STUDIES IN PYROLYSIS

PART I : Pyrolytic Formation of p-Diacetylbenzene
from Vinyl p-Acetylbenzoate.

PART II : Pyrolysis of Anilino-nitriles and
Benzoyloxy-nitriles.

Thesis

by

Adam Ellis Wright

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fulfilment of the regulations governing the award
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The work described in Part I of this thesis

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SUMMARY

PART I: Resulting from the work of Allan, Iengar and
Ritchie[1] on the pyrolysis of 2-benzoyloxyethyl
terephthalate as a model compound for the study of the
pyrolysis of polyethylene terephthalate ("Terylene"),
vinyl p-acetylbenzoate has been prepared and characterised;
on pyrolysis at ca.500° in the vapour phase, it yields a
pyrolysate containing p-diacetylbenzene as a major compon-
ent. Other predictable products were also observed (carbon
monoxide and dioxide, acetylene, p-acetylbenzoic acid,
acetophenone and an acid anhydride). The various break-
down routes and their products are discussed.

PART II: Following the work of Bain[2] on the pyrolysis of
anilino-nitriles at ca.200-250°, 1-anilino-1-
cyanocyclohexane and the cis-trans isomeric pair 1-anilino-
1-cyano-2-methylcyclohexane have been prepared and pyrolysed
at 400-600°. These compounds decompose thermally by a
primary reversible dissociation to hydrogen cyanide and the
corresponding anil at the temperatures used. There also
takes place to a minor extent a secondary self-condensation
reaction between the anils formed producing aniline and a
condensation product/ identified /as 2-cyclohex-1-enyl-cyclo-
hexylideneaniline and 2-methyl-6, 2-methylcyclohex-1-enyl-
cyclohexylideneaniline. Carbazole has also been detected

in these pyrolysates, produced by secondary decomposition
of aniline.   The rates of decomposition of cis and trans 1-
anilino-1-cyano-2-methylcyclohexane have been studied and
the cis isomer has been found to be considerably more stable
than the trans.   The trans isomer has also been found to be
converted to a large extent to the cis during the course of
the pyrolysis.   These results are discussed in the light
of the molecular conformations of the isomers and it is
suggested that the anil 2-methylcyclohexylideneaniline
exists in interconvertible syn and anti forms.

The cis and trans isomers of 1-benzoyloxy-1-cyano-
2-methylcyclohexane have also been prepared and pyrolysed.
The results obtained show that elimination of benzoic acid
takes place by a cis eliminatory mechanism, following the
Saytzeff rule.   These results are discussed in the light
of related work in this field.

The structural conformations of both pairs of
isomers have been investigated and established from
physical and chemical evidence.

PART I.

PART I: Pyrolytic Formation of p-Diacetylbenzene
from Vinyl p-Acetylbenzoate.

General Introduction

Smith[3] first demonstrated that esters could be decomposed by heat yielding an acid and an olefin. Since then, the pyrolysis of esters has been widely investigated and considerable controversy has arisen, concerning the possible /4 decomposition routes and their mechanism.

A survey of the literature on the pyrolysis of carboxylic esters shows that esters and their behaviour on pyrolysis may be divided into two classes. The first consists of alkyl and alkenyl carboxylates which have available β-hydrogen atoms. These decompose mainly by an alkyl-oxygen or alkenyl-oxygen scission, yielding a carboxylic acid and an olefin or acetylene respectively, thus:

Alkyl $R.CO_2CH_2CH_2.R_1 \longrightarrow R.CO_2H + CH_2:CHR_1$

Alkenyl $R.CO_2CH:CH.R_2 \longrightarrow R.CO_2H + CH:C.R_2$

The second class consists of esters which have no available β-hydrogen atoms. These esters require higher temperatures before decomposition takes place, and the products of their pyrolysis suggest a free radical mechanism, the main breakdown route being an acyl-oxygen scission forming two carbonyl compounds. Few esters, however, pyrolyse exclusively by the one route, minor products formed by competitive breakdown

routes and rearrangement reactions usually being present in small quantities in most pyrolysates. Secondary breakdown of the products of primary scission also often takes place, and occasionally primary breakdown products interact yielding secondary compounds of high molecular weight whose presence may be difficult to explain. These secondary products must be distinguished from the products of primary scission in any interpretation of results. The various types of breakdown routes are discussed below under the general classification of headings used in these laboratories.

Alkyl-oxygen scission A[1]

In this type of scission, esters containing one or more β-hydrogen atoms split into a carboxylic acid and an olefin.

$$R.CO_2 - C - C - H \longrightarrow R.CO_2H + C : C \ldots \ldots A^1$$

Ethyl acetate[4] decomposes by this route to give mainly acetic acid and ethylene.

$$Me.CO_2Et \longrightarrow Me.CO_2H + CH_2:CH_2 \quad \ldots \ldots \ldots A^1$$
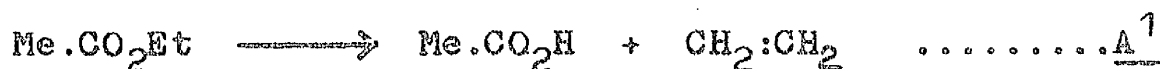
In many cases decomposition by this route takes place in almost quantitative yield under the correct conditions, and is often used as a method for preparing olefins.

A comparative study of t-, s-, and n-alkyl esters by Hurd and Blunck[5] has shown that the thermal stability of these esters decreases as the number of available β-hydrogen atoms increases, as in the series:

$$R.CO_2CH_2.Me > R.CO_2CH.Me_2 > R.CO_2.CMe_3$$
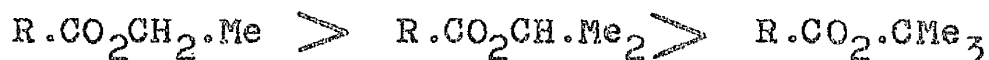
Thus, pyrolysis of t-butyl acetate, isopropyl acetate and ethyl acetate gave the following results.

$$AcO.CMe_3 \xrightarrow{360^o} AcOH + CH_2{:}CMe_2 \quad \dots\dots\dots\dots A[1]$$
(only products)

$$AcO.CHMe_2 \xrightarrow{430\text{-}460^o} AcOH + CH_2{:}CHMe \text{ (main products)}\dots A[1]$$
$$+ MeCHO + COMe_2 + CO \text{ (by-products)}$$

$$AcO.CH_2Me \xrightarrow{525\text{-}530^o} AcOH + CH_2{:}CH_2 \text{ (main products)}\dots A[1]$$
$$+ MeCHO + H.CHO + Ac_2O + CH_4$$
$$+ H_2 + CH_2{:}CO \qquad \text{(by-products)}$$
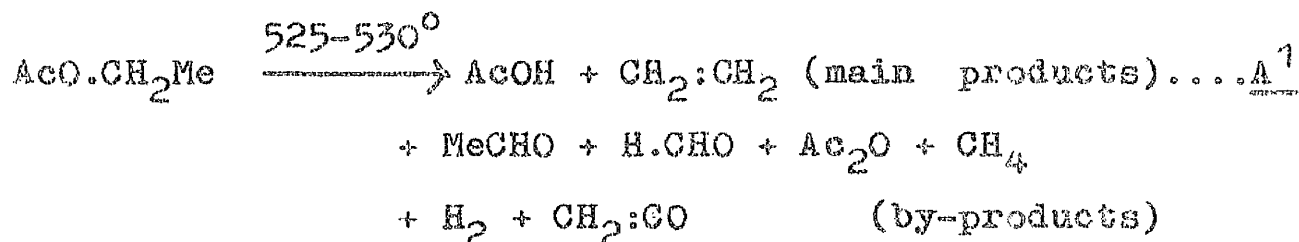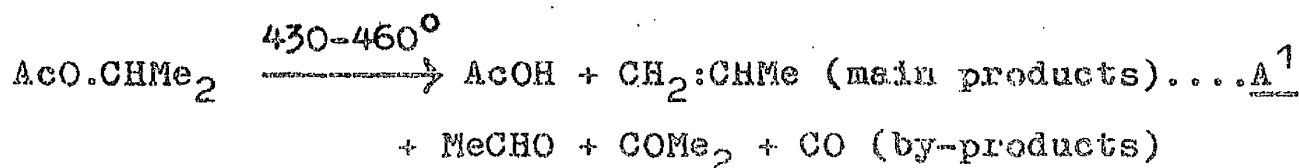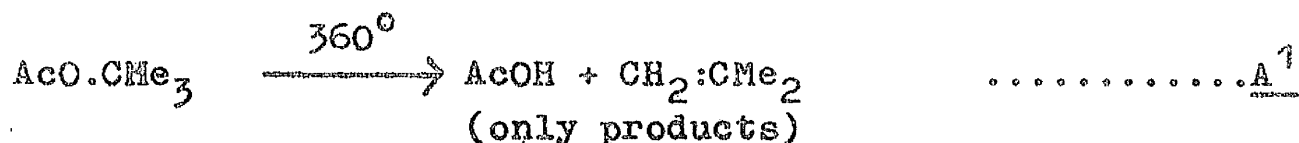
These results also illustrate the increasing complexity of breakdown routes as the temperature of pyrolysis is increased, though alkyl-oxygen scission remains the predominating route. The pyrolysis of secondary and tertiary esters may take place either according to the Hofmann rule[6] in which elimination takes place to produce the least highly alkylated olefin or by the Saytzeff rule[7] in which the most highly alkylated olefin is produced.

Following the work of Bailey and King[8] and Bailey, Hewitt, and King[9], who claimed that unsymmetrical secondary

and tertiary esters pyrolysed under mild conditions produced the least highly alkylated olefin exclusively in accordance with the Hofmann rule, the direction of elimination in ester pyrolysis has been extensively studied, thus:

$$AcO.CHMe.CHMe_2 \longrightarrow AcOH + CH_2:CH.CHMe_2 \quad \ldots\ldots A^1$$

$$\ldots\ldots A^1$$
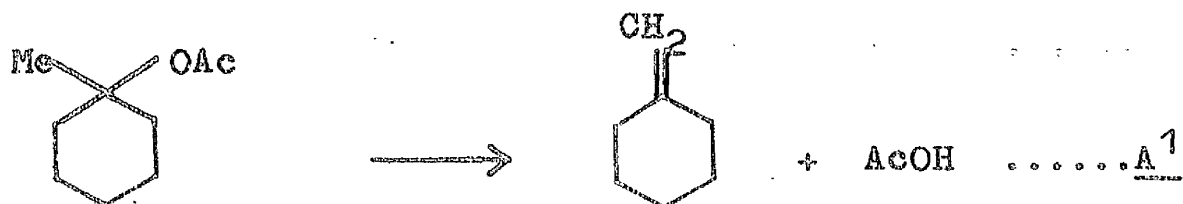
These results were contrary to those of Haay and Pines[10], who found that when s-butyl acetate was pyrolysed at 410-525° the concentration of 1-butene varied from 55-69%, approximating to the figure expected from statistical elimination of the neighbouring hydrogen atoms. The remainder of the pyrolysate was _cis_ and _trans_ 2-butene in proportions approximating the thermodynamic equilibrium mixture. The previous example (pyrolysis of 1-methylcyclo-hexyl acetate) has been intensively studied since the alternative product of pyrolysis, 1-methylcyclohexene, has the less strained structure and is the more thermodynamically stable.

Royals[12], reinvestigating the work of Bailey _et al._ by using the more accurate analytical techniques of gas-liquid chromatography, found that all secondary and tertiary acetates pyrolyse to mixtures of olefins, and concluded that Bailey's work was in error owing to his basing his results on infrared spectroscopy. The work of Royals and other

workers has established that methylenecyclohexane is formed in only about 21% yield by pyrolysis of 1-methylcyclohexyl acetate.

21%   79%
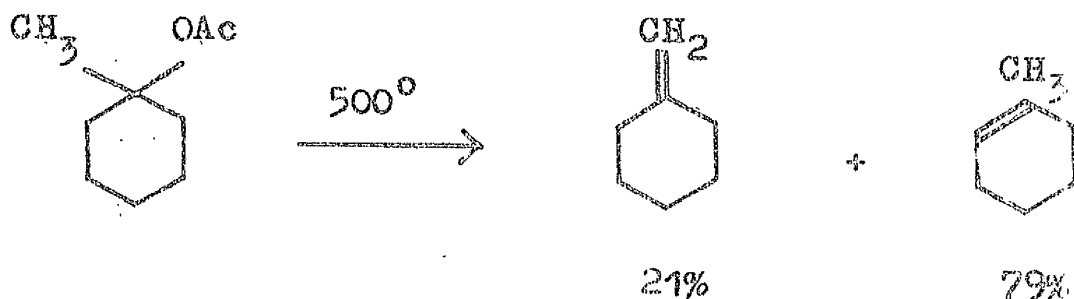
Eglinton and Rodger[13], pyrolysing the acetates of 1-methyl-cyclopentanol, cyclohexanol, and cycloheptanol at 450°, found no specificity with regard to exo- and endo-isomers. The main product in all cases is the endo-isomer. Benkeser and Hazdra[14] found that the acetate and xanthate of alkylcyclo-hexylcarbinols both gave similar olefin distributions, and concluded that the unifying feature of their results was the preferred formation of the more thermodynamically stable olefin. Similarly, De Puy and Leary[15] concluded that in some cases the thermodynamic stability of the two olefin products can be so widely different as to become the over-riding factor in determining the direction of elimination.

Froemsdorff et al.[16], pyrolysing a series of aliphatic acetates where the olefins produced were of comparable stability, found that the proportions of the olefins formed were close to the theoretical statistical values.

		1-olefin	2-olefin	1-olefin calcd. statistically
AcO.CHMeEt	$\xrightarrow{450^{\circ}}$	57%	43%	60%
AcO.CHMe.CHMe$_2$	$\xrightarrow{400^{\circ}}$	80%	20%	75%

Following the results of the workers quoted above, Benkeser, Hazdra and Burrows[17] pyrolysed the acetates and xanthates of the series of alcohols $R'O.CHEt.CH_2R$ where $R = CH_3$, C_2H_5, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$ and $R' = Ac$ or CS_2Me and concluded that ester pyrolysis is governed by an interplay of three factors: (1) statistical effects, (2) relative thermodynamic stability of the olefin products, (3) steric effects, which help or hinder the formation of the cyclic coplanar transition state.

Effect of Temperature on the Direction of Elimination.

Houtman et al.[18] have found that the temperature of pyrolysis has an effect on the olefin distribution in the pyrolysis of s-butyl acetate.

$$AcO.CHMeEt \begin{cases} \xrightarrow{500^{\circ}} CH_2:CHEt + MeCH:CHMe \\ \qquad\qquad 56\% \qquad\qquad 44\% \\ \xrightarrow{400^{\circ}} CH_2:CHEt + MeCH:CHMe \\ \qquad\qquad 25\% \qquad\qquad 75\% \end{cases}$$
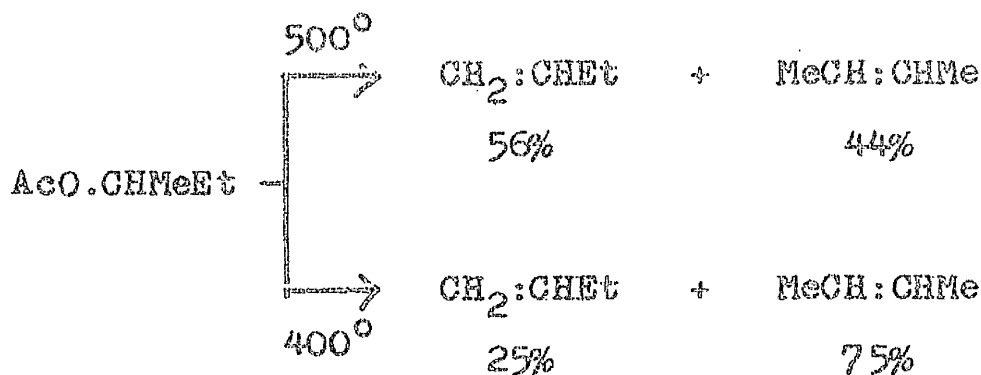
The Hofmann rule holds at the higher temperature, the Saytzeff rule at the lower. More recently, Bailey and Hale[19]

obtained similar results for t-amyl acetate.

$$AcO.CMe_2Et \xrightarrow{400^\circ} Me_2C:CH.Me + CH_2:CMeEt$$

$$\phantom{AcO.CMe_2Et \xrightarrow{400^\circ} Me_2C:CH.Me} 26\% 74\%$$

$$AcO.CMe_2Et \xrightarrow{225^\circ} Me_2C:CH.Me + CH_2:CMeEt$$

$$\phantom{AcO.CMe_2Et \xrightarrow{225^\circ} Me_2C:CH.Me} 58\% 42\%$$
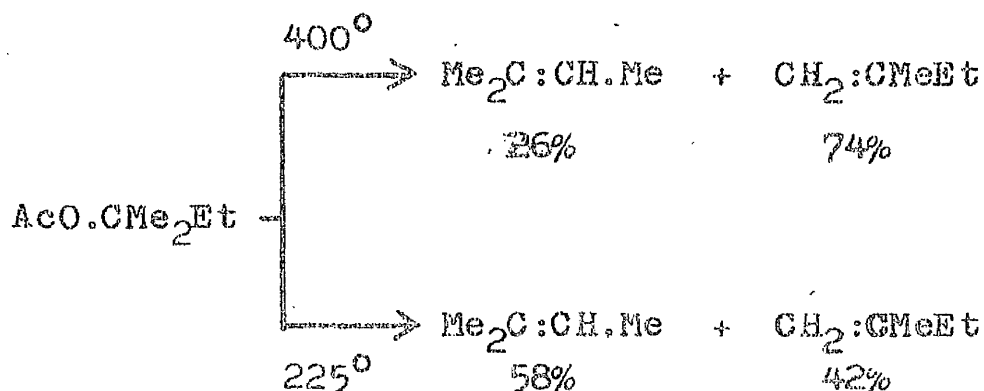
These results must remain in some doubt, since Froemsdorff et al.[16], repeating the latter pyrolysis, found similar olefin distributions at all temperatures. Bailey[19] has suggested that Saytzeff elimination is favoured in low-temperature liquid-phase pyrolysis, and Hofmann elimination in high-temperature vapour phase pyrolysis, and cites the example of dimethylisopropylcarbinyl acetate which at 400° gives 88% of 2,3-dimethylbut-1-ene

$$AcO.CMe_2Et \longrightarrow CH_2:CMe.CHMe_2$$

$$88\%$$

$$+$$

$$Me_2C:CMe_2$$

$$12\%$$
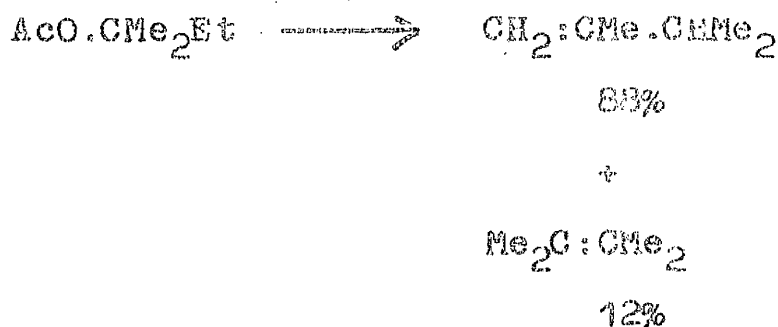
It should be noted, however, that these figures are very close to the statistically predicted figures of 86% and 14%.

Effect of Substituent Groups on the Direction of Elimination.

Bailey and Nicholas[20] investigating the effect of polar

groups substituted in the alkyl portion of the molecule found that β-methoxy or β-dimethylamino groups did not alter the direction of elimination.   Extending their investigations, Bailey and King[8] examined the introduction of unsaturated electron-withdrawing groups into the β-position of the alkyl group and found that the direction of elimination tended to revert to Saytzeff elimination.   Thus, β-phenylisopropyl acetate at 450° produces a mixture of olefins containing 75% 1-phenylprop-1-ene and 25% allylbenzene.

$$AcO.CHMe.CH_2Ph \xrightarrow[450°]{} PhCH:CHMe + PhCH_2.CH:CH_2$$
$$75\% \qquad 25\%$$
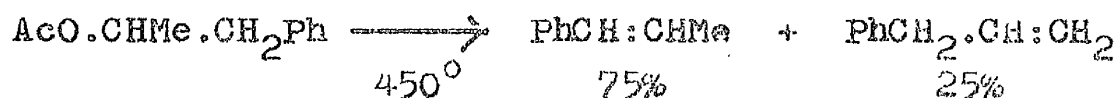
The introduction of a second phenyl group into the molecule caused exclusive Saytzeff elimination.   Thus, β,β-diphenyl-isopropyl acetate yields only 1,1-diphenylprop-1-ene, completely reversing the direction of elimination.

$$AcO.CHMe.CH_2Ph \xrightarrow{} AcOH + MeCH:CPh_2$$

Similarly, Gold[21] has found that the nitro group affects the direction of elimination;   β-nitroisopropyl acetate yields 1-nitroprop-1-ene, not 1-nitroprop-2-ene.

$$AcO.CHMe.CH_2NO_2 \xrightarrow{} MeCH:CH.NO_2 + AcOH$$

Eliminations from Cyclic Systems

While the factors affecting elimination reactions in aliphatic esters are now well understood, eliminations from cyclic systems would appear to be of a slightly different

character. Barton[22] has concluded that the marked prefer-
ence for Saytzeff elimination from such systems was the
decreasing activation energy of unimolecular elimination HX
(where X is the electronegative ion, OH, Cl, Br, I, etc.) in
the following order:

$$primary \; > \; secondary \; > \; tertiary$$
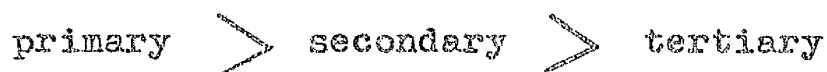
He considered that these decreases in activation energy were
the main factors influencing the reaction velocity and causing
preferential elimination towards the bridgehead. Thus,
Barton et al.[22] have shown that (-)-menthyl benzoate on
pyrolysis yields a mixture of two isomeric olefins, (+)-p-3-
menthene and (+)-p-2-menthene
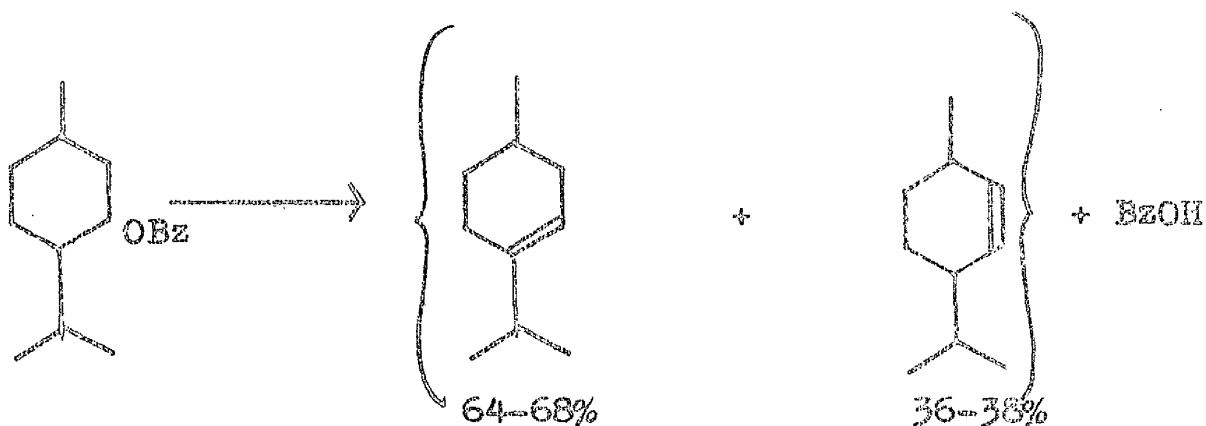
An even more striking example[24] is the almost exclusive
Saytzeff elimination of acetic acid from trans-1-acetoxy-2-
acetoxycyclohexane, giving 1-acetoxycyclohex-1-ene.
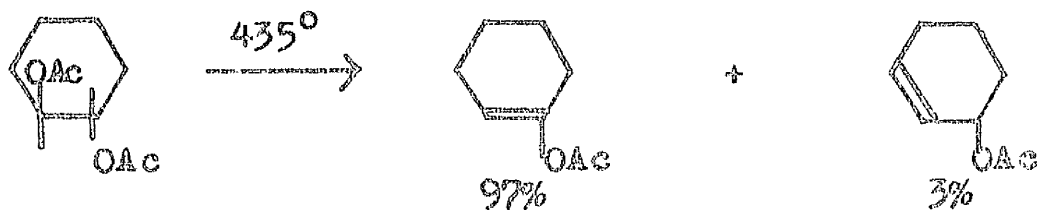
Recently, however, there have been many conflicting results
in this field.   These will be discussed later in relation
to the analogous work of the author.

