IN THE NAME OF ALLAH
THE MOST GRACIOUS
THE MOST MERCIFUL
WHOSE HELP WE SOLICIT
REACTIONS OF
1:9
ETHYL-2-OXO-Δ-OCTALIN-10-CARBOXYLATE

THESIS

By
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Institute of Chemistry
University of Sind
Jamshoro
November - 1975
REACTIONS OF

$^{1:9}$ ETHYL - 2 - OXO - $\Delta$ - OCTALIN - 10 - CARBOXYLATE

A THESIS SUBMITTED TO THE UNIVERSITY OF SIND
FOR THE DEGREE OF DOCTOR OF
PHILOSOPHY IN CHEMISTRY

By

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SYNOPSIS

1. The problems related to the synthesis of ethyl-2-oxo- $\Delta_{1:9}$-octalin-10-carboxylate (4) have been reviewed.

2. The work described in this thesis is largely concerned with the substitution in the ethyl-2-oxo- $\Delta_{1:9}$-octalin-10-carboxylate (4) by the following three methods.

   a) Ethyl-2-oxo- $\Delta_{1:9}$-octalin-10-carboxylate (4) was treated with suitable alkyl and acyl halides, in presence of sodium ethoxide, to form its 1-substituted derivatives (178) which on subsequent hydrolysis and decarboxylation, were converted into $\alpha$-R-unsaturated ketones (181).

   ![Chemical Reaction Diagram]

   b) The alkylation and acylation of ethyl-2-oxo- $\Delta_{1:9}$-octalin-10-carboxylate (4) was accomplished by preparing its sodio-derivative in liquid ammonia and dry ether or benzene, refluxing with suitable alkylating or acylating agents, to form its 1-substituted derivatives (178): The latter were hydrolysed and decarboxylated as above to give the corresponding $\alpha$-R-unsaturated ketones (181).
c) In this method the carbonyl group at 2-position of the ethyl-2-oxo- \( \Delta^{119} \)octalin-10-carboxylate (4) was blocked by introducing a removable substituent (Eg. pyrrolidine) which prevents the formation of the corresponding enolates and results into a resonance stabilized anion \((208-11)\) which undergoes kinetically controlled, alkylation or acylation giving the monoalkyl or acyl derivatives of \( \beta \)-keto ester \((178)\) at the \( \alpha \)-position. The 1-substituted derivatives \((178)\) were hydrolysed and decarboxylated as in the above two method into the corresponding \( \alpha \)-\( \beta \)-unsaturated Ketones \((181)\).

![Chemical structures](image)

The refractive index, ultraviolet absorption infrared spectrum and 2:4 dinitrophenyl hydrazone of the 1-substituted derivatives \((178)\) and \((181)\) prepared by the above methods were found to be identical.

The enamine method was found to be the best, because of its easier working procedure and better yield of the product.
3) 2-oxo-\(\Delta^{1:9}\)octalin and some of its 1-substituted have been dehydrobrominated with N-bromo succinimide to the corresponding phenols.

4) Ethyl 2-oxo-\(\Delta^{1:9}\)octalin-10-carboxylate (4) reacts with diethylamino-hydrochloride and paraformaldehyde to yield ethyl-1-methyl(N-diethyl amino)-2-oxo-\(\Delta^{1:9}\)octalin-10-carboxylate (263). Its methiodide (271) on treatment with sodium derivative of ethyl acetoacetate gave ethyl 2-oxo-1-(3'-keto butyl-2'-ethyl carboxylate)-\(\Delta^{1:9}\)octalin-10-carboxylate (267).

\[
\begin{align*}
\text{Ethyl-2-oxo-1-(3'-keto butyl-2'-ethyl carboxylate)} \\
\Delta^{1:9}\text{octalin-10-carboxylate (267) was also prepared by the onamine method,}
\end{align*}
\]
Ethyl-2-oxo-1-(3'-keto butyl-2-ethyl carboxylate)  

$\Delta^{19}$-octalin-10-carboxylate (267) on cyclization yields diethyl-2-oxo-2,3,4,5,6,7,8,9,10,14-decahydro phenanthrene -3:14 - dicarboxylate (278), which on hydrolysis and decarboxylation gave -2-oxo-2,3,4,5,6,7,8,9,10-decahydrophenanthrene (279).
A series of 1-alkylated and 1-acylated derivative (288) of diethyl-2-oxo-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene 3:14 dicarboxylate (270) have been prepared by the enamine method. These have been hydrolysed and decarboxylated to the corresponding \( \alpha \)-\( \beta \)-unsaturated tricyclic ketones (289).
INTRODUCTION

A detailed study of the literature on the preparation and synthetic applications of keto-esters led to the conclusion that it would be interesting to explore cyclic keto-esters which could be used as intermediates for the synthesis of larger molecules such as terpenoids and steroids and in the preparation of camphorone analogues and pyrethins. Such keto-esters described in the literature are Hagemann's ester (1), Ethyl isoprophorone carboxylate (2), Ethyl-2-methyl-4-oxo-cyclopent-2 ene-1-carboxylate (3), and Ethyl 2-oxo-Δ^11:9 octalin-10-carboxylate (4).
These cyclic keto-esters appear to have two main advantages. Firstly, they can be readily prepared from comparatively cheaper and commercially available starting materials e.g., ethyl acetocetate, ethyl malonate and ethyl cyclohexanone-2-carboxylate. Secondly, these esters on hydrolysis and subsequent decarboxylation would yield the corresponding ketones. These ketones if suitable method of dehydrogenation are made available, may lead to aromatic compound which may not be otherwise accessible by conventional methods.

Of the four esters described above Hagemann's ester (1) has undergone considerable investigation for its possible use in the synthesis of compounds of interest in connection with the chemistry of vitamins E and other larger molecules. It has been shown that the Hagemann's ester undergoes alkylations at 3-position on treatment with alkyl halides in presence of sodium ethoxide or sodium amide. The 3-substituted derivatives (5) thus obtained when hydrolysed and decarboxylated yielded corresponding ketones (6)
The first positive evidence that alkylation occurs exclusively at 3-position was provided by Hogg. Hagemann’s ester was alkylated with m-methoxy-phenyl ethyl bromide (7) in presence of sodiumamide in liquid ammonia. The product obtained was cyclized and dehydrogenated to a known phenanthrene derivative 7-methoxy-1-methyl phenanthrene (8).

A further evidence that Hagemann’s ester alkylates at 3-position and not at 1-position was provided by Harper et al. They condensed Cis-crotyl chloride with Hagemann’s ester, followed by hydrolysis and decarboxylation to give 2-cis-crotyl-3-methyl cyclohex-2-enone (9). This ketone was found to be identical with the ketone prepared by Robinson Mannich condensation of 4-dimethyl-amino-butan-2-one methiodide (10) and ethyl-sodio-3-oxo-oxo-6-enoate (11) followed by cyclization and decarboxylation. This, therefore conclusively proved that the substitution of Hagemann’s ester occurs exclusively at 3-position.
The alkylation of ethyl isophorone carboxylate (2) has been studied by Kazi et al. The gem-dimethyl group present in Ethyl Isophorone carboxylate as expected does not change the course of substitution in this compound. It has been shown that like Hagemann's ester, this compound also, could be alkylated at 3-position. The derivatives (12) thus obtained, on hydrolysis and decarboxylation will give a variety of isophorone-homologues, i.e., 2-alkyl-3,5,5-tri-methyl-cyclohex-2-enone (13).

\[ R = \text{Cis-CH}_2\text{-CH=CH}_2\text{-CH}_3 \]
A direct synthetic evidence to show that the alkylation of ethyl isophorone carboxylate occurs exclusively at 3-position has also been provided by Kazi et al. They alkylated ethyl isophorone carboxylate (2) with ethyl bromide to give ethyl-derivative (12, R = C₆H₅) which on hydrolysis and decarboxylation yielded the corresponding ketone (13, R = C₂H₅). This ketone was found to be identical with the ketone (13a, R = C₂H₅) prepared by Michael condensation of ethyl isophorone propylidene acetacetate (14) and ethyl 3-oxo-hexanoate (15) in the presence of potassium-t-butoxide.

Alkylation of ethyl-2-methyl-4-oxo-cyclopent-2 ene-carboxylate (3) at 3-position have also been studied with a view to open up a new route to the synthesis of compounds like cineole, pyrethins, jasmones, and also of some other cyclopentanone derivatives in-accessible by other routes.

Survey of the literature showed that unlike the above mentioned keto esters (1,2,3) which have been studied extensively the synthetic applications of ethyl-2-\(\triangle^{1,2}\) octalin-10-carboxylate (4) have remained almost completely
unexplored. The structural similarity between ethyl isoporphorone carboxylate (2) and ethyl 2-oxo- Δ\(^{1:9}\)octalin-10-carboxylate (4) suggested that this compound could also undergo similar alkylation reaction yielding important intermediate derivatives which might be difficult to obtain by usual methods. In addition to this, another interesting feature of this compound (4) which attracted the attention of the present worker, is that it is bicyclic. Hence if this β-keto-ester be subjected to Michael condensation, it will lead to important intermediates for the synthesis of tricyclic compounds. It could thus provide a very important basic skeleton for the synthesis of steroid and other natural products. Further the bicyclic and tricyclic derivatives thus obtained on dehydrogenation may lead to aromatic compound of naphthalene and phenanthrene series which may not be accessible by conventional methods. The present worker therefore considered it worthwhile to first explore into the various methods available for the synthesis of Ethyl-2-oxo- Δ\(^{1:9}\)octalin-10-carboxylate (4) and try to introduce an improved method for its preparation. Secondly, to undertake the alkylation and acylation of this compound.

**Preparation of Ethyl 2-oxo- Δ\(^{1:9}\)octalin-10-carboxylate.**

The two reported methods for the preparation of ethyl 2-oxo-Δ\(^{1:9}\)octalin-10-Carboxylate are as follows:

It was first prepared by Robinson et al.\(^6\), by the
condensation of ethyl cyclohexenone-2-carboxylate (14) with di-ethylamino-butane-methiodide (10) in presence of sodium ethoxide.

\[
\begin{align*}
&\text{Ethyl Cyclohexenone-2-Carboxylate (14)} \\
&\text{Di-Ethylamino-Butanone-Methiodide (10)} \\
&\text{Sodium Ethoxide (11)}
\end{align*}
\]

The reaction is supposed to proceed through the following steps.

\[
\begin{align*}
&\text{Ethyl Cyclohexenone-2-Carboxylate (14)} \\
&\text{Di-Ethylamino-Butanone-Methiodide (10)} \\
&\text{Sodium Ethoxide (11)}
\end{align*}
\]

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\begin{align*}
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&\text{Sodium Ethoxide (11)}
\end{align*}
\]

\[
\begin{align*}
&\text{Ethyl Cyclohexenone-2-Carboxylate (14)} \\
The probable steps involved in the preparation are as follows:

(i) Preparation of ethyl 2-(3′-oxo-buty1) cyclohexanone-2-carboxylate (15).

(ii) Cyclization of ethyl 2-(3′oxobuty1)-cyclohexenone -2-carboxylate (15), into ethyl 2-oxo-Δ^1,9-octalin-10-carboxylate (4).

The first operation i.e., the preparation of the intermediate ethyl 2-(3′-oxobuty1) cyclohexenone-2-carboxylate (15) has been performed in the above mentioned method. By
making use of the Michael condensation and its Robinson modification. The reactants involved in both the methods are readily accessible and the working method in both the cases are easy and smooth. Again since both methods produced ethyl 2-(3'-oxo-butyl) cyclohexanone-2-carboxylate in high yield (80 - 90%) the present worker decided not to look for any modification or alternative route for this step. However it was considered necessary for the purpose of this thesis to review the Michael condensation and its Robinson Modification.

The Second operation i.e., the cyclization of ethyl 2-(3'-oxo-butyl) cyclohexanone-2-carboxylate (15%) into the ethyl 2-oxo-\(\Delta^{11}\) -octaline-10-carboxylate (4) has been achieved by Robinson in alkaline conditions (35-39% yield) and by Michael under buffered conditions (42-44% yield).

The present worker therefore decided to reinvestigate the above two cyclization conditions and also look for other cyclization procedures, which might give the ethyl 2-oxo-\(\Delta^{11}\) -octaline-10-carboxylate in better yields.

The Michael reaction and its modifications.

The nucleophilic addition of an enolate anion e.g., (17a) to the carbon-carbon double bonds of \(\alpha,\beta\)-unsaturated ketones, aldehydes or carboxylic acid derivatives is known as Michael, reaction. This reaction provides a very useful method for the alkylation of active methylene compounds. The unsaturated Compound used in this reaction often called Michael acceptors, may include any unsaturated...
system having a functional group e.g. (carbonyl, ester, nitrocyano, sulphone or phenyl group, capable of stabilizing carbanionic intermediate (19):

\[
\text{CH}_2(\text{COOC}_2\text{H}_5)_2 + \text{NaOC}_2\text{H}_5/\text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_2 = \text{CH} - \text{CN} \quad (17)
\]

25° - 30°C  \quad (17a)  \quad (18)

\[
\begin{align*}
\text{CN} - \text{CH} - \text{CH}_3 - \text{CH} & \quad (\text{COOC}_2\text{H}_5)_2 \quad \text{CH}_2 = \text{CH} - \text{CN} \\
\rightarrow & \\
\text{CN} - \text{CH}_2 - \text{CH}_2 - \text{CH} & \quad (\text{COOC}_2\text{H}_5)_2 \quad \text{CH}_2 = \text{CH} - \text{CN} \\
\end{align*}
\]

(19b)

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow \text{CN} - \text{CH}_2 - \text{CH}_2 - \text{CH} & \quad (\text{COOC}_2\text{H}_5)_2 \quad (57-63\%)
\end{align*}
\]

(20)

Ref. 12

\[
\begin{align*}
\text{CH}_3 - \text{CH}(\text{COOCCH}_2\text{CH}_3)_2 + \text{NaOC}_2\text{H}_5/\text{C}_2\text{H}_5\text{OH} & \rightarrow \\
\rightarrow \text{CH}_3\text{C}(\text{COOCH}_2\text{CH}_3)_2 \quad \text{Na}^+ \quad (21a)
\end{align*}
\]

(21)

\[
\begin{align*}
\text{CH}_3\text{C}(\text{COOCH}_2\text{CH}_3)_2 \quad \text{Na}^+ + \text{C}_6\text{H}_5 - \text{CH} = \text{CH} - \text{C} & \quad \text{C}_6\text{H}_5 \rightarrow \\
\rightarrow \text{CH}_3 - \text{C}(\text{COOCH}_2\text{CH}_3)_2
\end{align*}
\]

(22)

Ref. 13
The Michael reaction differs from other alkylation reaction in that the base which generates the enolate-ion is regenerated, so that usually only a catalytic amount of the base is required. Furthermore, the reaction step ($a \rightarrow b$) which forms a new carbon-carbon bond is reversible, and the product, usually a 1,5-dicarbonyl compound is frequently capable of further transformation in the presence of base. These differences permit a variety of side reactions, not encountered in other commonly available alkylation procedures. It is therefore desirable to use the mildest reaction conditions, for affecting any given Michael reaction. It is because of this reason that these reactions are carried out, by selecting relatively weak basic catalysts, such as piperidine, pyridine, triethylamine, benzyl-trimethyl ammonium hydroxide (Triton B) and potassium hydroxide. If stronger bases, (e.g., sodium ethoxide) or potassium t-butoxide) are required, it is normally appropriate to use 0.1 to 0.3 equivalent of the bases and to employ low reaction temperatures ($25^\circ$C or less), and short reaction times in order to minimise side reactions. e.g:

$$\begin{align*}
\text{CH}_3 - \text{CO} - \text{NH} - \text{CH} - \text{COOC}_2\text{H}_5 + \text{CH} = \text{CH} - \text{CHO} & \xrightarrow{\text{NaOC}_2\text{H}_5} \\
& \xrightarrow{\text{C}_2\text{H}_5\text{OH}} \xrightarrow{25^\circ\text{C}} \\
\text{CH}_3 - \text{CO} - \text{NH} - \text{C} - \text{CH}_2 \text{CH}_2 - \text{CHO} & \xrightarrow{\text{Ref. 11 a.}} \\
& \text{COOC}_2\text{H}_5 \\
\end{align*}$$

(25) (26) (27)
The same Michael product may in principle be expected from its two different pairs of reactants. For example, a combination either of benzalacetophenone (30) and diethyl malonate, or, of diethyl-benzal-malonate (32) and acetophenone (33), could theoretically effect the preparation of the adduct (31). In this case, however, diethyl malonate rather than acetophenone as the active methylene component, is the proper choice, because formation of its anion can be accomplished with a weaker base and less vigorous conditions.

$$C_6H_5-CH=CH-CO-C_6H_5 + CH_2(COCH_2CH_3)_2$$

(30) $$\xrightarrow{\text{Piperidine}} C_2H_5OH$$

$$C_6H_5-CO-CH_2-CH=CH(COOC_2H_5)_2$$

(31) $$\xrightarrow{\text{Reflux}}$$

$$C_6H_5-CH=C\left(COOC_2H_5\right)_2 C_6H_5COCH_3$$

(32) (33) Ref. 15

The use of a full equivalent of base, elevated reaction temperature, and long reaction time frequently promote reversal of Michael reaction (called a retrograde Michael
reaction) or further transformation of the initial product. Since a retrograde Michael reaction may lead to compounds other than the original starting materials (e.g., 32 & 33 from 31) complex mixture may result. Examples of further transformations of Michael products are as follows.

\[
\begin{align*}
\text{CH}_3 - \text{C} &= \text{C} - \text{COCH}_3 + \text{CH}_2(\text{COOCH}_2\text{CH}_3)_2 \\
(34) \\
\rightarrow (\text{CH}_3)_2\text{C} &\rightarrow \text{COCH}_3 \\
\text{CH} - \text{COOC}_2\text{H}_5 \\
\text{COOC}_2\text{H}_5 \\
(35)
\end{align*}
\]

\[
\begin{align*}
(\text{H}_3\text{O})_2 &\rightarrow \text{(36)} \\
&\text{Ref. 16} \\
\text{CH}_3 - \text{CH} = \text{CH} - \text{COOC}_2\text{H}_5 + \text{CH}_3 - \text{CH} (\text{COOCH}_2\text{CH}_3)_2 \\
(37) \\
\text{CH}_3 - \text{CH} - \text{CH} - \text{COOC}_2\text{H}_5 &\xrightarrow{\text{NaOC}_{2}\text{H}_5} \text{H}_3\text{C} - \text{C} (\text{COOC}_2\text{H}_5)_2 \\
\text{NaOC}_{2}\text{H}_5 &\xrightarrow{\text{Reflux}} \text{CH}_2 - \text{CH} - \text{CH} - \text{COOC}_2\text{H}_5 \\
\text{H}_3\text{C} - \text{C} - \text{C} = 0 \\
\text{COOC}_2\text{H}_5 \\
\text{NaOC}_{2}\text{H}_5 &\xrightarrow{\text{H}_3\text{O}^+}
\end{align*}
\]
A variant of the usual procedure for the Michael reaction consist of treating the active methylene compound with a \( \beta \)-halo-carbonyl compound or the quaternary salt from a \( \beta \)-dialkylamino-carbonyl compound. These reactants are rapidly converted to \( \beta \)-unsaturated-carbonyl compounds in the reaction mixture by base catalyzed elimination, and a normal Michael reaction then occurs. The \( \beta \)-halocarbonyl compounds and quaternary ammonium salts consume a full equivalent of base during elimination reaction. Consequently the Michael reactions using these reactants are often run like conventional alkylation reactions. The most useful precursors of Michael acceptors are the \( \beta \)-dialkylamino carbonyl compounds and corresponding quaternary salts\(^{18}\) which are readily available from Knoevenagel reaction:

\[
\begin{align*}
\text{(39)} \quad \text{CH}_2\text{N}(\text{CH}_3)_2 & \quad \text{CH}_2\text{NO}_2 \\
\text{(40)} \quad \text{NaOCH}_3 & \quad \text{CH}_3\text{OH} \\
\text{(41)} \quad \text{O} & \quad \text{CH}_2 \quad \text{CH}_2\text{NO}_2 \\
\text{(42)} \quad \text{H}_2\text{O} & \quad \text{CH}_2\text{CH}_2\text{-NO}_2 \\
\end{align*}
\]

A very important Michael acceptor is methyl vinyl ketone. It has been shown\(^{19}\) that where as the \( \alpha \) cyclic ketones
showed little or no (0-15,5%) tendency to add to methyl vinyl ketone, the cyclic ketones, cyclopentanone, cyclohexanone and 2-methyl-cyclo-hexanone, reacted rapidly to give fair to good yields of condensation products. Thus cyclopentanone, when converted to its anion, was acetoethylated to give 2-(3-keto-butyl)-cyclopent-anone in 40% yields. Where as this compound had been earlier prepared in only 28% yield, by Gil et al. by the high temperature reaction of cyclopentanone with methiodide of 4-diethyl-amino-butanone in presence of catalytic amount of base.

\[
\begin{align*}
\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + CH_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{H}_5 \quad &\xrightarrow{\text{base}} \quad \text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \\
(43) &\quad \quad &\quad \quad (44)
\end{align*}
\]

Ref 19.

Both cyclohexanone and 2-methyl cyclohexanone reacted with methyl vinyl ketone to give the decalone derivatives, via, the intermediates (48) & (52) respectively.
Robinson Modification of the Michael condensation:

The use of a masked form of the \(\alpha,\beta\)-ethylenic-carbonyl compound, which produces the latter in situ, is of practical importance with sensitive ketones and in condensations requiring stringent experimental conditions. Although saturated \(\beta\)-chalcoketones had some use, as precursors of the corresponding \(\alpha,\beta\)-ethylenic ketones\(^\text{21}\), Robinson and his coworkers\(^\text{22,23,24}\) introduced the use of \(\beta\)-dialkylaminoketones or their quaternary salts; these decompose gradually into a dialkylamino or trialkylammonium salt and the desired \(\alpha,\beta\)-ethylenic ketones. These starting materials are readily accessible by appropriate Mannich reactions of saturated ketones and, if necessary, subsequent quaternization as shown in the following reaction sequence.

\[
\begin{align*}
\text{CH}_3\text{COCH}_2\text{CH}_3 & \quad \text{CH}_3\text{COCH}_2\text{CH}_2\text{N(CH}_3\text{)}_2 \\
& \quad \overset{\text{+}}{\rightarrow} \text{CH}_3\text{COCH}_2\text{CH}_2\text{N} (\text{CH}_3)_2 \overset{\text{II}}{\rightarrow} \\
& \quad \overset{\text{II}}{\rightarrow} \text{CH}_3\text{-COCH} = \text{CH}_2 + (\text{CH}_3)_2\text{NHII} \\
\end{align*}
\]

A recent study of these reaction has led to the conclusion that olefinic intermediate, as outlined by Robinson, occurs whenever there is a hydrogen atom on the
carbon atom beta to the nitrogen. One of the most useful synthetic applications of the Michael reaction has been the Robinson annelation reaction, illustrated by the following examples:

\[
\text{CH}_2=\text{CH-CCCH}_3 + \text{(C}_2\text{H}_5)_3\text{N} \xrightarrow{\text{C}_6\text{H}_6/25^\circ\text{C}} \text{CH}_2=\text{CH-CCCH}_3
\]

(55)  \quad 92\%

\[
\text{Al} \left[ (\text{C}-\text{C(CH}_3)_3\right]_3 \xrightarrow{\text{C}_6\text{H}_6/\text{Reflex}} \text{COCC}_2\text{H}_5
\]

(57)  \quad 34\%

\[
\text{CH}_2=\text{N(CH}_3)_2\text{C} + \text{CH}_3=\text{C-CH-CCOC}_2\text{H}_5 \xrightarrow{\text{NaO CH(CH}_3)_2/}\text{(CH}_3)_2\text{CHCH}_2} \text{CH}_3
\]

(58)  \quad (60)  \quad (61)  \quad 59\%

(62)  \quad \text{Ref. 27}  \quad \text{Ref. 28}

**Cyclization of Michael adducts:**

Michael's adducts are known to undergo cyclization and cycloisomerization reactions, giving a variety of ring compounds. In particular, the Robinson modification of the Michael reaction has been utilized for the synthesis of
Alicyclic ring systems. We will however, restrict ourselves to its use in the synthesis of cyclohexanone and condensed ring systems. Michael adducts of unsaturated aldehydes and ketones with ethyl acetoacetate are known to undergo a secondary condensation between the terminal methyl group of the adduct and the carbonyl group of the original acceptor molecule. In a fair number of cases this cyclization reaction is accompanied by the elimination of the carbethoxy group. This reaction is illustrated by the synthesis of the following keto-esters (64, 66).

Obviously, the same reaction will take place whenever 1:5 diketones (63, 65) of the above type are formed, e.g., the condensation product of ethyl cyclohexanone-2-carboxylate and ethyldene acetone or benzylidene acetone, yielding...
A similar cyclization takes place with the adducts of I-tetrolone and ethyldene acetoacetate or ethyl cyclopentanone, the tricyclic keto ester \(32\) (70) and the tetra-cyclic ketone(72) respectively.

A related reaction is the cyclization of diethyl alkylidene bisacetoacetate, diethyl-methyle \(\alpha\)-bisacetoacetate (73) for example forms (74). Then this loses water and one
carboethoxy group to give the Hagemanns ester (75).

There are few examples in which methyl of an acetyl group other than that of the ethyl acetoacetate component supplies the hydrogen of the water molecule to be eliminated, e.g. in the formation of cyclohexanone (a)\(^\text{34}\) and (b)\(^\text{35}\).
This cyclization is also possible with unsaturated 1,5 diketones; obviously, the configuration of the double bond must be cis for cyclization to take place. The product (86) from acetyl acetylene and 2-methyl cyclohexanone gives the dienone (81).

\[
\begin{align*}
    \text{CH}_3 & \quad \longrightarrow \\
    \text{CH}_3 & \quad \text{O} \\
\end{align*}
\]

(80) 

(81)

The importance of the Robinson annelation reaction for the ring closure can be understood by the following examples:

\[
\begin{align*}
    \text{COOCH}_3 & \quad \text{Na} \rightarrow \text{OCH}_3 \\
    \text{CH}_3 & \quad \text{OCH}_3/\text{C}_6\text{H}_6 \\
\end{align*}
\]

(82) 

(83) 92%

\[
\begin{align*}
    \text{C}_2\text{H}_5\text{N} & \quad \text{CH}_2-\text{CH}_2-\text{COCH}_3 \\
    \text{C}_6\text{H}_5\text{OH} & \quad 25^\circ \text{C} \\
\end{align*}
\]

(84) 90%

\[
\begin{align*}
    \text{CH}_3 & \quad \text{CH}_3 \\
    \text{CH}_3 & \quad \text{H}_2\text{O} \\
\end{align*}
\]

38%
The reaction of unsaturated carbonyl compounds with enamones. These reactions have been introduced by Stork et al. to overcome the serious limitations which were encountered during the alkylation of enolates and the related Michael reactions. Two of the major limitations are (1) The necessity of using relatively stronger bases (e.g., amide ions, triphenylmethide ions, and alkoxide ions) to transform the carbonyl compounds into its anions, may result in side reactions e.g., for example the self condensation of cyclopentanone by bases under the conditions of the Claisen or Michael condensation, the transformation, of 4-hydroxy-cyclo-hexanone benzoate, into cyclopropane derivatives with t.butoxide, and the well known condensation of acetalddehyde and its mono substituted derivatives even with mild bases. The proton transfer reaction between the alkylated ketones formed initially and the unreacted enolate ion. This problem will be illustrated by a typical example. Attempted mono alkylation of...
6-methoxy-3-tetralone with an equivalent of methyl-iodide in the presence of a strong base, leads to almost no mono-methyl compound a mixture of 6-methoxy-1,1-dimethyl-3-tetralone and the starting material is obtained instead.

While this is perhaps an extreme case, this experience is very general and is a result of the rapid equilibration of enolates, via, proton transfer which takes place under the reaction conditions. The same difficulty is also encountered in Michael addition reaction e.g., the reaction of acrylonitrile with cyclohexanone in the presence of a variety of bases which leads to a mixture of the mono-, tri-, and tetracyanoethylated ketones:

\[
\text{O} + \text{CH}_2 = \text{CH} = \text{CH} \rightarrow \text{base} \rightarrow \text{base}
\]

\[(R = \text{H}, \text{CH}_2 = \text{CH} = \text{CN})\]
Stork et al., therefore suggested a new method for the alkylation and acylation of ketones and aldehydes which emerged from the possibility that the enamines derived from an ordinary ketone or aldehyde might react with an electrophilic/to some extent on carbon as well as on nitrogen. The carbon alkylation product could be hydrolyzed by water to an alkylated ketone or aldehyde. The possibility of this reaction had not been earlier explored which may be due to the fact that in the earlier literature apparently exclusive N-alkylation had been reported by vinyl amines:

\[
\begin{align*}
\text{N} & \quad \text{R} \\
\text{R}^+ & \quad \text{N} \quad \text{R}
\end{align*}
\]

However when stork et al., started work on this problem it had already been established, that the enamine of ketone (and of aldehydes in some cases), generally lead to predominant carbon alkylation and acylation. Since no base or other catalyst is needed for these reactions, the first of the two difficulties mentioned above is avoided. At the same time it is not be-set by the second problem (Polyalkylation). The base-catalyzed alkylations and the Michael addition further differ from the behaviour of the enamines of the ketones e.g., an unsymmetrically substituted ketone such as 2-methyl cyclohexanone reacts with an alkyl halide in the presence of
the an strong base, or with acrylonitrile and other electrophilic olefins to give, in general, the product in which the newly introduced group appears on the more substituted carbon, \[ \text{Page 25} \]

\[
\text{(O} \rightarrow \text{C} \text{Q)} \]

The enamines derived from such ketones, however, normally lead to substitution on the less substituted carbon \[ \text{(O} \rightarrow \text{C} \text{Q}) \] (Page 25).

There are two very important application of this reaction:

I. The amine alkylation of carbonyl compounds with electrophilic olefins.

II. The amine alkylation of carbonyl compounds with alkylhalides.

---

I. The Enamine alkylation of the carbonyl compounds with Electrophilic olefins:

Enamines of ketone and aldehydes can react with electrophilic olefins to give high yields of mono-alkylated carbonyl compounds. This type of reaction is especially successful because competition from N-alkylation is inconsequential. The zwitterion ions formed by addition on nitrogen can readily regenerate the two components and N-alkylation is thus reversible. On the other hand, there exists a simple path for proton transfer leading to a neutral molecule in the case of \( \text{c-alkylation} \). This is illustrated in the following example using acrylonitrile as the electrophilic olefin and cyclopentanone as the ketone.
It is interesting that the enamine which results from the reaction (96) is that which derives from the transfer of the proton marked by an arrow (Possibly via an intramolecular-6-membered transition state). Thus leading to the more stable, less substituted enamines. In the case of aldehydes the possibility of such a proton transfer via, a six-membered ring is unavailable and the formation of a stable neutral alkylated enamine can only result from the intervention of a 4-membered transition state (or from intermolecular reactions).

\[
R - CH_2 - CHO \quad \xrightarrow{-27-} \quad R - CH = CHN \quad \xrightarrow{H_2O} \quad (97)
\]

(99)

(101)

(100 a)
The molecule can also become neutral by addition of the anion to the \( \text{\textgreater} C = \overset{\text{\textbullet}}{N} \). In a number of cases it is possible to isolate the cyclobutane derivative formed by direct neutralization of charges. This is of course especially true when the aldehyde enamine adduct cannot become neutral by proton transfer e.g., with \( \text{\textbullet}N\text{\textbullet} \)-disubstituted aldehydes.

\[
R - C = \overset{\text{\textbullet}}{N} \quad \overset{\text{\textbullet}}{\text{\textgreater}} \quad \overset{\text{\textbullet}}{\text{\textbullet}} \\
(103)
\]

\[
R - \overset{\text{\textbullet}}{C} - \overset{\text{\textbullet}}{\text{\textgreater}} - N \quad \overset{\text{\textbullet}}{\text{\textbullet}} \\
(104)
\]

\[
R - C = \overset{\text{\textbullet}}{\text{\textbullet}} - N \quad \overset{\text{\textbullet}}{\text{\textbullet}} \\
(105)
\]

This method of alkylation had some important advantages. In the first case, no catalyst is needed for the addition reaction, it means that the base-catalyzed polymerization (of the unsaturated ketones, nitriles, ester etc) is not generally a factor to content with, in contrast to the situation with usual base-catalyzed reactions Michael type. This means further that the carbonyl compound itself is not subject to aldol condensations which often preclude the use of the base catalysis. In the case of cyclopentanone for instance, the direct condensation with methyl vinyl ketone and base leads mainly to cyclopentylidene-cyclopentanone. The formation of the desired indanone (110) leading to (46) by the enamine procedure is easily achieved and may be
contrasted from the previously available method:

\[
\text{CH}_2=\text{CH}-\text{CO}-\text{CH}_3 + \text{cyclohexanone} \rightarrow \text{Product} \\
(107)
\]

In the case of aldehydes with a methylene group \(\alpha\)-to-carbonyl, the enamine method is about the only way to achieve the desired reaction, since base-catalyzed Michael reaction would lead to aldolization. Finally, mono-alkylation is easily achieved in contract to the results obtained. For instance in the usual enamo ethylation procedures,

Mono, di, tri or tetra enamo ethylation.

\[
\text{Enamine} \rightarrow \text{Product} \\
(113)
\]
This considerably greater rate of the first alkylation step than of further alkylation is remarkable and is responsible for the successful monoalkylation of enamines. Since in the reaction under discussion, the product is itself an alkylatable enamine (96). The transition state for e-alkylation necessitates, the coplanarity of the starred atom in (113) and the resulting interference between the hydrogen on the methylene to the nitrogen atom and R is obviously greater when R is alkyl (the monoalkylated product) than, when R is H (in the starting material) hence the higher energy of the transition state for the second alkylation. This factor is of course absent with the usual enolate ion.

A further point of difference with base-catalyzed Michael addition, is illustrated with 2-methyl-cyclohexanone:

\[ C(=O)O \rightarrow S \text{ Vs } O \rightarrow P \]

this is of course, the result to be expected from the structure which we have considered earlier.

Following examples will illustrate the synthetic importance of this reaction.

![Diagram of chemical structures]
(II) The Enamine alkylation of carbonyl compounds with alkyl halides.

Simple unactivated primary alkyl bromide or iodides give only a fair yield of 2-alkyl ketone by enamine method with the exception of β-tetralone derivatives which are thus mono alkylated in very high yield. The alkylation with alkyl halides, gives good yield with strongly electrophilic halides, such as alkylhalides, benzyl halides, propargyl halides, α-halo others, α-halo-ketones, κ-halo-esters and nitriles. Since these are the very substance which would often not be compatible with the conventional sequence involving transformation of a ketene into a β-keto ester followed by alkylation acid-hydrolysis and decarboxylation, the enamine alkyl halide reaction has turned out to be very valuable in such cases. A few example are as follows:
Furrolidine enamines have been found, most generally useful in alkylation with alkyl halides. One would of course expect the rate of the reaction to be higher with pyrrolidine than with morpholine on the basis of the difference in the strength of the bases. Since the electron removal from nitrogen is involved in the transition state for the alkylation reaction the

That this is not a whole story as shown by the fact that pyrrolidine enamines give considerably higher yields than the piperidine. It has been suggested to be due to the greater ease of formation of a trigonal carbon in a five-membered ring than in a six-membered one (compare the relative rates of solvolysis of 1-methyl cycloalkyl chlorides). Since the transition state for C-alkylation (but not N-alkylation) involves a trigonal atom in the amine portion of the molecule one would expect (and one observed) the most favourable ratio of C to N alkylation
to be obtained with the cyclic five and seven membered amines.

Alkylation of this type have been carried out, and a great variety of substances are thus made readily available. For example, the diketones derived from halo ketones can be cyclized to cyclopentanones. The product from pyrrolidine enamines of cyclohexanone and bromo acetic ester has been transformed into thioctic acid, the ketenitrile from cyclohexanone enamine and chloroaceto nitrile has been used to make hydroindole derivatives.

\[
\text{Methylation of the pyrrolidine enamine from 6-isoproyl-2-tetralone provides the starting material for the total synthesis of d,1-dehydroebiotic acid, and the synthesis of lactone (127) one of the constituent of the essential oil of jasmine from (125) obtained/enamine alkylation of cyclopentanone.}
\]
α, β-unsaturated ketones have not been studied so extensively, it has been shown that methylation of the pyrrolidine enamine of 1:9-octol-2, (129) leads to the 1-methyl compound (130) rather than a priori possible α-alkylated product.

The alkylation of an α,β-unsaturated ketone when it proceeds on carbon is a possible solution to the problem of mono alkylation of β-unsaturated carbonyl compounds with which dialkylation by the base-catalyzed alkyl halide method is sometimes even more of a complication than with saturated ketones: The high yields obtained in mono alkylation of ketones of the β-tetralone type have already been mentioned. The alkylation of a β-tetralone is formally related to that of an unsaturated ketones in the sense that the enamine is here also a conjugated enamine:
The usefulness of the enamine alkylation method over direct alkylation in the case of enones has been noted by Julia et al. who obtained 46% yield of the keto-ester (132) in the alkylation of the pyrroldine enamine (133) while direct base catalyzed alkylation led to 24% of the desired substance which was used in an ingenious synthesis of chrysanthemum carboxylic acid.

Again, alkylation of the unsaturated ketones (137) by the enamine method has been found to be superior to direct alkylation.

Recently it has been shown by Kuchae to be applicable to certain activated aryl halides. These reaction are,
however, really reactions with electrophilic olefins since they involve an addition-elimination mechanism.

The Enamine acylation of carbonyl compounds.

The enamine could be used for the synthesis of $\beta$-diketones by reactions with acid-chlorides followed by aqueous acid hydrolysis e.g., reaction of pyrrolidine enamine of cyclohexanone with benzoyl chloride to give 2-benzoyl cyclohexanone (138) and with ethyl carbonate to form 2-carbethoxy cyclohexanone (14).

\[
\begin{align*}
    \text{Enamine} & \quad \text{Acid Chloride} \quad \text{Product} \\
    \text{C} & \quad \text{Cl-COOC_2H_5} \quad \text{C_6H_5COCl} \\
    \text{(14)} & \quad \quad \quad \text{(138)}
\end{align*}
\]

Huang and co-workers$^{50}$ have subsequently made valuable contributions to this $\beta$-diketones synthesis. They showed that the less reactive morpholine enamines give better results than the pyrrolidine enamines in these reactions, and that the extra-mole of enamine used to take up the hydrogen chloride liberated in the reaction could be avoided in most cases by substituting a mole of triethylamine.
\[ \text{HO}_2C-(CH_2)_n + 6 \text{ COOH} \]

\[ \text{HO}_2C-(CH_2)_5-R \ (151) \]
Bromination with N-Bromosuccinimide:

The possibility of dehydrohalogenating the β-keto ester ethyl-2-oxo Δ^1:9-octalin-10-carboxylate (4) also its alkylated derivatives, and the corresponding ketone 4, e.g.

2-oxo- Δ^1:9-octalin and also its alkylated derivative to aromatic compound led the present worker to investigate into the use of N-bromosuccinimide for this purpose. The utility of N-Bromosuccinimide (Usually called NBS), as a reagent for allylic brominations was first pointed out by zeigler in 1942. The N-bromosuccinimide has a very wide application, which usually gave rise to nuclear mono bromo derivatives of various hydro-carbon, arylalkyl ethers, aromatic amines etc. Thus difficulty accessible bromo derivative were formed.

