# STUDIES IN PYROLYSIS

## PART I: A REVERSIBLE REARRANGEMENT IN THE PYROLYSIS OF ENOL CARBOXYLATES.

## PART II: COMPETITIVE ROUTES IN THE THERMAL BREAKDOWN OF SOME OPEN-CHAIN $\alpha$-ANILINO-CARBOXYLIC ACIDS.

THESIS

SUBMITTED TO THE UNIVERSITY OF GLASGOW
IN FULFILMENT OF THE REGULATIONS FOR
THE DEGREE OF DOCTOR OF PHILOSOPHY.

June, 1959.

JAMES McGEE.

ProQuest Number: 13850404

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

ProQuest 13850404

Published by ProQuest LLC (2019). Copyright of the Dissertation is held by the Author.

All rights reserved.
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

# ACKNOWLEDGMENTS.

The author wishes to express his thanks to Professor P.D. Ritchie, B.Sc., Ph.D., F.R.I.C., F.R.S.E., F.P.I., "Young" Professor of Chemical Technology, for his help and encouragement throughout the research, and also to the Department of Scientific and Industrial Research for a Maintenance Allowance.

Thanks are also due to the Staff of the Chemical Technology Department, and to the Staff of the Microanalysis Laboratory, Chemistry Department, the Royal College of Science and Technology, Glasgow.

## PUBLICATIONS.

The work described in Part I of this Thesis has been published in the following paper: Studies in Pyrolysis. Part XII. Reversible Thermal Rearrangement as a Competitive Route in the Pyrolysis of Enol Carboxylates, R.J.P. Allan, J. McGee, and P.D. Ritchie, Journal of the Chemical Society, 1957, 4407-4414.

A further paper based upon Part II of the Thesis has been prepared and will be shortly submitted for publication: Studies in Pyrolysis. Part XVI. Pyrolysis of Some Open-Chain $\alpha$-Anilino-carboxylic Acids, J. McGee and P.D. Ritchie.

# CONTENTS.

## PART I: A REVERSIBLE REARRANGEMENT IN THE PYROLYSIS OF ENOL CARBOXYLATES.

EXPERIMENTAL.

## PART II: COMPETITIVE ROUTES IN THE THERMAL BREAKDOWN OF SOME OPEN-CHAIN $\alpha$-ANILINO-CARBOXYLIC ACIDS.

EXPERIMENTAL

## SUMMARY.

**PART I:** The previously described formation of β-diketones by thermal rearrangement (1) of enol carboxylates (other than vinyl esters) is shown to be reversible. In the vapour phase at *ca.* 500° the equilibrium strongly favours the β-diketone. The enol carboxylates studied (*iso*propenyl acetate, *cyclo*hex-1-enyl acetate and *cyclo*hex-1-enyl benzoate) undergo, in addition to the above change, a series of competitive scissions, including decarboxylation to an alkene. The major component of the gaseous pyrolysate in each case studied is carbon monoxide. The various breakdown routes and their products are discussed.

**PART II:** Four straight-chain α-anilino acids have been pyrolysed in the liquid phase at *ca.* 240° in a static reactor. α-Anilino*iso*butyric acid and α-anilino-α-methyl-*n*-butyric acid give aniline, water, the corresponding unsaturated acid and a curious type of "lactone-lactam". Apart from the absence of a rearrangement product (a hydroxy-anilide) these two acids behave, on pyrolysis, similarly to their cyclic analogues (76) even in the increased yield of olefinic acid at the expense of the lactone-lactam, as molecular weight increases. Proof is given of the structure of the lactone-lactams and their possible origin is discussed. A third acid, $\alpha$-anilino-$\alpha$-phenylpropionic acid yields only aniline and an unsaturated acid. Reasons for this are suggested. The last acid in the series, $\alpha$-anilinodiphenylacetic acid is structurally precluded from giving an unsaturated acid and breaks down in quite a different manner from the other acids studied. The pyrolysis products indicate that a dilactone (benzilide) is the key intermediate. In the gaseous phase (*ca.* 550°) the above anilino acids and lactone-lactams are very largely decomposed with the formation of much carbon monoxide.

# PART I: A REVERSIBLE REARRANGEMENT IN THE PYROLYSIS OF ENOL CARBOXYLATES.

## 1. INTRODUCTION.

## Pyrolysis of Esters.

### 1.1. General.

A survey of the literature on thermal breakdown of carboxylic esters reveals that pyrolysis can take place by several competitive routes. In the case of alkyl carboxylates two of the major routes of decomposition are alkyl-oxygen scission to a carboxylic acid and an olefin or an acetylene; and acyl-oxygen scission to give either two carbonyl compounds or a ketone and a hydroxyl compound.

More recently it has been shown (1, 2) that enol carboxylates (with the exception of vinyl esters, see page (15) rearrange on pyrolysis to give good yields of $\beta$-diketones.

These types of breakdown routes, including decarboxylation and decarbonylation will be discussed under the headings used in these laboratories.

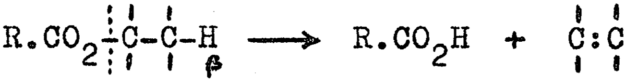
### 1.2. Alkyl-oxygen scission (A).

$$\mathrm{R.CO.O}\ \vdots\ \mathrm{R'}$$

This type of scission may be subdivided into two types - $A^1$ for alkyl, alkylidene, and alkylene esters and $A^2$ for alkenyl esters.

Type $A^1$

A carboxylic acid and an olefin are formed.



$$R.CO_2\vdots\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|\ \beta}{C}}-H \longrightarrow R.CO_2H + \overset{|}{\underset{|}{C}}:\overset{|}{\underset{|}{C}} \ldots\ldots\ldots\ldots (A^1)$$

An example of this type of breakdown is the pyrolysis of ethyl acetate (3), to give mainly acetic acid and ethylene.

$$Me.CO_2.Et \longrightarrow Me.CO_2H + CH_2:CH_2$$

A comparative study of tert.-, sec.-, and n-alkyl esters (4) has shown that thermal stability of the ester decreases as the number of available β-hydrogen atoms increases. It can also be seen from the following examples that as the stability of the ester increases so also does the complexity of the breakdown routes. Thus tert.- butyl acetate pyrolyses simply at a relatively low temperature, while isopropyl acetate and ethyl acetate require higher temperatures and give more complex results.

$$AcO.CMe_3 \xrightarrow{360^{\circ}} AcOH + CH_2:CMe_2 \ldots\ldots\ldots\ldots A^1$$

(only products)

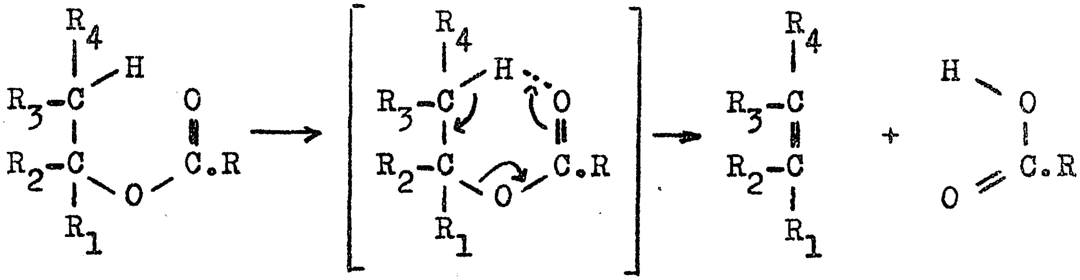
$$AcO.CHMe_2 \xrightarrow{430-460^{\circ}} AcOH + CH_2:CHMe\text{(main products)}\ldots A^1$$

$$+ Me.CHO + COMe_2 + CO \text{ (by products)}$$

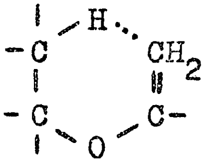
$$AcO.CH_2Me \xrightarrow{525-530^{\circ}} AcOH + CH_2:CH_2 \text{ (main products)}\ldots\ldots A^1$$

$$+ Me.CHO + H.CHO + Ac_2O + CH_4 + H_2$$

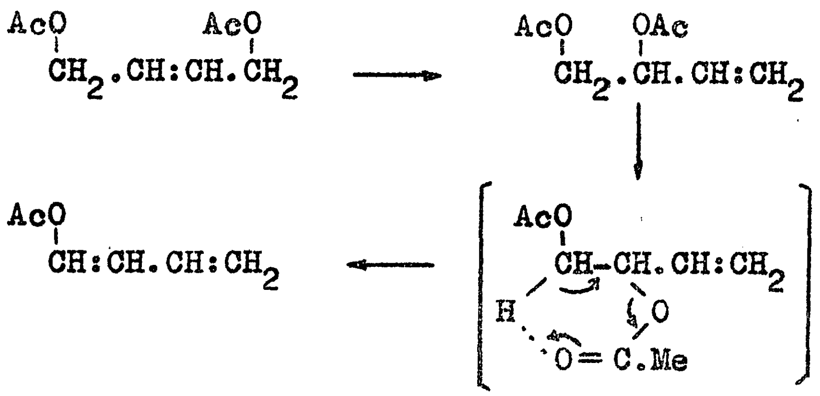
$$+ CO + CH_2:CO \text{ (by-products)}$$



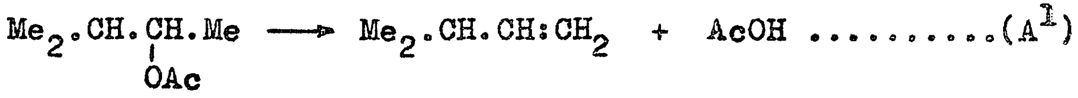
Recent studies in the decomposition of vinyl alkyl ethers (5,6) suggest a similar type of activated complex involved.



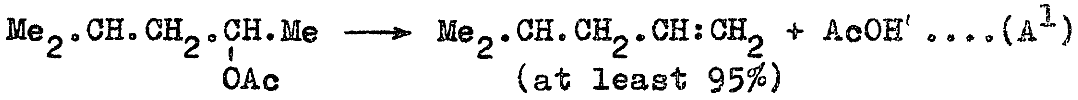
Alexander and Mudrak (7) have also favoured a cylic transition-state complex in their work on xanthates and acetates, although they point out that other mechanisms are possible. The xanthate esters have been further studied by Stevens and Richmond (8), who have postulated hydrogen-bonding prior to proton elimination, and other evidence for this mechanism of pyrolysis of esters has been produced by Arnold, Smith and Dodson (9). This mechanism has been further endorsed, more recently, by Baily and Barclay (10), who suggest that 1:4-diacetoxybut-2-ene pyrolyses by first undergoing a thermal allylic rearrangement to the 1:2-diacetoxybut-3-ene, which subsequently decomposes by a quasi-six-membered ring to form the 1-acetoxy-1:3-butadiene.



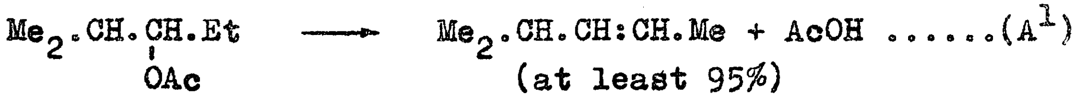
It has been shown that the pyrolysis of esters proceeds in a highly selective manner to produce almost exclusively the least highly alkylated olefin according to the Hofmann rule (11). Thus, Baily and King (12) have found that when unsymmetrical secondary esters were pyrolysed under mild conditions only the least highly alkylated olefin was produced.



$$Me_2.CH.\underset{OAc}{CH}.Me \longrightarrow Me_2.CH.CH{:}CH_2 \;+\; AcOH \ldots\ldots\ldots\ldots(A^1)$$



$$Me_2.CH.CH_2.\underset{OAc}{CH}.Me \longrightarrow \underset{\text{(at least 95\%)}}{Me_2.CH.CH_2.CH{:}CH_2} + AcOH \ldots\ldots(A^1)$$



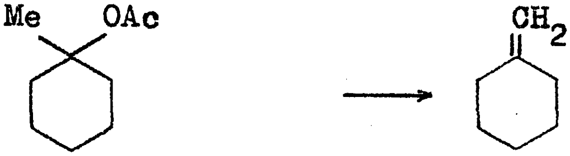
$$Me_2.CH.\underset{OAc}{CH}.Et \longrightarrow \underset{\text{(at least 95\%)}}{Me_2.CH.CH{:}CH.Me} + AcOH \ldots\ldots(A^1)$$

Bailey, Hewitt and King (13) have further shown that this selectivity also includes tertiary esters, thus:

$$\mathrm{Me_2.CH.CMe_2.OAc} \longrightarrow \mathrm{Me_2.CH.CMe{:}CH_2} + \mathrm{AcOH} \ldots \mathrm{A}^1$$

(at least 98%)

$$\mathrm{Et.CMe_2.OAc} \longrightarrow \mathrm{Et.CMe{:}CH_2} + \mathrm{AcOH} \ldots \mathrm{A}^1$$



$+ \mathrm{AcOH} \ldots \mathrm{A}^1$

This last example is a very good illustration of the selectivity of ester pyrolysis, since the alternative product, 1-methylcyclohexene, is considered to have a less strained structure. This has been illustrated by Birch, Kon and Norris (14), who have shown that a double bond is more stable <u>endo</u>cyclic to a <u>cyclo</u>hexane ring than <u>exo</u>cyclic to it.

In the above examples the pyrolyses were intentionally carried out under mild conditions, since it has been pointed out by several workers (15,7,16) that carbonisation of the pyrolysis tube leads to isomerisation of the olefins produced.

There are, however, some apparent contradictions to this rule of selectivity. Thus, Houtman *et al.* (17) found that pyrolysis of *sec.*-butyl acetate yielded a mixture of but-1-ene and but-2-ene.

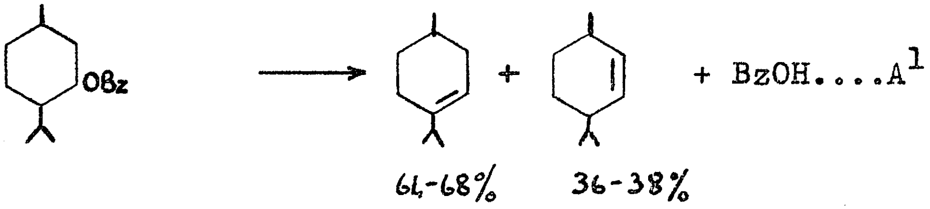
$$Me.CH_2.CHMe.OAc \xrightarrow{500^\circ} \underset{56\%}{Me.CH_2.CH{:}CH_2} + \underset{44\%}{Me.CH{:}CH.Me}$$

$$Me.CH_2.CHMe.OAc \xrightarrow{400^\circ} \underset{25\%}{Me.CH_2.CH{:}CH_2} + \underset{75\%}{Me.CH{:}CH.Me}$$

However, both Bailey <u>et</u> <u>al</u>. and Houtman <u>et</u> <u>al</u>. agree that a proton is lost in the following decreasing order of ease:

$$-CH_3 > {:}CH_2 > \vdots CH$$

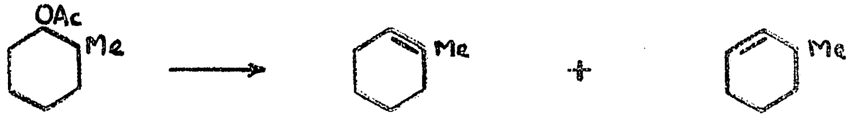
Similarly, Barton <u>et</u> <u>al</u>. (18) have shown that (-) - menthyl benzoate on pyrolysis yields a mixture of (+) - p-3-menthene and (+) -p-2- menthene.



These results are in accordance with the <u>Saytzeff</u> <u>Rule</u> (11,19) (when an alkyl halide is converted to an olefin, the main product will be the most highly branched olefin).

In contrast to the work of Arnold <u>et</u> <u>al</u>. (9), the pyrolysis of a mixture of <u>cis</u>- and <u>trans</u>-2-methyl<u>cyclo</u>hexyl acetate or pure <u>trans</u>-2-methyl<u>cyclo</u>hexyl acetate was found by Bailey and

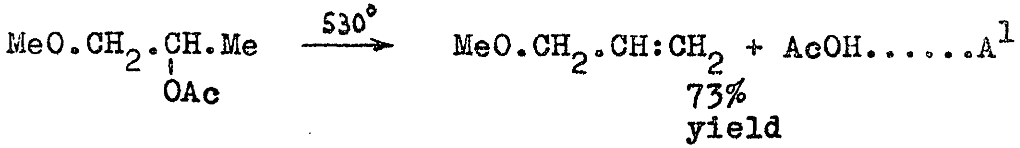
Nicholas (20) to produce almost entirely 3-methyl*cyclo*hexene, with only a trace of the isomeric 1-methyl*cyclo*hexene. The authors pointed out that the result was in agreement with earlier work (12,13).



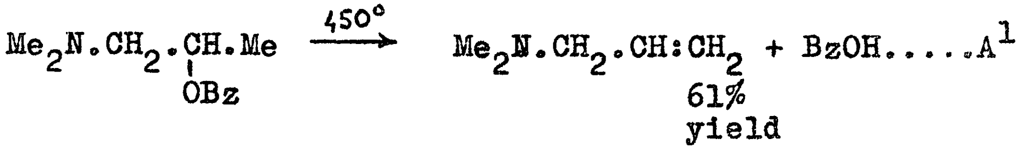
(trace) (main product)

They also pointed out that very high temperatures promoted extensive charring and gasification, and caused rearrangements and aromatisation. The presence of carbonaceous deposits, they stated, was found to reverse to some extend the direction of elimination during the pyrolysis of esters.

During a research programme designed to determine the effect of polar groups on the direction of elimination in the pyrolysis of esters, Bailey and Nicholas (21) found that the introduction of a β-methoxy or β-dimethylamino group in the alkyl portion of the ester did not alter the direction of elimination. Thus, β-methoxy*iso*propyl acetate produced on pyrolysis methyl allyl ether, while β-dimethylaminoisopropyl benzoate gave allyldimethylamine

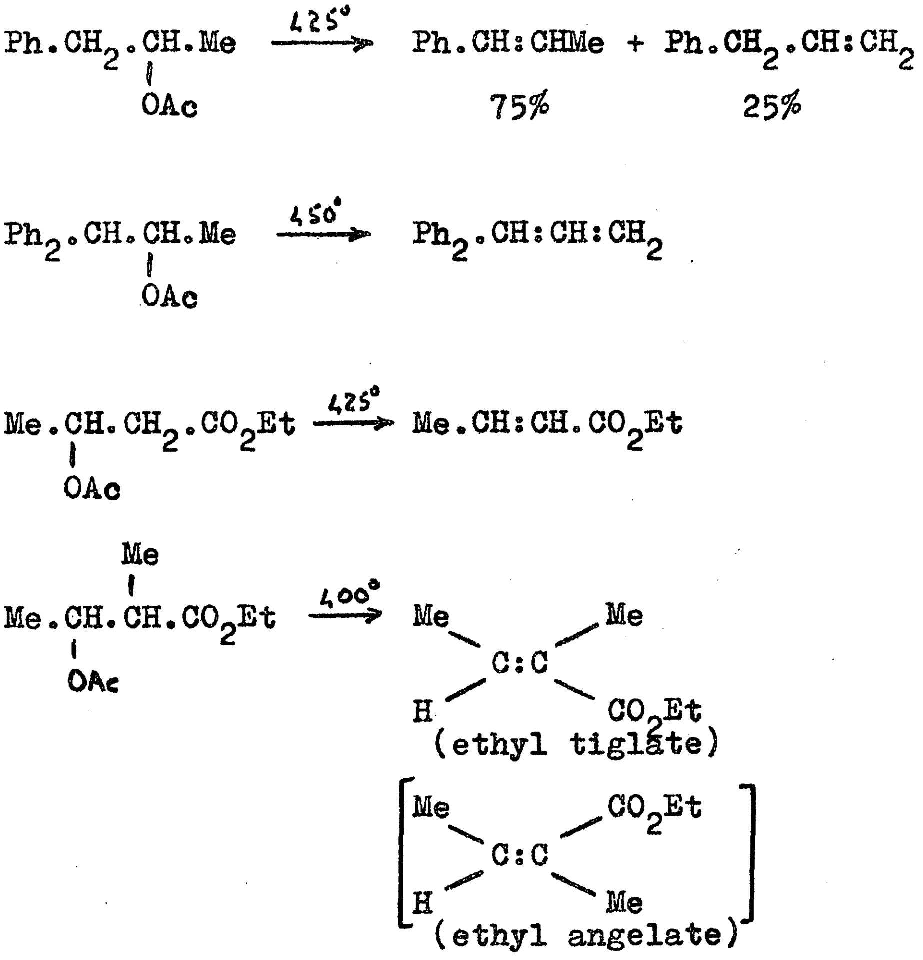


$$\mathrm{MeO.CH_2.}\underset{\substack{|\\ \mathrm{OAc}}}{\mathrm{CH}}\mathrm{.Me} \xrightarrow{530^\circ} \underset{\substack{73\%\\ \mathrm{yield}}}{\mathrm{MeO.CH_2.CH{:}CH_2}} + \mathrm{AcOH}.....\mathrm{A}^1$$



$$\mathrm{Me_2N.CH_2.}\underset{\substack{|\\ \mathrm{OBz}}}{\mathrm{CH}}\mathrm{.Me} \xrightarrow{450^\circ} \underset{\substack{61\%\\ \mathrm{yield}}}{\mathrm{Me_2N.CH_2.CH{:}CH_2}} + \mathrm{BzOH}.....\mathrm{A}^1$$

Since the above work showed that simple inductive effects did not appear to change the direction of elimination, Bailey and King (22) went on to investigate the effect of unsaturation on the direction of elimination in the pyrolysis of esters. They found that the introduction of unsaturated electron-withdrawing groups in the β-position of the alkyl portion of an ester tends to reverse the direction of elimination during pyrolysis. They state that the acidity of the β-hydrogen atom appears to be an important factor in determining the direction of elimination. Thus, the pyrolysis of β-phenyl*iso*propyl acetate produced a mixture of olefins consisting of 75% of 1-phenylprop-1-ene and 25% allylbenzene, while the pyrolysis of ββ'-diphenylisopropyl acetate gave substantially only 1,1-diphenylprop-1-ene. The pyrolysis of ethyl β-acetoxy-*n*-butyrate was found to produce only ethyl crotonate and the pyrolysis of the related ethyl α-methyl- β-acetoxy-*n*-butyrate gave essentially ethyl tiglate. In all these pyrolyses mild conditions were chosen to permit maximum selectivity in the elimination and to avoid any carbonisation in the pyrolysis tube.



$$\mathrm{Ph.CH_2.}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{.Me} \xrightarrow{425^\circ} \underset{75\%}{\mathrm{Ph.CH{:}CHMe}} + \underset{25\%}{\mathrm{Ph.CH_2.CH{:}CH_2}}$$

$$\mathrm{Ph_2.CH.}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{.Me} \xrightarrow{450^\circ} \mathrm{Ph_2.CH{:}CH{:}CH_2}$$

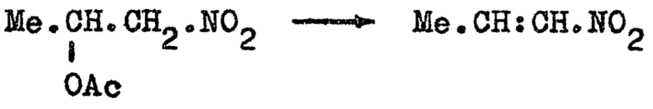
$$\mathrm{Me.}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{.CH_2.CO_2Et} \xrightarrow{425^\circ} \mathrm{Me.CH{:}CH.CO_2Et}$$

$$\mathrm{Me.}\underset{\mathrm{OAc}}{\mathrm{CH}}\mathrm{.}\overset{\mathrm{Me}}{\mathrm{CH}}\mathrm{.CO_2Et} \xrightarrow{400^\circ}$$

(ethyl tiglate)

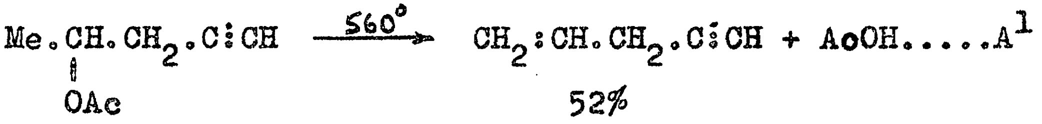
(ethyl angelate)

Similarly, Gold (23) found that the pyrolysis of 2-acetoxy-1-nitropropane gave 1-nitropropene



$$\mathrm{Me.}\underset{\substack{|\\ \mathrm{OAc}}}{\mathrm{CH}}\mathrm{.CH_2.NO_2} \longrightarrow \mathrm{Me.CH{:}CH.NO_2}$$

Bailey and King, however, point out that Paul and Tchelitcheff (24) found that the pyrolysis of 4-acetoxypent-1-yne at 560° gave a 52% yield of allylacetylene.



$$\mathrm{Me.}\underset{\substack{|\\ \mathrm{OAc}}}{\mathrm{CH}}\mathrm{.CH_2.C}\vdots\mathrm{CH} \xrightarrow{560^{\circ}} \underset{52\%}{\mathrm{CH_2{:}CH.CH_2.C}\vdots\mathrm{CH}} + \mathrm{AcOH.....A^1}$$

It is clear from this example that all unsaturated groups do not reverse the direction of elimination. The above work of Bailey and King, however, shows that although the Hofmann rule of elimination in the pyrolysis of esters is followed by most simple esters the direction of elimination can be reversed by the presence of an unsaturated electron-withdrawing group in the $\beta$-position to the acetoxy group.