Mechanism of the Elimination Reaction.

The mechanism of olefin formation, proposed by Hurd
and Blunck[5] is a molecular mechanism involving the formation
of a transient six-membered ring by hydrogen bonding of the
β-hydrogen atom.
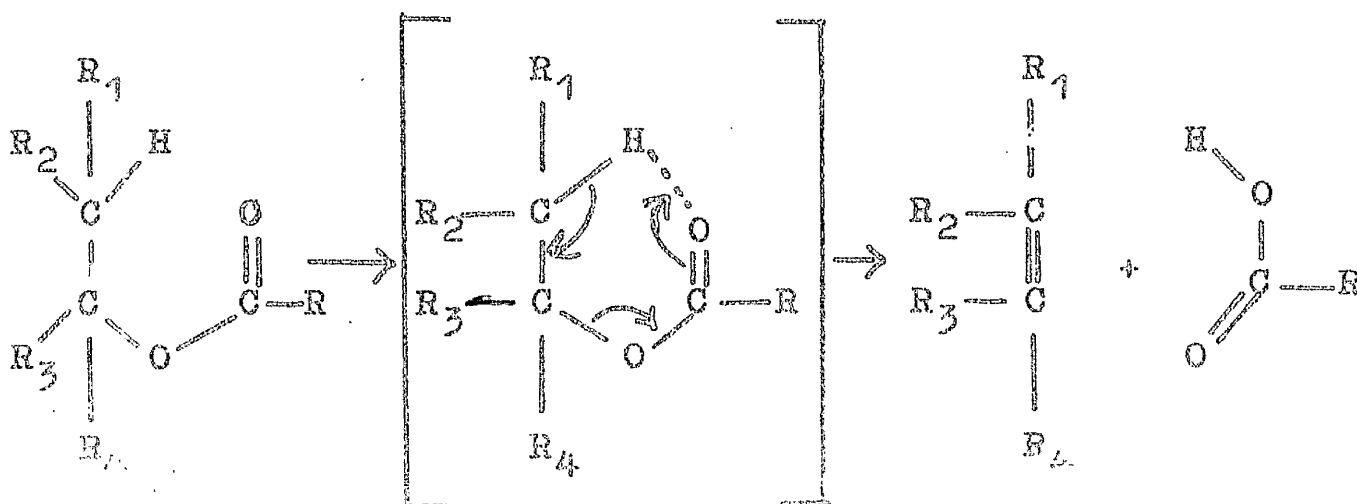
This mechanism, though criticised by Houtman et al.[18] on the
grounds that there is no evidence for hydrogen bonding at
high temperatures, is now generally accepted.   Alexander and
Mudrak[25,26] also favoured a cyclic transition state in elim-
inations from xanthates.   The mechanism has also been
supported by Arnold, Smith, and Dodson,[27] from their work on
cyclic acetates.   De Puy et al.[16] have shown that the carbon-
hydrogen bond is being broken in the transition state but that

the acidity of the hydrogen atom being removed is not of
primary importance, though this may not be true for extremely
acidic hydrogens.   Bordwell and Landis[28] considered that the
transition state is best described as one in which both carbon
hydrogen bonds and carbon-oxygen bonds are to a large extent
broken and a great deal of double bond character has developed
but in which no appreciable change-separation is evident.

Influence of the Acidic Portion of the Ester.

Although most pyrolysis work has been done with
acetates, other acid esters are occasionally preferred. Thus,
Ritchie[29] pyrolysed benzoates, and Barton[22] has reviewed the
pyrolysis of the benzoates of several sterols.   Benzoates may
have advantages over acetates in this work, as they are more
easily purified and characterised owing to their higher melting
point.   It has been found[30,31] that benzoates give higher
conversions than acetates, and that the extent of pyrolysis is
directly related to the pKa of the corresponding acid.

cis Eliminations from Cyclic Esters.

Hurd[32] first pointed out that the formation of C_3O_2 by
the pyrolysis of the diacetate of tartaric anhydride must
proceed via acetoxy maleic anhydride formed by cis elimination
of acetic acid.

$$\text{(structure)} \longrightarrow \text{(structure)} + \text{AcOH}$$
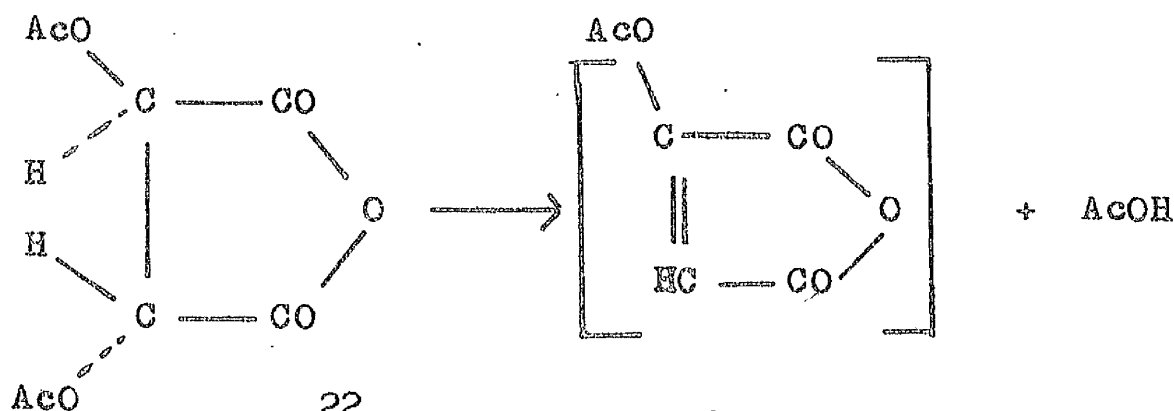
Barton[22] has concluded from a survey of the elimination
reactions of a large number of xanthate esters that as a gener-
al rule for elimination by unimolecular thermal decomposition,
the four centres of elimination must lie suitably disposed
with respect to each other in one plane to ensure the mini-
misation of the activation energy, and therefore cis stereo-
chemistry must be demanded in the reactant.   Thus iso and
neo thujyl alcohols give only products formed by cis
elimination.

iso
$\xrightarrow{130^{o}}$
α thujene

neo
$\xrightarrow{183^{o}}$
β thujene
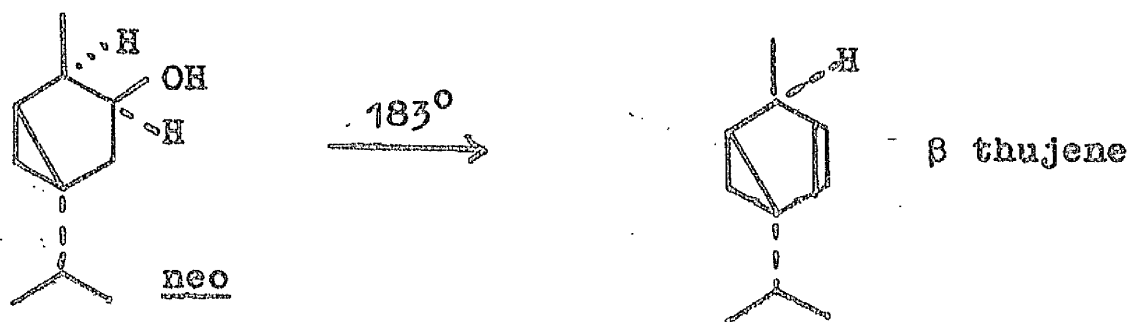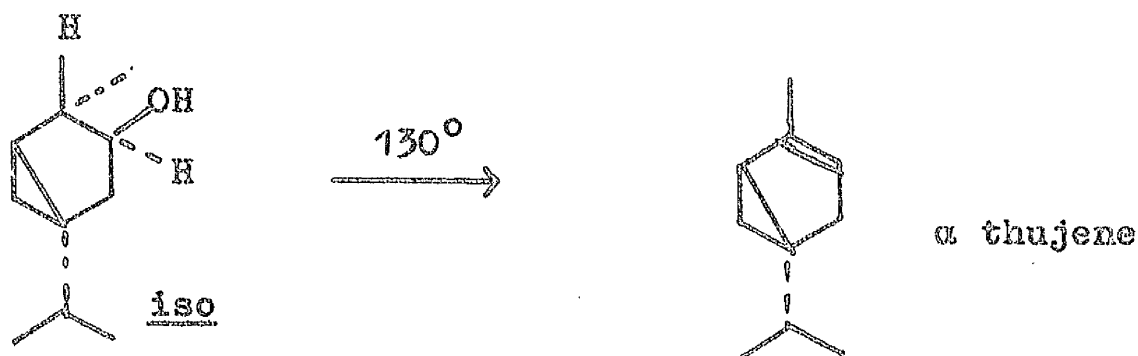
The concept of <u>cis</u> elimination will be discussed more fully later in this work in the light of related results by recent workers.

Alkenyl-Oxygen Scission A^2

This type of scission, which may be regarded as a subdivision of the $\underline{A}^1$ scission is confined to alkenyl esters which may break down to give a carboxylic acid and an acetylene.

$$RCO_2 \overset{|}{\underset{\alpha}{C}} : \overset{|}{\underset{\beta}{CH}} \xrightarrow{\hspace{2cm}} RCO_2H + \overset{|}{C} : \overset{|}{C} \quad \ldots\ldots\ldots\underline{A}^2$$

The mechanism for this scission is probably similar to that of the $\underline{A}^1$ scission. Vinyl benzoate[33] has been shown to break down by several competitive routes, among them being a minor scission to benzoic acid and acetylene.

$$BzOCH:CH_2 \xrightarrow{\hspace{0.5cm}400^o\hspace{0.5cm}} BzOH + CH:CH \quad \ldots\ldots\ldots\underline{A}^2$$

Similarly vinyl acetate gives small amounts of acetic acid and acetylene on pyrolysis.

$$AcO.CH:CH_2 \xrightarrow{\hspace{2cm}} AcOH + CH:CH \quad \ldots\ldots\ldots\underline{A}^2$$

Alkyl-Oxygen Scission in Methyl Esters A^o

Methyl esters, having no β-hydrogen atoms, thus preventing alkyl-oxygen scission, require much higher temperatures before decomposition takes place. Alkyl-oxygen scission

has however been shown to occur in certain methyl esters at very high temperatures yielding an acid and an olefin as in a normal A^1 scission, the olefin presumably being formed via a transient diradical.

$$RCO.OCH \longrightarrow RCO.OH + \left[\overset{|}{\underset{|}{>C}} \right] \qquad \ldots\ldots\ldots A^0$$

$$RCO.OH + \tfrac{1}{2}\, \overset{|}{\underset{|}{C}} : \overset{|}{\underset{|}{C}}$$
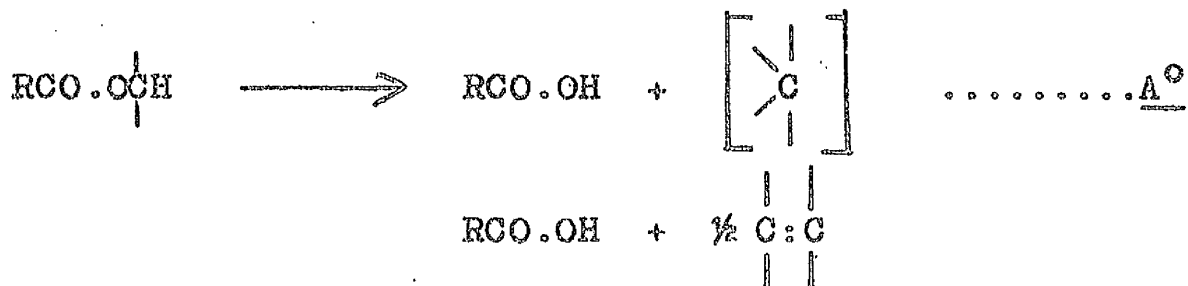
This type of scission has been designated $\underline{A}^0$. Peytral[34] has shown that methyl acetate at $1100^{\circ}C$ gives small amounts of acetic acid and ethylene although the predominating reaction is a $\underline{B}^2$ acyl-oxygen scission.

$$AcO.Me \xrightarrow{1100^{\circ}} \begin{cases} AcOH + \tfrac{1}{2}\,CH_2:CH_2 & \ldots\ldots\ldots \underline{A}^0 \\ MeCHO + H.CHO \longrightarrow 2\,CO + CH_4 + H_2 & \ldots\ldots \underline{B}^2 \end{cases}$$
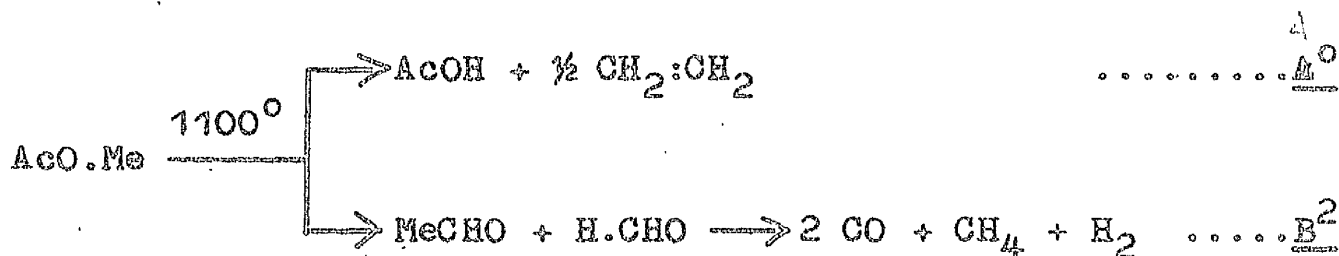
$\underline{A}^0$ scission has occurred only as a minor breakdown route in all recorded cases.

Acyl-Oxygen Scission

An ester with no β-hydrogens usually requires a higher temperature before rupture of the molecule takes place owing to its increased thermal stability. The predominating reaction when breakdown of the ester does occur is an acyl-oxygen scission. In this type of scission, rupture occurs between the acyl group of the ester and the ether oxygen

followed by transfer of a hydrogen atom from the acyl group
or from the alkyl portion of the molecule. These types of
breakdown are designated $\underline{B}^1$ and $\underline{B}^2$ respectively.

B^1 Scission

This type of scission occurs rarely in ester pyrolysis:
in it a keten and a hydroxyl compound are formed

$$>CH.CO - OCH< \longrightarrow >C:C:O + HO.CH< \quad \ldots\ldots\ldots\underline{B}^1$$
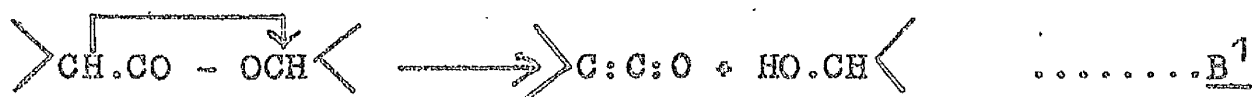
This route takes place only to a minor extent if at all. An
important exception is the decomposition of phenyl acetate
which breaks down entirely by a $\underline{B}^1$ scission forming keten and
phenol.

$$AcO.Ph \longrightarrow CH_2:C:O + HOPh \quad \ldots\ldots\ldots\underline{B}^1$$

This pyrolysis has been extensively studied[5] as a method for
the preparation of keten. Similarly phenyl propionate
decomposes at 600° to give small amounts of methyl keten and
phenol.

$$MeCH_2.COOPh \longrightarrow MeCH:C:O + HOPh \quad \ldots\ldots\ldots\underline{B}^1$$
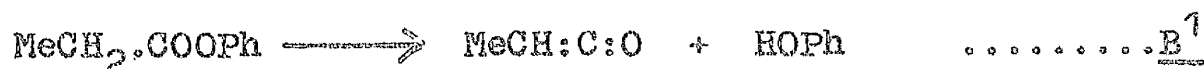
More recently[35] it has been found that $\underline{B}^1$ scission is a major
competitive route in the pyrolysis at 500° of isopropenyl
acetate, producing keten and acetone.

$$MeCO:O.CMe:CH_2 \longrightarrow CH_2:CO + (HO.CMe:CH_2) \rightleftharpoons MeCOMe$$
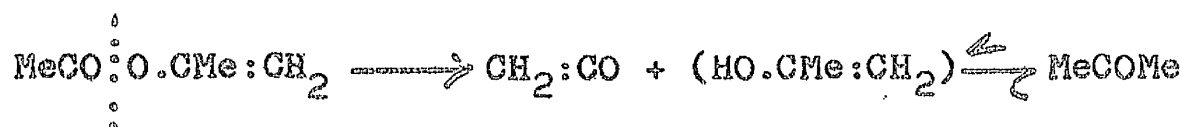
B^2 Scission

This is the more normal type of acyl-oxygen scission met with in ester pyrolysis.   In it, two carbonyl compounds are formed by migration of a hydrogen atom from the α position in the alkyl portion of the molecule to the carbonyl group of the ester.

$$>CHCO:OCH< \longrightarrow >CHCHO + O:C< \quad \ldots\ldots\ldots\ldots B^2$$
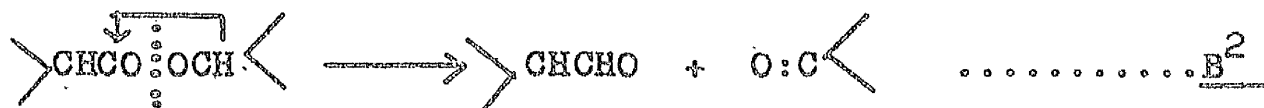
B^2 scission is the predominating scission with these esters which do not possess β-hydrogen atoms.   Many examples are quoted in the literature.   Thus Hurd and Bennett[36] have shown that the major scission product of benzyl benzoate is benzaldehyde via a B^2 acyl-oxygen scission.

$$PhCO:OCH_2Ph \longrightarrow 2 \, PhCHO$$
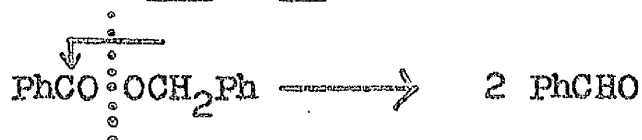
This is a straight thermal reversal of the Tischtschenko reaction used to prepare this ester.

Similarly Hurd and Blunck[5] have found that isopropyl acetate although it decomposes mainly by an A^1 scission to acetic acid and propene also yields acetone and acetaldehyde by a minor B^2 scission.

$$AcO.CH(Me)_2 \xrightarrow{430-460^0} MeCHO + COMe_2 \quad \ldots\ldots\ldots B^2$$

An interesting feature of the B^2 scission is that there are several examples of B^2 scission taking place via an atom or group other than a hydrogen atom.   Thus Bennett and Ritchie[37]

found that 1-cyanoisopropyl benzoate decomposes by two
primary routes, one being a $\underline{B}^2$ scission involving migration
of the cyano group.

$$BzO.CMe_2CN \longrightarrow \begin{cases} BzOH + CH_2:CMeCN & \dots\dots\dots A^1 \\ BzCN + COMe_2 & \dots\dots\dots \underline{B}^2 \end{cases}$$
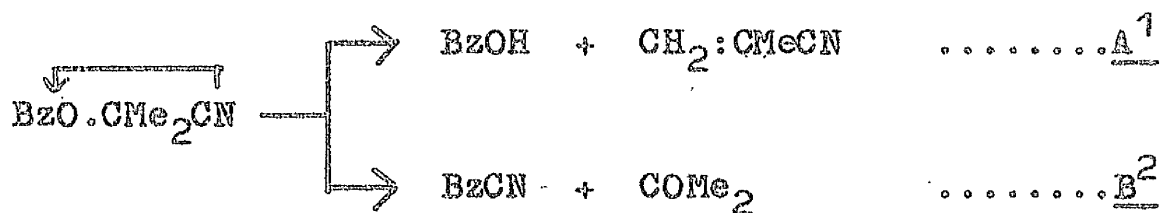
Similarly Jones[38] has found that the main breakdown route of
α-cyanobenzyl acetate is a $\underline{B}^2$ scission involving migration of
the cyano group.

$$AcO.CHPhCN \longrightarrow \left[AcCN\right] + PhCHO \qquad \dots\dots\dots \underline{B}^2$$
$$\downarrow$$
$$MeCN + CO$$
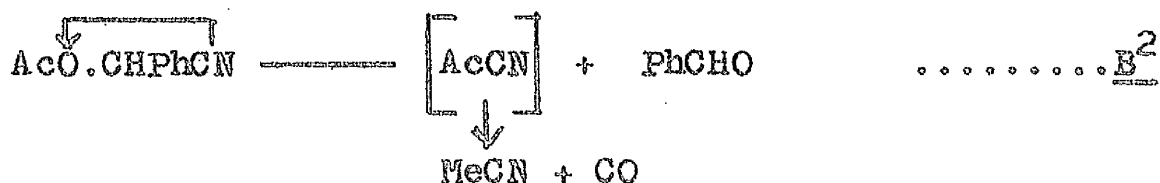
Decarbonylation and Decarboxylation

Decarbonylation C^1

Decarbonylation reactions are frequently met with in
ester pyrolysis, not as primary scissions but as secondary
reactions of carboxyl compounds produced by primary scission.
Thus/acetaldehyde/a common product of ester pyrolysis/,
decarbonylates at 400° to methane[39].

$$MeCHO \longrightarrow MeH + CO \qquad \dots\dots\dots \underline{C}^1$$
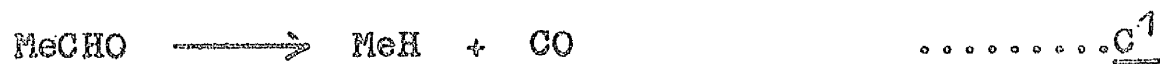
Similarly benzoyl cyanide has been shown to decarbonylate
easily to benzonitrile

$$PhCOCN \xrightarrow{470°} PhCN + CO \qquad \dots\dots\dots \underline{C}^1$$
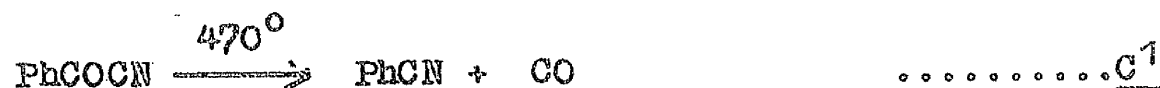
There are few examples of ester decarbonylation in the literature.   Phenyl formate decomposes quantitatively at 550° by the $\underline{C^1}$ route

$$HCO.OPh \longrightarrow HOPh + CO \qquad \dots\dots\dots\underline{C^1}$$
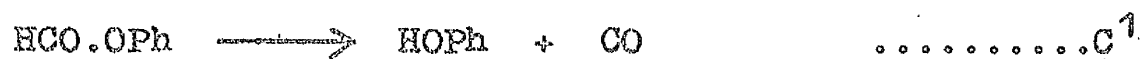
Pyruvic esters have been found by isotopic tracer techniques to decarbonylate $\underline{via}$ the ester carbonyl group rather than the α-carbonyl group.[42]   e.g. ethyl pyruvate:

$$MeCO.CO_2Et \xrightarrow{100\text{-}130^{\circ}} CO + CO_2 \left(\begin{array}{c} + \text{ other} \\ \text{products} \end{array}\right) \dots\underline{C^1}$$
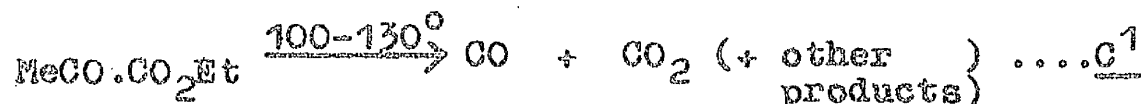
Decarboxylation C^2

Until recently, very few examples of ester decarboxyl-ation had been recorded in the literature, possibly since it usually occurs only to a very minor extent and the resulting products may be difficult to identify.   Roberts and Bowden[43] have reported the decarboxylation of triphenylmethyl formate at 100°.

$$HCO_2.CPh_3 \longrightarrow HCPh_3 + CO_2 \qquad \dots\dots\dots\dots C^2$$

The formation of methyl benzoate from dimethyl phthalate was considered[44] to proceed predominantly $\underline{via}$ a decarboxylation step to methyl-$\underline{o}$-toluate followed by decomposition to methyl benzoate.
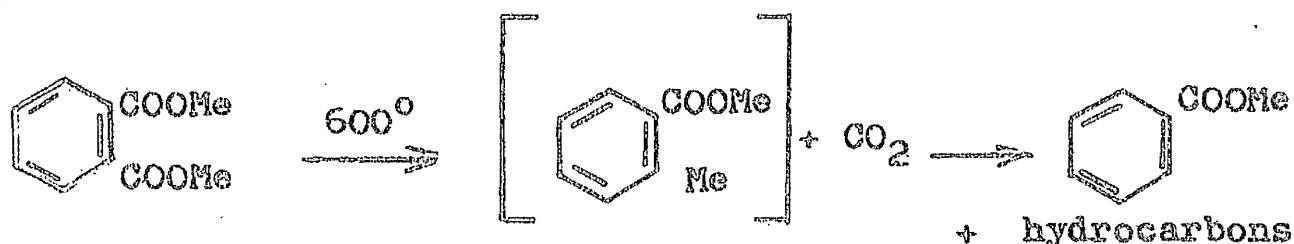
Similarly Szwarc and Taylor[45] have found that benzyl benzoate decarboxylates at 650-700° to diphenyl methane.

$$PhCO_2CH_2Ph \longrightarrow Ph_2CH_2 + CO_2 \qquad \ldots\ldots\ldots C^2$$
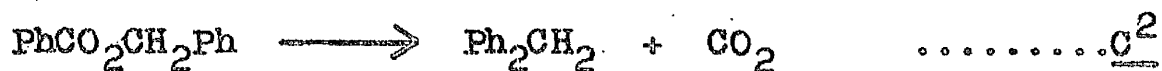
More recently vinyl benzoate[33] and phenyl acrylate[47] have also been shown to undergo decarboxylation reactions.

$$BzOCH:CH_2 \xrightarrow{400-500°} PhCH:CH_2 + CO_2 \qquad \ldots\ldots\ldots C^2$$

$$CH_2:CHCO_2Ph \xrightarrow{550°} CH_2:CHPh + CO_2 \qquad \ldots\ldots\ldots C^2$$
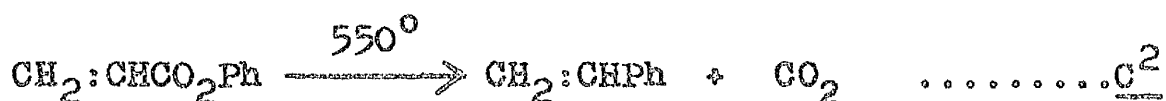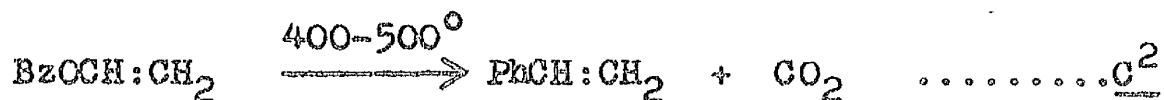
The thermal decarboxylation of esters is probably/ therefore, a much more common reaction than was at first thought.