Bloomfield originally suggested a chain carrying sequence involving the succinimide radical which until recently has been accepted by most workers.
However, Goldfinger\textsuperscript{58} proposed an alternative scheme of utilization of a bromine atom chain made possible by the presence of traces of bromine or H3R in the reaction system.

\[
\begin{align*}
\text{Br} + \text{RH} & \rightarrow \text{R} + \text{HBr} \\
\text{Br}_2 + \text{R} & \rightarrow \text{RBr} + \text{Br} \\
\text{HBr} + \text{NBS} & \rightarrow \text{Br}_2 + \text{Succinimide}.
\end{align*}
\]

Here the bromosuccinimide acts simply as a reservoir capable of sustaining a low steady-state concentration of bromine during the reaction. However, it is possible that the succinimidyl radical attacks on N-bromosuccinimide followed by reaction of the succinimide radical with bromine. Their presence is certainly suggested by the occasional report of N-bromo succinimide addition products to olefins during halogenation and also by the occurrence of the N-bromosuccinimide \( \beta \)-bromo propionylisocyanate rearrangement. This reaction discovered independently by Bartlett and Martin\textsuperscript{59}; Johnson and Sublitz\textsuperscript{60}, evidently arise from a competing radical chain since it requires the presence of radical sources. The most plausible formulation is certainly the following sequence.

\[
\begin{align*}
\text{H}_2\text{C} - \text{CO} & \rightarrow \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{N} - \text{CO} \\
\text{H}_2\text{C} - \text{CO} + \text{Br} & \rightarrow \text{H}_2\text{C} - \text{CO} + \text{Br} - \text{CH}_2 - \text{CH}_2 - \text{CO} - \text{N} - \text{CO}
\end{align*}
\]
Bartlett and Martin obtained the isocyanate by refluxing N-Bromosuccinimide in carbon tetrachloride, but Johnson and Zublitz reported that the presence of chloroform and an olefin (Allyl bromide) were required for the reaction. Isocyanate is detected by the infrared spectra. Conclusion drawn is that radicals may attack N-Bromosuccinimide but that succinimide radical is too unreactive to attack the carbon-hydrogen bonds. 61 The N-H bond dissociation energies of succinimide has been estimated as 74 K-cal, which would make such hydrogen abstraction endothermic, and it is perhaps significant that N-Iodosuccinimide is reported to be ineffective as a free radical halogenating agent. Here the succinimide radical chain, were it possible, should be easily realised, but an iodine atom chain is energetically prohibited. This clearly indicates that succinimide is not the chain carrying species in a free radical chain reaction.

Work by Goldfinger on allylic chlorination with N-chlorosuccinimide has suggested that halogen atom rather than succinimidyl radicals, may function as the chain carrying species. He has developed kinetic arguments to show that low chlorine concentration should favour substitution, rather than addition. The halogen presumably is kept in a low concentration by an ionic reaction of hydrogenchloride and N-chlorosuccinimide. Sixma and Rieman and McGrath and Tedder, have pointed out the possibility of an analogous mechanism for N-Bromo- succinimide bromination by showing that allylic substitution is competitive with addition, in reaction of bromine with
olefin at low bromine concentration.

Pearson and Martin\textsuperscript{63} have shown that identical selectivity
with brominations of substituted toluenes are
evidenced by the N-Bromosuccinimide, N-Bromotetrafluorosucc-
minide, N-Bromo tetramethyl succinimide and molecular brom-
ine. These results make it possible to discount some of the
evidence which has been interpreted in terms of the succini-
idyl radical mechanism and make the bromine atom mechanism
more attractive indeed. Koeing and Brewer\textsuperscript{62} with a view to estab-
lish the existence of succinimidyl radical prepared N.N.-bis-
succinimidyld with the expectation that it would dissociate
and serve as an unequivocal source of the radical. It was
found that this dimer is remarkably stable even under extreme
conditions. This shows that succinimidyl radical is highly
unstable with respect to the dimer, succinimide and even
N-bromosuccinimide. Simple molecular orbital calculations
suggest that a highly developed system involving lone pair
on the nitrogen and the adjacent carbonyl group exists in
both the ground state molecule and in radical and that no
net stabilisation of the radical is realised. The mechanism
\textit{mix mechanism} of bromination with NBS then involves very slow
production of molecular bromine which then attacks the sub-
strate. Support for this mechanism comes also from the fact
that at low concentration levels and in absence of hydrogen
bromide, bromine react with cyclohexene to form allylicbrom-
ide rather than 1,2 addition product. Horner and Winkelmann
had shown the reaction of NBS to be an free radical surface
reaction.
Wohl-Zeigler bromination of unsaturated substances is highly specific, occurring invariably on the carbon atoms adjacent to the unsaturated centres. This follows from the mechanism of the reaction in which the radical intermediate involved is established by resonance by the unsaturated groups. In a substance $XCH_2CHY$, therefore, in which both $X$ and $Y$ are unsaturated substituents, both methylene groups would be open to attack, and provided steric complications are absent, bromination would proceed by the route involving the radical intermediate of greater stability. Selective bromination, therefore, provides a means by which such stabilising effects can be compared.

This wide interest in NBS has been occasioned by both its paradoxically clean-cut specificity and diverse reactivity. Thus, under mild but different conditions, N-Bromo succinimide reacts to substitute bromine in the allyl position or to add NOBr or Br$_2$ to the double bond. Similarly, it can be made to substitute in the carbon of the side chain of an alkyl substituted aromatic hydrocarbon or heterocyclic compound or it may substitute in nucleus, depending upon conditions. In many cases, at least, the desired direction of reaction can be directed almost exclusively by catalysts or conditions.

The effect of environmental factors (oxygen, light) reactant impurities (water, hydrogen-bromine, hydroperoxides) and added substances of potential catalytic or inhibitory
activity on the course and the relative reaction times of the reaction of N-bromo-succinimide has been investigated by 
Eyp. J. Dauben, Jr., and Layton L. Macoy. 67

The role of the solvent in influencing the course of NBS brominations is obscure. It would appear that water has a distinct tendency to promote additions of HOBr. It is therefore customary to dry solvents carefully when allylic bromination is desired. The presence of alcohol in solvents is also undesirable, because alcohol appears to promote the addition of bromine to the double bond.

In general, little difference is noted between chlorinated solvent and hydrocarbons. Buchman and Hutton 68 however found that benzene provided better yield of allyl-substituted methylene cyclobutane than did although the reaction was more rapid in the latter solvent. Normal hexane led to small yield of addition product without increasing allylic reaction, and an excess of reactant as solvent completely inhibited the reaction with NBS.

Carbon tetrachloride has a distinct advantage in the investigation of new reactions in that it is less dense than NBS but more dense than succinimide. The conclusion of reaction is therefore signalled by the disappearance of all NBS from the bottom of the reaction flask and the collection of succinimide on the surface of the liquid.69

N-Bromo-succinimide reactions in acetic acid as a solvent indicates that they are exceptionally rapid. The low temperatures required make this solvent more attractive than
CCl₄ or benzene in instances where rearrangement and spontaneous dehydro-halo-genations are probable. The reactions thus far studied in acetic acid gave better yields than did the same reactions run in CCl₄. It is not surprising that acetic acid should speed up the reaction (granted that it does not change the whole direction of the reaction because of its polar character) because of its much greater solvent power for NBS. Perhaps acetamide, with its high boiling point and exceedingly high solvent power for NBS, might provide a medium for the reaction of NBS compounds which react only difficultly.

The reaction of N-Bromo succinimide with alkenes is conducted in normal diffuse light and in a contact with air (through the condenser).

In a few cases nitrogen atmosphere or precautions to maintain the reaction mixture anhydrous have been employed but these measures have been used to protect the bromination product from decomposition rather than to change the course or the rate of bromination reactions. Strong light irradiation has been shown to catalyze the reaction of NBS with alkene and an incandescent bulb below the reaction flask frequently has been used to catalyze the allylic bromination and to furnish heat needed for refluxing. To determine the effect of diffuse light and of atmospheric oxygen on the course and the time of complete reaction, a series of runs were conducted under various combination of light-free, oxygen-free and peroxide-free conditions. The similarity
of reaction times, for runs 4 and 5, which were carried out under the normal conditions and different only in the access of diffuse light, indicates that light does not contribute significantly to catalysis of the reaction when peroxide are also present. When performed, peroxides and access of oxygen and moisture are excluded, the reaction time than diffuse light is almost doubled, when access of light is additionally removed reaction occurs very slowly and the reaction time is increased almost ten-fold. The difference between the latter two reaction times indicates that, in the absence of peroxides, even diffuse light may catalyze the allylic bromination reaction. Further, it has been shown that a sluggish reaction may be activated by addition of peroxide that normally would have been present in the reaction mixture. These observations that reaction times become successively longer as peroxides, light, and oxygen are eliminated provide convincing evidence of the radical chain nature of the NBS-alkene reaction, and of the importance of these catalysts, usually inadvertently present, in synthetic applications of the reaction. The very slow reaction still found when these catalysts are excluded may be attributable to initiation by bromine radicals, formed by thermal homolysis of bromine or, possibly of NBS, or to slow formation of peroxides from residual traces of oxygen not removed by the sweeping with nitrogen.

Product analysis of these runs clearly indicates that gradual exclusion of environmental catalysts does not
alter the fundamental course of the reaction but by prolonging reaction time, causes a subsequent reaction to become increasingly important.

Schmid and Karrar had demonstrated that benzoyl peroxide was an effective catalyst for allylic bromination reactions by NBS, and Buch, Scitz and Jeger had used suspended barium carbonate to prevent excessive dehydro-bromination of the allylic bromide product. Ford and Waters showed that allylic and benzylic brominations by NBS were accelerated by Azo-bis-\( \alpha \)-methyl-butyro-nitrile and were retarded by iodine or chloroanil.

The accelerators have been divided into two main groups.

i) Normal initiators of radical reactions (benzoyl peroxide azo-bis-iso-butyronitrile);

ii) Bromine-producing group (bromine, hydrogen bromide ethanol, water etc).

Some of the important applications of N-Bromosuccinimide are as follows.

1. Allylic substitution.

Of all the reactions of N-Bromosuccinimide, undoubtedly allylic substitution is the most useful and mostly used. Ziegler's original papers demonstrated the specificity of NBS in reacting with a variety of olefinic compounds to substitute bromine in the allylic position.
He also made the general observations that methylene groups were easier to substitute than methyl groups, that tertiary hydrogens could not be substituted under his conditions, and even methylene groups adjacent to conjugated double bonds resisted bromination in his hands.

These limitations have been removed by the introduction of catalysts. Schmid and Karrer used benzoyl peroxide to catalyse the reaction.

\[
\begin{align*}
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3 & \quad \xrightarrow{\text{NBS}} \quad \text{Br-CH}_2-\text{CH} = \text{CH} - \text{CH} = \text{CH} - \text{COOCH}_3 \\
\text{CH}_3 - \text{C} - \text{CH} = \text{CH} - \text{COOCH}_3 & \quad \xrightarrow{\text{NBS}} \\
\text{H}_3\text{C} - \text{C} - \text{CH}_2 = \text{CH} - \text{COOCH}_3
\end{align*}
\]

In addition to the conjugated unsaturated esters which Schmid and Karrer and other have brominated with NBS, a variety of bromination of conjugated unsaturated ketones have been carried out.\(^{70-73}\) For example, Bjerass and his collaborators\(^{70}\) have brominated testosterone-acetate in the 6-position.
Similarly aldehydes have been brominated and dehydro-brominated by Karrer and Ochener.\textsuperscript{69c}

2a. Side Chain Bromination.

Although toluene is not attacked by NBS in the absence of catalyst, Schmid and Karrer demonstrated that benzoyl peroxide brought about the formation of benzyl bromide in 64% yield, where activating influences are present the catalyst is not usually required. For example p-nitro toluene produced p-nitrobenzyl bromide in 50% yield in the absence of catalyst, methyl and ethyl naphthalene\textsuperscript{73a} and di and tri phenyl methane all reacted without catalyst to produced \(\alpha\)-brominated side chains. This affords a convenient approach for the synthesis of aryl acetic acids and styrenes\textsuperscript{73a}.

\[ \text{CH}_3 \quad \rightarrow \quad \text{CH}_2\text{Br} \]

\[ \text{CH}_2\text{-CN} \quad \rightarrow \quad \text{CH}_2\text{COOH} \]

\[ \text{CH}_3 \quad \rightarrow \quad \text{CH}_2\text{-CH}_3 \quad \rightarrow \quad \text{CHBr}_2\text{-CH}_3 \quad \rightarrow \quad \text{CH}=\text{CH}_2 \]
The hydro-aromatic hydrocarbons are so readily brominated by NBS and the product loses HBr so readily that the method affords a convenient method for aromatization.

\[
\begin{array}{c}
\text{Benzene} \\
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\end{array}
\]

The side-chain bromination of hetero-cyclic compounds has received a great deal of attention. Much of this work has been done on derivatives of thiophene.

Dehydrogenation.

Since many dehydrogenations of hydroaromatic compounds are accompanied by the rearrangements, migrations and ring closures, the use of a low temperature bromination-dehydriobromination process has been studied by Roderick A. Barennes using N-Bromosuccinimide as the reagent. A procedure has been developed which is satisfactory specially for compounds of the tetratin type which have one hydroaromatic ring attached to a benzenoid ring. Barennes has found that tetratin gave a 74% yield of naphthalene.

\[
\begin{array}{c}
\text{Tetratin} \\
\begin{array}{c}
\text{Br} \\
\text{Br}
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{Naphthalene} \\
\end{array}
\]
Equimolar amount of decalin and NBS reacted in presence of Benzoyl peroxide to form a tetra-bromoocatlin as major product.

Early attempts to aromatize cyclohexene by reaction with 2-3 moles of NBS failed: However 6 moles of the reagent produced a mixture of dibromo benzene in 58% yield. The liquid mixture was found to be largely the meta-isomer containing about one third of the solid para isomer. Since benzene does not react with NBS at an appreciable rate, the dibromobenzene must have resulted by the aromatization of a dibromocyclohexene or dibromo cyclohexadiene intermediate.

The present worker therefore considered it worthwhile to use the N-bromosuccinimide for the dehydrohalogenation of ethyl-2-oxo-Δ\(^{1:9}\)-octalin-10-carboxylate into 2-naphthol-10-ethyl-carboxylate while 2-oxo-Δ\(^{1:9}\)-octalin was converted into 2-naphthol. Since it appeared to be a very promising and interesting route for the synthesis of aromatic compounds of naphthalene and phenanthrene series which may not be accessible by conventional methods.
A survey of the literature on the preparation and synthetic application of cyclic keto esters led to the observation that an interesting keto-ester reported in the literature which could be used for the synthesis of larger molecules such as terpenoids, steroids and in the preparation of cinnamone analogues and pyrethins is ethyl 2-oxo-Δ1,2 octalin-10-carboxylate (4). The present worker further observed that this ester although prepared as early as 1937 but somehow it had not received the attention of research workers; consequently little details are available about its synthesis and its synthetic applications have remained completely unexplored. It was therefore thought interesting to investigate the methods of the preparation of the above compound, and to explore its importance as a synthetic intermediate.

The present worker prepared ethyl cyclohexanone-2-carboxylate by three different methods. In the first method cyclohexanone was condensed with diethyl oxalate in the presence of sodium ethoxide followed by the pyrolysis of the resulting 2-keto cyclohexyl glyoxalate (152) to yield the required ethyl cyclohexanone-2-carboxylate in 58-59% yield.
The ethyl oxalate first splits into the type \( \text{H}_5\text{C}_2\text{O}^-\text{C}^-\text{C}^+ \) ion which reacts directly with the carbanion of cyclohexanone. After the substitution at 2-position, the carbonyl group is removed by the thermal decarbonylation of the 2-keto cyclohexyl glyoxalate. \( \text{Fe}_2\text{O}_3 \) acts as a catalyst to remove carbonyl group from 2-keto-cyclohexylglyoxalate. Iron is reduced, and a complex is formed with the 2-keto cyclohexyl glyoxalate. The mechanism how this complex exists in the reaction mixture is still unknown.

The second method used for the preparation of ethyl cyclohexanone-2-carboxylate is by stork et al. In this method morpholino-enamine of cyclohexanone was prepared and treated with ethyl chloroformate in the presence of catalytic
amount of p-toluenesulphate. The water formed during the reaction was removed continuously with Dean and Stark trap.

The above method was slightly modified and pyrrolidine base was used in place of morpholine. The yield of the final product was thus raised to 64%. All the steps of the above reaction are reversible, and enamine if hydrolysed by water during refluxing will reform the carbonyl compound thus resulting in the poor yield of the final product. Therefore the reactions of enamine must be conducted under strictly anhydrous conditions. Once the reaction has been effected, the modified carbonyl compound is easily liberated from the product by the addition of water in the reaction mixture. Following mechanism has been suggested for the above reaction:
The third method for the preparation of ethyl cyclohexanone-2-carboxylate is a modification of the second method. Morpholine-enamine of cyclohexanone was mixed with diethyl aniline and dry chloroform in nitrogen atmosphere and then treated with ethyl chloroformate. The mixture was refluxed and finally hydrolysed to give the above product (14). Triethylamine used as a catalyst in the above reaction, neutralizes the hydrogen chloride formed, which would otherwise combine with the enamine and effect the yield. The mechanism suggested is as under.
Ethylcyclohexanone-2-carboxylate obtained by the methods described above was found to be identical in all respects (I.R. spectra, M.P of the 2:1 dinitro phenyl hydrazones and the mixed melting point). Further it was found that the second method gives the best result. It was therefore followed during the course of this work.

1-Dimethyl amino butanone:

1-diethylamino-5-butanone was prepared\(^5\) by the condensation of paraformaldehyde, dimethyl aminehydrochloride acetone and few drops of concentrated hydrochloric acid in 68-72 % yield. The reaction is believed to follow the following reaction path.

\[
\begin{align*}
\text{(CH}_3\text{)}_2 & \text{N} + \text{CH}_2 \rightarrow \text{(H}_3\text{C)}_2 & \text{N} - \text{CH}_2 - \text{O} \\
\text{(CH}_3\text{)}_2 & \text{N} \text{Cl} \rightarrow \text{CH}_2 \rightarrow \text{H}_2\text{O} \\
\left[ \text{(CH}_3\text{)}_2 & \text{N} \text{CH}_2 \text{C}_2 \text{(CH}_3\text{)}_2 \text{N} = \text{CH}_2 \right] \rightarrow \text{H}_3\text{C} - \text{C} \rightarrow \text{CH}_3
\end{align*}
\]

This reaction is initiated by the attack of the unshared electron present at the nitrogen of dimethylamine hydrochloride on the carbonyl carbon atom of paraformaldehyde to yield an unstable resonating ion. This is immediately attacked by the carbanion derived from the acetone giving the so-called Mannich base.
I-dimethyl ammino-3-butanone was treated with methyl iodide and the methiodide (16) thus obtained, being highly hygroscopic, was directly used for the preparation of ethyl-2-oxo-Δ¹¹,9 octalin-10-carboxylate (4).

\[
\text{CH}_3 - \overset{\text{O}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{N(CH}_3)_2}{\text{CH}_2} + \text{CH}_3\text{I} \quad \rightarrow
\]

\[
\text{CH}_3 - \overset{\text{O}}{\text{C}} - \text{CH}_2 - \text{CH}_2 - \overset{\text{N(CH}_3)_2}{\text{CH}_2} + \overset{\text{CH}_3}{\Phi}
\]

Methyl vinyl ketone:

Methyl-vinyl ketone (16) was prepared by the present worker on the lines of the method suggested for the preparation of ethyl vinyl ketone by McNohan et al.: The method makes use of the acylation of ethylene in presence of anhydrous aluminium chloride. The ketone was thus obtained in 45% yield.

The reaction is believed to proceed, via an electrophilic attack on the olefin by a complex (a) of the lewis acid (AlCl₃) with the acid chloride (acetyl chloride), alternatively the acylating agent may be formulated as an acylation. The ketone formed in the reaction mixture is converted to its conjugated acid(b) by the aluminium chloride present. For this reason it was necessary, to use at least one equivalent of the aluminium chloride catalyst to ensure complete reaction:
The present worker had three alternate routes for the preparation of Ethyl-2-oxo-Δ^{11.9}-octalin-19-carboxylate(4).

Each of these routes make use of the Michael reaction and consist of treating the active methylene compound i.e. ethyl cyclohexanone-2-carboxylate (14) with:

A) a halo carbonyl compound, (4-chlorobutanone)(16 a)

B) a P-vinyl-carbonyl compound, (methyl vinyl ketone) (16).

C) a quaternary salt from α,β-amino carbonyl compound.
These reactants are rapidly converted to \( \alpha_2 \beta \) -unsaturated carbonyl compounds in the reaction mixture by base catalysed elimination, and a normal Michael reaction then occurs. The \( \beta \)-halocarbonyl compound and the corresponding quaternary ammonium salts consume a full equivalent of base during the elimination reaction and thus the reaction runs like conventional alkylation reaction.

A) The preparation of ethyl-2-oxo- \( \Delta^{119} \) -octalin-10-carboxylate (4) by the interaction of the ethyl cyclohexanone-2-carboxylate (14) with 4-chlorobutanone (16 a).

The sodium enolate of ethylcyclohexanone-2-carboxylate was prepared by heating the ester and sodium in equimolar quantities. This was cooled and refluxed with 4-chlorobutanone. The reaction mixture on dilution and extraction with benzene gave ethyl-2-(3'-keto butyl) cyclohexanone-2-carboxylate (15).

\[
\begin{align*}
\text{(a)} & \quad \text{(b)} \\
\text{(c)} & \quad \text{(d)} \quad \text{(15)} \\
\text{(16 a)}
\end{align*}
\]
Ethyl-2-3-keto butyl) cyclohexanone-2-carboxylate (15) was cyclised into Ethyl-2-oxo-Δ¹⁻octalin-10-carboxylate (4) by refluxing the di-keto ester (15) with a mixture of acetic acid and hydrochloric acid (5:1 by volume) under nitrogen for 20-24 hours. Dilution of the reaction mixture and extraction with benzene gave ethyl-2-oxo Δ¹⁻octalin-10-carboxylate (4) in 56% yield; b.p. 140-141°C/2 mm nD 1.508 following mechanism has been suggested for the above reaction.
The preparation of ethyl-2-oxc-\(\Delta^{1,9}\) octalin-10-carboxylate (\(4\)) by the interaction of ethyl cyclohexanone-2-carboxylate with methyl vinyl ketone (\(16\)) in presence of triethylamine.

Condensation of a mixture of ethyl cyclohexanone-2-carboxylate, anhydrous methyl vinyl ketone and few mls of the triethylamine in an atmosphere of nitrogen gave ethyl-2-(3''keto butyl)cyclohexanone-2-carboxylate 80-85% yield %
b.p. 85-92° 4mm.
Ethyl-2(3'-keto butyl)cyclohexanone-2-carboxylate (5) was cyclised into Ethyl-2-oxo-octalin-10-carboxylate (4) by refluxing the diketo ester (15) with a mixture of tert-butyl-alcohol and benzene under nitrogen for six hours. Dilution of the reaction mixture and extraction with ether gave the above product, in 34% yield b.p. 138-145° C / 2.5 - 3 mm nD 27 1.508.

Following mechanism has been proposed for this reaction.
The preparation of ethyl-2-\( \Delta^{1:9} \) octalin-10-carboxylate by the condensation of ethyl cyclohexanone-2-carboxylate with methyl vinyl ketone in presence of sodium hydroxide.

Condensation of ethyl cyclohexanone-2-carboxylate and methyl vinyl ketone in presence of 30% alcoholic sodium hydroxide gave ethyl-2(3-keto-butyl)cyclohexanone-2-carboxylate in 60 % yield.

The \( \delta \)-keto ester (15) was cyclised as in (B-1) to give the desired product (4) in 45 % yield.
(B-III) The preparation of ethyl-2-oxo-octalin-10-carboxylate by the condensation of the enamine of ethyl cyclohexanone-2-carboxylate (145) with methyl vinyl ketone.

The enamine of the Ethyl cyclohexanone-2-carboxylate was prepared using ethyl cyclohexanone-2-carboxylate and a slight excess of pyrrolidine in benzene and the mixture was refluxed under nitrogen atmosphere. The water removed azeotropically by means of water separator.

\[
\text{COOC}_2\text{H}_5 + \text{C}_5\text{H}_5\text{N} \rightarrow \text{COOC}_2\text{H}_5 \quad \text{(14)}
\]

\[
\text{COOC}_2\text{H}_5 \quad \text{(165 a)} \quad \text{COOC}_2\text{H}_5 \quad \text{(165 b)} \quad \text{COOC}_2\text{H}_5 \quad \text{(165 c)}
\]

The enamine of the \(\beta\)-keto \(\text{ester}\) was then condensed with methyl vinyl ketone in dioxane, followed by the removal of the excess of vinyl ketone and treatment again with pyrrolidine, using acetic acid as a catalyst, gave ethyl-2-oxo-

\[
\text{COOC}_2\text{H}_5 \quad \text{(165 d)} \quad \text{(166)}
\]

\(\Delta^1\) octalin-10-carboxylate in 42% yield. Following
A mechanism has been proposed for the above reaction.

\[
\begin{align*}
\ce{\text{COOC}_2\text{H}_5} + \ce{\text{H}_3\text{C}==\text{CH}==\text{CH}_2} &\rightarrow \ce{\text{COOC}_2\text{H}_5} \\
\ce{\text{H}_3\text{C}==\text{CH}==\text{CH}_2} &\rightarrow \ce{\text{H}_3\text{C}==\text{C}==\text{CH}_2}
\end{align*}
\]

The preparation of ethyl-2-oxo-\(\Delta^{119}\)octalin-10-carboxylate by the interaction ethyl cyclohexanone-2-carboxylate with a quaternary salt of an \(\alpha\)-amino carboxyl compound.

The sodium enolate of ethyl cyclohexanone-2-carboxylate was prepared by heating the \(\beta\)-keto ester(14) and sodium in equimolar ratio in benzene absolute ethyl alcohol. The mixture was cooled and refluxed with 1-dimethyl
amino-3-butanoic methiodide (10) giving ethyl-2(3'-ketobutyl) cyclohexanone-2-carboxylate in 80% yield.

\[
\begin{align*}
&\text{COOC}_2\text{H}_5 \\
\stackrel{\text{+NaCO}_2\text{H}}{\text{c}_5\text{H}_5} &\rightarrow \text{H}_3\text{C}-\text{CCH}_2-\text{CH}_2\text{N(CH}_3\text{)}_2\text{H} \\
&\text{COOC}_2\text{H}_5 \\
\end{align*}
\]

The reaction proceeds by the initial formation of the resonance stabilised \(\beta\)-keto ester (14) which undergoes kinetically controlled alkylation at the \(\alpha\)-position to give the mono-alkylated diketone (15). The \(\alpha\)-proton in this case is more readily removed by the reaction with the base (sodium metal) than in either the starting material or the final product, since it is activated by the carbonyl group and an ethylenic double bond. The carbonium ion (3'-ketobutyl) obtained during the thermal
decomposition of the $\alpha$-amino-carbonyl compound (10) alkylated at the $\alpha$-position.

Ethyl-2(3'-keto butyl) cyclohexanone-2-carboxylate was cyclized into ethyl-2-oxo-$\Delta^1:9$-octalin-10-carboxylates as in the previous cases giving ethyl-2-oxo-$\Delta^1:9$-octalin-10-carboxylate in 56% yield b.p. 140-141°C/2 mm.

Ethyl-2-oxo-$\Delta^1:9$-octalone-10-carboxylate obtained by the different methods (A, 3, C) described above was found to be identical in all respects. The infrared spectra of the samples from different methods showed the same frequencies; the melting points of their 2:4 dinitrophenyl hydrazones were same and further the mixed melting points of thin 2:4 dinitro-phenylhydrazones showed no depression. The identity of this $\beta$-keto ester was also confirmed by its analysis and by the fact that its physical constant are same as reported in the literature (Table 1, p-60).
**Table of Values for the Preparation of (4)**

<table>
<thead>
<tr>
<th>Name of the Compound</th>
<th>D.P. C</th>
<th>Refractive Index</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt;</th>
<th>η&lt;sub&gt;max&lt;/sub&gt;</th>
<th>2;4'En_2C_6</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ethyl-2-oxo- Δ-octalin 1:9 10-carboxylate 54</td>
<td>133-44 C°</td>
<td>1.503</td>
<td>232</td>
<td>16,300</td>
<td>178-78.5</td>
<td>43%</td>
</tr>
<tr>
<td>2. Ethyl-2-oxo- Δ-octalin 1:9 10-carboxylate 54</td>
<td>138-45 C°</td>
<td>1.503</td>
<td>232</td>
<td>16,800</td>
<td>178-178.5</td>
<td>42%</td>
</tr>
<tr>
<td>3. Ethyl-2-oxo- Δ-octalin 1:9 10-carboxylate 6</td>
<td>170-78 C°</td>
<td>1.503</td>
<td>232</td>
<td>16,800</td>
<td>178.5</td>
<td>39%</td>
</tr>
<tr>
<td>4. Ethyl-2-oxo- Δ-octalin 1:9 10-carboxylate 55°</td>
<td>142-144 C°</td>
<td>1.503</td>
<td>232</td>
<td>16,800</td>
<td>177-78</td>
<td>60%</td>
</tr>
<tr>
<td>5. Ethyl-2-oxo- Δ-octalin 1:9 10-carboxylate 55°</td>
<td>141-42</td>
<td>1.503</td>
<td>232</td>
<td>16,800</td>
<td>178.5</td>
<td>76%</td>
</tr>
</tbody>
</table>
The alkylation and acylation reaction of ethyl-2-oxo-Δ1:9 octalin-10-carboxylate(4) were accomplished by three methods:

1. Sodium ethoxide method
2. Sodamide method
3. Enamine method

1. Sodium ethoxide method.

The alkylation of ethyl-2-oxo-Δ1:9 octalin-10-carboxylate (4) was accomplished by preparing its sodio-derivative in sodium ethoxide solution and treating this with suitable alkyl halides. The alkylated derivatives were isolated by vacuum distillation in 40-60% yields as high boiling reddish yellow liquid and showed characteristic frequencies in the infra-red and ultraviolet spectra. They were further characterized by their 2:4 dinitrophenyl hydrazones.

These 1-substituted alkyl derivatives (178) of ethyl-2-oxo-Δ1:9 octalin-10-carboxylate were refluxed with ethanolic sodium hydroxide for 6-10 hours, followed by acidification with hydrochloric acid. The keto acids thus liberated on brief refluxing underwent decarboxylation to yield the ketones (181). The alkylated ketones were isolated by vacuum distillation and collected mostly as yellow coloured, sweet smelling liquids. These ketones showed characteristic frequencies in the infrared and ultra violet absorption spectra and were characterized by their 2:4 dinitrophenylhydrazones.
The mechanism suggested for the above reaction and the alkyl groups substituted at 1-position are as follows:

1) NaOH
2) HCl
Reflux

The other possibility of a by product.

\[ R = \text{methyl, ethyl, } n\text{-propyl, isooctyl, } n\text{-butyl, sec-butyl tert butyl, allyl, tolyl, benzyl ortho hydroxy(phenyl) 1-naphthyl.} \]
The anions (173 and 174) derived from the 
\( \beta \)-unsaturated ketoester (4) by abstraction of a gamma proton is alkylated at the \( \alpha \) -position to form an \( \beta_2 \beta \gamma \)-unsaturated ketoester (175). This initial product (175) may be isomerized to an \( \alpha \)-alkyl \( \alpha \beta \)-unsaturated ketoester (178) or may undergo further alkylation (180). Dialkylation has often been reported in such cases because a proton is abstracted more readily from the intermediate unsaturated ketoester (176) than from the starting material (4) or the alkylated \( \beta \)-unsaturated ketoester (175). Dialkylation is suppressed by the slow addition of alkylating agents. This permits the isomerization of the \( \beta_2 \beta \gamma \)-unsaturated ketoester (175) to the less acidic \( \alpha \beta \)-unsaturated ketoester (178) to occur more rapidly than the alkylation of the intermediate anion (176) & (177).

The reactions were carried out under complete anhydrous conditions, since in the presence of moisture, the actual reaction will not follow, because the water is much stronger acid than the activated methylene compound, and will ultimately protonate the carbanion ion produced in the reaction mixture, as a result the yield of the final product will decrease.

A possible side reaction which may be assumed to take place during the direct alkylation and acylation (using sodium ethoxide/ethylalcohol, as the basic medium) of ethyl-2-oxo-octalin-10-carboxylate leading to di or poly alkylated or acylated product through the interaction of the ori-
Original enolate ion, instead of forming the mono alkylated or acylated product. This difficulty was supposed to be due to the weak basic agent and the alcohol used as a solvent. The problem of polyalkylation and acylation was avoided by addition of an inert solvent, and large amount of the alkylating or acylating agents. In this way the enolate ion will be rapidly consumed before equilibration with the alkylated or acylated β-keto-ester leading to polyalkylation or polyacylation.

The mechanism for acylation reactions is as follows:

R = acetyl, propionyl, n-butyryl, iso-butyryl, valeryl, iso-valeryl, succinyl and glutaryl, benzyl, m-nitrobenzyl, aminomethyl, and naphthyl.
The alkylation and acylation of ethyl-2-oxo-\(\Delta^1\)\textsubscript{9} octalin-10-carboxylate (4) was accomplished by preparing its sodio derivative in liquid ammonia and dry ether or benzene and refluxing with suitable alkylating or acylating agents. The required derivatives were isolated by vacuum distillation in yields of 40-60% as high boiling reddish yellow liquids. The 1-substituted derivatives (150) of the ethyl-2-oxo-octalin-10-carboxylate were hydrolysed and decarboxylated as described in the sodium ethoxide method to yield ketones (18). The infrared absorption spectrum 2,4-dinitrophenylhydrazones and...
refractive index of the esters (178) and the ketones (181),
were identical with the corresponding esters and their ketones
prepared by the sodium ethoxide method.
The action of one equivalent of a strong base, such as sodium amide on ethyl-2-oxo-octalin-10-carboxylate (4) converts the ester essentially quantitatively into an anion, and the composition of the mixture of the enolate ion, formed under such condition of the kinetic control may differ substantially from that of the mixture formed under equilibration conditions. In general, enolate mixture formed under such conditions contain more or less highly substituted enolate than in the equilibrium mixture, indicating that the less hindered proton are removed more rapidly by the strong base (sodium amide in liquid ammonia). The alkylation and acylation reactions carried out by sodium amide method have been summarised on page [76].
Enamine Method.

In this method the carbonyl group at 2-position of the ethyl-2-oxo-\(\Delta^1,9\) octalin-10-carboxylate, is blocked by introducing a removable substituent (pyrrolidine) which prevents the formation of the corresponding enolates; the conversion of the (4) into the enamine with secondary base (pyrrolidine or morpholine) facilitates the removal of \(\alpha\)-proton in these compounds. Further the ethylenic double bond also change their position due to the conversion of carbonyl group into enamine finally, resulting into the resonance stabilized anion. The enamine reactions thus proceed by the initial formation of a resonance stabilized anion (206 - 211) and which undergoes kinetically controlled, alkylation or acylation at the \(\alpha\)-position to give the mono alkylated or acylated derivative (178) of the \(\beta\)-keto ester.

The alkylation or acylation of ethyl-2-\(\tilde{\text{H}}\)-pyrrolidyl-octalin-10-carboxylate (209) was accomplished by treating this with the slight excess of suitable alkylating or acylating agents, usually in solvents like benzene, toluene, dioxane or acetonitrile under nitrogen and refluxed for 10-15 hours. The 1-substituted enamine (215) was stirred at room temperature, then it was hydrolyzed with 5-10% hydrochloric acid and further refluxed for a short time. Finally the \(\beta\)-keto ester derivatives, (178) were isolated under vacuum distillation in yield of 40-50% as high boiling reddish yellow liquids. The refractive, infrared spectrum and 2:4-dinitrophenyl hydrazones of the derivatives (178) prepared by
prepared by this method were found identical in all respect with the corresponding derivatives prepared by the first two methods. These ester derivatives (176) were hydrolysed and decarboxylated by the usual method to give the ketones (181) in 35-40% yield. The infrared spectrum, refractive index and 2:4 dinitrophenylhydrazones of these ketones (181) were found to be identical with the corresponding ketones prepared by the first two methods. Following mechanism has been suggested for these reaction.
The halogenation reactions carried out by the cumins method have been summarized on page 30, No. 30 at one consideration of the scheme of reaction of the cumins.
It was observed that the rate of reaction is higher with the pyrrolidyl-enamine than with morpholinyl enamine of the keto ester. This is due to the difference in the strength of the parent bases, since electron is removed in the transition state for the alkylation and acylation reactions.

The alkylation and acylation reactions of the ethyl \(-2\)-oxo-\(\Delta^1,9\)-octalin-10-carboxylate proceed on carbon-1 rather than the a priori possible \(\gamma\)-alkylated or \(\delta\)-alkylated product. This situation is analogous to the methylation.

So have found methylation of the pyrrolidine enamine of \(\Delta^1,10\)-octalin-2 \(\beta\) giving the 1-methyl compound \(\beta\) rather than a priori possible \(\gamma\)-alkylated product.
Such type of alkylation of an $\alpha,\beta$-unsaturated ketone, when it proceeds on carbon $^3$ is a possible solution of the monoalkylation of $\alpha,\beta$-unsaturated carbonyl compound with which dialkylation by the usual base alkylhalide method is sometime even more of a complication than with a saturated ketone ($\beta$-tetralone). The high yield obtained in the monoalkylation of the ketone of the $\beta$-tetralone type have already been mentioned. The alkylation of a $\beta$-tetralone is formally related to that of an $\alpha,\beta$-unsaturated bicyclic keto ester (4) in the sense that the enamine is here also a conjugated enamine ($F_1$). But it remains to be determined whether even with cyclic keto ester enamine, the first step is direct carbon alkylation or involves reversible quaternary salt formation. It is interesting in connection with the later possibility that those halides which give satisfactory yields might be expected to be most easily removed from nitrogen by reaction with the halide ion, thus regenerating the starting material for the eventual C-alkylation. Further study will be required to elucidate this point.
Ethyl-2N-pyrrolidyl-octalin-10-carboxylate (209) reacts with acid chlorides to give only the C-acylated compound that is ethyl-2N-pyrrolidyl-1-acetyl-octalin-10-carboxylate (234).

\[ \text{Similiar results were obtained by the reaction of} \]
\[ \text{(209) with benzoyl or p-nitrobenzoyl chloride. In each case} \]
\[ \text{the C-acylated product was obtained with an equimolar amount} \]
\[ \text{of the hydrochlorides (232).} \]

\[ \text{R = benzoyl or p-nitro benzoyl} \]
The formation of the hydrochloride (232) rather than that of the C-acylated products (235, 236) reflects the facts that enamine derivative i.e. (209) is a stronger base than (234, 235 and 236).

Thus, the enamine keto ester (238) is a strong base to dehydrohalogenate acyl chloride to ketones, which is rapidly converted to a dimer under the reaction conditions. The difference in the behaviour of (209, 210) toward acetyl chloride must lie in the basicities of enamine as well as in the greater ease of formation of a trigonal atom in a five membered ring compared with a six membered ring in the transition state. Thus in the acylation reaction the more a reactive i.e., pyrrolidine enamine-ketone react to give C-acylated product while the morpholino enamine which is less reactive is nevertheless a strong base to effect the dehydrohalogenation of the acetyl chloride. This preference in reactivity is well illustrated by the reaction of (210) and (211) with acetic anhydride. The pyrrolidine enamine-keto ester (209) reacts with boiling acetic anhydride to give
the required product, while the morpholino-enamino keto ester
remains uncharged under the same conditions.85

The reaction of aliphatic acid chlorides (acetyl, propionyl, n-butyryl, isobutyryl, valeryl and isovaleryl chlorides) with ethyl-2-N-pyrrolidyl octalin-10-carboxylate (209) gave the expected acylated product; the resulting acyl enamines were hydrolysed to the diketones in good yields. The intermediate acylenamic was not isolated since the position of the double bond in the intermediate cannot be fixed.

The reaction of aryl acid chlorides (benzoyl, p-nitro benzoyl and cinnamoyl chloride) with ethyl-2-N-pyrrolidyl-octalin-10-carboxylate gave the expected product; the resulting acyl enamines however were hydrolysed to the diketones in low yields. The failure of the stork reaction to give monobenzoylation was especially acute in the case of ortho-substituted benzoyl chloride.

Some features of the mechanism of the stork acylation are elucidated by our results. The final product of the first benzoylation (236) loses a proton from the alpha carbon atom at which the attack occurred. In the stork acylation reaction, the proton loss occurred at the opposite, or the \( \alpha \) carbon atom.
Thus in the above example the formation of the conjugated system of (239) is the controlling factor. Subsequent attack at the α position by a second molecule is possible only if the non-conjugated benzoyl enamine (242) is formed. The second benzoylation must then occur at the alpha carbon or at the oxygen. The preference for C-acylation over O-acylation can be explained by noting that the resonance form (241) must be available for C-acylation. Examination of the molecular models reveals that when the \[ \equiv N - C - C = C = C - \] system is co-planar as required crowding between the carbonyl oxygen and the hydrogens on carbon-2- of the pyrrolidine
moiety exceeds by some limits of van der wall radii. Steric inhibition of form (241) resonance suppresses the negative character of oxygen, and the acylation attack occurs at alpha carbon as suggested by form (240) and (241).