<u>Type $A^2$</u> <u>An Alkenyl-oxygen scission</u>.

A carboxylic acid and an acetylene are formed:

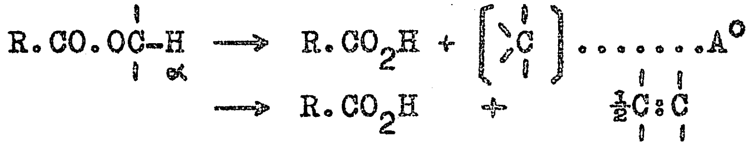
$$\mathrm{R.CO.O{-}}\overset{|}{\mathrm{C}} = \underset{\beta}{\overset{|}{\mathrm{C}}}\bullet\mathrm{H} \longrightarrow \mathrm{R.CO_2H} + \overset{|}{\mathrm{C}}\vdots\overset{|}{\mathrm{C}}$$

The mechanism for this type of scission is very similar to the $A^1$ scission.

Vinyl benzoate (25) has been shown to breakdown by several competitive primary routes, one of which yields minor amounts of benzoic acid and acetylene.

$$BzO.CH{:}CH_2 \xrightarrow{400^\circ} BzOH + CH{⋮}CH \ldots\ldots\ldots\ldots\ldots\ldots A^2$$
$$+ CO_2 + Ph.CH{:}CH_2 + CO + Me.CO.Ph$$

The absence of $\beta$-hydrogen atoms in the alkyl group of the ester prevents <u>acyl-oxygen</u> scission, with decomposition setting in at a higher temperature than normal (26). However, alkyl-oxygen scission has been shown to occur in certain methyl esters. This type of scission has been designated $A^o$.



$$\begin{array}{l} R.CO.OC\text{-}H \longrightarrow R.CO_2H + \left[ >\!C< \right] \ldots\ldots\ldots A^o \\ \qquad\qquad\quad\ \ \longrightarrow R.CO_2H + \tfrac{1}{2}C{:}C \end{array}$$

These methyl esters yield an acid and an olefin as in an $A^1$ scission, but the olefin occurs presumably *via* a transient diradical. Methyl acetate (27) has been shown by Peytral to breakdown at 1,100°, an $A^o$ scission to ethylene and acetic acid competing with the predominating $B^2$ acyl-oxygen scission.

$$AcO.Me \xrightarrow{1100^\circ} \left\{ \begin{array}{l} \longrightarrow AcOH + \tfrac{1}{2}CH_2{:}CH_2 \ldots\ldots\ldots\ldots\ldots A^o \\ \\ \longrightarrow Me.CHO + CH_2O \longrightarrow 2CO + CH_4 + H_2 \ldots B^2 \end{array} \right.$$

In all recorded cases where an $A^o$ scission occurs it is only a minor breakdown route; other scissions predominate.

### 1.3. Acyl-oxygen scission (B).

$$\mathrm{R.CO} \,\vdots\, \mathrm{O.R}$$

This type of scission involves the transfer of an α-hydrogen atom from either the alkyl or acyl portion of the molecule, resulting in one of the two following breakdowns ($B^1$ or $B^2$):

Type $B^1$. A keten and a hydroxyl compound are formed.

$$\mathrm{{>}CH.CO} \,\vdots\, \mathrm{O.CH{<}} \longrightarrow \mathrm{{>}C{:}CO + HO.CH{<}}$$

Of the two types of acyl oxygen scission the $B^1$ route is the less common. Allan *et al.* (25) found that vinyl *iso*butyrate decomposed to acetaldehyde and secondary products attributable to dimethylketen, while phenyl acetate was found by Hurd and Blunk (4) to decompose at 600-650° to give keten and phenol:

$$\mathrm{Me_2.CH.CO_2.CH{:}CH_2} \longrightarrow \mathrm{Me_2.C{:}CO + (CH_2{:}CHOH) \rightarrow Me.CHO\,..\,B^1}$$

$$\qquad\qquad \hookrightarrow \mathrm{CO + \tfrac{1}{2}\,Me_2.C{:}C.Me_2}$$

$$\mathrm{AcO.Ph} \longrightarrow \mathrm{CH_2{:}CO + PhOH}\ \ldots\ldots\ldots\ldots\ldots\ldots\ \mathrm{B^1}$$

Type $B^2$. Two carbonyl molecules are formed.

$$\mathrm{{>}CH.CO} \,\vdots\, \mathrm{O.CH{<}} \longrightarrow \mathrm{{>}CH.CHO + O{:}C{<}}$$

As mentioned previously, esters which do not possess a β-hydrogen atom are normally much more thermally stable than esters possessing such an atom. However, when such esters do break down, very often they do so by a $B^2$ acyl-oxygen scission as the major route (28).

Ethyl acetate as mentioned previously, decomposes (3) to give acetaldehyde as one of the products, although the $A^1$ route predominates.

$$\mathrm{AcO.Et} \longrightarrow \begin{cases} \mathrm{AcOH} + \mathrm{CH_2{:}CH_2} \ \ldots\ldots\ldots\ldots\ldots \ A^1 \\[2ex] \mathrm{2Me.CHO} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ B^2 \end{cases}$$

Methyl formate has been shown by Muller and Peytral (29) and Peytral (30) to decompose at 1,150° to give formaldehyde and its breakdown products

$$\mathrm{H.CO.OMe} \longrightarrow \mathrm{2CH_2O} \longrightarrow \text{secondary products} \ \ldots\ldots\ldots\ldots \ B^2$$

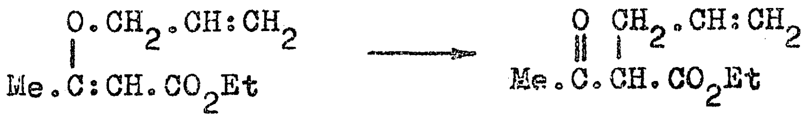
Methyl acetate (27) already mentioned has been found to decompose predominantly by a $B^2$ route, although an $A^0$ scission to some extent competes with this route:

$$\mathrm{Me.CO_2.Me} \longrightarrow \begin{cases} \mathrm{Me.CO_2H} + \tfrac{1}{2}\mathrm{CH_2{:}CH_2} \ \ldots\ldots\ldots \ A^0 \\[2ex] (\mathrm{Me.CHO} + \mathrm{H.CHO}) \ \ldots\ldots\ldots\ldots \ B^2 \\ \qquad \hookrightarrow \mathrm{2CO.} + \mathrm{CH_4} + \mathrm{H_2} \end{cases}$$

Acyl oxygen scission is normally the major route of the more thermally stable esters, the lack of thermal stability being associated, as mentioned previously, with the lack of available β-hydrogen atoms. There are, however, few examples of the $B^1$ scission mentioned in the literature, the $B^2$ scission being by far the more common. It has been suggested by Hurd and Blunk (4) that a free radical mechanism is likely to occur with these esters, requiring high temperatures for their decomposition.

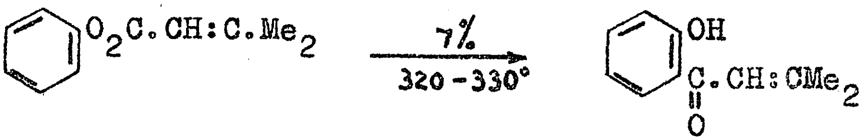
## 1.4. Rearrangement (R).

A search of the literature reveals that apart from the Claisen rearrangement, there are few reported ester rearrangements which occur apparently without the use of a catalyst. Laner and Kelburn (31) have proved that the Claisen rearrangement of ethyl O-allyloxycrotonate, originally reported by Claisen (32) to take place under the influence of ammonium chloride, could be brought about purely by thermal means to give ethyl α-allylacetoacetate.



$$\begin{array}{l} \mathrm{O.CH_2.CH{:}CH_2} \\ | \\ \mathrm{Me.C{:}CH.CO_2Et} \end{array} \longrightarrow \begin{array}{l} \mathrm{O\;\;CH_2.CH{:}CH_2} \\ \|\;\;\;| \\ \mathrm{Me.C.CH.CO_2Et} \end{array}$$

Skraup and Beng (33) have reported that the aryl esters of β,β-dimethylacrylic acid rearrange to give an o-hydroxyketone, thus:



Similarlly, Skraup and Beifuss (34) have shown that phenyl cyclohexanecarboxylate, heated in a sealed tube, rearranges to form cyclohexyl o-hydroxyphenyl ketone.

More recently it has been found by Boese and Young (2) that enol carboxylates of the following form undergo rearrangements to the corresponding $\beta$-diketone.

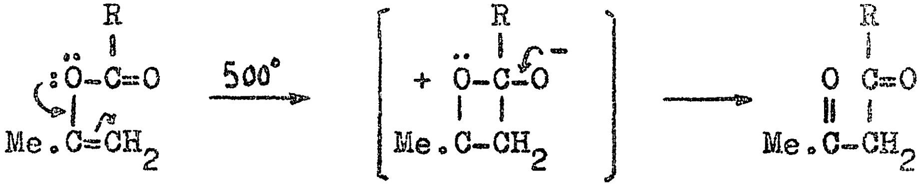
$$R'.CO.OC(R''):C<$$

where $R'$ and $R''$ may be aliphatic or aromatic radicals or where $R'$ together with the ethylenic carbon atoms may be part of an aliphatic ring.

An example of this type of rearrangement is given by the pyrolysis of isopropenyl acetate.

$$Me.CO_2.C(Me):CH_2 \xrightarrow{500^\circ} Me.CO.CH_2.CO.Me.......R$$

It has been suggested by Young et al. that the rearrangement proceeds through a four-centre transition state, a concept possibly applicable to other thermal rearrangements (35).



Allan *et al.* (25) have shown that vinyl esters undergo a similar rearrangement, but the product is a labile β-keto-aldehyde instead of a stable β-diketone. It is further suggested by Young *et al.* that the above reaction proceeds by an intramolecular mechanism, while the same rearrangement, which may be effected at low temperatures (1) under the influence of boron trifluoride, proceeds by an intermolecular reaction mechanism, involving a complex addition compound as the intermediate.

## 1.5. Decarbonylation and Decarboxylation (C).

### Type $C^1$ Decarbonylation.

This type of scission is frequently shown by aldehydes or compounds containing an aldehydic grouping.

It has been found that acetaldehyde and propionaldehyde (36) pyrolyse to give carbon monoxide and the appropriate hydrocarbon. Most simple aldehydes decompose in this manner.

It has also been found that esters containing an α-carbonyl group (*e.g.* pyruvic esters) may also pyrolyse with the elimination of carbon monoxide *e.g.* ethyl pyruvate (37).

$$\mathrm{Me.CO.CO_2Et} \xrightarrow{100-130^\circ} \mathrm{CO} + \mathrm{CO_2} \text{ ( + other products)..}C^1$$

However, it has unexpectedly been shown by the use of isotopic tracer techniques, that here the ester carbonyl group rather than the $\alpha$-carbonyl group is eliminated as carbon monoxide.

Type $C^2$ Decarboxylation.

This type of reaction was believed until recently to occur only rarely in ester pyrolysis. Hence, few examples are reported in the earlier literature.

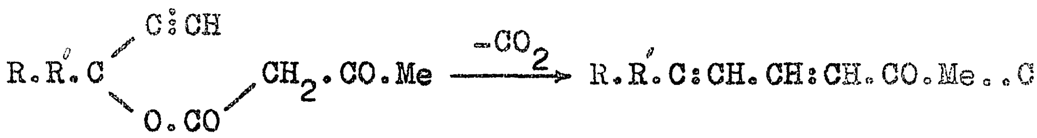
Triphenyl-methyl formate has been reported to lose carbon dioxide at *ca.* 100°C (38).

$$\mathrm{HCO_2CPh_3} \longrightarrow \mathrm{CO_2} + \mathrm{CHPh_3}$$

Aryl esters of cinnamic acid have been reported by Anschutz (39) to decompose to carbon dioxide and stilbene:

$$\mathrm{Ph.CH{:}CH.CO_2Ar} \longrightarrow \mathrm{Ph.CH{:}CH.Ar} + \mathrm{CO_2} \text{ .........}C^2$$

An unusual type of ester decarboxylation was observed by Lacey (40), who discovered that dienones were formed in the thermal decomposition of acetoacetates of ethynylcarbinols.



$\ldots C^2$

As one of several competitive breakdown reactions, decarboxylation has been found to occur in the breakdown of vinyl benzoate (25) at ca. 450°.

$$\mathrm{BzOCH{:}CH_2} \xrightarrow{400-500^\circ} \mathrm{Ph.CH{:}CH_2} + \mathrm{CO_2} \quad \ldots\ldots\ldots\ldots C^2$$

Both phenyl acrylate and phenyl α-methacrylate (41), stable up to ca. 500°, breakdown at ca. 550° by a series of competitive reactions, including decarboxylation:

$$\mathrm{CH_2{:}CH.CO_2Ph} \xrightarrow{550^\circ} \mathrm{CO_2} + \mathrm{CH_2{:}CHPh} \quad \ldots\ldots\ldots\ldots C^2$$

$$\mathrm{CH_2{:}CMe.CO_2Ph} \xrightarrow{550^\circ} \mathrm{CO_2} + \mathrm{CH_2{:}CMe.Ph} \quad \ldots\ldots\ldots\ldots C^2$$

It now seems probable, therefore, that thermal decarboxylation of esters is a much more common reaction than at first thought, and the present work adds to the growing list of this type of reaction.

## 1.6. Enol carboxylates.

As mentioned previously, enol carboxylates have been found to rearrange to isomeric β-diketones on pyrolysis.

Both isopropenyl acetate and cyclohex-1-enyl acetate have been found by Young *et al.* (1,2) to rearrange in this way. *No mention was made, however, of products of any other competitive decompositions.*

On studying the pyrolysis of a similar type of compound, *cyclo*hex-1-enyl benzoate, Allan (42) obtained several unexpected results, *viz.* the presence of *cyclo*hexanone and benzoic acid. Further, on pyrolysis of the isomeric $\beta$-diketone 2-benzoyl*cyclo*hexanone, Allan found definite traces of the enol ester, once more together with *cyclo*hexanone, as well as a new product, benzene.

It seemed likely, therefore, that the $\beta$-diketones, obtained from the enol carboxylates, themselves rearrange on pyrolysis to give traces of the parent ester. To confirm and study this unexpected preliminary observation, the following work was planned and carried out.

## 2.1. OBJECTS OF RESEARCH.

The objects of the present investigations were:

1. To discover other routes of decomposition of both isopropenyl acetate and cyclohex-1-enyl acetate.
2. To find the source of the unexpected products from cyclohex-1-enyl benzoate and 2-benzoylcyclohexanone and to determine any other decomposition routes.
3. To confirm the unexpected preliminary observation (42) that 2-benzoylcyclohexanone yielded cyclohex-1-enyl benzoate on pyrolysis, and to determine whether acetylacetone behaved in a similar manner, yielding isopropenyl acetate.

## 3. DISCUSSION OF RESULTS.

In their work on the thermal rearrangement of enol esters to the isomeric $\beta$-diketones, Boesne and Young (2) found (with the exception of a small amount of tarry material) no signigicant by-products or side reactions. They observed, however, that until a thin deposit of carbon had been formed, some decomposition of enol carboxylate to lower boiling substances took place with a resultant lower yield; but no by-products were recorded.

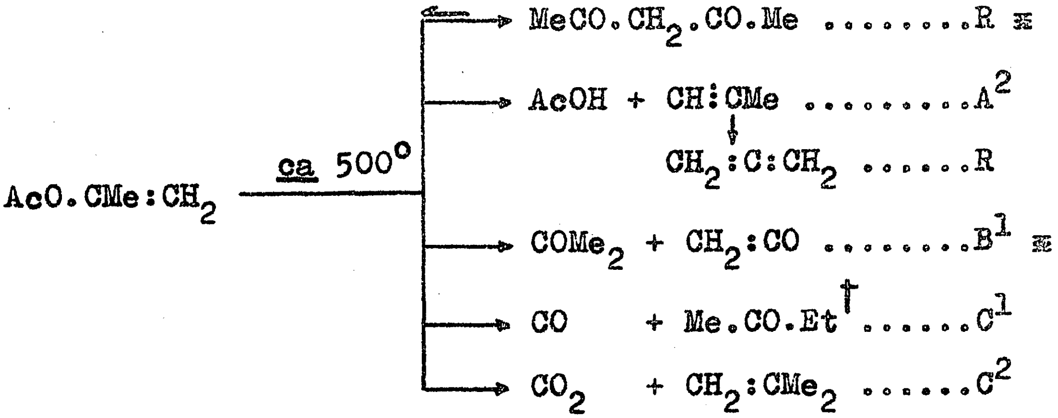
$$\mathrm{R.CO_2.CR'{:}CH_2 \longrightarrow R.CO.CH_2.COR'} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathrm{R}$$

It was shown later by Allan, Forman, and Ritchie (25) that vinyl carboxylates (i.e. those enol carboxylates in which $R' = H$) breakdown under similar conditions by a complex series of competitive scissions. It is now shown that this is true of enol carboxylates in general, and that in addition an equilibrium exists between the enol ester and the isomeric $\beta$-diketone in the vapour phase. It must be emphasised that Boesne and Young (2) had no evidence for the reversability of this reaction R. Boesne and Young state that conversion of the enol ester to the isomeric $\beta$-diketone appears to be brought about primarily by a thermal reaction, since such basic or acidic materials as were tested for catalytic activity had a deleterious affect on the yield. However, Bailey et al. (12,15) have shown that carbonised deposits (presumed to be acidic) formed during the pyrolysis of an ester can catalytically induce rearrangements of certain of the primary products, notably olefins. In the present work it was found that carbonisation, though slight, was unavoidable at the high temperatures necessary for scission, so that carbonised deposits may possibly affect catalytically the competitive scissions noted. Certainly, the rearrangements (R) of enol carboxylates can be caused not only thermally, but also catalytically (e.g. by bases (43) or boron trifluoride (1), though in the special case of vinyl esters the latter caused violent polymerisation even at - 40°, rather than detectable rearrangement (42).

## 3.1. isoPropenyl acetate.

Pyrolysis of isopropenyl acetate in a flow system confirmed that the isomeric $\beta$-diketone acetylacetone is a major product. The best yield obtained was approximately 46% (Boesne and Young (2) claimed 45.3%). This yield was obtained from Run 3 (see Table 1), and it is of interest that the yield for

Run 2 (which has a similar contact time) is only 25%. However, the amount of ester pyrolysed in Run 3 was approximately double that of Run 2, and it may well be that the higher yield is due to increased carbon deposit having a catalytic affect. However, several other major decomposition routes were apparent in the pyrolysis, and each will now be discussed in turn under the appropriate heading. The best overall interpretation of the results is offered by the following scheme, in which ≋ indicates a major route and † a product identified in the pyrolysate from the ester only, not from the $\beta$-diketone.

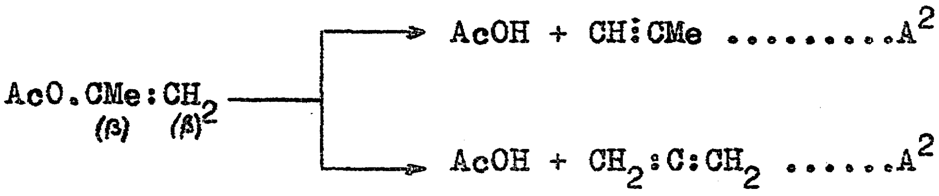


(Also small amounts of $Ac_2O, CH_4$, and $CH_2:CH_2$).

<u>Alkenyl-oxygen scission $A^2$.</u>

It is to be expected that *iso*propenyl acetate, which has two sources of available

$\beta$-hydrogen atoms should decompose, to some extent, by an $A^2$ scission.



$$AcO.\underset{(\beta)}{CMe}:\underset{(\beta)}{CH_2} \rightarrow \begin{cases} AcOH + CH\vdots CMe \ldots\ldots\ldots A^2 \\ AcOH + CH_2:C:CH_2 \ldots\ldots A^2 \end{cases}$$

Formally it is possible for both methylacetylene and allene to be formed. In the first, the acetoxy-group of the *iso*propenyl acetate abstracts a hydrogen from the methylene group (essentially an $A^1$ scission); in the second, it abstracts a hydrogen from the $\alpha$-methyl group (an $A^2$ scission). In fact only methylacetylene was identified in the pyrolysate, no trace of allene being found. The work of Bailey *et al*. (13) suggests that a clean reactor should favour the formation of allene, but the present work is in agreement with that of Bailey and Rosenberg (15) who pointed out that carbonisation leads to some extent to the reversal of the normal direction of elimination, which in this case would lead to the formation of methylacetylene. It is, however, possible that both methylacetylene and allene could be formed directly (i.e. competitively) from *iso*propenyl acetate and that the allene could rearrange during pyrolysis to methylacetylene. Hurd *et al.* (44) showed that an alk-1-yne is partially isomerised to an alka-1:2-diene at *ca.* 500°, but that the reverse change does not appear to occur thermally (though it can be induced catalytically). This, coupled with the fact that an alkyne is formed from vinyl (25) as well as from *iso*propenyl acetage, by a minor scission, suggests that methylacetylene is a primary product of the latter.

### Acyl-oxygen scission $B^1$.

It is somewhat unusual to find an acyl-oxygen scission competing successfully with an alkenyl-oxygen scission in the pyrolysis of an ester, containing available $\beta$-hydrogen atoms. In the pyrolysis of *iso*propenyl acetate, however, a major competitive route, was found to be the acyl-oxygen scission of the $B^1$ type to form acetone (enol) and keten.

$$CH_3.CO\vdots O.CMe{:}CH_2 \longrightarrow CH_2{:}CO + (HO.CMe{:}CH_2 \rightleftharpoons Me.CO.Me)\,..\,B^1$$

Normally, a $B^2$ scission is more common than a $B^1$; but here this is impossible, as there are no available $\alpha$-hydrogen atoms on the alkyl group.

It is of interest to compare this result with those obtained by Allan *et al.* (25) in a study of vinyl carboxylates (*cf.* also Bennet *et al.* (28)).

$$\mathrm{\overbrace{CHRR'.CO\vdots O}.CH{:}CH_2 \longrightarrow CRR'{:}CO + (HO.CH{:}CH_2 \rightleftharpoons MeCHO)\ldots B^1}$$

$$\mathrm{CHRR'.\overbrace{CO\vdots O.CH}{:}CH_2 \longrightarrow CHRR'.CHO + CH_2{:}CO \ldots\ldots\ldots\ldots B^2}$$

For vinyl acetate (R = R' = H) it is clear that both routes lead to the same pair of products, keten and acetaldehyde, and both were found by Allan _et al_. in the pyrolysate. Thus, in this case, it was not possible to say which of the two routes was followed. In the case of vinyl _iso_butyrate (R = R' = Me), they found that the pyrolysis yielded acetaldehyde and secondary products attributable to dimethylketen (route $B^1$), with no detectable quantity of _iso_butyraldehyde and keten (route $B^2$). They found also in the case of vinyl benzoate whose acyl group lacks the α-hydrogen atoms needed for a $B^1$ scission, that although a $B^2$ scission was formally possible the benzoate in fact showed no trace of acyl-oxygen scission, benzaldehyde and keten being entirely absent from the pyrolysis.

$$\mathrm{Ph.\overbrace{CO\vdots O.CH}{:}CH_2 \not\longrightarrow Ph.CHO + O{:}C{:}CH_2}$$

Allan _et al_. suggest from these results that vinyl carboxylates in general can undergo acyl-oxygen scission by route $B^1$ only.

The present work on _iso_propenyl acetate would appear to underline the fact that a $B^1$ scission is a major route of pyrolysis for enol carboxylates.

## $C^1$ Scission.

The formation of a trace of ethyl methyl ketone from *iso*propenyl acetate was unexpected.

$$AcO.CMe:CH_2 \longrightarrow CO + Me.CO.Et \quad \ldots\ldots\ldots\ldots\ldots \quad C^1$$

Although this is described as a $C^1$ type of scission, yielding carbon monoxide and ketone, no simple rearrangement of the type proposed by Young *et al.* (1) could lead to a readily decarbonylated β-keto-aldehyde precursor, such as $Me.CO.CH.Me.CHO$ or $Et.CO.CH_2.CHO$, the latter of which is claimed (25) to be the direct precursor of the ethyl methyl ketone formed on pyrolysis of ethylene dipropionate (45).