Mechanism of Decarboxylation and Decarbonylation

Szwarc and Taylor[45] in their work with benzyl benzoate attribute the carbon monoxide and carbon dioxide in the pyrolysate gas to free radical reactions. Thus they assumed the first decomposition reaction to be the formation of benzoate radicals followed by their decomposition.

$$PhCOO.CH_2Ph \longrightarrow PhCOO\cdot + \cdot CH_2Ph \qquad \ldots\ldots(1)$$

$$PhCOO\cdot \longrightarrow Ph\cdot + CO_2 \qquad \ldots\ldots(2)$$
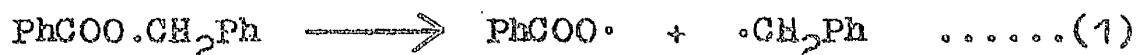
In support of this mechanism diphenyl, diphenylmethane and dibenzyl were identified as main products of the decomposition reaction. The carbon monoxide produced was attributed to the reaction sequence

$$Ph\cdot + Ph.COOCH_2Ph \longrightarrow PhH + PhCOOCHPh$$

$$PhCOO.CHPh \longrightarrow Ph\cdot + CO + PhCHO$$

The benzaldehyde in the pyrolysates was roughly proportional to the carbon monoxide evolved.

Rearrangement Reactions R

There are few examples of purely thermal ester rearrangements in the literature. There are however several examples of an allylic rearrangement by crotyl esters.

Thus Morell et al.[46] found that 3-acetoxybut-1-ene underwent rearrangement to 1-acetoxybut-2-ene.

$$AcOCHMe.CH:CH_2 \xrightarrow{\;495^\circ\;} MeCH:CH.CH_2OAc$$
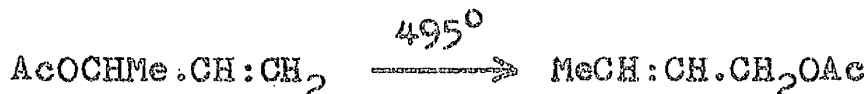
Similarly Manuel and Brace[45] found that during the pyrolysis of 3-acetoxy-3-cyanobut-1-ene some 1-acetoxy-3-cyanobut-2-ene was formed.

$$AcO.CCNMeCH:CH_2 \longrightarrow AcO.CH_2CH:CCNMe$$
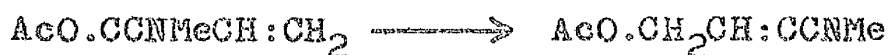
Rearrangements may take another form in which the product may be a ketone rather than an ester. Young et al.[48] have shown that isopropenyl acetate and cyclohex-1-enylbenzoate rearrange to isomeric β-diketones on pyrolysis.

$$MeCO_2.CMe:CH_2 \xrightarrow{\;500^\circ\;} MeCO.CH_2COMe \qquad \ldots\ldots\ldots R$$
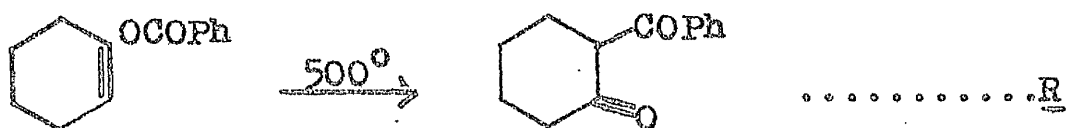
This reaction has now been found to be reversible at 500° [35]. Allan and Ritchie[49] have shown that vinyl benzoate undergoes a thermal rearrangement to a labile keto-aldehyde followed by decarboxylation.

$$PhCO \cdot OCH:CH_2 \longrightarrow PhCOCH_2CHO \qquad \dots\dots\dots\dots R$$
$$\downarrow$$
$$PhCOMe \quad + \quad CO \qquad \dots\dots\dots\dots C^1$$

Introduction

In recent years polyethylene terephthalate ("Terylene")
has achieved considerable commercial importance as a textile
fibre.   The fibre is produced from the polyester chips by the
melt spinning process at 280°.   This temperature is critical
since at ca. 300° decomposition of the polyester occurs with
the production of low molecular weight material which dimin-
ishes the desirable properties of the polyester.   Consider-
able attention has therefore been directed to a study of the
thermal breakdown of the polyester and the resultant product.
Owing to difficulties encountered in studying the thermal
breakdown of the polyester itself, the work was continued by
studying the pyrolysis of model compounds representing various
segments of the polyester chain.   Two of the principal com-
pounds studied[1] were 2-benzoyloxyethyl terephthalate and its
chlorine labelled analogue.

$$BzOCH_2CH_2CO_2 \langle\!\!\langle\bigcirc\rangle\!\!\rangle O_2CCH_2CH_2OBz$$

$$Cl\langle\!\!\langle\bigcirc\rangle\!\!\rangle CO_2CH_2CH_2O_2C\langle\!\!\langle\bigcirc\rangle\!\!\rangle CO_2CH_2CH_2O_2C\langle\!\!\langle\bigcirc\rangle\!\!\rangle Cl$$
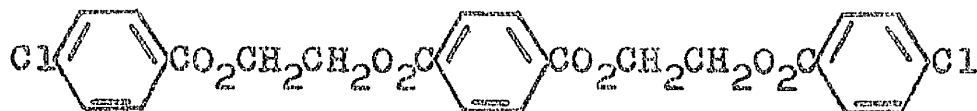
From pyrolysis of these compounds and related work[33,49], a
fairly complete picture of the behaviour of the polyester on
pyrolysis has been obtained.   Because of the presence of
available β-hydrogen atoms it was to be expected that the
primary reaction on pyrolysis would be alkyl-oxygen scission

at the ester linkages a, a', b, b' giving different vinyl esters

$$BzOCH_2CH_2O_2C \diagramphenyl CO_2CH_2CH_2OBz$$

a   b   b'   a'
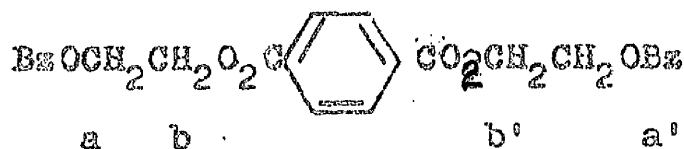
One of the expected products from pyrolysis of these compounds was p-diacetylbenzene, produced by two successive A^1 scissions of the molecule followed by two rearrangement/decarbonylation reactions described by Allan and Ritchie[49].

$$BzOCH_2CH_2O_2C \diagramphenyl CO_2CH_2CH_2OBz$$

$$\downarrow 2\ A^1$$

$$CH_2:CHO_2C \diagramphenyl CO_2CH:CH_2 + 2\ BzOH$$

$$\downarrow 2\ R/C^1$$

$$MeCO \diagramphenyl COMe + 2\ CO$$
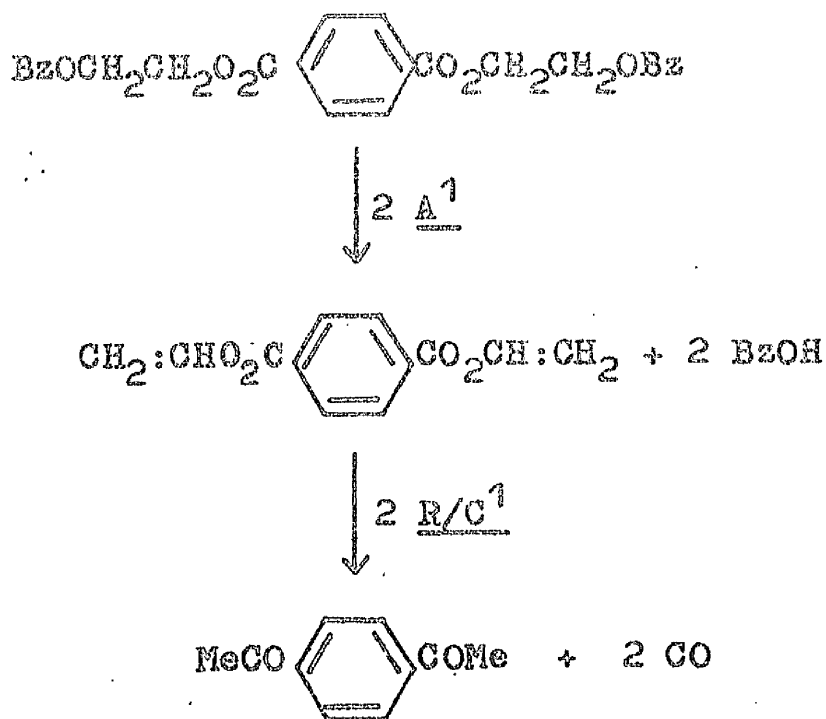
Nevertheless, though carefully sought, p-diacetylbenzene was not detected as a breakdown product.

This was surprising since the work of Pohl[50], and

Marshal and Todd[51] has indicated that the competitive A^1 scissions of the polyester chain are truly random and thus terephthalic acid and its mono and divinyl ester should have been formed in roughly equivalent amounts, the latter compound divinyl terephthalate being the precursor of p-diacetylbenzene.

$$CH_2:CHO_2C \langle \bigcirc \rangle CO_2CH:CH_2 \xrightarrow{R/C^1} CH_2:CHO_2C \langle \bigcirc \rangle COCH_3$$

$$\downarrow R/C^1$$

$$MeCO \langle \bigcirc \rangle COMe$$
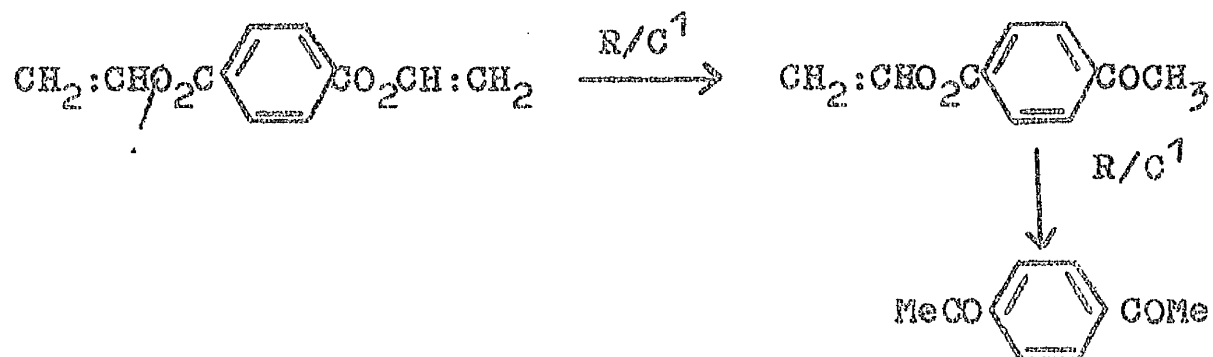
p-Diacetylbenzene should therefore have been present in detectable amounts since the R/C^1 route has been shown to be the major scission route of vinyl esters[49] and terephthalic acid itself was identified as a major product of pyrolysis of both esters.

To account for the non-identification of p-diacetyl-benzene it was suggested[1] that either divinyl terephthalate decomposes predominantly by the A^1/D reaction by reaction with carboxyl end-groups in the pyrolysate, shown[52] to be a major scission route of ethylene dibenzoate or that the electronic structure of the intermediate vinyl p-acetylbenzoate is so modified that the second vinyl ester group breaks down by one of the other possible competitive routes.

It was considered that the former explanation was the more likely. In order to verify this theory therefore it was decided to prepare and pyrolyse vinyl p-acetylbenzoate in order to find out whether p-diacetylbenzene was a major product of pyrolysis.

Discussion of Results

Pyrolysis of Vinyl p-Acetylbenzoate

The present work has shown that in accord with the
work of Allan and Ritchie[49] on vinyl benzoate, the predom-
inating breakdown route of vinyl p-acetyl benzoate at 500°
is the R/C[1] reaction already described yielding p-diacetyl-
benzene.

$$\text{MeCO}\text{—}\text{(ring)}\text{—}\text{CO}_2\text{CH:CH}_2 \xrightarrow{R} \text{MeCO}\text{—}\text{(ring)}\text{—}\text{COCH}_2\text{CHO}$$

$$\downarrow \text{-CO}$$

$$\text{MeCO}\text{—}\text{(ring)}\text{—}\text{COMe}$$
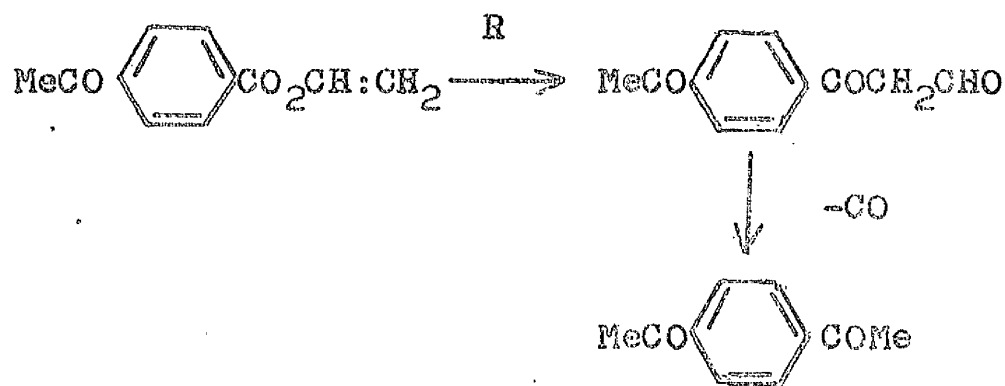
The view of Allan, Iengar and Ritchie[1], therefore, that, their
failure to detect p-diacetylbenzene as a breakdown product
of 2-benzoyloxyethyl terephthalate and 2-p-chlorobenzoylethyl
terephthalate was caused by the diketone being produced in
amounts too small to be detected is/therefore/confirmed. It /₅₇
was suggested that vinyl p-acetylbenzoate and its precursor
divinyl terephthalate formed during pyrolysis, reacted with
carboxyl end groups in the pyrolysate forming ethylidene com-
pounds which then disproportionated into acetaldehyde and an
acid anhydride. It is of interest, therefore, that an acid
anhydride was detected in the pyrolysate of the ester possibly
formed by the combination of p-acetylbenzoic acid - a product

of pyrolysis ~ and the ester to an ethylidene compound

followed by disproportionation

MeCO⟨benzene ring⟩CO$_2$CH:CH$\backslash$ + HO$_2$C⟨benzene ring⟩COMe

→

Me
|
MeCO⟨benzene ring⟩CO$_2$CH ~ O$_2$C⟨benzene ring⟩COMe ⟹ MeCO⟨benzene ring⟩CO
|
Me†CHO

MeCO⟨benzene ring⟩CO
\
O
/
MeCO⟨benzene ring⟩CO
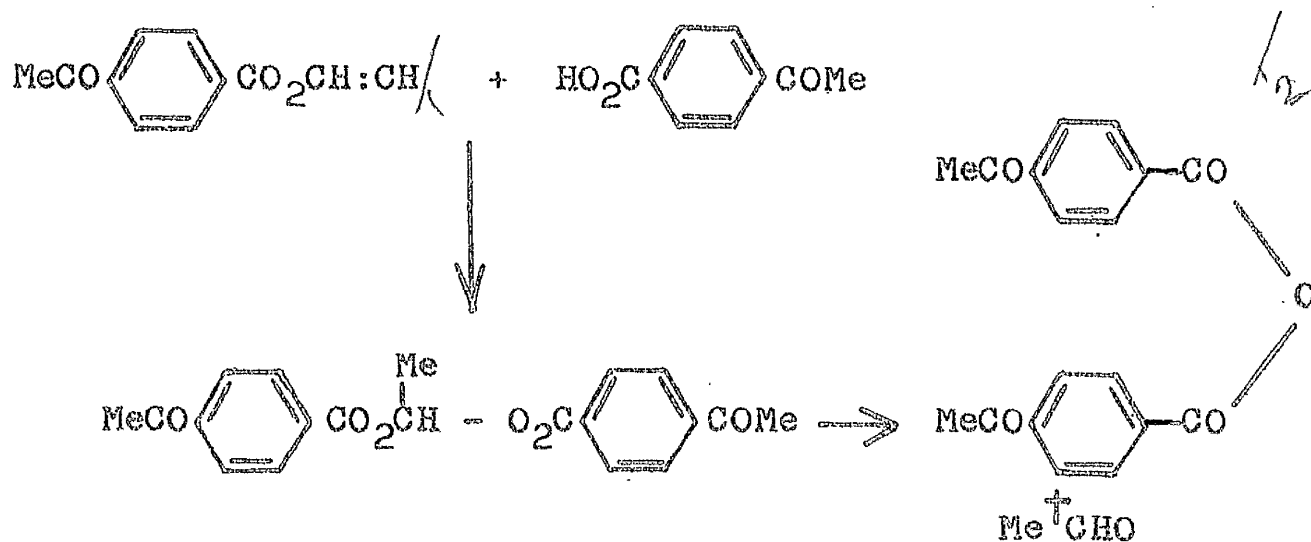
The anhydride may also possibly have been formed by the

dehydration of 2 molecules of benzoic acid.

One of the possible scission products of vinyl p~

acetylbenzoate is p~vinylacetophenone formed by a decarboxyl~

ation of the ester itself thus:

MeCO⟨benzene ring⟩CO$_2$CH:CH$_2$ $\xrightarrow{-CO_2}$ MeCO⟨benzene ring⟩CH:CH$_2$
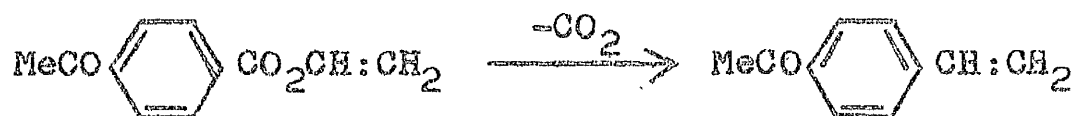
Allan, Forman and Ritchie[33] have shown that vinyl benzoate

undergoes a similar reaction yielding styrene, though only

to a very minor extent.   Nevertheless p~vinylacetophenone

was not detected in pyrolysates of the ester, though very

carefully sought for.   Paper chromatography of the mixture

of 2,4 dinitrophenylhydrazones from the pyrolysates showed

two unidentified spots, one of which may possibly have been

that of p-vinylacetophenone. Column chromatography of the 2,4 dinitrophenylhydrazones also failed to detect the ketone. It must be concluded therefore that p-vinylacetophenone if formed is present only in very small amounts if at all.

Other Products of Decomposition

(a)   Acetylene and p-Acetylbenzoic acid

These two compounds found in the pyrolysate are formed together by an A^2 alkenyl-oxygen scission of the ester

$$MeCO\langle\rangle CO_2CH{:}CH_2 \longrightarrow MeCO\langle\rangle COOH + CH{:}CH$$

This is a minor reaction only. Acetylene formed 1-2% of the pyrolysate gas. It can be seen therefore that only small amounts of acid are available for reaction with the ester by the A^1/D reaction. During pyrolysis of the larger model compounds, however, carboxylic end groups are formed in large numbers by A^1 scissions.

(b)   Carbon Monoxide

Carbon monoxide is present in the pyrolysis gas in large quantities, formed by decarboxylation of the inter-mediate rearrangement product/p-acetylbenzoylacetaldehyde, the major breakdown product of the ester.

$$MeCO\langle\rangle COCH_2CHO \xrightarrow{-CO} MeCO\langle\rangle COMe$$
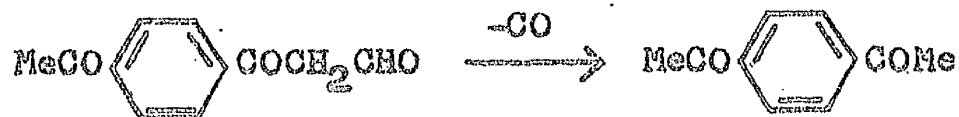
(c)   <u>Carbon dioxide and Acetophenone</u>

Carbon dioxide is almost certainly formed by decarboxylation of p-acetylbenzoic acid to acetophenone although decarboxylation of the ester to p-vinylacetophenone is formally possible.   Allan, Iengar and Ritchie[1] have shown that p-acetylbenzoic acid pyrolysed for 10 min. at 500° is decarboxylated to the extent of about 25%.

EXPERIMENTAL

Apparatus and Procedure

Flow Reactor:- The pyrolysis unit was similar to that shown in the accompanying diagram. The reactor consisted of a Pyrex tube packed with small lengths of glass tubing held vertically inside an electric furnace. The temperature of the furnace could be controlled to $\pm 5^{\circ}$ by a series of resistances and a "Simmerstat" energy controller. The temperature inside the furnace was measured by a chromel-alumel thermocouple. Various reaction vessels were used as required. Their dimensions are given below.