An alternative explanation of the absence of O-acylation products is that while both O- and C-acylation might occur, only the latter leads to products. The O-acylation intermediate could revert to reactants, while the C-acylation intermediate leads to stable product by the proton loss to excess base.
Of the three methods described above for the alkylation and acylation of ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (4), best results were obtained by the enamine method. The advantages of this method over the other methods have already been discussed in the introduction and further the working procedure is also simple.

It has already been briefly discussed above that during these reactions, the alkyl and acyl groups enter the 1-position in the ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (4), rather 3 or 8-positions. This assumption is further supported by the alkylation and acylation reactions of a structurally analogous compound Hagemann's ester (1) where it has been conclusively proved \( \text{1, 2, 3, 5} \) that the alkyl and acyl groups enter the 3-position. Using similar arguments, we can also assume that in ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (4) the alkyl and acyl groups will enter at the 1-positions.

A more positive evidence for the alkyl and acyl groups entering the 1-position in ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (4) is as follows:

Ethyl-1-methyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (192) in addition to its preparation from the above three described alkylation methods was also prepared by the

1. Sodium ethoxide method
2. Sodium amide
3. Enamine method

\[ \text{COOC}_2\text{H}_5 \text{CH}_2\text{I} \]
Robinson's method\textsuperscript{24} from ethyl cyclohexanone-2-carboxylate\textsuperscript{(14)} and 1-diethyl amino-pentan-3-one methiodide (10 a), and characterized as semicarbazone and 2:4 dinitrophenyl hydrazone.

\[
\begin{align*}
\text{CCOC}_2\text{H}_5 & + \text{CH}_2\text{CH}_2\text{CO}-\text{CH}_2\text{CH}_2-N\left(\text{C}_2\text{H}_5\right)\text{I}_2 & \xrightarrow{\text{NaCOC}_2\text{H}_5} & \text{CCOC}_2\text{H}_5 \\
(14) & & (10 a) & \\
\end{align*}
\]

The comparison of physical constants (table 2) and the mixed melting points of the derivatives from the four different sources provided a conclusive proof that all the products (193) are identical and that the methyl group is present at 1-position in these products.

**Table 2.**

Physical constants of Ethyl-1-methyl-2-oxo-\textsuperscript{1:9} octalin-10-carboxylate and its derivatives.

<table>
<thead>
<tr>
<th>Product</th>
<th>B.Ps $^\circ C$</th>
<th>$n_D$</th>
<th>$\lambda_{max}$</th>
<th>$\varepsilon_{max}$</th>
<th>2:4 DNP/Semicarbazone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Product\textsuperscript{(193)} obtained by sodium ethoxide</td>
<td>143-144</td>
<td>$n_D^{25}$</td>
<td>238</td>
<td>18000</td>
<td>163-163.5C 166-77</td>
</tr>
<tr>
<td>2. Product\textsuperscript{(193)} obtained by sodium amide &amp; enamime methods</td>
<td>140-144</td>
<td>$n_D^{26}$</td>
<td>238</td>
<td>18000</td>
<td>163-163.5C 166-77</td>
</tr>
</tbody>
</table>

Robinson et al\textsuperscript{24} prepared ethyl-1-methyl-2-oxo-\textsuperscript{1:9} octalin-10-carboxylate, $b.p. 135-66^\circ C/0.2$ mm, $n_D^{16} 1.514$, semi-
carbazone recrystallized with alcohol m.p. 166-7 (prism).

A further evidence for the alkylation and acylation taking place at 1-position in ethyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate was provided by the fact that ethyl-1-methyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate (193) on hydrolysis and decarboxylate furnishes 1-methyl-2-oxo-$\Delta^{1:9}$ octalin(130). This compound was also prepared directly by three other known routes. First involving a Robinson-Mannich condensation\(^87\) of cyclohexanone and 1-(diethyl amino)-3-pentanone methiodide (10 a) followed by cyclization of the resulting 11,5-diketone

\[
\begin{align*}
\text{COOC}_2H_5 & \quad \xrightarrow{\text{i) NaOH}} \quad \xrightarrow{\text{ii) HCl}} \\
\text{CH}_3 & \quad \text{(193)} & \quad \text{(130)}
\end{align*}
\]

The second route\(^88\) involved a Reformatsky reaction between ethyl-cyclohexanone-2-$\beta$-propionate (251) and ethyl $\beta$-bromo propionate (252) followed by a treatment of the crude condensation product with aqueous alkali:
The third route for the preparation of (130) involved a condensation of cyclohexanone enamine and ethyl-vinyl ketone (16 a) followed by cyclization of the resulting \(1-(2\text{-oxo-cyclohexyl})\)-pentanone-3.

\[
\begin{align*}
(47) & \quad + \quad \text{CH}_3\text{CH}_2\text{COCH} = \text{CH}_2 \\
(16\ a) & \quad \Rightarrow \quad (130) \quad \text{CH}_3
\end{align*}
\]

The comparison of physical constants of the above products (Table No. 2) and the mixed melting points of the derivatives from the four sources showed that the product were identical and that the methyl group in these product is present at 1-position.
Physical constants of 1-methyl-2-oxo- $\Delta^{1:9}$octalin and its derivatives.

<table>
<thead>
<tr>
<th>Product (130)</th>
<th>BP $^0$</th>
<th>$n_D$</th>
<th>$\lambda_{max}$</th>
<th>$\epsilon_{max}$</th>
<th>2:4 DNP</th>
<th>SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>obtained by the hydrolysis and decarboxylation of (493).</td>
<td>124-127</td>
<td>1.521</td>
<td>249</td>
<td>log 176-77</td>
<td>2120 $^0$</td>
<td></td>
</tr>
<tr>
<td>@ 10 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Product (130)</td>
<td>140-145</td>
<td>1.523</td>
<td>25</td>
<td></td>
<td>177 $^0$</td>
<td>2120 $^0$</td>
</tr>
<tr>
<td>@ 17 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Product (130)</td>
<td>125-127</td>
<td>1.528</td>
<td>249</td>
<td>4.1</td>
<td>177 $^0$</td>
<td>2120 $^0$</td>
</tr>
<tr>
<td>@ 8 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Product (130)</td>
<td>150-55</td>
<td>1.528</td>
<td>249</td>
<td>4.1</td>
<td>177 $^0$</td>
<td>2120 $^0$</td>
</tr>
<tr>
<td>@ 18 mm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The identity authenticity and the position of the methyl group in the compound (130) has been further confirmed by comparison of its physical constants with that of 3-methyl-2-oxo- $\Delta^{1:9}$octalin (61) and 8-methyl-2-oxo- $\Delta^{1:9}$octalin (119).
Thus the above argument prove conclusively that the alkylation and acylation of ethyl-2-oxo-1:9-octalin-10-carboxylate (4) occurs exclusively at 1-position rather than at 3 or 8-positions.

It is worth mentioning here that no rearrangement was observed while using n-propyl-n-butyl and sec-butyl halides as the alkylating agents.

The physical constants of the various 1-alkylated acylated ethyl-2-oxo-1:9-octalin-10-carboxylate their corresponding ketones and derivatives have been reported in Table 6, 7, 8, 9 and 10.
The use of N-bromo succinimide as a dehydrogenating reagent and its superiority over other similar reagent is well known. Thus while dehydrogenation of cyclohexanone with other dehydrogenating reagents either failed or gave poor yield, N-bromo succinimide has been successfully used for this purpose leading to aromatized products in suitable yields. Mousern et al. have also used this reagent successfully for the dehydrogenation of cyclohex-2-one. It was therefore considered desirable to investigate the use of N-bromo succinimide as the dehydrogenation agent for ethyl-2-oxo-\(\triangle^{119}\)-octalin-10-carboxylate, its 1-alkylated/acylated derivatives and the corresponding ketones.

**REACTION WITH N-BROMOSUCINIMIDE.**

2-oxo-\(\triangle^{119}\)-octalin was treated with N-Bromosuccinimide in dried carbon tetrachloride; the reaction proceeded smoothly in the beginning but after some time it was followed with concomitant evolution of hydrogen bromide. After filtering off the succinimide the crude tri-bromo ketone was dehydrobrominated with 3 M-sodium hydroxide and sulphuric acid to give an unsaturated intermediate which being unstable passed on to the corresponding phenol (\(\beta\)-naphthol) by enolisation. The reaction is supposed to proceed as follows:
The β-naphthol was identified by its characteristic reactions and mixed melting with an authentic sample.

In another experiment 2-oxo-1-methyl-Δ¹⁻ ninhydrin on treatment with N-bromosuccinimide and subsequent dehydrobromination gave 10-methyl-2-naphthol, which was identified by its characteristic chemical reactions and by comparison with an authentic sample.
A number of other 1-alkylated 2-oxo-\( \Delta^{1:9} \) octalin (Table No. 5) were similarly converted into corresponding naphthalols and characterized (a) by their characteristic reactions (b) by comparison of their physical constants with those of the authentic compounds.

**Table No. 5**

<table>
<thead>
<tr>
<th>1-alkylated 2-oxo-( \Delta^{1:9} ) octalin</th>
<th>Corresponding 1-alkylated 2-hydroxy naphthalene</th>
<th>( B_p, N_p, d )</th>
<th>( n_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-oxo-1-methyl-( \Delta^{1:9} ) octalin</td>
<td>1-methyl hydroxy naphthalene</td>
<td>180-2/12</td>
<td>m.p.; 11-2</td>
</tr>
<tr>
<td>2-oxo-1-ethyl-( \Delta^{1:9} ) octalin</td>
<td>1-ethyl-2-hydroxy naphthalene</td>
<td>143-5/3</td>
<td></td>
</tr>
<tr>
<td>2-oxo-1-n-propyl-( \Delta^{1:9} ) octalin</td>
<td>1-propyl-2-hydroxy naphthalene</td>
<td>143-5/3</td>
<td></td>
</tr>
<tr>
<td>2-oxo-1-iso-propyl-( \Delta^{1:9} ) octalin</td>
<td>1-iso-propyl-2-hydroxy naphthalene</td>
<td>143-5/3</td>
<td></td>
</tr>
<tr>
<td>2-oxo-1-n-butyl-( \Delta^{1:9} ) octalin</td>
<td>1-n-butyl-2-hydroxy naphthalene</td>
<td>180-2/12</td>
<td>m.p.; 80-1</td>
</tr>
<tr>
<td>2-oxo-1-tert-butyl-( \Delta^{1:9} ) octalin</td>
<td>1-tert-butyl-2-hydroxy naphthalene</td>
<td>180-2/12</td>
<td>m.p.; 66-7</td>
</tr>
<tr>
<td>2-oxo-1-allyl-( \Delta^{1:9} ) octalin</td>
<td>1-allyl-2-hydroxy naphthalene</td>
<td>177-3/12</td>
<td>m.p.; 55-6</td>
</tr>
</tbody>
</table>

\( n_D = 26.1, 6.7 \)
<table>
<thead>
<tr>
<th>Name of the Compound</th>
<th>Method of Preparation</th>
<th>Boiling point</th>
<th>Refractive Index</th>
<th>max</th>
<th>max</th>
<th>2:4 DNP</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethyl-2-oxo-1-methyl-10-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△8-octalin-10-carboxylate</td>
<td>a) Sodium ethoxide</td>
<td>143-9°C @ 2 mm</td>
<td>nD 1.512</td>
<td>238</td>
<td>18000</td>
<td>167-8°C</td>
<td>52.1%</td>
</tr>
<tr>
<td></td>
<td>b) sodium amide</td>
<td>142-46°C @ 2 mm</td>
<td>1.512</td>
<td>238</td>
<td>18000</td>
<td>157-8°C</td>
<td>54%</td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>155-36°C @ 0.5-1 mm</td>
<td>1/512</td>
<td>238</td>
<td>18000</td>
<td>5C 166-7°C</td>
<td>49%</td>
</tr>
<tr>
<td>Ethyl-2-oxo-1-ethyl △9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-octalin-10-carboxylate</td>
<td>a) Sodium ethoxide</td>
<td>147-5°C @ 2-3 mm</td>
<td>nD 1.527</td>
<td>235</td>
<td>18300</td>
<td>159-60°C</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td>146-50°C @ 2 mm</td>
<td>1.527</td>
<td>235</td>
<td>18300</td>
<td>160°C</td>
<td>52%</td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>170-71°C @ 2.5 mm</td>
<td>nD 1.527</td>
<td>238</td>
<td>18500</td>
<td>169-70°C</td>
<td>53%</td>
</tr>
<tr>
<td>Ethyl-2-oxo-1-n-propyl-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△9-octalin-10-carboxylate</td>
<td>a) Sodium ethoxide</td>
<td>172-4°C @ 3 mm</td>
<td>nD 1.521</td>
<td>234</td>
<td>18500</td>
<td>169-70°C</td>
<td>48-51%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td>172-75°C @ 2 mm</td>
<td>nD 1.520</td>
<td>238</td>
<td>18500</td>
<td>169-70°C</td>
<td>42-44%</td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>170-71°C @ 2.5 mm</td>
<td>nD 1.527</td>
<td>238</td>
<td>18500</td>
<td>169-70°C</td>
<td>53%</td>
</tr>
<tr>
<td>Ethyl-2-oxo-1-iso-propyl-</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△9-octalin-10-carboxylate</td>
<td>a) Sodium ethoxide</td>
<td>178-81°C @ 2 mm</td>
<td>nD 1.530</td>
<td>230</td>
<td>10000</td>
<td>142-144°C</td>
<td>50-51%</td>
</tr>
<tr>
<td></td>
<td>b) enamine</td>
<td>182-83°C @ 2.5 mm</td>
<td>nD 1.532</td>
<td>230</td>
<td>10000</td>
<td>142-144°C</td>
<td>49%</td>
</tr>
<tr>
<td>Ethyl-2-oxo-1-n-butyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>△9-octalin-10-carboxylate</td>
<td>a) Sodium ethoxide</td>
<td>192-95°C @ 3.4 mm</td>
<td>nD 1.537</td>
<td>237+1</td>
<td>19500</td>
<td>191-2°C</td>
<td>49%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td>189-3°C @ 3 mm</td>
<td>nD 1.537</td>
<td>237+1</td>
<td>19500</td>
<td>191-2°C</td>
<td>4-41%</td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>184-86°C @ 2.5 mm</td>
<td>nD 1.532</td>
<td>--</td>
<td>--</td>
<td>144-45°C</td>
<td>28%</td>
</tr>
<tr>
<td>Ethyl-2-oxo-1-tert-butyl</td>
<td>a) Sodium ethoxide</td>
<td>178-81°C @ 2.5-3 mm</td>
<td>nD 1.532</td>
<td>--</td>
<td>--</td>
<td>144-45°C</td>
<td>34%</td>
</tr>
<tr>
<td></td>
<td>b) sodium amide</td>
<td>184-86°C @ 2.5 mm</td>
<td>nD 1.532</td>
<td>--</td>
<td>--</td>
<td>144-45°C</td>
<td>34%</td>
</tr>
<tr>
<td>Name of the Compound</td>
<td>Method of Preparation</td>
<td>Boiling Point °C/mm</td>
<td>Refractive Index</td>
<td>max</td>
<td>max</td>
<td>2:4 DNP m.p. °C</td>
<td>Yield</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------</td>
<td>---------------------</td>
<td>-----------------</td>
<td>-----</td>
<td>-----</td>
<td>----------------</td>
<td>-------</td>
</tr>
<tr>
<td>7. Ethyl-2-oxo-1-acetyl-(\Delta^{1:9}) octalin-10-carboxylate.</td>
<td>a) Sodium ethoxide</td>
<td>188-93 °C/2</td>
<td>(n_D^{26}) 1.528</td>
<td>235</td>
<td>19500</td>
<td>160-61</td>
<td>47%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>192-05 °C/4</td>
<td>(n_D^{26}) 1.528</td>
<td>235</td>
<td>19500</td>
<td>160.5</td>
<td>42-44%</td>
</tr>
<tr>
<td>8. Ethyl-2-oxo-1-propionyl-(\Delta^{1:9}) octalin-10-carboxylate.</td>
<td>a) Sodium ethoxide</td>
<td>191-93 °C/1.5</td>
<td>(n_D^{25}) 1.524</td>
<td>238</td>
<td>21500</td>
<td>160-61</td>
<td>47-48%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>204-205 °C/2</td>
<td>(n_D^{27}) 1.529</td>
<td>238</td>
<td>21500</td>
<td>160-61</td>
<td>58%</td>
</tr>
<tr>
<td>9. Ethyl-2-oxo-1-benzoyl-(\Delta^{1:9}) octalin-10-carboxylate.</td>
<td>a) Sodium ethoxide</td>
<td>210-211 °C/4</td>
<td>(n_D^{25}) 1.549</td>
<td>241</td>
<td>22300</td>
<td>183.4</td>
<td>68%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>180-4 °C/5</td>
<td>(n_D^{25}) 1.549</td>
<td>241</td>
<td>22300</td>
<td>183.4</td>
<td>68%</td>
</tr>
<tr>
<td>10. Ethyl-2-oxo-1-cinnamoyl-(\Delta^{1:9}) octalin-10-carboxylate.</td>
<td>a) Sodium ethoxide</td>
<td>200-4 °C/</td>
<td>(n_D^{25}) 1.553</td>
<td>-</td>
<td>-</td>
<td>194.0</td>
<td>55-56%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td>2-3.5.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>199-200 °C/1</td>
<td>(n_D^{25}) 1.552</td>
<td>-</td>
<td>-</td>
<td>194.5</td>
<td>51-52%</td>
</tr>
<tr>
<td>11. Ethyl-2-oxo-1-allyl-(\Delta^{1:9}) octalin-10-carboxylate.</td>
<td>a) Sodium ethoxide</td>
<td>193-4 °C/3</td>
<td>(n_D^{28}) 1.530</td>
<td>247</td>
<td>22000</td>
<td>179.0</td>
<td>25-30%</td>
</tr>
<tr>
<td></td>
<td>b) Sodium amide</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>c) enamine</td>
<td>182-84 °C/1</td>
<td>(n_D^{26}) 1.533</td>
<td>247</td>
<td>22000</td>
<td>170.80</td>
<td>68%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>195-7 °C/2.5</td>
<td>(n_D^{26}) 1.533</td>
<td>247</td>
<td>22000</td>
<td>170.80</td>
<td>55%</td>
</tr>
</tbody>
</table>
TABLE No. 7

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>Boiling Point C/mm</th>
<th>Refractive Index</th>
<th>2:4 DNP m.p. C</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 2-oxo-1-methyl-(\Delta^{1:9})-octalin</td>
<td>124-5°C/10</td>
<td>(n_D^{25}) 1.523</td>
<td>162-4</td>
<td>45</td>
</tr>
<tr>
<td>2. 2-oxo-1-ethyl-(\Delta^{1:9})-octalin</td>
<td>165-75°C/12</td>
<td>(n_D^{28}) 1.520</td>
<td>162.4</td>
<td>43</td>
</tr>
<tr>
<td>3. 2-oxo-1-n-propyl-(\Delta^{1:9})-octalin</td>
<td>164-6°C/10</td>
<td>(n_D^{29})</td>
<td>179-80</td>
<td>43-50%</td>
</tr>
<tr>
<td>4. 2-oxo-1-iso-propyl-(\Delta^{1:9})-octalin</td>
<td>168-71°C/4</td>
<td>(n_D^{25}) 1.542</td>
<td>162-4</td>
<td>45</td>
</tr>
<tr>
<td>5. 2-oxo-1-nebutyl-(\Delta^{1:9})-octalin</td>
<td>168-71°C/10</td>
<td>(n_D^{27}) 1.538</td>
<td>201</td>
<td>54</td>
</tr>
<tr>
<td>6. 2-oxo-1-sec-butyl-(\Delta^{1:9})-octalin</td>
<td>159-70°C/15</td>
<td>(n_D^{27}) 1.540</td>
<td>241</td>
<td>53</td>
</tr>
<tr>
<td>7. 2-oxo-1-tert-butyl-(\Delta^{1:9})-octalin</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. 2-oxo-1-allyl-(\Delta^{1:9})-octalin</td>
<td>182-3°C/5</td>
<td>(n_D^{27}) 1.543</td>
<td>135-6</td>
<td>58</td>
</tr>
<tr>
<td>9. 2-oxo-1-acetyl-(\Delta^{1:9})-octalin</td>
<td>186-91°C/109</td>
<td>(n_D^{26}) 1.513</td>
<td>162-1</td>
<td>52</td>
</tr>
<tr>
<td>10. 2-oxo-1-propionyl-(\Delta^{1:9})-octalin</td>
<td>188-90°C/5</td>
<td>(n_D^{25}) 1.530</td>
<td>171-3</td>
<td>48</td>
</tr>
<tr>
<td>11. 2-oxo-1-benzoyl-(\Delta^{1:9})-octalin</td>
<td>182-4°C/10</td>
<td>(n_D^{26}) 1.541</td>
<td>148-9</td>
<td>50</td>
</tr>
<tr>
<td>12. 2-oxo-1-cinnamoyl-(\Delta^{1:9})-octalin</td>
<td>188-9°C/10</td>
<td>(n_D^{27}) 1.543</td>
<td>157-8</td>
<td>40</td>
</tr>
<tr>
<td>Name of the compound</td>
<td>Method of preparation</td>
<td>Boiling Point °C/mm</td>
<td>Refractive Index</td>
<td>2:1 DNP m.p. °C</td>
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<tr>
<td>-------------------------------------------------------------------------------------</td>
<td>-----------------------</td>
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</tr>
<tr>
<td>1. Ethyl-2-oxo-1-2'-nitrophenyl $\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Enamine</td>
<td>175-9°C/1.5</td>
<td>26 $n_D$ 1.531</td>
<td>198-5°C</td>
</tr>
<tr>
<td>2. Ethyl-2-oxo-1-(4'-nitro)phenyl $\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Enamine</td>
<td>175-81°C/1.5</td>
<td>25 $n_D$ 1.538</td>
<td>216°C</td>
</tr>
<tr>
<td>3. Ethyl-2-oxo-1-(2'-hydroxy)phenyl $\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Sodium ethoxide</td>
<td>168-76°C/1</td>
<td>27 $n_D$ 1.549</td>
<td>159.5°C</td>
</tr>
<tr>
<td>4. Ethyl-2-oxo-1-naphthyl $\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Enamine</td>
<td>170-80°C/3</td>
<td>26 $n_D$ 1.543</td>
<td>159.5°C</td>
</tr>
<tr>
<td>5. Ethyl-2-1-(2'-chloro)phenyl $\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Sodium ethoxide</td>
<td>196-8°C/4</td>
<td>26 $n_D$ 1.539</td>
<td>195-6°C</td>
</tr>
<tr>
<td>7. Ethyl-2-oxo-1-benzyl-$\Delta^{1:9}$-octaline-10-carboxylate.</td>
<td>Sodium ethoxide</td>
<td>156-61°C/1</td>
<td>26 $n_D$ 1.538</td>
<td>203.0°C</td>
</tr>
<tr>
<td>NAME OF THE COMPOUND</td>
<td>Method of Preparation</td>
<td>Boiling Point C/mm</td>
<td>Refractive Index</td>
<td>2:4 DHP m.p. C</td>
</tr>
<tr>
<td>----------------------</td>
<td>-----------------------</td>
<td>-------------------</td>
<td>-----------------</td>
<td>--------------</td>
</tr>
<tr>
<td>1. Ethyl-2-oxo-1-n-butyryl-(\Delta^{1:9})-octalin-10-carboxylate.</td>
<td>Sodium ethoxide Enamine</td>
<td>181-89°C/2</td>
<td>(n_D^{26}) 1.540</td>
<td>197-8°C</td>
</tr>
<tr>
<td>2. Ethyl-2-oxo-1-Iso-butyryl-(\Delta^{1:9})-octalin-10-carboxylate</td>
<td>Sodium ethoxide Enamine</td>
<td>185-6°C/2-5</td>
<td>(n_D^{25}) 1.542</td>
<td>138-9°C</td>
</tr>
<tr>
<td>3. Ethyl-2-oxo-1-n-valeryl-(\Delta^{1:9})-octalin-10-carboxylate.</td>
<td>Sodium ethoxide Enamine</td>
<td>186-8°C/2</td>
<td>(n_D^{26}) 1.561</td>
<td>147-8°C</td>
</tr>
<tr>
<td>4. Ethyl-2-oxo-1-glutaryl-(\Delta^{1:9})-octalin-10-carboxylate.</td>
<td>Sodium ethoxide Enamine</td>
<td>178-80°C/1</td>
<td>(n_D^{25}) 1.543</td>
<td>164-6°C</td>
</tr>
<tr>
<td>5. Ethyl-2-oxo-1-Iso-valeryl-(\Delta^{1:9})-octalin-10-carboxylate</td>
<td>Sodium ethoxide Enamine</td>
<td>182-91°C/2</td>
<td>(n_D^{26}) 1.544</td>
<td>164.5</td>
</tr>
<tr>
<td>6. Ethyl-2-oxo-1-succinyl-(\Delta^{1:9})-octalin-10-carboxylate.</td>
<td>Sodium ethoxide Enamine</td>
<td>178-82°C/2</td>
<td>(n_D^{25}) 1.562</td>
<td>163.8°C</td>
</tr>
<tr>
<td>7. Ethyl-2-oxo-1-p-nitrobenzoyl-(\Delta^{1:9})-octalin-10-carboxylate</td>
<td>Sodium ethoxide Enamine</td>
<td>192-4°C/2</td>
<td>(n_D^{25}) 1.562</td>
<td>148-9</td>
</tr>
<tr>
<td>8. Ethyl-2-oxo-1-Iso-phthalyl(\Delta^{119})-octalin-10-carboxylate</td>
<td>Sodium ethoxide Enamine</td>
<td>178-2°C/0.5</td>
<td>(n_D^{29}) 1.538</td>
<td>148-9</td>
</tr>
<tr>
<td>Name of the Compound</td>
<td>TABLE NO. 10</td>
<td>Boiling point C/mm</td>
<td>Refractive Index</td>
<td>2:4 DNP m.p. °C</td>
</tr>
<tr>
<td>----------------------</td>
<td>--------------</td>
<td>--------------------</td>
<td>------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>1.2-oxo-1-(2′-nitro)phenyl-Δ1:9-octalin.</td>
<td></td>
<td>168°C/10 mm</td>
<td>$n_D^{25}$ 1.544</td>
<td>141-2°C</td>
</tr>
<tr>
<td>2.2-oxo-1-(4′-nitro)phenyl-Δ1:9-octalin.</td>
<td></td>
<td>162-4/8</td>
<td>$n_D^{25}$ 1.541</td>
<td>191-3°C</td>
</tr>
<tr>
<td>3.2-oxo-1-(2′hydroxy)phenyl-Δ1:9-octalin.</td>
<td></td>
<td>163-4/6</td>
<td>$n_D^{27}$ 1.538</td>
<td></td>
</tr>
<tr>
<td>4.2-oxo-1-(2′chloro)phenyl-Δ1:9-octalin.</td>
<td></td>
<td>178-9/10</td>
<td>$n_D^{26}$ 1.548</td>
<td>200-2°C</td>
</tr>
<tr>
<td>5.2-oxo-1-benzyl-Δ1:9-octalin</td>
<td></td>
<td>142-4/10</td>
<td>$n_D^{26}$ 1.521</td>
<td>181-2°C</td>
</tr>
<tr>
<td>6.2-oxo-1-isopropyl-Δ1:9-octalin</td>
<td></td>
<td>153-8/8</td>
<td>$n_D^{25}$ 1.523</td>
<td>214-15°C</td>
</tr>
<tr>
<td>7.2-oxo-4-naphthyl-Δ1:9-octalin</td>
<td></td>
<td>183-1/10</td>
<td>$n_D^{25}$ 1.532</td>
<td>163-4°C</td>
</tr>
<tr>
<td>8.2-oxo-1-n-butyryl-Δ1:9-octalin</td>
<td></td>
<td>183-4/13</td>
<td>$n_D^{25}$ 1.530</td>
<td>138-9°C</td>
</tr>
<tr>
<td>9.2-oxo-1-iso-butyryl-Δ1:9-octalin</td>
<td></td>
<td>178-80/14</td>
<td>$n_D^{26}$ 1.531</td>
<td>145-4°C</td>
</tr>
<tr>
<td>10.2-oxo-1-n-valeryl-Δ1:9-octalin</td>
<td></td>
<td>175-81/12</td>
<td>$n_D^{27}$ 1.558</td>
<td></td>
</tr>
<tr>
<td>11.2-oxo-1-iso-valeryl-Δ1:9-octalin</td>
<td></td>
<td>167-71/3</td>
<td></td>
<td>158-60°C</td>
</tr>
<tr>
<td>12.2-oxo-1-glutaryl-Δ1:9-octalin</td>
<td></td>
<td>168-9/10</td>
<td>$n_D^{27}$ 1.529</td>
<td>174-5°C</td>
</tr>
<tr>
<td>13.2-oxo-1-succinyl-Δ1:9-octalin</td>
<td></td>
<td>181-6/5</td>
<td>$n_D^{27}$</td>
<td>156-7°C</td>
</tr>
<tr>
<td>14.2-oxo-1-p-nitrobenzoyl-Δ1:9-octalin</td>
<td></td>
<td>192-3/5</td>
<td>viscos</td>
<td>179.80°C</td>
</tr>
<tr>
<td>15.2-oxo-1-iso-phthalyl-Δ1:9-octalin</td>
<td></td>
<td>181-5/4-6</td>
<td>$n_D^{27}$ 1.543</td>
<td>210-1°C</td>
</tr>
</tbody>
</table>
Diethyl-2-oxo-2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene-3:4 dicarboxylate (278).

The synthesis of this compound involves the preparation of the intermediate ethyl-2-oxo-1-(3'-keto butyl-2-ethylcarboxylate) - $\Delta^{1:9}$ octalin-10-carboxylate followed by its cyclisation:

Ethyl-2-oxo-1-(3'-keto butyl-2-ethylcarboxylate)

$\Delta^{1:9}$ octalin-10-carboxylate (267).

Ethyl-2-oxo-1-(3'-keto butyl-2-ethyl-carboxylate)

$\Delta^{1:9}$ octalin-10-carboxylate has been prepared by two different routes. Each of these routes involved Mannich reaction.

1. Ethyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate (4) was converted into its enamine (163) and the latter on condensation with a mixture of diethylamine and paraformaldehyde gave ethyl, 1-methyl (N-diethyl amino)-2-N-pyrrolidyl octalin-10-carboxylate (265). This was converted into its methiodide (264) which was immediately used for the preparation of tricyclic compound. The enamine is such that B-carbon atom bears an appreciable negative charge and may serve as a nucleophile while the reactive carbonyl group is blocked.

![Chemical structures](image-url)
The use of making enamine of β-keto ester, was to avoid the polycondensations of (iminium salt) methyl (N-diethyl amino) ion \( \text{H}_2\text{C} = \text{N} (\text{C}_2\text{H}_5)^2 \) to other active centres of the above β-keto ester. This ensures that the main reaction will be predominant at the more highly substituted position.
The sodium enolate of ethyl acetoacetate was prepared by heating the keto ester and sodium in equimolar ratio in benzene/absolute ethyl alcohol. The mixture was cooled and refluxed with ethyl-1-methyl (N-diethyl amino)-2-pyrrolidyl \( \Delta^{1:9} \) octalin-10-carboxylate methiodide (264) for fifteen hours, giving ethyl-2-oxo-1-(3'-ketoetyl-2-ethyl carboxylate) \( \Delta^{1:9} \) octalin-10-carboxylate in 80% yield b.p. 160-166°C/7 mm. The following mechanism has been suggested:

\[
\begin{align*}
\text{COOC}_2\text{H}_5 & \quad \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{COOC}_2\text{H}_5 \\
\text{NaC}_2\text{H}_5 & \quad \text{Reflux} \\
\end{align*}
\]

The second method for the preparation of ethyl-1-methyl \( \Delta^{1:9} \) (N-diethylamino-2-oxo)octalin-10-carboxylate (270) involved the condensation of active methylene compound i.e. ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (4) with diethyl amine and paraformaldehyde. The reaction is believed to involve
electrophilic attack by an iminium salt on the enol of the active methylene compound.

\[
\begin{align*}
(C_2H_5)_2NH + CH_2O & \xrightarrow{H^+} [ (C_2H_5)_2N = CH_2 \rightleftharpoons (C_2H_5)_2N^+CH_2] \\
\end{align*}
\]

\[
\begin{align*}
(C_2H_5)_2NH - CH_2 - N(C_2H_5)_2 \\
(268) \\
\end{align*}
\]

\[
\begin{align*}
(C_2H_5)_2NH - CH_2 - N(C_2H_5)_2 \\
(269) \\
\end{align*}
\]

Ethyl, 1-methyl-(N-diethyl amino)-2-oxo- \(\Delta^{1:2}\) octalin-10-carboxylate was converted into its methiodide, and the latter was used directly for the preparation of tricyclo 3 diketo-ester (267')

\[
\begin{align*}
\text{CH}_3\text{I} + \text{CH}_2 = \text{N} - (C_2H_5)_2 & \xrightarrow{\text{NaCC}_2H_5 / C_2H_5OH \ \text{Reflex}} \text{CH}_3\text{C-CH}_2 - \text{COOC}_2H_5 \\
(270) & \xrightarrow{\text{CH}_3\text{C-CH}_2 - \text{COOC}_2H_5} \text{CH}_2 = \text{N} - (C_2H_5)_2 \\
(271) & \xrightarrow{\text{CH}_3\text{C-CH}_2 - \text{COOC}_2H_5} \text{CH}_2 = \text{N} - (C_2H_5)_2 \\
(267) & \xrightarrow{\text{CH}_3\text{C-CH}_2 - \text{COOC}_2H_5} \text{CH}_2 = \text{N} - (C_2H_5)_2 \\
\end{align*}
\]
Cyclization of ethyl-2-oxo-1-(3'-keto butyl-2-ethyl carboxylate) $\Delta^{1:9}$ octaline-10-carboxylate into diethyl-2-oxo-2,3,4,5,6,7,8,9,10,14-decahydro phenthrene 3:14 dicarboxylate:

Reflexing of the ester (267) with a mixture of acetic acid and hydrochloric acid (5:1 by volume) under nitrogen for 16 hours, followed by dilution of the reaction mixture and extraction with benzene gave the tricyclic keto β-ester (273) in 50% yield b.p. 195-201°C / 2 mm $n_D^{25}$ 1.534; Following mechanism has been suggested for the above reaction.
\[ -108 - \]

\[ \text{H}^+ \]

\[ \text{H}_2\text{O} \]

[Equation 276]

[Equation 277]

[Equation 278]

[Equation 279]

\text{Boil Hydrolysis and Decarboxylation}
The alkylation and acylation of Diethyl-2-oxo-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene-3:14-dicarboxylate (270) were accomplished by the enamine method. The carbonyl group at 2-position in the tricyclic β-keto ester was blocked by the introduction of a removable substituent e.g. pyrrolidine, which prevents the formation of the corresponding enolate the ethylenic double bond at 1:11 position changing their position, due to the conversion of carbonyl group into the enamine, resulting into the resonance stabilized anion (236-282) which undergoes kinetically controlled alkylation or acylation giving the mono alkyl or acyl derivatives at the α-position.

The reactions were carried out by refluxing the pyrrolidine enamine of tricyclic β-keto ester in benzene or toluene with slight excess of suitable alkyl or acyl enamine derivatives for 10-15 hours. The α-substituted derivatives were stirred at room temperature. Finally the tricyclic-β-keto ester derivatives (282) were isolated under vacuum in 40-50 % yields, as high boiling reddish yellow liquids. The infrared absorption spectra show the characteristic frequencies of the groups present in these compounds.

The α-Substituted acyl and alkyl derivative when refluxed with ethanolic sodium hydroxide for 6-8 hours, followed by the acidification with hydrochloric acid gave the free keto acid, which on brief refluxing underwent decarboxylation to the ketones (289) in 40-50 % yield as sweet smelling yellow coloured liquids. The infrared spectrums shows characteristic frequencies which are in conformity.
with the group present in the compounds. Following mechanism has been suggested for the alkylation and acylation.
(284) \[ \text{HCl} \rightarrow \text{Reflux on a water bath with stirring.} \]

(285) \[ \rightarrow \text{NaOH/CH}_3\text{CO}_2\text{H} \rightarrow \text{Aq.HCl reflux (2 steps)} \]

(286) (287) (288) (289)
It is thus concluded that ethyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate reacts with alkyl and acyl halides giving a variety of 1-substituted keto-esters which can be hydrolysed and decarboxylated into the corresponding ketones. These in turn can easily be dehydrobrominated with N-bromo succinimide to the corresponding aromatic compounds.

Further ethyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate reacts with diethylamine and paraformaldehyde to yield ethyl-1-methyl(N-diethyl amino)-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate (263). Its methiodide (264 & 271) reacts with sodio derivative of ethyl acetoacetate to give ethyl-2-oxo-1-(3'-keto butyl-2-ethyl carboxylate) $\Delta^{1:9}$ octalin-10-carboxylate (267). This compound was also prepared from ethyl-2-oxo-$\Delta^{1:9}$ octalin-10-carboxylate by the enamino method. Ethyl-2-oxo-1-(3'-keto butyl-2'-ethyl carboxylate)-$\Delta^{1:9}$ octalin-10-carboxylate (267) on cyclization yields diethyl-2-oxo-3,4,5,6,7,8,9,10-octa-decachydro phenanthrene-3:14 dicarboxylate (278) which on hydrolysis and decarboxylation gave 2-oxo-3,4,5,6,7,8,9,10-14-decachydrophenanthrene (279). This $\alpha\beta$-unsaturated tricyclic keto ester reacts with alkyl and acyl halides giving a variety of 1-substituted keto esters which on hydrolysis and decarboxylation was converted into the corresponding $\alpha\beta$-unsaturated tricyclic ketones.