It is just possible that the ketone might arise from the semidecarbonylation of acetylacetone itself, but this seems unlikely as no ethyl methyl ketone could be detected in the pyrolysate from the pure diketone. This negative result agrees with an earlier study of this pyrolysis (46).

A further explanation may be found in high temperature free radical reactions. The radical $\cdot OCMe:CH_2$, formed by initial scission could possibly react in its alternative canonical form as follows:

(1) $\mathrm{Me.CO.O.CMe{:}CH_2 \longrightarrow MeCO\cdot + \cdot O.CMe{:}CH_2}$

(2) $\mathrm{Me.CO\cdot \longrightarrow Me\cdot + CO}$

(3) $\mathrm{\cdot O.CMe{:}CH_2 \longleftrightarrow O{:}CMe.CH_2\cdot}$

(4) $\mathrm{O{:}CMe.CH_2\cdot + Me\cdot \longrightarrow Me.CO.CH_2.Me}$

It must be recorded, however, that although this free radical mechanism should apply equally well to _cyclo_hex-1-enyl acetate, pyrolysis of this compound (see pages 33 and 55) yielded no evidence for the formation of 2-methyl_cyclo_hexanone, the ketone corresponding to ethyl methyl ketone, on the above basis.

A second free radical explanation may be found in the thermal breakdown of acetone, a product of the pyrolysis. It has been shown by McNesby _et al_. (47) that the thermal decomposition of acetone at 500°C proceeds almost entirely by a free radical mechanism, in accordance with the Rice-Herzfeld mechanism (48). This sequence has been written as:

(1) $\mathrm{Me.CO.Me \longrightarrow Me\cdot + Me.CO\cdot}$

(2) $\mathrm{Me.CO\cdot \longrightarrow Me\cdot + CO.}$

(3) $\mathrm{Me\cdot + Me.CO.Me \longrightarrow CH_4 + \cdot CH_2.CO.Me}$

(4) $\mathrm{\cdot CH_2.CO.Me \longrightarrow \cdot Me + CH_2{:}CO}$

(5) $\mathrm{\cdot Me + \cdot CH_2.CO.Me \longrightarrow Et.CO.Me}$

There is good evidence in the literature for the first four of the above reactions (49). McNesby *et al.* however, found no evidence for the presence of ethyl methyl ketone in the products of decomposition of acetone, but they did find traces of ethane and acetonylacetone, possible chain-ending products. The only evidence for the existence of ethyl methyl ketone in the products of acetone decomposition is the work of Allan (50) on the pyrolysis of acetone, and McNesby and Gordon (51) who confirmed that ethyl methyl ketone is a product of the photolysis of acetone in the temperature range 100 - 250°.

This possible explanation of the formation of a trace of ethyl methyl ketone in the pyrolysis of *iso*propenyl acetate would, of course, account for the fact that no 2-methyl*cyclo*hexanone was found in the pyrolysate from *cyclo*hex-1-enyl acetate.

## $C^2$ Scission.

Although carbon dioxide was found on pyrolysis of *iso*propenyl acetate, no trace of the other decarboxylation product, *iso*butene, could be found.

$$Me.CO_2.CMe{:}CH_2 \longrightarrow CO_2 + CH_2{:}CMe_2$$

It is of course possible that the small amount of isobutene formed breaks down during the pyrolysis to methane and methylacetylene (both products identified), a reaction known to occur at high temperatures and low contact times (52).

## Other products of decomposition.

### a). Carbon Monoxide.

The carbon monoxide found in the pyrolysis is present in relatively large quantities, and another possible source, apart from those stated above, might be the partial breakdown of keten (53) to ethylene and carbon monoxide:

$$2CH_2{:}CO \longrightarrow CH_2{:}CH_2 + 2CO$$

This source of carbon monoxide would also explain the presence of ethylene (identified by infra-red).

### b). Methane.

An infra-red analysis of the pyrolysis gases showed methane to be present. This can be accounted for in two ways, either by the breakdown of acetone to keten and methane (a well-known thermal reaction) or by the decarboxylation of acetic acid to methane and carbon dioxide. The latter route could account at least in part for the presence of carbon dioxide.

### c). Acetic anhydride.

Traces of acetic anhydride in the pyrolysate can be readily explained by the interaction of acetic acid (from $A^2$) and keten (from $B^1$).

$$AcOH + CH_2{:}CO \longrightarrow (Me.CO)_2O$$

## 3.2. Acetylacetone.

Acetylacetone was pyrolysed under similar conditions to those used for the parent ester, isopropenyl acetate. Among other breakdown products, definite evidence was obtained by infra-red and ultra-violet spectroscopy for the presence of the enol acetate.

The diketone was found, as would be expected, to be much more thermally stable than the parent enol acetate, and relatively large amounts survived pyrolysis (30-70%). Even on prolonged heating (154 hours) at its boiling point, acetylacetone remained unchanged (96% recovered).

At first it proved extremely difficult to find evidence for the presence of isopropenyl acetate, owing to the fact that only a very small amount was formed and it was thus impossible to separate it from the other products by distillation. Eventually, isopropenyl acetate was detected in the following manner. The entire pyrolysate was dissolved in ether and washed with aqueous sodium hydrogen carbonate to remove acid. On removal of the ether a very small amount of liquid was isolated, most of the pyrolysate being extracted in the alkali. This residual liquid, distilled and examined by ultra-violet and infra-red spectroscopy, was found to contain acetylacetone (ultra-violet absorption band $\lambda_{max.}$ 273) together with isopropenyl acetate (ultra-violet absorption band $\lambda_{max.}$ 206, and infra-red bands at ca. 1745 (C=O) and 1200 cm.$^{-1}$ (C-O-C)). Control experiments showed that these bands, characteristic of isopropenyl acetate, persisted strongly when a sample of pure ester was progressively diluted down to a concentration of 8% by the addition of acetylacetone. Also, a control sample of pure acetylacetone, treated as above with ether and aqueous sodium hydrogen carbonate, showed none of the absorption bands of the ester, showing that the observed enol carboxylate was not produced by an alkali-catalysed rearrangement of the diketone.

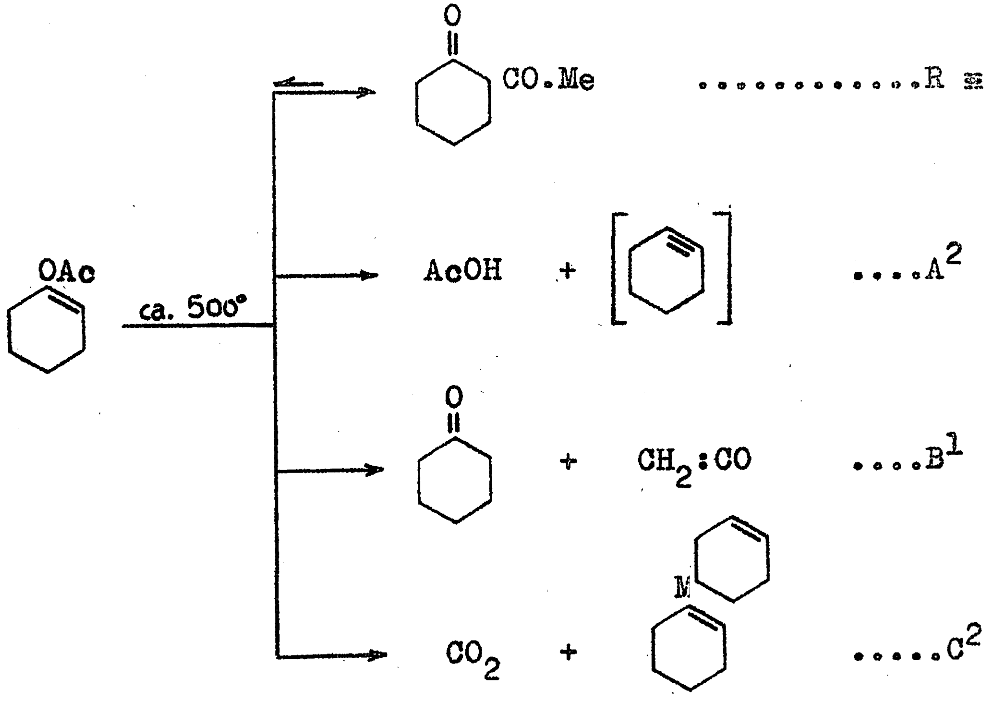
The equilibrium itself must lie well over to the $\beta$-diketone side, since at temperatures below 500° the diketone is very stable and no trace of ester could be found in the pyrolysate by using the above methods. It would be expected that at higher temperatures any ester formed would rapidly decompose. Thus, although higher temperatures might favour the formation of the enol ester, they would also cause its immediate breakdown.

All the breakdown products obtained on pyrolysis of *iso*propenyl acetate (see page 22) were detected in the pyrolysis from the $\beta$-diketone, with the exception of ethyl methyl ketone. The presence of acetic acid in the pyrolysate from the diketone would appear to be another proof of an equilibrium, as it seems unlikely that the acid could be produced *directly* from the diketone without some sort of prior rearrangement. Coupled with this is the fact that on pyrolysis the ester produces more acetic acid than does the diketone.

Since several of the observed products might formally originate both from the enol carboxylate and from its isomeric $\beta$-diketone, the fact that an equilibrium exists raises some doubt as to the actual source of certain products of pyrolysis (e.g. acetone and keten). In the case of ethyl methyl ketone this doubt no longer exists, as this compound is obtained from the ester only. In this connection, the suggestion that ethyl methyl ketone may be produced by a free radical mechanism involving acetone does not appear to agree with the fact that acetone is found in the pyrolysate from acetylacetone.

## 3.3. cycloHex-1-enyl acetate.

Boesne and Young (2) found that *cyclo*hex-1-enyl acetate rearranged thermally to 2-acetyl*cyclo*hexanone in yields of 43%, with no recorded by-products. The present work confirms this rearrangement, but the best yield obtained was *ca*. 25%. As in the case of *iso*propenyl acetate, several other competitive routes of decomposition have been found. An overall picture of the breakdown routes is presented by the following scheme, where * indicates a major route of decomposition:



(also CO, *and small amounts* of $AC_2O$, $COMe_2$, $CH_2$:CH *and* cyclo*hexene*).

*Alkenyl-oxygen scission. $A^2$.*

By analogy with the results obtained from isopropenyl acetate the acetic acid formed on pyrolysis of the cyclohex-1-enyl acetate should be accompanied by an acetylene (cyclohexyne) and/or an alkene (cyclohexa-1:2-diene). As expected, there was no evidence for these transient entities (cyclohexyne (54) is incapable of stable existence); but neither was there evidence for any of their probable secondary reactions - for example, rearrangement to cyclohexa-1:3-diene, trimerisation to dodecahydrotriphenylene, or disproportionation to benzene plus cyclohexene. This $A^2$ reaction is, therefore, less well established than that of isopropenyl acetate.

Another explanation of the presence of acetic acid might be the reaction of keten with water, possibly formed from self condensation of cyclohexanone (see page 63) to give cyclohexylidene-cyclohexanone (56).

Acyl-oxygen scission. $B^1$.

As in the case of isopropenyl acetate, an acyl-oxygen scission of the $B^1$ type was found to compete quite successfully with the main pyrolysis route to the isomeric β-diketone. Thus, cyclohexanone and keten were both found in the pyrolysate. This again confirms that a $B^1$ scission is a major route for enol carboxylates in general (see page 25).

### Decarboxylation. $C^2$.

*cyclo*Hex-1-enyl acetate was found to provide a further example of ester decarboxylation, yielding carbon dioxide and 1-methyl*cyclo*hexene. Formally this reaction requires the splitting of the ester molecule at two points, elimination of carbon dioxide, and subsequent reunion of the two terminal portions (in this case alkenyl and alkyl). This is difficult to visulise except through a free radical mechanism although Mackinnon and Ritchie (41) found that inhibitors did not seem to effect this type of reaction.

### Other products of decomposition.

#### a). Acetic anhydride.

Traces of acetic anhydride, presumably due to the interaction of keten ($B^1$ scission) and acetic acid, were also found. At least one ester, benzyl benzoate (55), yields an acid anhydride and an ether, by disproportionation; but this reaction is an unlikely origin for the anhydride observed in the present pyrolysis or in that of *iso*propenyl acetate, since *cyclo*hex-1-enyl benzoate yields no benzoic anhydride, and vinyl carboxylates (25) no divinyl ether.

#### b). Acetone and cyclohexene.

Two unexpected products of the pyrolysis were acetone and *cyclo*hexene. They possibly have their source in some type of complex free radical mechanism.

### c). Carbon monoxide.

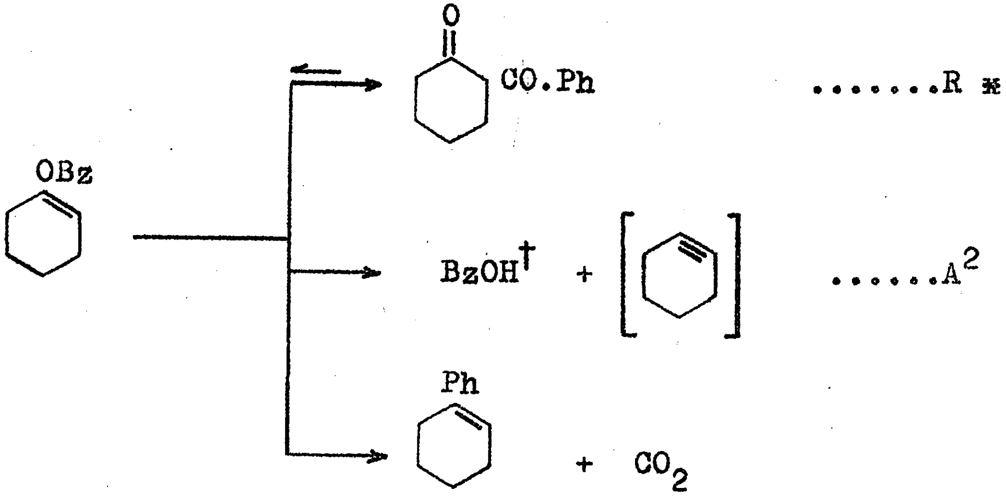
As in the previous pyrolysis, carbon monoxide is produced in fair quantity. Secondary breakdown of the observed *cyclo*hexanone (56) may be responsible, since this ketone yields carbon monoxide on pyrolysis (see page 63). In addition, partial breakdown of keten (53) may contribute to the formation of carbon monoxide and this reaction would also explain the presence of ethylene.

### Identification of 2-acetylcyclohexanone.

The characterisation of 2-acetyl*cyclo*hexanone produced in the present pyrolyses gave rise to some rather surprising results. On treatment with semicarbazide hydrochloride a crystalline derivative, m.p. 156-7°, was formed. (Found C, 60.1; H, 7.0; O (direct), 8.7%; M (cryo in benzene), 203,182). An authentic sample of the $\beta$-diketone prepared as described by Levine *et al.* (57) yielded the same derivative, m.p. and mixed m.p. 157-158°. However, Leser (58) has described a so-called semicarbazone of 2-acetyl*cyclo*hexanone, m.p. 159°; in a later paper (59) he gives m.p. 162-3°, but in neither case is an analysis reported. It is now clear that the derivative is not, in fact, the expected semicarbazone (calc. for $C_9H_{15}O_2N_3$: C, 54.8; H, 7.7; O, 16.2; N, 21.3%; M, 197) but a dehydration product thereof (calc. for $C_9H_{13}ON_3$: C, 60.3; H, 7.3; O, 8.9; N, 23.5%; M, 179). The compound loses its nitrogen on analysis with some difficulty and reliable figures could not be obtained (Found: N ca. 20% by micro-Dumas, ca. 10% by micro-Kjeldahl). This reluctance to lose its nitrogen is possibly due to the formation of some type of ring compound on dehydration of the normal semicarbazone derivative.

### 3.4. cycloHex-1-enyl benzoate.

The pyrolysis of cyclohex-1-enyl benzoate confirmed its rearrangement to 2-benzoylcyclohexanone, and the presence of cyclohexanone together with a trace of benzoic acid as previously reported by Allan (42). As in the case of the other two enol carboxylates, isopropenyl acetate and cyclohex-1-enyl acetate, it was found that rearrangement of the ester to the isomeric β-diketone 2-benzoycyclohexanone (27% yield) was not the only pyrolysis route; several other routes competed successfully. The following scheme represents the various pyrolysis routes:



(also CO, $CH_2{:}CH_2$, benzene and cyclohexanone).

✱ represents a major route; † signifies that the compound was obtained from the ester only.

In addition to the products first reported by Allan (42) several new products of pyrolysis have been observed in the present work.

### Alkenyl-oxygen scission.

Benzoic acid was identified in the pyrolysate, but as in the case of cyclohex-1-enyl acetate no trace was found of any of the transient entities (cyclohexyne etc.) which should have accompanied the acid on the basis of an alkenyl-oxygen scission.

### Acyl-oxygen scission.

Although this reaction competes quite strongly in the pyrolysis of the two acetates it is structurally precluded from an enol benzoate.

### Decarboxylation $C^2$.

The present work provides yet another example of decarboxylation of esters to be added to the growing list of this type of reaction. Both carbon dioxide and 1-phenyl*cyclo*hexene are products of the pyrolysis. It will be noted that the enol carboxylates studied in the present work are structurally similar to the vinyl carboxylates studied by Allan *et al.* (25) which undergo ester decarboxylation (*cf.* Mackinnon and Ritchie (41)).

### Other products of Decomposition.

### a). Benzene.

Although not previously reported by Allan (42), a fairly large quantity of benzene (ca. 50% Theory) was found in the pyrolysate from *cyclo*hex-1-enyl benzoate. Indeed, the benzene and diketone appear in almost equal quantities. The source of the benzene is, however, somewhat obscure, and it is felt that it must be due to some type of free radical mechanism. The benzoic acid, of which a trace is found in the pyrolysate, might be considered as a possible alternative source; but if this were the case, it is rather surprising that although benzene is found in the pyrolysate from 2-benzoyl*cyclo*hexanone no trace of benzoic acid was found. It will be noted at this stage that no benzene was found in the pyrolysate from cyclohex-1-enyl acetate, which would seem to indicate that benzene has its source in the aroyl half of the ester molecule.

b). cycloHexanone.

Like the benzene, it is felt that cyclohexanone, obtained in quite large amounts, must have its source in some free radical mechanism. The fact that cyclohex-1-enyl benzoate was vigorously dried before pyrolysis must rule out a partial hydrolysis to cyclohexanone and benzoic acid by adventitious water.

c). Carbon monoxide.

The partial breakdown of cyclohexanone may once more account for the presence of carbon monoxide (see page 63).

d). Ethylene.

This was identified in the pyrolysate gases by the aid of infra-red spectroscopy. It is present in the breakdown products from all three enol carboxylates. For isopropenyl acetate and cyclohex-1-enyl acetate it can be explained by partial breakdown of keten from the major $B^1$ scission, but in the present case it must have some other origin. It could arise from partial breakdown of a labile intermediate such as the postulated cyclohexyne.

## 3.5. Benzoylcyclohexanone.

The $\beta$-diketone breaks down on pyrolysis to give all the products (see page 39) obtained from the enol ester *cyclo*hex-1-enyl benzoate. The present work confirms and extends the results previously obtained by Allan (42). The presence of the enol ester in the pyrolysate was confirmed both by infra-red spectroscopy and hydrolysis to benzoic acid, and the benzene was confirmed by conversion to *m*-dinitrobenzene.

In addition, evidence was found for decarboxylation to carbon dioxide and 1-phenyl-*cyclo*hexene as in the case of *cyclo*hex-1-enyl benzoate. No evidence was found for the presence of benzoic acid or its anhydride, nor for any of the transient entities mentioned previously, which would form the other half of the breakdown products. This seems to suggest that benzoic acid is a product of the ester only. It will be remembered that pyrolysis of *iso*propenyl acetate gave more acetic acid than pyrolysis of the isomeric $\beta$-diketone acetylacetone.

As was the case with acetylacetone, however, it is formally possible for several of the observed products to arise from both the enol carboxylate and from the isomeric diketone. Thus, it is difficult to say whether the products of pyrolysis arise in practice from both sides of the equilibrium system or from one only.

In this pyrolysis of 2-benzoyl*cyclo*hexanone as with all the compounds pyrolysed, carbon monoxide is the major component of the pyrolysate gases. In all the cases studied the molar ratio $CO:CO_2$ always lies within the range *ca.* 2-9 (cf. tables 1-4).

### 3.6. Co-pyrolysis of Benzoic acid and cyclohexanone.

As recorded above, *cyclo*hexanone was identified in the pyrolysates of both 2-benzoyl *cyclo*hexanone and *cyclo*hex-1-enyl benzoate, while benzoic acid was observed only in the pyrolysate from the ester. It was felt, therefore, that although benzoic acid might have been formed during the pyrolysis of the diketone it possibly reacted with the *cyclo*hexanone to give water and *cyclo*hex-1-enyl benzoate, thus explaining its non-appearance in the final pyrolysate. The present work was, therefore, designed to find whether the two components (each reported to be thermally stable when pyrolysed alone) affected each other when pyrolysed as a mixture. Both constituents were recovered unchanged. It was noted, however, that the pyrolysate on standing overnight turned a bright red colour. On distillation, traces of water were found in the pyrolysate, presumably due to some self-condensation of cyclohexanone. The pyrolysate gases contained a large proportion of carbon monoxide.

### 3.7. Pyrolysis of cycloHexanone.

This pyrolysis confirmed the thermal stability (56) of cyclohexanone. Carbon monoxide was the major constituent of the small amount of gas evolved. Traces of water were also noted. Again, this was probably due to self-condensation of the ketone to give cyclohexylidene-cyclohexanone.

## 4. GENERAL ASSESSMENT OF RESULTS.

The present work has revealed the new and unexpected fact that thermal rearrangement of enol carboxylates (1) to β-diketone, is reversible. The rearrangement of 2-benzoylcyclohexanone first reported by Allan (42) has been confirmed, and in addition it has been found that acetylacetone rearranges to give traces of isopropenyl acetate. The equilibrium in both cases lies well over to the β-diketone side. Young et al. (1) recorded no by-products from pyrolysis of the esters now studied. It was, however, shown by Allan, Forman and Ritchie (25) that vinyl carboxylates break down under similar conditions by a complex series of competitive scissions; this has now been shown by the present work to be true of enol carboxylates in general. In particular, in the case of isopropenyl and cyclohex-1-enyl acetates, an acyl oxygen scission of the $B^1$ type has been found to compete with the thermal rearrangement. Further, two more examples of ester decarboxylation have been observed.