Reactor	Heated length (cm.)	Bore (cm.)	Free Volume ccs.
Pyrex medium	30	2.3	76
Pyrex small	18	2	30
Pyrex semi-micro	5	1	4

Before each pyrolysis, the system was evacuated several times with dried oxygen-free nitrogen to prevent combustion of the vapours. Liquid pyrolysands were introduced into the furnace by a tap funnel fitted with a side arm to equalise the pressures above and below the liquid pyrolysand. Solid pyrolysands were melted in the tap funnel by means of a heating tape and then run into the furnace in the normal manner. Liquid and solid pyrolysates issuing from the reaction tube passed through an air condenser and up a vertical water condenser, being collected in a flask beneath the water

FLOW REACTOR
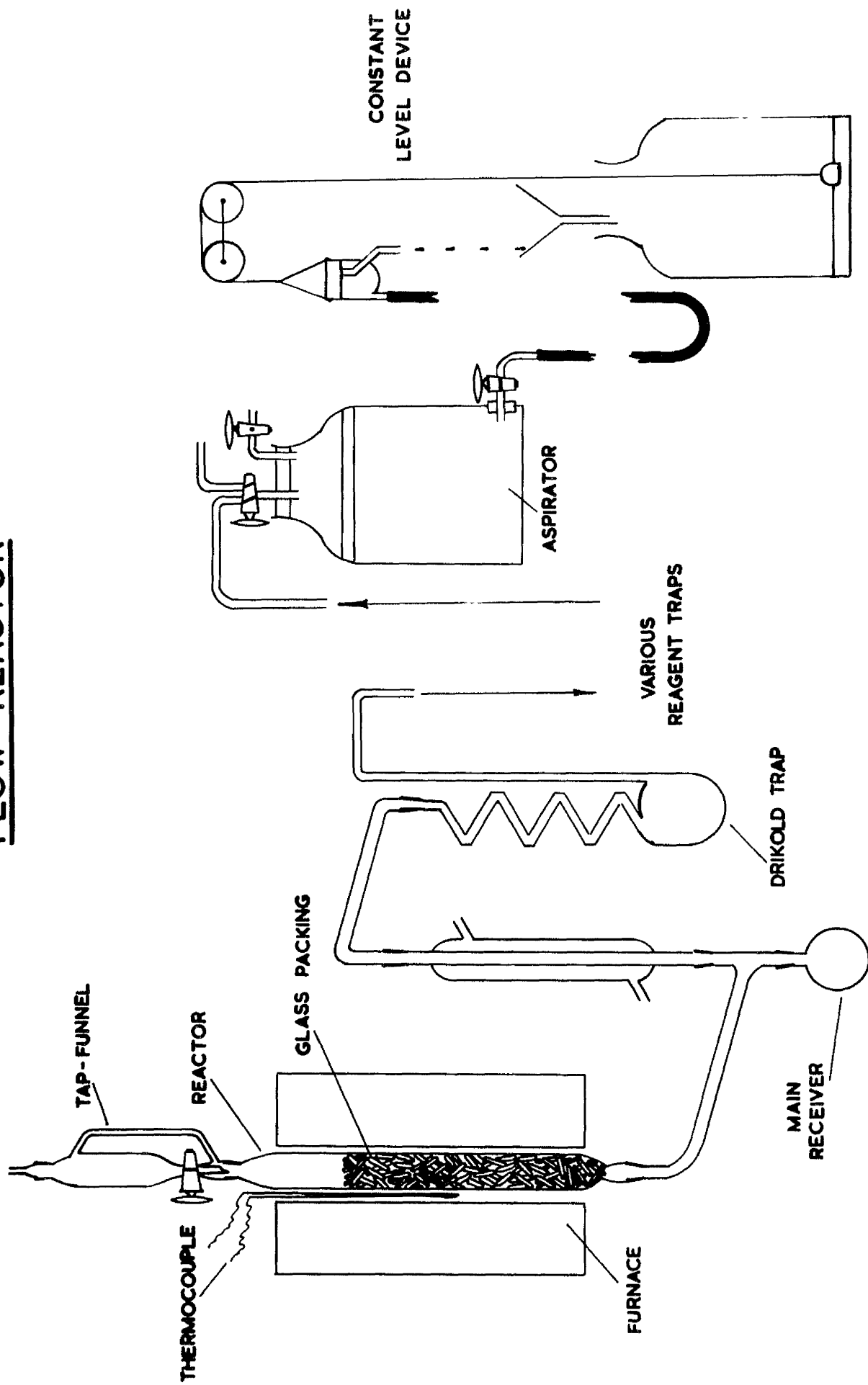
FIGURE 1.

condenser. The gaseous products remaining, passed through a second receiver cooled to ~70° in an acetone/Drikold freezing mixture and then through various reagent traps, inserted as required. The gases remaining were collected over water covered with gas saturated paraffin in a 20 l. aspirator. The whole system was maintained at atmospheric pressure by means of a constant level device. After each pyrolysis, the reactor tube was cleaned by blowing a stream of air for 4 hr. through the tube, maintained at 500°.

Residence Time

The term residence time is now preferred to contact time as a description of this factor. The residence time of the pyrolysand was calculated according to the formula:

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

where the residence time t_R is equated to the free volume (V_c) of the reactor, the number of gram-moles per second of pyrolysand (N_v) and nitrogen (N_n), the pressure (p) and the absolute temperature (T) of the system. If it is assumed that pyrolysis takes place at 1 atmosphere and that there is no flow of nitrogen during the pyrolysis, the expression may be written as:

$$t_R = \frac{12.2 \times V_c}{N_v \times T}$$

Analytical Methods

Chemical Analysis

Pyrolysates were separated into fractions by distillation. The fractions were then examined by standard chemical methods. In many instances infrared and ultraviolet spectroscopy were utilised as additional analytical aids. Whenever possible, compounds were identified by a mixed melting point with standard samples. Mixtures of carbonyl compounds were separated by column chromatography[53] and identified by paper chromatography[54] or by mixed melting point determination. Anhydrides were detected by the Davidson and Newman colour reaction[55].

Infrared Spectroscopy

Infrared spectroscopy was used extensively for the preliminary investigation of pyrolysate fractions and also for examining the products of preparative reactions. The instrument used was a double-beam Perkin-Elmar "Infracord". Liquids were examined in a standard rock salt cell. Solids were examined as a Nujol mull or more conveniently by the potassium chloride disc procedure. The various samples examined were compared with standards whenever this was possible. Care is needed when examining mixtures as certain compounds, such as benzoic anhydride have been found to mask the characteristic spectra of other compounds in the mixture.

Many compounds also have very similar spectra.

Chromatography

Column Chromatography

Column chromatography[53] was used for separating mixtures of 2,4-dinitrophenylhydrazones. The eluate was collected in 5 ml. fractions and the concentration of each fraction followed by means of a colorimeter. The various fractions were concentrated and the 2,4-dinitrophenyl-hydrazones identified as described above.

Paper Chromatography

Mixtures of 2,4-dinitrophenylhydrazones were also studied using paper chromatography, by the method of Burton[54] as modified by Jones[38]. Control samples were always run alongside unknown mixtures. At the end of each run the paper was dried, examined under ultraviolet light and the distance travelled by each spot from the base line noted. This method was found to be only partially successful since all the derivatives studied tended to give long streaks on the paper and consistent results from run to run could not be obtained.

Preparation of Vinyl p-Acetylbenzoate

Preparation of this compound caused some difficulty owing to difficulty in preparing p-acetylbenzoic acid and preparing the ester from the acid by ester-exchange methods. The main problem in preparation of the ester was one of preparing p-acetylbenzoic acid in sufficiently large quantities for use in the ester-exchange reaction where yields are low.

Preparation of p-Acetylbenzoic Acid

The first attempt at preparing this compound was via p-aminoacetophenone, prepared by the method of Raadsveld[56] followed by conversion of the amine to p-cyanoacetophenone by a Sandmeyer reaction. The p-cyanoacetophenone was then hydrolysed with 10% potassium hydroxide solution to p-acetyl-benzoic acid. Very low yields (5-10%) of acid were obtained in this way. It was also found that a rather impure product was obtained by this method which was difficult to purify by crystallisation.

Various modifications of the above procedure were tried without success.

1. Anhydrous aluminium chloride was used as a catalyst instead of zinc chloride, in the preparation of p-aminoacetophenone. Only acetanilide was produced.

2. Acetic anhydride, zinc chloride and acetanilide were refluxed and the reaction product worked up as before.

No better yields were obtained.

3.   p-Aminoacetophenone was prepared by the method of Dippy and Wood[57] using N,N-diacetylaniline. Yields improved only slightly.

In view of the low yields of amine obtained and the large amount of p-acetylbenzoic acid required it was decided to try an alternative method of preparation. The method used was that of Emerson and Deebel[58].

p-Ethylacetophenone was prepared from ethyl benzene and acetyl chloride by a Friedel-Craft's reaction and oxidised to p-ethylbenzoic acid with sodium hypochlorite solution. The acid was then converted to the methyl ester, followed by air oxidation to methyl p-acetylbenzoate, using a chromium sesquioxide/calcium carbonate catalyst. The product, obtained from the reaction mixture by distillation, was hydrolysed to p-acetylbenzoic acid with 15% sodium hydroxide solution.

The sodium hypochlorite solution for the oxidation of p-ethylacetophenone was initially made by mixing solutions of calcium hypochlorite and sodium carbonate/sodium hydroxide and filtering. This method was found to be unsatisfactory giving poor yields ca.15%, and instead the hypochlorite solution was made by the method of Newman and Holmes[59] using chlorine and sodium hydroxide solution. Yields of p-ethylbenzoic acid of up to 90-95% were obtained.

Oxidation of more than 100 g. of ester at a time resulted in a large amount of tar being formed during the

distillation of the reaction product, thus cutting down yields.

p-Acetylbenzoic acid prepared by this method was a fine white powder m.p.208°; lit.,[60] m.p.208°. It yielded a 2,4-dinitrophenylhydrazone as orange needles (from glacial acetic acid), m.p. ca. 280° (decomp.) Allan[1] gives m.p. 280° (decomp.) (Found: C, 52.7; H, 4.0; N, 16.4. Calc. for $C_{15}H_{12}O_6N_4$: C, 52.3; H, 3.5; N, 16.3%)

Vinyl p-Acetylbenzoate

The method of preparation used was that of Burnett and Wright[61] but with certain modifications[62].

p-Acetylbenzoic acid (50 g.) was partially dissolved in vinyl acetate (172 g.) by warming to 60°. Mercuric acetate (1.34 g.) was added and the mixture shaken for 30 min., when 100% sulphuric acid (0.125 ml.) was added dropwise. After cooling, the solution was filtered free of excess acid and sodium acetate trihydrate (0.83 g.) added to neutralise any free sulphuric acid. Excess vinyl acetate was distilled off under reduced pressure in a nitrogen atmosphere and the distillation continued at low pressure yielding three fractions (i) b.p.50-60°/18 mm., (ii) b.p.128-138°/4 mm., and (iii) b.p.138-150°/4 mm. Fraction (i) was acetic acid: fractions (ii) and (iii) solidified to crude vinyl p-acetyl-benzoate, from which 8 g. (14%) of the solid ester were obtained as colourless needles (from methanol) m.p.88°. A

second preparation with a reflux period of 18 hr. gave a yield of 38%. (Found: C, 69.5; H, 5.7%; M(cryoscopic in benzene), 196. Calc. for $C_{11}H_{10}O_3$: C, 69.5; H, 5.3%; M, 190). The ester decolourises bromine water and aqueous potassium permanganate: it is sparingly soluble in ether, cold methanol, and hot light petroleum (b.p. 60-80°) , and very soluble in benzene and hot methanol. It yields a 2,4-dinitrophenylhydrazone as orange needles m.p.221° (v. high?) from glacial acetic acid (Found: C, 55.0; H, 4.3%. Calc. for $C_{17}H_{14}O_6N_4$: C, 55.1; H, 3.8%).

Preparation of Reference Compounds

p-Ethylacetophenone was converted to p-diacetylbenzene by a 24 hr. oxidation with chromium sesquioxide/calcium carbonate catalyst at 140° after the method of Iengar[63]. The reaction product was filtered and distilled under vacuum. Crude p-diacetylbenzene distilled at 120°/1 mm.; obtained as colourless needles (from methanol) m.p. 114° lit.[63] 114°. As might be expected, the substance formed two 2,4-dinitrophenyl-hydrazones. The fully substituted derivative was prepared using a large excess of reagent. No suitable solvent for the product was found. After boiling for several hours with glacial acetic acid, the solution was filtered hot and the insoluble residue washed and dried; m.p.340 (decomposes, not quoted in lit.). The half-substituted derivative was prepared by adding small quantities of reagent solution to a solution

of p-diacetylbenzene in methanol. The derivative was obtained as orange-red needles m.p.223-224° (from glacial acetic acid). (Found: C, 56.0; H, 4.4; N, 16.0. Calc. for $C_{16}H_{14}O_5N_4$: C, 56.1; N, 16.4%

X value for H ?

Attempted Preparation of p-Acetylbenzoic acid

In view of the difficulty of preparation of this compound, an attempt was made to prepare it by the method of Sladkov[64] in which p-methylacetophenone is oxidised directly to p-acetylbenzoic acid with air using a nickel benzoate catalyst. No acid product was obtained. Certain modifications[65] in which alumina was added during the course of the oxidation using cobalt benzoate as a catalyst were tried. A very low yield of acid (0.5 - 1%) was obtained.

Attempted Preparation of Vinyl benzoate.

Sladkov and Petrov[66] have described a method of preparation of vinyl benzoate in 90% yield using pure dry pyridine and acetaldehyde with benzoyl chloride. The acetaldehyde reacts in pyridine in its enol form forming vinyl benzoate by elimination of hydrogen chloride. The preparation of vinyl benzoate was tried out as a trial run for the preparation of vinyl p-acetylbenzoate. Although the reactants were rigorously dried and purified, no vinyl benzoate was obtained.

Details of Pyrolysis

Run 1

24.5 g. of the ester was pyrolysed at 500° — the temperature at which 2-benzoyloxyethyl terephthalate was pyrolysed[1]. The gas consisted of carbon monoxide (79%) carbon dioxide (5.5%) and unsaturated hydrocarbons (15.5%). The pyrolysate itself was a pale yellow solid which could be forced into a paste. The pyrolysate gave a positive reaction for anhydrides by the Davidson-Newman[55] colour reaction. A small portion of the pyrolysate was converted into a mixture of the 2,4-dinitrophenylhydrazones of all carboxyl compounds present, and this mixture was examined by paper chromatography without further purification.

The pyrolysate was dissolved in ether, and the ether-insoluble fractions filtered off. The extract was washed twice with potassium carbonate solution. Acidification of the alkaline extract yielded a pale yellow solid. This solid and the ether insoluble fraction were identified as p-acetylbenzoic acid (m.p. and mixed m.p. $207-208^{\circ}$). The residue from the ether-soluble fraction was distilled yielding three fractions: (i) 12.5 g., b.p. $106^{\circ}/1$ mm. (solidified), (ii) 1 g., b.p. $106-112^{\circ}/1$ mm., (liquid), and (iii) a residue. Fraction (i) was unchanged ester (mixed m.p. 87°). Fraction (ii), after several days slowly deposited a white crystalline solid (0.1 g.) identified as p-diacetylbenzene (m.p. and mixed m.p. $110-111^{\circ}$).

Paper chromatography of the 2,4-dinitrophenylhydrazone of the pyrolysate, using reference samples of p-acetylbenzoic acid, vinyl p-acetylbenzoate and p-diacetylbenzene identified all these compounds in the pyrolysate. The eluent employed was acetone (20%) in light petroleum (b.p.60-80°)(80%). There were two unidentified spots in the pyrolysate.

Run 2

Since the previous run had appeared to indicate that the R/C[1] route was only a very minor one for the ester, the material was pyrolysed for a second time with a much higher residence time in the reactor. There was considerable carbonisation in the pyrolysis tube.

The pyrolysate was worked up as in run 1. A test for anhydrides was negative. Distillation of the pyrolysate residue after removal of the ether yielded four fractions: (i) 7.2 g., b.p.130-135°/4 mm.;(solidified), (ii) 0.5 g., b.p. 130-135°/4 mm.(liquid), (iii) 19 g., b.p.135-140°/4 mm. (solidified), and (iv) a dark brown residual tar. Fraction (i) was unchanged ester; fraction (ii) was a mixture of the ester and acetophenone (infrared); fraction (iii) was p-diacetylbenzene (m.p. and mixed m.p.112-113°).

A mixture of the 2,4-dinitrophenylhydrazones of the carbonyl compounds in the pyrolysate was separated into its individual components by column chromatography after the method of Elvidge and Whalley[53]. 200 mg. of the 2,4-dinitro-phenylhydrazone mixture was dissolved in chloroform and

adsorbed on a 20 cm. x 1.7 cm. column of bentonite/kieselguhr.
Elutriation was begun with chloroform, working up to 1:1
chloroform/ethanol.   The results are summarised below.

Compound	Eluent	M.Pt.	Mixed M.Pt.
Acetophenone	1:50 EtOH/CHCl$_3$	247-248°	248°
Vinyl p-acetylbenzoate	1:20 EtOH/CHCl$_3$	220-220.5°	220.5-221°
p-Diacetylbenzene	1:10 EtOH/CHCl$_3$	233-234°	233-234°
p-Acetylbenzoic acid	1:1 EtOH/CHCl$_3$	280°(decomp.)	280°(decomp.)

The eluent was collected in 10 ml. fractions and the fraction
number plotted against optical density in order to follow the
separation.   The major component of the mixture was the mono-
substituted derivative of p-diacetylbenzene.   All the sub-
stances identified had previously been detected by other
means.   Any unidentified substance must have been present in
very small quantity.

Infrared Data

The following are the principal infrared absorption bands of the compounds studied.

Vinyl p-acetylbenzoate

2880 s, 1725 s, 1675 s , 1540 m, 1500 w , 1450 m , 1410 w, 1375 m, 1360 m, 1325 m, 1295 m, 1264 s, 1195 m, 1188 m, 1170 m, 1107 s, 1025 m, 956 m, 950 m, 882 m, 865 m cm.$^{-1}$

p-Diacetylbenzene

3480 w, 3000 m (shoulder), 2900 s, 2650 w, 2520 w, 1680 s, 1578 w, 1500 w, 1460 m (shoulder), 1430 s, 1410 m (shoulder), 1380 m, 1365 m, 1325 m (shoulder), 1310 m (shoulder), 1295 s, 1265 s, 1185 w, 1135 w, 1123 w, 1035 w, 1023 w, 1000 w, 970 m, 940 m, 875 m, 853 w, 830 w, 818 w, 777 s, 735 m, 695 m. cm^{-1}.

p-Acetylbenzoic acid

3350 w, 2900 s, 2650 w, 2530 w, 1680 s, 1575 m, 1500 m, 1460 m, 1430 s, 1410 m (shoulder), 1380 m, 1360 m, 1325 m (shoulder), 1310 s (shoulder), 1295 s, 1270 s, 1190 w, 1037 w, 1022 w, 1000 w, 970 m, 940 m, 875 m, 852 w, 830 w, 818 w, 778 s, 736 m, 696 m. cm^{-1}.

Tabulated Results

Table 1

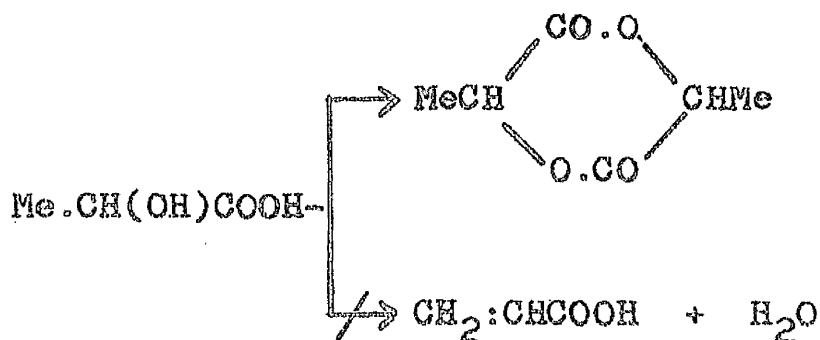| Pyrolysand		Vinyl p-acetylbenzoate	
Run No		1.	2.
Temperature		500°	500°
Feed Rate (g./min.)		0.175	0.153
Contact time (sec.)		51.5	151
Wt. pyrolysed (g.)		24.5	41.5
(a) In cold trap (ml.)		–	–
(b) In main receiver (g.)		22.5	34.5
(c) Gaseous pyrolysate (l.)		0.9	2.9
Composition (%) of (c) (approx.):			
CO		79	77.1
CO_2		5.5	11.9
Unsat. hydrocarbons		5.5	9.3
Acetylene		*	1.7

* Not analysed.

PART II.

PART II: The Pyrolysis of Anilino-nitriles and

Benzoyloxy-nitriles.

Introduction

Pyrolysis of lactic acid in attempts to prepare commercially useful acrylic acid gives only a lactide condensation product and no acrylic acid.

$$Me.CH(OH)COOH \begin{cases} \rightarrow MeCH \overset{CO.O}{\underset{O.CO}{\diamond}} CHMe \\ \nrightarrow CH_2{:}CHCOOH + H_2O \end{cases}$$

Burns, Jones and Ritchie[67] have shown that substituted olefins may be prepared by vapour phase pyrolysis at 450-550° of α-acyloxy esters and acylated cyanohydrins, yielding the desired olefinic ester or nitrile in high yield by elimination of carboxylic acid.

Thus methyl methacrylate and 1-cyanocyclohexene may be prepared from the corresponding esters. $/\alpha$

$$BzOCMe_2CO_2Me \longrightarrow BzOH + CH_2{=}CMeCO_2Me$$

$$\longrightarrow \quad \text{(cyclohexene)} \; CN \; + \; AcOH$$

In a similar manner, 1-anilino-1-cyanocyclohexane breaks down on simple distillation to aniline and cyclohex-1-ene-

carboxylic acid[68]
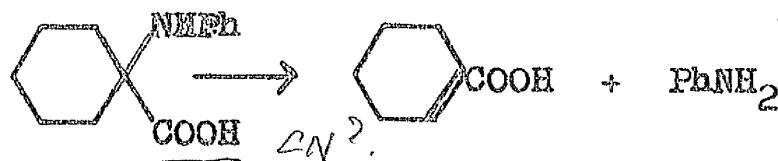


Recent work, however, by Bain and Ritchie[69] has shown that though scission into an unsaturated acid and aniline is the primary reaction for the C_5, C_6 and C_7 cyclic anilino-acids, secondary reactions also take place yielding a complex pyrolysate, containing a 1-hydroxyanilide formed through an unexpected rearrangement reaction, and a compound with a lactone-lactam type of structure formed by a condensation reaction between the starting material and the unsaturated acid.
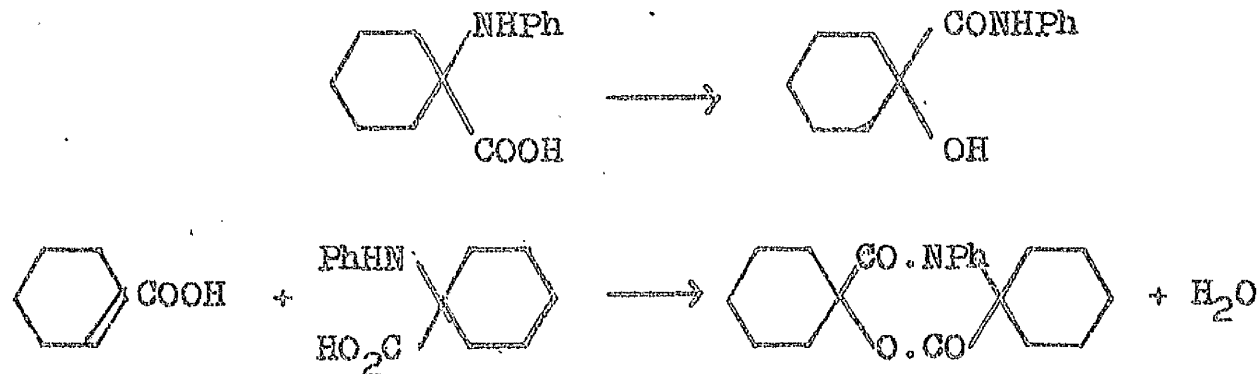

These by-products gave a rather complex pyrolysate, which was difficult to purify.

Plant and Facer[70] have reported briefly that 1-anilino-1-cyanocyclopentane "decomposes on distillation with the formation of some aniline", which suggested the formation of the corresponding product 1-cyanocyclopentene
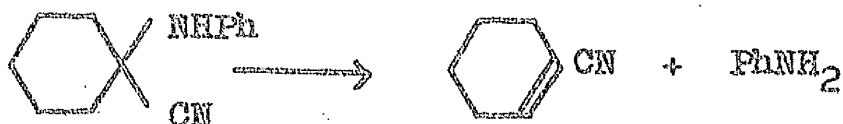
This seemed very likely on the basis of the previous work with anilino-acids and these reports on the pyrolysis of anilino-acids and nitriles led Burns, Jones and Ritchie[67] seeking new general routes to olefinic nitriles, to investigate further the pyrolysis of the readily accessible α-anilino nitriles which may be prepared in almost quantitative yield from the corresponding ketone by condensation with aniline and hydrogen cyanide.