It is expected that these $\alpha\beta$-unsaturated tricyclic ketones can be dehydrobrominated to the corresponding phenanthrene derivatives.
<table>
<thead>
<tr>
<th>R = alkyl &amp; acyl</th>
<th>Boiling Point</th>
<th>Refractive index.</th>
<th>Semi Carbazones</th>
<th>Yield.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Methyl</td>
<td>207-9°C @ 3 mm</td>
<td>n_D 1.543</td>
<td>213-14°C</td>
<td>33-39%</td>
</tr>
<tr>
<td>2. Ethyl</td>
<td>203-4°C @</td>
<td>n_D 1.561</td>
<td>241-2°C</td>
<td>43%.</td>
</tr>
<tr>
<td>3. n-propyl</td>
<td>213-15°C @ 3-4 mm</td>
<td>n_D 1.549</td>
<td>227-9°C (dec)</td>
<td>44%.</td>
</tr>
<tr>
<td>4. n-butyl</td>
<td>216-17°C @ 3 mm</td>
<td>n_D 1.540</td>
<td>235-36°C</td>
<td>53%.</td>
</tr>
<tr>
<td>5. sec-butyl</td>
<td>217-21°C @ 2.5 mm</td>
<td>n_D 1.546</td>
<td></td>
<td>53-4%.</td>
</tr>
<tr>
<td>6. tert-butyl</td>
<td>230-2°C @ 6 mm</td>
<td>n_D 1.551</td>
<td>221-3°C</td>
<td>52%.</td>
</tr>
<tr>
<td>7. n-butyl</td>
<td>203-7°C @ 2 mm</td>
<td>n_D 1.572</td>
<td>197-198°C</td>
<td>65%.</td>
</tr>
<tr>
<td>8. iso-butyl</td>
<td>201-2°C @ 2-3 mm</td>
<td>n_D 1.567</td>
<td>202-5°C</td>
<td>55-8%.</td>
</tr>
<tr>
<td>9. n-valeryl</td>
<td>212-16°C @ 6-8 mm</td>
<td>n_D 1.563</td>
<td>216-17°C</td>
<td>46%.</td>
</tr>
<tr>
<td>10. iso-valeryl</td>
<td>218-25°C @ 4-5 mm</td>
<td>n_D 1.563</td>
<td>201-2°C</td>
<td>60-61%.</td>
</tr>
<tr>
<td>11. Cinnamoyl</td>
<td>213-24°C @ 2-3 mm</td>
<td>semi solid</td>
<td>238-9°C</td>
<td>48-51%.</td>
</tr>
<tr>
<td>12. isophthalyl</td>
<td>215-9°C @ 0.5-1 mm</td>
<td>semi solid</td>
<td></td>
<td>56-58%.</td>
</tr>
<tr>
<td>Residue (alkyl &amp; acyl)</td>
<td>Boiling Point</td>
<td>Refractive index</td>
<td>Semi carbazones</td>
<td>Yields</td>
</tr>
<tr>
<td>------------------------</td>
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<td>--------</td>
</tr>
<tr>
<td>methyl</td>
<td>201°C @ 7-8 mm</td>
<td>n_p^26 1.553</td>
<td>194-195°C</td>
<td>43 %</td>
</tr>
<tr>
<td>ethyl</td>
<td>195-7°C @ 7 mm</td>
<td>n_p^26 1.566</td>
<td>203-203.5°C</td>
<td></td>
</tr>
<tr>
<td>n-propyl</td>
<td>206-7°C @ 7-8 mm</td>
<td>n_p^27 1.559</td>
<td>209-11°C(decc)</td>
<td>55 %</td>
</tr>
<tr>
<td>n-butyl</td>
<td>204-6°C @ 4-6 mm</td>
<td>n_p^26 1.561</td>
<td>183°C</td>
<td>57 %</td>
</tr>
<tr>
<td>sec-butyl</td>
<td>214-15°C @ 9-10 mm</td>
<td>n_p^26 1.563</td>
<td>194-5°C</td>
<td></td>
</tr>
<tr>
<td>tert-butyl</td>
<td>198-04°C @ 3-4 mm</td>
<td>n_p^27 1.561</td>
<td>177°C</td>
<td>49 %</td>
</tr>
<tr>
<td>n-butyryl</td>
<td>218-22°C @ 15-8 mm</td>
<td>n_p^26 1.557</td>
<td>219-20°C</td>
<td>64 %</td>
</tr>
<tr>
<td>iso-butyryl</td>
<td>213-22°C @ 18-10 mm</td>
<td>n_p^26 1.562</td>
<td>189°C</td>
<td>66 %</td>
</tr>
<tr>
<td>n-valeryl</td>
<td>230-35°C @ 10 mm</td>
<td>n_p^26 1.547</td>
<td>194°C</td>
<td>66-7 %</td>
</tr>
<tr>
<td>iso-valeryl</td>
<td>218-24°C @ 5-6 mm</td>
<td>n_p^27 1.540</td>
<td>163-4°C</td>
<td>62° %</td>
</tr>
<tr>
<td>cinnamyl</td>
<td>235-8°C @ 2-3 mm</td>
<td>semi solid</td>
<td>236-7°C</td>
<td>61-3 %</td>
</tr>
<tr>
<td>isophthalyl</td>
<td>241-5°C @ 6-8 mm</td>
<td>semi solid</td>
<td></td>
<td>45-8 %</td>
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</table>
Experimental Memoranda:

1. Melting points were determined on a Kofler micro heating stage.

2. Infra-red absorption spectra were recorded with a Perkin-Elmer spectro-photometer, Infrared No. 137 using sodium chloride plates.

3. The Ultra-Violet absorption measurement were made in Iso-propanol using a Beckman-Spectrophotometer.

4. Microanalysis were carried out by Mikro analytisches laboratorium, 5251, Elbachuber Engelskirchen, Fritz Pregl-Strabe 1416 West Germany, microanalytical staff of Reading University, (U.K) and microanalytical staff of the Queen Elizabeth College, London (England).
EXPERIMENTAL

2-Carbethoxy-cyclohexanone (14)

Method 1

The morpholine-enamine of cyclohexanone (160.7 gm; 1.1 mole) and diethyl aniline (160.4 gm; 1.11 mole) were dissolved in 1.0-litre of dry chloroform, while the system was kept under nitrogen atmosphere, ethyl chloroformate (70.2 gm; 101.66 mole) was added and the mixture refluxed for 14 hours. The resulting solution was then transferred to a separating funnel. 30 ml of conc. hydrochloric acid and 350 ml of water was added. The mixture was shaken at intervals over a period of 15-30 minutes. The chloroform layer was separated from the aqueous layer and washed successively with 4 x 25 ml portions of 10% aqueous hydrochloric acid finally with water. These washings were mixed with the aqueous layer (mentioned earlier and the mixture was extracted with benzene (3 x 100 ml portions). The benzene extract and chloroform layer (mentioned earlier) were combined and dried. The solution was filtered and the solvent was distilled off. Fractionation of the residue gave 94.7 gm. of the above product, b.p. 110-112°C at 10 mm, yield 63% nD²⁵ 1.456 L.R. absorption, 3000, 1760-1750, 1470-1450, 1330-1320, 1275-1260, 1210, 985 and 745-720 cm⁻¹.
A 2:4 dinitrophenyl hydrazone was prepared and twice recrystallized from ethanol m.p.; 154-155°C.

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2-Carbethoxy-cyclohexanone (14).

Method 2. To a solution of (20.0 gm; 0.12 mole) of morpholine enamine of cyclohexanone in 400 ml of dry benzene, ethyl chloroformate (9.2 gm; 0.6 mole) was added under nitrogen, while the enamine solution was being stirred rapidly. After refluxing for about ten hours, the solution was cooled and filtered. The precipitates of enamine hydrochloride were washed with ether. The combined filtrate and washing were returned to the reaction flask. 22 ml. of 10% aqueous hydrochloric acid was added and the mixture was stirred vigorously for 15-30 minutes. The organic layer was separated, and the aqueous layer was extracted with benzene. The combined organic layer and the extracts were distilled at atmospheric pressure to remove the solvent. Fractionation of the residue gave 60.2 gm of the above product, b.p.; 112-115°C at 10 mm. yield 62% nD 26 1.456. The infrared spectrum of this product was identical with the product obtained by the method (1).

A 2:4 dinitrophenyl hydrazone was prepared and recrystallized from a mixture of aqueous alcohol and ethyl acetate m.p.; 154-155°C.
2-Carbethoxy cyclohexanone

A solution of sodium ethoxide was prepared by the addition of (46.00 gm, 2.0 gm atom) of sodium to 600 ml of absolute ethyl alcohol. The solution was cooled to 10 °C and to this was added dropwise an ice-cold solution of freshly distilled cyclohexanone (196.0 gm; 2.0 mole) in ethyl-exalate (292.0 gm, 2.0 mole) over a period of about 15 minutes. The mixture was stirred at room temperature for six hours.

The reaction mixture was then decomposed by the careful addition of ice-cold dilute sulphuric acid (50.00 ml; of conc. sulphuric acid in 450–450 gm of ice). During the neutralisation, the temperature of the mixture was maintained at 5–10 °C. The solution was diluted with cold water to a volume of four litres, ethyl-2-keto cyclohexylglyoxalate separated as a heavy oil, and was removed. The aqueous solution was extracted with benzene (5 x 100 ml portions). The benzene solution was dried, and the solvent was distilled off, the residue was distilled and the fraction obtained between 105–175 °C at 10 mm was collected. The yield was 260 gms (i.e. 67% of the theoretical amount).

The above distillate was transferred to a 500 ml claisen flask, and poured few grams of iron-oxide along with fine ground glass pieces. The mixture when distilled under vacuum gave 200 gm of the above product, b.p. 110–112 °C at 10 mm, yield 59% n_D^25 = 1.456

The infrared spectrum of this compound was identical with that of authentic 2-carbethoxy-cyclohexanone, and prepared by method (i) and (ii).
2:4 dinitrophenyl hydrazone derivative of the above product was prepared and recrystallised from ethanol, m.p. 154-154.5 °C.

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1-Dimethylamino-3-butanone (1c).

In a three litre-round bottomed flask equipped with a condenser was placed dimethylamine-hydrochloride (261.0 gm, 3.2 mole) paraformaldehyde (136.0 gm, 4.5 mole) acetone (1200 ml, 16.40 mole) 80 ml of methanol and 2 ml of conc. hydrochloric acid. The mixture was refluxed for 12 hours, at a moderate to a vigorous rate of reflux. The light yellow solution in which a small amount of gelatinous solid enamine was cooled, and a cold solution of 140 gm, of sodium hydroxide, 450-500 mls of water was added. The mixture was extracted with ether (3 x 100 ml portions).

The combined ethereal solution was dried and filtered, the solvent was distilled off. The residue was then distilled under vacuum to give 180-185 gm of the above product, b.p. 44-47 °C at 10 mm yield 76 % nL 1.414.

1-Dimethylamino-3-butanone methiodide.

The methiodide was prepared by adding (142.0 gm, 1.0 mole) of freshly distilled methyl iodide, to (247 gm, 1.0 mole) of 1-dimethylamino-3-butanone. The mixture was
allowed to stand protected from moisture for one hour at zero degree, and for one hour at room temperature. A crystalline methiodide was obtained. Due to its hygroscopic nature it was not further purified, it was however, washed twice by decantation with ether to remove excess of methyl iodide. 400 gm of 1-dimethylamino-3-butanone methiodide was obtained.

4-Chlorobutane

Method (1):

Acetyl chloride (510 gm, 6.50 mole) was added with stirring and cooling during thirty minutes to a mixture of anhydrous aluminum chloride (910 gm, 6.80 mole) and chloroform (500 ml). At the end of the addition the temperature had risen to 25 °C, cooling was continued until the temperature had fallen to zero degree. Ethylene gas was bubbled into the mixture at such a rate that all was absorbed, the internal temperature being kept between 5-10 °C by continuous ice salt cooling. Ethylene gas started escaping after two hours. The reaction mixture was poured into a mixture of one litre of conc. hydrochloric acid and 5 kg. of ice. The organic layer was washed successively with sodium bicarbonate solution, and finally dried. Then it was distilled through a short column to remove the lower boiling fractions, the residue when fractionally distilled under vacuum gave 420-425 gm of the required product, b.p. 43-47° at 16 mm. yield 61 % nD 1.429.
A 2:4 dinitrophenyl hydrazone was prepared and recrystallised from ethanol, pale yellow shining crystals m.p. 126-126.5 °C and a semicarbazone also prepared m.p. 138-139 °C.

Method (2).

Freshly distilled methyl vinyl ketone (104.0 gm; b.p. 75-82 °C) was saturated at zero degree, with a rapid stream of dry hydrochloric acid. The solution was allowed to stand at room temperature for one hour, then it was poured into ice-water neutralised with dilute sodium hydroxide solution and extracted with ether (3 x 100 ml portions). The colourless extract was washed with water and dried. The solvent was removed and the residue when distilled under reduced pressure, gave 68-72 gm of the required product, b.p. 48-50 °C at 15 mm yield 65-70% nD25 1.429.

A 2:4 dinitrophenyl hydrazone of the chloro ketone was prepared, recrystallised from ethyl alcohol, m.p. 106 °C.

Methyl vinyl ketone.

Acetyl chloride (355.0 gm, 4.5 mole) was added slowly to a mixture of carbon disulphide (2 litres) and aluminum chloride (575 gm, 4.3 mole) with constant stirring. The mixture was cooled to zero, and dry ethylene gas was passed into the mixture for about seven hours. The mixture was heated on a water bath for 45-49 °C until the brisk evolution of hyeogen chloride gas diminished, then it was allowed to stand overnight. The residue was poured in ice, this treatment decomposes the aluminium chloride complexe and gave a brownish coloured liquid. The
organic layer was washed successively with dilute hydrochloric acid, water and finally neutralized by sodium bicarbonate solution. It was again washed with water and dried (Na$_2$SO$_4$). The bulk of the carbon disulphide was removed by distillation, through a short column at atmospheric pressure. The residue when fractionally distillation gave $\frac{103}{4}$ gm of the required product, bp: 53-4 °C/ 130 mm $n_D^{20}$ 1.4086. 33-35% yield, absorption infrared: $\sqrt{\nu}$ 3000, 1760, 1480, 1340, 1245, 1150 975; 920 and 875 cm$^{-1}$.

A semicarbazone of the above compound was prepared, and recrystallized from hot ethyl alcohol melting point 140-141°C.

\[
3\text{ethyl-2-oxo} \triangle 1:9\text{-octalin-10-carboxylate (4)}
\]

\[n_D^{26}=1.503\]

A solution of pyrrolidine enamine of ethyl cyclohexanone-2-carboxylate (20.9 gm, 0.1 mole) in 100 ml of dry benzene was added to methyl vinyl ketone (7.0 gm, 0.1 mole) in an atmosphere of nitrogen. The mixture was then refluxed for 24 hours. A buffer solution was made up of 25 ml of acetic acid, 25 ml of water and 12.5 gm of sodium acetate was then added and refluxing was then continued for six hours. The organic layer was separated and the aqueous layer was extracted with benzene. The organic layer and the combined extracts were washed successively with 10% aqueous hydrochloric acid, saturated sodium bicarbonate solution and finally with water. It was dried and filtered, the solvent was distilled off, and the residue when distilled under reduced pressure gave 0.6 gm of the above product; b.p. $133-144^\circ$C at 2.5 mm yield 43% $n_D^{26}$ 1.503.

See page 127.
Light absorption (a) Ultraviolet \( \lambda \text{ max } 232 \ E \text{ max } 16,800 \\
(b) Infrared \ \nu 3000, 1760, 1480, 1340, 1230, 1125, 1130, 975, 920 870, 875 \ \text{cm}^{-1}.

(Found C, 70.24; H, 8.21; O, 21.59% \ C_{15}H_{18}O_{3}

Requires C, 70.24; H, 8.29; O, 21.56%)

A 2:4 Dinitrophenyl hydrazone prepared and recrystallized from ethyl alcohol and ethyl acetate mixture m.p. 178-178.5°C. (Found C, 56.72; H, 3.31; N, 13.903 \ C_{14}H_{22}O_{6}N_{4} \text{ requires } C, 56.78, H, 5.15; N, 13.72%).

Ethyl-2-oxo- \( \Delta^11 \)-octalin-10-carboxylate. (4)

Meth.-3 Ethyl-cyclohexanone-2-carboxylate (34.0 gm, 0.2 mole) freshly distilled methyl vinyl ketone (14.1 gm 0.2 mole) 12 gm of sodium hydroxide in 150 mls of absolute ethyl alcohol were mixed together, and the mixture was refluxed for six hours. It was distilled under atmospheric pressure to remove unreacted methyl vinyl ketone and ethyl alcohol. To remove water and last traces of ethyl alcohol, 200 mls of benzene and 15 mls of piperidine was added. A dean-stark water separator was used and the mixture was refluxed for few hours. During this time all the water present in the mixture separated. After the removal of benzene from the mixture, it was diluted with 10% aqueous hydrochloric acid, when the organic layer separated. The aqueous layer was washed with ether (2 x 100 mls portions). The organic layer combined with ethereal layer was washed with water and neutralized with saturated sodium bicarbonate solution, followed by washing with water, and finally dried \( (\text{Na}_2\text{SO}_4) \). The solvent was evaporated and the residue was fractionally distilled to give 20.2 gm of the required
A 2:4 dinitrophenyl hydrazone derivative of the above compound m.p. 178°C was prepared according identical with that of \( \text{I} \).

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**Ethyl-2-oxo-\( \Delta^{1:9} \)-octalin-10-carboxylate (4).**

**Method-3.**

A solution of ethyl cyclohexanone-2-carboxylate (34.5 gm, 0.2 mole) in sodium ethoxide (4.6 gm atoms in 300 ml of absolute ethyl alcohol) was cooled in ice and 1-dimethylamine \(-3\)-butanone methiodide (51.4 gm, 0.2 mole) in absolute alcohol (100 ml) was added with stirring within five minutes. Cooling was continued for fifteen minutes. The mixture was then left at room temperature for one hour, and refluxed for three hours, was then allowed to cool to room temperature, and acidified with 2 N sulphuric acid (congo red) followed by enough water to dissolve the sodium sulphate. It was then extracted with ether, dried (Na\(_2\)SO\(_4\)) and filtered. After the removal of the solvent, the residue when distilled under reduced pressure gave 17-18 gm of the above product. b.p. 170-178°C @ 10 mm yield 39% \( n_d^{26} = 1.508 \).

A 2:4 Dinitrophenyl hydrazone prepared and recrystallized from ethyl alcohol and ethyl acetate mixture, m.p. 178-178.5°C.

**Ethyl-2-oxo-\( \Delta^{1:9} \)-octalin-carboxylate (4)**

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**Method-4**

a) Ethyl-2-oxo-(3-keto butyl)-cyclohexanone-2-carboxylate (15).

Ethyl cyclohexanone-2-carboxylate (48.0 gm, 0.3 mole) anhydrous methyl vinyl ketone (25.5 gm, 0.35 mole) 12 mls of
triethylamine and 200 mls. of dry benzene were mixed together in a reaction flask and allowed to stand for 150 hours at room temperature with constant magnetic stirring. The mixture was then refluxed at low temperature for six hours. The benzene layer was separated and washed with 10% aqueous hydrochloric acid and water. It was then neutralized with sodium bicarbonate solution dried and the lower boiling fractions were removed. The residue was fractionally distilled to give 62.3 gm on redistillation b.p. 85-92 °C/4 mm of the above product, b.p. 100-115/9 mm (80-85% yield nD0 1.473. The distillate did not give a positive ferric chloride test; it produced a yellow precipitate with 2:4 dinitrophenyl hydrazine reagent in dilute sulphuric acid.

b) Cyclization.

A mixture of 500 mls of benzene, 500 mls of glacial acetic acid and 100 mls of concentrated hydrochloric acid and 60 gms of the diketo ester \( \text{H} \) was refluxed under an atmosphere of nitrogen for twenty four hours, the product obtained by dilution and extraction with benzene gave the same \( \text{B}-\text{keto-ester} \) b.p. 142-144 °C @ 2 mm 99-50% yield.

\[ \text{Ethyl-2-oxo-} \Delta_{1:9} \text{octalin-10-carboxylate} \] (4).

Method 5.
a) Ethyl-2-oxo(3-keto butyl) cyclohexanone-2-carboxylate. (15).

In a three-necked one litre round bottom flask, fitted with a mechanical stirrer, a condenser, and a dropping funnel was placed dry ether (225 mls) and sodium wire (7.00 gm 0.3 gm atom). Ethylene-cyclohexanone-2-carboxylate (51 gm, 0.3 mole) was added dropwise with stirring at room temperature. Stirring 

was continued with slight warming over a water bath till all the sodium had dissolved. 4-Chlorobutanone (31.10 gm, 0.3 mole) was then added dropwise with stirring, and the mixture refluxed for two hours. It was then cooled to room temperature and acidified with dilute acetic acid. The upper organic layer was separated and the aqueous layer extracted with ether (3 x 100 ml portions). The etheral layer and the organic layer were combined, washed with water, and dried (Mg SO₄). The solvent was removed and the residue was fractionally distilled under reduced pressure to give 58.5 gm of the above product b.p. 123°C 5-6 mm 67% yield. nD²⁵ 1.473.

b) Cyclization.

A mixture of 500 ml of methanol, 150 ml of 45% of sodium hydroxide solution and 50 gm of the above compound was refluxed under an atmosphere of nitrogen for twenty four hours. The solution was then diluted and the product was extracted with warm benzene (3 x 100 ml portions). The extract was washed with water and dilute hydrochloric acid, then it was concentrated. The residue when fractionally distilled under reduced pressure to give 23 gm of the required product b.p. 141-2°C @ 2 mm 56 % yield. Ethyl 3-oxo-3-hydroxy-1-p-oxoylethyl (4) prepared by the method (2), (3), (4) and (5), were found to be identical in all respects.
Modified method 1

After refluxing the mixture of pyrrolidine enamine of ethyl cyclohexanone-2-carboxylate (0.1 mole) and methyl vinyl ketone for twenty four hours, it was cooled at room temperature. A mixture of 10 ml of acetic acid, 20 ml of water and 5 gm. of sodium acetate was then added and the solution was heated on the steam bath for 30 minutes. Addition of water, extracted with ether etc., gave 24-26 gm unacyclized product (15) b.p. 100-115/3 mm yield 60-85 ml D 1.4750 infrared absorption Vmax 3000, 1710(s) 1680, 1525 1445, 1350, 1290, 1220-25, 1180, 1050, 1080, 1004 940, 860, 800, and 710 cm⁻¹. This product was directly cyclized in good yield by the method of Shunk and Wills giving the ethyl-2-oxo- Δ1:9-octalin-10-carboxylate (4), b.p. 139-144/2-2.5 mm D 1.508 λ max 232 

Shrinking method 2

The clear solution was diluted with water, then extracted with ether, washed and dried. The ether was evaporated and the residue distilled under vacuum to give unacyclized substance (15) b.p. 104-111/2.5 mm yield 70-80 %. The infrared spectrum and refractive index were found identical with the product obtained by the method (10).

Modified method 3

Cyclization of ethyl-2-(3-keto butyl)cyclohexanone-2-carboxylate into ethyl-2-oxo- Δ1:9-octaline-10-carboxylate.

To ethyl-2-(3'-keto butyl) cyclohexanone-2-carboxylate b.p. 104/1.5 mm and added a mixture of aluminum tert-butoxide in a tert butyl alcohol/dry benzene 500 ml heated to reflux for six hours under nitrogen. It was cooled to room temperature and hydrolyzed with aqueous HCl, washed and extracted with ether gave only 23 % of the cyclized product (4) b.p. 141-43°C/2 mm D 1.508 λ max 232, 

Shrinking method 3

The infrared spectrum identical with that of authentic compound prepared by the method (1,2,3,4,5,6).
2-oxo- \( \Delta^{11:9} \) octalin.

A solution of ethyl-2-oxo- \( \Delta^{11:9} \) octaline-10-carboxylate (15.5 g, 0.05 mole), sodium hydroxide (6.00 g, 0.15 mole) in 25-26 ml of water, and 20 ml of ethyl alcohol (95 %) was placed in a reaction flask and heated under reflux for three to four hours. The warm solution was acidified by the addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes cooled and extracted with ether. The ether layer washed well with 2 % aqueous acetic acid and finally with water. It was dried (Na₂SO₄) and filtered. The solvent was evaporated, and the residue when distilled under reduced pressure gave the above product. B.p. 140-141 °C @ 14 mm n²⁰ 1.523 yield 45 %. Light absorption a) Ultraviolet \( \lambda_{\text{max}} \) 238 cm⁻¹ \( \lambda_{\text{max}} \) 12.900

(found C, 79.8; H, 8.3 % C₁₀H₁₄O required C, 80.0 % H, 9.3 %).

A 2:4 dinitrophenyl hydrazone derivative was prepared and recrystallized from a mixture of methanol and ethyl acetate m.p. 168-169°C.

A semi-carbazone of \( \Delta^{11:9} \) octalone-2 was also prepared as white needles (alcohol) m.p. 208°C.

(found C, 58.2; H, 5.5; N, 17.0 % C₁₀H₁₈O₄N₂ requires C, 58.1; H, 5.70; N, 16.8%.

A throttling compound

A.L. Wilds and W.H. Shunk \(^{91}\) prepared from formyl cyclohexanon and diethyl amino butanone methiodide in methanolic solution yield, 13.69° gm (68 %), b.p. 100-110°C @ 1 mm; \( \lambda_{\text{max}} \) 238 mu (logE 4.1).
Ethyl-2-oxo-1-methyl-\(\Delta^{119}\)-octalin-10= carboxylate.

(Sodium ethoxide melted).

Ethyl-2-oxo- \(\Delta^{119}\) octalin-10= carboxylate (22 gm., 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm., 0.1 mole) in dry ethyl alcohol; cooled to room temperature. The reaction mixture was stirred for further forty five minutes to complete the formation of sodium derivative of the \(\beta\)-keto ester. Freshly distilled methyl iodide (42.5 gm., 0.3 mole) was added during one hour. The mixture was stirred for two hours and refluxing for three hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 ml). The organic layer was separated and the aqueous layer was extracted with ether (3 x 100 ml portions). The extracts were mixed with the organic layer and the mixture was washed with dilute sodium bisulphite solution then with water, finally it was dried (Mg SO\(_4\)). The solvent was removed and the residue when fractionally distilled under vacuum gave 7.2 gms. of the above product. B.p. 143-149°C @ 2 mm \(T_d\) 1.512 \(n_d\) 1.523 yield 52.1 %. Light absorption a) Ultraviolet violet isoprop. \(\lambda_{\text{max}} 238 \varepsilon_{\text{max}} 18,000.\) b) Infrared \(\sqrt{3600, 3100, 1650, 1535, 1360, 1120, 1110, 875, 750 \text{ and } 765 \text{ cm}^{-1}.\)

(Found C, 73.14; H, 8.54; O, 20.30% C\(_{14}\)H\(_{20}\)O\(_3\) requires C, 70.93 H, 8.45, and O, 20.50%)

A 2:4 Dinitrophenyl hydrazone prepared and recrystallized from ethyl alcohol, m.p. 167-8°C

(Found C, 56.74; N, 13.45; H, 15.85% C\(_{20}\)H\(_{24}\)N\(_4\)O\(_6\) requires C, 56.31; H, 5.32, N, 13.97%).
Ethyl-2-oxo-1-methyl-$\Delta^{1;9}$-octalin-10-carboxylate.

(Sodium amide method)

In a three-necked round bottomed flask placed in bath of liquid air, was taken sodium (4.6 gm, 0.2 mole) and about 150 mls of liquid ammonia was added along with 2.5 gm of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-$\Delta^{1;9}$ octalin-10-carboxylate (44 gm, 0.2 mole) was then added carefully, dropwise over a period of fifteen minutes with constant stirring. A yellowish red amorphous salt formed immediately. 400 mls of sodium dried diethyl ether was added, and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier became increasingly viscous but the stirring was continued. Freshly distilled methylamide (94 gm, 0.3 mole) was added in small portions as the mixture was heated under reflux with continuous stirring under nitrogen for nine hours. After addition of water, the organic solution was separated washed with 5% aqueous acetic acid and water. Dried over sodium sulphate. Ether-toluene were removed by normal distillation and the residue when fractionally distilled under vacuum gave the above product b.p. 142-146°C 0.2 mm nD²⁰ 1.512 54% yield.

A 2:4 Dinitrophenyl hydrazone prepared and recrystallised from ethyl alcohol m.p. 157-8°C.

Ethyl-2-oxo-1-methyl-$\Delta^{1;9}$-octalin-10-carboxylate.

(Benzine method).

A solution of pyrrolidine (10.6 gm, 0.15 mole) in 10 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-$\Delta^{1;9}$ octalin-10-carboxylate.
late (22.0 gm, 0.1 mole) in 100 mls of benzene. The mixture was then refluxed for three to five hours during this time the water produced in the reaction mixture was removed with Dean and Starks water separator. Then about 160 mls of the solvent was distilled off and the remaining light red solution was cooled. A solution of methyl iodide (21.78 gm 1.15 mole) in 100 mls of dry dioxane was added and the mixture refluxed for 24 hours. 5% aqueous hydrochloric acid (100 mls) was then added and the mixture was refluxed for another two hours. About two third of the solvent was distilled off, diluted with water and the mixture extracted with ether (200 mls) The aqueous layer was further extracted with ether (2 x 100 mls) combined ether extract was washed successively with an aqueous sodium bisulphite solution, water, and dried. The ether was removed and the residue when fractionally distilled under vacuum gave 18.30 gm of the above product, b.p. 135-6°C @ 0.5-1 mm Hg 1.5141 yield 49%

A semi carbazone derivative was prepared and recrystallized from ethyl alcohol m.p. 165-7°C (Found C, 63.51; H, 8.15; N, 14.80; C6H23O3N3 requires C, 63.54; H, 8.18; N, 14.82 %).

\[2\text{-oxo-1-methyl-}\Delta^{119}\text{-octalin}(136)\]

Ethyl-2-oxo-1-methyl-\Delta^{119}\text{-octaline -10-carboxylate (23.63 gm, 0.1 mole) Sodium hydroxide (6.0 gm, 0.15 mole) 25-16 mls of water and the 10-15 mls of ethyl alcohol were mixed in the reaction flask. It was heated under refluxed for 3-4 hours. The warm solution was acidified by the slow addition of 11 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled}
under reflux for 90-minutes, cooled and extracted with ether. The ether layer was washed well with 5% sodium hydroxide solution, followed by washing with 2% aqueous acetic acid and finally with water. It was dried (Na$_2$SO$_4$) the solvent was distilled under vacuum. The residue when distilled under vacuum gave 12.3 gm of the above product, b.p. 124-127$^\circ$C @ 10 mm $^2$H$_2$O yield 47 %. Light absorption (a) Ultraviolet isopropyl

$\lambda$ max 249 nm (log $\varepsilon$ 4.1) (b) infrared $\tilde{\nu}$ 3000, 1745, 1480

1385, 1240, 1125, 1110, 1016, 935 and 870 cm$^{-1}$. R$_e$ N$_o$.

(Found C, 80.56; H, 9.68; and O, 9.75% C$_{11}$H$_{10}$O requires C, 80.54; H, 9.63 and O, 9.84%)

The 2:4 dinitrophenyl hydrazone was prepared and recrystallized from ethyl acetate m.p. 176-177$^\circ$C.

(Found C, 59.31, N, 16.26; and H, 5.86% C$_{17}$H$_{20}$N$_4$O$_4$ requires C, 59.77; N, 16.60; and H, 5.23%)

(Sodium ethoxide method)

Ethyl-2-oxo-1:9-octalin-10-carboxylate (22 gm, 0.1 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol cooled to room temperature. The reaction mixture was stirred for further forty five minutes to complete the formation of sodioderivative of keto ester. Freshly distilled ethyl iodide (23.38 gm, 0.15 mole) dissolved in 50 ml of alcohol was added during one hour, and the mixture was stirred for two hour at 10$^\circ$C, then it was refluxed for three hours. Most of the ethyl alcohol was removed at the suction pump. The residue
was distilled diluted with water 100-150 mls. The organic layer was separated, aqueous layer extracted with ether (4 x 150 mls portions). The resulting solution was worked out in the usual manner as described in the previous experiment. The solvent was removed and the residue fractionally distilled under reduced pressure gave 154 gm of the above product b.p. 147-155°C @ 2-3 mm Hg N0. 16517 yield 49%. Light absorption

a) Ultraviolet Absorption Λ max 235; E max 18330, b) Infrared

ν 3100, 1750; 1475; 1245; 1130, 1025, 930, 872 and 770 cm⁻¹

(Found C, 71.96; H, 8.86; and O. 19.17 % C₁₅H₂₂O₃ requires C, 71.2; H, 8.82; and O. 19.95 %)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallised from alcohol b.p. 159-60°C

(Found C, 50.85; H, 6.68; O, 22.30 % and N, 10.62 %; C₂₁H₂₆O₆N₄ requires C, 50.91; H, 6.23; O, 22.57 and N, 10.72 %)

Ethyl-2-oxo-1-ethyl-A⁺⁻octalin-10-carboxylate:

(Examining method)

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 60 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-A⁺⁻octalin-10-carboxylate (22.0 gm, C, 1 mole) in 150 mls of benzene. The mixture was refluxed for three hours during this time the water produced in the reaction mixture was removed with Dean and stark water separator. Then 200 mls of the solvent was distilled off, and the remaining red solution was cooled. A solution of ethyl iodide (23.38 gm, 0.15 mole) in 100 mls of dry dioxane was added and the mixture was refluxed for 24 hours, after then
5% aqueous hydrochloric acid (100 mls) was added, and the mixture refluxed for another two hours.

The resulting mixture was worked out in the usual manner as described in the previous experiment; the residue fractionally distilled under reduced pressure gave 23.1 gm. of the product b.p. 146-150°C @ 2 mm, nD27 1.519 yield 52%.

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallised from alcohol, m.p. 160°C.

2-oxo-1-ethylΔ119-octalin:

Ethyl-2-oxo-1-ethyl-Δ119-octalin-10-carboxylate (25.03 gm, 0.1 mole) sodium hydroxide (6.0 gm, 0.15 mole). 25 mls of water, and 10 ml of ethyl alcohol 95% were taken in the reaction flask. The mixture was heated under reflux for five hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution under reflux carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was worked out in the usual manner as described in the previous experiment.

The residue obtained when fractionally distilled under vacuum gave 11.4 gms. of the required product b.p. 165-75°C @ 1212,5 mm nD 28 1.520, yield 43%. Light absorption a) Ultra violet isoprop. λ max 232 ε max 14,500.

(Found C, 80.87%; H, 10.15; and O, 8.97% C12H18O
requires C, 80.83%; H, 10.25; and O, 8.91%)

A 2:4 dinitrophenyl hydrazone was prepared and recrystallised from pet.ether and aqueous alcohol m.p. 162.4°C.
(Found C, 55.14; H, 6.18; and N, 15.62 % C_{15}H_{22}N_{4}O_{4}.
Required C, 63.14; H, 6.25; and N, 15.43 %.)

**Ethyl-2-oxo-propyl-Δ^{119}octalin-carboxylate**

(Sodiummethoxide method).

Ethyl-2-oxo-Δ^{119}octalin-10-carboxylate (22.0 gm 0.1 mole) was added during 30 minutes to a stirred solution of sodium (2.3gm, 0.1 mole) of sodium (2.3g) reaction mixture was stirred for further 45-60 minutes to complete the formation of sodio derivative of β-keto ester. Freshly distilled n-propyl iodide (25.49 gm, 0.15 mole) dissolved in 50 mls of ethyl alcohol was added during the one hour. The mixture was stirred for two hours and refluxed three hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls). The organic layer was separated and the aqueous layer was extracted with ether. The extracts were mixed with the organic layer and the mixture was washed with water, finally dried (Na_{2}SO_{4}). The solvent was removed the residue was fractionally distilled under reduced pressure gave 13.3 gm, of the above required product. b.p. 172-174°C 3 mm yield 48-51 % n_{D}^{26} 1.521 Light absorption a) Ultraviolet isoprop., λ max 234 ε max 18500 b) Infrared ν 3100, 1760, 1475, 1380; (s) 1165, 1035 and 875 cm^{-1}. (Found C, 72.72; H, 9.15; and O, 18.1; % C_{16}H_{24}O_{3} requires C, 72.69; H, 9.32 and O, 18.02 %).

A 2:4 dinitrophenyl hydrazone of the product was prepared and recrystallized from alcohol m.p. 169-70°C.
(Found C, 50.94; H, 6.35; O, 21.59; and N, 12.60 % C_{22}H_{28}O_{6}N_{4} requires C, 50.82; H, 6.43; O; 21.63; and N, 12.2%).

**Ethyl-2-oxo-1-propyl-\Delta^{11}9-octalin-10-carboxylate.**

(Sodium ethoxide method).

In a three necked round bottomed flask placed in a bath of liquid air was taken (4.6 gm 0.2 mole) and about 150 mls of liquid ammonia was added along with 2.5 gm. of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-\Delta^{11}9-octalin-10-carboxylate (44 gm, 0.2 mole) was then added drop-wise over a period of fifteen minutes with constant stirring. A yellowish red amorphous salt formed immediately. 400 mls of sodium dried diethyl ether. Several excess was added, and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier become increasingly viscous, but the stirring was continued in an atmosphere of nitrogen. and n-Propyl iodide (50.98 gm, 0.3 mole) was added in small portions as the mixture was brought to refluxing temperature, and finally 100 mls of dry toluene was added and the mix refluxed for further nine hours. The mixture was worked out in the usual manner as described in the earlier experiment. The solvent was removed and the residue distilled under reduced pressure gave 19.6 gm. of the above product. b.p. 170-175 @ 2 mm. n^D_{25} 1.520 yield 42-44 %.

The product obtained by sodium ethoxide method have identical infrared spectra and have no depression in the melting points of the 2:1 dimethoxydiphenyl sulfoxide.
Ethyl-2-oxo-1-propyl-Δ¹¹⁻²⁻octalin-10-carboxylate (C₉H₁₀O₅)

(Enamine method): A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ¹¹⁻²⁻octalin-10-carboxylate (22.0 gm 0.1 mole) in 150 ml of benzene. The mixture was refluxed for three hours, during this time the water produced in the reaction mixture was removed with Dean and Stark water separator. Then 200 ml of the solvent was distilled off, and the remaining red solution was cooled. A solution of H-propyl iodide (25.49 gm, 0.15 mole) in 100 ml of dry dioxane was added and the mixture was refluxed for 14 hours, 5% aqueous hydrochloric acid (100 ml) was then added and the mixture was refluxed for another two hours.

About two third of the solvent was distilled off, and the mixture was extracted with ether (2 × 100 ml portions). The combined ether extracts was washed successively with an aqueous sodium bisulphite solution, water and dried. The solvent was distilled off, the residue fractionally distilled under vacuum gave 45.4 gm of the above product b.p. 170-171 °C @ 2.5 mm. nD²⁷ 1.527 53% yield.

A 2:4 dinitrophenyl hydrazone of the product was prepared and recrystallized from alcohol m.p. 169-70 °C. Compound prepared by the above dinitrophenyl method were found to be identical in all respects.

2-oxo-propyl-Δ¹¹⁻²⁻octalin.

Ethyl-2-oxo-1-propyl-Δ¹¹⁻²⁻octalin-10-carboxylate (26.43 gm, 0.1 mole) 6.00 gm of sodium hydroxide, 25 ml of ethyl alcohol (95%) were mixed in the reaction flask. The
mixture was heated under refluxed for five hours. The warm solution was added by the slow addition of 1:1 sulphuric acid a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for about ninety minutes cooled and extracted with ether. The resulting mixture was proceeded as described in the previous experiment. The residue obtained when fractionally distilled under vacuum gave 15.3 gm of the required product b.p. 164-166°C @ 10-14 mm nD 26 yield 48-50%. Recrystallization of the product following the same physical constant.

(Pound C, 81.20; H, 10.47; O, 8.32 % C13H20O requires C, 81.23; H, 10.51; O, 8.24 %).

A 2:4 dinitrophenyl hydrazone of the product was prepared and recrystallised from pet. ether alcohol m.p. 179-180°C.

(Pound C, 61.27; H, 64.9; N, 15.83 % C19H24N4O4 requires Cp 61.32; H, 64.32; and N, 15.91%).

The infrared spectrum is in conformity with the structure of the compound showing characteristic frequencies of the groups present.

**Ethyl-2-oxo-1-isopropyl- Δ**1,9**octalin-10-carboxylate.**

(Sodium ethoxide method).

**Ethyl-2-oxo- Δ**1,9**octalin-10-carboxylate** (22.0 gm 0.1 mole) was added during 30 minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further 45-60 minutes to complete the formation of sodium derivative of D-keto ester. Freshly distilled isopropyl bromide
(18.45 gm, 0.15 mole) dissolved in 50 mls of ethyl alcohol was added during one hour. The mixture was stirred for two hours, and refluxed for three hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 ml). The organic layer was separated, and aqueous layer was extracted with ether (3 x 100 ml portions). The extracts were mixed with the organic layer and the mixture was washed with water; finally dried (Na₂SO₄). The solvent was removed, residue was fractionally distilled under reduced pressure gave 12.8 gm of the above required product, b.p. 178-181°C @ 2 mm nD 25° 1.530 yield 50-51%. Light absorption:

a) Ultraviolet isoprop 
λ max 236 + 1, E₄₁₅ 18,600; b) Infra-red absorption: v C=O 3100, 1655;
1545, 1445, 1245, 1170, 1040, 880, and 765 cm⁻¹.

(Found C, 72.72; H, 9.47; C₁₆H₂₄O₅ requires 72.69; H, 9.32; O, 13.22%)

A 2:1 dinitrophenyl hydrazone was prepared and recrystallized from ethyl acetate/ethyl alcohol mixture m.p. 142-14°C (Found C, 50.84; H, 6.28; C, 21.5% and N, 12.61% C₂₂H₂₈N₄O₆ requires C, 50.82; H, 6.43; O, 21.63 and N, 12.2%).