# FLOW REACTOR

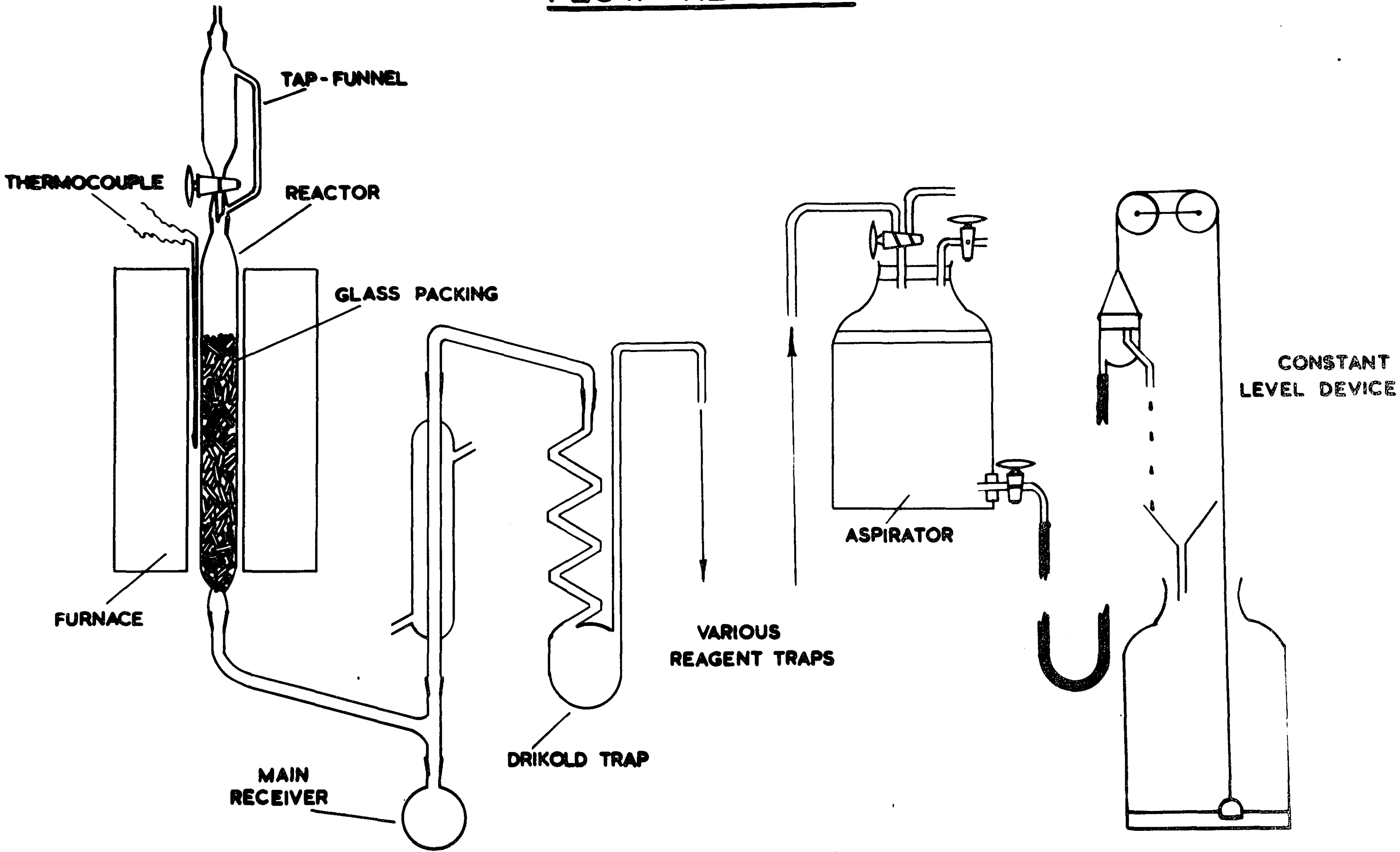


FIGURE I.

# EXPERIMENTAL.

## 5. APPARATUS AND PROCEDURE.

### 5.1. Flow reactor.

The pyrolysis unit consisted of a vertically located Pyrex-glass tube (as shown in fig.1). The dimensions of the reactor were: total length 70 cms; heated length 30 cms; diameter 2.3 cms and contact volume of 50 mls. It was heated by an electric furnace, which kept the central section of the reaction vessel at a temperature controlled ($\pm 5^{\circ}$) by a series of resistences and a "Sunvic" energy controller. The temperature was measured by a chromel-alumel thermocouple. Before each pyrolysis the system was evacuated and filled with oxygen-free nitrogen several times to avoid combustion of the vapours.

Liquid pyrolysands were introduced by means of a tap-funnel fitted with a side arm to equalise the pressure above and below the feed liquid. Solid pyrolysands were melted in the tap-funnel by means of a heating jacket and run into the reactor in a liquid form.

The liquid and solid pyrolysates were collected in a first receiver by means of an air condenser. The exit gases were passed through a water condenser to a second receiver cooled in a freezing mixture of acetone and solid carbon dioxide ("Drikold" trap). The final uncondensed gases were then passed either through appropriate reagent traps to a gas aspirator or direct to the aspirator. The gases were collected over water covered in gas saturated paraffin to prevent absorption of the gas. The whole system was maintained at atmospheric pressure by means of a constant level device (see fig. 1). After a pyrolysis, the reactor tube was cleaned by heating in a stream of air.

### 5.2. Contact times.

The contact times were calculated according to the formula (60):

$$t_c = \frac{273 \times V_c \times p}{22.4 \times (N_v - N_n) \times T}$$

The contact time in seconds ($t_c$) is related by this expression to the volume ($V_c$) of the reaction vessel, the number of gram - molecules per sec. of pyrolysand ($N_v$) and nitrogen ($N_n$) and the pressure (p) and the absolute temperature (T) of the system. Assuming that pyrolysis takes place at 1 atmosphere, and that there is no flow of nitrogen during the pyrolysis then the expression may be simplified thus:

$$t_c = \frac{12.2\ V_c}{N_v T}$$

## 5.3. Analytical Methods.

The pyrolysate fractions were examined by standard chemical methods. In some cases this was supplemented by infra-red and ultra-violet spectroscopy. Carbonyl compounds were identified by their 2:4-dinitrophenylhydrazones or by their semicarbazones. Mixtures of carbonyl compounds were identified by paper chromatography of their 2:4-dinitrophenylhydrazones (61). Benzene and cyclohexene were identified by conversion to m-dinitrobenzene (m.p. 90°) and adipic acid (m.p. 150°) respectively.

Acetic anhydride was identified by the Davidson and Newmann colour reaction (62). Keten and acetic acid were characterised by conversion to acentanilide (m.p. 113°). (To identify keten, the exit gases from the pyrolysis were bubbled through aniline to form acetanilide). Methylacetylene was identified by its infra-red spectrum and by formation of its cuprous derivative by bubbling the gases through ammoniacal cuprous chloride. All solid material was identified by mixed melting points. Tables 1-5 summarise the general overall conditions and results for 17 Runs.

## 6. PREPARATION OF PYROLYSANDS.

### 6.1. isoPropenyl acetate.

Pure ester obtained from L. Light & Co. was redistilled and the fraction used had b.p. 92-94°, $n_D^{20}$ 1.406.

### 6.2. Acetylacetone.

Pure diketone obtained from L. Light & Co. was redistilled and the fraction used had b.p. 134-138°, $n_D^{20}$ 1.452.

### 6.3. cycloHex-1-enyl acetate.

cycloHexanone, acetic anhydride and p-toluenesulphonic acid were refluxed for 4 hours as described by Bedoukian (63). The pure enol acetate had b.p. 92°/34 mm. and $n_D^{20}$ 1.464 (lit. (63) b.p. 74-76°/17 mm., $n_D^{25}$ 1.4585). Found: C, 68.6; H, 8.8. Calc. for $C_8H_{12}O_2$: C, 68.5; H, 8.6%.

### 6.4. cycloHex-1-enyl benzoate.

Attemps to prepare this compound by ester-interchange between cyclohex-1-enyl acetate and benzoic acid, or by direct Schotten-Baumann benzoylation of (enolic) cyclohexanone, were unsuccessful. Ultimately, it was prepared as described by Nesmeyanov, Lutsenko, and Tumanova (64). cycloHex-1-enyl acetate was converted into 2-chloromercuricyclohexanone (m.p. 134-135°) which was dried and treated with freshly distilled benzoyl chloride in sodium-dried xylene (50°; 12 hr.; rapid stirring). The product was fractionated, washed free from mercuric chloride (dilute ammonia), and refractionated yielding pure *cyclo*hex-1-enyl benzoate, b.p. 144-145°/7 mm., $n_D^{20}$ 1.547 (lit. (64) b.p. 146-147°/6 mm., $n_D^{20}$ 1.5386). Found: C, 77.0; H, 7.2. Calc. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9%. It appears that the use of rigorously dry Xylene is important; this precaution led to yields of *ca*. 40% (Nesmeyanov *et al*. (64) claim 63%), whereas various preparations in which ordinary technical xylene was used gave yields of only *ca*. 5/10%.

### 6.5. 2-Benzoylcyclohexanone.

This was prepared as described, by Hauser, Ringler, Swarmer and Thomson (65), who claim a yield of 69%. Preliminary work gave very low yields, but it was found that increasing the amount of sodamide used from 2 equivalents to 3 equivalents, and increasing the time of reaction from 2 hours to 12 hours (Steam-Bath) gave a yield of 22%. The diketone had m.p. 88-89° (needles from ethanol or light petroleum; lit., (65) m.p. 88-89°) Found: C, 77.2; H, 7.2. Calc. for $C_{13}H_{14}O_2$: C, 77.2; H, 6.9%.

## 7. PREPARATION OF REFERENCE COMPOUNDS FOR INFRA-RED SPECTROMETRY.

### 7.1. 1-Methylcyclohexene.

The olefin was prepared by dehydrating (66) 1-methylcyclohexanol with zinc chloride at 160°C. The alcohol was prepared by the Grignard method (67) using magnesium, methyl iodide and cyclohexanone. The 1-methylcyclohexene had b.p. 110-112°, $n_D^{15}$ 1.458 (lit., (66) b.p. 110-111°, $n_D^{12}$ 1.458).

### 7.2. 1-Phenylcyclohexene.

This compound was prepared, as described above. It had b.p. 126-128°/18 mm., $n_D^{14}$ 1.569 (lit. (66) b.p. 128-130°/20 mm., $n_D^{14}$ 1.5676. Found: C, 91.2; H, 9.2. Calc. for $C_{12}H_{14}$: C, 91.1; H, 8.9%.

## 8. DETAILS OF PYROLYSIS.

### 8.1. Pyrolysis of isoPropenyl Acetate - Runs 1-3.

The analytical results of these runs were similar; those for Run 1 are given as typical. 60g. of ester were pyrolysed at 500° in the flow reactor and yielded 1.8 l. of gas. The gas consisted of carbon monoxide (87%), carbon dioxide (10%) and unsaturated hydrocarbons (3%). The liquid found in the Drikold trap contained acetone. The main pyrolysate yielded eight fractions on distillation, (i) 6.2 g., b.p. 60-86°, (ii) 7.1 g., b.p. 86-100°, (iii) 13.3 g., b.p. 100-126°, (iv) 20.3 g., b.p. 126-148°, (v) 1 g., b.p. 148-164°, (vi) ca. 1 g., b.p. 48-60°/1.3 mm., (vii) ca. 0.5 g., b.p. 60-84°/1.3 mm., and (viii) ca. 0.2 g., b.p. 84-96°/ 1.3 mm. There was a small tarry residue. Fraction (i) contained acetone. Fraction (ii) contained unchanged starting material, along with traces of ethyl methyl ketone, identified by paper chromatography (61) of the 2:4-dinitrophenylhydrazone derivative. Fraction (iii) contained acetic acid. Fraction (iv) contained acetylacetone identified as a semicarbazone (it proved impossible to form a 2:4-dinitrophenylhydrazone), and an acid anhydride (colour reaction (62)). Fraction (v) was similar. Fraction (vi) and (vii) appeared to be mainly acetylacetone contaminated with a little tar. The tar was examined but yielded no useful product. The exit gases contained keten (aniline-ether trap), together with methylacetylene identified by formation of a red precipitate with ammoniacal cuprous chloride and confirmed by infra-red analysis. The infra-red analysis of the exit gases also indicated traces of ethylene and methane gases.

## 8.2. Pyrolysis of Acetylacetone.

### Runs 4-6.

The analytical results of Run 4 are given as typical. 50 g. of acetylacetone were pyrolysed at 550° in the flow reactor and yielded 5.3 l. of gas. The gas consisted of carbon monoxide (63%), carbon dioxide (22%) and unsaturated hydrocarbons (15%). A small amount of liquid obtained in the Drikold trap contained acetone. The pyrolysate, itself, was distilled and yielded five fractions, (i) 13.1 g., b.p. 54-72°, (ii) 0.7 g., b.p. 82-100°, (iii) 2.2 g., b.p. 110-130°, (iv) 20.1 g., b.p. 130-150° and (v) 1.0 g., b.p. 150-160°. There was a small tarry residue, which yielded no useful product. Fraction (i) was mainly acetone; there was no evidence for ethyl methyl ketone in fraction (ii) and evidence for *iso*propenyl acetate (infra-red and ultra-violet) was inconclusive; fraction (iii) contained acetic acid; fractions (iv) and (v) were mainly unchanged acetylacetone, containing a little acetic anhydride (colour reaction (62)). The exit gases contained keten.

Run 7.

50 g. of the diketone were pyrolysed at 500°C. 3.8 l. of gas were collected, consisting of carbon monoxide (57%), carbon dioxide (29%) and unsaturated hydrocarbons (14%). As before, the liquid found in the Drikold trap contained acetone and the exit gases contained keten. In this run the total pyrolysate was dissolved in ether and washed free from acid with aqueous sodium hydrogen carbonate. The ether layer was dried over magnesium sulphate and after removal of the ether yielded four fractions on distillation. Fraction (i) ca. 0.5 g., b.p. 54-86°, fraction (ii) ca. 0.7 g., b.p. 86-100°, fraction (iii) ca. 0.8 g., b.p. 100-110°, and fraction (iv) ca. 1 g., b.p. 110-112°. There was also a small tarry residue. Fractions (i) to (iii) contained unchanged acetylacetone (ultra-violet absorption band $\lambda_{max}$ 273), together with isopropenyl acetate (ultra-violet absorption band $\lambda_{max}$ 206 and infra-red absorption at ca. 1745 and 1200 $cm^{-1}$). Control experiments showed that these bands characteristic of isopropenyl acetate

persisted strongly when a sample of pure ester was progressively diluted down to a concentration of 8%, by addition of acetylacetone. Also, a control sample of pure acetylacetone, treated as above with ether and aqueous sodium hydrogen carbonate, showed none of the absorption bands characteristic of the ester viz. 1745 and 1200 cm$^{-1}$. The exit gases were passed through ammoniacal cuprous chloride and a red precipitate observed. Methylacetylene was confirmed, as in the case of isopropenyl acetate, by infra-red absorption bands at ca. 2155 m, 1462 m, 1452 m, 1269 w, and 920 w cm$^{-1}$) (lit. (68) 2160, 1459, 1448, 1264 and 921 cm$^{-1}$). Ethylene and a trace of methane were also present.

Runs 8 and 9.

10 g. of diketone were pyrolysed at temperatures of 450° and 400°. Both runs showed that pyrolysis below 500° was very slight, there being almost no carbonisation in the reaction vessel. The pyrolysates in each case were treated with sodium hydrogen carbonate as above and analysed by infra-red spectroscopy, but no trace of isopropenyl acetate could be found.

Run 10.

This run was carried out in a static system.

The apparatus, used, consisted of a standard reflux set-up, heated by an isothermal mantle controlled by a "Sunvic" controller. The gases were passed through a "Drikold" trap to a gas aspirator as in the flow system. This pyrolysis was carried out to find the effect of prolonged heating on acetylacetone. 100 g. of acetylacetone were refluxed for a total of 154 hours. It was noted that although the b.p. of the diketone is given in the literature as 135°, the liquid was boiling steadily at 148°. The temperature, however, fell slowly throughout the pyrolysis to 137°. About 1.5 ml. of liquid was found in the "Drikold" trap and this proved to be acetone. No evidence could be found for the presence of keten, acetic anhydride and acetic acid. The liquid in the static reactor proved to be unchanged acetylacetone, confirmed by boiling point, refractive index, infra-red spectrum and its semicarbazone derivative.

### 8.3. Pyrolysis of cycloHex-1-enyl Acetate.

#### Run 11.

30 g. of ester were pyrolysed at 500° in the flow reactor, giving 1.7 l. of gas. The gas consisted of carbon monoxide (69%), carbon dioxide (9%) and unsaturated hydrocarbons (22%); it also contained keten,

acetone vapour (2:4-dinitrophenylhydrazone trap) and ethylene and methane (infra-red). The liquid pyrolysate was distilled and yielded six fractions: (i) 1.0 g., b.p. 74-90°; (ii) 0.8 g., b.p. 90-130°; (iii) 2.0 g., b.p. 130-150°; (iv) 6.5 g., b.p. 150-160°; (v) 8.5 g., b.p. 86-100°/28 mm., and (vi) 6.0 g., b.p. 110-114°/28 mm. There was a small tarry residue (ca. 0.5 g.). Fraction (i) was found to contain acetone, identified by paper chromatography (61); there was also evidence for an olefin (ultra-violet). Fraction (ii) contained acetic acid and anhydride (infra-red); fraction (iii) contained acetic anhydride (infra-red; colour reaction (62)), and *cyclo*hexanone; fraction (iv) contained acetic anhydride (trace), *cyclo*hexanone and unchanged pyrolysand (infra-red). The acetic anhydride and acetic acid were confirmed by conversion to acetanilide and the *cyclo*hexanone characterised as its 2:4-dinitrophenylhydrazone. Separate tests showed that although the pure pyrolysand yields *cyclo*hexanone 2:4-dinitrophenylhydrazone, owing to its partial hydrolysis by the test reagent even in the cold, this source of possible error is eliminated if the ketone is first separated from the rest of the fraction by aqueous sodium hydrogen sulphite, hydrolysis of the ester under these conditions being negligible. Fraction (v) was unchanged pyrolysand, and fraction (vi) 2-acetyl*cyclo*hexanone. On treatment with semicarbazide hydrochloride, fraction (vi) yielded a crystalline derivative, m.p. 156-157°. Found: C, 60.1; H, 7.0; O (direct), 8.7; M (cryoscopic in benzene), 203, 182); an authentic sample of 2-acetyl*cyclo*hexanone prepared as described by Levine *et al.* (57) (b.p. 110°/19 mm., $n_D^{20}$ 1.510; lit. (57) b.p. 111-112°/18 mm., $n_D^{20}$ 1.5138), yielded the same derivative m.p. and mixed m.p. 157-159°. Leser (58) has described a so-called semicarbazone of 2-acetyl*cyclo*hexanone m.p. 159°; in a later paper (59) he gives m.p. 162-163°, but in neither case is an analysis reported. It is now clear that the derivative is not, in fact, the expected semicarbazone, but a dehydration product thereof (Calc. for $C_9H_{13}ON_3$: C, 60.3; H, 7.3; O, 8.9; N, 23.5%; M, 179. (Calc. for $C_9H_{15}O_2N_3$; C, 54.8; H, 7.7; O, 16.2; N, 21.3%; M, 197). The compound loses its nitrogen, on analysis, with some difficulty, and reliable figures could not be obtained. (Found: N, *ca.* 20% by micro-Dumas, *ca.* 10% by micro-Kjeldahl). There are several formal possibilities for *cyclo*dehydration of the semicarbazone, but it was not possible to study this compound further in the present work.

Run 12.

27 g. of the ester were pyrolysed at 500° and gave 2.1 l. of gas. The gas analysed as carbon monoxide (63%), carbon dioxide (9%) and unsaturated hydrocarbons (28%). The liquid pyrolysate gave similar results to the previous run; in addition the first fraction (1.5 g., b.p. 40-72°) obtained by distillation contained 1-methyl*cyclo*hexene (its infra-red spectrum showed all 15 absorption bands listed (page 65 ) for the pure olefin) and *cyclo*hexene (infra-red).

Run 13.

61 g. of ester pyrolysed at 500° to give 2.3 l. of gas. This pyrolysis was carried out with a larger amount of starting material, in order to confirm some of the unexpected results (acetone, *cyclo*hexene) obtained in the previous runs.

The liquid pyrolysate distilled to yield seven fractions, (i) 0.5 g., b.p. 56°, (ii) 2.0 g., b.p. 78°, (iii) 0.8 g., b.p. 78-130°, (iv) 20 g., b.p. 130-150°, (v) 3.8 g., b.p. 150-160°, (vi) 40.2 g., b.p. 62-88°/ 24 mm. and (vii) 5.7 g., b.p. 106-110/24 mm. There was a small tarry residue (*ca.* 1.0 g.). Fraction (i) contained acetone, confirmed by formation of the 2:4-dinitrophenylhydrazone and mixed m.p. Fraction (ii) was treated with tetranitromethane (70) and gave a yellow colour (cyclohexene gives a yellow and cyclohexa-1:3-diene a red colour); redistilled fraction (ii) had b.p. 78-81°, $n_D^{20}$ 1.440 and yielded adipic acid on oxidation (alkaline permanganate) confirming the presence of cyclohexene. Fraction (ii) also contained a trace of acetone and cyclohexanone. Fractions (iii) to (vii) confirmed the results from Run 11. In Runs 11-13, 2-methylcyclohexanone was carefully sought by paper chromatography (61) of the mixed 2:4-dinitrophenylhydrazones of the overall ketonic products, the 2:4-dinitrophenylhydrazone of this ketone being used as a control; no evidence for its presence could be obtained.

### 8.4. Pyrolysis of cycloHex-1-enyl Benzoate.

Run 14.

30 g. of the ester were pyrolysed in the flow reactor at 500°, 4.2 l. of gas being evolved. The gas contained carbon monoxide (69%), carbon dioxide (12%) and unsaturated hydrocarbons (19%). Ethylene and methane were identified by infra-red.

The liquid in the cold trap was mainly benzene, although surprisingly a little cyclohexanone was also found in the cold trap. The main pyrolysate was distilled to yield seven fractions, (i) 6.2 g., b.p. 78-84°, (ii) 1.7 g., b.p. 84-144°, (iii) 1.4 g., b.p. 144-148°, (iv) 0.9 g., b.p. 20-90°/3 mm., (v) 1.5 g., b.p. 90-120/3 mm., (vi) 8.7 g., b.p. 120-140/3 mm. and (vii) 4.0 g., b.p. 140-164/3 mm. There was also *ca*. 1.5 g., of tarry residue. Fraction (i) was mainly benzene, with a little *cyclo*hexanone; fractions (ii) and (iii) were mainly *cyclo*hexanone. Fraction (iv) contained 1-phenyl*cyclo*hexene; its infra-red spectrum showed all six absorption bands listed above for the pure olefin. Fraction (v) was mainly unchanged pyrolysand (infra-red), from which a trace of benzoic acid separated during the distillation; fractions (vi) and (vii) consisted of a mixture of unchanged pyrolysand (*ca*. 4.5 g., infra-red) and 2-benzoyl*cyclo*hexanone (*ca*. 8.2 g.), the latter separating out on standing.

## 8.5. Pyrolysis of 2-Benzoylcyclohexanone.

### Run 15.

30 g. of β-diketone were pyrolysed at 500° and gave 2.9 l. of gas, consisting of carbon monoxide (71%), carbon dioxide (16%) and unsaturated hydrocarbons (13%). Ethylene was identified by infra-red.

The liquid pyrolysate was filtered free from suspended unchanged pyrolysand (6.0 g.). The filtrate distilled to give five fractions, (i) 2.3 g., b.p. 78-84°,

(ii) 2.5 g., b.p. 84-168°, (iii) 1.6 g., b.p. 76-130°/2 mm., (iv) 4.4 g., b.p. 130-150/2 mm., and (v) 1.1 g., b.p. 150/162°/2 mm. There was a small tarry residue (ca. 2 g.). Fraction (i) was mainly benzene (characterised as m-dinitrobenzene), containing no cyclohexa-1:3-diene (infra-red; no adduct with maleic anhydride); fraction (ii) was mainly cyclohexanone. Fraction (iii) was examined for benzoic acid by taking the whole fraction up in ether and shaking with a 5% solution of sodium hydrogen carbonate, with negative result. The fraction was then examined by infra-red and proved to be mainly cyclohex-1-enyl benzoate (the infra-red spectrum showed all 10 absorption bands listed (page 65 ) for the pure ester). In addition, there seemed to be some evidence for 1-phenylcyclohexene. To confirm this the fraction was hydrolysed by alcoholic potassium hydroxide and gave benzoic acid, as one of the hydrolysis products, (a further proof of the presence of cyclohex-1-enyl benzoate). The hydrolysis products also contained 1-phenylcyclohexene (infra-red showed all 6 absorption bands listed (page 65 ) for the pure olefin). Fractions (iv) and (v) solidified on standing and consisted of unchanged pyrolysand.

Run 16.

In this pyrolysis the contact time was increased, with a consequent increase in the gas production and an increase in the amount of benzene and cyclohexanone formed. The pyrolysate was liquid and contained no solid material. On distillation five fractions were obtained as before. Fraction (i) 4.6 g., b.p. 74-86°, fraction (ii) 3.4 g., b.p. 86-166°, (iii) 5.1 g., 50-130°/2 mm., (iv) 3.1 g., 130-150°/2 mm., (v) 1.9 g., b.p. 150-166°/2 mm. and 2.3 g. of tar. The fractions analysed as before.

### 8.6. Pyrolysis of cycloHexanone.

#### Run 17.

30 g. of cyclohexanone were pyrolysed at 500°, giving 0.25 l. of gas. The gas consisted of carbon monoxide (57%), carbon dioxide (5%) and unsaturated hydrocarbons (38%). The liquid pyrolysate was substantially unchanged pyrolysand. A little water was observed, probably due to self-condensation of the ketone to cyclohexylidene-cyclohexanone (56).

### 8.7. Copyrolysis of cycloHexanone and Benzoic acid.

#### Run 18.

16.7 g. of benzoic acid were dissolved in 25.9 g. of cyclohexanone, giving a saturated solution. This solution was pyrolysed at 500° in the flow reactor. 0.4 l. of gas were collected, consisting of carbon monoxide (60%), carbon dioxide (9%) and unsaturated hydrocarbons (31%). The liquid pyrolysate (which became red on standing overnight) was substantially unchanged pyrolysand; a little water was observed (cf. Run 17). The colour test (62) for acid anhydride gave a negative result.