Initial experiments showed that pyrolysis of these compounds in a flow reactor at 450-550° yielded mainly unchanged α-anilino-nitrile along with traces of hydrogen cyanide but no aniline. These results were explained when Drew and Ritchie[71] demonstrated that anilino-nitriles refluxed in a static system in a stream of nitrogen (to carry off hydrogen cyanide formed) yield hydrogen cyanide and an anil as the main products. The reaction was found to be reversible at room temperature which explained why only starting material was found in the pyrolysate.
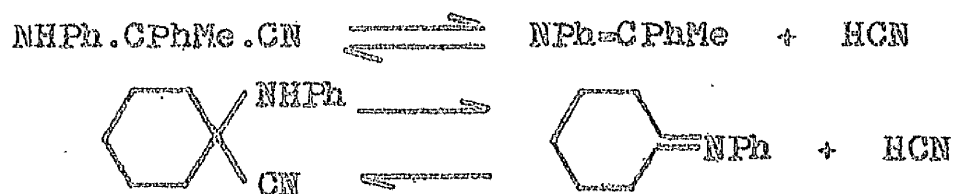
It was shown that the anil could be formed in up to 85% yield by this method.

Bain[2] intensively studied the liquid-phase pyrolysis of 1-anilino-1-cyanocyclopentane at low temperatures and found that a complex pyrolysate formed, containing aniline but no 1-cyanocyclopentene. It was found that the aniline was formed by a secondary condensation of the anil cyclopentylideneaniline to 2-cyclopentylidenecyclopentylideneaniline splitting off aniline.
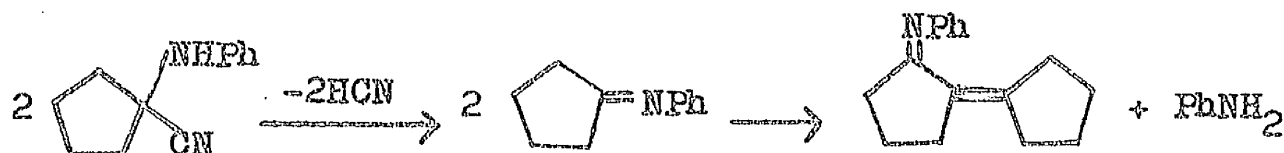
The thermal self-condensation of the anil was analogous to the well-known base-catalysed self-condensation of cyclopentanone. It was found that for the C_5, C_6 and C_7 cyclic anils the reaction with hydrogen cyanide was violent at room temperature.

The negative work with the C_5 and C_6 cyclic anilino-nitriles led Bain[2] to investigate the pyrolysis of 1-anilino-1-cyano-2-methylcyclohexane in the hope that the electron repelling influence of the o-methyl group might promote the splitting off of aniline to give the desired unsaturated nitrile. Static pyrolysis at 200 and 250°, however, gave similar results to those for the C_5 and C_6 compounds: 95-98% yields of hydrogen cyanide and the anil 2-methyl-cyclohexylideneaniline were obtained.

Of additional interest in the pyrolysis of 1-anilino-1-

cyano-2-methylcyclohexane is the fact that this compound can exist in a cis or trans isomeric forms which (neglecting "boat" and "chair" conformations) may be written thus:
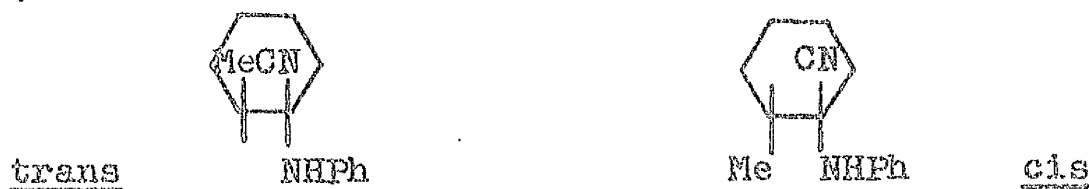
The work of Alexander and Mudrak[25,26] with xanthate esters and of Barton[22] with the benzoate esters of steroid and terpene alcohols has shown that eliminations from ring systems by pyrolysis are almost exclusively cis in nature and that cis-trans isomeric pairs give different products or different proportions of products on pyrolysis. If these concepts are applied to the cis-trans pair under consideration, it can be seen that cis elimination of aniline to give an unsaturated nitrile would produce the following products - assuming C_1-C_2 elimination predominates over C_1-C_6 because of the electron repelling influence of the o-methyl substituent.
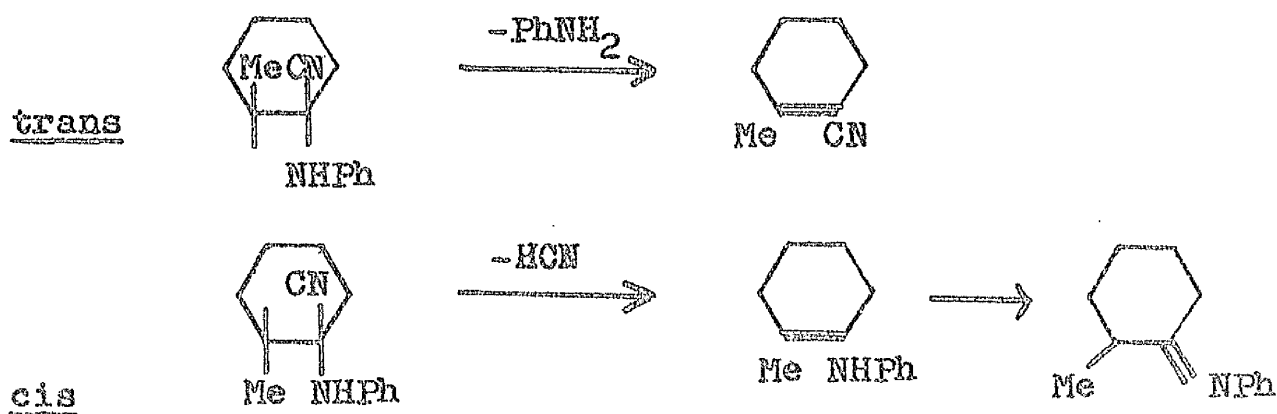
The trans compound will produce mainly the olefin 1-cyano-2-

methylcyclohex-1-ene whereas the cis isomer will give the
anil 2-methylcyclohexylideneaniline via the intermediate
vinylamine.   Bain however was unable to find any trace of
aniline or an unsaturated nitrile in pyrolysates of the
isomers.   Both isomers gave very similar pyrolysates contain-
ing the anil and hydrogen cyanide in 95-96% yield.

Concurrent with this work, Ritchie and Shim[72] attempted
to prepare the corresponding isomeric benzoates.
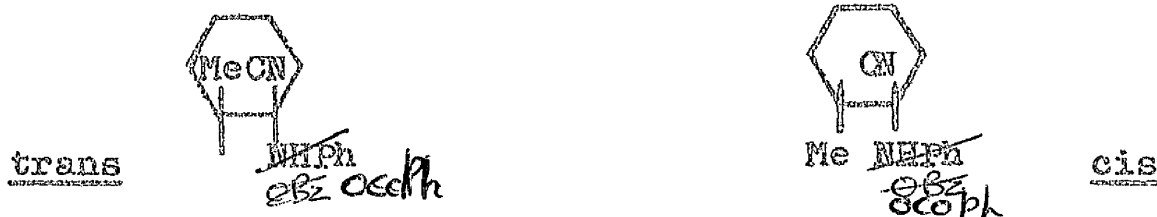
These isomers should easily eliminate benzoic acid by an A^1
scission giving different pyrolysis products because of the
cis elimination of benzoic acid.   They were only able,
however, to prepare and pyrolyse what has now been found to
be the trans isomer, but, because of the similarity of the
properties of the nitriles were unable to identify them
positively in the pyrolysate.

Objects of Research

In view of the results obtained by Bain on pyrolysis of the isomeric anilino-nitriles, an investigation of the high temperature pyrolysis of these compounds seemed desirable in the hope that at 500-600°, the major pyrolysis route might be that of scission into aniline and an unsaturated nitrile. At the same time, it was hoped that the newly available technique of gas-liquid chromatography would enable aniline and any nitriles formed to be detected in the pyrolysates, even if present only as minor products. Similarly/gas-liquid/, chromatography would be of great help in accurately determining the percentage distribution of any mixture of nitriles in the pyrolysates. Comparison of these results with those of previous workers[22,25,26] would be of great interest.

Concurrent with the above work it was also intended to prepare and pyrolyse the cis/trans pair of benzoates, one isomer of which was known to break down mainly to benzoic acid and an unsaturated nitrile or mixture of nitriles. Theoretically, provided cis elimination is the rule, the trans benzoate should give a mixture of olefins whereas the cis benzoate should yield a pure olefin product.
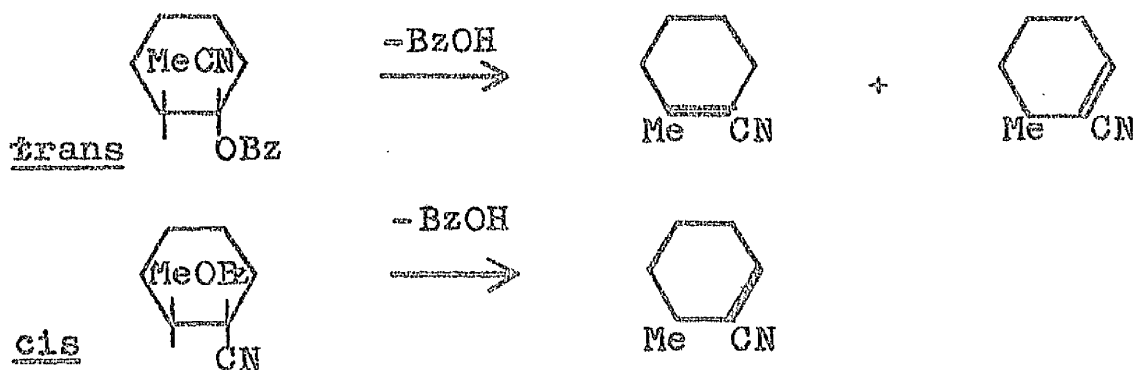
It was hoped to compare the olefin distributions in the pyrolysates of the anilino-nitriles and the benzoyloxy-nitriles.

The products of pyrolysis of the benzoates were of great interest for another reason in that, whereas initial work in this field had demonstrated consistent cis elimination by the Saytzeff rule, more recent work by Bailey et al. and Arnold, Smith and Dodson[27] on the pyrolysis of 2-methyl-cyclohexyl acetate had demonstrated not only trans elimination but almost exclusive elimination away from the bridgehead in accordance with the Hofmann rule. These results are of doubtful validity since widely different results are reported for the same compounds pyrolysed under similar conditions. It was hoped therefore to throw fresh light on these results. Another point of interest was the effect of temperature on the olefin distribution; Bailey and Hale[19] have reported that s-butyl acetate shows a marked change in favour of the Saytzeff rule at low temperatures whereas De Puy et al.[16] have found no variation of the olefin distribution of this ester from $300-500^{\circ}$.

Lastly, it was hoped to establish beyond doubt the molecular conformations of the cis/trans isomeric pairs in order that the pyrolysis results might be correctly interpreted.

Discussion of Results

The Molecular Conformations of cis and trans-1-Anilino-1-cyano-2-methylcyclohexane and 1-Benzoyloxy-1-cyano-2-methyl-cyclohexane

In order to arrive at a correct interpretation of the results from the pyrolyses of these compounds, it was necessary to establish their molecular conformations. The best method for attacking this problem seemed to be to establish the structure of the solid 2-methylcyclohexanone cyanohydrin already prepared and then to prepare from it the corresponding anilino and benzoyloxy compounds, which would presumably have the same conformation. The structure of one isomer being known, the conformation of the other could then be deduced easily.

Bain[2] has reported that cyclohexanone cyanohydrin reacts very slowly with aniline to give the corresponding anilino compound by elimination of water. It was found that 2-methylcyclohexanone cyanohydrin (trans-form, m.p.56-59°) and aniline kept at 50-60° for 72 hr. yielded the high melting isomer trans 1-anilino-1-cyano-2-methylcyclohexane, already prepared by standard methods.

The cyanohydrin reacted smoothly with benzoyl chloride in pyridine, yielding trans-1-benzoyloxy-1-cyano-2-methyl-cyclohexane, m.p.91-92°; Ritchie and Shim,[72] m.p.90-91°.

The Molecular Conformations of trans and cis 2-Methylcyclo-
hexanone Cyanohydrin.

The "Chair" form rather than the "boat" form has been shown to
be the most stable form of the cyclohexane ring from infra-
red [73], Raman spectroscopy[74], electron diffraction[75], and
thermodynamic considerations[76].   The "boat" form may/therefore/,,
be ignored in a discussion of cyclohexane isomers.   The possible
"chair" conformations of the isomers of the cyanohydrin may then
be represented as follows:

CN
OH
Me
H

I

OH
CN
Me
H

II

CN
OH
H
Me

III

OH
CN
H
Me

IV
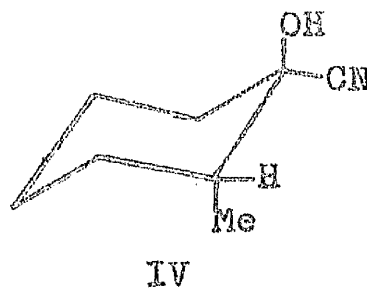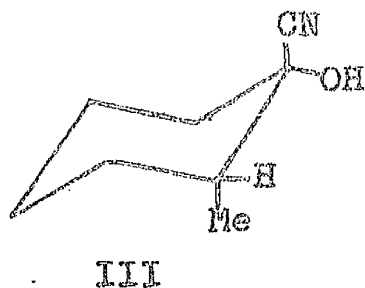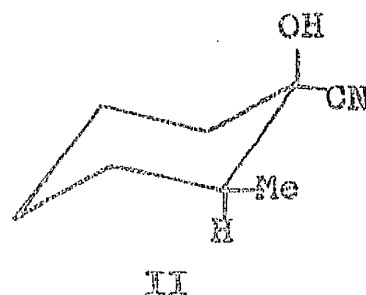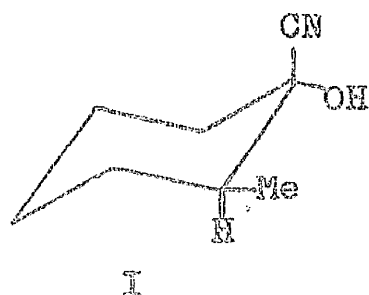
Hassel et al.[76] have shown that a cyclohexane derivative
normally exists predominantly in the "chair" conformation which
has the maximum number of equatorial substituents.   If this is
so, then conformations III and IV can be neglected and structures
I and II taken as those in which 2-methylcyclohexanone cyano-
hydrin normally exists.   These are, referring to the methyl and
hydroxyl groups, the 1,2 trans diequatorial (I) and 1,2 cis (II)

conformations.

The solid isomer of the cyanohydrin has been shown[77] to be dehydrated by phosphorus oxychloride and pyridine to 1-cyano-6-methylcyclohex-1-ene exclusively, uncontaminated by any other product, a result now confirmed by the present work using gas-liquid chromatography.
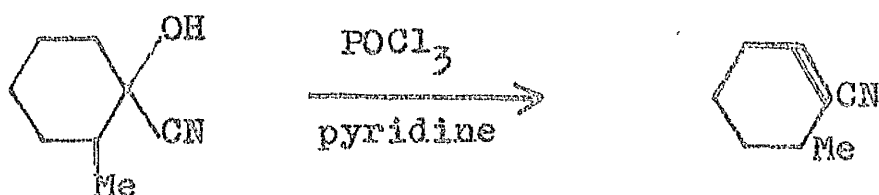
If, therefore, the mechanism of the dehydration reaction can be determined this should provide valuable evidence for the structure of the cyanohydrin, provided that the course of the dehydration is kinetically not thermodynamically controlled and that the structure of the product is a function of the stereo-chemistry of the cyanohydrin and the reaction sequence. Parham, Moulton and Zuckerbraun[78], in a detailed study of the dehydration reactions of the isomers of 2-phenylcyclohexanone cyanohydrin, showed that the high-melting isomer dehydrated exclusively to a low-melting olefinic nitrile identified as 1-cyano-6-phenylcyclo-hex-1-ene. Since this was thermodynamically the less stable isomer, they concluded that the above assumptions on the reaction sequence were correct. The mechanism of the dehydration they represented as being replacement of the hydroxyl group by a chlorine atom, with inversion, followed by trans elimination of hydrogen chloride. This mechanism represents the solid isomer as being the one in which the nitrile and phenyl groups bear a

trans relationship.
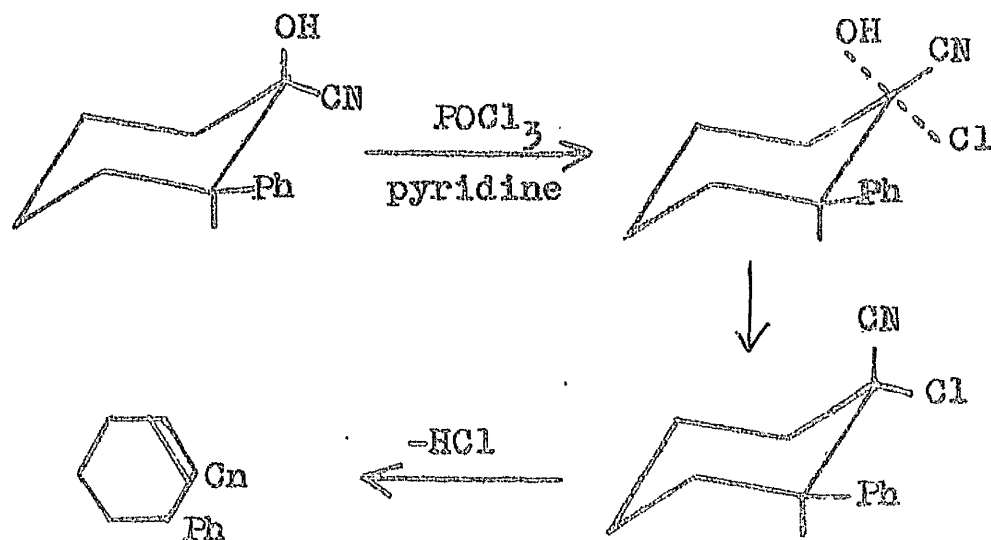
They were unable, however, to bring forward any chemical or physical evidence for these structures and mechanism, the inversion step being that in which there lies considerable doubt.

The steroid field has recently provided valuable evidence for the mechanism of dehydration. Fieser et al.[79] showed that in the steroid allocholane series, the position of a hydroxyl group at the 7-position could be determined by dehydration with phosphorus oxychloride and pyridine, followed by trans elimination without inversion. Their results were confirmed by Barton and Rosenfelder[80] by pyrolysis of the corresponding benzoates, which they concluded, on the basis of related work on steroids, to proceed via a cis eliminatory mechanism.

These results can be represented as:
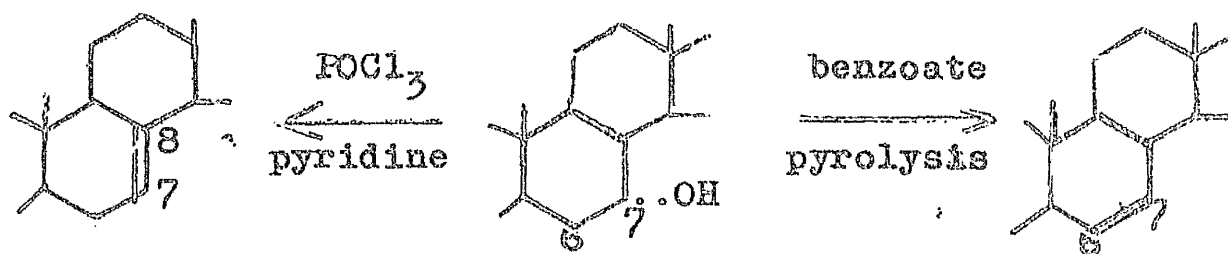
It can be seen that the method of Fieser has no inversion step. Fieser concluded that the ready _trans_ elimination probably took place through an ionic transition state by an E_2 type reaction. The electron pair of the C_8 - H bond enters the C_7 octet from the front as the hydroxyl group departs from the rear with the shared pair of electrons.

The epimeric alcohol was found[79] to be very resistant to dehydration, and on treatment with phosphorus oxychloride and pyridine yielded the corresponding chloride, but no olefin. The resistance of the chloro compound to boiling pyridine also suggested that it was formed without inversion, the _cis_ relationship to the hydrogen on C_8 being maintained.
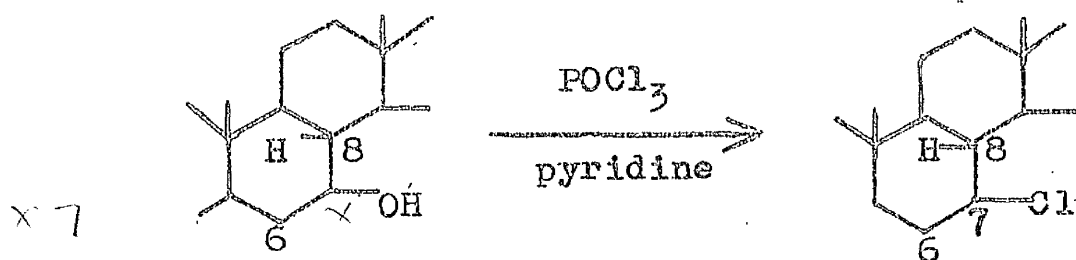
Barton[22] has given many examples in the steroid field in which _cis_ eliminations in benzoate pyrolysis, similar to the example given, conveniently explain the configuration of epimers.

As a guide to the behaviour of _trans-2-methylcyclo-_ hexanone cyanohydrin on dehydration, the results of Fieser[79] and Barton[80] are preferred to those of Parham, Moulton and Zuckerbraun[78] on account of the large volume of experimental evidence supporting the former.

The dehydration reaction can then be represented as:
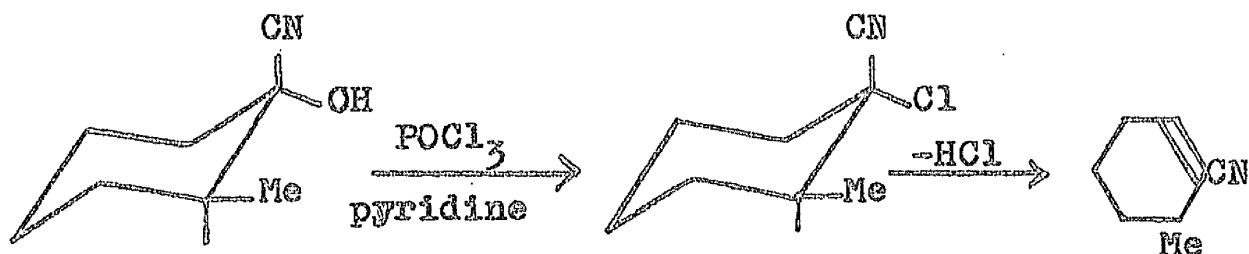
The <u>trans</u> elimination of hydrogen halide is a well-established reaction.   Barton and Cookson[81] review many reactions of this type in the cyclohexane series.   These results, however, cannot be taken as a definite indication of the cyanohydrin conformation, since Ingold <u>et al</u>[82] have shown that dehydrohalogenation may take place with or without inversion depending on the compound and its substituent groups.

Additional evidence has, therefore, been sought in favour of the above structure.

Infrared Spectroscopy

It has been shown[83] that in hydroxyl-substituted cyclo-hexanes, the intensity of infrared absorption at 2.9 m/u (hydrogen bonded hydroxyl) relative to that at 2.75 m/u (unassociated hydroxyl) is markedly greater in the isomer in which the hydroxyl group occupies an unhindered equatorial position. Consideration of the cyanohydrin structures shows that the solid isomer should have a greater bonded/unbonded ratio than the other because of the equatorial hydroxyl group.   Infrared spectra in carbon tetrachloride solution confirmed this view, the solid isomer having a much higher ratio than a liquid mixture of the isomers. The values for the mixture were not, of course, absolute values

for the _cis_ isomer, which would be expected to have an even lower ratio.