Ethyl-2-oxo-1-isopropyl-Δ₁¹⁻octalin-10-carboxylate (1%) (Enamine method)

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ₁¹⁻octalin-10-carboxylate (22.0 gm 0.1 mole) in 150 ml of dry benzene. The mixture was refluxed for three hours during this time the water formed
in the reaction mixture was removed with Dean and Stark water separator. Then 200 mls of the solvent was distilled off, and the remaining red solution was cooled. A solution of isopropyl bromide (18.45 gm, 0.15 mole) in 100 mls of dry dioxane was added and the mixture was refluxed for fourteen hours. 5% aqueous hydrochloric acid (100 mls) was then added and the mixture was refluxed for another two hours.

About two third of the solvent was distilled off and the mixture was extracted with 200 mls ether. The aqueous layer was further extracted with ether (2 x 100 mls portions). The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue was fractionally distilled under vacuum gave 10.9 gm of the above product b.p. 182-183 2.5 mm nD 1.532 49% yield.

The two samples have identical infrared spectra and undegreased mixed melting point of the 2:4 dinitrophenyl hydrazone showed no depression.

2-oxo-1-isopropyl-Δ1:9 octalin.

Ethyl-2-oxo-1-isopropyl-Δ1:9-octalin-10-carboxylate (26.43 gm 0.1 mole), 6.00 gm of sodium hydroxide, 25 ml of water and 15 ml of ethyl alcohol (95%) were mixed in the reaction flask; the mixture was heated under reflux for seven hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for one hour; cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as described in the
previous experiment. The residue obtained was fractionally
distilled under vacuum gave 11.2 gm of the above required \( p \)
product b.p. 168-171°C/3-4 mm \( n_0^D \) 1.542 yield 44-45%.
Light
absorption spectra a) Ultraviolet isoprop. \( \Lambda \) max 233 +1 mu
\( E \) max 19,600 b) Infrared spectrum in the conformity with the
structure.

\[(\text{Found C}, 61.47; \text{H}, 64.43; \text{and N}, 15.78 \% \text{C}_{19}H_{24}O_{4}N_{4} \text{ requires C, 61.32; H, 64.32, N,15.91 \%}).\]

A 2:14 dinitrophenylic hydrozone was prepared and recryst-
tallized from ethyl alcohol/dioxane, shining yellow crystals
m.p. 162-4°C. Analysis of 2-oxo-\( \Delta \) \( 1:9 \)-octalin-10-carboxylate.)

\[(\text{Found C, 81, 18; H, 10.50; O, 19.29 \% \text{C}_{13}H_{10}O \text{ requires C, 81, 23; H, 10.57}
O, 19.24 \%).}\]

**Ethyl-2-oxo-1-butyl- \( \Delta \) \( 1:9 \)-octalin-10-carboxylate.**

**(Sodium ethoxide method)**

Ethyl-2-oxo-\( \Delta \) \( 1:9 \)-octalin-10-carboxylate (22.0 gm,
0.1 mole) 0.1 mole) was added during thirty to forty minutes
to a stirred solution of sodium (2.3 gm 0.1 mole) in a absol-
ute ethylalcohol, cooled to room temperature. The reaction was
stirred for further 45.50 minutes to complete the formation
of sodio derivative of \( \beta \)-keto. n-Butyl bromide (20.55 gm,
0.15 mole) dissolved in 50-60 ml of ethyl alcohol was added
during one hour. The mixture was stirred for two hours and
was continued
refluxing for the eight to ten hours. Most of the ethyl alco-
hol was distilled off, and the residue was diluted with water
(100 ml). The organic layer was separated, and the aqueous
layer was extracted with ether. The extracts were mixed with
the organic layer and the mixture was washed with water. Finally dried, the solvent was distilled off, and the residue was fractionally distilled under reduced pressure gave 15.4 gm of the required product b.p. 190-193°C @ 3-4 mm yield 49%
\( n_D^25 = 1.537 \). Light absorption a) Ultraviolet b) Isopropyl \( \lambda_{	ext{max}} 237\pm \text{mu} \; \text{E}_{	ext{max}} 19500 \).
(Found C, 73.34; H, 9.45; O, 17.24% \( C_{17}H_{26}O_3 \) requires C, 73.49 H, 9.51; O, 17.00%).

A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallized twice with hot ethanol 191-2°C m.p.
(Found C, 60.24; H, 6.39; O, 20.91 and \( \text{N} \) 12.22% \( C_{23}H_{32}O_6\) \( \text{N} \) 12.27).

Ethyl-2-oxo-1-butyl- \( \Delta^1\)octalin-10-carboxylate,
(Enawine method).

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo- \( \Delta^1\)octalin-10-carboxylate (22.0 gm 0.1 mole) in 150 mls of benzene. The mixture was refluxed for three hours, water produced was removed with Dean and Stark water separator. The 200 mls of the solvent was distilled off, and the remaining red solution was cooled.

A solution of n-butyl bromide (20.55 gm, 0.15 mole) in 100 mls in dry dioxide was added and the mixture was refluxed for ten hours, 5% aqueous hydrochloric acid (100 mls) was then added and the mixture was refluxed for another two hours.

About two third of the solvent was distilled off, and
the mixture was extracted with 200 mls ether. The aqueous layer was further extracted with ether (2 x 100 mls portions). The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue was fractionally distilled under vacuum gave 15.5 gm of the above product b.p. 189-193°C 3 mm nD 1.534 yield 40-41%.

The two samples to have identical infrared spectra and undepressed melting points of the 2:4 dinitrophenyl hydrazone derivatives, showed no depression.

2-oxo-1-butyl-△119-octalin:

Ethyl-2-oxo-1-butyl-△119-octalin-10-carboxylate (27.33 gm, 0.1 mole) 6.00 gm of sodium hydroxide, 25 mls of water and 10 ml of ethyl alcohol 95 % were mixed in a reaction flask. The mixture was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as described in the earlier experiment. The residue obtained when fractionally distilled under reduced pressure gave 15.1 gm of the required product b.p. 168-171°C/10mm nD 1.538. Light absorption a) Ultraviolet λmax 239 max 18,500 b)Infrared

\[ \tilde{\nu} 3100, 1785, 1675, 1540, 1500, 1320, 1260, 1140, 920 and 875 \text{ cm}^{-1} \]

(Found C, 81.49; H, 10.75; O, 7.75; C14H22O requires C, 81.43; H, 10.71 %).

A 2:4 dinitrophenyl hydrazone of the product was
and prepared recrystallized from ethyl alcohol and ethyl acetate (1:1) mixture m.p. 201°C.

(Found C, 62.16; H, 6.78; N, 14.49, C, 16.56 requires C_{20}H_{26}^{14}C_{2}, 62.23; H, 6.48; C, 16.66 and N, 14.39%).

**Ethyl-2-oxo-1-sec-butyl-Δ^{1:9}-octalin-10-carboxylate.**

(Sodium ethoxide method).

Ethyl-2-oxo-Δ^{1:9}-octalin-10-carboxylate (22.0 gm 0.1 mole) was added during 30 minutes to stirred solution of sodium (2.3 gm; 0.1 mole) in absolute ethyl alcohol cooled to room temperature. The reaction mixture was stirred for further 45-60 minutes to complete the formation sodium-derivative of β-ketone ester. Freshly distilled sec-butyl β

bromide (20.53 gm, 0.15 mole) dissolved in 50 ml of ethyl alcohol was added during one hour. The mixture was stirred for two hours and refluxed for seven hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (500 ml) The organic layer was separated and the aqueous layer was extracted with ether. The extracts were mixed with the organic layer and the mixture was washed with water, finally dried. The solvent was removed, and the residue fractionally distilled under reduced pressure gave 6.9 gm of the above product. b.p. 178-181°C @ 2.5-3 yield 28 %.

The infrared spectrum of the product, showing the characteristic group frequencies.

(Found C, 73.34; H, 9.43; O, 17.24, C_{17}H_{26}O_{3} requires C, 73.29 H, 9.39; O, 17.21%)
A 2:4 dinitrophenyl hydrazone of the product was prepared and re-crystallized from ethyl alcohol m.p. 144-145°C (Found C, 60.24; H, 6.59; O, 20.91 and N, 12.22 %
\( \text{C}_{25}\text{H}_{29}\text{O}_{7}\text{N}_{4} \) requires C, 60.17; H, 6.43; O, 20.94; and N, 12.62%)

**Ethyl-2-oxo-1-sec.butyl-\( \Delta^{119} \)-octalin-10-carboxylate**

(Enamine method).

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\( \Delta^{119} \)-octalin-10-carboxylate (22.0 gm, 0.1 mole) in 150 mls of dry benzene. The mixture was refluxed for three hours, during this time the water formed in the reaction mixture was removed with Dean and Stark water separator. Then 200 mls of the solvent was distilled off, and the remaining red solution was cooled, a solution of sec. butyl bromide (20.53 gm 0.15 mole) in 100-150 mls of dry dioxane was added, and the mixture was refluxed for ten hours 5% aqueous hydrochloric acid was then added and the mixture was refluxed for another two hours.

About two third of the solvent was distilled off, and the mixture was extracted with 200 mls ether. The aqueous layer was further extracted with ether (3 x 100 mls portions). The resulting mixture was proceed in the usual manner as described in the previous experiment. The residue was fractionally distilled under vacuum gave 3.2 gm of the above product b.p. 184-186°C @ 2.5 mm \( n_{D}^{27} = 1.532 \) yield 34%. 
A 2:4 dinitrophenyl hydrazone of the product was prepared and recrystallized from ethyl alcohol m.p. 144-145°C.

2-oxo-1-sec-buty1- Δ^{1:9} -octalin.

Ethyl-2-oxo-1-sec-buty1- Δ^{1:9} -octalin-10-carboxylate (27.83 gm 0.1 mole), 6400 gm of sodium hydroxide, 25 mls of water, and 15 mls of ethyl alcohol 65% were mixed in a reaction flask. The mixture was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue obtained was fractionally distilled under vacuum gave 15.3 gm of the above required product b.p. 159-170°C at 15 mm. \( n_d^27.1.540 \) yield 53%. Light absorption a) Ultraviolet A_{max} 241, E_{max} 203000, b) Infrared ν=3100, 1735, 1675, 1540, 1500, 1320, 1260, 1132, 920 and 875 cm\(^{-1}\), (Found C, 81.34, H, 10.67, C\(_{10}\)H\(_{12}\)O requires C, 81.43; H, 10.71%). A 2:4:9.1% prepared mp. 157-8°C (A(c). (Found C, 62.13, H, 6.41, N, 14.40, \( C_{10} H_{16} N_2O_4 \) requires C, 62.23, H, 6.48, N, 14.39%).

Ethyl-2-oxo-1-tert-buty1- Δ^{1:9} -octalin-10-carboxylate.

(Sodium ethoxide)

Ethyl-2-oxo- Δ^{1:9} -octalin-10-carboxylate (33.0 gm 0.15 mole) was added during 30 minutes to stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol cooled to room temperature. The reaction mixture was stirred for further 45-60 minutes to complete the formation of sodium-derivative of
\( \beta \)-keto ester. Freshly distilled tert-butyl chloride (27.74 gm 0.3 mole) dissolved in 50 ml. of ethyl alcohol was added during one hour. The mixture was stirred for two hours and refluxed for seven hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 ml). The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were mixed with the organic layer and the mixture was washed with water; finally dried. The solvent was removed, and the residue fractionally distilled under reduced pressure gave 18.5 gm of the above product b.p. 178-181°C @ 2.5-3 n\text{D}^26 1.540 yield 50-52%. Light absorption a) Ultraviolet, Isopropλ max 238 & max 18,500

b) Infrared \( \nu \): 3400, 1625, 1535, 1325, 1235, 1025-1030 cm\(^{-1}\).

(Found C 73.34; H 9.43; O 17.24%, \( \text{C}_{17}\text{H}_{26}\text{O}_3 \) requires
C 73.29; H 9.38; O 17.28 %).

A 2:4 dinitrophenyl hydrazone derivative of the product was prepared and recrystallised twice with ethyl alcohol/dioxane m.p. 154-155°C.

(Found C 60.24; H 6.59; O 20.91 and N 12.62 %,
\( \text{C}_{23}\text{H}_{30}\text{O}_6\text{N}_4 \) requires C 60.29; H 6.57; O 20.87 and N 12.86%.

**Ethyl-2-oxo-\( \Delta^1 \)octalin-3-carboxylate.**

(Sodium amide method).

In a three-necked round bottomed flask placed in a bath of liquid air was taken sodium (4.6 gm - 0.2 mole) and about 150 mls of liquid ammonia was added, along with 2.5 gm of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-\( \Delta^1 \)
\( \Delta^{1:9} \)-octalin-10-carboxylate (44.0 gm, 0.2 mole) was then added carefully, dropwise over a period of fifteen minutes with constant stirring. A yellowish red amorphous salt formed immediately 400 mls diethyl ether was added, and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier become increasingly viscous, but the stirring was continued. Freshly distilled tert butyl chloride (27.74 gm, 0.3 mole) was added in small portions as the mixture was brought to refluxing temperature, and finally dry toluene was added. The mixture was heated under reflux for twelve hours. After the refluxing, water was added to the mixture and separated the organic layer. Then washed with 5% aqueous acetic acid, and the water. Dried (Na\(_2\)SO\(_4\)) and solvent was removed, the residue when fractionally distilled under reduced pressure gave 24.1 gm of the above product b.p. 192-194°C @ 2 mm. \( n_D^{26} \) 1.541 yield 49%.

A 2:4 dinitrophenyldrazone derivative of the product was prepared and recrystallised twice with ethyl alcohol m.p. 134,5°C

\textbf{Ethyl- 2-oxo-1-tert-butyl- \( \Delta^{1:9} \)-octalin-10-carboxylate.}

(Enamine method)

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo- \( \Delta^{1:9} \)-octalin-10-carboxylate (22.0 gm, 0.1 mole) in 150 mls of dry benzene. The mixture was refluxed for three hours, during this time the
water formed in the reaction mixture was removed with Dean and Stark water separator. Then 200 mls of the solvent was distilled off, and the remaining red solution was cooled. A solution of tert butyl chloride (13.87 gm 0.15 mole) in 100 mls of dry dioxane was added, and the mixture was refluxed for ten hours. 5% aqueous hydrochloric acid (100 mls) was then added and the mixture was refluxed for another two hours.

About two third of the solvent was distilled off and the mixture was extracted with 200 mls of ether. The aqueous layer was further extracted with ether (2 x 100 mls portions). The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residual portion when fractionally distilled under vacuum gave 15.4 gm of the above product b.p. 195-198 @ 2 mm nD 26 1.549 yield 49-50 %.

Compound (1982) obtained by the above three methods were identical in all respects. Duct obtained by method (1) and (2) and showed no depression in the mixed melting points of 2% binary phenyl hydrazones derivatives.
2-oxo-1-tert-butyl $\Delta^{1,9}$ octalin.

Ethyl-2-oxo-1-tert-butyl $\Delta^{1,9}$ octalin-10-carboxylate (27.33 gm, 0.1 mole) 6.00 gm of sodium hydroxide $\Delta^{25}$ ml of ethyl alcohol 95% were mixed in a reaction flask. The mixture was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was then boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner. The residue obtained when fractionally distilled under reduced pressure gave 14.3 gm of the required product, B.p; 170-81 C° @ 4-5 mm nD £25 1.539 Yield 58% Light absorption
a) Ultra violet Isoprop max 243 $\varepsilon$ max 21,300 b) Infra-red $\gamma$
3500, 3050, 1785, 1640, 1530, 1325, 1125, 915, 875 and 765 cm$^{-1}$. (Found C, 81.49; H, 10.75; 0, 7.75; C$\text{H}_{14}$ requires C, 81.47; H, 10.73; 0, 7.24%).

A 2:4 dinitrophenyl hydrazone of the above $\beta$-ketone was prepared and recrystallized from ethyl alcohol 167-6 C°.
(Found C, 62.16; H, 6.78; N, 14.49% C$\text{H}_{20}$O$_2$N$_4$ requires C, 62.23; H, 6.82; N, 14.53%).

Ethyl-2-oxo-1-allyl-$\Delta^{1,9}$ octalin-10-carboxylate.
(Sodium ethoxide method).

Ethyl-2-oxo $\Delta^{1,9}$ octalin-10-carboxylate (22.2 gm, 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in ethyl alcohol, was cooled to room temperature. The reaction mixture was stirred for another 40-60 minutes to complete the formation.
of sodo derivative of β-keto ester. Allyl bromide (18.13 gm, 0.15 mole) dissolved in 50-60 mls of ethyl alcohol was added during one hour. The mixture was stirred for another two hours and refluxed for twelve hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water 1 litre. The organic layer was extracted with ether (4 x 100 mls portions). Ethersal extract was combined with the organic layer and the mixture was washed with water, finally dried (Na₂SO₄). The solvent was distilled off, and the residue was fractionally distilled under reduced pressure gives 8.3 gm of the above product b.p. 193-194°C at 3 mm yield 25-30 %.

ν₃ = 1.530. Light absorption a) Ultra violet Isoprop. λ max 247 (max 22000 b) Infrared ν= ν 3100, 1790, 1500, 1340, 1240, 1130, 1025, 915, 875 and 765 cm⁻¹.

(Found C, 75.67; H, 8.43; O, 17.33; %; C₁₆H₂₂O₃ requires C, 73.61; H, 8.31; O, 17.41 %)

A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallized from pet ether and ethyl acetate m.p. 179°C.

(Found C, 58.33; H, 6.26; N, 12.95% C₂₁H₂₆O₆N₂ requires C, 58.39; H, 6.21; N, 12.83%)

Ethyl-2-oxo-1-allyl- Δ¹₁octalin-10-carboxylate

(Sodium-amide method).

In a three-necked round bottomed flask placed in a bath of liquid air was taken sodium (4.6 gm, 0.2 mole) and about 150 mls of liquid ammonia was added along with 2.5 gm
of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-Δ<sup>11:9</sup> octalin-10-carboxylate (44.00 gm, 0.2 mole) was then added carefully, dropwise over a period of fifteen minutes with constant stirring. A yellowish red amorphous salt formed immediately; 400 mls of sodium dried diethyl ether was added and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier became increasingly viscous but the stirring was continued. Allyl chloride (22.95 gm, 0.3 mole) was added in small portions as the mixture was brought to refluxing temperature and finally 100 mls of dry toluene was added. The mixture was heated under reflux with stirring in nitrogen for nine hours. After addition of water the organic layer was separated, washed successively with 5% aqueous acetic acid and water. Dried over sodium sulphate. The ether-toluene were distilled off, and the residue was on fractionation under vacuum give 34.7 gm. of the above product. b.p. 180-184 c @ 1 mm n<sup>D</sup> 1.523 yield 68%.

A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallized from pet ether and ethyl acetate m.p. 179-80°C.

**Ethyl-2-oxo-1-allyl-Δ<sup>11:9</sup>-octalin-10-carboxylate.**

(Enamine method)

A solution of pyrrolidine (10.66 gm, 0.15 mole) in 100 mls dry benzene was added drop-wise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ<sup>11:9</sup>-octalin-10-carboxylate (22.00 gm, 0.1 mole) in 150 mls of dry benzene. The
mixture was refluxed for three hours during this time, the water formed in the reaction mixture was removed with Dean and Stark waterseparator. Then 200 mls of the solvent was distilled off, and the remaining red solution was cooled. A solution of allyl bromide (18.13 gm, 0.15 mole) in 100 mls of dry dioxane was added and the mixture was refluxed for twelve hours. 5% aqueous hydrochloric acid (100 mls) was then added and the mixture was refluxed for another two hours. About two thirds of the solvent was distilled off, and the mixture was extracted with 200 mls ether. The aqueous layer was further extracted with ether (4 x 50 mls portions). The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue was fractionally distilled under reduced pressure gives 14.2 gm of the above product, b.p. 195-197 °C/12.5 mm, yield 55 % $^n_D$ 1.529.

The I.R. Spectrum of this product was identical with the spectra of the product obtained by the above described method and showed no depression in the mixed melting point of 2:4 dinitrophenyl hydrazone derivatives.

2-oxo-1-allyl- $\Delta^{119}$ octalin.

Ethyl-2-oxo-1-allyl- $\Delta^{119}$ octalin-10-carboxylate (26.23 gm, 0.1 mole) 6.00 gms of sodium hydroxide, 25 mls of water, and 15 mls of ethyl alcohol (95 %) were mixed in a reaction flask. The mixture was heated under refluxed for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbox-
dioxide resulted. The acidified mixture was boiled under reflux for one hour, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue obtained was fractionally distilled under vacuum; gives 18.20 grams of the above product b.p. 182-183 °C @ 5-6 mm Hg, nD 1.543 yield 58%. Infrared absorption V → 3000, 1650, 1530, 1335-40, 1265 1275 (s) and 765 cm⁻¹

(Found C, 82.08; H, 9.51; O, 8.41 %. C₁₃H₁₈O requires C, 82.18; H, 9.53; O, 8.31 %)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from hot ethyl alcohol m.p. 135-6°C.

(Found C, 61.64; H, 5.93; N, 15.12 %. C₁₉H₂₂N₂O₄ requires C, 61.59; H, 5.80; N, 15.10 %)

**Ethyl-2-oxo-1-benzyl-Δ¹⁻[9]-octalin-10-carboxylate.**

(Sodium ethoxide method)

**Ethyl-2-oxo-Δ¹⁻[9]-octalin-10-carboxylate**

(33.0 gms, 0.15 mole) was added dropwise during thirty minutes to a well-stored solution of sodium (3.45 gms, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further 35-40 minutes to complete the formation of sodio derivative of β-keto ester. Benzyl chloride (37.97 gms, 0.3 mole) diluted with 50 ml of dry alcohol, added dropwise for a period of about one hour. Then, it was then refluxed for eight hours. Most of the ethyl was distilled, and the residue was diluted with water. The organic
Layer was separated and the aqueous layer was extracted with ether (3 x 100 mls portions). The organic layer was separated and the aqueous layer was extracted with ether (2 x 100 mls portions). The extract were mixed with organic layer and the mixture was proceeded as usual described in the previous experiment. The ether extracts was concentrated and the residue when distilled under reduced pressure gave 25.0 gm of the above product. b.p. 156-161 @ 1 mm, n° 1.538 yield 71.73 %. Infrared absorption Vmax 3000, 1772, 1480, 1340, 1120, 920, 875 and 765 cm⁻¹.

(Found C, 76.92; H, 7.74 %, C₂₀H₂₄O₃ requires C, 76.83; H, 7.69 %

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol dioxane m.p. 203°C

(Found C, 63.33; H, 5.69; N, 41.23 % C₂₆H₂₈O₆N₄ requires 63.40; H, 5.70; N, 41.35 %)

**Ethyl-2-oxo-1-benzyl- Δ¹:⁹octalin-10-carboxylate.**

(Enamine method).

A solution of pyrrolidine (21.33 gm, 0.3 mole) in dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ¹:⁹-octalin-10-carboxylate (33.0 gms 0.15 mole) in 150 mls of dry benzene. The mixture was refluxed for four hours, during this time the water formed in the reaction mixture was removed with Dean and Stark™.
150 ml of the solvent was removed and the remaining solution was cooled to room temperature. It was diluted with 250 mls of acetonitrile. Freshly distilled benzyl chloride (37.95 gms added and the mixture 0.3 mole) was refluxed for thirteen hours under nitrogen. After the removal of most of the solvent, the residue was neutralized with 5% aqueous hydrochloric acid and the reaction mixture was heated on the steam bath for one hour and then cooled and processed as usual. The ether was dried, concentrated, and the residue distilled under reduced pressure to give 20.4 gms of the above product b.p. 168-175 @ 2 mm nD26 1.532 yield 62.5%.

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol dioxide and m.p. 205°C.

**-2-oxo-1-benzyl- \( \Delta^{1:9} \) octalin:**

Ethyl-2-oxo-1-benzyl- \( \Delta^{1:9} \) octalin-10-carboxylate (12.16 gm 0.05 mole) 6 gms of sodium hydroxide, 25-30 mls of water, 30-90 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes. Cooled and extracted with ether. The resulting mixture was proceeded in the usual manner. The residue then fractionally distilled under vacuum gives 8.1 gm of the product, b.p. 142-4°C @ 10 mm nD26 1.521 yield 58%.
Infrared absorption $\tilde{\nu}$ 3100 (w) 1755, 1500, 1480, 1320, 1235, 1035, and 730 cm$^{-1}$

(Found C, 83.22; H, 8.40; O, 8.41 %. C$_{17}$H$_{20}$O requires C, 83.19; H, 8.35; O, 8.40 %)

The 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallized from ethyl alcohol m.p. 181-2°C. (Found, C, 85.90; H, 7.67; N, 17.41; C$_{23}$H$_{15}$O$_{4}$N$_{4}$ requires C, 85.94; H, 7.93; N, 17.42 %).

**Ethyl-2-oxo-1-tolyl-\(\Delta^{4,9}\) octalin-10-carboxylate.**
(Sodium ethoxide).

**Ethyl-2-oxo-\(\Delta^{4,9}\) octalin-10-carboxylate** (33.0 gms, 0.15 mole) was added during thirty minutes, to a well stirred solution of sodium (5.45 gm, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further five to ten minutes to complete the formation of sodium derivative of \(\beta\)-keto ester. Freshly distilled bromotoluene (51.30 gm, 0.3 mole) diluted with 50-60 mls of dry ethyl alcohol, added dropwise for a period of about one hour, it was then refluxed for ten hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water. The organic layer was separated and the aqueous layer was extracted with ether (2 x 1000 mls) portions. The extracts were mixed with the organic layer and the mixture was washed with water and finally dried. The solvent was removed and the residue fractionally distilled under reduced pressure gave 19.2 gm of the required product, b.p. 168-177 @ 3 mm yield 38 % n$^2$D 1.541.
The infrared spectrum showed all the frequencies of the characteristic groups present in the structure:

\[ \nu = 3000, 1765, 1510, 1445, 1300, 1265, 1125, 1020, 810 \text{ and } 775 \text{ cm}^{-1}. \]

(Found C, 76.88; H, 7.73; O, 15.36 %; \( \text{C}_{20}\text{H}_{24}\text{O}_{3} \) requires C, 75.79; H, 7.69; O, 15.36 %).

A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallized from ethyl alcohol mp. 213-214°C.

(Found C, 62.99; H, 5.73; N, 11.37 %; \( \text{C}_{26}\text{H}_{28}\text{O}_{6}\text{N}_{4} \) requires C, 62.91; H, 5.68; N, 11.29 %).

**Ethyl-2-oxo-1-toly-\( \Delta^{119} \)-octalin-10-carboxylate.**

(Enamine method)

A solution of pyrroldine (21.33 gms, 0.3 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\( \Delta^{119} \)-octalin-10-carboxylate (33.00 gms, 0.15 mole) in 150 mls of dry benzene. The mixture was refluxed for six hours, during this time the water formed in the reaction mixture was removed with the trap, 150 mls of the solvent was distilled off, and the remaining solution was cooled. It was diluted with 250 mls of acetonitrile. Freshly distilled \( \text{p} \)-bromo toluene (51.30 gms, 0.3 mole) was added dropwise to this mixture. The mixture was refluxed for eight hours, under nitrogen. After the removal of most of the acetonitrile, the residue neutralized with 5% aqueous hydroxide and the reaction mixture was heated.
on a steam bath for one hour. The resulting solution was
cooled and washed as usual as mentioned in the previous exp-
eriment. The ether extract was dried, concentrated. The res-
idue when distilled under reduced pressure gives 34.2 gms
of the above product b.p. 174-181°C @ 2.5 mm, \( n_D^{26} 1.543 \)
yield 72%.

A 2:4 dinitrophenyl hydrazone of the above comp-
ound was prepared and recrystallized from ethyl alcohol
m.p. 2130-214°C.

2-oxo-1-tolyl-\( \Delta^{1;9} \)-octalin

Ethyl-2-oxo-1-tolyl-\( \Delta^{1;9} \)-octalin-10-carboxylate
(15.6 gms, 0.05 mole), 6.00 gm of sodium hydroxide, 25 mls
of water and 30-40 mls of ethyl alcohol 95 % were mixed in a
reaction flask. The mixture was heated under refluxed for
eight hours. The warm solution was acidified by the slow
addition of 1:1 sulphuric acid, a vigorous evolution of
carbon dioxide resulted. The acidified mixture was boiled
under reflux for one hour, cooled and extracted with ether.
The resulting mixture was proceeded in the usual manner as
described in the previous experiment. The residue obtained
when fractionally distilled under vacuum gives 5.6 gm of the
above product b.p. 153°C @ 8 mm \( n_D^{26} 1.523 \) yield 42 - 45 %.
Infrared absorption \( \nu \) 3100, 1800, 1680, 1550, 1500, 1490,
1345, 1245, 1140, 925, 870 and 765 cm\(^{-1}\).
A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallised from ethyl alcohol m.p. 214-5°C.

Found C, 84.67; H, 8.77; O, 6.55 %; \( \text{C}_{17}\text{H}_{21}\text{O} \) requires C, 84.63; H, 8.73; O, 6.49 %.

Ethyl-2-oxo-1-(2-chloro)phenyl- \( \Delta^1\text{19} \) octalin-10-carboxylate

(Sodium ethoxide).

Ethyl-2-oxo- \( \Delta^1\text{19} \) octalin-10-carboxylate

(33.00 gm, 0.15 mole) was added during thirty minutes to a well stirred solution of sodium (3.45 gm, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further fifteen minutes to complete the formation of sodio-derivative of \( \beta \)-keto ester. Freshly distilled O-dichlorobenzene (44.10 gm, 0.3 mole), diluted with 100 mls of dry ethyl alcohol, added dropwise for a period of about one hour, it was then refluxed for ten hours. Most of the ethyl alcohol was distilled off and the residue was diluted with water. The organic layer was separated and the aqueous layer was extracted with ether (2 x 100 mls) portions. The extracts were mixed with the organic layer and the mixture was washed with water and finally dried. The solvent was removed, and the residue when fractionally distilled under reduced pressure gave \( \text{LCO}_{18} \) gm of the product b.p. 196-198°C/ 4 mm \( n^D_25 \) 1.539 yield 39%. 
Infrared absorption: $\bar{\nu}$ 3050, 1750, 1640, 1550, 1440, 1360, 1330, 1245, 1130, 1035, 1070, 920 and 765 cm$^{-1}$.

(Found C, 68.55; H, 6.35; O, 14.42; Cl, 16.06 %. $C_{19}H_{21}O_3Cl$
requires C, 68.61; H, 6.41; O, 14.39; Cl, 16.66%).

A 2:1 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol and pet. ether 185-185.6 °C.

(Found C, 58.51; H, 4.91; N, 10.92; Cl, 6.92 %. $C_{25}H_{25}O_6N_4Cl$
requires C, 58.38; H, 4.87; N, 10.79 %).

**Ethyl-2-oxo-1-(2'-chlorophenyl)-Δ⁴⁺octalin-10-carboxylate:**

(Enamine method)

A solution of pyrrolidine (21.33 gms, 0.3 mole) in 100 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ⁴⁺octalin-10-carboxylate (33.00 gms, 0.15 mole) in 150 mls of dry benzene. The mixture was refluxed for four hours, during this time the water formed was removed with water separator; 150 mls of the solvent was distilled off and the remaining solution of pyrrolidine enamine of p-keto ester was cooled. It was diluted with 250 mls of acetonitrile. Freshly distilled O-dichlorobenzene (44.10 gms, 0.3 mole) was added dropwise to this mixture. The mixture was refluxed for ten hours under nitrogen. After the removal of most of the acetonitrile, the residual portion was neutralized with 5 % aqueous hydrochloric acid (100 mls), the reaction mixture was heated on the steam bath for one hour. Then it was extracted with ether. The resulting mixture was washed as usual as mentioned in the
earlier experiment. The residue obtained when fractionally distilled under reduced pressure gave 24.0 gms of the above product b.p. 195-197°C @ 2.5 mm. n_D^27 1.528 yield 52%.

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol and pet ether m.p. 186-6°C.

2-oxo-1-(2'-chloro) phenyl-Δ^1:9-octalin:

Ethyl-2-oxo-1-(2'-chloro) phenyl-Δ^1:9-octalin-10-carboxylate (16.8 g, 0.05 mole), 6 g of Sodium hydroxide 25 mls of water and 30-40 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for one hour, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as described in the previous experiment. The residue obtained, when fractionally distilled under vacuum gave 7.9 gms of the above product b.p. 178°C @ 10 mm n_D^26 1.548 yield 48%.

Infrared absorption:

\[ \tilde{\nu} \begin{align*} &3500, \ 1630, \ 1510, \ 1430, \ 1335, \ 1170, \ 1125, \ 1100, \ 875, \ \text{and} \ 825 \ \text{cm}^{-1}. \end{align*} \]

(Found C, 73.60; H, 6.58; Cl, 13.23%; C_{26}H_{17}Cl, requires C, 73.63; H, 6.56; Cl, 13.33 %)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol m.p. 200-2°C.
Ethyl-2-oxo-1-naphthyl-Δ¹⁹-octalin-10-carboxylate,

(Sodium ethoxide)

Ethyl-2-oxo-Δ¹⁹-octalin-10-carboxylate (33.0 gm, 0.15 mole) was added dropwise during the thirty minutes, to a well-stirred solution of sodium (3.45 gm, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further 35-40 minutes to complete the formation for sodio derivative of keto ester. Freshly distilled 2-bromonaphthalene (62.10 gm, 0.3 mole) diluted with 50 mls of dry ethyl alcohol, introduced dropwise for a period of one hour; it was then refluxed for six-eight hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water. The organic layer was separated and the aqueous was extracted with ether. The mixture was washed as usual and dried with Na₂SO₄. The solvent was removed and the residue, fractionally distilled under reduced pressure gave 25.8 gm of the above product b.p. 201-203°C @ 1 mm nD²⁸ 1.548; Yield 54-55 %.

Infrared absorption Vmax 3060, 1700, 1610, 1525, 1384, 1260, 1230, 960; 610 and 775 cm⁻¹ .

(Found C, 79.39; H, 6.54; C, 13.77%; C₂₂H₂₁O₄ requires C, 79.63; H, 6.51; C, 13.67%)

A 2:1 4-nitrophenyl-hydrazone of the product was prepared and recrystallized from pet. ether and ethyl alcohol.
m.p. 193°C.

(Found C, 66.20; H, 4.90; O, 18.23; N, 10.62. C₂₉H₂₆O₆N₉

Ethyl-2-oxo-1-naphthyl- Δ¹:⁹octaline-10-carboxylate.

(Enamine method).

A solution of pyrrolidinone (21.33 gm, 0.3 mole) in
100 mls of dry benzene was added dropwise under nitrogen to
a refluxing solution of ethyl-2-oxo- Δ¹:⁹octaline-10-carbox-
ylate (33 gm 0.15 mole) in 150 mls of dry benzene. The mix-
ture was refluxed for four hours, during this time the water
formed in the reaction mixture was removed with Dean and Stark
water separator. 150 mls of the solvent was distilled off, and
the remaining solution of pyrrolidinone enamine was cooled. It
was diluted with 200 mls of acetonitrile. Freshly distilled
bromonaphthalen (62.10 gm, 0.3 mole) was added dropwise
to this mixture. The mixture was refluxed for thirteen hours
under nitrogen. After the removal of most of the acetonitrile
the residue was neutralized with 5% aqueous hydrochloric acid
and the reaction mixture heated on the stem bath for one hour.
The resulting mixture was cooled and extracted with ether.
The ether extract was dried, concentrated and distilled under
reduced pressure to give the above product 20.4 gms b.p.
210-215°C @ 3 mm nD²⁵ 1.543. Yield 57-58 %.

A 2:4 dinitrophenyl hydrazone of the product was
prepared and recrystallized from pet. ether and ethyl alcohol
m.p. 193°C.
2-oxo-1-naphthyl-Δ¹⁻⁹-octalin:

Ethyl-2-oxo-1-naphthyl-Δ¹⁻⁹-octalin-10-carboxylate

(17.41 gm, 0.05 mole), 6.00 gm of sodium hydroxide 25-30 mls of water and 30-40 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for eight to ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner as mentioned in the earlier experiment. The residue when fractionally distilled under vacuum gives 8.3 gm of the above product b.p. 183 °C 10 mm nD²⁵ 1.552 yield 50.52 %, Infrared absorption ν max 3050, 1765, 1635, 1510, 1365, 1260, 1200, 1050, 965, 895, and 775 cm⁻¹, found

(Found C, 86.94%; H, 7.29; O, 5.76 %. C₂₀H₂₀O requires.
C, 86.39; H, 7.30; O, 5.73%)

A 2:4 dinitrophenyl hydrazone of the product was prepared and recrystallized from alcohol/pet. ether m.p. 163-40°C.

(Found C, 68.41; H, 5.08; N, 12.26 %. C₂₆H₂₄O₄N₄ requires.
C, 68.39; H, 5.39; N, 12.25 %.

Ethyl-2-oxo-1-(2-hydroxy)naphthyl-Δ¹⁻⁹-octalin-10-carboxylate.

(Sodium ethoxide method).

Ethyl-2-oxo-Δ¹⁻⁹-octalin-10-carboxylate (35.0 gm,
0.15 mole) was introduced dropwise during thirty minutes to a well stirred solution of sodium (3.45 gm, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further 5-10 minutes to complete the formation of sodium derivative of \(\beta\)-keto ester. Freshly distilled \(\beta\)-chlorophenol (38.55 gm, 0.3 mole), was added dropwise for thirty minutes, it was then refluxed for ten hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water. The organic layer was separated and the aqueous layer extracted with ether. The mixed organic layer was washed with water and dried with \(\text{Na}_2\text{SO}_4\) anhydrous. The solvent was removed, and the residue fractionally distilled under vacuum gave 10.4 gm of the above product b.p., 168-176°C @ 1 mm yield n\(_D^2\) 1.549 42 % yield, Infrared \(\nu\) 3700, 3100, 1650, 1520, 1465, 1320, 1260, 1020, 750 and 765 cm\(^{-1}\). (Found C, 72.58; H, 7.05; O, 20.35 %, \(\text{C}_{19}\text{H}_{22}\text{O}_4\) requires C C, 72.58; H, 7.09; O, 20.31 %).

A 2:4 dinitrophenyl hydrozone of the compound was prepared and recrystallized from ethyl alcohol \& ethyl acetate m.p. 159.5°C.
(Found C, 60.10; H, 5.31; N, 11.31 %, \(\text{C}_{25}\text{H}_{25}\text{N}_4\) requires C, 60.01; H, 5.24; N, 11.21 %)

**Ethyl-2\(\omega\)-oxo-1-(2'hydroxy)-phenyl-\(\Delta^{1,9}\)-octaline-10-carboxylate.** (Enamine method).

A solution of pyrrolidine (21.33 gm, 0.3 mole) in 100 mls of dry benzene was added dropwise under nitrogen to a
to a refluxing solution of ethyl \( \Delta^{119} \)-octaline-10-carboxylate (33.0 gm, 0.15 mole) in 150 mls of dry benzene. The mixture was refluxed for four hours during this time the water formed in the reaction mixture was removed with water separator, 150 mls of the solvent was distilled off, and the remaining solution of pyrroolidine-enamine of \( \beta \)-keto ester was cooled. It was diluted with 250 mls. of acetonitrile. Freshly distilled (0-chlorophenol (38.55 gm, 0.3 mole) was added dropwise to this mixture. The mixture was refluxed for ten hours under nitrogen. After the removal of the most of the acetonitrile the residue was neutralized with 5% aqueous hydrochloric acid heated on steam bath for one hour, and the reaction mixture was cooled and extracted with ether. The ether extract was dried (\( \text{Na}_2\text{SO}_4 \)) and concentrated residue was distilled under reduced pressure to give 13.0 gm of the above product b.p. 170-180/2-3 mm yield 39 % \( n_D^{26} \) 1.543 yield 39%.

A 2:4 dinitrophenyl hydrazone of the compound was prepared and recrystallised from ethyl alcohol + ethyl acetate m.p. 159-160°C.

\[ -2\text{-oxo-1-(2-hydroxy)-phenyl-} \Delta^{119} \text{octalin} \]

\[ \text{Ethyl-2-oxo-1-(2-hydroxy)-phenyl-} \Delta^{119} \text{octalin} \]

-10-carboxylate (15.51 gm, 0.05 mole) 6 gm of sodium hydroxide 25-30 mls of water and 30-40 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for eight to ten hours. The warm solution was acidified by the
slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether the resulting mixture was proceeded in the usual manner. The residue when fractionally distilled under vacuum gave 9.7 gm of the above product b.p. 163-4°C @ 8-6 mm \( n_D^27 = 1.538 \) yield 51.52%. Infrared absorption \( \nu/v_{cm} \): 3700, 3000 (s), 1650, 1500, 1320, 1280, 1145, 1040, 1065, 950, 850, and 775 cm\(^{-1}\).