## 9. INFRA-RED DATA.

The following are the principal infra-red absorption bands of the compounds studied.

cyclo*Hex-1-enyl acetate*.

2941 *s*, 2857 *m*, 1767 *s*, 1695 *m*, 1449 *m*, 1443 *m*, 1366 *s*, 1217 *s*, 1121 *s*, 1073 *m*, 1043 *m*, 1010 *m*, and 905 *m* cm.$^{-1}$.

cyclo*Hex-1-enyl benzoate*.

1730 *s*, 1595 *m*, 1308 (shoulder), 1250 *s*, 1215 (shoulder) 1120 *s*, 1068 *m*, 1029 *m*, and 710 *m* cm.$^{-1}$.

*2-Benzoyl*cyclo*hexanone*.

1709 *s*, 1672 *s*, 1600 *m*, 1580 *m*, 1361 *s*, 1316 *m*, 1282 *s*, 1250 *s*, 1236 *s*, 1183 *s*, 1129 *s*, 1104 *m*, 1072 *m*, 958 *m*, 913 *m*, 787 *m*, 744 *s*, 693 *m*, and 684 *s* cm.$^{-1}$.

*1-Methy*cyclo*hexene*.

1442 *s*, 1370 *m*, 1305 *m*, 1260 *m*, 1135 *s*, 1089 *s*, 1050 *s*, 1014 *s*, 960 *m*, 910 *s*, 890 *s*, 820 *s*, 790 *s*, and 750 *s* cm.$^{-1}$, in good agreement with published figures (68).

*1-Phenyl*cyclo*hexene*.

1600 *m*, 1494 *s*, 1445 *s*, 754 *s*, 734 *s*, 685 *m* cm.$^{-1}$.

## 10. TABULATED RESULTS.

### TABLE 1.

| Pyrolysand. | isoPropenyl Acetate. | | |
|---|---|---|---|
| Run No. | 1 | 2 | 3 |
| Temperature ................ | 500° | 500° | 500° |
| Feed Rate (g./min.)........ | 0.33 | 0.20 | 0.19 |
| Contact time (sec.)........ | 14 | 24 | 25 |
| Wt. pyrolysed (g.)......... | 60.0 | 30.0 | 57.0 |
| (a) In cold trap (ml.)..... | 6.0 | 3.0 | 6.0 |
| (b) In main receiver (g.).. | 53.6 | 27.0 | 53.2 |
| (c) Gaseous pyrolysate (l.) | 1.8 | 1.3 | 2.7 |
| Composition (%) of (c) (approx.): | | | |
| CO ........................ | 87 | 63 | 80 |
| $CO_2$ ........................ | 10 | 20 | 16 |
| Unsat. hydrocarbons ....... | 3 | 17 | 4 |
| $CH_4$ ........................ | ※ | ※ | ※ |
| $CO:CO_2$ (molar ratio)....... | 8.7 | 3.2 | 5.0 |

※ Traces observed by infra-red spectrometry.

## TABLE 2.

| Pyrolysand. | Acetylacetone | | | | | |
|---|---|---|---|---|---|---|
| Run No. | 4 | 5 | 6 | 7† | 8 | 9 |
| Temperature ................ | 550° | 500° | 500° | 500° | 450° | 400° |
| Feed Rate (g./min.)........ | 0.15 | 0.40 | 0.20 | 0.20 | 0.20 | 0.14 |
| Contact time (sec.)........ | 30 | 12 | 24 | 24 | 25 | 39 |
| Wt. pyrolysed (g.).......... | 50.0 | 50.0 | 73.4 | 50.0 | 10.0 | 10.0 |
| (a) In cold trap (ml.)..... | 1.5 | Nil | Nil | 0.5 | Nil | Nil |
| (b) In main receiver (g.).. | 40.0 | 46.5 | 62.5 | 39.1 | 9.2 | 9.0 |
| (c) Gaseous pyrolysate (l.) | 5.3 | 1.0 | 4.3 | 3.8 | 0.3 | 0.1 |
| Composition (%) of (c.) (approx.) | | | | | | |
| CO ........................ | 63 | 60 | 59 | 57 | - | - |
| CO$_2$ ........................ | 22 | 20 | 29 | 29 | - | - |
| Unsat. hydrocarbons ....... | 15 | 20 | 12 | 14 | - | - |
| CH$_4$ ........................ | * | - | * | * | - | - |
| CO:CO$_2$ (molar ratio) ...... | 2.9 | 3.0 | 2.0 | 2.0 | - | - |

* Traces observed by infra-red spectrometry.

† Carbonised reaction vessel from Run 6 used.

\- Not observed.

## TABLE 3.

Pyrolysand. cycloHex-1-enyl Acetate.

| Run No. | 11 | 12 | 13 |
|---|---|---|---|
| Temperature | 500° | 500° | 500° |
| Feed Rate (g./min.) | 0.27 | 0.23 | 0.51 |
| Contact time (sec.) | 25 | 29 | 13 |
| Wt. pyrolysed (g.) | 30.0 | 27.0 | 61.0 |
| (a) In cold trap (ml.) | - | - | - |
| (b) In main receiver (g.) | 25.2 | 24.0 | 58.0 |
| (c) Gaseous pyrolysate (l.) | 1.7 | 2.1 | 2.3 |
| Composition (%) of (c) (approx.) | | | |
| CO | 69 | 63 | - |
| $CO_2$ | 9 | 9 | - |
| Unsat. hydrocarbons | 22 | 28 | - |
| $CH_4$ | - | * | - |
| $CO:CO_2$ (molar ratio) | 7.7 | 7.0 | - |

* Traces observed by infra-red spectrometry.

## TABLE 4.

| Pyrolysand. | cycloHex-1-enyl benzoate. | 2-Benzoylcyclohexene | |
|---|---|---|---|
| Run No. | 14 | 15 | 16 |
| Temperature ................ | 500° | 500° | 500° |
| Feed Rate (g./min.)........ | 0.22 | 0.32 | 0.25 |
| Contact time (sec.)........ | 44 | 30 | 38 |
| Wt. pyrolysed (g.).......... | 30.0 | 30.0 | 30.0 |
| (a) In cold trap (ml.)..... | 2.0 | Nil | Nil |
| (b) In main receiver (g.).. | 27.0 | 21.5 | 21.4 |
| (c) Gaseous pyrolysate (l.) | 4.2 | 2.9 | 4.6 |
| Composition (%) of (c) (approx.) | | | |
| CO ........................ | 69 | 71 | - |
| $CO_2$ ...................... | 12 | 16 | - |
| Unsat. hydrocarbons ....... | 19 | 13 | - |
| $CH_4$ ...................... | * | - | * |
| $CO:CO_2$ (molar ratio)....... | 5.7 | 4.4 | - |

* Traces observed by infra-red spectrometry.

## TABLE 5.

| Pyrolysand. | cycloHexanone. | cycloHexanone + Benzoic acid. |
|---|---|---|
| Run No. | 17 | 18 |
| Temperature ................ | 500° | 500° |
| Feed Rate (g./min.)........ | 0.2 | 0.45 |
| Contact time (sec.)........ | 23 | 11 |
| Wt. pyrolysed (g.)......... | 32.0 | 42.6 |
| (a) In cold trap (ml.)..... | Nil | Nil |
| (b) In main receiver (g.).. | 31.5 | 41.6 |
| (c) Gaseous pyrolysate (l.) | 0.25 | 0.4 |
| Composition (%) of (c) (approx.) | | |
| CO ...................... | 57 | 60 |
| $CO_2$ ...................... | 5 | 9 |
| Unsat. hydrocarbons........ | 38 | 31 |
| $CH_4$ ...................... | - | - |
| $CO:CO_2$ (molar ratio) ...... | 11.4 | 6.5 |

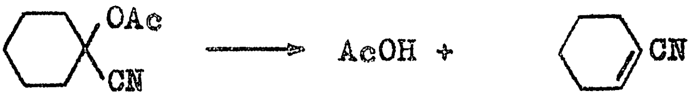
Sat. solution (ketone 25.9 g., acid 16.7 g.).

# PART II: COMPETITIVE ROUTES IN THE THERMAL BREAKDOWN OF α-ANILINO-ACIDS.

## 1. INTRODUCTION.

During a research programme on new general routes to polymerisable substituted olefins, of the acrylic and related types, it was found that vapour phase pyrolysis (*ca*. 450-550°) of α-acyloxy-esters (71,72) and acylated cyanohydrins (72), leads in general to smooth elimination of carboxylic acid, with the formation of the desired olefinic ester or nitrile respectively:

$$BzO.CMe_2.CO_2Me \longrightarrow BzOH + CH_2{:}CMe.CO_2Me$$

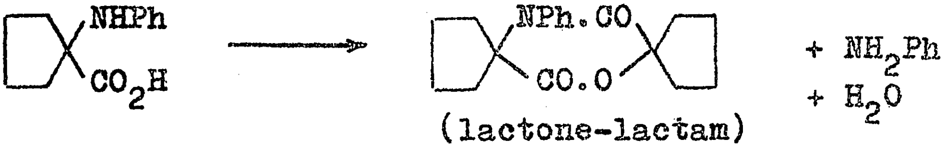


This method fails, however, when applied to α-acyloxy-acids, which break down thermally by a more complex route and do not yield olefinic acids (73):

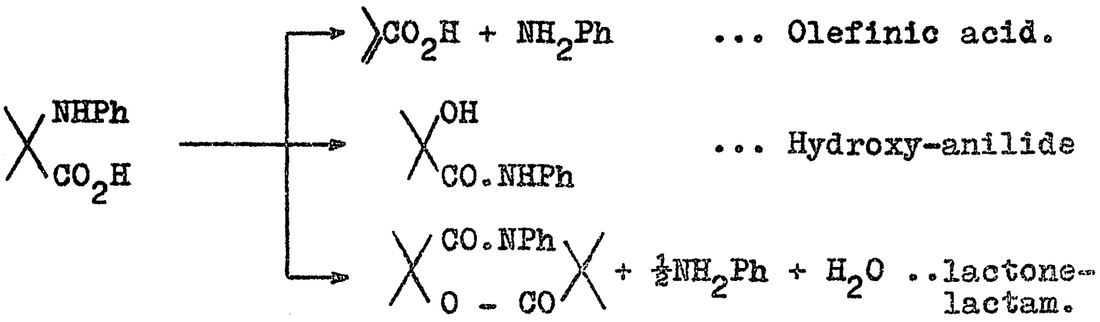
$$AcO.CHR.CO_2H \longrightarrow AcOH + CO + R.CHO$$

Nevertheless, it is recorded that α-anilino-α-carboxy*cyclo*hexane breaks down on distillation, to aniline and *cyclo*hex-1-enecarboxylic acid (74):

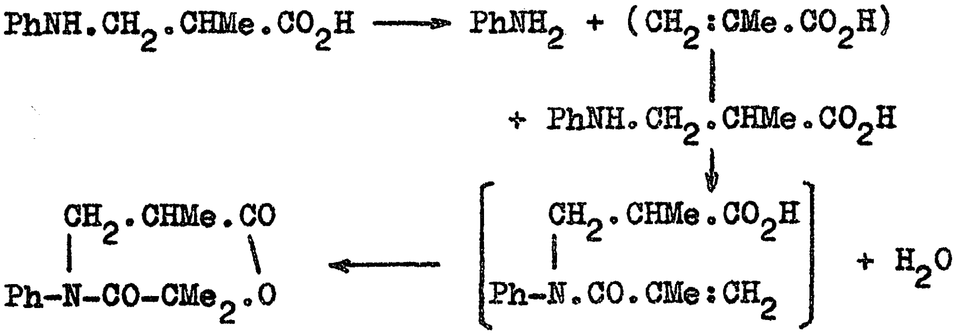
This suggested that pyrolysis of suitable anilino (instead of acyloxy) compounds might provide a simple alternative route to olefinic acids, and perhaps to all the desired types of olefinic monomers. However, $\alpha$-anilino-$\alpha$-carboxy*cyclo*~~hexane~~pentane, the five-membered homologue of the above $\alpha$-anilino-acid, was reported (75) to break down thermally in quite a different way, yielding the curious "lactone-lactam" shown below, which seemed to suggest that the size of the *cyclo*alkane ring exerts some specific controlling influence on the degradation route. The lactone-lactam structure was named by Plant and Facer (75) as the lactone of $\alpha$-($\alpha$-hydroxy*cyclo*pentanecarboxyanilido)*cyclo*pentane-carboxylic acid, but for convenience such structures will be called lactone-lactams throughout this thesis.



$\alpha$-Anilino-$\alpha$-carboxy*cyclo*hexane and $\alpha$-anilino-$\alpha$-carboxy*cyclo*pentane were studied by Bain and Ritchie (76) in greater detail, along with their $C_7$ homologue $\alpha$-anilino-$\alpha$-carboxy*cyclo*heptane. Bain and Ritchie found that all three acids showed precisely the same qualitative type of breakdown in the liquid phase at *ca*. 250° in a static reaction vessel, yielding not only aniline, water, olefinic acid, and a lactone-lactam, but also a wholly unexpected minor product, the α-hydroxy*cyclo*alkanecarboxyanilide isomeric with the parent anilino acid. The results can be represented by the following generalised scheme of competitive pyrolytic changes:



It is further recorded in the literature by Bischoff and Mintz (77) that a straight-chain anilino-acid, β-anilino*iso*butyric acid (m.p. 184°) breaks down on simple distillation to give aniline and a 7-membered ring lactone; and they proposed the following mechanism:



It is also recorded in the same paper that α-anilino*iso*butyric acid (m.p. 142°) distils to give an amine. There is some doubt, however, in the literature (77,78) as to which of these two anilino acids (m.p. 184° and 142°) is the $\alpha$-form and which is the $\beta$-form and additional new evidence on this question is presented on a later page.

## 2. OBJECTS OF RESEARCH.

In view of the unexpected products (hydroxy-anilides) found by Bain and Ritchie (76) on pyrolysis of the cyclic anilino-acids, as previously mentioned, it seemed desirable to discover whether this type of rearrangement reaction was a general reaction for all types of anilino-acids. Also, as the α-anilino-*iso*butyric acid studied by Bischoff and Mintz (77) appeared to give on distillation only an amine whereas the β-form gave a seven-membered lactone, it was decided to investigate these compounds further.

Thus, it was planned to study a series of straight-chain anilino-acids: α-anilino*iso*butyric acid (I), α-anilino-α-methyl-*n*-butyric acid (II), α-anilino-α-phenylpropionic acid (III), and α-anilinodiphenylacetic acid (IV), and to compare the results obtained with those obtained by Bain and Ritchie (76) especially as regards formation of the hydroxy-anilides.

$NHPh.CMe_2.CO_2H$ (I)

$NHPh.CMeEt.CO_2H$ (II)

$NHPh.CMePh.CO_2H$ (III)

$NHPh.CPh_2.CO_2H$ (IV)

It was also intended to elucidate still further, if possible, the structure of the lactone-lactam which should be formed on pyrolysis.

## 3. DISCUSSION OF RESULTS.

The three cyclic anilino-acids,
α-anilinocyclopentanecarboxylic acid,
α-anilinocyclohexanecarboxylic acid, and
α-anilinocycloheptanecarboxylic acid studied by Bain and Ritchie (76) were found to decompose on pyrolysis to give aniline and the corresponding unsaturated acid. The yield, however, was by no means theoretical, though it increased with the ring-size. The other products of pyrolysis (lactone-lactam and hydroxy-anilide) were found to have the same functional-group structure for the three ring-sizes, the effect of the ring-size being merely to vary the yields of the products rather than the type of products themselves.

The present work on straight-chain anilino acids (I) to (IV), shows that no rearrangement product (hydroxy-anilide) is formed on pyrolysis. This was a disappointment, since it rendered useless what had been planned as the next stage in the work - namely, to resolve (say) α-anilino- α-methyl-n-butyric acid (II) into its optical antipodes, and to find whether pyrolytic rearrangement of these to a hydroxy-anilide occurred with or without retention of the original optical configuration. Positive evidence on this first point would have given a valuable indication of the rearrangement mechanism - whether, for example, detachment of the anilino group from the asymmetric carbon atom was ionic, molecular, or free-radical in character.

It was found that on pyrolysis the first two anilino-acids in the series, α-anilino*iso*butyric acid (I) and α-anilino-α-methyl-*n*-butyric acid (II), gave similar results to those of the cyclic anilino acids studied by Bain and Ritchie (76) apart from the absence of a rearrangement to hydroxy-anilide. The remaining two acids studied, α-anilino-α-phenylpropionic (III) and α-anilinodiphenylacetic (IV) acids, gave somewhat different results. For this reason, the first two anilino-acids can conveniently be discussed together, while the remaining two acids will be discussed separately.

## 3.1. Preparation of α-Anilino-acids.

The methods used for the preparation of the α-anilino-acids, with the exception of α-anilinodiphenylacetic acid (IV) were similar to those used by Bain and Ritchie (76), *viz.* preparation of an anilino-nitrile from the appropriate ketone with subsequent hydrolysis to the α-anilino-acid, thus:

$$RR'.CO \xrightarrow[NH_2Ph]{HCN} PhNH.CRR'.CN \xrightarrow{hydrolysis} PhNH.CRR'.CO_2H$$

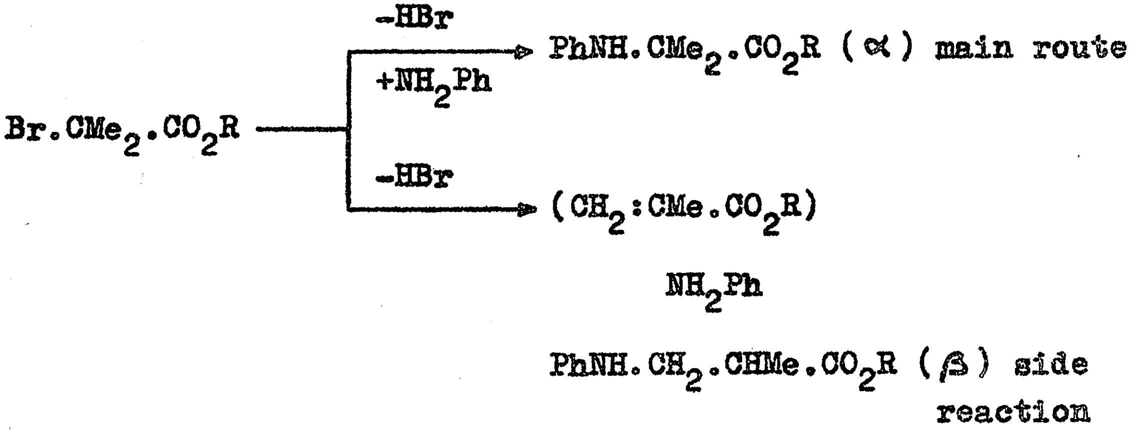
(I: R = R' = Me; II: R = Me, R' = Et; III: R = Me, R' = Ph)

α-Anilino- α-methyl-n-butyric acid (II) and α-anilino- α-phenylpropionic acid (III) are not recorded in the literature, but α-anilinoisobutyric acid (I) is mentioned, though with some doubt. The anilinoisobutyric acid obtained by the method used in the present work has m.p. 184° and is presumed to be the α-form. A similar method of preparation used by Von Tiemann (78) led to an anilinoisobutyric acid (m.p. 184°) which he also called the α-form. However, Bischoff and Mintz (77) have claimed that the anilinoisobutyric acid (m.p. 184°) isolated by Von Tiemann was not the α-form, but the β-form. They suggest that the OH group of the cyanohydrin is not replaced by the anilino group in the α-position but in the β-position, because of congestion of the alkyl group. They further claim that the bromo-ester used by them in the preparation of anilinoisobutyric acid would react in a similar fashion and give the β-form as the main product, thus:

$$2NH_2Ph + Br.CMe_2.CO_2Et \longrightarrow PhNH.CH_2.CHMe.CO_2Et + PhNH_3Br$$

They also suggested that the main product of the above method (m.p. 184°) is the β-anilino*isobutyric* acid, and that the small amount of anilino-acid (m.p. 142°) also obtained is the α-form.

It is the opinion of the present author, however, that the hydroxy group of the cyanohydrin is in fact replaced in the α-position by the anilino-group (*cf.* the Strecker Synthesis (79) of α-amino acids and subsequent hydrolysis). It will be noted here that the method of preparation used in this work produced only a single product. There is always the possibility that the bromo-ester used by Bischoff and Mintz (77) might have reacted by two competing routes - (i) direct replacement of bromine by the anilino group, and (ii) removal of hydrogen bromide, followed by re-addition of aniline to the resulting double bond, thus:



Such a scheme would explain the two observed products, the main product being the α-anilino*isobutyric* acid (I) (m.p. 184°) and the β-anilino acid (m.p. 142°) being a by-product. In support of this argument, it is known that methyl acrylate ($CH_2:CH.CO_2Me$) reacts with aniline to give $PhNH_2.CH_2.CH_2.CO_2Me$.

A further proof that the anilino*iso*butyric acid (m.p. 184°) obtained in the present work is the α-form is suggested by an infra-red absorption band at 1193 $cm.^{-1}$ (also observed for the lactone-lactam at 1190 *m* and for the α-hydroxy*iso*butyranilide at 1190 *s*) characteristic of the structure $(Me)_2C<$ with no free hydrogen atom on the central carbon atom (80).

Again, it will be noted that in the preparation of α-anilino-α-methyl-*n*-butyric acid (II) (m.p. 144°) two different β-forms should be produced if the method of preparation does in fact give the β-form rather than the α-form, as suggested by Bischoff and Mintz, thus:

$PhNH.CMeEt.CO_2H$
α (II)

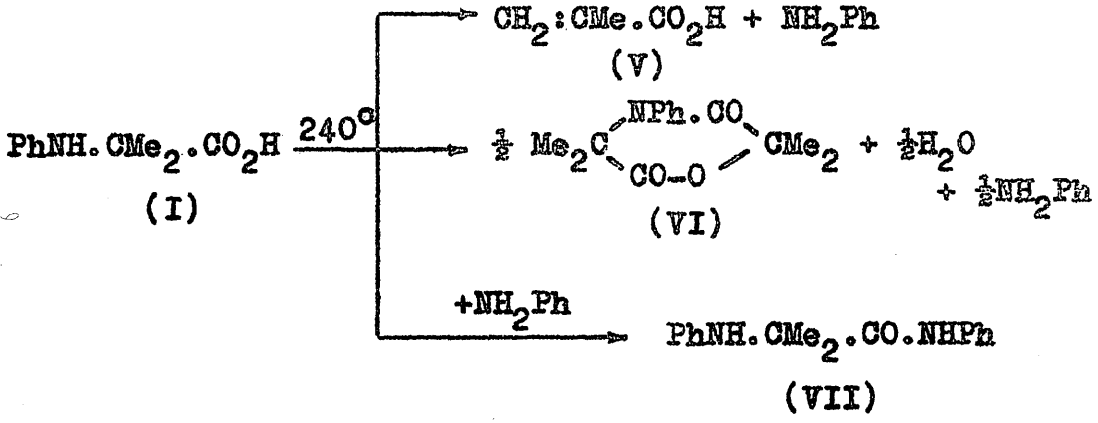
$PhNH.CHMe.CHMe.CO_2H$
β

$PhNH.CH_2.CHEt.CO_2H$
β

In fact, only a single product was obtained, as with all the other preparations; and this was taken to be the α-form, for reasons already listed.

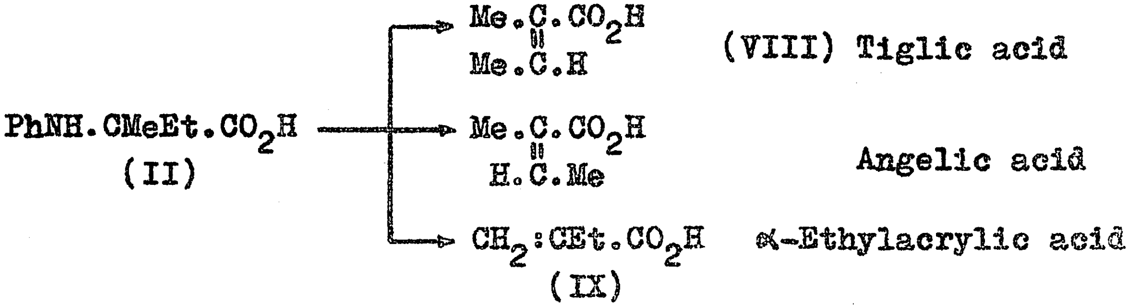
## 3.2. Pyrolysis of α-anilinoisobutyric (I) and α-anilino-α-methyl-n-butyric acids (II).