An interesting confirmation of these results was found by Bain[2], who reported the relative intensities of bonded and unbonded N-H in carbon tetrachloride solution for the isomers of 1-anilino-1-cyano-2-methylcyclohexane. The _trans_ isomer, of similar structure to the solid cyanohydrin, had a much higher relative intensity of bonded to unbonded hydrogen than the _cis_ isomer. These are very similar results to those for the cyano-hydrins and are very probably due to the same causes - inter-molecular bonding by the hydrogen of an equatorial anilino group.

Rates of Esterification of the Cyanohydrin Isomers

Additional chemical evidence has also been found for the cyanohydrin structure. It has been shown[81] that equatorial alcohols are esterified much more readily than axial alcohols owing to there being much less steric compression in the equa-torial bond. This most probably explains why the normal method of preparation of the benzoyloxy isomers yields a single isomer (m.p.92-92.5^{o}). Esterification of a 50:50 mixture of the cyano-hydrin isomers with benzoyl chloride in pyridine solution for 72 hr. at 100°, followed by fractional crystallisation of the product, yielded only 0.5 g. of the _cis_ isomer and much unchanged cyanohydrin. The extreme difficulty of preparing the _cis_ isomer is most probably due to its being prepared _via_ an axial hydroxyl group.

These results confirm the supposition of Bain[2] that the anilino-nitriles are not formed via the cyanohydrin by simple elimination of water on the following lines:
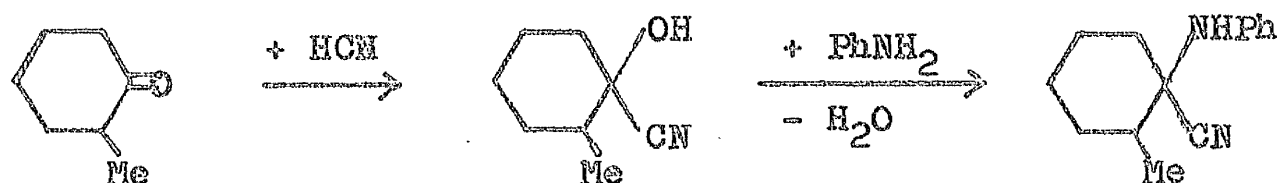
As well as being a slow reaction, it should produce only one isomer, as with the benzoates whereas the isomers are actually formed in the ratio 55:45 of trans to cis. Indeed, preliminary work with a catalyst produced only the trans isomer and a liquid residue containing the solid isomer of 2-methylcyclohexanone cyanohydrin. The present work has shown that the cyanohydrin isomers are formed in the ratio trans to cis of 75:25. Comparison of the ratios shows that the anilino-nitriles must be formed by the alternative route previously suggested[2].
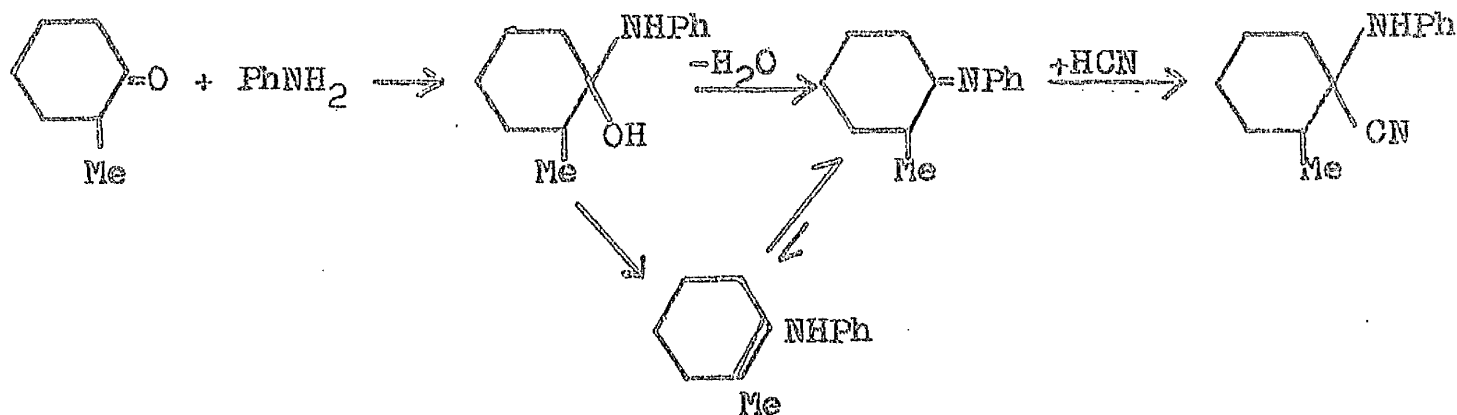
These results all indicate an equatorial hydroxyl group in the solid cyanohydrin isomer. The conformations of the anilino and benzoyloxy isomers can then be represented as follows:

trans m.p.56-59°

CN / OCOPh / Me   m.p.92-92.5°

CN / NHPh / Me   m.p.126-126.5°

OH / CN / Me

cis not isolated pure

OCOPh / CN / Me   m.p.86.5-87°

NHPh / CN / Me   m.p.86-86.5°
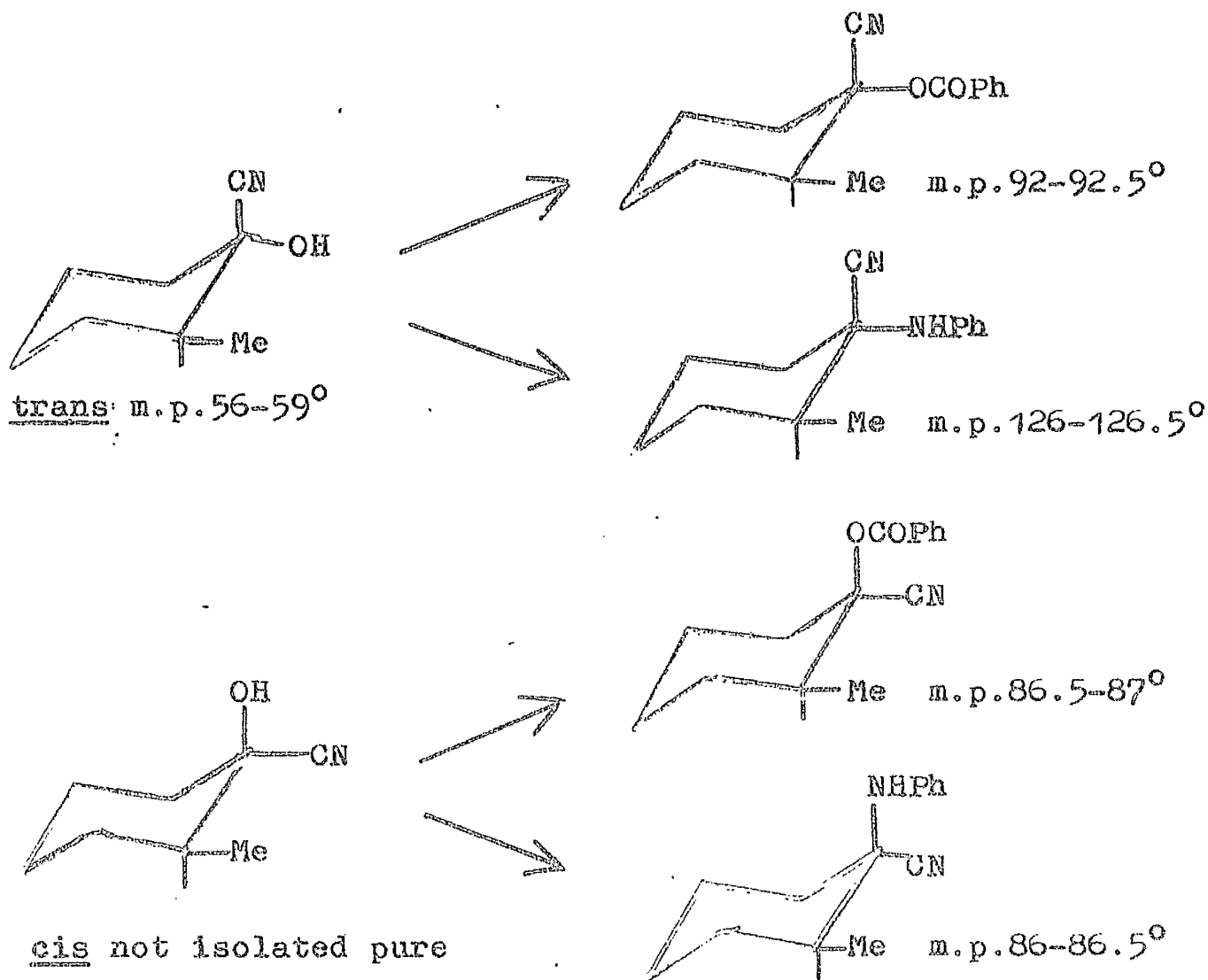
A study of Stuart models of the two isomeric anilino-nitriles showed that they had the following conformations.

trans   Me CN / NHPh

CN / N—H / Ph / Me   (1)

or

CN / Ph / N / H / Me   (2)

cis
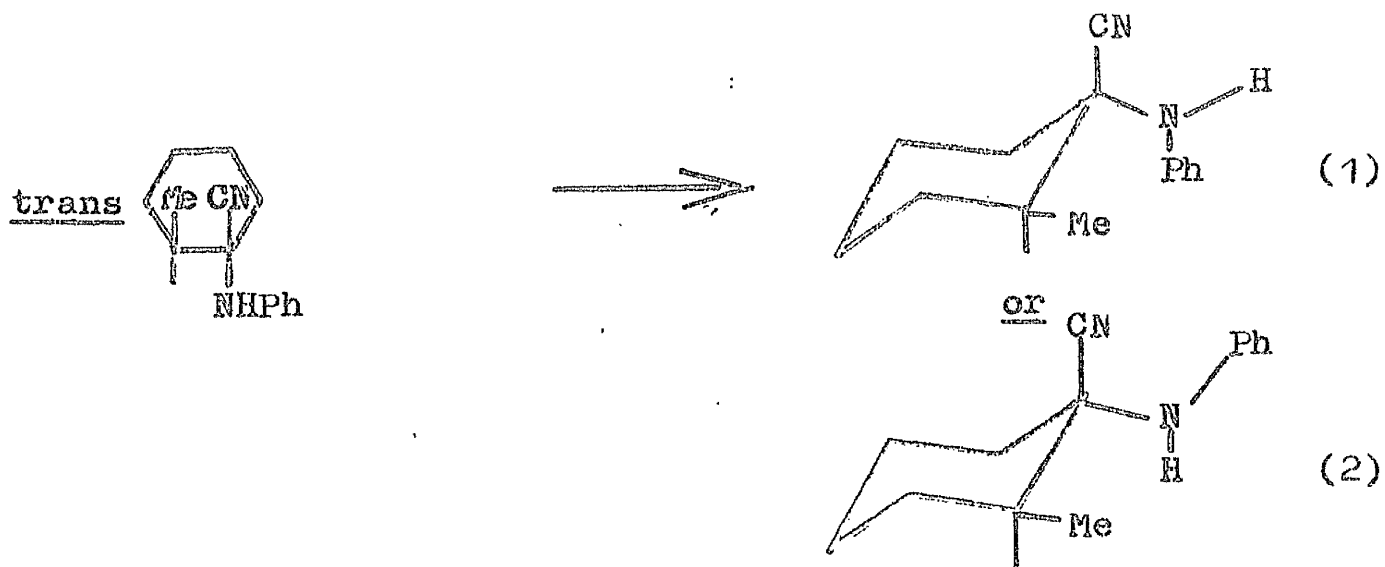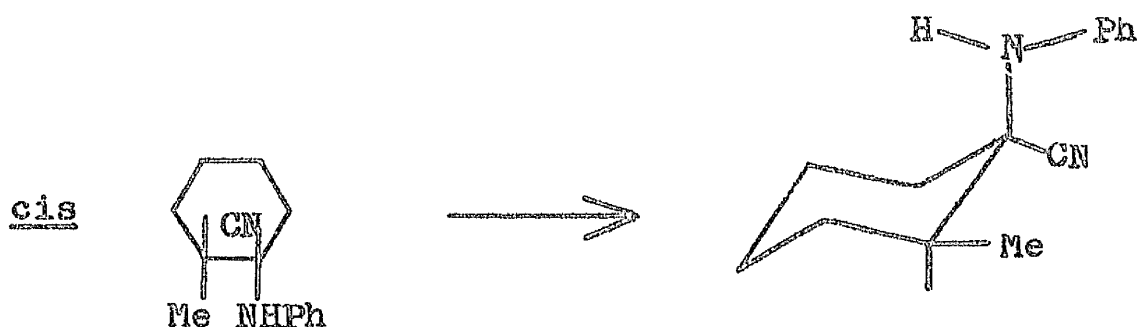
There are two possible conformations of the trans isomer:
conformation (1) is preferred to conformation (2) owing to
a degree of steric hindrance between the nitrile and phenyl
groups in (2).   Hereafter the trans isomer will be assumed
to have the former conformation.   In the trans isomer, the
hydrogen attached to the nitrogen atom and the nitrile group
are close together, and the hydrogen atom is equatorially
orientated similarly to the hydroxyl hydrogen of the trans
cyanohydrin isomer.   The cis isomer has the hydrogen atom
of the anilino group and the nitrile group comparatively far
apart, with the phenyl group approximately coplanar with the
cyclohexane ring.

Mechanism of the Elimination Reaction.

The elimination reaction has therefore been shown to
be of the type found by Fieser[79] rather than that deduced by
Parham, Moulton and Zuckerbraun[78].   This elimination reaction
without inversion, found for the cyanohydrins, is an interest-
ing reversal of the general rule found by Ingold et al.[82] of
consistent inversion of configuration in a large series of
elimination reactions with phosphorus halides.

The results can be explained consistently with the theory of elimination reactions if the presence of the nitrile group at the seat of substitution is considered. Hughes[84] has shown that the elimination reaction consists of the formation of an ester halide which can either be followed by an inversion step or an intramolecular rearrangement with the elimination of an inorganic oxyhalide. The presence of a nitrile group at the seat of substitution, however, can cause retention of configuration by the latter reaction, and is the probable cause of the apparent reversal of the general rule. The reaction may then be represented as follows:
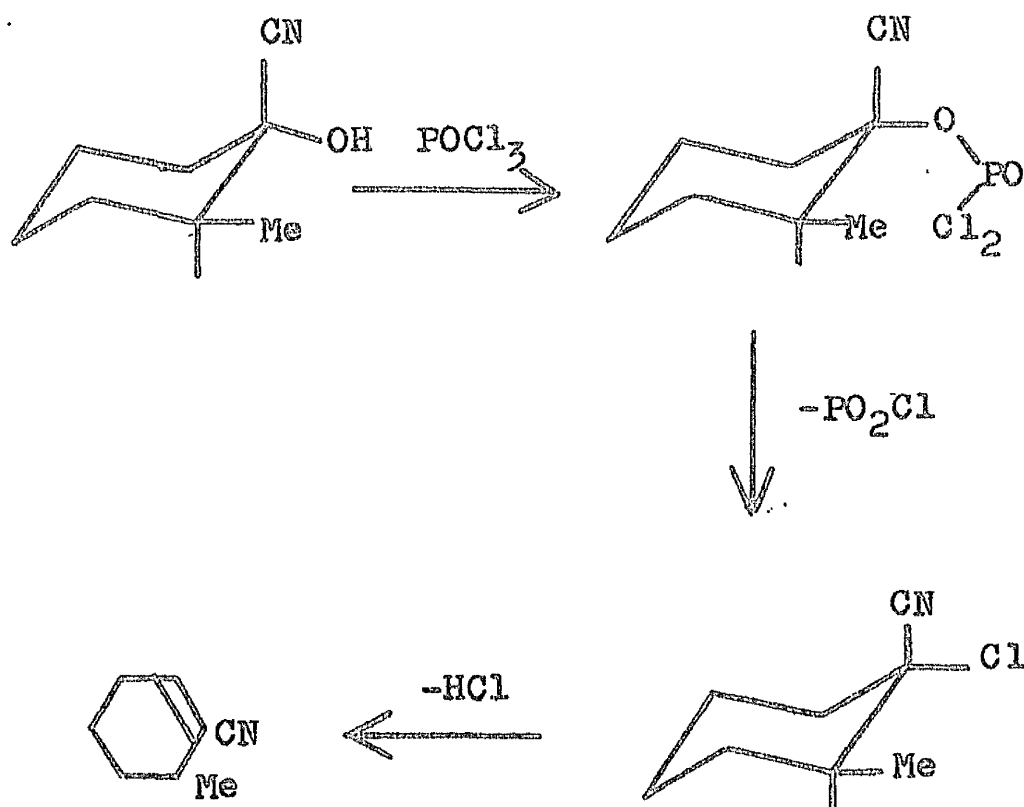
The Preparation and Identification of 1-Cyano-2-methylcyclohex-1-ene and 1-Cyano-6-methylcyclohex-1-ene 2.

It was found necessary to prepare the above olefinic nitriles and establish their structures as standards for analysis of the pyrolysates from the isomeric anilino-nitriles and benzoyloxy-nitriles.

Several groups of workers have prepared 2-methylcyclohexanone cyanohydrin and dehydrated the reaction product, obtaining an olefinic nitrile or mixture of nitriles.   None, however, has made a full study of the products formed or assigned structures to them.

Linstead and Millidge[85] mention a semi-solid cyanohydrin mixture, which they did not investigate but considered to be a mixture of 2-methylcyclohexanone cyanohydrin isomers. They considered their dehydration product to be 1-cyano-6-methylcyclohex-1-ene.   Braude and Wheeler[77] obtained a liquid cyanohydrin mixture which they dehydrated with phosphorus oxychloride and pyridine, obtaining a product which was at least partly the above nitrile, since hydrolysis with phosphoric acid gave 6-methylcyclohex-1-ene carboxylic acid. They also identified the nitrile by ultraviolet spectroscopy, obtaining a spectrum characteristic of the system $:C \cdot C:N$, though this is of course characteristic of both isomers.
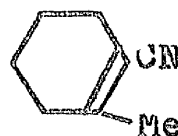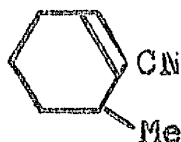
Phosphoric acid has recently been shown[86] to cause double bond shifts in substituted cyclohexenes, which possible accounts for only one acid product being obtained, the 1,2-nitrile being isomerised to the 1,6-nitrile during the hydrolysis. More recently, Kamernitskii and Ahrem[87] showed that 2-methylcyclohexanone cyanohydrin prepared from the ketone, potassium cyanide, and mineral acid yields a mixture of isomers which contains 73.6% of the solid trans isomer and 26.4% of a liquid cis isomer.

2-Methylcyclohexanone cyanohydrin has been prepared by several methods, the most convenient being addition of glacial acetic acid to a stirred mixture of ketone and potassium cyanide in methanol. After standing for 48 hr. the reaction product crystallised to a semi-solid mass. The solid, filtered off and recrystallised from light petroleum (b.p.60-80°), proved to be identical with that prepared by Bain[2] from the ketone and liquid hydrogen cyanide (m.p.56-59°). The liquid residue continued to deposit crystals over a period of weeks, leaving a viscous liquid which gas-liquid chromatography showed to be a mixture of the cyanohydrin isomers in about equal proportions. Overall, the isomers were in the proportions 75% solid : 25% liquid which agrees well with Kamernitskii and Ahrem's results. The solid isomer was smoothly dehydrated by phosphorus oxychloride and pyridine to a pure olefinic nitrile, shown by hydrolysis with hydrochloric acid to be 1-cyano-6-methylcyclohex-1-ene.

Isomerisation of 1-Cyano-6-methylcyclohex-1-ene

The nitrile from the above preparation was refluxed for 24
hr. in a solution of sodium isopropoxide in isopropyl alcohol
in an attempt to isomerise it by the method of Parham, Moulton
and Zuckerbraun[78]. The product from the isomerisation con-
tained 5-10% of a new higher boiling material, assumed to be
1-cyano-2-methylcyclohex-1-ene. A 56 hr. reflux yielded
about 40% of the new material, which could not be separated
from its isomer by distillation. The 1,2-isomer has also
been prepared in much greater purity by the pyrolysis of
trans-1-benzoyloxy-1-cyano-2-methylcyclohexane.

Dehydration of the liquid mixture of cyanohydrin
isomers gave a ratio of 79% 1,6-isomer: 21% 1,2-isomer.
Since the solid isomer gives 100% of 1,6-isomer, the 1,2-
isomer must give 58% 1,6-isomer and 42% 1,2-isomer, if both
cyanohydrin isomers dehydrate at the same rate. The liquid
isomer, therefore, probably dehydrates by the Hofmann rule.

Pyrolysis of cis- and trans-1-Anilino-1-cyano-2-methylcyclo-hexane

Six preliminary pyrolyses of the anilino-nitriles at 400,
500, and 600° showed that[2] as at the lower temperatures of
200 and 250°, the major breakdown route was loss of hydrogen
cyanide from the molecule with formation of an anil, the
reaction being reversible at room temperature.
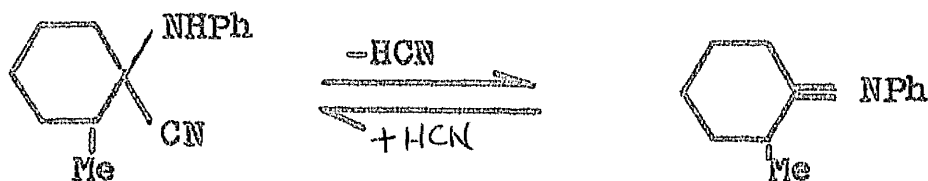
Gas-liquid chromatography has now shown the unexpected formation of aniline without formation of the expected related compounds 1-cyano-2-methylcyclohex-1-ene and 1-cyano-6-methylcyclohex-1-ene. Consideration of the possible modes of formation of aniline showed that there were three possible routes.

(1)   A direct scission of the molecule into aniline and the corresponding nitrile: a route already investigated and found to be absent. Control runs with mixtures of aniline and the olefinic nitriles have shown that they are distinguishable by gas-liquid chromatography.

(2)   The self-condensation of the anil 2-methyl cyclohexylideneaniline to 2-methyl-6, 2'-methylcyclohex-1-enylcyclohexylideneaniline and aniline.
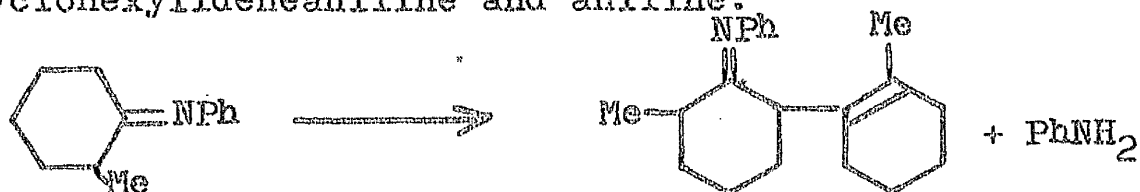
Cyclopentylideneaniline has been found[2] to self-condense very readily at 250° in this manner. In addition, Reddelien and Meyn[88] have reported a similar catalysed self-condensation of cyclohexylideneaniline at 60°, and Sapiro and P'eng[89] observed a slow uncatalysed self-condensation of cyclohexylideneaniline. There would appear, therefore, to be a strong possibility that this reaction takes place to some

extent during the pyrolysis.

(3)   A third but less likely possibility is an inter-
       molecular reaction such as the following:
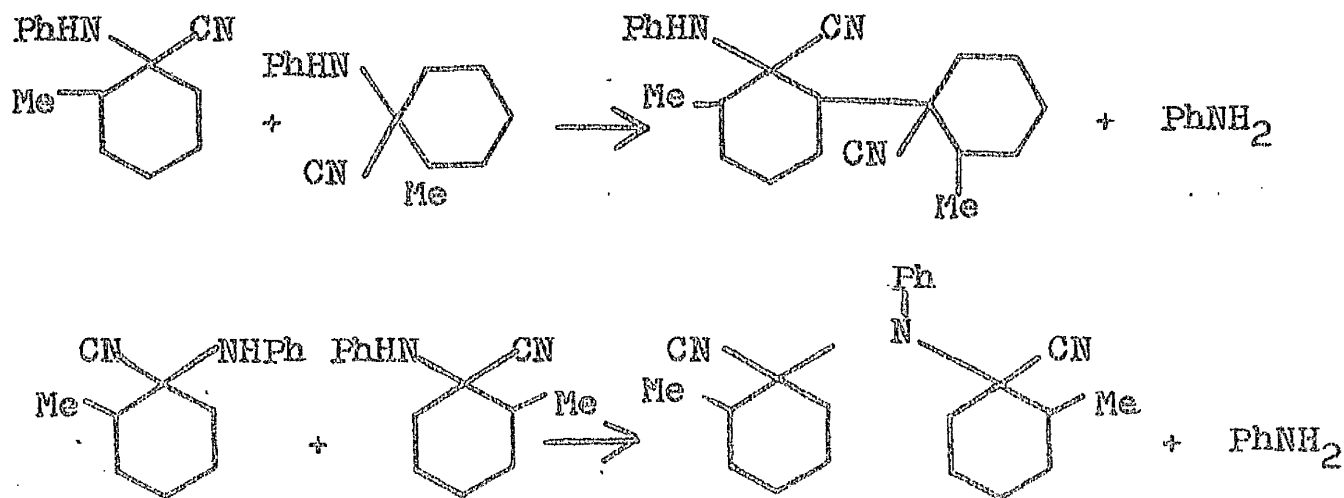
       This type of reaction should yield aniline and a
condensation product, possibly similar to the unknown com-
pound[2] found in the pyrolysate from 1-anilino-1-cyanocyclo-
pentane.   Since the first possibility had been discounted,
attention was turned to the other two.   Several different
lines of approach were tried.