**Ethyl-2-oxo-1-(4\(^\prime\)-nitro-) phenyl-\(\Delta_{1:9}\) octalin-10-carboxylate.**

(Enamine method).

A solution of pyrrolidine (21.33 gms, 0.3 mole) in 150 mls of dry toluene, was added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo- \(\Delta_{1:9}\) octalin-10-carboxylate (33.0 gms, 0.15 mole) in 100 mls of toluene. The mixture was refluxed for four hours, during refluxing the water formed in the reaction mixture was removed with Dean and Stark trap the solvent was distilled off and remaining solution of pyrrolidine-enamine of \(\beta\)-keto-ester was cooled, it was diluted with 200 mls of dioxane, p-Chloronitro benzene (47.25 gms, 0.3 mole) was added dropwise to the mixture. Then it was refluxed for eight hours under nitrogen, the mixture was cooled to room temperature and filtered with suction. The precipitates of enamine-hydrochloride was washed with ether (4 x 50 mls portions). Combined the filtrate and washing were returned to the reaction flask, neutralized with 10% aqueous
hydrochloric acid (100 mls) and the mixture was refluxed on a water-bath for one hour. The organic layer was separated and the aqueous layer was extracted with ether. The reaction mixture was proceeded the usual manner as described in the earlier experiment. The solvent was removed and the residue fractionally distilled under reduced pressure to give 17.5 gms of the above product b.p. 176-181°C @ 1-1.5 mm nD25 1.538 yield 43 %. The infrared absorption spectrum is in conformity with the above structure.

(Found C, 59.81; H, 6.17; O23.27%, N, 4.07; C19H21O5N requires, 56.79; H, 6.32; O, 23.24; N, 4.17 %.)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallised from pet. ether and ethyl acetate m.p. 216°C.

(Found C, 57.35; H, 4.81; N, 13.39 %; C25H22O8N4 requires C, 57.35; H, 4.89; N, 13.41 %)

2-oxo-(4'-nitro)phenyl- Δ 1:9-octalin.

Ethyl-2-oxo-1-(4-nitropheryl- Δ 1:9-Octalin-10-carboxylate (13.62 gm ; 0.05 mole), 6.00 gm of sodium hydroxide 25-30 mls of water, and 30-40 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for eight to ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evol-ution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted
with ether, the resulting mixture was proceeded in the usual manner. The residue when fractionally distilled under vacuum gives 53 gms of the product b.p. 162-4°C @ 8 mm \( n_D^26.531 \) yield 39-41%. The infrared spectrum of the above compound is in conformity with the structure. Analysis of 2-[4-phenylglycyl]pyrrolidine (Found \( C, 58.51; H, 6.63; N, 15.63 \). \( C_{22}H_{21}O_3N_5 \) requires \( C, 58.53; H, 6.64; N, 15.67% \).

**Ethyl-2-oxo-1-(2'-nitro)-Phenyl-\( \Delta^{11.9} \)octalin-10-carboxylate.**

(Enamine method)

A solution of pyrrolidine (21.33 gms, 0.3 moles) in 150 mls of dry toluene added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\( \Delta^{11.9} \)octalin-10-carboxylate (53.0 gms, 0.1 mole) in 100 mls of toluene. The mixture was refluxed for four hours, during refluxing the water was formed in the reaction mixture was removed with Dean and St Starktrap. The solvent was distilled off, and the remaining solution of pyrrolidine of enamine of \( \beta \)-keto-ester was cooled. It was diluted with 200 mls of dry dioxane. Freshly distilled o-chloro nitrobenzene (47.25 gms, 0.3 mole) was added dropwise to the mixture. Then mixture was cooled to room temperature and the mixture was refluxed for eight hours under
The mixture was again cooled and filtered with suction; the precipitates of enamine hydrochloride washed with dry ether (3 x 100 mls portions); combined the filtrate and washing returned to the reaction flask, neutralized with 10% aqueous hydrochloric acid (100 mls); layer separated and the aqueous layer was extracted with ether and worked out as described in the previous experiment. The solvent was distilled off and the residue when distilled under reduced pressure gave 18.3 gms of the required product, b.p. 175-179°C @ 15 mm; [α]D 1.531 yield 44.45%.

(Found C₂₆H₂₆O₁₈N₁₂; H₆.17; N, 4.07%; requires C₂₆H₂₆O₁₈N₁₂; H₆.21; N, 4.21%).

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol m.p. 198.5-199°C.

(Found C₂₅H₂₅O₈N₄; requires C₂₅H₂₅O₈N₄; H, 4.69%; N₂ 13.43%).

The infrared spectrum is in conformity with the above structure.

2-oxo-1-(2'-nitro)phenyl-Δ¹⁻⁹-octalin.

Ethyl-2-oxo-1-(2'nitro)phenyl-Δ¹⁻⁹-octalin-10-carboxylate (13.62 gm, 0.05 mole) 6.00 gms of sodium hydroxide 25 mls of water, 50 mls of ethyl alcohol were mixed in a reaction flask. The mixture was heated under reflux for ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid; a vigorous evolution of carbondioxide
resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The resulting mixture was proceeded in the usual manner. The residue when fractionally distilled under reduced pressure give 8.3 gm of the product 168°C @ 10 mm, nD25 1.544 yield 65%.

(Found C, 70.53; H, 6.63; N, 5.18) C14H18O3N requires C, 70.84; H, 6.63; N, 5.20%.)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallised twice with ethyl acetate and ethyl alcohol m.p. 141-2°C.

(Found C, 58.48; H, 4.61; N, 15.49; C12H16O6N2 requires C, 58.53; H, 4.66; N, 15.67%) 15.55%)

The infrared spectrum is in conformity with the structure of the above compound.

**Ethyl-2-oxo-4-acetyl-Δ119 octalin-10-carboxylate.**

(Sodium ethoxide).

Ethyl-2-oxo-Δ119 octalin-10-(22.0 gm, 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further five minutes to complete the formation of sódio derivative of the β-keto ester. Acetyl chloride (15.70 gm, 0.2 mole) was mixed with 100 mls of ethyl alcohol, and added dropwise for a period of one hour. The mixture was stirred for further
one hour, it was then refluxed for eight hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls). The organic layer was separated and the aqueous layer was extracted with ether (4 x 50 mls portions). The extracts were mixed with the organic layer and the mixture was washed with water and finally dried. The solvent was removed, and the residue was fractionally distilled under reduced pressure, gave 14.8 gm of the required product b.p., 183-193°C @ 2 mm, n\text{D} 1.528, yield 47%. Light absorption a) Ultraviolet Isopropyl max, 235 Emax 19500,
b) Infrared, wavenumbers (cm\textsuperscript{-1}): 3100, 3300, 1760, 1450, 1360, 1340, 1140, 1030, 980, 870, and 770cm\textsuperscript{-1}.

(Found C, 68.15; H, 7.24; O, 24.51% C\textsubscript{15}H\textsubscript{20}O\textsubscript{4} requires C, 68.25; H, 7.25; O, 24.47%)

A 2:4 dinitrophenyl hydrasone of the compound prepared and recrystallized by ethyl alcohol/pet.ether (1:1) m.p. 160-161°C.

(Found C, 56.76; H, 5.44; N, 18.60%; C\textsubscript{2}\textsubscript{2}.H\textsubscript{2}C.N\textsubscript{4} requires C, 56.73; H, 5.43; N, 18.58%)

Ethyl-2-oxo-1-acetyl-\textsuperscript{1:9} octalin-10-carboxylate.

(Sodium amide method).

In a three necked bottomed flask placed in a bath of liquid air was taken (4.6 gm 0.2 mole) and about 150 mls of liquid ammonia was added along with 2.5 gm of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-
-20-octalin-10-carboxylate (44 gm, 0.2 mole) was then added drop wise over a period of fifteen minutes with constant stirring. A yellowish red amorphous salt formed immediately 400 mls of sodium dried diethyl ether diethyl ether was added, and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier became increasingly viscous, but the stirring was continued in an atmosphere of nitrogen and acetyl chloride (31.40 gm, 0.4 mole) was added in small portions as the mixture was brought to refluxing temperature, and finally 100 mls. of dry toluene was added and the mixture refluxed for further nine hours. The mixture was worked out in the usual manner as described in the earlier experiment. The solvent was removed and the residue distilled under reduced pressure gave 17.3 gm. of the above product b.p. 190-192°C @ 4 mm, nD 1.520 yield 42-44%.

A 2:4 dinitrophenyl hydrazone of the compound was prepared and recrystallized by ethyl alcohol/pet ether (1:1) m.p. 160.5°C.

**Ethyl-2-oxo-1-acetyl-Δ^1:9-octalin-10-carboxylate.**

(Enamine method).

A solution of pyrrolidine (23.3 gms, 0.3 mole) in 150 mls of dry toluene was added dropwise to a refluxing solution of ethyl-2-oxo-Δ^1:9-octalin-10-carboxylate (33.0 gms, 0.15 mole) in 100 mls of toluene. The mixture was refluxed for four hours, during refluxing the water was
formed in the reaction mixture was removed with Dean and Stark water separator. The solvent was distilled off, and the remaining solution of pyrrolidine enamine of \( \beta \)-keto ester was cooled. It was diluted with 200 mls. of dioxane acetyl chloride (23.55 gm, 0.3 mole) was added in portions to the cold solution. The reflux was prefluxed for twelve hours under nitrogen and the mixture was cooled to room temperature. The precipitate of enamine-hydrochloride formed during refluxing was filtered and washed with ether; combined the filtrate and washing to the reaction flask, then it was neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated while the aqueous layer was extracted with ether. Washing of the mixture was carried out in the usual way as described in the previous experiment. The solvent was removed, and the residue distilled under reduced pressure to give 42.1 gm of the required compound b.p. 192-205°C @ 4 mm 20°C 1.524 yield 41%.

A 2:4 dinitrophenyl hydrazone of the compound prepared and recrystallized by ethyl alcohol/pet. ether (1:1) m.p. 160.5°C.

2-oxo-1-acetyl- \( \Delta^{1:9} \)-octalin.

A solution of 26.43 gm (0.05 mole) of ethyl
\[ \text{2-oxo-acetyl-} \quad \Delta \quad \text{octalin-10-carboxylate, 6.00 gm of the sodium hydroxide 25 mls of water, and the 25 mls of ethyl} \]
alcohol (95%) was heated under reflux for five hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid and a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for one hour, cooled and extracted with ether. The ether layer was washed well with 5% sodium hydroxide. Solution, followed by washing with 2% aqueous acetic acid, then with water. It was dried (Na$_2$SO$_4$).

The solvent was evaporated and the residue when distilled under reduced pressure gave 14.2 gm of the above product b.p. 186-191°C @ 10 mm n$^D$ 1.513 yield 52%. Light absorption Ultraviolet, Isopropyl max 242, E max 23000, b) Infrared $\tilde{\nu}$ 3000, 1764, 1650, 1540, 1480, 1360, 1260, 1140, 1040, 945, 870, and 765 cm$^{-1}$. (Found C, 76.15; H, 7.2; O, 16.65% C$_{12}$H$_{16}$O$_2$ requires C, 76.21; H, 7.21; O, 16.43%).

A 2:4 dinitrophenylhydrazone of the compound was prepared and recrystallised from pet. ether and ethyl alcohol m.p. 168-169°C. (Found C, 58.05; H, 5.69; N, 15.03%, C$_{18}$H$_{20}$O$_2$N$_4$ requires C, 58.25; H, 5.61; N, 15.21%).

**Ethyl-2-oxo-1-propionyl-\[11\] octalin-10-carboxylate.**

(Sodium ethoxide method)

Ethyl-2-oxo-\[1\] octalin-10-carboxylate (33.0 gms, 0.15 mole) was added during thirty minutes to a stirred sol-
ution of sodium (3.45 gm; 0.15 mole) in absolute alcohol, cool
cooled to room temperature. The reaction mixture was stirred
for further ten minutes to complete the formation of sodio
derivative of the β-keto ester. Freshly distilled propionyl
chloride (27.75 gm; 0.3 mole) was mixed with 50 mls of ethyl
alcohol and added dropwise for a period of one hour; it was
then refluxed fourteen hours. Most of the ethyl alcohol was
distilled off, and the residue was diluted with water. The
organic layer was separated and the aqueous layer was extr-
acted with ether. The extract were combined with the organic
layer, and the mixture was washed with water and finally dr
ried. The solvent was removed and the residue was fraction-
ally distilled under reduced pressure gave 14.3 gm of the
required product b.p. 191-193°C @ 171.5 mm nD 1.524
yield 97-98 %. Light absorption  a) Ultraviolet Isoprop
λ max 238, Emax 21500, b) Infrared ν 3000, 1760, 1470,
4365, 1334, 1245, 1140, 1040, 870 and 750 cm⁻¹.
(Found C, 69.30; H, 8.02; C₁₆H₂₂O₄ requires
 C, 69.03; H, 7.99 %).

A 2:4 dinitrophenyl hydrazone of the product
was prepared and recrystallised from ethyl alcohol, m.p.
160-161°C.
(Found C, 57.63; H, 5.97; N, 11.85 %. C₂₂H₂₆O₇N₄ requires
 C, 57.62; H, 5.69; N, 11.99 %).
Ethyl-2-oxo-1-propionyl-\(\Delta_{1:9}\)-octaline-10-carboxylate

(Enamine method)

A solution of pyrrolidine (21.33 gm, 0.3 mole) in 150 mls of dry toluene added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\(\Delta_{1:9}\)-octaline-10-carboxylate (33.0 gm, 0.15 mole) in 150 mls of toluene. The mixture was refluxed for four hours during refluxing, the water formed in the reaction mixture was removed with water separator. The solvent was distilled off, and the remaining solution of pyrrolidine enamine of \(\beta\)-keto ester was cooled. It was diluted with 200 mls of dioxane. Propionyl chloride (27.75 gm, 0.3 mole) was added in two portions to the cold reaction mixture then refluxed for twelve hours under nitrogen, and the mixture was cooled to room temperature. The precipitates of enamine-hydrochloride formed during refluxing was filtered and washed with ether. Combined the filtrate and washing to a reaction flask, it was neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated while the aqueous layer was extracted with ether (4 x 50 ml portions).

Washing of the mixture was carried out in the usual way as described in the previous experiment. The solvent was removed and the residue distilled under reduced pressure to give 23.1 gms of the above product b.p. 204-205°C/ 2mm n_D \(^\text{27}\) 1.529 yield 58%.

A 2,4 dinitrophenyl hydrazone of the product was prepared and recrystallised from thyl alcohol m.p. 160-1°C.
2-oxo-1-propionyl-\Delta^{1;9}\text{-octalin.}

A solution of 13.92 gm, (0.05 mole) of ethyl-2-oxo-1-propionyl-\Delta^{1;9}\text{-octalin-10-carboxylate, 6.00 gm of sodium hydroxide, 25 mls of water and 25 mls of ethyl alcohol (95%) was heated under reflux for five hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of CO_2 resulted. The acidified mixture was boiled under reflux for one hour, cooled and extracted with ether. The ether-layer was washed well with 5% sodium hydroxide solution, followed by washing with 2\% aqueous acetic acid, then with water. It was dried (Na_2SO_4). The solvent was evaporated, and the residue when distilled under reduced pressure gave 7.2 gm of the above product, b.\text{D.}, 188\text{°C} @ 2.5 mm, n_D^{25} 1.530, yield 48\%. Light absorption

a) Ultraviolet Isoprop \lambda \text{max} 241 \ E\text{max} 22,300, b) Infrared \ \sqrt{\text{V}} 3000, 1775, 1480, 1450, 1365, 1325, 1250, 1130, 1065, 925, 875, and 765 cm^{-1}.

(Found C, 75.7; H, 8.78; O, 15.52 \% C_{15}H_{18}O_2 requires C, 75.3; H, 8.74; O, 15.39\%).

A 2:4 dinitrophenyl hydrazone of the diketone was prepared and recrystallised from pet.ether m.p. 171-173\text{°C}

(Found C, 59.14; H, 5.47; N, 14.75 \% C_{19}H_{22}O_5N_4 requires C, 59.21; H, 5.52; N, 14.68 \%).

Ethyl-2-oxo-1-butyryl-\Delta^{1;9}\text{-octalin-10-carboxylate.}

(Sodium ethoxide)

Ethyl-2-\ o\ c=\Delta^{1;9}\text{-octaline-10-carboxylate}
(33.0 gm, 0.13 mole) was added during thirty minutes to stirred solution of sodium (5.45 gm, 0.15 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further ten minutes to complete the formation of sodio derivative of the \( \beta \)-keto-ester. Butyryl chloride (31.97 gm, 0.3 mole) was mixed with 100 mls of ethyl alcohol, and added dropwise for a period of one hour. The mixture was stirred for another one hour. It was then refluxed for ten hours. Most of the ethyl alcohol was distilled off, and the residue was washed with water and finally dried. The solvent was removed, and the residue was fractionally distilled under reduced pressure gave 8.3 gm of the required product b.p. 181-189°C @ 2 mm Hg 1.540 yield 28%. The infrared \( \overline{\nu} \) 3000, 1785, 1465, (s) 1365, 1340, 1140, 1090, (s) 1075, 1025, 1000, 915, 875 and 750 cm\(^{-1}\).

(Found C, 69.83; H, 8.27; \( \text{C}_{17}\text{H}_{24}\text{O}\text{X} \) requires O, 69.71; H, 8.43%)

A 2: dinitrophenyl hydrazone was prepared of the above product recrystallized from dioxane/pet. ether (4:1) m.p. 197-198°C (fine yellow shining crystals).

(Found C, 58.45; H, 5.97; N, 11.85 %, \( \text{C}_{23}\text{H}_{20}\text{O}_{7}\text{N}_{4} \) requires C, 58.43; H, 5.83; N, 11.86%)

Ethyl-2-oxo-1-butyryl-\( \Delta^{1:9} \)-octaline-10-carboxylate.

(Enamine method)

A solution of pyrrolidine (10.66 gm, 0.25 mls) in 100 mls of dry benzene \( \text{H}_2 \) added dropwise under nitrogen to
a refluxing solution of ethyl-2-oxo-\(\Delta^{1:9}\)octalin-10-carboxylate (22.0 gm, 0.1 mole) in 150 mls. of benzene. The mixture was refluxed for four hours during refluxing the water formed in the reaction was removed with water separator. (Dean and Stark). The solvent was distilled off, and the remaining solution of pyrolidine enamine of 3-keto ester was cooled. It was diluted with 200 mls. of dioxane, butyl chloride (31.97 gm, 0.30 mole) was added in portions to the cold reaction mixture. The refluxed for six hours under nitrogen and the mixture was cooled to room temperature.

The precipitate of enamine-hydrochloride formed during refluxing, was filtered and washed with ether (4 x 50 mls portions) combined the filtrate and washing to the reaction flask, it was neutralized with 10% aqueous hydrochloric acid and refluxed for one hour. The organic layer was separated and the aqueous layer was extracted with ether. Washing of the mixture was carried out in the usual way to as described in the previous experiments. The solvent was removed, and the residue fractionally distilled under vacuum gave 13.5 gm of the required compound b.p. 180-192\(^\circ\)C @ 3 mm \(n_D^{25}\) 1.541 yield 42%.

A 2:4 dinitrophenyl hydrazone was prepared of the above product recrystallised from dioxane/pet. ether (4:1) m.p. 197-198\(^\circ\)C.
2-oxo-1-butyl-Δ\(^{1;9}\)octalin.

A solution of 16.42 gm (0.05 mole) of ethyl-2-oxo-1-butyl-Δ\(^{1;9}\)octalin-10-carboxylate, 6 gm (0.15 mole) of sodium hydroxide 5 mls of water, and 25-30 mls of ethyl alcohol (95%) was heated under reflux for five to eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux of for 90 minutes, cooled and extracted with ether. The ether-layer was washed well with 5% sodium hydroxide, followed by 2% aqueous acetic acid, then with water. It was dried (Na\(_2\)SO\(_4\)).

The solvent was evaporated, and the residue when distilled under reduced pressure gave 6.20 gm of the above product, b.p. 183-184°C @ 13 mm. \(n_D^{25}\) 1.530, yield 43%. The infrared spectrum is in conformity with the structure of the compound.

(Found C, 73.96; H, 10.07; O, 15.97 %. \(C_{14}H_{20}O_2\) requires C, 75.91; H, 10.12; O, 15.81 %).

A 2:4 dinitrophenyl hydrazone of diketone was prepared and recrystallized from pet. ether/dioxane m.p. 138-39°C.

(Found C, 59.99; H, 6.04; N, 13.98 %. \(C_{20}H_{24}O_{5}N_4\) requires C, 59.99; H, 6.14; N, 13.68 %).

Ethyl-2-oxo-iso-butyl-Δ\(^{1;9}\)octalin-10-carboxylate.

(Sodium ethoxide method).

Ethyl-2-oxo-Δ\(^{1;9}\)octalin-10-carboxylate

(44.0 gm, 0.2 mole) was added during thirty minutes to a stirred solution of sodium (4.6 gm, 0.2 mole) in absolute
ethyl alcohol, cooled to room temperature. The reaction was stirred for 30-40 minutes to complete the formation of sodio-derivative of the \( \beta \)-keto ester. Freshly, distilled iso-butryryl chloride (31.95 gm, 0.3 mole) was diluted with 50 mls of dry ethyl alcohol and added dropwise for a period of forty five minutes. The mixture was stirred for another one hour, it was then refluxed for ten hour. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls). The organic layer was separated and the aqueous layer was extracted with ether (2 x 100 mls portions). The extract were combined with the organic layer and the mixture washed with water and finally dried. The solvent was removed and the residue when distilled under reduced pressure gave 11.1 gm, of the required product b.p. 185-186°C @ 2.25 mm \( n^2_{D} \) 1.542 yield 34-35%. Infrared absorption \( \nu \) 3000, 1760, 1480, 1340, 1240, 1025, 1000, 915, 873, and 750 cm\(^{-1}\).

(Found C, 69.83; H, 8.27%; \( \text{C}_{17} \text{H}_{24} \text{O}_{4} \) requires C, 69.69; H, 8.41%)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallised from ethyl alcohol/dioxane m.p. 138-139°C.

(Found C, 58.45; H, 5.97; N, 11.85 %, \( \text{C}_{27} \text{H}_{28} \text{O}_{7} \text{N}_{4} \) requires C, 58.41; H, 5.93; N, 11.83 %).
Ethyl-2-oxo-1-iso-butyrll-Δ\(^{1:9}\)-octalin-10-carboxylate.
(Enamine method)

Pyrollidine (10.66 gm, 0.15 mole) in 100 mls of dry benzene, added drop wise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ\(^{1:9}\)-octalin-10-carboxylate (22.0 gm, 0.1 mole) in 150 mls of benzene. The mixture was refluxed for four hours during refluxing the water formed in the reaction was removed with water separator. The solvent was distilled off, and the remaining solution of pyrrolidine-enamine of β-keto ester was cooled. It was diluted with 200 mls of dioxane, Isobutyryl chloride (15.97 gm, 0.15 mole) was added in portion to cold reaction mixture. Then refluxed for eight hours under nitrogen and the mixture was cooled to room temperature. The precipitate of enamine hydrochloride formed during refluxing, was filtered and washed with ether. (Combined the filtrate and washed with ether). Combined the filtrate and washing to the reaction flask it was neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated and the aqueous layer was extracted with ether. Washing of the mixture was carried out in the usual way as described in the previous experiment. The solvent was removed and the residue distilled under reduced pressure to give 12.4 gm of the required product. b.p. 192-198 @ 2 mm Hg 26 \(n_D\) 1.539 yield 39-40 %. Both the samples have identical infrared spectra and the mixed melting point of the 2:4 dimitrophenyl hydrazones derivative showed no depression in their melting point.
2-oxo-1-Isobutyryl- $\Delta^{1:9}$-octalin.

A solution of 14.6 gm (0.05 mole) of ethyl 2-oxo-1-Isobutyl- $\Delta^{1:9}$-octalin-10-carboxylate, 6.00 gm (0.15 mole) of sodium hydroxide in 25 mls of water and 25 mls of ethyl alcohol (95 %) was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes. Cooled and extracted with ether. The ether layer was washed well with 5 % sodium hydroxide solution, followed by washing with 2 % aqueous acetic acid, then with water. It was dried ($\text{Na}_2\text{SO}_4$). The solvent was evaporated and the residue when distilled under reduced pressure gave 6.3 gm of the above product b.p. 178-180°C @ 14 mm, n$\text{D}^{26}$ 1.530 yield 43%.

(Found C, 73.96; H, 10.07; O, 15.97 %. C$_{12}$H$_{20}$O$_2$ requires C, 73.91; H, 10.17; O, 15.94 %.)

A 2:4 dinitrophenyl hydrazone of the diketone was prepared and recrystallised from pet. ether 6 ethyl alcohol (3:2) m.p. 143-4°C.

(Found C, 59.99; H, 6.04; N, 13.98 %. C$_{20}$H$_{24}$O$_5$N$_4$ requires C, 59.69; H, 6.21; N, 13.92 %.)

Ethyl-2-oxo-1-n-valeryl- $\Delta^{1:9}$-octalin-10-carboxylate.

(Sodium ethoxide)

Ethyl-2-oxo- $\Delta^{1:9}$-octalin-10-carboxylate

(22.0 gm, 0.1 mole) was added during twenty minutes to
stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for another five minutes to complete the hydroxyl derivative. Distilled valeryl chloride (18.30 gm, 0.15 mole), was added dropwise for a period of one hour it was then refluxed for six hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls). The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were mixed with the organic layer and the mixture was washed with water, finally dried. The solvent was removed, the residue was fractionally distilled under reduced pressure to give 8.3 gm of the required product b.p. 186-188°C 0 2 mm, yield 22% nD 1.561.

(Found C, 70.55; H, 8.55; O, 20.88 %. C18H26C4 requires C, 70.51; H, 8.53; O, 20.82 %). A 2:4 dinitrophenyl hydrazone was prepared of the above product and recrystallized from dioxane/ethyl alcohol m.p. 147-48°C.

(Found C, 59.24; H, 6.21; N, 11.51 %. C24H30O7N4 requires C, 59.21; H, 6.29, N, 11.62 %.)

**Ethyl-2-oxo-1-n-valeryl-Δ1:9-octaline-10-carboxylate.**

(Enamine method)

A solution of pyrrolidine (21.33 gm, 0.3 mole) in 150 mls of dry toluene added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ1:9-octaline-10-
carboxylate (33.0 gm, 0.15 mole) in 100 mls of toluene. The mixture was refluxed for four hours during refluxing the water formed in the reaction mixture was removed with water separator (Dean and Stark). The solvent was distilled off, and the remaining solution of pyrrolidine enamine of 3-keto ester, was cooled. It was diluted with 250 mls of dioxane; Valeryl chloride (36.15 gm, 0.3 mole) was added dropwise to the cold solution. Then it was refluxed for eight hours under the influence of nitrogen atmosphere, and the mixture was cooled to room temperature. The precipitates of enamine-hydrochloride formed during refluxing was filtered and washed with ether, combined the filtrate and washing to the reaction flask, it was neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated while the aqueous layer was extracted with ether (4 x 50 mls portions), washing of the mixture was carried out in the usual manner as described in the previous experiment. The solvent was removed, and the residue distilled under reduced pressure to give 11.4 gm, of the required product b.p. 183-194°C @ 1.5-2 mm, nD^26 1.562, yield 33-34%.

A 2:4 dinitrophenyl hydrazone was prepared of the above product and recrystallised from dioxane/ethyl alcohol m.p. 147-8°C.

2-oxo-1-valeryl- △^{1:9} octalin.

A solution of 15.32 gm (0.05 mole) of ethyl 2-oxo-1-valeryl- △^{1:9} octalin-10-carboxylate, 6.0 gm
(0.15 mole) of sodium hydroxide, 25 mls of water and 25 mls of ethyl was refluxed for ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The ether-layer was washed well with 5% sodiumhydroxide solution followed by washing with 2% aqueous acetic acid then with water. It was dried (Na$_2$SO$_4$). The solvent was evaporated, and the residue when distilled under reduced pressure gave 8.20 gm of the above product b.p. 175-181/12 mm yield 49-51%, $n_D^{27} 1.558$. The infrared spectrum showed the characteristic frequencies of the groups present in the diketo compound, which confirms the structure.

(Found C, 76.86; H, 9.46; O, 13.67 % C$_{15}$H$_{22}$O$_2$ requires C, 76.82; H, 9.43; O, 13.65%).

**Ethyl-2-oxo-1-Iso-valeryl-$\Delta^{119}$octalin-10-carboxylate:**

(Sodium ethoxide)

**Ethyl-2-oxo-$\Delta^{119}$-octalin-10-carboxylate**

(33.0 gm, 0.15 mole) was added during thirty minutes, to a stirred solution of sodium (3.45 gm, 0.15 mole) in absolute ethyl alcohol, and cooled to room temperature. The reaction mixture was stirred for further ten minutes to complete the formation of sodium-derivative of $\beta$-keto-ester. Iso-valeryl chloride (36.15 gm, 0.3 mole) diluted with of dry ethyl alcohol, was added dropwise over a period of one hour, it
was then refluxed for eight to ten hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water. The organic layer was separated while the aqueous layer was extracted with ether. The extracts were combined with the organic layer and the mixture was washed with water and finally dried. The solvent was removed and the residue was fractionally distilled under reduced pressure gave 8.5 gm of the required product b.p. 175-180°C/2 mm $n_D^{25}$ 1.561 yield 23%. Infrared Vmax 3100, 1760, 1480, 1360, 1340, 1250, 1140, 1050, (s) 925, and 760 cm$^{-1}$.

(Found C, 40.55; H, 8.55; O, 20.88%; C$_{18}$H$_{26}$O$_4$ requires C, 70.62; H, 8.61; O, 20.92%).

A 2:4 dinitrophenyl hydrazone was prepared of the above compound and recrystallised from ethyl alcohol/ethyl acetate (2:1) m.p. 168-170°C.

(Found C, 59.24; H, 6.21; N, 11.51%; C$_{24}$H$_{30}$O$_7$N$_4$ requires C, 59.23; H, 6.18; N, 11.58%)

Ethyl-2-oxo-1-iso-valeryl-$\Delta^{1:9}$-octalin-10-carboxylate.

(Enamine method).

A solution of pyrrolidine (21.53 gm, 0.3 mole) was in 150 mls of dry toluene added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-$\Delta^{1:9}$-octaline-10-carboxylate (33.0 gm, 0.15 mole) in 100 mls of toluene. The mixture was refluxed for four hours during refluxing the water formed in the reaction mixture was removed with the water separator (H. Dean & Stark). The solvent was distilled off,
and the remaining solution of pyrrolidine-enamine of β-keto ester was cooled. It was diluted with 250 mls of diowane, Isovaleryl chloride (36.15 gm, 0.3 mole) was added dropwise to the cold solution. Then it was refluxed for ten hours under nitrogen, and the mixture was cooled to room temperature. The precipitates of enamine hydrochloride formed during refluxing was filtered and washed with ether, combined the filtrate and washing to the reaction flask, it was neutralized with 10 % aqueous hydrochloride acid and refluxed for one hour on a water bath. The organic layer was separated while the aqueous layer was extracted with ether (4 x 50 mls portions) washing of the mixture was carried out in the usual way as described in the previous experiment. The solvent was removed and the residue when distilled under reduced pressure gave 12.3 gm of the above product 178-183°C 2 2 mm nD25 1.5623, yield 40-41 %.

A 2:4 dinitrophenyl hydrazone was prepared of the above compound and recrystallised from ethyl alcohol/ethyl acetate (2:1) m.p. 163.5°C.

Ethyl-2-oxo-1-Isovaleryl-Δ119-octaline.

A solution 15.32 gm, (0.05 mls of ethyl-2-oxo-1-Isovaleryl-Δ119-octaline-10-carboxylate, 6.0 gm, (0.15 mole) of sodium hydroxide, 25 mls of water, and the 20 mls of ethyl alcohol (95 %) was heated under reflux for five hours. Then the warm solution was acidified by the slow addition. The acidified mixture was boiled under reflux for ninety minutes,
cooled and extracted with ether. The ether layer was washed well with 5% sodium hydroxide solution, followed by the washing with 2% aqueous acetic acid, and finally with water. It was dried with sodium sulphate anhydrous. The solvent was evaporated, and the residue distilled under reduced pressure gave 6.2 gm of the above product b.p. 157-171°C @ 3 mm yield 39%. Infrared absorption Vmax 3000, 1765, (w), 1635, 1456, 1135, 1065, 1050, 980, 850, and 750 cm⁻¹.

(Found C, 76.36; H, 9.46; O, 13.67%; C₁₅H₂₂O₂ requires C, 76.84; H, 9.44; O, 13.64%).

A 2:4 dinitrophenyl hydrazone of the diketo compound was prepared and recrystallised from pet. ether m.p. 158-60°C.

(Found, C, 60.81; H, 6.56; N, 13.51%; C₂₁H₂₆N₄C₅ requires C, 60.75; H, 6.52; N, 13.49%).

**Ethyl-2-oxo-1-succinyl- Δ₁⁹-octalin-10-carboxylate.**

Sodium ethoxide method.

**Ethyl-2-oxo- Δ₁⁹-octalin-10-carboxylate** (31.0 gm 0.2 mole) was added during thirty minutes to a stirred solution of sodium (4.6 gm 0.1 mole) in absolute ethyl alcohol and then stirred for another ten minutes to complete the formation of sodium derivative of the 3-keto ester. Freshly distilled succinyl chloride (31.0 gm, 0.2 mole) was added dropwise for a period of 45 minutes. The mixture was stirred for further one hour, it was then refluxed for twelve hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water,
The organic layer was separated and aqueous layer was extracted with ether. The extracts were combined with water and finally dried. The solvent was removed, and the residue was fractionally distilled under reduced pressure gave 24 gm of the required product b.p. 192-194°C @ 1 mm yield 47 % Semi-solidified on cooling. Infrared absorption ν 3100, 1785, 1465, 1456, 1365, 1340, 1245, 1135, 1050, 940 and 870 cm⁻¹.

(Found C, 59.90; H, 6.21 % C₁₇H₂₁O₅Cl requires C, 59.83; H, 16.18%).

A 2:4 dinitrophenyl hydrazone was prepared of the above product and recrystallised twice with ethyl alcohol m.p. 148-149°C.

(Found C, 53.02; H, 4.33; N, 10.20 %, C₂₃H₂₅O₅N₄Cl requires C, 52.21; H, 4.79; N₄C₂.27 %).

**Ethyl-2-oxo-1-succinyl-Δ¹¹⁻octaline-10-carboxylate.**

(Enamine method)

Pyrrolidine (21.33 gm, 0.3 mole) in 100 mls of dry benzene, added dropwise under nitrogen to a refluxing solution of ethyl -2-oxo-Δ¹¹⁻octalin-10-carboxylate (33.0 gm 0.15 mole) in 250 mls of benzene. The mixture was refluxed for four hours during refluxing the water formed in the reaction was removed with water separator (Dean and Stark). The solvent was distilled off, and the remaining solution of pyrrolidine-enamine of β-keto ester was cooled. It was diluted with 200 mls of dioxane, succinyl chloride (46.47 gm,
0.3 mole) was added in the portions to the cold reaction mixture. The refluxed for eight hours under nitrogen, and the mixture was cooled to room temperature. The precipitate of oxamino-hydrochloride formed during refluxing, was filtered and washed with ether; combined the filtrate and washing returned to the reaction flask it was neutralized with 10% aqueous hydrochloride acid and refluxed for one hour on a water bath. The organic layer was separated and the mixture was carried out in the usual way as mentioned in the previous experiment. The solvent was removed and the residue distilled under reduced pressure to give 26 gm of the required product b.p. 200-210° C @ 2mm nD 1.538, Yield 44%.

A 2:4 dinitrophenyl hydrazone was prepared of the above product and recrystallized twice with ethyl alcohol m.p. 148-149° C.

Ethyl-2-oxo-1-succinyl-Δ1:9-octalin.

A solution of 34.0 gm (0.15 mole) of ethyl-2-oxo-1-succinyl-Δ1:9-octalin-10-carboxylate 6.00 gm (0.15 mole) of sodium hydroxide, 25 mls of water, and 25 mls of ethyl alcohol (95%) was heated under reflux for four hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evaluation of carbon dioxide for one hour, and cooled and extracted with ether. The ether layer was washed as usual as described in the previous experiment. The solvent was evaporated, and the residue distilled under vacuum gave
15.3 gm of the above product b.p. 181-186°C @ 5 mm yield 48 %.

The infrared spectrum is in conformity with the structure found C, 62.58; H, 6.35; O, 17.86; Cl, 13.2 %, C₁₄H₁₇O₃Cl requires, C, 62.51; H, 6.39 %.

A 2,4 dinitrophenylhydrazone of the diketoc compound was prepared and recrystallised from ethyl alcohol n.p. 156-157°C.

(Found C, 53.51; H, 4.71; N, 12.71 %, C₂₀H₂₁O₆N₄Cl requires C, 53.49; H, 4.63; N, 12.89 %).

**Ethyl-2-oxo-glutaryl- Δ¹¹octaline-10-carboxylate.**

(Sodium ethoxide method).

Ethyl-2-oxo- Δ¹¹ carboxylate (22.0 gm, 0.1 mole) was added during the thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol cooled to room temperature. The reaction mixture was stirred for further ten minutes to complete the formation of sodium derivative of Δ₁¹-keto ester. Freshly distilled glutaryl chloride (32.18 gm, 0.2 mole) was added dropwise for a period of one hour. The mixture was stirred for further thirty minutes, it was then refluxed for eight hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water. The organic layer was separated, and the aqueous layer was extracted with ether. The extracts were combined with the organic layer and the mixture was washed with water and finally dried. The solvent was removed, and the residue was fractionally distilled.
under reduced pressure gave 18.7 gms of the above product. 

Bi.P. 178-180°C @ 1 mm Hg. Infrared absorption \( \tilde{\nu} \):

3000, 1700, 1460, 1365, 1275, 1125, 1000, (s), 920, 875 and 765 cm\(^{-1}\).

(found, C, 60.83, H, 6.50, N, 9.80, \( \text{C}_{18} \text{H}_{23} \text{O}_{5} \text{Cl} \).

requires C, 60.91; H, 6.52; N, 9.86%)

A 2:4 dinitrophenyl hydrazone of the above compound

was prepared and recrystallised from ethyl alcohol + pet. ether

n\(_D\), 164-6°C.

(found C, 53.97; H, 5.08; N, 10.47 %, \( \text{C}_{24} \text{H}_{27} \text{O}_{5} \text{N}_{4} \text{Cl} \).

requires C, 53.69; H, 5.28; N, 10.39%)

Ethyl-2-oxo-1-glutaryl-\( \text{\Delta}^{1:9} \) octaline-10-carboxylate.

Enamine method).

A solution of pyrrolidine (21.33 gm, 0.3 mole) in 150 mls of dry toluene, added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\( \text{\Delta}^{1:9} \) octaline-10-carboxylate (33.0 gm, 0.15 mole) in 100 mls of dry toluene. The mixture was refluxed for four hours, during the refluxing, the water formed in the reaction mixture was removed with water separated (Dean and Stark). The solvent was distilled off, and the remaining solution of pyrrolidine-enamine of \( \beta \)-keto ester was cooled. It was diluted with 200 mls of dioxane, glutaryl chloride b.p. (48.27 gm, 0.3 mole) was added
dropwise to the cold solution. Then it was refluxed four
eight hour under nitrogen, and the mixture was cooled to
room temperature. The precipitates of enamine-hydrochloride
formed during refluxing was filtered and washed with ether.
Combined the filtrate and washing to the reaction flask, it
was neutralized with 10% aqueous hydrochloride acid, and
refluxed for one hour on a water bath. The organic layer was
separated, while the aqueous layer extracted with ether
(4 x 50 mls portions). Washing of the mixture was carried
out in the usual way as described in the previous experiment.
The solvent was removed and the residue distilled under redu-
ced pressure to give 22.5 gm; of the above product b.p.
182-191°C @ 1.5-2 mm Hg 26 1.544 yield 45%.