Acid (I) gave aniline and methacrylic acid (V), along with the expected lactone-lactam (VI) and traces of water. There was also a small amount of the anilide (VII) of the parent anilino-acid and a large amount of tarry material. The routes of decomposition are illustrated by the following scheme.



It will be noted (Table 6) that the amount of unsaturated acid found is surprisingly small, the main product being the lactone-lactam (*cf.* Bain & Ritchie (76)).

Similarly, the pyrolysis of acid (II) yielded a lactone-lactam, aniline, and unsaturated acid, along with traces of water and a large amount of tar. The yield of unsaturated acid is higher than that from anilino acid (I), and the yield of lactone-lactam is correspondingly smaller. This increase in the yield of unsaturated acid with increase in molecular weight is in agreement with the results of Bain and Ritchie. α-Anilino-α-methyl-n-butyric acid (II) can formally break down to give three unsaturated acids, as in the following scheme:



In fact, only tiglic acid (VIII) and α-ethylacrylic acid (IX) were observed. It is known that ethyl methyl ketone cyanohydrin (81) is dehydrated by heating with $P_2O_5$ to give a mixture of angelic, tiglic, and α-ethylacrylic acids. However, it has been found by Bennett et al. (28) that pyrolysis of the acetate of the above cyanohydrin proceeds mainly by an $A^1$ scission (plus a little $B^2$ scission) to acetic acid, and a mixture of tiglic and α-ethylacrylic acids (but no angelic acid). This is an agreement with the present observations. Tiglic acid (VIII) is the stable member of the cis-trans pair (it is known to be formed from angelic acid on heating the latter), and at the temperature used (ca. 450-500°) by Bennett et al. (28) it is not surprising that no angelic acid survives, even if originally formed. The same may apply to this present work, although a lower temperature was used (240°); but the Belgian workers Bruylante _et al._ (81) used temperatures of 100° or less, which may explain the angelic acid which they observed.

The tiglic acid (VIII) obtained from the acid (II) was identified by mixed melting point, but the $\alpha$-ethylacrylic acid (IX) proved more difficult to identify. Because of the small amount of unsaturated acid formed during pyrolysis and the similarity of the boiling points, tiglic acid (b.p. 198.5°) and $\alpha$-ethylacrylic acid (b.p. 180°) were both collected in the same fraction. It proved relatively easy to separate off the solid tiglic acid, but the liquid remaining was always contaminated with dissolved tiglic acid. Thus, infra-red analysis of the liquid could not differentiate between tiglic acid and $\alpha$-ethylacrylic acid (both spectra very similar).

However, oxidation (82) of tiglic acid yields among other products acetic acid, while $\alpha$-ethylacrylic acid yields among other products propionic acid (83) and this fact was used to identify $\alpha$-ethylacrylic acid.

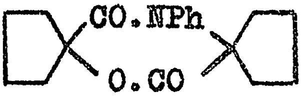
The appropriate fraction of the pyrolysate was oxidised with alkaline potassium permanganate and the oxidised products containing the acetic and propionic acids were then extracted with ether. The ether solution was dried over magnesium sulphate and was then examined by means of a vapour phase chromatography unit. On comparison with control samples acetic acid and propionic acid were both identified in the sample. The identification of propionic acid is taken as proof of the presence of α-ethylacrylic acid in the pyrolysate.

It is of some interest to compare the fact that α-anilino-α-methyl-n-butyric acid (II) gives both possible unsaturated acids on pyrolysis, with the postulate of Bailey and King (22) that unsymmetrical esters on pyrolysis yield the least highly alkylated alkene, except when there is heavy carbonisation.

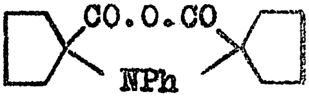
## 3.3. The elucidation of the structure of the lactone-lactam.

Of the four anilino acids studied, only two (α-anilino-isobutyric acid (I) and α-anilino-α-methyl-n-butyric acid (II) yielded a lactone-lactam on pyrolysis. The molecular formulae of both lactone-lactams were confirmed by molecular weight determination and micro-analysis. Both compounds crystallised in the form of large plates; both dissolved in dilute alkali and were reprecipitated by the addition of dilute acid. Infra-red analysis showed both compounds to have the same functional group structure.

There was, however, the problem of assigning an actual structure to the lactone-lactam. Plant proposed the structure (A) for the lactone-lactam obtained on pyrolysis of α-anilino*cyclo*pentanecarboxylic acid and the present work confirms this proposed structure. Plant supported his view of the structure by (a) elementary analysis, (b) the fact that it dissolves slowly in dilute alkali and is reprecipitated slowly by dilute acid (a characteristic of a lactone), (c) the fact that it is not basic, and (d) the fact that it does not react with aniline or dry ammonia at elevated temperatures:



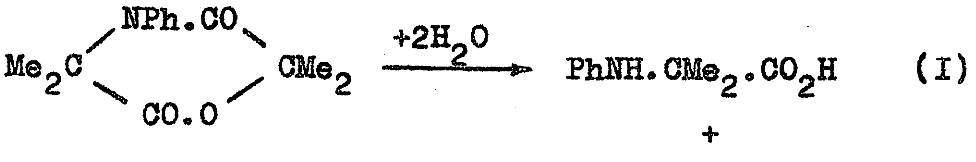
(A)



(B)

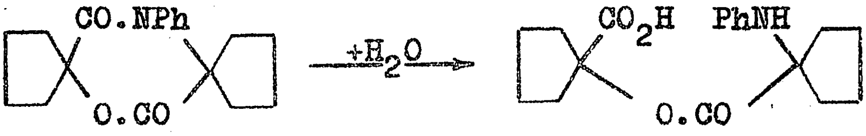
The structure (B) was also considered by Plant, but was rejected because it would be expected to be basic (owing to the tertiary amine group present) whereas the compound isolated showed no basic properties.

Properties (a), (b), and (c) listed above have been confirmed in the present work and further evidence confirming the structure (A) has been obtained. A hydrolysis of the lactone-lactam (VI) (obtained from α-anilino*iso*butyric acid) by boiling with $4\overline{N}$ sulphuric acid for 25 hours split the molecule to α-anilino<u>iso</u>butyric acid (I) and α-hydroxy<u>iso</u>butyric acid (X):



(VI) (I) (X)

A similar experiment by Bain and Ritchie (76) with the lactone-lactam (A) from α-anilino<u>cyclo</u>pentanecarboxylic acid, led only to a partial hydrolysis giving a new compound believed to have the structure (C):



(A) (C)

## 3.4. Source of the Products.

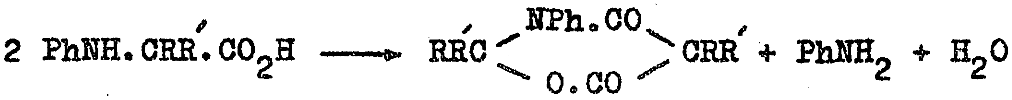
### 1. Aniline and unsaturated acid.

The aniline present in the pyrolysate from anilino-acids (I) and (II) can be readily accounted for by the primary scission to an unsaturated acid and aniline:

$$\underset{(I,\ II)}{PhNH.CRR'.CO_2H} \longrightarrow CH_2{:}CR'.CO_2H + PhNH_2$$

(I: R = R' = Me; II: R = Me, R' = Et)

The amount of aniline formed (see table 6) cannot, however, be wholly accounted for in this way; but water was always noted in the pyrolyses, and the excess aniline can be explained by the following formation of the lactone-lactam:



$$2\ \mathrm{PhNH.CRR'.CO_2H} \longrightarrow \mathrm{RR'C}\left\langle\begin{matrix}\mathrm{NPh.CO}\\ \mathrm{O.CO}\end{matrix}\right\rangle\mathrm{CRR'} + \mathrm{PhNH_2} + \mathrm{H_2O}$$

### 2. Hydroxy-anilides.

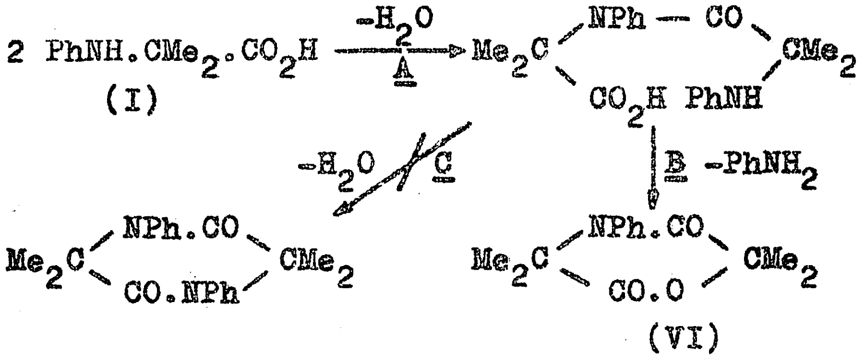
$$\mathrm{PhNH.CRR'.CO_2H} \not\longrightarrow \mathrm{HO.CRR'.CO.NHPh}$$

Although this type of reaction occurs in the pyrolysis of cyclic anilino-acids (76), no evidence could be found in the present work for the presence of such compounds. A sample of α-hydroxy*iso*butyranilide was prepared and pyrolysed under conditions similar to those used for the parent α-anilino*iso*butyric acid (I), in order to check the thermal stability of the former. It was found to be thermally stable at 240°; hence, it would have survived if in fact it was a product of the pyrolysis of the anilino acid (I) (Bain and Ritchie (76) found that α-hydroxy*cyclo*hexanecarboxyanilide was similarly thermally stable). A further check (infra-red) was made on the appropriate fraction of the pyrolysate from α-anilino*iso*butyric acid (I), but no trace could be found of the characteristic OH band (3279 *s*). Bain and Ritchie (76) noted that the yield of hydroxy-anilide from

$\alpha$-anilino*cyclo*hexanecarboxylic acid varied with the duration of pyrolysis and temperature of pyrolysis (13% at 160°, 48 hrs.; 8% at 250°, ½ hr.). However, on heating acid (I) for 48 hrs. at 180° no hydroxy-anilide was detected. It must, therefore, be concluded that acids (I) and (II) do not rearrange thermally under the conditions studied.

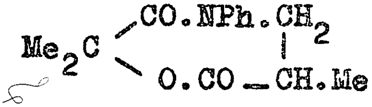
3. *Lactone-lactam.*

The following discussion is based upon the lactone-lactam (VI) obtained from $\alpha$-anilino*iso*butyric acid (I); but it applies equally well, of course, to the lactone-lactam from $\alpha$-anilino-$\alpha$-methyl-*n*-butyric acid (II). Although the formation of the lactone-lactam is rather difficult to explain, the following reaction appears to be a formal possibility:



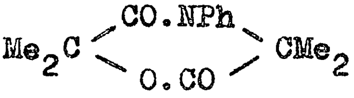
Reaction *A* is the predictable interaction of an acid and aniline yielding an anilide. This anilide might then be expected to yield a diketopiperazine by a symmetrical ring-closure (reaction *C*); there was, however, no evidence of this (*cf.* also Bain and Ritchie (76)), and it can only be concluded that the lactone-lactam is formed by a rather unexpected intramolecular esterification (reaction *B*).

Bischoff and Mintz (77) on pyrolysis of the anilino-acid with m.p. 184° (called β-anilino*iso*butyric acid by them, but in the present work called α-anilino*iso*butyric acid (I), obtained a lactone, to which they assigned the following possible structure:

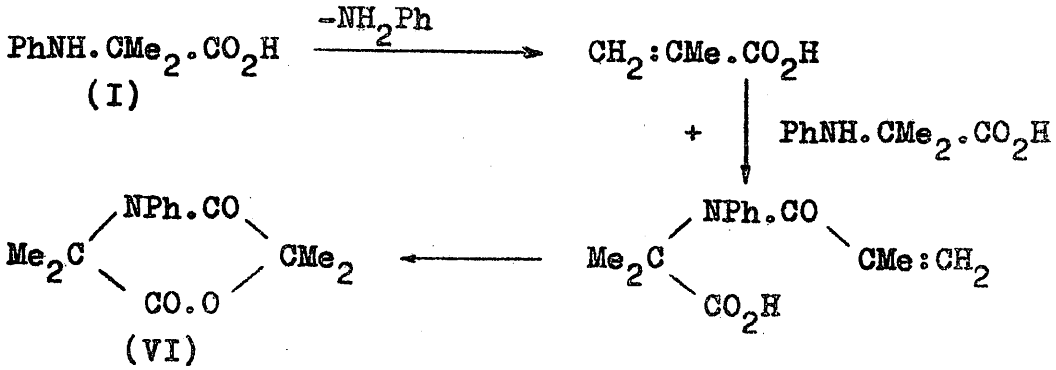


(7 - membered ring)

As a result of the present work, a 6-membered rather than a 7-membered ring is preferred, and the lactone-lactam is now considered to have the following structure:



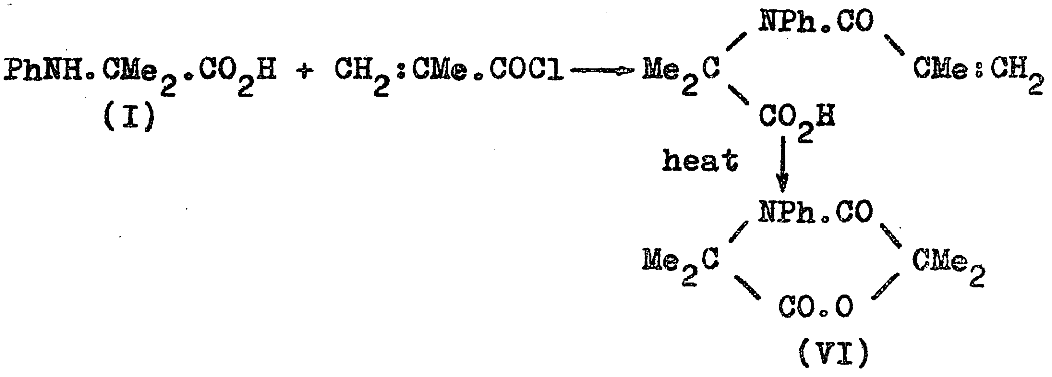
However, the method of formation suggested by Bischoff and Mintz (77) must still be considered as possible; namely, that the unsaturated acid formed in the first instance reacts with the parent anilino-acid as follows:



It should be noted at this stage that the so-called α-anilino*iso*butyric acid (m.p. 142°) distilled by Bischoff and Mintz (77) does not yield a lactone but an amine. It is suggested by the present author that this is a further indication that this so-called α-form was in fact the β-form, and that an amine was formed rather than a seven-membered ring lactone as above.

## 3.5. Attempted synthesis of the lactone-lactam.

In an attempt to find the method of formation of the lactone-lactam the following synthesis was attempted:



However, on reacting $\alpha$-anilinoisobutyric acid (I) with the acid chloride of methacrylic acid no positive conclusion could be reached.

## 3.6. Pyrolysis in Semi-Micro flow reactor.

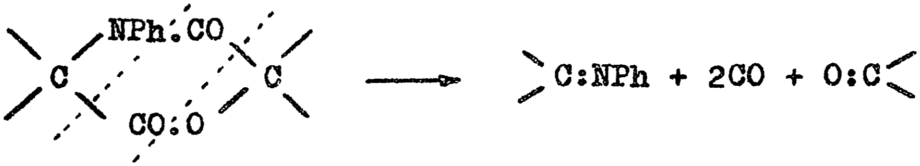
At 240° for 1 hour, in the static system, the anilino acids yielded very little gas. The semi-micro flow reactor offered a useful method of pyrolysing materials available (like the lactone-lactam) in only very small amounts, and thus obtaining sufficient gas to enable an analysis to be made.

The present series of experiments was planned to provide information on the composition of the gas evolved at high temperatures (540°), and to provide a comparison with the results obtained by Bain and Ritchie (76) for cyclic anilino-acids.

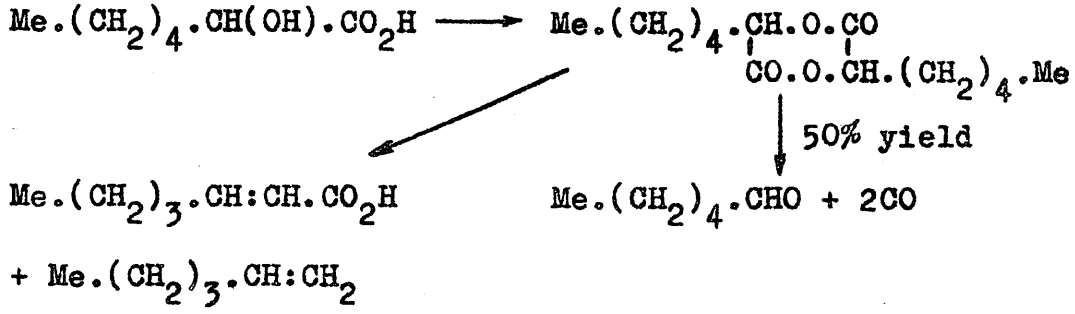
Both $\alpha$-anilinoisobutyric acid (I) and $\alpha$-anilino-$\alpha$-methyl-n-butyric acid (II) gave, on high temperature pyrolysis, quite large quantities of carbon monoxide (see tables 8 and 9). Similar results were obtained from $\alpha$-anilinocyclopentanecarboxylic acid and $\alpha$-anilinocyclohexane carboxylic acid (76), but here the hydroxy-anilides obtained on low temperature pyrolysis of both these compounds, gave quite large quantities of carbon monoxide at high temperature. Formation of hydroxy-anilide, with subsequent break down, was therefore suggested as a possible source of the carbon monoxide from the anilino-acids. In the present work, however, no hydroxy-anilide was obtained from the low temperature pyrolysis of either anilino-acids (I) or (II) and it was felt that the carbon monoxide must have some other source.

With this idea in view, the lactone-lactams obtained from both the above anilino-acids were pyrolysed in the semi-micro flow-unit; and much carbon monoxide was found in the gaseous pyrolysate.

The following scheme is suggested as a possible break down route for lactone-lactams in general:



In support of this idea, acetone and methyl ethyl ketone were identified in the pyrolysates of the lactone-lactams from α-anilinoisobutyric (I) and α-anilino-α-methyl-n-butyric (II) acids respectively. In further agreement, Blaise (84) found that aldehydes could be prepared in good yield by the distillation of lactides; and Bagard (73), using the same method, obtained a 50% yield of caproic aldehyde from α-hydroxyheptoic acid, though he obtained in addition hex-1-ene and an unsaturated acid (possibly heptenoic acid) and, as expected, some α-hydroxyheptilactide, thus:



$$\mathrm{Me.(CH_2)_4.CH(OH).CO_2H} \longrightarrow \begin{array}{l} \mathrm{Me.(CH_2)_4.CH.O.CO} \\ \qquad\qquad\quad\;\; \mathrm{CO.O.CH.(CH_2)_4.Me} \end{array}$$

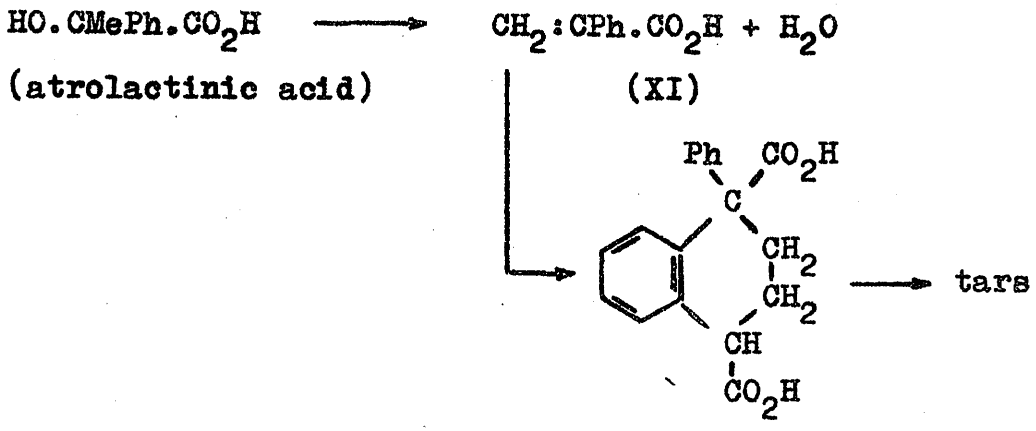
$$\xrightarrow{50\%\ \text{yield}} \mathrm{Me.(CH_2)_4.CHO + 2CO}$$

$$\swarrow\ \mathrm{Me.(CH_2)_3.CH{:}CH.CO_2H + Me.(CH_2)_3.CH{:}CH_2}$$

## 3.7. Pyrolysis of α-anilino- α-phenylpropionic acid (III).

Pyrolysis of anilino acid (III) at 240° for 1 hour yielded a very large amount of tar. The only other products which could be isolated were water (trace), aniline, and a very small amount of the anilide of atropic acid. There was no trace of the expected unsaturated acid, atropic acid, nor the lactone-lactam.

It is known (85) that in the preparation of atropic acid (XI) from atrolactinic acid, isatropic acid is also formed; and, if the distillation is carried out slowly, a viscous residue of isatropic acids is obtained. This is a possible explanation of the large amount of tar formed during the pyrolysis:



(XII)

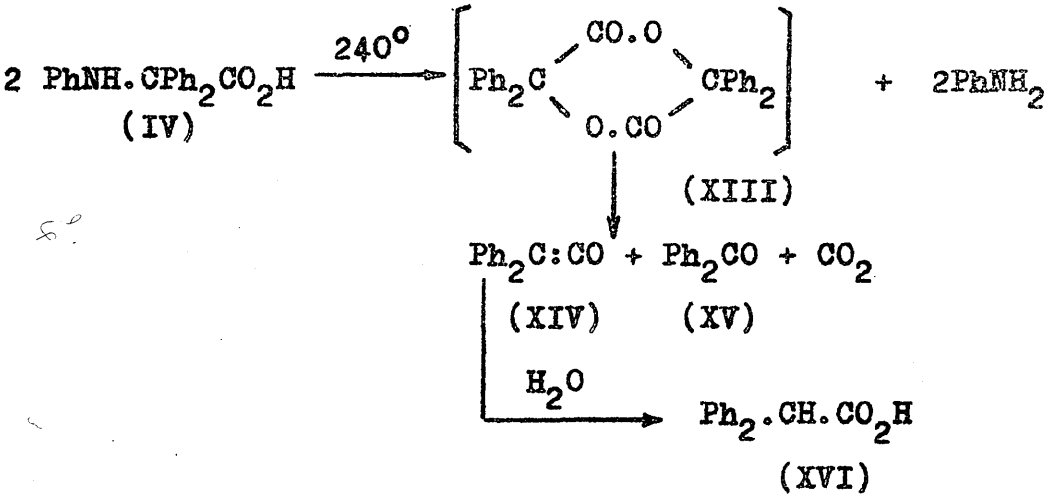
Since it was thought that the relatively high temperature of the pyrolysis (240°) might be destroying the atropic acid, a second pyrolysis was carried out at a much lower temperature (180°). This led to a much lower yield of aniline; but this time the unsaturated acid (atropic acid) was identified in the pyrolysate, which seems to confirm that higher temperatures are responsible for tar-formation.

Investigation of the tars from the first (high-temperature) pyrolysis yielded no crystalline products, but the tar produced in the low-temperature (180°) pyrolysis yielded two unexpected products. The residue from the pyrolysate was taken up in benzene-light petroleum and after standing the solution for a week, traces of solid (A) were observed on the sides of the flask. The solid was recrystallised to m.p. 206°

(prisms from benzene/light petroleum) (0.75% by weight). The mother liquors yielded another crystalline product (B) m.p. 168° (2% by weight) (prisms from benzene/light petroleum). A mixed m.p. proved these two compounds to be different, while a sodium fusion test indicated that carbon, hydrogen and oxygen were the only elements present. Tests for acidity and unsaturation gave negative results, for both compounds; and there was no reaction with 2:4-dinitrophenylhydrazine. A micro-analysis of both compounds indicated a molecular formula $C_{7n}H_{6n}O_n$, while a molecular weight determination (camphor method) gave 135 for compound A and 380 for compound B. Infra-red analysis indicated that both compounds had similar functional groups (see page 119), their spectra suggesting the presence of one of the following groups: ketone, aldehyde, keto-ester, ester, or anhydride. An attempted hydrolysis of compound B with both acid and alkaline reagents produced only the original starting material. For the present, substances A and B remain unidentified.