(1)   The trans isomer was pyrolysed on a large scale at
       500° and high boiling products carefully sought in
the distillate of the pyrolysate.

(2)   1-Anilino-1-cyanocyclohexane itself was pyrolysed.
       It was hoped that the positive identification of any
condensation product of cyclohexylideneaniline would be
simpler owing to previous reports in the literature.

(3)   The anils were pyrolysed under the same conditions as

their anilino-nitrile precursor.   Any aniline produced

would confirm that self-condensation took place on pyrolysis.

In addition, it was hoped to compare the quantity of aniline

produced per mole of anilino-nitrile and of anil.

Large Scale Pyrolysis of trans-1-Anilino-1-cyano-2-methyl-cyclohexane.

Two large scale pyrolyses of the anilino-nitrile at 500°

yielded after successive distillations a few drops of a

thick viscous yellow liquid, b.p.160-163°/4 mm.   Ultraviolet

spectroscopy indicated that this fraction contained a com-

pound with two double bonds in the molecule.   Hydrolysis of

the fraction, followed by estimation of the aniline liberat-

ed, indicated the presence of a compound with the formula:
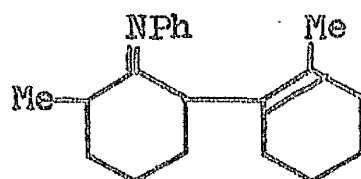
The ketone product of the hydrolysis had an infrared spectrum

very similar to that of the ketone of corresponding structure

prepared synthetically by the method of Mleziva[90].
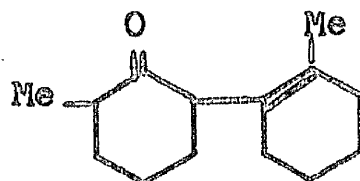
Positive identification was difficult, since the ketone did

not form any solid derivatives, possibly owing to steric

hindrance by the ortho substituents.

Pyrolysis of 1-Anilino-1-cyanocyclohexane.

Confirmation of the formation of aniline by secondary self-condensation of an anil was obtained by pyrolysis of this compound. From the pyrolysate, a viscous yellow liquid was obtained, b.p.160-170°/1 mm. (lit.,[88] b.p.212-214°/18 mm.) whose hydrolysis, followed by estimation of the aniline and preparation of solid derivatives of the ketone showed it to be 2-cyclohex-1-enylcyclohexanone. There was a small amount of an even more viscous material, which on cooling solidified to a glassy yellow solid, but which could not be induced to crystallise. The condensation reaction and the resultant products will be discussed in more detail later.

Pyrolysis of Anils.

Pyrolysis of the anils 2-methylcyclohexylideneaniline and cyclohexylideneaniline confirmed that their self-condensation was the cause of formation of aniline. Both anils, shown by gas-liquid chromatography to be pure before pyrolysis, produced aniline in their pyrolysates. Gas-liquid chromatography also indicated a small peak with the same retention time as the synthetic condensation products.

Pyrolysis of Cycloheptylideneaniline.

The close similarity between the reactions of cyclic ketones and cyclic anils was further emphasised by pyrolysis of

cycloheptylideneaniline at 500th. Wallach[91] has shown that
the ease of condensation of cyclic ketones is in the
following order:

$$c_5 \; > \; c_6 \; > \; c_7$$
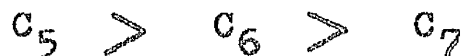
If self-condensation is the reaction producing aniline,
cycloheptylideneaniline pyrolysed in the same way as the other
anils should be very stable. This was found to be so, only
a minute trace of aniline being detected in the pyrolysate.

Investigation of the Tarry Residues from Runs 3-10.

A third possibility, previously mentioned, that aniline might
be formed by some unknown route along with an unknown compound
was further investigated. High vacuum distillation of these
tarry residues yielded a very high boiling fraction which
solidified to a sticky yellow-brown non-crystalline solid,
crystallised from light petroleum (b.p.60-80°) as fine silvery
crystals m.p.231-232°. Microanalysis indicated a carbon
percentage characteristic of a wholly aromatic compound. The
material must, therefore, have been formed only from the aromat-
ic anilino part of the molecule. A survey of the literature
showed that aniline gives small amounts of carbazole on
pyrolysis, thus:
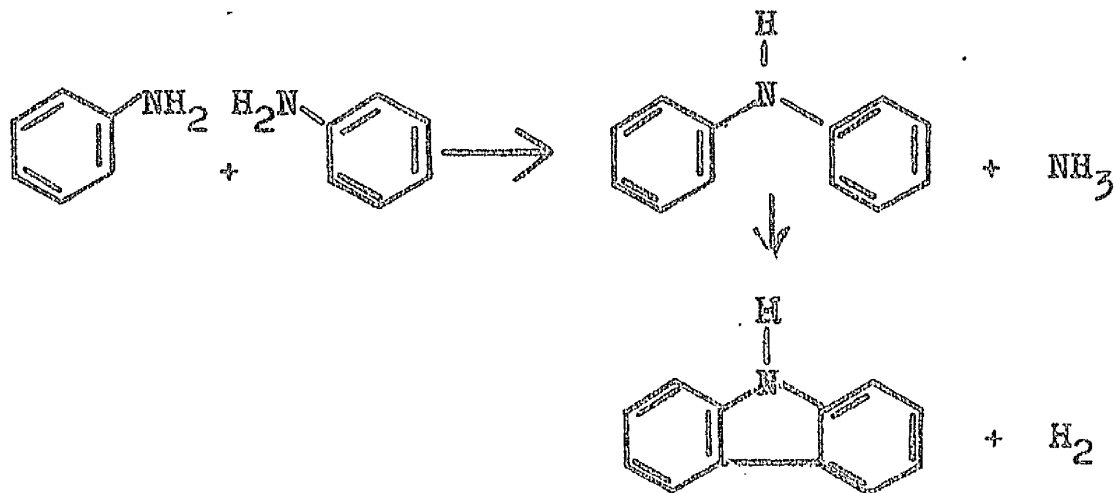
The compound was identified as carbazole by a mixed melting point determination. No diphenylamine was detected in the pyrolysate; but, since it dehydrogenates easily to carbazole, the rate-determining step being the formation of diphenylamine from aniline, it is probable that very little was present.

Structure of the Self-Condensation Product of the Anils.

The structure of the self-condensation product of the six-membered ring anils was at first thought to be 2-cyclohexyl-idenecyclohexylideneaniline (V) and 2-(2'-methyl cyclohexyl-idene)-6-methylcyclohexylideneaniline (VI) as suggested by Mannich[92].

V

VI
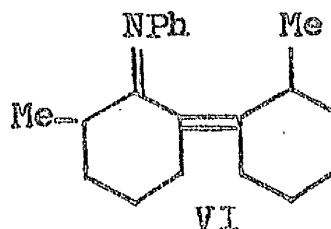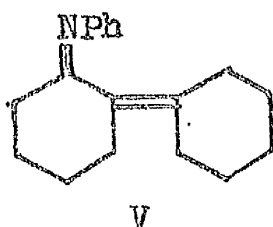
These structures are analogous to the well established structures of 2-cyclopentylidenecyclopentanone (VII) and 2-cyclopentylidenecyclopentylideneaniline (VIII).
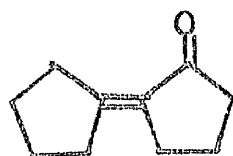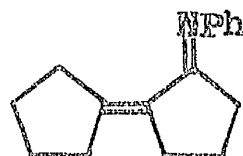
VII   VIII

It has been shown, however,[93] that the condensation product
of cyclohexanone is 2-cyclohex-1-enylcyclohexanone (IX) and
not 2-cyclohexylidenecyclohexanone (X) as originally thought.
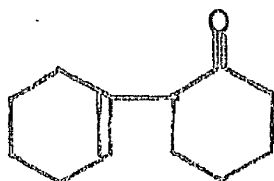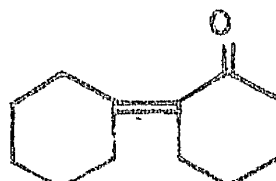
IX   X.

In addition, Sapiro and P'eng[89] have identified the structure
of the condensation product of cyclohexylideneaniline as
2-cyclohex-1-enylcyclohexylideneaniline, and this has been
confirmed by the present work.   The product of the self-
condensation of 2-methylcyclohexylideneaniline has, therefore,
been regarded as having a structure analogous to that of the
unsubstituted compound.   There are two possible isomeric
structures: 2-methyl-6, 2'-methylcyclohex-1-enylcyclohexyl-
ideneaniline (XI) and 2-methyl-6,6'-methylcyclohex-1-enyl-
cyclohexylideneaniline (XII).
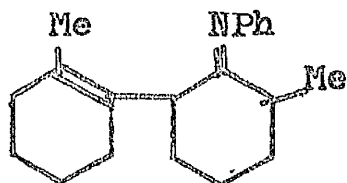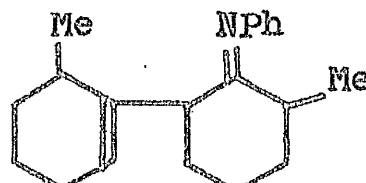
XI   XII

The high boiling fraction obtained from the pyrolysates will
most likely be a mixture of isomers rather than the one pure

compound.

There is, however, some doubt at present regarding
the structure of the product obtained from the condensation
of three molecules of cyclohexanone. The triple-condensa-
tion product of cyclopentanone was long accepted as having
the structure 2',6-dicyclopentylidenecyclopentanone (XIII),
though this had neither been proved nor disproved.
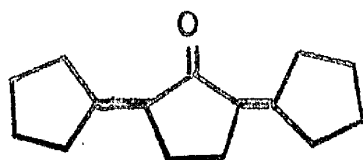
XIII

Recently, Mleziva[94] brought forward evidence for the alter-
native structure 2,2'cyclopentylidenecyclopentylidenecyclo-
pentanone (XIV)
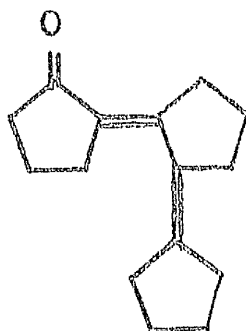
XIV

Mleziva also isolated a new product, m.p.79°, from the self-
condensation of cyclohexanone, which he suggested had the
structure 2,2'-cyclohex-1-enylcyclohexylidenecyclohexanone
(XV).
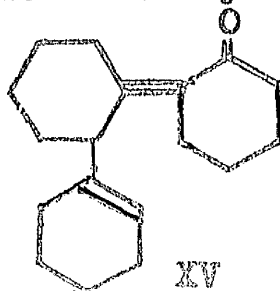
XV

More recently, Plesek[95] reinvestigated the evidence for the structure of these compounds and obtained evidence for the structure (XIII) originally proposed by Mannich for the tri-condensation product of cyclopentanone. Cyclohexanone was found to have a more complex reaction. The main product of the tricondensation was found to be 2,6-dicyclohex-1-enyl-cyclohexanone (XVI).

XVI
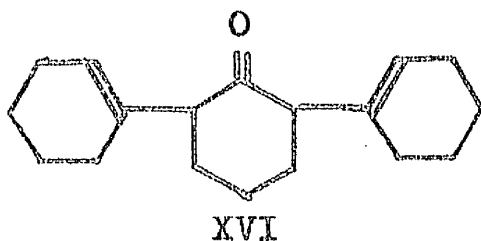
There was also present a liquid mixture of 2,6-dicyclohexyl-idenecyclohexanone (XVII) and 2-cyclohex-1-enyl-6-cyclo-hexylidenecyclohexanone (XVIII).

XVII

XVIII
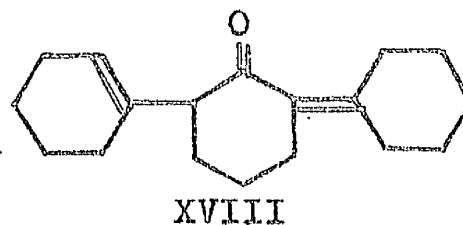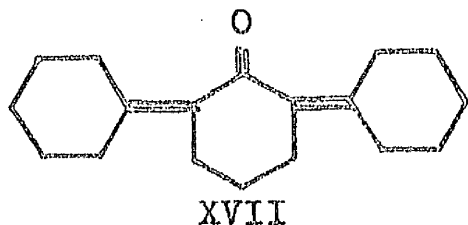
Some measure of confirmation of the results of Plesek has come from Svetozarskii et al.[96], who prepared and identified the ketone (XV) of the structure proposed by Mleziva, finding it to have m.p.44° and to have different properties from the ketone prepared by Mleziva and Plesek. The results of Plesek, however, cannot be regarded as conclusive, since Edgar and Johnson[97], while investigating the products obtained from the condensation of ammonia with cyclopentanone and cyclohexanone,

identified compounds which must have been formed via the
ketones (XIV, XV) having the structures proposed by Mleziva.
On the basis of these results, therefore, the very high boil-
ing fraction from the pyrolysis of 1-anilino-1-cyanocyclo-
hexane is best regarded as a complex mixture of the following
isomeric anils:

XIX

XX

XXI
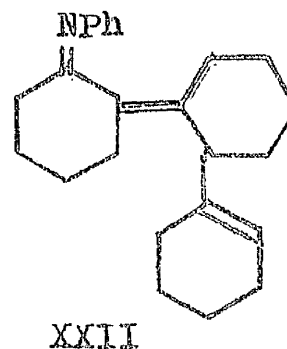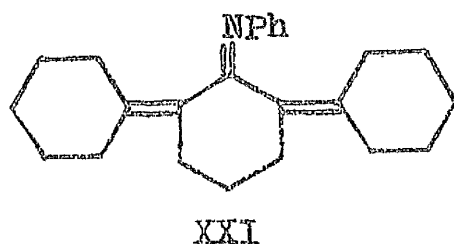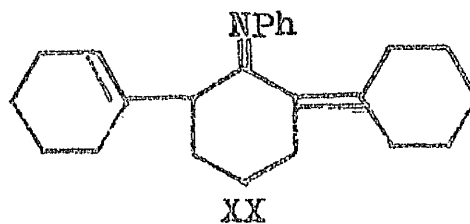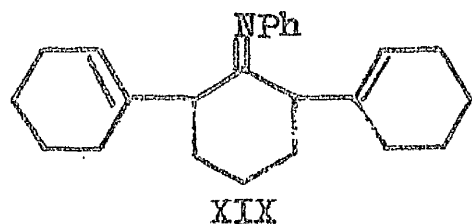
XXII

The other possible structure, 2-(2'-cyclohexylidenecyclo-
hexylidene)cyclohexylideneaniline (XXIII), was considered to
be inadmissible[96] since it has too high a degree of steric
hindrance (as indicated by a study of molecular models).

XXIII
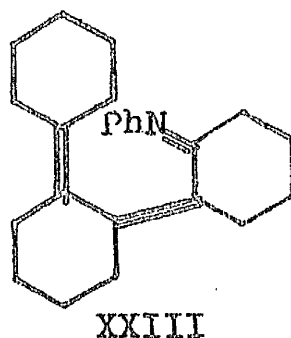
The cis, trans isomers of 1-anilino-1-cyano-2-methylcyclo-
hexane did not yield a similar high boiling fraction from

their pyrolysates, but a small amount of a tarry residue was always left after distillation of their pyrolysates, which was probably a complex mixture of anils similar to those already discussed.   The _ortho_ methyl group in 2-methylcyclohexylideneaniline blocks one of the positions by which condensation may occur, and thus self-condensation will be much slower.

The structures of the ketones (VII, IX) and their corresponding anils are now well established, but as yet, the unconjugated structures of the six-membered ring compounds have not been satisfactorily explained.

X   IX
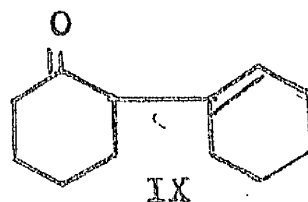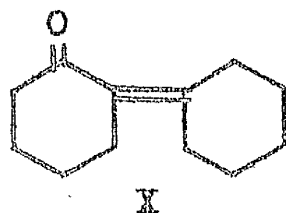
Birch, Ken and Norris[98] have shown that double bonds _exo_ to a six-membered ring tend to migrate into the ring and increase the stability of the compound; it seems probable, therefore, that the unconjugated ketone (IX) is more stable than the ketone (X) which has two adjacent _exocyclic_ double bonds in ring one.   Similarly, for the anils the unconjugated structure should be the more stable.   It is probable that even if the conjugated anils (V, VI) are formed to some extent during pyrolysis, the high temperatures at which condensation takes place will pause their rearrangement to the unconjugated structures.   For these reasons the condensation of three

molecules of cyclohexanone at 500° should produce mainly the
ketone (XIX), since all other possible structures have cyclo-
hexane rings with two or three exocyclic double bonds. The
findings of Plesek[95] that this ketone is the major product
of condensation lends some confirmation to this theory.

(XVI)

Mechanism of the Condensation Reaction.

The self-condensation reaction of the anil probably takes
place through the labile vinylamine form of the anil,
analogous to the enolic form of ketones and aldehydes through
which the aldol condensation proceeds.
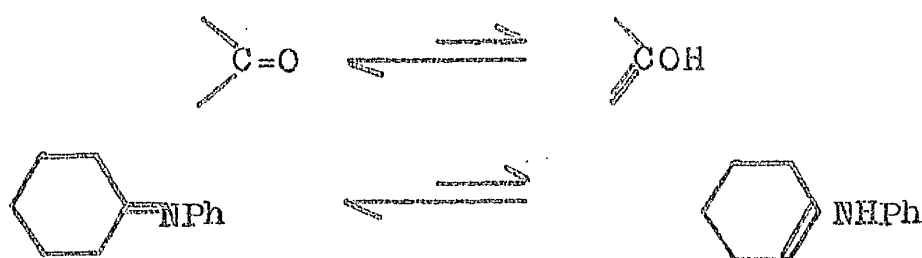
The lability of vinylamines is well known, though there is
evidence[99] that certain such pairs may exist separately. The
anils discussed in this work therefore probably exist in
equilibrium with the corresponding vinylamine. The condensa-
tion reaction can then be represented as follows:
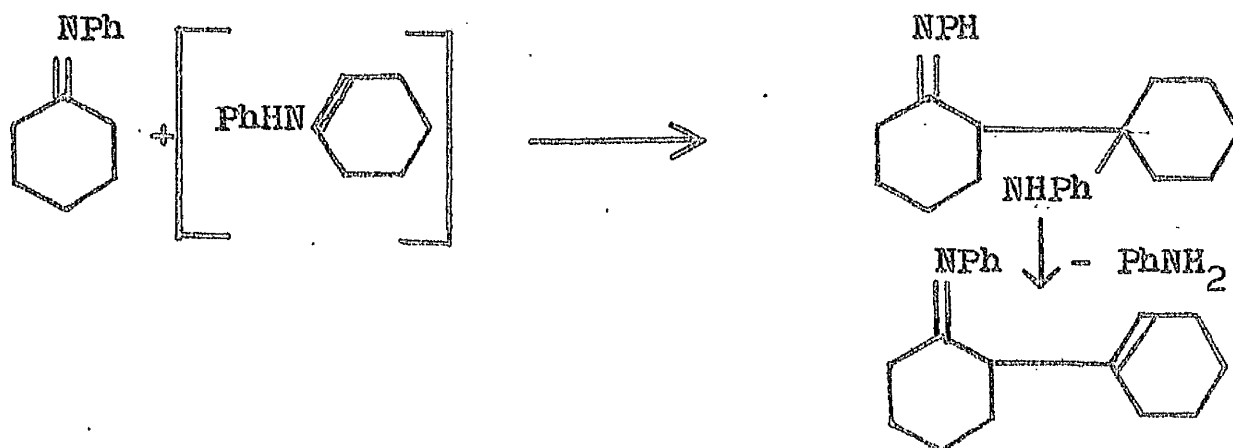
Elimination Reactions of the Anilino-nitriles.

The present results have confirmed previous conclusions[2,71] that at lower temperatures pyrolysis of anilino-nitriles takes place by a predominating scission to hydrogen cyanide and an anil, thus:

Gas-liquid chromatography has confirmed that the unsaturated nitriles 1-cyano-2-methylcyclohex-1-ene and 1-cyano-6-methyl-cyclohex-1-ene are not present even in small amounts in the pyrolysates, though small quantities of aniline occur, formed by a self-condensation of the anils.

The reactions of anilino-nitriles are therefore very different from those of anilino-acids, which readily eliminate aniline leaving the unsaturated acid.

Rates of Elimination of Hydrogen Cyanide from cis- and trans-1-Anilino-1-cyano-2-methylcyclohexane.

The study of the elimination of hydrogen cyanide from these molecules at high temperatures has also given fresh evidence for the C_1-N elimination of hydrogen cyanide rather than C_1-C_2 or C_1-C_6 elimination.