A 2:4 dinitrophenyl hydrazone of the above compound
was prepared and recrystallised from ethyl alcohol in pet. ether
m.p. 164-6°C.

\[ 2-\text{oxo-1-glutaryl-} \Delta^{1:9} \text{octalin.} \]

A solution of 18.74 gm (0.05 mole) of ethyl-2-
-oxo-1-glutaryl- \( \Delta^{1:9} \) octalin-10-carboxylate, 6.0 gm
(0.15 mole) of sodium hydroxide, 25 mls of water, and 25 mls
of ethyl alcohol (95 %) was heated under reflux for eight
hours, the warm solution was acidified by the slow addition
of 1:1 sulphuric acid, a vigorous evolution of carbon-dioxide
resulted. The acidified mixture was boiled under reflux for
ninety minutes, cooled and extracted with ether. The ether-layer was washed well with 2% sodium hydroxide followed by washing with 2% aqueous acetic acid, then with water. It was dried (Na₂SO₄). The solvent was evaporated and the residue when distilled under reduced pressure gave 8.3 gm of the above product b.p. 168-9°C/10 mm. nD²⁷ 1.529, yield 32%.

(Found, C, 63.70; H, 6.68; Cl, 12.59; C₁₅H₁₉O₅Cl
requires C, 63.73; H, 6.77, Cl, 12.55%)

A 2:4 dinitrophenyl hydrazone of the above compound was prepared and recrystallised from hot ethyl alcohol.
m.p. 174-5°C.

(Found C, 54.74; H, 5.01; N, 12.09% ; C₂₁H₂₃C₆N₄Cl, requires C, 54.62; H, 5.49, N, 12.34%)
Ethyl-2-oxo-1-benzoyl- \( \Delta^{1:9} \) octalin-10-carboxylate.
(Sodium ethoxide method),

Ethyl-2-oxo- \( \Delta^{1:9} \) octalin-10-carboxylate (33.0 gm), 15 mole) was added during thirty minutes, to a stirred solution of sodium (3.45 gms, 0.15 mole in absolute alcohol cooled to room temperature. The reaction mixture was stirred for further 30 minutes, to complete the formation of sodio-derivative of \( \beta \)-keto ester. Freshly distilled benzoyl chloride (28.10 gms 0.2 mole) dilute with 50-60 mls of dry ethyl alcohol, added dropwise for a period of one hour, it was then refluxed for ten hours. Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls) The organic layer was separated and the aqueous layer was extracted with ether (@ 50 mls portion) The extract were mixed, and the mixture was washed with water and dried (\( \text{Na}_2\text{SO}_4 \), \( \text{SO}_4 \) anhydrous). The solvent was removed, and the residue when fractionally distilled under reduced pressure gave 24.0 gm of the required product b.p. 210-211°C @ 4 mm yield 66-68 % \( \eta_0 \) 1.549. Light absorption (a) Ultraviolet Isoprop \( \lambda_{\text{max}} \) 241 8\( \text{max} \) 225,300,000 b) Infrared absorption \( \nu_{\text{max}} \) 3000, 1750, 1765 (w), 1630, 1433, 1200, 1120-1140 (w), 1092, 1055, 940, 350 (w) and 735 cm\(^{-1}\). (Found C, 73.59; H, 6.82; O, 16.54 %; \( C_{20}H_{22}O_4 \) requires C, 73.58; H, 6.79; O, 16.53 %.

A 2:4 dinitrophenyl hydrazone was prepared of the above product recrystallised from ethyl alcohol/ethyl acetate m.p. 183-184°C.
(Found C, 61.88; H, 5.17; N, 11.61 %, \( \text{C}_26\text{H}_{26}\text{O}_7\text{N}_4 \) requires C, 61.43; H, 5.16; N, 11.59 %).

\[ \text{Ethyl-2-oxo-1-benzoyl-1-octalin-10-carboxylate,} \]

(Sodium amide method)

In three necked round bottomed flask placed in a bath of liquid air was taken sodium (4.6 gm, 0.2 mole) and about 150 mls of liquid ammonia was added along with 2.5 gm of ferric nitrate monohydrate as a catalyst. Ethyl-2-oxo-

\[ \Delta^1:2 \text{octalin-10-carboxylate (44.00 gm, 0.2 mole) was then added carefully, dropwise over a period of fifteen minutes with constant stirring.} \]

A yellowish red amorphous salt formed immediately, 400 mls of sodium dried diethyl ether was added and the excess of ammonia was allowed to evaporate. The amorphous salt separated earlier became increasingly viscous but the stirring was continued. Benzoyl chloride (42.15 gm, 0.3 mole) was added in small portions as the mixture was brought to refluxing temperature, and finally 100 mls of dry toluene was added. The mixture was heated under reflux with stirring in nitrogen for nine hours. After addition of water, the organic layer was separated, washed successively with 5% aqueous acetic acid and water. Dried over sodium sulphate. The ether-toluene were distilled off, and the residue were on fractionation under vacuum give 32.4 gm of the above product, b.p. 180-184°C @ 0.5 mm \( n_D^{25} \) 1.542 yield 48%.
Ethyl-2-oxo-1-benzoyl-\(\Delta^{1:9}\)octalin-10-carboxylate.

(Enamine method)

A solution of pyrrolidine (21.33 gms, 0.3 mole in a 100 mls of dry benzene, added drop wise under nitrogen to a refluxing solution of ethyl-2-oxo-\(\Delta^{1:9}\)octalin-10-carboxylate (53.0, 0.15 mole) in 150 mls of benzene. The mixture was refluxed for four hours during refluxing the water formed in the reaction was removed with Dean and Stark trap. The solvent was distilled off, and the remaining solution of pyrrolidine- enamine of \(\beta\)-keto ester was cooled. It was diluted with 200 mls of dioxane, then benzoyl chloride (42.15, 0.3 mole) was added in the cold mixture. Remx then refluxed for ten hours under nitrogen and the mixture was again cooled to room temperature. The precipitate of enamine hydrochloride formed, was filtered and washed with ether (3 x 100 mls)

Combined the filtrate and washing in to the reaction flask neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was extracted with ether. Both layer were combined and washed in the usual manner as mentioned in the previous experiment. The solvent was removed and the residue when distilled under reduced pressure gave 22.9 gms of the required product. b.p. 201-4°C 3 3 mm \(n^2\) 1.545 yield 90 %.

Compound obtained by the three method were identical as all properties of the product obtained by the above described method, and showed no depression in the mixed melting point of 3:4 dinitrophenyl hydrazone derivative.
2-oxo-1-benzoyl-Δ^1:9-octalin:

A solution of 16.32 gms, 0.05 mole) of ethyl-2-oxo-1-one benzoyl-Δ^1:9-octalin-10-carboxylate, 6.00 gms (0.15 mole) of sodium hydroxide 25 mls of water, and 30 mls of ethyl alcohol (95 %) was heated under refluxed by slow addition of 1:1 sulphuric acid a vigorous evolution of carbon-dioxide resulted. The acidified mixture was boiled under reflux for one hour, cooled and extracted with ether. The ether-sol-frag layer was washed well with 5 % sodium hydroxide solution, followed by washing with 2% aqueous acetic acid and finally with water. It was dried (Na₂SO₄ anhydrous) and the solvent was distilled off, the residue distilled under reduced pressure gave 10.2 gms of the above 3-ketone b.p. 182-184°C @ 10 mm n⁰₂₅ 1.541 yield 49.50 %. Light absorption a) ultraviolet isoprop λ max 241, 18,300 b) Infrared ν C=O 3000, 1765, 1485, 1390, 1340, 1245, 1135, 1035, 872, 765 and 730 cm⁻¹

(Found C, 80.3; H, 7.12; O, 12.58 %; C₁₇H₁₈O₂ requires C, 80.31; H, 7.25; O, 12.39 %.

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from pet.ether/ethyl alcohol m.p. 148-149°C.

(Found C, 63.61; H, 5.14; N, 12.86 %; C₂₅H₂₂O₂N₄ requires C, 63.59; H, 5.12; N, 12.83 %).
Ethyl-2-oxo-1-(4'-nitro)benzoyl-\(\Delta^{19}\)octalin-10-carboxylate

(Sodium ethoxide method)

Ethyl-2-oxo-\(\Delta^{19}\)octalin-10-carboxylate (22.0 gm 0.1 mole) was added during the thirty minutes to a stirred solution of sodium (2.5 gm, 0.1 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred further for forty-five minutes to complete the formation of sodium-derivative of the \(\beta\)-keto ester. 4-Nitrobenzoyl chloride (37.10, 0.2 mole), was diluted with 100 mls, of dry ethyl alcohol, and added dropwise over a period of one hour. The mixture was stirred for thirty minutes at room temperature, the solvent was then distilled off, and the residue was diluted with water (100 mls). The organic layer was separated and the aqueous layer was extracted with ether (2 x 100 mls portion). The extracts were mixed with the organic layer and the mixture was washed with water, finally dried. The solvent was removed and the residue when fractionally distilled under reduced pressure gave 8.6 gm of the above product b.p. 198-200°C @ 1.5-2.5 mm yield 50.53 %. Infrared absorption \(\nu\) 3100, 1760, 1575, 1460, 1300, 1120, 1070, 720.

(Found C, 64.67; H, 5.67 % \(\text{C}_{20}\text{H}_{20}\text{O}_{5}\text{N}\) requires C, 64.66; H, 5.66 %).

A 2:4 dinitrophenyl hydrazone of diketester was prepared and recrystallised from ethyl alcohol m.p. 211-13°C dec.

(Found C, 56.62; H, 4.56; N, 12.79 %, \(\text{C}_{26}\text{H}_{25}\text{O}_{9}\text{N}_{5}\) requires C, 56.92; H, 4.52; N, 12.79 %).
Ethyl-2-oxo-1-(4'-nitro)benzoyl-Δ^1:9 octalin-10-carboxylate.

(Examine method).

Pyrrolidine (21.33 gm, 0.3 mole) in 100 ml of dry benzene, added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-Δ^1:9 octalin-10-carboxylate (33.0 gm, 0.15 mole) in 150 ml of benzene. The mixture was refluxed for four hours during refluxing the water formed in the reaction was removed with water separator (Dean and Stark). The solvent was distilled off, and the remaining solution of pyrrolidine enamine of p-keto-ester was cooled. It was diluted with 200 ml of dioxane 4-nitrobenzoyl chloride (55.65 gm, 0.3 mole) was added in portions to the cold reaction mixture. It was refluxed for fourteen hours under nitrogen and the mixture was cooled to room temperature. The precipitate of enamine hydrochloride formed in the mixture was filtered and washed with ether. Combined the filtrate and washings, returned into the reaction flask, neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated and the aqueous layer was extracted with ether. Washing of the reaction mixture was carried out in the usual way as mentioned in the previous experiment. The solvent was removed, and the residue distilled under reduced pressure to give 29.3 gms of the required product b.p. 206-211°C @ 3 mm yield 62-63% semisolid. The mixed melting point of 2:4 dinitrophenyl hydrazone of the two sample was found undepressed, and the samples have identical infrared spectra which is in confir-
mity with the structure.

\[ \text{2-oxy-1-(4-nitrobenzoyl-} \Delta^1,9 \text{octalin.} \]

A solution of 10.56 gm (0.05 mole) of sodium hydroxide in 25 mls of water and 25 mls of ethyl alcohol 95% was heated under reflux for six hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The ether layer was washed well with 5% sodium hydroxide solution, followed by washing with 2% aqueous acetic acid then with water. It was dried, the solvent was evaporated and the residue distilled under reduced pressure gave 14.1 gm of the above product b.p. 192-193°C & 5 mm yield 51%. Red viscous oil refractive index could not identified by several trials. Infrared absorption Vmax 3100, 1780, 1490, 1365, 1245, 1144, 1035, 920, 870, and 775 cm\(^{-1}\).

(Found C, 72.67; H, 5.02; O, 16.94% N, 4.94% C\(_{17}\)H\(_{17}\)O\(_3\)N requires C, 72.63; H, 6.11; N, 4.92%).

A 2:4 dinitrophenyl hydrazone of the compound was prepared and recrystallised from pet. ether/ethyl alcohol m.p. 170-180°C.

(Found C, 57.67; H, 4.41; N, 14.60% C\(_{25}\)H\(_{21}\)O\(_7\)N\(_5\) requires C, 57.65; H, 4.39; N, 14.52%).
Ethyl-2-oxo-1-cinnamoyl-\(\Delta^1\)-octalin-10-carboxylate, 
(Sodium ethoxide method).

1.9

Ethyl-2-oxo-\(\Delta^1\)-octalin-10-carboxylate (22.0 gm, 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol, cooled to room temperature. The reaction mixture was stirred for further forty-five minutes to complete the formation of sodium-derivative of \(p\)-keto-ester, freshly distilled cinnamoyl chloride (33.52 gm, 0.2 mole) was added with 100 ml of ethyl alcohol, and added drop-wise over a period of one hour. The mixture was stirred for further one hour. It was then refluxed for ten hours.

Most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 ml). The organic layer was separated, and the aqueous layer was extracted with ether (4x 50 ml portions). The extracts were mixed with the organic layer and the mixture was washed with water, and finally dried.

The solvent was removed and the residue was fractionally distilled under reduced pressure gave 20.1 gms of the above product b.p. 200-204 C \(\alpha\) 2.3-3.5 mm, \(nD^25\) 1.553 yield 55-56% Infrared absorption \(V_{max}\) 3100, 1765, 1465, 1340, 1245, 1035, 1010, (S), 920, 880, and 750 cm\(^{-1}\).

(Found; C, 75.37; H, 6.32; \(\text{C}_{22}\text{H}_{24}\text{O}_4\) requires, C, 75.29; H, 6.29%)

A 2:4-dinitrophenyl hydrazone of the diketo ester was prepared and recrystallized from ethyl alcohol, m.p. 194 C.

(Found; C, 63.14; H, 5.29; N, 10.52% \(\text{C}_{28}\text{H}_{26}\text{O}_4\text{N}_4\) requires, C, 63.21; H, 5.29; N, 10.49%)
Ethyl-2-oxo-\(\Delta^1\)-cinnamoyl-\(\Delta^1\)octalin-10-carboxylate.

(sodium amide method).

In a three-necked reaction flask, placed in a bath of liquid air was taken sodium (4.6 gms, 0.2 mole) and about 150 mls of liquid ammonia was added, along with 2.5 gm of ferric-nitrate monohydrate as a catalyst. Ethyl-2-oxo-\(\Delta^1\)
ocatalin-10-carboxylate (44.0 gm, 0.2 mole) was then added carefully, drop-wise over a period of fifteen minutes with constant stirring. A yellowish red crystalline salt formed immediately, 400 mls of ether was added, and the excess of ammonia was allowed to evaporate. The salt separated earlier became increasingly viscous, but the stirring was continued. Freshly distilled cinnamoyl chloride (56.64 gm, 0.4 moles) was mixed with 100 mls of ethyl alcohol, and added drop-wise over a period of one hour. The mixture was stirred for further one hour, it was then refluxed for ten hours. Most of ethyl-alcohol was distilled off, and the residue was diluted with water. The organic layer was separated, and the aqueous layer was extracted with ether (4 X 50 mls portions). The extract were mixed with the organic layer and the mixture was washed with water, and finally dried. The solvent was removed and the residue when fractionally distilled under reduced pressure gave 33.3 gms of the above product, b.p; 196-199°C @ 1mm, yield 51-52% \(n^2_0\) 1.552

A 2:4 dinitrophenyl hydrazone was prepared and re-
crystallized from ethyl alcohol, m.p; 194.5°C
Ethyl-2-oxo-1-cinnamoyl-\(\Delta^1\)-octalin-10-carboxylate (Enamine method).

Pyrrolidine (21.35 gm, 0.3 mole) in 100 mls of dry toluene added dropwise under nitrogen to a refluxing solution of ethyl-2-oxo-\(\Delta^1\)-octalin-10-carboxylate (33.0 gm, 0.15 mole) in 150 mls of benzene. The mixture was refluxed for 3-4 hours, during refluxing the water formed in the reaction mixture was removed. The solvent was distilled off, and the remaining solution of enamine of \(\beta\)-keto ester was cooled. It was diluted with 200 ml of dry dioxane, cinnamoyl chloride (49.98 gm, 0.3 mole) was added in portion to the cold reaction mixture. Then it was refluxed for six hours under nitrogen. The mixture was cooled to room temperature and filtered with suction, the precipitates of enamine-hydrochloride washed with dry ether. Combined the filtrate and washing, refluxed again into the reaction flask, neutralized with 10% aqueous hydrochloric acid and refluxed for one hour on a water bath. The organic layer was separated and the aqueous layer was extracted with ether. Washing of the reaction mixture was carried out in the usual way. The solvent was removed and the residue was distilled under vacuum to give 35.0 gm of the required product, \(\beta,p\):

210-213 C° @ 4-6mm \(n_D^{25}\) 1.552, yield 59-60%

The X.R. spectrum of this product was identical with the spectra of the product obtained by the above described methods and showed no depression in the mixed melting point of 2:4 dinitrophenyl hydrazone derivatives.
A solution of 17.6 gm (0.05 mole) of ethyl-2-oxo-1-cinnamoyl-\( \Delta \) - octalin-10-carboxylate, 6.0 gm of sodium hydroxide, 25 ml of water and 25 ml of ethyl alcohol was heated under refluxed for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The ether layer washed well, with 5% sodium hydroxide, followed by washing with 2% aqueous acetic acid then with water. It was dried and the solvent was evaporated, the residue when distilled under reduced pressure gave 14.8 gm of the above product. b.p. 181-185 C\(^{0} \) @ 10 mm n\(_D^2\) 1.543 yield 39-40%, Infra red absorption \( \tilde{\nu} \) 3100, 1785, 1500, 1345, 1245, 1135, 1010, 920, 870, and 750 cm\(^{-1} \) (found, C, 81.39; H, 7.19; C, 11.41% C\(_{19}H_{21}O_2 \) requires, C, 81.41 H, 7.21; O, 11.39%)

A 2:4 dinitrophenyl hydrazone was prepared of the above compound, recrystallized from ethyl alcohol/ethyl acetate m.p. 157-58 C\(^{0} \).

(Found C, 65.20; H, 5.26; N, 12.16% C\(_{25}H_{24}N_5O_5 \) requires C, 65.07 H, 7.31; N, 12.25%)

Ethyl-2-oxo-1-iso-phthaloyl-\( \Delta \) - octalin-10-carboxylate.

(Sodium ethoxide method).

Ethyl-2-oxo-\( \Delta \) - octalin-10-carboxylate (22.0 gm, 0.1 mole) was added during thirty minutes to a stirred solution of sodium (2.3 gm, 0.1 mole) in absolute ethyl alcohol, cooled
to room temperature. The reaction mixture was stirred for further forty five minutes to complete the formation of sodio derivative of the β-keto ester. Freshly distilled Iso-phthalyl chloride (40.6 gm, 0.2 mole) was mixed with 100 mls of ethyl alcohol, and added dropwise over a period of one hour. The mixture was stirred for one hour, and refluxed for 12 hours, and most of the ethyl alcohol was distilled off, and the residue was diluted with water (100 mls). The organic layer was separated, and the aqueous layer was extracted with ether (4X50 mls portions). The extracts were mixed with the organic layer and the mixture was washed with water and finally dried. The solvent was removed, and the residue when fractionally distilled under vacuum gave 26.1 gm of the above product 5-p;195-204 3\ tell (semi solid mass) Infra red absorption \( \nu_r 3000, 1300, \) 1500, 1345, 1275, 1135, 1010, 930, 870 and 750 cm\(^{-1}\).

(Pound C, 64.85; H, 5.44; O, 20.57; Cl, 9.12% \( \text{C}_{21}\text{H}_{15}\text{O}_5\text{Cl} \) requires C, 64.95; H, 5.39; O, 20.53; Cl, 9.09%)

A 2:4dinitrophenyl hydrazone of the compound was prepared and recrystallized several times by ethyl alcohol m/p;172 C°

(Pound C, 56.97; H, 4.42; N, 9.6% \( \text{C}_{27}\text{H}_{25}\text{C}_{8}\text{H}_{4}\text{Cl} \) requires C, 56.97; H, 4.42; N, 9.67%).

Ethyl-2oxo-1-Iso-phthalyl- \( \Delta \) octalin-10-carboxylate,

(Enamine method).

Pyrrolidine (21.33 gm, 0.3 mole) in 100 mls of dry benzene, added dropwise under nitrogen to a refluxing solution
ethyl-2-oxo-\( \Delta \)-octalin-10-carboxylate (33.0 gm, 0.15 mole) in 150 mls of benzene. The mixture was refluxed for three-four hours, during the refluxing the water formed was removed. The solvent was distilled off, and the remaining solution of pyrrolidine-enamine off-keto-ester was cooled. It was diluted with 200 mls of dioxane. Iso-phthalyl chloride (50.50 gm, 0.3 mole) was added in portions to the cold reaction mixture. Then it was refluxed for six hours under nitrogen. The mixture was cooled to room temperature and filtered with suction. The precipitates of enamine-hydrochloride were washed with dry ether (4 x 50 mls portions). Combined filtrate and washing returned into the reaction flask, neutralised with 10% aqueous hydrochloric acid and the mixture was refluxed on a water bath for about one hour. The organic layer was separated and the aqueous layer extracted with ether. Washing of the reaction mixture was carried out in the usual way as described in the previous experiment. The solvent was removed, and the residue distilled under vacuum to give 20.0 gm of the above product, \( \text{b.p.} 178-182\text{C} \) yield 28%.

2:4 dinitrophenyl hydrazone of the compound was prepared and recrystallized from ethyl alcohol, \( \text{mp.} 172.5\text{C} \).

2-oxo-1-Iso-phthalyl \( \Delta \)-octalin.

A solution of 28.45 gm (0.05 mole) of ethyl-2-oxo-1-Iso-phthalyl-\( \Delta \)-octalin-10-carboxylate, 6.0 gm (0.15 mole) of sodium hydroxide, 25 ml of water, and 25 ml of ethyl alcohol
was heated under reflux for six hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes cooled and extracted with ether. The ether layer was washed well with 5% sodium hydroxide followed by washing with 2% aqueous acetic acid then with water. It was dried and the solvent was removed, the residue when distilled under vacuum gave 14.8 gm of the above product, b.p. 181-185°C @ 4-6 mm n_D 1.543 yield 39.41%

Infra-red absorption ν 3100, 1785, 1500, 1245, 1135, 1010, 920, 870, and 750 cm⁻¹. (Found C, 81.39; H, 7.19; O, 11.41% C₁₉H₂₁C₂
requires, C, 81.41; H, 7.21; O, 11.39%)

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl acetate and pet- ether, m.p. 210-211°C.

(Found C, 65.20; H, 5.26; N, 12.16% C₂₅H₂₄N₅ requires, C, 65.27; H, 5.24; N, 12.24% ).
2-hydroxy-naphthalene.

To a solution of 15.00 gms (0.1 mole) of 2-oxo-\( \Delta^1 \) 9 octalin, in 250 mls of dry carbon tetrachloride was added 59.33 gms (0.3 mole) of N-bromosuccinimide. The resulting mixture was refluxed while being illuminated with two 100 Watt light bulbs. Hydrogen bromide was evolved during reflux. After two hours the original precipitates were completely replaced by supernatent succinimide, which was removed by filtration of the cooled mixture. Evaporation of the filtrate afforded 10-12 gms of resinous gummy solid, which was stirred with 300 mls of 3N-sodium hydroxide solution at room temperature for 20-24 hours, and the mixture was heated on the water bath for three hours to complete the dissolution of the solid. After being cooled, the reaction mixture was acidified with 3N sulphuric acid, causing the formation of a slightly yellowish precipitates, which were collected by filtration. The solid product was dissolved in ether and the solution was dried over sodium sulphate. The solvent was evaporated and the residue triturated with pet. ether (40-60°C) to give a crystalline product. It was recrystallised from alcohol pet ether mixture. m.p. 120-12°C. The identity of the sample was confirmed by characteristic tests of 2-naphthol. Further a mixed melting point with an authentic sample of 2-naphthol showed no depression. Thus confirming it to be 2-naphthol.
1-methyl-2-hydroxy-naphthalone.

To a solution of 16.5 gms (0.1 mole) of 1-methyl-2-oxo-Δ1:9-cetaline in 250 mls of dry CCl₄ was added 59.33 gms (0.3 mole) of N-Bromosuccinimide. The resulting mixture was refluxed for 2½ hours, hydrogen bromide was evolved during reflux. The original precipitates were completely replaced by the supernatant succinimide which was removed by filtration of the cooled mixture. The solvent was evaporated, resulting in a resinous gummy solid, which was stirred with 300 mls of 3 N NaOH solution, at room temperature for 20 hours, and the mixture was heated to reflux on a water bath, to ensure the complete dissolution of the solid. Then, it was cooled and the mixture was acidified with 2N H₂SO₄ solution, causing the formation of a whitish yellow precipitates, which were collected by filtration. The solid product was dissolved in ether dried and concentrated. The residue triturated with a mixture of pet. ether (40-60°C)/ ethyl alcohol to give a crystalline product. m.p. 112-13°C. It was recrystallized with diethyl ether, to give fine needles m.p. 111.5°C.

D.p. 180/12 mm. Readily soluble in alcohol, ether acetic acid acetone, benzene. Readily soluble in alkali hydroxide with blue violet fluorescence with conc. H₂SO₄ it gives a red yellow solution.

(Found C₂₈₂.79; H₆.54% C₉H₁₀O requires C₂₈₂.73; H₆.56%)
1-ethyl-2-hydroxy naphthalene.

A solution of 17.9 gm (0.1 mole) of 1-ethyl-2-oxo-\(\Delta^{1+9}\)octaline, in 250 mls of dry CCl\(_4\) was added 59.33 gms (0.3 mole) of N-bromo succinimide. The resulting mixture was refluxed for three hours. HBr was evolved during reflux. The original precipitates were completely replaced by the supernatent succinimide, which were removed by filtration of the cooled mixture. The solvent was evaporated, resulting in a resinsous gummy mass which was stirred with 250 mls of 3 N NaOH solution, at room temperature for 24 hours, and then the mixture was heated to reflux on a water bath, to ensure the complete dissolution of the solid. Then it was cooled and the reaction mixture was acidified with 3N H\(_2\)SO\(_4\), Causing the formation of yellow precipitates, which were collected by filtration. The solid product was dissolved in diethyl ether, dried and concentrated. The residue were triturated with a mixture of pet. ether (40-60°C) ethyl alcohol to give a crystalline product m.p. 106°C.

It was recrystallized with ethyl alcohol (dry) to give fine crystals m.p. 105°C. Needles (ligrion) m.p. 105°C; readily soluble in CH\(_3\)COOH, benzene, ether, CHCl\(_3\) and also soluble in dil NaOH. (Found C, 83.65; H, 7.02; C\(_{12}\)H\(_{12}\)O requires C, 83.68; H, 7.02%).

1-Propyl-2-hydroxy-naphthalene.

To a solution of 19.3 gm (0.1 mole) of 1-propyl-2-oxo-\(\Delta^{1+9}\)octaline, in 250 mls of dry CCl\(_4\), was added 59.33 gms, (0.3 mole) of N-bromosuccinimide. The resulting
mixture was refluxed for three hours; HBr was evolved during reflux. The original precipitates were completely replaced by the supernatant succinimide, which was removed by filtration of the cooled mixture. The solvent was evaporated, resulting in a resinosgummy solid, which was stirred with 250 mls of 2 N NaOH solution at room temperature for 24 hours, and then it was heated to reflux on a water bath, to ensure the complete dissolution of the solid, finally it was cooled, and acidified with 2N H₂SO₄ solution; slight yellow precipitates were formed which were collected by filtration. This precipitates were then dissolved in benzene, dried with Na₂SO₄ (anhydrous). The solvent was evaporated, and the residue when distilled fractionally under vacuum gave 6.2 gm (pale brown oil) of the above product b.p. 138-140/2-2.5 mm yield. In alkaline solution with chloroform on boiling it gives a blue colour, which disappear on standing).

(Found C₆H₈O₂; H₇.62; C₆H₄O literature requires C, 84.74;
H, 7.65%;)
1-Isopropyl-2-hydroxy naphthalene.

To a solution of 19.3 gms (0.1 mole) of 1-Isopropyl
2-oxo-4,1,9-octalin in 300 mls of dry CC1₄, was added 59.33
gms (0.3 mole) of N-bromo succinimide. The resulting mixture
was refluxed for five to six hours, HBr was found evolving
during reflux. The original precipitates were completely
replaced by the supernatant succinimide, which was removed
by filtration of the cooled mixture. The solvent was evaporated, resulting in a resinosgummy mass, which was stirred with
250 mls of 3N NaOH solution at room temperature for 24 hours
and the mixture was heated to reflux on a water bath to ensure the complete dissolution of the gummy mass. Then it was cooled and the mixture was acidified with 3 N-H$_2$SO$_4$ solution, causing the formation of dark brown precipitates which were collected by filtration. The precipitates dissolved in dry benzene dried. The solvent was evaporated and the residue when fractionally distilled under vacuum gave 8.3 gm of the required product b.p. 141-2 C/1 mm $n_D^{27}$ 1.547. In alkaline solution with chloroform on boiling it gives a blue colour, which disappears on standing.

(Found C, 84.71; H, 7.68% C$_{13}$H$_{14}$O, requires C, 84.74, H, 7.65 %)

1-butyl-2-hydroxy naphthalene.

To a solution of 20.7 gm (0.1 mole) of 1-butyl 2-oxo- $\Delta^{1:2}$ octalin, in 300 mls of dry CCl$_4$, was added 59.33 gms (0.3 mole) of N-bromo succinimide. The resulting mixture was refluxed for eight hours, HBr was found evolving during reflux. The original precipitates were completely replaced by the supernatent succinimide which was removed by filtration of the cooled mixture. The solvent was evaporated resulting in a gummy mass, which was stirred with 250 mls of 3 N NaOH solution, at room temperature for 24 hours, the mixture was heated to reflux on a water bath, to ensure the complete dissolution of the solid. Then it was cooled and mixture was acidified with 2 NH$_2$SO$_4$ solution, causing the formation of brown precipitates which were collected by filtration. The precipitates dissolved in dry benzene, dried.
The solvent was evaporated and the residue when fractionally distilled under vacuum gave 10 gms of the required product. Cream coloured needles (pet. ether) m.p. 80-81°; b.p. 190/3 \text{°C}; in alkalin solution with CHCl₃ on boiling gives a blue colour which dissappears on standing.

(Found C, 83.92; H, 8.107 \% C₁₄H₁₀O requires C, 83.95 H, 8.05 \%)

1-tert-butyl-2-hydroxy-naphthalene.

To a solution of 20.7 gm. (0.1 mole) of 1-tert-butyl-2-oxo-\(\Delta^{119}\) octalin, in 250 mls of dry CCl₄ was added 59.33 gms (0.3 mole) of N-bromo-succinimide. The resulting mixture were refluxed for ten hours. HBr was found evolving during reflux. The original precipitates were completely replaced by the supernatent succinimide, which was removed by filtration of the cooled mixture. The solvent was evaporated, resulting to a resinaceous mass, which was stirred with 250 mls of 3 N-NaOH solution at room temperature for 2½ hours, and the mixture was heated to reflux on a water bath to ensure the complete dissolution of the gummy; then it was cooled and the mixture was acidified with 3N-H₂SO₄ solution, causing the dark brown precipitates which were collected by filtration. The precipitates were dissolved in dry benzene, dried with anhydrous sodium sulphate. The solvent was evaporated, and the residue when fractionally distilled under vacuum gave 12.5 gms of the above product. Needles (alcohol) m.p. 66°C b.p. 188°C / 14 mm. Volatile in steam.

(Found C, 83.88 ; H, 0.01 \%, C₁₄H₁₆O requires C, 83.95 H, 0.05 \%).
1-alkyl-2-hydroxy naphthalene.

To a solution of 19.1 gms (0.1 mole) of 1-alkyl-2-oxo \( \Delta^1:9 \)-octalin in 300 ml of dry \( \text{CCl}_4 \), was added 59.33 gms (0.3 mole mole) of \( N \)-bromosuccinimide. The resulting mixture was refluxed for eight hours; \( \text{HBr} \) was found evolving during reflux. The original precipitates were completely replaced by supernatant succinimide which was removed by filtration of the cooled mixture. The solvent was evaporated, and resulting gummy mass, which was stirred with 250 ml of 3\( N \)-\( \text{NaOH} \) solution at room temperature for 24 hours, and the mixture was heated to reflux on a water bath to ensure the complete dissolution of the gummy mass. Then it was cooled and the mixture was acidified with 3\( N \)-\( \text{H}_2\text{SO}_4 \) solution, causing the formation of the dark brown precipitates which were collected by filtration. The precipitates were dissolved in dry ether. The solvent was distilled off, and the residue when fractionally distilled under vacuum gave 7.8 gm of the required product. Prism (ligroin) m.p. 55°C. b.p. 177-8°C/12 mm. 

\( n^D_{20} \) 1.617 with \( \text{FeCl}_3 \) in alcohol gives a green solution. 

(Found C, 84.72; H, 6.58\% \( \text{C}_{13}\text{H}_{12} \) requires C, 84.75; H, 6.56 \%).
A solution of 220 gms (1.00 mole) of ethyl-2-oxo-
$\Delta^{1:9}$ octalin-10-carboxylate, 123.55 gms (1.75 mole) of
pyrrolidine, and 1.5 gms of p-toluene-sulphonate in a 500
mls of toluene was heated in a litre round bottomed flask,
to which attached a Dean and Stark water separator trap,
under a reflux condenser. The separation of water begins at
once and ceases, eight to ten hours. An indented Cloissen
still-head was attached to the flask and the mixture was
distilled. Most of the toluene was removed at atmospheric
pressure, and the residue when distilled under reduced
pressure gave about 200 gms of the above product D.p. 175-
182 C/12 mm n$^2_0$ 1.538 yield 70-75 %. The infrared spectrum
is in conformity with the structure. Infra-red absorption n$^\nu$
3600, 3000, 1640, 1500(w), 1330, 1290(s) 1125, 1100, 1025, 880, 840
and 750 cm$^{-1}$.

2. Ethyl-1-methyl(N-diethyl amino)-2-pyrrolidyl-$\Delta^{1:9}$
octalin-10-carboxylate(263)

In a two litre round bottomed flask equipped with
a reflux condenser was placed 179.0 gms (1.50 mole) of
diethyl amino-hydrochloride, 68.00 gm (2.26 mole) of para-
formaldehyde, 276 gm of the ethyl-2-N-pyrrolidyl-$\Delta^{1:9}$
octalin-10-carboxylate, 100 mls of dry isopropanol, 5 mls
of concentrated hydrochloric acid. The mixture was heated
for twelve hours at a moderate to vigorous rate of reflux,
Then it was cooled to room temperature, and added a cold solution of 65-70 gms of sodium hydroxide in 250 mls of water. The mixture was extracted with ether (4 x 200 mls portions). Combined etheral extracts were treated with saturated sodium chloride solution and it was again extracted with ether. The etheral layers dried with anhydrous sodium sulphate. The solvent was distilled off, and the residue when distilled under vacuum gave 315-20 gms. of the required product b.p. 190-205°C/10-12 mm nD 27 1.542. The infrared spectrum is in conformity with the structure.


The methiodide was prepared by adding one mole of freshly distilled above product (263) and freshly distilled methyl iodide (1.00 mole) the mixture was allowed to stand protected from moisture for three hours at room temperature. A crystalline methiodide was formed, due to its hygroscopic nature it was not further purified. It was however, washed twice with dry ether.

4. Ethyl-2-oxo-1-(3′keto butyl-2′-ethyl carboxylate)

Δ 119 octalin-10-carboxylate (267)

In a three necked a one litre flask with a mechanical stirrer, a condenser was placed thiophene free benzene (500 mls) and 23 gms (1.00 mole) of sodium wire, ethyl acetate-acetate 130,14 gms (1.00 mole) was added dropwisewith constant
stirring under ice bath. After three hours the mixture was
left at room temperature for 45 minutes, then methiodide
of Ethyl-1-methyl (N-diethyl amino)-N-pyrrolidyl \( \Delta \)
-10-carboxylate (1.00 mole) with 250 mls of dry ethyl alc-
hol was added with stirring for two hours, then the mixture
was refluxed for six hours under nitrogen atmosphere. The
clear solution was then diluted with 10% aqueous hydroch-
loric acid and refluxed on a water bath under nitrogen. The
organic layer was separated and aqueous layer extracted with ether. Combined the organic portion and washed again
with conc. Na\(_2\)CO\(_3\) solution, finally it was washed with wa-
ter and dried with sodium sulphate. The solvent was remo-
vved and the residual portion was cyclized into tri cyclic-\(\beta\)-
ketoo ester, both in the acidic and basic medium. Both meth-
ods gave identical result.

Cyclisation (Acidic medium).

A. Acidic medium. The above compound No. (261)

About 180 gms of glacial acetic acid and 150 mls of concentrated hydro-
hloric acid under nitrogen atmosphere, for twenty hours.
The solution was then diluted with water and the product
extracted with three portions of 200 mls warm benzene.
The extract was washed with water and saturated sodium bi-carbonate solution and again with water finally it was
dried (Na\(_2\)SO\(_4\)). The solvent was removed and the residue
when distilled under reduced pressure gave 90 gms of the
required product. D.P. 205-6°C @ 3 mm yield 46%.
(Found C, 69.34; H, 7.56; O, 9%; C_{20}H_{26}O_{5} requires
C, 69.29; H, 7.51; O, 23.19%.)

A 2:4 dinitrophenyl hydrazone was prepared and
recrystallised with ethyl alcohol and dioxane after
keeping several hours in ice cold mixture shining yellow
 crystals were obtained m.p.

A semicarbazone of the above compound was prepared
and recrystallised with alcohol m.p. C
(Found C, 62.50; H, 7.24; O, 19.84; N, 10.41%; C_{21}H_{29}O_{5}N_{3}
requires C, 62.49; H, 7.21; O, 19.81; N, 10.34%.

D. Basic Medium.

A mixture of one litre methyl alcohol, 1000 mls
of potassium hydroxide and 180/_{2}ethy-2-oxo-1-methyl(3'keto-
butyl-2-ethyl carboxylate) M1:9 octalin-10-carboxylate,
was heated under reflux under nitrogen atmosphere for
24 hours. The solution was diluted and the product extrac-
ted with 4 x 200 mls portions of benzene. The extract were
washed with water and dilute hydrochloric acid and then
concentrated. The residue when distilled under reduced
pressure gave 90-95 gms of the above product, b.p. 205-10°C
at 3-4 mm

The two samples were found identical in all respects.
Ethyl-2-oxo-1-(\(\Delta^1\)-Keto butyl-2-ethyl carboxylate) - \(\Delta^1\)-octalin-10-carboxylate (267)

1. Ethyl-2-oxo-1-methyl-(N-dimethyl) - \(\Delta^1\)-octalin-10-carboxylate (263)

In a 2 litres round bottomed flask equipped with a condenser, was placed (130 gm, 1.60 mole) of dimethyl amine-hydrochloride, 68.0 gm (2.26 mole) of paraformaldehyde, 222 gms of ethyl-2-oxo- \(\Delta^1\) - octalin-10-carboxylate, 30 ml of dry methanol and 0.2 ml of concentrated hydrochloric acid. The yellow solution in which small quantity of gelatinous water ink was heated for ten hours at a moderate to vigorous rate of reflux, then it was cooled to room temperature and added a cold solution of sodium hydroxide (70 gm in 300 ml of water). The mixture was extracted with ether (3 x 250 mls portions). The ethereal layers were washed with 2x 150 mls of saturated sodium chloride solution and then with water. The ether solution was dried over night with sodium sulphate. The solvent was removed and the residue when distilled under reduced pressure gave 185-190 gms of the above product, b.p. 180-195 \(\pm\) 1 mm.

C\(_7\)H\(_{14}\)N\(_2\)O\(_2\) yield 52-56% Infra red absorption V

2. Ethyl-2-oxo-1-methyl-(N-dimethyl) - \(\Delta^1\)-octalin-10-carboxylate-methiodide.

The methiodide was prepared by the addition of one mole of
freshly distilled above product (and methyl iodide (1.0 mole)
the mixture was allowed to stand protected from moisture for
three hours at room temperature. A crystalline mass was formed
due to its hygroscopic in nature it was not further purified.