### 3.8. Pyrolysis of $\alpha$-Anilinodiphenylacetic acid (IV).

Owing to difficulty in preparing this compound only 6 g. could be obtained for pyrolysis. As with all the anilino-acids, pyrolysis (240°, 1 hr.) yielded aniline and tar. In this case, however, it is not formally possible for the anilino-acid to breakdown to an unsaturated acid along with aniline. Rather unexpectedly, however, diphenylacetic acid (XVI) was identified in the pyrolysate. There was no trace of a lactone-lactam. At first sight it is rather difficult to explain the presence of diphenylacetic acid, but the following scheme is suggested as a possibility:



Benzilide (XIII) is known to break down (86) to carbon dioxide (80.6% of theory), benzophenone (XV), and diphenylketen (XIV). The diphenylketen thus formed would be expected to react with the aqueous sodium carbonate solution used to extract the pyrolysate, yielding the salt of acid (XVI). In agreement with this theory, benzophenone was identified in the pyrolysate from a second smaller pyrolysis. Identification of benzophenone, however, does not really confirm the above scheme, although it does not contradict it; there is always the likelihood that benzilide breaks down, in part, to give carbon monoxide and benzophenone. As in all the other pyrolyses of anilino-acids, a large amount of tar was formed, from which no useful product could be isolated.

## 4. GENERAL ASSESSMENT OF RESULTS.

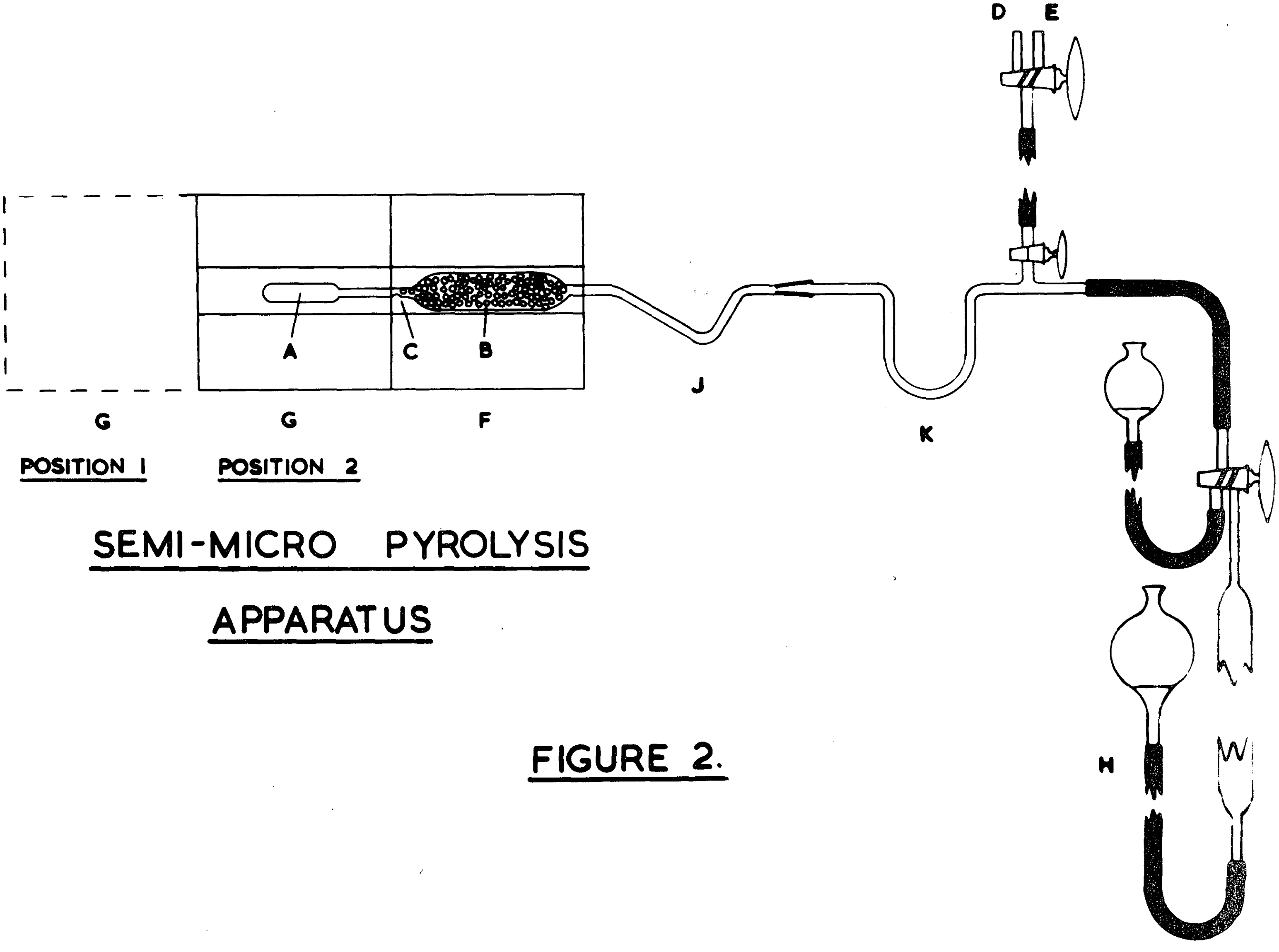
Of the four straight-chain anilino-acids covered by the present work, α-anilinoisobutyric acid (I) and α-anilino- α-methyl-n-butyric acid (II) yielded on pyrolysis aniline, water, unsaturated acid, and a lactone-lactam; α-anilino- α-phenylpropionic acid (III) yielded the first three of these products, but no lactone-lactam. None of them yielded a hydroxy-anilide, so that this thermal rearrangement is not a general feature of the pyrolysis of anilino-acids, though previously observed (76) for cyclic anilino-acids. α-Anilinodiphenylacetic acid (IV), which is structurally precluded from yielding an unsaturated acid, breaks down in quite a different way; the observed decomposition products indicate that a dilactone (benzilide) rather than a lactone-lactam is the key intermediate.

In agreement with the work of Bain and Ritchie (76), the yield of unsaturated acid was greater from anilino-acid (II) than from acid (I); i.e. the yield of unsaturated acid increased with an increase of molecular weight. Acid (III) as expected gave a still greater yield of unsaturated acid.

If it is assumed that the unsaturated acid generally produced on pyrolysis of anilino-acids combines in turn with the anilino-acid to give a lactone-lactam, then the fact that a lactone-lactam is obtained from both anilino-acids (I) and (II) is in obvious agreement. The anilino-acid (IV), which cannot yield an unsaturated acid, would not, on this basis, be expected to give a lactone-lactam; and it is suggested that a dilactone is formed in its place. The anilino-acid (III) yields an unsaturated acid on pyrolysis, though no lactone-lactam could be identified in the pyrolysate. Here, however, the unsaturated acid produced (atropic acid) is very readily converted to tarry material, which may account for the non appearance of a lactone-lactam.

Hydrolysis of the lactone-lactam isolated from the pyrolysate of anilino acid (I) into the parent anilino-acid and $\alpha$-hydroxy*iso*butyric acid confirms the structure proposed by Plant *et al*. (75), while pyrolysis in a semi-micro flow apparatus would seem to indicate that lactone-lactams break down thermally in a similar manner to dilactones (84, 73), to give carbon monoxide and a carbonyl compound.

Finally, it is felt that sufficient evidence has been collected to claim that the anilino*iso*butyric acid (m.p. 184°), prepared in the present work is in fact the $\alpha$-isomer, and not the $\beta$-isomer as claimed by Bischoff and Mintz (77).



SEMI-MICRO PYROLYSIS APPARATUS

FIGURE 2.

## EXPERIMENTAL.

## 5. Apparatus.

### 5.1. Macro-method, (Static Reaction Vessel).

The pyrolysand was heated under reflux in a small flask, immersed in a bath of Wood's Metal. The metal bath was heated by an electric hot-plate controlled by a "Simmerstat". Temperatures were controlled to within $\pm 5^\circ$. To prevent oxidation during pyrolysis, the system was evacuated and filled with oxygen-free nitrogen several times. The pyrolysate in most cases was fractionally distilled.

### 5.2. Semi-micro method, (Flow Reaction Vessel).

The Pyrex-glass apparatus shown in fig.2 was used primarily for the collection and study of gaseous pyrolysates (see tables 8, 9). The pyrolysand (300 m.g.) was placed in bulb A; bulb B was then filled with glass beads (diam. *ca.* 3 mm.) up to a constriction at C, and the whole repeatedly evacuated and filled with nitrogen via inlets D and E. A short cylindrical electric furnace F and the similar furnace G (in position 1), were both raised to $540^\circ$; after 2 hours, G was moved to position 2, enclosing bulb A. The barometric leg H was adjusted during the run so as to collect the gaseous pyrolysate at approximately atmospheric pressure. Any non-gaseous pyrolysate was removed at the leg J, or the cold trap K. After pyrolysis (10 mins.) the reactor was removed from the furnace and cooled (20 mins.): the total gas evolved was measured by the difference between the initial and final volume readings on the gas-burette. By lowering the mercury level of the collecting limb of the burette before closing the stopcock, ca. 80% of the gas in the system can be collected for analysis. The Sleigh gas analysis apparatus (87) was found to be accurate and particularly suitable for the gas analysis of the small amounts available. By measuring the total volume of the reaction vessel (29 ml.) the amount of gas evolved could be calculated.

## 5.3. Methods of analysis.

The aniline was determined as described by Siggia (88). The solid products were identified by mixed m.p., supplemented in some cases by infra-red analysis, vapour phase-chromatography and hydrolysis. The gas analyses are reported on a nitrogen free basis. The light petroleum used was the fraction b.p. 60 - 80°. Tables 6 and 7 summarise the results from the static system and tables 8 and 9 summarise the results obtained from the semi-micro pyrolysis unit.

## 6. Preparation of Pyrolysands.

### 6.1. α-Anilinocarboxylic acids.

The anilino-acids were prepared from the anilino-nitriles by the method of Plant and Facer (75) and Betts, Muspratt and Plant (74).

The anilino-nitrile was prepared by the method of Von Walter and Hubner (89). The appropriate ketone was added to a mixture of aniline and potassium cyanide in a large conical flask. This was well cooled ($0^\circ - 5^\circ$) and then glacial acetic acid was added, along with small quantities of water to dissolve the potassium cyanide. After several hours a solid separated out. This was filtered off and recrystallised from alcohol and water.

The anilino-nitrile was then dissolved in cold concentrated sulphuric acid and, after two days, poured onto crushed ice. On making the solution alkaline with ammonium carbonate and ammonium hydroxide the amide was precipitated. The amide on hydrolysis for two hours by concentrated hydrochloric acid (8 hours required for α-anilino- α-phenylpropionic acid) gave the α-anilinocarboxylic acid. The following three anilino acids were prepared by this method:

6.2. α-Anilinoisobutyric acid (I) crystallised from hot water in fine needles m.p. 184-5°, (lit. 184-5°)

overall yield 17%. (Found: C, 67.3; H, 7.4; N, 8.1. Calc. for $C_{10}H_{13}O_2N$, C, 67.0; H, 7.3; N, 7.8%).

6.3. α-Anilino- α-methyl-n-butyric acid (II) crystallised from benzene m.p. 144°, overall yield 10%. (Found: C, 68.7; H, 7.9; N, 7.3. $C_{11}H_{15}O_2N$ requires C, 68.4; H, 7.8; N, 7.3%.)

6.4. α-Anilino- α-phenylpropionic acid (III) crystallised from carbon tetrachloride m.p. 146°, overall yield 12%. (Found: C, 74.3; H, 6.3; N, 6.0; $C_{15}H_{15}O_2N$ requires C, 74.5; H, 6.3; N, 5.8%).

6.5. α-Anilinodiphenylacetic acid (IV). This acid was prepared by a different method to that used above, because of the difficulty of forming benzophenone cyanohydrin. The methods used were those recommended by Stohle (90).

1st Method.

78 g. of thionyl chloride were added to 50 g. of benzilic acid in carbon tetrachloride and left for 7 days. On removing the solvent a viscous oil was obtained (the lit. (90) claimed a high yield of diphenyl-chloracetic acid m.p. 118° at this stage). This oil was treated with excess aniline in ether and 4 g. of α-anilino-diphenylacetic acid (IV) m.p. 170° were obtained.

## 2nd Method.

290 g. of benzilic acid were refluxed with 810 g. of thionyl chloride in carbon tetrachloride for 7 days. After this time the solvent was removed and a viscous oil was obtained (lit. (90) claimed diphenylchlor-acetic anhydride m.p. 124° formed at this stage). The oil was treated with excess aniline in ether and after filtering off the aniline hydrochloride it was extracted with sodium carbonate. The alkali extract on neutralisation yielded 5 g. of α-anilino-diphenylacetic acid m.p. 168°, recrystallised from benzene m.p. 174° (lit. claimed 168°, 174°). (Found: C, 78.9; H, 5.6; N, 4.2; Calc. for $C_{20}H_{17}O_2N$, C, 79.2; H, 5.7; N, 4.6%).

## 6.6. α-Hydroxy*iso*butyranilide (X).

Acetone cyanohydrin prepared by the method of Welch and Clemo (91) was hydrolysed by the method of Bucherer and Brandt (92) to give 7 g. of α-hydroxy*iso*butyric acid m.p. 79° (lit. 79°). (Found: C, 46.3; H, 8.0. Calc. for $C_4H_8O_3$, C, 46.2; H, 7.8%).

2.15 g. (0.021 mole) of α-hydroxy*iso*butyric acid were then heated with 3.92 g. (0.042 mole) of aniline at 200° for 10 mins. The solid obtained on cooling was washed with dilute hydrochloric acid to remove excess aniline. The α-hydroxy*iso*butyranilide(X) recrystallised to a m.p. 132-133° (lit. 132-133°) yield 0.6 g. (Found: C, 67.1; H, 7.2; N, 7.6; Calc. for $C_{10}H_{13}O_2N$, C, 67.0; H, 7.3; N, 7.8%).

## 7. DETAILS OF PYROLYSIS (STATIC SYSTEM).

### 7.1. Pyrolysis of $\alpha$-Anilinoisobutyric acid (I).

**Run 1.**

44 g. of the anilino acid (I) were heated for 1 hour at 220° in the static system and the residue distilled to 9.5 g. of a mixture, b.p. 150-200°. This mixture contained water, aniline (7.5 g.) and a trace of solid (0.5 g.) m.p. 116-120°.

The water was identified by removing the droplets with a small pipette and then shaking with benzene to remove any aniline present, and then testing with anhydrous copper sulphate. The aniline was separated from the mixture by taking the mixture up in ether and then extracting with hydrochloric acid solution. The amount of aniline present was determined by sodium nitrite titration (88) and the aniline confirmed by conversion to acetanilide. The ether extract yielded a solid m.p. 116-120°, subsequently proved to be the expected lactone-lactam.

The distillation residue (i) 30 g. was extracted for 1 hour with a 5% sodium carbonate solution to give a solution (ii) and a residue (iii). The solution (ii) was acidified and extracted with ether to give 3 g. of solid product, which recrystallised to 1.5 g. of lactone-lactam, m.p. 116-120°. The residue (iii) was extracted with dilute hydrochloric acid solution to give a solution (iv) and a residue (v). The solution (iv) contained 0.5 g. of aniline. The extract was then made alkaline and 1.5 g. of solid material, recrystallised from methanol-water as plates m.p. 154-156° (lit. (93) m.p. 155° for α-anilino<u>iso</u>butyranilide). (Found: C, 75.8; H, 6.8; N, 11.0%). Calc. for $C_{10}H_{12}ON_2$: C, 75.6; H, 7.1; N, 11.0%. The identification was confirmed by hydrolysis to the original anilino acid and aniline.

The residue (v) was recrystallised from benzene/light petroleum to give 15 g. of crude lactone-lactam. This was recrystallised to give 7 g. of pure lactone-lactam (VI) (large plates) m.p. 116-120°. Found: C, 68.3; H, 7.1; N, 5.6; M (cryoscopic in benzene), 243. Calc. for $C_{14}H_{17}O_2N$; C, 68.0; H, 6.9; N, 5.7%; M, 247. The overall losses are accounted for by distillation losses, water and a tarry residue which was not analysed further.

## 7.2. Hydrolysis of the Lactone-lactam (VI).

The lactone-lactam was hydrolysed for 25 hours with $4\bar{N}$ sulphuric acid. The solution was neutralised (pH <u>ca</u>. 5) with dilute sodium hydroxide solution, and extracted with ether. The ether extract yielded α-anilino<u>iso</u>butyric acid, identified by mixed m.p.

The remaining solution was evaporated to dryness and a yellow solid obtained. This was recrystallised from benzene as fine needles of pure $\alpha$-hydroxy_iso_butyric acid, m.p. 79°, confirmed by a mixed m.p. with a synthetic sample of $\alpha$-hydroxy_iso_butyric acid, m.p. 79°.

Run 2.

As the expected unsaturated acid was not identified on the previous pyrolysis, this second run was carried out. 25 g. of the anilino acid were pyrolysed as before for 1 hour at 240°. The pyrolysate was distilled to give 5 g. of liquid b.p. 140-220° and a residue (i). The liquid was a mixture of aniline (4.1 g.), water and methacrylic acid.

The mixture was taken up in ether and extracted with hydrochloric acid to remove the aniline, as before. The ether extract in this case yielded a semi-solid material. This semi-solid was taken up in benzene, leaving behind a residue. The benzene was removed and the liquid obtained analysed by infra-red spectroscopy. Methacrylic acid was shown to be present on comparison with a control spectrum. The residue left behind, after extraction with benzene, started to decompose at 200° and became liquid at 300°. This was almost certainly polymethacrylic acid (94). A further 0.5 g. of aniline was recovered from the residue (i) and 5 g. of pure lactone-lactam m.p. 116-120° were isolated. The residue (i) was found to be entirely soluble in benzene, while a sample of synthetic $\alpha$-hydroxy<u>iso</u>butyric acid anilide was found to be insoluble in benzene. The residue (i) was also submitted for infra-red analysis, but no evidence could be found for the presence of the hydroxyanilide (no infra-red absorption band found at 3279<u>s</u>, characteristic of OH grouping).

<u>Run 3</u>.

Bain and Ritchie (76) found that the yield of hydroxy-anilide from $\alpha$-anilino<u>cyclo</u>hexanecarboxylic acid varied with duration of heating (i.e. effective "contact time") and temperature of pyrolysis (13% at 160°, 48 hrs.; 8% at 250°, ½ hr.). To find the effect, therefore, of long contact time and low temperature on $\alpha$-anilino<u>iso</u>butyric acid the present pyrolysis was carried out.

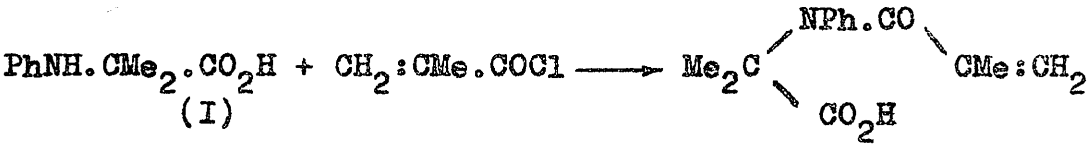
2.0 g. of the anilino acid were heated for 48 hrs. at 160°. A very tarry residue was obtained, which yielded <u>ca</u>. 0.1 g. of solid m.p. 150° on extraction with benzene. This solid recrystallised to m.p. 155-6° (methanol-water) and proved to be the anilide of the starting material ($\alpha$-anilino<u>iso</u>butyric acid anilide). No trace could be found of $\alpha$-hydroxy<u>iso</u>butyranilide.

## 7.3. Pyrolysis of α-Hydroxy*iso*butyranilide.

This pyrolysis was carried out to determine the stability of the hydroxy-anilide under the conditions of pyrolysis used for α-anilino*iso*butyric acid. 0.34 g. of α-hydroxy*iso*butyranilide were pyrolysed for 1 hr. at 240° in the static system. All the starting material was recovered unchanged; confirmed by m.p. and mixed m.p.

## 7.4. Attempted Synthesis of the Lactone-lactam (VI).

An attempt was made to synthesise the lactone-lactam of α-anilino*iso*butyric acid (I) by reacting the acid chloride of methacrylic acid with the acid (I) as below:



$$\underset{\text{(I)}}{\mathrm{PhNH.CMe_2.CO_2H}} + \mathrm{CH_2{:}CMe.COCl} \longrightarrow \mathrm{Me_2C}\left\langle\begin{matrix}\mathrm{NPh.CO.CMe{:}CH_2}\\ \mathrm{CO_2H}\end{matrix}\right.$$

It was thought that by heating the product, ring closure might take place to give the desired lactone-lactam. No conclusive result was obtained.

## 7.5. Preparation of the acid chloride of methacrylic acid

6 g. of acid chloride were prepared by heating methacrylic acid and phosphorus trichloride (95). The pure acid chloride had b.p. 94-97°, $n_D^{15}$ 1.448 (lit., b.p. 95-96°, $n_D^{15}$ 1.444).

## 7.6. Attempted reaction of α-anilinoisobutyric acid (I) with the acid chloride of methacrylic acid.

0.8 g. of the anilino acid (I) and an excess of the acid chloride were dissolved in benzene and left overnight. A very small amount of solid m.p. 196-200° was isolated. This solid gave a positive reaction for an acid and for unsaturation. It was soluble in water and methanol and insoluble in ethanol, benzene and light petroleum.

The product, 0.07 g. was heated under a stream of nitrogen for 10 mins. at 240°. The only material isolated from the pyrolysate had a m.p. 158°. When mixed with acid (I) m.p. 184° the m.p. was raised to 160°.

## 7.7. Pyrolysis of α-anilino- α-methyl-n-butyric acid (II).

### Run 4.

40 g. of the anilino acid (II) were pyrolysed at 240° for 1 hr. in the static reactor. The pyrolysate distilled, as before, to give 9.7 g. of a liquid b.p. 140-190° and a residue (i).

The liquid was found to be a mixture of aniline (7.7 g.) water and tiglic acid. The mixture was taken up in ether and the aniline extracted with hydrochloric acid. The ether portion yielded a brown liquid which on cooling to $0^{\circ}$ deposited a white solid m.p. $40-58^{\circ}$. This was recrystallised from hot water to a m.p. $58-62^{\circ}$ (lit. tiglic acid m.p. $58-62^{\circ}$). Tiglic acid was confirmed by mixed m.p.

The residue (i) yielded a further 0.5 g. of aniline on extraction with hydrochloric acid. The residue was then dissolved in a benzene-light petroleum mixture. On cooling 7 g. of crystals (plates) m.p. $117^{\circ}$ were obtained. These were recrystallised to give 5 g. (plates) of pure lactone-lactam m.p. $124-5^{\circ}$. (Found: C, ~~68.9~~ 69.8; H, 7.9; N, 5.0; M (cryoscopic in benzene), 279, 270. $C_{16}H_{21}O_3N$ requires: C, 69.8; H, 7.7; N, 5.1%; M 275).

<u>Run 5</u>.

At this stage it was felt that $\alpha$-ethylacrylic acid was a possible product of the thermal breakdown of anilino acid (II). This second pyrolysis was carried out to discover if this was the case.

21 g. of the anilino acid were pyrolysed for 1 hr. at $240^{\circ}$ as before. The total pyrolysate was then dissolved in ether and extracted with a 5% sodium carbonate solution and then with a $2\bar{N}$ hydrochloric acid solution.

The alkali extract (100 mls.) was divided into two equal portions. One portion was oxidised with potassium permanganate and the oxidised products extracted with ether. The ether extract was dried and then examined by vapour phase chromatography. This indicated on comparison with control samples the presence of acetic and propionic acids. The identification of propionic acid as one of the oxidised products confirmed the suspected presence of $\alpha$-ethyl acrylic acid. The other alkali portion was acidified and extracted with ether. The ether gave ca. 0.05 g. of tiglic acid (confirmed by mixed m.p.) and ca. 0.1 g. of brown liquid. This liquid was analysed by infra-red, but it proved impossible to distinguish between tiglic and $\alpha$-ethyl acrylic acid.

The acid extract of the pyrolysate contained 4.7 g. of aniline, while 6 g. of crude lactone-lactam were isolated from the residue. This was recrystallised to 4 g. of pure lactone-lactam m.p. 124-5°. There was no trace of a hydroxy-anilide. The remainder of the residue was tar, which was not analysed further.

## 7.8. Pyrolysis of $\alpha$-anilino- $\alpha$-phenylpropionic acid (III).

### Run 6.

50 g. of the acid (III) were pyrolysed at 240° for 1 hr. in the static system. Distillation of the pyrolysate gave 10 g. of liquid. This proved to be a

mixture of water (ca. 1.5 g.) and aniline (7.0 g.). The mixture was separated in the usual way by taking up in ether and shaking with $2\bar{N}$ hydrochloric acid. The ether layer yielded a trace of sticky solid m.p. 220°, but it proved impossible to recrystallise.