Ethyl-2-oxo-1-(3-keto butyl-2-ethylcarboxylate) \( \Delta \)
\[ \text{catalin-10-carboxylate} \uparrow \]

In a three necked reaction flask fitted with a mech-
anical stirrer, was placed dry thiophene free benzene (500 mls)
23 gms of sodium wire, ethyl acetate 130.14 gms (1.0 mole)
was added dropwise with constant stirring under ice bath.
After three hours the mixture was left for forty five minutes,
the methiodide of ethyl-2-oxo-1-methyl-(N-diethyl amino)- \( \Delta \)
catalin-10-carboxylate, alongwith 200 mls of dry ethyl alcohol unpadded
and continued stirring for two hours. The clear solution was
then diluted with water and extracted with ether (4X50 mls
portions). The two portions were combined and washed with
water, and dried. The solvent was removed and the residual
portion was distilled under vacuum to give the above produ ct
b.p. 191-195 \( \Delta \) 1.5 mm \( \text{m} \uparrow \) 271.5

Cyclization:

Take 103.8 gms (0.3 mole) of \( \text{di-keto-ester} \uparrow \)
250 mls of glacial acetic acid, 50 mls of hydrochloric acid in
a reaction flask and \( \text{refluxed} \) under nitrogen for
Twenty-four hours. This was then diluted with water, and the product was extracted with benzene. The extract was washed with water, saturated sodium bicarbonate solution and again with water, finally it was dried. The solvent was removed and the residue when distilled under reduced pressure gave 46.34 gm of the required product b.p. 205-206°C @ 3 mm nD 1.538.

Infra-red absorption V max

(Found C, 69.34; H, 7.56; O, 23.09% C 20–25.05 requires, C, 69.29; H, 7.51; O, 23.19%).

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized with ethyl alcohol and dioxane after keeping several hours in the cold ice mixture, shining yellow crystals were obtained m.p. 182–3°C dec. A semicarbazone prepared and recrystallized from alcohol m.p. 213-4°C.

(Found C, 62.52; H, 7.24; O, 19.84% N, 10.41% C 21–20.5 H 3 requires C, 62.49; H, 7.21; O, 19.81; N, 10.34%).
Diethyl-2-oxo-1-methyl-2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene-3:14-dicarboxylate.

(Enamine method).

A solution of pyrrolidine (10.6 gm, 0.15 mole) in 150 mls of dry benzene was placed dropwise under nitrogen to a refluxing solution of tri-cyclic-β-keto ester, (34.4 gm, 0.1 mole) in 250 mls of benzene. The mixture was refluxed for six hours, during this time the amount of water formed was removed, then about 300 mls of solvent was removed and the remaining portion was cooled. A solution of methyl iodide (42.58 gm 0.3 mole) in 200 ml of dry dioxane added, and the mixture was cooled and filtered with suction, the precipitated enamine-hydrochloride was washed with dry ether. Combined filtrate and washing were returned to the reaction flask, then 150 ml of 10% aqueous hydrochloric acid was added and the mixture was refluxed on a water bath with vigorous stirring for one hour. The organic layer was separated and the aqueous layer extracted with ether. The ethereal layer was washed with saturated sodium bicarbonate solution, then with water. The solvent was distilled off, and the residue when fractionally distilled under reduced pressure gave 19.3 gms of the above product, b.p. 207-209 C° @ 3 mm, n\textsubscript{D} 1.543 yield 38-39%.

Infra red absorption \( \bar{V}_{\text{max}} \) 3100, 1785, 1475, 1365, 1344, 1248, 1141, 1072, 1035, 940, 872 and 760 cm\textsuperscript{-1}.

(Found C, 69.95; H, 7.33% C\textsubscript{21}H\textsubscript{28}O\textsubscript{5} requires C, 69.21; H, 7.37%).
A semicarbazone of the above compound was prepared and recrystallized from hot ethyl alcohol, m.p.; 213-214°C.

(Found C, 62.99; H, 7.45; O, 19.07; N, 10.49% C_{22}H_{31}O_5N_3 requires C, 62.91; H, 7.46; O, 19.07 N, 10.49% )

2-oxo-1-methyl-2,3,4,5,6,7,8,9,10,14-decahydrophanthrene.

A solution of 16.83 gm (0.05 mole) of tri-cyclic-\( \beta \)-ketone ester, 8.0 gm of sodium hydroxide, 25 ml of water and 50 ml of ethyl alcohol was added under reflux for ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for ninety minutes, cooled and extracted with ether. The ethereal layer was worked up as usual, finally dried. The solvent was evaporated and the residue when distilled under reduced pressure gave 7.2 gm of the above product, b.p.; 201°C @ 7-8 mm, n_D 1.55; yield 43%; infra red absorption \( \vec{\nu} \), 3100, 1785, 1480, 1374, 1335, 1240, 1065, 941, 870 and 760 cm\(^{-1}\).

(Found C, 83.24; H, 9.32; O, 7.43% C_{15}H_{20}O requires C, 83.21; H, 9.37; O, 7.39% )

A semicarbazone of the above compound prepared and recrystallized from ethyl alcohol/pet. ether, m.p.; 194-195°C.

(Found C, 75.75; H, 9.69; N, 16.53; C_{16}H_{23}O_5N_3 requires C, 75.84; H, 9.53; N, 16.57% ).
Diethyl-2-oxo-1-ethyl 3,4,5,6,7,8,9,10,14-decahydro-phenanthrene 3:14-dicarboxylate.

(Enamine method).

A solution of pyroplidin (10.6 gm, 0.15 mole) in 200 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of tri-cyclic-β-keto ester (34.4 gm, 0.1 mole), in 150 ml of dry benzene. The solution was refluxed for six hours during this time the amount the amount of water formed was removed. The excess amount of the solvent was removed, and the remaining was cooled to room temperature. Then added ethyl iodide (23.4 gm, 0.15 mole) in 100 mls of dry dioxane was added dropwise, and the mixture was refluxed for twelve hours, under nitrogen with constant stirring. The mixture was cooled and filtered, the precipitated enamine hydrochloride washed several time with ether. Combined the filterate and washing were returned to the reaction flask, 100 mls of 10% aqueous hydrochloric acid added and the mixture was refluxed on a water bath with vigorous stirring for three hours. The organic layer was separated and extracted with ether (4×100 ml portions). The ethereal layer combined with the previous layer and then washed with saturated sodium bicarbonate solution, water and finally dried. The solvent was distilled off, and the residue when distilled practically under reduced pressure gave 22.1 gm of the above product, b.p. 203-204°C nD 25 1.561 yield 43% Infra red absorption \( \tilde{\nu} \) 3100, 1350, 1470, 1365, 1335, 1240 1140, 925, 865 cm\(^{-1}\).
A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol/ethyl acetate, mp 241-242°C.

A solution of 8.5 gm (0.05 mole) of tri-cyclic β-keto β-ester, 8.0 gm of sodium hydroxide, 20 ml of water and 50 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for another two hours, cooled and extracted with ether. The ethereal layer was washed well as usual. The solvent was distilled off, and the residue when distilled under reduced pressure gave 7.2 gm of the above product, b.p. 195-197°C. nD20 1.566

Infra red absorption V̄ 3100, 1765, 1485, 1375, 1275, 1250, 1145, 1035, 945, 875 and 765 cm⁻¹

A semicarbazone of the above compound was prepared and recrystallized from hot ethyl alcohol, mp 203-203.5°C.

A solution of 8.5 gm (0.05 mole) of tri-cyclic β-keto β-ester, 8.0 gm of sodium hydroxide, 20 ml of water and 50 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for another two hours, cooled and extracted with ether. The ethereal layer was washed well as usual. The solvent was distilled off, and the residue when distilled under reduced pressure gave 7.2 gm of the above product, b.p. 195-197°C. nD20 1.566

Infra red absorption V̄ 3100, 1765, 1485, 1375, 1275, 1250, 1145, 1035, 945, 875 and 765 cm⁻¹.
Diethyl-2-oxo-1-n-propyl-2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene-3:14-dicarboxylate.

(Enamine method).

A solution of pyrrolidine (10.5 gm, 0.15 mole) in 200 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of tri cyclic-\(\beta\)-keto ester \(\text{(25.4 gm, 0.1 mole)}\) in dry benzene. The solution was refluxed for six hours, during this time the amount of water formed was removed. The solvent was distilled off, and the remaining portion was cooled to room temperature. Then a solution of n-propyl iodide (25.49 gm, 0.15 mole) in dry dioxane was added dropwise, and the mixture was refluxed for sixteen hours under nitrogen with constant stirring. The mixture was cooled and filtered, the precipitated enamine hydrochloride washed several times with ether. Combined the filtrate and washing were returned to the reaction flask, 100 ml of 10% aqueous hydrochloric acid added and the mixture was refluxed on a water bath with constant stirring for two hours. The organic layer was separated and the aqueous layer extracted with ether (5x30 ml portions). The ethereal layer combined with the organic portion, washed with saturated sodium bicarbonate solution, dilute sodium bisulphite solution finally with water and dried. The solvent was distilled off, and the residue when distilled under reduced pressure gave 16.45 gm of the required product, \(\delta\) pr 213-215 'C. 3-4 mm n\textsubscript{D} 1.549. Yield 44% Infra red absorption \(\nu\): 3100, 1765, 1475, 1365, 1340, 1240, 1135, 940, 875 and 775 cm.
(Found C, 70.36; H, 8.50% \( C_{23}H_{34}O_5 \) requires C, 70.10; H, 8.49%)

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol/ethyl acetate, m.p. 227-229°
(Found C, 64.69; H, 8.01; O, 17.96% \( C_{24}H_{35}O_5 \) requires C, 64.69; H, 8.09; O, 18.01; N, 9.41%).

2-oxo-1-n-propyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 19.42 g (0.05 mole) of tricyclic-3-keto ester, 8.0 g of sodium hydroxide, 25 ml of water, 30 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid; a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for two hours, cooled and extracted with ether. The ether layer was washed well with 3% sodium hydroxide solution, followed by washing with 2% aqueous acetic acid, then with water. It was dried. The solvent was distilled off, and the residue when distilled under reduced pressure gave 11.7 g of the above product, m.p. 205-7°C @ 7-8 mm \( \text{Hg} \)\(^{27} \cdot 559 \) yield 55% Infra red absorption
\( v_{\text{max}} \) 3100, 1765, 1475, 1375, 1340, 1245, 1135, 1065, 1035, 940, 870 and 765 cm\(^{-1}\).
(Found C, 83.52; H, 9.90; O, 6.57% \( C_{17}H_{24}O \) requires C, 83.58; H, 9.96; O, 6.53%).

A 2:4 dinitrophenyl hydrazone of the above product was prepared and recrystallized from ethyl alcohol m.p. 209-211°C.
(Found C, 71.28; H, 8.96; N, 14.59% \( C_{18}H_{27}O_N_3 \) requires C, 71.72; H, 8.93; N, 14.98%).
Diethyl-2-oxo-1-n-butyl-2,3,4,5,6,7,8,9,10,14-decahydro-phenanthrene3:14 dicarboxylate.

(Enamine method).

A solution of pyrrolidine (10.6 gm, 0.15 mole) in 200 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of tricyclic-β-ketoester (34.4 gm, 0.1 mole) in dry benzene. The solution was refluxed for six hours, during this time the amount of water formed was removed. About 250 mls of the solvent was distilled off, and the remaining portion was cooled to room temperature, then n-butyl bromide (20.2 gm, 0.15 mole) in dry dioxane was added, and the mixture was refluxed for sixteen hours under nitrogen, then it was cooled and filtered the precipitated enamine hydrochloride washed several times with ether. Combined the filtrate and washing were returned to the reaction flask 100 mls of 10% aqueous hydrochloric acid added and the mixture was refluxed on water bath with constant stirring for two hours. The organic layer was separated and extracted with ether (5 X 50 mls portions). The etheral layer, combined, the above organic portion, then washed with sodium bicarbonate solution and water. It was dried and solvent was distilled off, and the residue when fractionally distilled under vacuum gave 23.3 gm of the required product.

\[ \text{bp} 216-17 \degree C \& 3 \text{ mm} \ n_D^26 1.540 \text{ Infra red absorption spectrum is in confirmity with the structure.} \]

( Found C, 71.1; H, 8.51% C_{24}H_{34}O_5 requires C, 71.03; H, 8.20%).
A semicarbazone of the above product was prepared and recrystallized twice hot ethyl alcohol, mp 235-236 C°.
(Found C, 65.33; H, 8.12; O, 8.12; N, 9.13%; C_25 H_37 O_5 N_3 requires C, 65.29; H, 8.20; O, 8.15; N, 9.15%).

2-oxo-1-n-butyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene

A solution of 20.12 gm (0.05 mole) of tricyclic-8-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and 50 ml of ethylalcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 11 sulphuric acid, vigorous evolution of carbon dioxide resulted.
The acidified mixture was boiled under reflux for two hours cooled and extracted with ether. The ethereal layer was washed well as usual, finally it was dried. The solvent was evaporated and the residue distilled under reduced pressure gave 13.1 gm of the above product. bp 204-6 C° n_D 1.561 yield 57% The infra red absorption V_max 3000, 1765, 1500, 1339, 1245, 1135, 1040 (s), 915 and 875 cm^-1 (Found C, 63.62; H, 10.17; O, 6.15% C_18 H_26 O requires C, 63.62; H, 10.17; O, 6.15%).

A semicarbazone of the above compound was prepared recrystallized from pet ether 40-60 C°, mp 183 C°.
(Found, C, 69.71; H, 9.02; N, 16.17; C_1 H_2 O_3 N requires C, 69.35; H, 9.02; N, 16.50%).
Diethyl-2-oxo-1-sec.butyl-2,3,4,5,6,7,8,9,10,14-decahydro-phenanthrene-3:14 dicarboxylate.

(Enamine method).

A solution of pyrrolidine (10.6 gm, 0.15 mole) in 200 mls of dry benzene was added dropwise under nitrogen to a refluxing solution of tricyclic-β-keto ester (34.4 gm, 0.1 mole) in dry benzene. The solution was refluxed for six hours, during this time the amount of water formed was removed. Then about 200 mls of the benzene was distilled off, and the remaining portion was cooled to room temperature, sec.butyl bromide (20.5 gm, 0.15 mole) in dry dioxane was added, and the mixture was refluxed for sixteen hours under nitrogen. The mixture was cooled and filtered, the precipitated enamine hydrochloride washed successively with ether and benzene. Combined the filtrate and washing were returned to the reaction flask, 100 mls of the 10% aqueous hydrochloric acid added and refluxed for three hours on a water bath with constant stirring. The organic layer separated and the aqueous layer extracted with ether. The ethereal layer was combined with the previous portion and worked out as earlier. The solvent was removed, and the residue when distilled under vacuum gave 24.1 gm of the above product, b.p. 217-21 C° @ 2.5 mm
nD 1.546; yield 55-54% Infra red absorption \( \tilde{\nu} \), 3100, 1765, 1475, 1345, 1245, 1135, 1040, 940 and 375 cm\(^{-1}\).

(Found C, 71.1; H, 8.51% \( C_{24} H_{34} O_5 \) requires C, 71.9; H, 8.02%).
2-oxo-1-sec.-butyl-2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene.

A solution of 20.12 gm (0.05 mole) of tricyclic-\( \beta \)-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and 50 mls of ethyl alcohol was heated under reflux for six to eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid. A vigorous evolution of carbon dioxide gas resulted. The acidified mixture was boiled under reflux for two hours, cooled and extracted with ether. The ethereal layer was worked up as usual. Finally it was dried. The solvent was evaporated, and the residue when distilled under reduced pressure gave 14.3 gm of the above product.

D.p: 214-5 C\(_0\) @ 9-10 mm n\(_D\) 1.563 Infrared absorption:

\[ \nu \text{ cm}^{-1} \]

\[ 3100, 1745, 1450, \text{and} 955 \]

(Found C, 83.66; H, 10.14; O, 6.20% \( C_{18}H_{26}O \) requires C, 83.63; H, 10.17; O, 6.11%).

A semicarbazone of the compound was prepared and recrystallized from ethyl alcohol/pet. other \( n_p; 194-5 \) C\(_0\).

(Found C, 69.09, H, 8.66; N, 16.68\% \( C_{12}H_{24}ON_{2} \) requires C, 69.27, H, 8.97, N, 16.10%).
Diethyl-2-oxo-1-tert.butyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene-3,4-dicarboxylate.

(Enamine method).

Pyrrolidine (10.6 gm, 0.15 mole) in 250 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of tricyclic-β-keto ester (34.4 gm, 0.1 mole) in 150 ml of benzene. The solution refluxed for six hours, and water formed during this time was removed. Then about 250 ml of the solvent was distilled off, and the remaining portion was cooled to room temperature, tert.butyl chloride (13.87 gm, 0.15 mole) in dry dioxane was added, and the solution was refluxed for six hours under nitrogen. After which it was cooled and filtered, the precipitated enamine hydrochloride was washed several times with ether. Combined the filtrate and washing were returned to the reaction flask, 100 ml of 10% aqueous hydrochloric acid added and the mixture was refluxed for 2 hours on a water bath with constant stirring. The organic layer was separated, the aqueous portion was extracted with ether (4 x 50 ml portion). The layers were combined and worked up as usual. The solvent was removed, and the residue distilled under reduced pressure gave 18.3 gm of the required product, m.p. 230-2 C° @ 6 mm nD 27.1551 yield 52% Infra red absorption V 3100,1785,1370, 1335, 1135,1065, and 935 cm⁻¹.

(Found C, 71.1; H, 8.51% C₈4 H₃₄ O₅ requires C, 70.35; H, 8.23)

A semicarbazone of the compound was prepared and recrystallized from pet. ether/ethyl alcohol m.p. 221-3 C°.
(Found C, 65.33; H, 8.12; O, 17.4%; N, 9.13% \( \text{C}_{25}H_{37}O_5N_3 \) requires C, 65.24; H, 8.09; O, 17.34; N, 9.17%).

2-oxo-1-tert. butyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 20.12 gm (0.05 mole) of tricyclic-\( \beta \)-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and 30 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid a vigorous evolution of carbon dioxide resulted. The acidified mixture was then boiled for two hours. It was cooled and extracted with ether. The ethereal layer was worked out as usual. The solvent was removed, the residue when distilled under reduced pressure gave 12.7 gm of the required product. \( \text{bp} \, 198-04 \, \circ \text{C} \), \( d_4^0 \, 3.4 \, \text{mm} \), \( n_D^2 \, 1.561 \) yield 49%

Infra red absorption \( V_{\text{max}} \) 3000, 1750, 1500, 1335, 1240, 1045 (w), 940, and 865 cm\(^{-1}\).

(Found C, 83.66; H, 10.14; O, 6.20% \( \text{C}_{18}H_{26}O_5 \) requires C, 83.63; H, 10.17%; O, 6.14%).

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol /pet. ether, \( m, p \); 177 \( \circ \). (Found C, 69.69; H, 8.86; N, 16.68; \( \text{C}_{19}H_{29}O_9N_6 \) requires C, 69.27; H, 8.87; N, 16.96%).
Diethyl-2-oxo-1-n-butyryl-2,3,4,5,6,7,8,9,10,14 decahydro-phenanthrene 3:14 dicarboxylate.

(Eamine method).

Fyrrolidine (10.6 gm, 0.15 mole) in 150 ml of dry toluene was added dropwise under nitrogen to a refluxing solution of tricyclic-3-keto ester (3.4 gm, 0.1 mole) in 100 ml of toluene. The mixture was refluxed for ten hours during this time the amount of water formed was removed. Then it was concentrated, and n. butyryl chloride (15.97 gm, 0.15 mole) in dry dioxane, added and the mixture was refluxed under nitrogen for twelve hours with constant stirring. The mixture was cooled filtered, and the enamine hydrochloride precipitate were washed with ether. Combined the filtrate and washing returned to the reaction flask, then add 100 ml of 10% aqueous hydrochloric acid and started refluxed on a water bath for one hour with stirring. The organic layer was separated and worked out as usual. The solvent was removed, the residue distilled under reduced pressure to give 27.4 gm of the above product, b.p. 203-7 C° 2 mm n, 27 1572, yield 65% Infra red absorption ν 3100, 1765, 1470, 1335, 1245, 1155, and 735 cm⁻¹.

(found C, 69.03; H, 7.07% C₂₀H₃₂O₆ requires C, 69.13; H, 7.21%).

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol/ethyl acetate m.p. 197-200°

(found C, 64.77; H, 7.66; N, 9.30%; C₂₁H₃₆O₆N₂C₂₅H₃₆C₅N₃ requires C, 64.77; H, 7.64; N, 9.24%).
2-oxo-1-n. butyryl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 22.42 gm (0.05 mole) of tricyclic-β-keto ester, 8.0 gm of sodium hydroxide 25 ml of water and 50 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition 1:1 sulphuric acid, vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for two hours, cooled and extracted with ether. The ethereal layer was worked out as usual, finally it was dried. The solvent was removed and the residue when distilled under vacuum gave 14.3 gm of the required product, b.p; 213-222 C⁰ @ 5-8 mm; n₂ 27.1, 557 yield 64%. The infra red spectrum of the above compound is in conformity with the structure of the compound.

(Found C, 75.70; H, 8.82% C₄₈H₂₄O₂ requires C, 75.72; H, 8.85%).

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol m.p; 219-20 C⁰.

(Found C₂₁H₂₁O₂N₂, H, 12.72% C₂₁H₂₁O₂N₂ requires C₂₁H₂₁O₂N₂).  

Diethyl-2-oxo-1-isobutyryl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene-3:14 dicarboxylate.

(Enamine method).

Pyrroolidine (10.6 gm, 0.15 mole) in 100 ml of dry toluene, added dropwise to refluxing solution of tricyclic-β-keto ester (34.4 gm, 0.1 mole) in 100 ml of toluene. The mixt-
ure refluxed for six hours, during this time the amount of water formed was removed and the excess solvent was removed finally the remaining portion was cooled. A solution of iso-butyryl chloride (15.97 gm, 0.15 mole) in dry dioxane was added to the above cold mixture, then started refluxing for sixteen hours with constant stirring. The mixture was cooled again, and filtered with suction, the enamine hydrochloride precipitates, washed with ether. Combined the filterate and washing and proceed as usual, finally it was dried. The solvent was removed and the residue when distilled under vacuum gave 23.1 gm of the above product. B. p. 201-2 C°@ 2-3 mm n D 26 1.557

Infra red absorption \( \tilde{\nu} 3000,1735,1456,1320,1235,1135,920, \) and 870 cm\(^{-1}\). (Found, C. 69.05; H. 7.07; C\(_{24}\)H\(_{33}\)O\(_6\) C. 69.33; H. 7.47%).

A semicarbazone of the above product was prepared and recrystallized from hot ethyl alcohol. B. p. 202.5 C°

\( \tilde{\nu} 3000,1735,1456,1320,1235,1135,920, \) and 870 cm\(^{-1}\). (Found, C. 64.59; H. 7.64; O. 40.76 % C\(_{25}\)H\(_{26}\)O\(_6\)N\(_3\) requires,

C. 64.77; H. 7.648 % O. 40.76 % and N. 9.34%).

2-oxa-1-iso-butyryl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 22.42 gm (0.05 mole) of tricyclic-3-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and 30 ml ethyl alcohol was added, and the mixture was refluxed for eight hours. The warm solution was then acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under
reflux for one hour, cooled and extracted with ether. The ethereal layer was worked up as usual, finally it was dried. The solvent was removed and the residue when distilled under vacuum gave 15.2 gm of the required product, b.p. 213-222 °C at 8-10 mm nD26 1.562 yield 66% Infra red absorption \( \bar{\nu} \) 3100, 1750, 1456, 1356, 1240, 1135, 1035, 940, 870, and 750 cm\(^{-1}\).

(Found C, 75.70; H, 8.82% \( \text{C}_{18} \text{H}_{29} \text{O}_2 \) required C, 75.72; H, 8.85%).

A semicarbazone of the above product was prepared and recrystallized from ethyl alcohol m.p. 189 °C.

(Found C, 69.34; H, 8.34; N, 12.62; \( \bar{\nu} \) 3130, 1705, 1240, 1125, 980, and 750 cm\(^{-1}\).

\( \text{Diethyl-2-oxo-1-n-valeryl-2,3,4-m, 6, 7, 8, 9, 10, 14-decachydro-phananthrene-3:14 dicarboxylate.} \)

(Enamine method).

Pyrrolidine (10.6 gm, 0.15 mole) in 250 ml of dry toluene was added drop wise under nitrogen to refluxing solution of tricyclic-\( \beta \)-keto-eater (34.4 gm, 0.1 mole) in 100 ml of toluene. The mixture was then refluxed for six hours, the water formed during refluxing was removed. The solvent was removed. The concentrated portion was cooled to room temperature. A solution of \( \text{n-valeryl chloride} \) (18.10 gm, 0.15 mole) in dry dioxane (200 mls) added, and the mixture was refluxed for ten hours under nitrogen with constant stirring. The mixture was cooled and filtered, the precipitated enamine hydrochloride was washed with ether. Combined the
filterate and washing to the reaction flask and 100 ml of 10% aqueous hydrochloric acid was added again the mixture was refluxed on a water bath under nitrogen, with constant stirring for one hour. The organic layer was separated and the aqueous layer was extracted with ether. The layers were combined and worked as usual. The solvent was removed and the residue when distilled fractionally under reduced pressure gave 21.3 gm of the required product, b.p.: 212-216°C, nD 27.1.563 yield 46%. Infra red absorption V max. 3000, 1785, 1490, 1375, 1350, 1250, 1145, 970, and 765 cm⁻¹.

(Found C, 69.57; H, 5.11% C₂₅H₃₅O₆ requires, C, 69.82; H, 5.49%)

A semicarbazone of the above product was prepared and recrystallized from ethyl alcohol m.p.: 216-17°C.

(Found C, 63.79; H, 7.80; N, 6.66% C₂₆H₃₆O₆ requires C, 63.91; H, 7.82; N, 6.57%).

2-oxo-1-n-valeryl-2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene.

A solution of 22.57 gm (0.05 mole) of tricyclic-3-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and 30 ml of ethyl alcohol was heated under reflux for six hours. The warm solution was acidified as usual, then warm mixture was boiled under reflux for one hour, it was cooled and extracted with ether. The ethereal layer was worked as usual. The solvent was evaporated and the residue when distilled under reduced pressure gave 14.5 gm of the required product. b.p.: 230-235°C @ 10 mm nD 27.947 yield 65-67%. Infra red absorption V max. 3000, 1735, 1465, 1445, 1370, 1335, 1240, 1135, 1035, 920.
875 and 765 cm⁻¹.

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol mp 194 °C. (Found C, 79.39; H, 8.45% C, 19.26; O, 20.2% C, 79.83; H, 8.41%).

Diethyl-2-oxo-1-isovaleryl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene-3:14 dicarboxylate.

(Pyrrrolidine (10.6 gm, 0.15 mole) in 150 ml of dry benzene was added under nitrogen to a refluxing solution of tricyclic-β-keto ester (34.4 gm, 0.1 mole) in 150 ml of benzene. The mixture was refluxed for six hours, during this time the amount of water formed was removed. This was concentrated and cooled to room temperature. A solution of Iso-valeryl chloride (18.10 gm, 0.15 mole) in 200 ml of dry benzene was added slowly and the mixture was refluxed for sixteen hours under nitrogen with constant stirring. The mixture was cooled and filtered with suction, the enamine hydrochloride precipitates washed with ether. Combined the filtrate and washing into the reaction flask, then added 100 ml of 10% aqueous hydrochloric acid, again the mixture was boiled under reflux on a water bath for two hours. The organic layer was separated and the aqueous layer was extracted with ether. Combined the layer and worked as usual as mentioned in the earlier experiments. The solvent was removed and the residue fractionally distilled under reduced pressure gave 24.7 gm.
of the required product, b.p. 218-25 C° @ 4.5 mm n_D 271.563
yield 60-1% Infra red absorption \( \bar{V}_{\text{max}} \) 3100, 1785, 1450, 1375,
1345, 1260, 1135, 940, 875, and 745 cm\(^{-1}\) (Found C, 69.56; H, 0.41
\( C_{15}H_{25}O_6 \) requires C, 69.82; H, 8.49%).

A semicarbazone of the above product was prepared
and recrystallized from methyl alcohol/ethyl acetate m.p. 201-2 C°.

( Found C, 63.87; H, 7.30; O, 19.10; N, 6.39% C_{16}H_{38}O_3 requires C, 63.91; H, 7.32; O, 19.15; N, 6.59% ).

2-oxo-1-4-so-valeryl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 22.57 gm (0.05 mole) of tricyclic-\( \beta \)-keto ester, 8.0 gm of sodium hydroxide, 25 ml of water and
50 ml of ethyl alcohol was heated under reflux for eight
hours. The warm solution was acidified by the slow addition
of 1:1 sulphuric acid a vigorous evolution of carbon dioxide
resulted. The acidified mixture was boiled under reflux
for one hour. The ethereal layer washed as usual, finally
it was dried. The solvent was evaporated and the residue
when distilled under reduced pressure gave 13.8 gm of the
above product, b.p. 218-24 C° @ 5-6 mm n_D 271.540 yield 62%
Infra red absorption \( \bar{V}_{\text{max}} \) 3100, 1500, 1450, 1385, 1345, 1290, 1260,
1140, 1040, 970 and 750 cm\(^{-1}\).

( found C, 79.39; H, 9.45% \( C_{19}H_{26}O_2 \) requires C, 79.40; H, 8.39% ).

A semicarbazone of the above compound was prepared and
recrystallized from ethyl alcohol, m.p. 163-4 C°.
(Found C, 67.28; H, 9.24; N, 15.62. \( \text{C}_2\text{H}_2\text{O}_2\text{N}_3 \) requires C, 67.49; H, 8.30; N, 15.66%).

Diethyl-2-oxo-1-cinnamoyl-2,3,4,5,6,7,8,9,10,14, decahydrophenanthrene -3:14-dicarboxylate,
(\( \text{amine method} \)).

Pyrrolidine (10.6 gm, 0.15 mole) in 150 ml of benzene was added under nitrogen to a refluxing solution of tricyclic \( \beta \)-keto ester \( \text{C}_4\text{H}_4 \text{O}_2 \) (34.4 gm, 0.05 mole) in 100 ml of benzene. The mixture was refluxed for six hours, during this time the amount of water formed was removed. The mixture was then concentrated and the remaining portion was cooled to room temperature. A solution of Cinnamoyl chloride (24.96 gm, 0.15 mole) in 200 ml of dioxane added, and the mixture was refluxed for sixteen hours, under nitrogen with constant stirring. The mixture was cooled to room temperature then filtered with suction, the precipitates of enamine hydrochloride were washed with ether. Combined the filtrate and washings to the reaction flask, 100 ml of 10% aqueous hydrochloric acid added and the mixture was refluxed on a water bath for two hours. The organic layer was separated and the aqueous layer was extracted with ether. Combined the two layers and washed as usual. The solvent was removed and the residue fractionally distilled under vacuum to give 20.3 gm of the above product. \( \text{D}^1 \text{P}^1 215-24 \text{C}^\circ \@ 2-3 \text{ mm} \text{ yield 48-51% Infra red absorption} \). \( \sqrt{3000, 1750, 1456, 1135, 1056, 980, 890, 775 \text{ cm}^{-1}} \).
A semicarbazone of the above product was prepared and recrystallized from ethyl alcohol, m.p.: 238-9 °C. (Found C, 69.23; H, 6.61; O, 18.01; N, 7.14% C₂₉H₂₂O₆ requires C, 69.19; H, 6.59; O, 18.43; N, 7.23%).

2-oxo-1-cinnamoyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene.

A solution of 23.82 gm (0.05 mole) of tricyclic β-keto ester, 8.0 gm of sodium hydroxide, 15 ml of water and 50 ml of ethyl alcohol was heated under reflux for eight hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled reflux for two hours, cooled and extracted with ether. The ethereal layer was worked up as usual, finally it was dried. The solvent was removed and the residue when distilled under vacuum gave 16.3 gm of the required product, m.p.: 235-8 °C @ 2-3 mm. Yield 61-3% Infra red absorption ν 3000, 1750, 1470, 1356, 1335, 1240, 1135, 1078, 920, and 875 cm⁻¹. (Found C, 79.81; H, 9.15% C₂₄H₂₆O₂ requires C, 79.33; H, 9.14%).

A semicarbazone of the above compound was prepared and recrystallized from ethyl alcohol, m.p.: 236-7 °C. (Found C, 71.82; H, 7.39; N, 13.40% C, 71.92; H, 7.01; N, 13.38%).
Diethyl-2-oxo-1-Isophthalyl-2,3,4,5,6,7,8,9,10,14-decahydrophenanthrene-3:14-dicarboxylate.

(Enamine method).

Pyrrolidine (10.6 gm, 0.15 mole) in 150 ml of dry benzene was added dropwise under nitrogen to a refluxing solution of tricyclic-β-keto ester(34.4 gm, 0.1 mole) in 250 ml of benzene. The mixture was refluxed for six hours during this time the water formed was removed from the reaction mixture. Then it was concentrated and cooled to room temperature. Isophthalyl chloride (30.1 gm, 0.15 mole) in 400 ml of dry dioxane was added, then it was refluxed for sixteen hours under nitrogen with constant stirring. The mixture was cooled and filtered with suction, the enamine precipitates were washed with ether. Combined the filtrate and washing, returned to the reaction flask, 100 ml of 10% aqueous hydrochloric acid and refluxed on a water bath. The organic layer was separated and the aqueous layer was extracted with ether. The ethereal layer was processed as usual. The solvent was removed and the residue distilled under vacuum gave 21.3 gm of the required product. D.p. 215-219 C° @ 0.5-1 mm yield 56-8% Infra red absorption

\[ \text{\nu} 3100, 1735, 1500, 1240, 1135, 1040, \text{and} 885 \text{ cm}^{-1} \].

( Found C, 62.48; H, 7.67; O, 20.84; Cl, 9.41%)

C_{28}H_{30}O_7Cl requires C, 62.10; H, 7.83; O, 20.56; Cl, 9.11% )
2-oxo-1-iso-phthalyl-2,3,4,5,6,7,8,9,10,14-deca hydrophenanthrene.

A solution of 24.7 gm (0.05 mole) of tricyclic-β-keto ester, 8.0 gm of sodium hydroxide, 15 ml of water, 50 ml of ethyl alcohol was heated under reflux for ten hours. The warm solution was acidified by the slow addition of 1:1 sulphuric acid, a vigorous evolution of carbon dioxide resulted. The acidified mixture was boiled under reflux for 2½ hours. The ethereal layer was worked out as usual. The solvent was evaporated and the residue when distilled under reduced pressure gave 12.2 gm of the above product. D.p. 241-5 C° @ 6-8 mm yield 45-8% semi solid at room temp. (Found C, 59.39; H, 8.81; Cl, 13. 50%, C_{23}H_{23}O_{3}Cl
requires C, 59.42; H, 8.81; Cl, 13.54%).
INFRA-RED SPECTRA.
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<th>REMARKS</th>
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SAMPLE: 2-oxo L-ethyl 3,4-aetalin.

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<th>CONC.</th>
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TRANSMITTANCE (%)
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**Sample**

- $\text{C}_8\text{H}_2\text{CH}_2\text{CH}_2\text{O}$

**Wavelength (Microns)**

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**Transmittance (%)**

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</table>

**Chemical Structure**

- $\text{C}_8\text{H}_2\text{CH}_2\text{CH}_2\text{O}$
SAMPLE

WAVELENGTH (MICRONS)

WAVENUMBER (CM⁻¹)

TRANSMITTANCE (%)

PHASE

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

SAMPLE

ETHYL 2-ORO-1-BENZYL Δ19 OCTALIN-10-CARBOXYLATE

ORIGIN

REFERENCE

NO. 263.
WAVELNUMBER (CM⁻¹)

WAVELENGTH (MICRONS)

SAMPLE

PHASE: Liquid

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

NO.

ORIGIN

Ethyl-2-oxo-1,6-bicyclo[6.1.0]nepental-10-carboxylate
SAMPLE ORIGIN

PHASE

SOLVENT

CONC.

CELL PATH

REFERENCE

WAVENUMBER (CM⁻¹)

WAVELENGTH (MICRONS)

TRANSMITTANCE (%)
Ethyl 2-cyclo-1 (2'-hydroxy) phenyl Δ19 octalin o-carboxylate.

SAMPLE

PHASE  Liquid.

SOLVENT

CONC. 

CELL PATH 

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS
WAVENUMBER (CM⁻¹)

WAVELENGTH (MICRONS)

SAMPLE

PHASE

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

ORIGIN

-273-

-273-

Ethyl 3-oxo-1-(D-methyl)phosphoryl-5-1% octanol-10-Carboxylate

No. 24
SAMPLE

PHASE

SOLVENT

CONC.

CELL PATH

REFERENCE

2-oxo-4-(4-nitro)phenyl-5:9-acalene

LIQUID

OPERATOR

DATE

REMARKS

NO. 25
Ethyl 2-oxo-1-propionyl 19-nor-10-Carbocyclate

SAMPLE

PHASE

SOLVENT

CONC.

CELL PATH

REFERENCE

WAVELENGTH (MICRONS)

WAVENUMBER (CM⁻¹)

NOMENCLATURE

No. 38
SAMPLE

PHASE  Liquid

SCAN SPEED

SOLVENT

OPERATOR

CONC.

DATE

CELL PATH

REMARKS

REFERENCE
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**Legend:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate

**Table:**

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<tbody>
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</table>

**Phase:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate

**Solvent:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate

**Concentration:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate

**Cell Path:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate

**Reference:**
- 3.4: Ethyl 2-oxo-1-benzyl 11-acetyl phenylacetate
Ethyl 2-oxo 1 (4'-nitro) benzyl Δ17 octadiene-10-carboxylate

SAMPLE

PHASE Liquid

SOLVENT

CONC.

CELL PATH

REFERENCE

SCAN SPEED

SLIT

OPERATOR

DATE

REMARKS

NO. 41
Ethyl 2-oxo-1-iso-phthalyl-11,19-octain-10-carboxylate

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SPECTRUM NO.   ORIGIN   LEGEND   REMARKS
SAMPLE   2-oxo 1-methyl 2,3,4,5,6,7,8,9,10,11-decahydrophenanthrene
PURITY   1.
PHASE   2.
LIQUID
THICKNESS
DATE
OPERATOR
SAMPLE: 2-oxo-1-n-propyl 9,3,4,5,6,7,8,9,10,11-decahydrophenanthrene

PHASE: Liquid

SOLVENT:

CONC.:

CELL PATH:

REFERENCE:

REMARKS:

SCAN SPEED

OPERATOR

DATE

SLIT

NO.
2-epoxy-10β-deoxy-∆5-3β-propyl-3,4,5,6,7,8,9,10,11-decahydrophenanthrene

SAMPLE

PHASE liquid

SOLVENT

CONC.

CELL PATH

REFERENCE

WAVELENGTH (MICRONS)

TRANSMITTANCE (%)

WAVELENGTH (CM\(^{-1}\))
Diethyl-2-oxo-1, 3, 4, 5, 6, 7, 8, 9, 10, 11-decahydrophanthrene-3,4-dicarboxylate
Diethyl 2-oxo-1-iso-butyryl 3,3',4,5,6,7,8,9,10,11-decahydrophanthrene-3',4'-dicarboxylate
SAMPLE: 2,0,0.1 iso-bulphyl, 8, 9, 10, 11, 12, 13, 14- decahydrophenanthrene.

PHASE: liquid

SOLVENT:

CONC.:

CELL PATH:

REFERENCE:

SCAN SPEED: 

SLIT: 

OPERATOR: 

DATE: 

REMARKS: 

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**TRANSMITTANCE (%)**

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**SPECIES**
2-oxo-1 Cinnamyl 2,3,4,5,6,7,8,9,10,11 decyhydrofuran 2,4,3

**PHASE**
Liquid

**THICKNESS OPERATOR**

**SPECTRUM NO.**
53.

**REMARKS**
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This greater difficulty of C-alkylation is presumably due to steric interference by the axial C-10 methyl group.


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