The acid extract, containing the aniline, was made alkaline and 0.2 g. of solid were obtained. This was recrystallised from methanol/water m.p. 132° (lit. (96) for atropanilide m.p. 134°. (Found: C, 80.8; H, 5.9; N, 5.9% Calc. for $C_{15}H_{13}ON$: C, 80.8; H, 5.9; N, 6.3%).

The residue from the distillation was taken up in benzene, but produced nothing but tar. A trace of material m.p. 238° was isolated (isatropic acid).

McKenzie and Wood (85) noted that in the preparation of atropic acid from atrolactinic acid, isatropic acid was also formed and if the distillation was carried out slowly a viscous residue of isatropic acids was obtained. This possibly explains the large amount of tar produced in this pyrolysis.

It was, therefore, decided to carry out the following pyrolysis at a much lower temperature, in an attempt to avoid the formation of large amounts of tar.

Run 7.

In this run 40 g. of the anilino acid were pyrolysed for 1 hr. at 180°. To avoid formation of tars, the pyrolysate was not distilled, as in the previous run, but was taken up in ether, leaving behind a resinous material (5.6 g.). This resinous material yielded no crystalline product on further investigation. The ether solution on extraction with $2\bar{N}$ hydrochloric acid gave 3 g. of aniline. The ether was then extracted with a 5% sodium carbonate to give 1.2 g. of solid. This was recrystallised from ethanol m.p. 106° (lit. (85) atropic acid m.p. 106-7°). This acid was oxidised with chromic acid to benzoic acid (confirmed by mixed m.p.). The atropic acid was then heated in a test tube and the residue extracted with benzene. A white solid m.p. 238° (lit. (97) m.p. 238° for isatropic acid) was left behind by the benzene. The ether was then evaporated and left a tarry residue. This was dissolved in benzene and light petroleum. On standing the solution for about a week, traces of solid were noticed on the sides of the flask. This was recrystallised from benzene m.p. 204° (0.3 g.). The mother liquors from the above were evaporated to dryness and yielded another crop of crystalline material. This recrystallised from benzene-light petroleum, m.p. 164° (small prisms) (0.8 g.). Both compounds were recrystallised from methanol to m.p.s of 206° and 168°

respectively. A mixed m.p. proved these two compounds to be different. A sodium fusion test showed that both compounds contained only carbon, hydrogen and oxygen. Tests for acidity and unsaturation on both compounds gave negative results. Similarly there was no reaction with 2:4-dinitrophenylhydrazine. Micro-analysis gave the following results: Compound A (m.p. 206°): C, 78.7; H, 5.8; O (direct), 15.7%; M (camphor method), 135; Compound B (m.p. 168°) C, 78.7; 78.4; H, 5.8; 6.2; O (direct), 14.3%; M (camphor method), 380. Repeated heating of both materials up to and beyond their m.p.s. did not alter their m.p.s. Since compound B was present in the larger amount, it was used for an attempted hydrolysis. In the first instance the compound was refluxed with 4$\bar{N}$ sulphuric acid for 4 hrs., but was recovered unchanged. Similarly refluxing with $\bar{N}$ alcoholic potassium hydroxide solution for 15 hrs. had no effect on the material.

### 7.9. Pyrolysis of α-Anilinodiphenylacetic acid (IV).

#### Run 8.

6 g. of the anilino acid (IV) were pyrolysed in the static reactor for 1 hr. at 240°. The pyrolysate was then dissolved in ether, leaving behind a resinous material (0.6 g.). The only products expected were the lactone-lactam and aniline. Thus the ether solution was

extracted with 2N hydrochloric acid to give 0.5 g. of aniline. A sodium carbonate extract of the ether solution, however, gave unexpectedly 0.8 g. of a white solid. This was recrystallised from a benzene - light petroleum mixture to a m.p. 148°. This compound was identified as diphenylacetic acid, confirmed by a mixed m.p. and infra-red analysis. Finally the other solution yielded a tar, which could not be purified further.

There was no trace of the expected lactone-lactam nor the corresponding dilactone benzilide. At this stage it was felt that benzilide if formed might have decomposed during the pyrolysis to give secondary products. The following pyrolysis was carried out to test this theory.

Run 9.

1 g. of the anilino acid (IV) was pyrolysed as above; the pyrolysate was taken up in methanol and tested with a solution of 2:4-dinitrophenylhydrazine. A red precipitate was obtained which was identified as the derivative of benzophenone (mixed m.p.), a known breakdown product of benzilide (86).

## 8. DETAILS OF PYROLYSES (SEMI-MICRO METHOD).

These pyrolyses were carried out to investigate the composition of the gaseous pyrolysates from high temperature pyrolysis of the α-anilino acids and lactone-lactams, since the present work has shown that low temperatures produce only very small traces of gas.

### 8.1. Pyrolysis of α-Anilinoisobutyric acid (I).

Run 10.

0.3 g. of acid (I) were pyrolysed at 540° in the semi-micro pyrolysis unit. The gas analysis gave the following results: carbon dioxide 11.8%; unsaturated hydrocarbons 1.4%; carbon monoxide 33.0%; and hydrogen 3.4%.

### 8.2. Pyrolysis of the lactone-lactam (VI) from α-anilinoisobutyric acid (I).

Run 11.

0.3 g. of the lactone-lactam (VI) were pyrolysed as above. The pyrolysate gas contained carbon dioxide 9.8%; unsaturated hydrocarbons 3.0%; carbon monoxide 27.9%; and hydrogen 3.72%. Acetone was identified in the pyrolysate; confirmed by m.p. and mixed m.p. of its 2:4-dinitrophenylhydrazone.

## 8.3. Pyrolysis of α-Anilino- α-methyl-n-butyric acid (II).

### Run 12.

0.3 g. of the anilino-acid (II) were pyrolysed at 540° as above. The gaseous pyrolysate contained carbon dioxide 12.6%; unsaturated hydrocarbons 2.2%; carbon monoxide 25.2%; and hydrogen 2.2%.

## 8.4. Pyrolysis of the lactone-lactam from α-anilino-α-methyl-n-butyric acid (II).

### Run 13.

0.3 g. of the lactone-lactam were pyrolysed at 540°. The pyrolysis gas analysed as carbon dioxide 3.15%; unsaturated hydrocarbons 2.89%; carbon monoxide 39.2%; and hydrogen 4.34%. Methyl ethyl ketone was identified in the pyrolysate by m.p. and mixed m.p. of the 2:4-dinitrophenylhydrazone derivative.

## 9. NEW INFRA-RED DATA.

The following are the principal infra-red absorption bands of the compounds studied.

### α-Anilinoisobutyric acid (I).

1618 s, 1495 m, 1404 s, 1359 s, 1218 m, 1193 m, 1156 m, 1030 m, 917 m, 897 m, 819 m, 806 m, 782 m, 741 s, 693 s cm.$^{-1}$.

**Assignments.**

| | |
|---|---|
| 1618 cm.$^{-1}$ | Carboxylate ion. |
| 1193 cm.$^{-1}$ | Isopropyl skeleton $(Me)_2C<$ with no free H atom attached to the central C atom. |

### α-Anilino- α-methyl-n-butyric acid (II).

1616 s, 1486 m, 1391 s, 1359 s, 1325 m, 1305 w, 1284 m, 1183 w, 1145 m, 1135 w, 1025 m, 885 m, 797 m, 763 w, 735 s, 692 s cm.$^{-1}$.

**Assignments.**

| | |
|---|---|
| 1616 cm.$^{-1}$ | Carboxylate ion. |

### α-Anilino- α-phenylpropionic acid (III).

1650 s, 1613 s, 1558 w, 1495 s, 1389 s, 1361 s, 1511 w, 1282 w, 1258 w, 1208 w, 1183 w, 1156 w, 1130 w, 1075 w, 1029 m, 912 w, 881 m, 797 w, 766 w, 739 s, 694 s cm.$^{-1}$.

**Assignments.**

| | |
|---|---|
| 1650 cm.$^{-1}$ | Acid C:O |

1613 cm.$^{-1}$ Carboxylate ion.

1558 cm.$^{-1}$ Benzene ring.

α-Anilinodiphenylacetic acid (IV).

1626 s, 1493 (shoulder), 1326 s, 1279 (shoulder), 1220 w, 1183 (shoulder), 1170 w, 1156 (shoulder), 1081 w, 1026 (shoulder), 985 w, 905 w, 890 w, 833 w, 785 w, 782 w, 746 s, 722 s, 687 s cm.$^{-1}$.

Assignments.

1626 cm.$^{-1}$ Carboxylate ion.

Lactone-lactam from α-anilinoisobutyric acid(I).

1745 s, 1661 s, 1595 w, 1490 w, 1406 s, 1389 (shoulder), 1305 s, 1250 m, 1220 m, 1190 m, 1147 s, 1053 m, 759 s, 702 s cm.$^{-1}$.

Lactone-lactam from α-anilino- α -methyl-n-butyric acid (II).

1727 s, 1667 s, 1590 m, 1495 m, 1437 w, 1416 s, 1340 s, 1309 s, 1259 s, 1233 s, 1211 m, 1176 m, 1156 s, 1130 s, 1080 m, 1070 m, 1036 s, 1030 (shoulder), 1022 (shoulder), 1000 m, 976 w, 961 m, 855 m, 848 (shoulder), 812 w, 806 w, 761 s, 735 w, 702 s cm.$^{-1}$.

Assignments.

| | |
|---|---|
| 1745, 1727 cm.$^{-1}$ | Lactone C:O |
| 1661, 1667 cm.$^{-1}$ | Lactam C:O |
| 1595, 1590 cm.$^{-1}$ | Benzene ring. |

### α-Hydroxyisobutyranilide.

3279 *s*, 1667 *s*, 1608 *s*, 1555 *s*, 1504 *w*, 1490 *w*, 1449 *s*, 1416 *w*, 1361 *w*, 1333 *w*, 1325 *m*, 1235 *m*, 1190 *s*, 1167 (shoulder), 1156 *s*, 976 *s*, 926 *m*, 908 *m*, 761 *s*, 751 *s*, 693 *s* cm.$^{-1}$.

### Assignments.

| | |
|---|---|
| 3279 cm.$^{-1}$ | OH group. |
| 1667 cm.$^{-1}$ | Amide group. |

### Compound A (m.p. 206°) from α-anilino- α-phenylpropionic acid (III).

1757 *s*, 1669 *s*, 1587 *w*, 1488 (shoulder), 1287 *w*, 1264 *s*, 1224 *w*, 1212 *w*, 1116 *m*, 1103 *m*, 1071 *m*, 1058 (shoulder), 971 *w*, 840 *w*, 787 *w*, 776 *w*, 741 *w*, 726 *w*, 700 *w* cm.$^{-1}$.

### Compound B (m.p. 168°) from α-anilino- α-phenylpropionic acid (III).

1745 *s*, 1687 *s*, 1590 *w*, 1486 (shoulder), 1209 *w*, 1266 *s*, 1220 *w*, 1114 *m*, 1071 *m*, 977 *w*, 897 *w*, 772 *w*, 760 *m*, 720 *m*, 692 *m* cm.$^{-1}$.

## 10. TABULATED RESULTS.

### TABLE 6.

### STATIC SYSTEM.

α-Anilinoisobutyric acid (I).

| Product. | % yield (theory) | | % yield (weight) | |
|---|---|---|---|---|
| Run No. | (1) | (2) | (1) | (2) |
| Aniline | 35.0% | 35.3% | 18.4% | 18.4% |
| Unsat. acid | - | 0.8% | - | 0.4% |
| α-Hydroxyanilide | - | - | - | - |
| Lactone-lactam | 24.8% | 29.0% | 17.0% | 20.0% |

α-Anilino- α-methyl-n-butyric acid (II).

| Product. | % yield (theory) | | % yield (weight) | |
|---|---|---|---|---|
| Run No. | (4) | (5) | (4) | (5) |
| Aniline | 42.5% | 47.0% | 20.5% | 22.4% |
| Unsat. acid | 1.0% | 2.8% | 0.5% | 1.4% |
| α-Hydroxyanilide | - | - | - | - |
| Lactone-lactam | 21.0% | 26.7% | 15.0% | 19.0% |

The figures representing % theory are based on conversion into a single product; the figures representing % by weight are based on the original acid.

## TABLE 7.

### STATIC SYSTEM.

### α-Anilino- α-phenylpropionic acid (III).

| Product. | % yield (theory) | | % yield (weight) | |
|---|---|---|---|---|
| Run No. | (6) | (7) | (6) | (7) |
| Aniline ............. | 36.3% | 19.5% | 14.0% | 7.5% |
| Unsat. acid ......... | - | 5.0% | - | 3.0% |
| α-Hydroxyanilide .. | - | - | - | - |
| Lactone-lactam ...... | - | - | - | - |

### α-Anilinodiphenylacetic acid (IV).

| Product. | % yield (theory) | % yield (weight) |
|---|---|---|
| Run No. | (8) | (8) |
| Aniline ............. | 27.0% | 8.3% |
| Unsat. acid ......... | - | - |
| α-Hydroxyanilide .. | - | - |
| Lactone-lactam | - | - |

The figures representing % theory are based on conversion into a single product; the figures representing % by weight are based on the original acid.

## TABLE 8.

### Semi-micro Flow Reactor (540°).

| Pyrolysand. | α-Anilinoisobutyric acid | Lactone-lactam |
|---|---|---|
| Run No. | (10) | (11) |
| Amount pyrolysed | 300.0 mg. | 300.0 mg. |
| Ml. of gas formed (N.T.P.) | 37.0 | 32.0 |
| Gas formed % theory | 98.5 | 58.6 |
| **Gas analysis (%).** | | |
| $CO_2$ | 11.8 | 9.8 |
| CO | 33.0 | 27.9 |
| Unsat. hydrocarbons | 1.4 | 3.0 |
| $H_2$ | 3.4 | 3.7 |
| **% theory** | | |
| $CO_2$ | 20.8 | 11.0 |
| CO | 58.0 | 31.2 |
| **Ratio** $CO:CO_2$ | 2.8/1 | 2.9/1 |

## TABLE 9.

### Semi-micro Flow Reactor ($540^{\circ}$).

| Pyrolysand. | α-Anilino- α-methyl-n-butyric acid | Lactone-lactam |
|---|---|---|
| Run No. | (12) | (13) |
| Amount pyrolysed ............ | 300.0 mg. | 300.0 mg. |
| Ml. of gas formed (N.T.P.).. | 34.0 | 48.0 |
| Gas formed % theory ........ | 97.0 | 98.0 |
| **Gas analysis (%).** | | |
| $CO_2$ ....................... | 12.6 | 8.2 |
| CO ....................... | 25.2 | 39.2 |
| Unsat. hydrocarbons ........ | 2.3 | 2.9 |
| $H_2$ ......................... | 2.2 | 4.3 |
| **% theory** | | |
| $CO_2$ ........................ | 21.2 | 12.9 |
| CO ........................ | 42.5 | 61.5 |
| Ratio $CO:CO_2$ ................ | 2/1 | 4.8/1 |

## REFERENCES.

1. Young, Frostick, Sanderson and Hauser, J. Amer. Chem. Soc., 1950, 72, 3635.
2. Boesne and Young, U.S.P. 2,395,800/1946; B.P.615,523/1949.
3. Oppenheim and Precht, Ber. dtsch. chem. Ges., 1876, 9, 325.
4. Hurd and Blunck, J. Amer. Chem. Soc., 1938, 60, 2419.
5. Blades and Murphy, ibid., 1952, 74, 1039.
6. Blades, Canad. J. Chem., 1953, 31, 418.
7. Alexander and Mudrak, J. Amer. Chem. Soc., 1950, 72, 1810 and 3194; ibid., 1951, 73, 59.
8. Stevens and Richmond, ibid., 1941, 63, 3132.
9. Arnold, Smith and Dodson, J. Org. Chem., 1950, 15, 1256.
10. Bailey and Barclay, ibid., 1956, 21, 328.
11. Hughes, Ingold, et al., J. Chem. Soc., 1948, 2097.
12. Bailey and King, J. Amer. Chem. Soc., 1955, 77, 75.
13. Bailey, Hewitt and King, ibid., 1955, 77, 357.
14. Birch, Kon and Norris, J. Chem. Soc., 1923, 1361.
15. Bailey and Rosenberg, J. Amer. Chem. Soc., 1955, 77, 73;also Bailey, Rosenberg and Young, ibid., 1954, 76, 2251.

16. v. Pelt Jr., and Wibaut, *Rec. trav. chim.*, 1941, **60**, 55.

17. Houtman, Steenis and Heertzes, *ibid.*, 1946, **65**, 781.

18. Barton, Head and Williams, *J. Chem. Soc.*, 1952, 453.

19. *Annalen*, 1875, **179**, 296.

20. Bailey and Nicholas, *J. Org. Chem.*, 1956, **21**, 854.

21. *Idem.*, *ibid.*, 1956, **21**, 648.

22. Bailey and King, *ibid.*, 1956, **21**, 858.

23. Gold, *J. Amer. Chem. Soc.*, 1946, **68**, 2544.

24. Paul and Tchelitcheff, *Compt. rend.*, 1951, **233**, 1116.

25. Allan, Forman and Ritchie, *J. Chem. Soc.*, 1955, 2717.

26. Bilger and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 823.

27. Peytral, *Bull. Soc. chim. France*, 1922, (4), **31**, 118.

28. Bennet, Deans, Harris, Ritchie and Shim, *J. Chem. Soc.* 1958, 4508.

29. Muller and Peytral, *Compt. rend.*, 1924, **179**, 831.

30. Peytral, *Bull. Soc. chim. France*, 1925, **37**, 562.

31. Laner and Kelburn, *J. Amer. Chem.* Soc., 1937, **59**, 107.

32. Claisen, *Ber. dtsch. chem. Ges.*, 1912, **45**, 3157.

33. Skraup and Beng, *ibid.*, 1927, **60**, 942.

34. Skraup and Beifuss, *ibid.*, 1927, **60**, 1070.

35. See e.g. Chapman, *J. Chem. Soc.*, 1927, 1743, Schonberg *et al.*, *Ber.*, 1930, *63*, 178; *Annalen*, 1930, *483*, 107; Wiberg *et al.*, *J. Amer. Chem. Soc.*, 1953, *75*, 2665; 1955, *77*, 2205, 2774; White, *ibid.*, 1955, *77*, 6011, 6014; Al-Kazami, Tarbel and Plant, *ibid.*, 1955, *77*, 2479.

36. *Annalen*, 1901, *318*, 198.

37. Calvin and Lemman, *J. Amer. Chem. Soc.*, 1947, *69*, 1232.

38. Roberts and Bowden, *Rec. Trav. Chim.*, 1930, *49*, 665.

39. Anschutz, *Ber.*, 1885, *18*, 1945.

40. Lacey, *J. Chem. Soc.*, 1954, 827.

41. Makinnon and Ritchie, *ibid.*, 1957, *498*, 2564.

42. Allan, Ph.D. Thesis, Glasgow University, 1956.

43. Claisen and Hasse, *Ber.*, 1903, *36*, 3674; Dieckmann and Stein, *ibid.*, 1904, *37*, 3370.

44. Meinent and Hurd, *J. Amer. Chem. Soc.*, 1930, *52*, 4549; Hurd and Meinent, *ibid.*, 1931, *53*, 292; Hurd and Christ, *ibid.*, 1937, *59*, 2161.

45. Chitwood, U.S.P. 2,251, 983/1949.

46. Hurd and Tallyn, *J. Amer. Chem. Soc.*, 1925, *47*, 1779.

47. McNesby, Davis and Gordon, *ibid.*, 1954, *76*, 823; *idem.*, *J. Chem. Phys.*, 1953, *21*, 956.

48. Rice and Hertzfeld, *J. Amer. Chem. Soc.*, 1934, 56, 284.

49. Steacie, "Atomic and Free Radical Reactions", Reinhold.

50. Allan, J. Amer. Chem. Soc., 1941, 63, 708.

51. McNesby and Gordon, ibid., 1954, 76, 4196.

52. Rice and Wall, ibid., 1925, 47, 1779.

53. Peytral, Bull. Soc. chim., 1921 (4), 31, 122.

54. Rodd, "Chemistry of Carbon Compounds", Elsevier, London, 1954, Vol IIa, p.5; Favorsky and Boshowsky, Annalen, 1912, 390, 122; Favorsky, Bull. Soc. chim. France, 1936, (v), 3, 1727.

55. Hurd and Bennett, J. Amer. Chem. Soc., 1929, 51, 1197

56. Hurd, "Pyrolysis of Carbon Compounds", Chemical Catalog Co., New York, 1929, p.258; Hurd, Greengard, and Roe, J. Amer. Chem. Soc., 1939, 61, 335.

57. Levine, Conroy Adams and Hauser, ibid., 1947, 69, 2649.

58. Leser, Compt. rend., 1905, 141, 1632.

59. Idem, Ann. Chem. (France), 1912, 26, 233.

60. Fisher, Ind. Eng. Chem., 1942, 34, 473.

61. Burton, Chem. and Ind., 1954, 576.

62. Davidson and Newman, J. Amer. Chem. Soc., 1952, 74, 1515.

63. Bedoukian, ibid., 1945, 67, 1430.

64. Nesmeyanov, Lutsenko and Tumanova, *Izvest. Akad. Nauk, S.S.S.R., Otdel. khim. Nauk*, 1949, 601.

65. Hauser, Ringler, Swarmer and Thomson, *J. Amer. Chem. Soc.*, 1947, *69*, 2649.

66. Sabatier and Mailhe, *Compt. rend.*, 1904, *138*, 1321.

67. Zelinsky, *Ber.*, *34*, 2880.

68. Amer. Petroleum Inst., Research Project 44, Nat. Bur. Stand., Washington, Serial No.897, 1949.

69. *Ibid.*, Serial No.45, 1943.

70. Werner, *Ber.*, 1909, *42*, 4235; Kaufmann, King and Haung, *ibid.*, 1942, *75*, 1201.

71. Burns, Jones and Ritchie, *J. Chem. Soc.*, 1935, *400*, 714; Ritchie, *ibid.*, 1935, 1054.

72. Ritchie, Jones, Burns and I.C.I. B.P. 425, 885; U.S.P. 2,183,357,2,265,184.

73. Bagard, *Bull. Soc. chim., France*, 1907, *1*, 307.

74. Betts, Muspartt and Plant, *J. Chem. Soc.*, 1927, 1310.

75. Plant and Facer, *ibid.*, 1925, *127*, 2037.

76. Bain and Ritchie, *ibid.*, 1955, 4402.

77. Bischoff and Mintz, *Ber.*, 1892, *25*, 2327.

78. Tiemann, *Ber.*, 1882, *15*, 2042.

79. Strecker, *Annalen*, 1850, *75*, 27; Cocker and Lapworth, *J. Chem. Soc.*, 1931, 1391; Fischer and Leucks, *Ber.*, 1902, *35*, 3787.

80. Bellamy, "Infra-red spectra of complex molecules", Methuen, London, 1958, p.26.

81. Bruylants, Ernould and Dekoker, *Bull. Soc. chim. Belg.*, 1925, *37*, 562.

82. Beilstein and Wiegand, *Ber.*, 1884, *17*, 2261.

83. Ssem, *J. der Russischen Physckalisch - chemischen Gesellschaft*, *23*, 208; *Chem. Zentr.*, 1899, *1*, 1071.

84. Blaise, *Compt. rend.*, 1904, *138*, 697.

85. McKenzie and Wood, *J. Chem. Soc.*, 1919, *115*, 834.

86. Hurd, *op. cit.*, p.434.

87. Sleigh, *J. Soc. Chem. Ind., Lond.*, 1937, 15, 430.

88. Siggia, "Quantitative Organic Analysis", Wiley and Sons, Inc., New York, 1st Edn., p.71.

89. Walther and Hubner, *J. Prakt. Chem.*, 1916, *93*, 119.

90. Stohl, *Ber.*, 1910, *43*, 2472.

91. Welch and Clemo, *J. Chem. Soc.*, 1928, 2629.

92. Brandt and Bucherer, *J. Prakt. Chem.*, 1934, *140*, 136.

93. Bischoff, *Ber.*, *30*, 2318.

94. Mjoen, *Ber.*, 1897, *30*, 1227; Fittig and Engelhorn, *Annalen*, *200*, 70.

95. Remberg, Dixon and Fisher, *J. Amer. Chem. Soc.*, 1945, *67*, 209.

96. v. Braun *et al*. Ber., 1934, 67B, 269; C.A., 28, 2328

97. Staudinger and Ruzicka, *Annalen*, 1911, *380*, 296.