The percentage of hydrogen cyanide eliminated at $400°$, 500 and $600°$ from the anilino-nitriles is shown in the adjoin-

ELIMINATION OF HYDROGEN CYANIDE FROM CIS AND TRANS ISOMERS

TRANS ISOMER

CIS ISOMER

T°C

700

600

500

400

300

0   10   20   30   40   50   60

% HYDROGEN CYANIDE EVOLVED
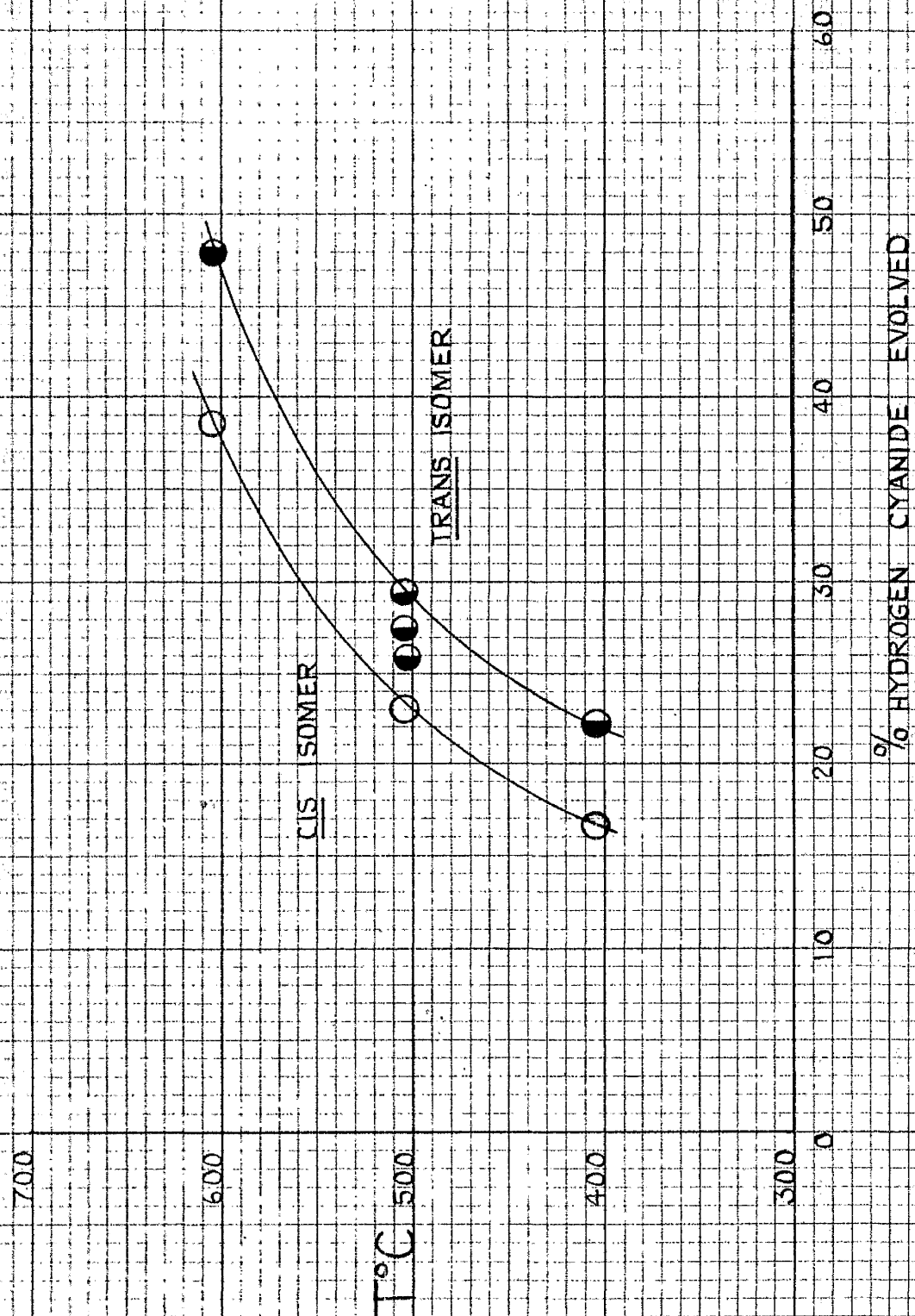
adjoining graph, which indicates clearly that at all temperatures the cis isomer is the more stable and eliminates an appreciably smaller amount of hydrogen cyanide. No definite conclusions can be drawn from these graphs, since the hydrogen cyanide eliminated depends on several factors. The primary factor will be the rate of the forward and back reactions in the furnace, thus:
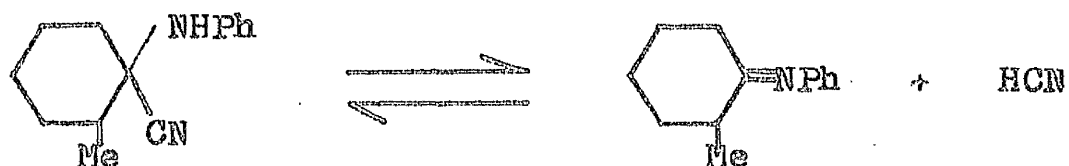
Scission will be favoured in the furnace, and recombination by the cooler conditions in the pyrolysate receiver. These reactions in turn depend on the effect of the nitrogen flow, the residence time, and slight variations in temperature during the pyrolysis.

The greater ease of elimination of hydrogen cyanide from the trans isomer may be conveniently explained by a study of Stuart models of the two isomers. The conformations of the isomers are represented thus:
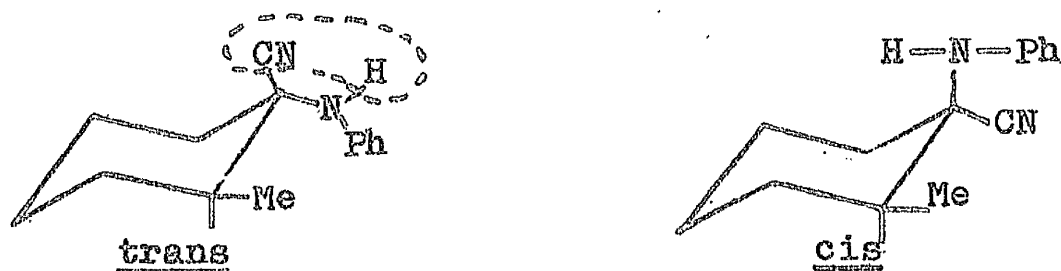
From these it can be clearly seen that whereas in the trans isomer the N-H atoms and CN atoms are close together on the same side of the molecule, in the cis isomer they are

comparatively far apart lying respectively above and beneath the plane of the cyclohexane ring. In the trans isomer, therefore, because of their proximity to each other, elimination of the hydrogen atom and the cyanide group will occur more readily than in the cis isomer.

This explanation is only valid if consistent C_1-N elimination of hydrogen cyanide from both isomers is assumed. This has already been considered[2] to be the most likely route. It is also significant that the cis-trans isomers of 1-benzoyl-oxy-1-cyano-2-methylcyclohexane, which have no hydrogen atom equivalent to the N-H atom in their molecules, yield only 0.1-0.5% of hydrogen cyanide on pyrolysis at 400-600°.

Stability of the cis-trans Anilino-nitrile Isomers

Because of secondary recombination of hydrogen cyanide and anil, regenerating the original anilino-nitriles, the presence of both isomers in the pyrolysate of either was to be expected. Fractional crystallisation of the pyrolysates of both isomers showed, however, that they contained predominantly cis isomer. This was surprising, since it has been shown[2] that addition of hydrogen cyanide to 2-methylcyclohexylideneaniline regenerates a mixture of the anilino-nitriles in the ratio cis to trans of 45:55. Hence, the trans and not the cis isomer should have been the major constituent formed by recombination. At first the results of the pyrolyses at 600° compared with those at 400° and 500° seemed anomalous, since no cis isomer was found

in their pyrolysates, though a small amount of <u>trans</u> material was obtained in the pyrolysate of the <u>cis</u> isomer. Further consideration showed that these results were a confirmation of the foregoing, since if the more soluble <u>cis</u> isomer predominates, it is likely to remain dissolved in these liquid pyrolysates and thus avoid detection. For this reason the ratio of <u>cis</u> to <u>trans</u> isomer was probably greater in all pyrolysates than that actually found.

At first the reason for the preponderance of <u>cis</u> material in the pyrolysates seemed to be that recombination of hydrogen cyanide and anil to give a mixture of anilino-nitriles occurred to quite a large extent, even at the high temperatures used. The proportion of <u>cis</u> material formed by this reaction would be mainly undecomposed because of its lower tendency to eliminate hydrogen cyanide, thus leaving more <u>cis</u> than <u>trans</u> material in the pyrolysates. Nevertheless this explanation must be excluded for several reasons. Although the <u>cis</u> isomer has been shown to be the more stable towards elimination of hydrogen cyanide, the difference in stability is small compared with the large quantities of <u>cis</u> isomer found in the pyrolysates. In addition, it seems unlikely that recombination could be favoured at the high temperatures used.

Even if recombination took place the residence time in the reactor is much less than the contact time between the cooled pyrolysate liquid and evolved hydrogen cyanide in the

receiving flask, where recombination should give a higher proportion of _trans_ than _cis_ isomer in the pyrolysate.

An alternative though improbable theory is that the more labile of the isomers is converted into the less labile by a direct interconversion. The pyrolysis of either isomer can then be represented thus:
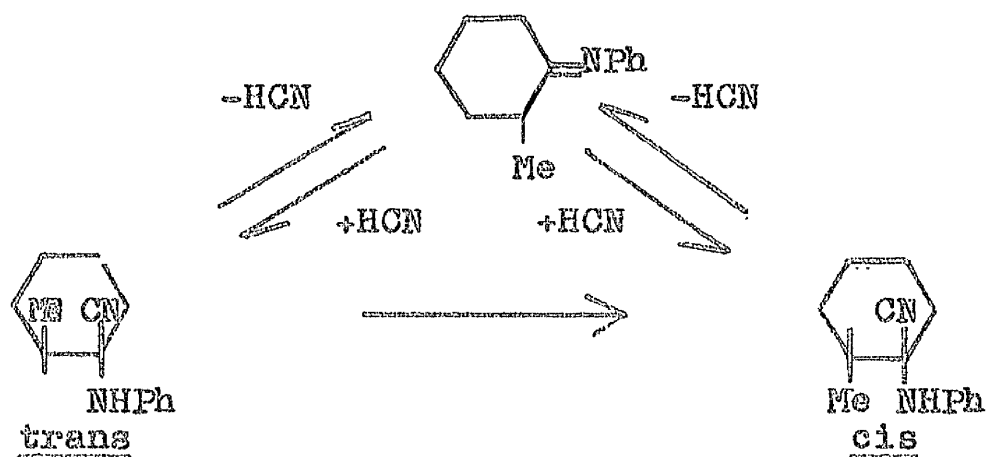
The most likely mechanism of interconversion of the isomers would appear to be _via_ an interconversion of _syn_ and _anti_ forms of the anil. Certain anils are known to exist in two separate interconvertible forms[100], the interconversion taking place by heating alone. There is also evidence[101] that certain anils exist normally in only one form and not as an equilibrium mixture. Bain[2] has found no evidence for different forms of the anil, but his static method of pyrolysis probably favoured an equilibrium mixture of the two forms.
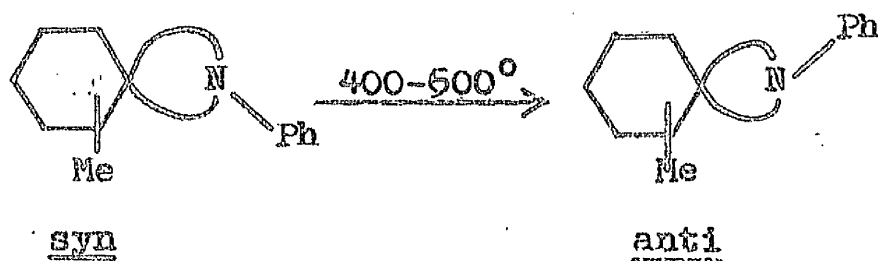
This discussion assumes that the anilino-nitriles exist in the conformations already discussed: also that reversal of the bond structure of the nitrogen atom occurs on elimination. This is the normal behaviour of an amine of the type $NR_1R_2R_3$, incapable of separation into optical isomers. The reaction for the trans isomer can then be represented as elimination of hydrogen cyanide giving the syn form of the anil by reversal of the bond structure of the nitrogen atom followed by conversion to the stable anti form at the high temperature employed. On cooling, the pyrolysate will consist mainly of the anti form of the anil which will recombine with the hydrogen cyanide evolved, forming cis isomer. There is probably a slow formation at room temperature of an equilibrium mixture of the anils, so that a small amount of trans material will also be formed. The reactions may then be represented thus:

Equilibrium Mixture
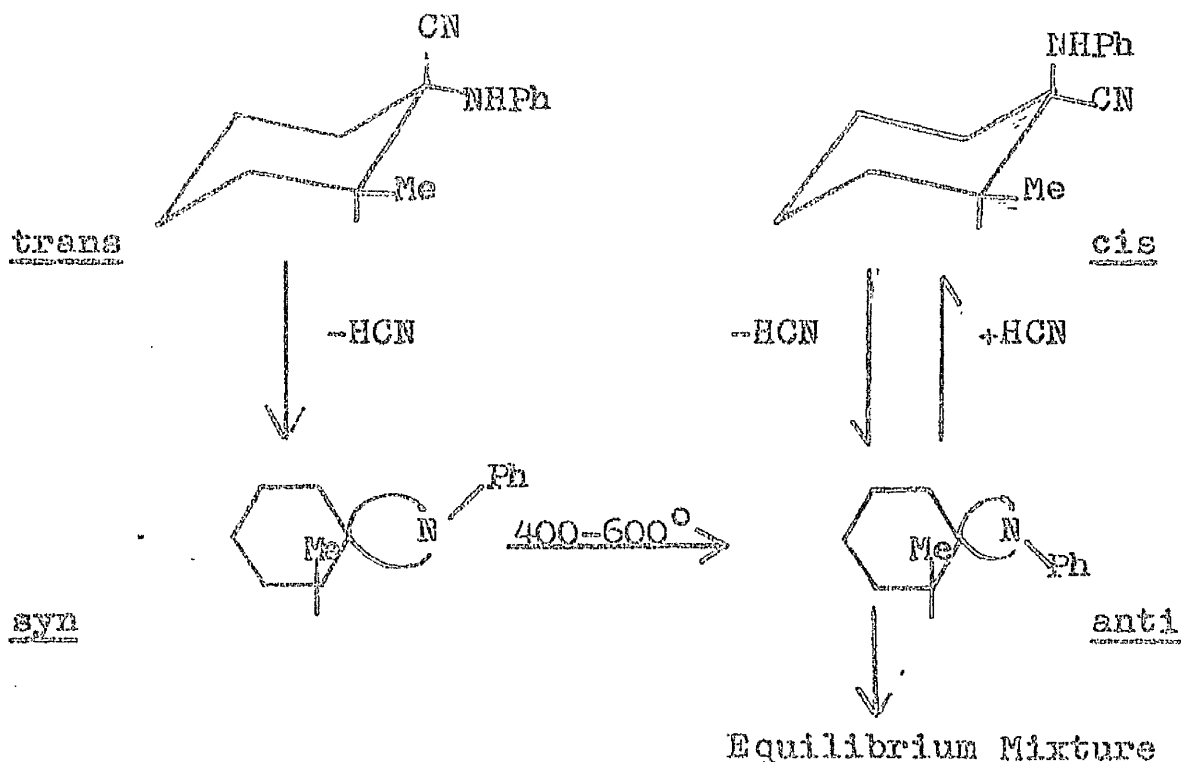
Pyrolysis of cis- and trans-1-Benzoyloxy-1-cyano-2-methyl-cyclohexane.

Cis- and trans-1-benzoyloxy-1-cyano-2-methylcyclohexane have been shown to give different products on pyrolysis in accordance with the following equations:

trans   Me CN   Me CH
          67%   33%

cis   Me CN   Mo CN
          96.5%   3.5%
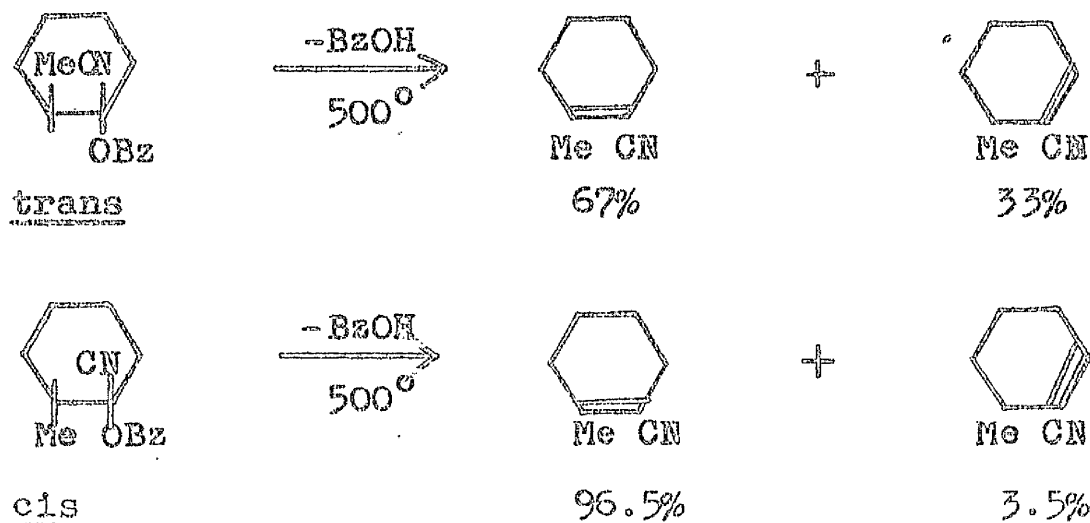
These results agree well with those of Alexander and Mudrak[25,26], who found cis eliminations to be the rule in acetate and xanthate pyrolyses.

($R = OAc$ or $O.CS_2Me$)

acetate	92.8%	7.2%
xanthate	96-100%	0.4%

cis

acetate	13.5%	86.5%
xanthate	11.7%	88.3%
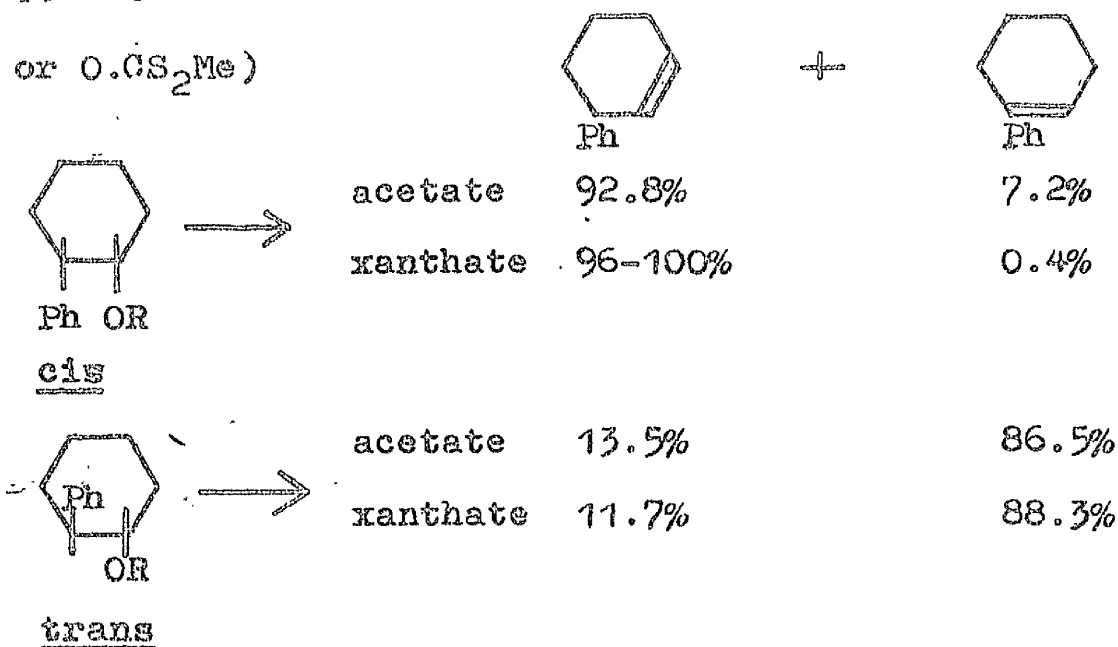
trans

The small amount of olefin indicating a trans elimination in the cis pyrolysis may either be due to a trace of trans impurity or to a very slight interconversion between the isomeric esters, similar to that suggested for the anilino-nitriles.

cis   trans
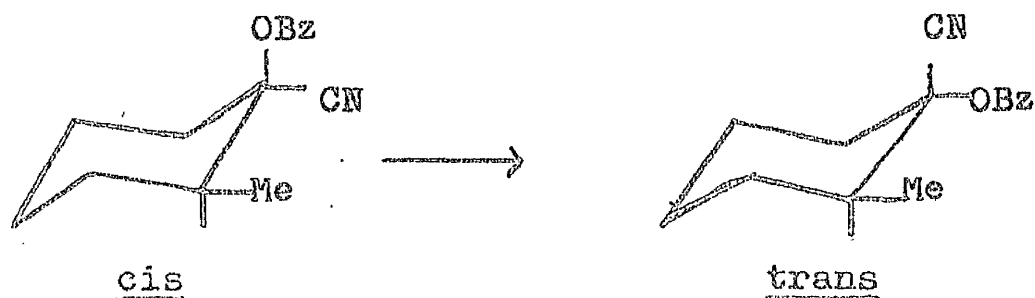
A third possibility, suggested by Barton[80], is that trans elimination in pyrolysis is indicative of an ionic mechanism. An interconversion of the type suggested would explain the small trans eliminations found by Alexander and Mudrak. Molecules which remain completely resistant to pyrolysis may be unable to undergo this type of interconversion because of structural considerations, e.g. an adjoining benzene ring[26].

No Reaction
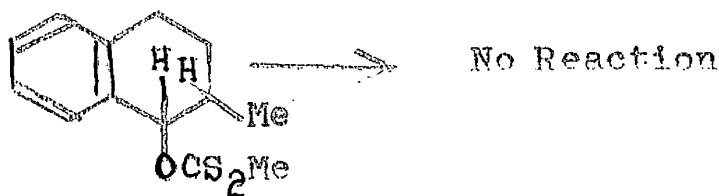
The results contrast markedly with those of Bailey and Nicholas[20] and Arnold, Smith and Dodson[27] who pyrolysed cis- and trans-2-methylcyclohexyl acetate and observed a trans elimination. Their results also differ widely in the proportions of methylcyclohexenes formed.

trans	91%	some. (Bailey and Nicholas)
	45%	55% (Arnold, Smith and Dodson)

68%	32%	95%	5%	(Bailey and Nicholas)
	100%	75%	25%	(Arnold, Smith and Dodson)
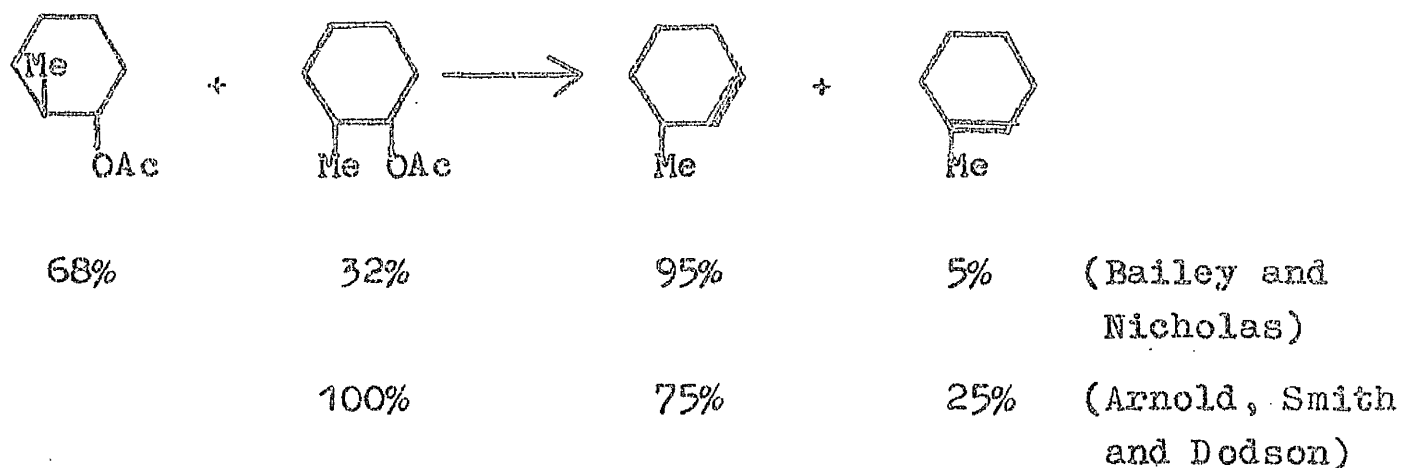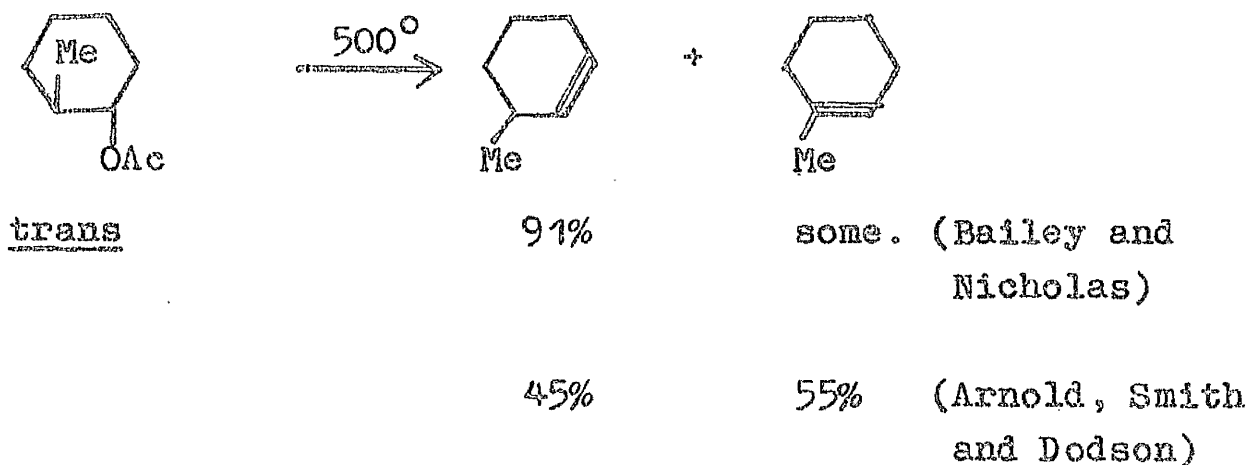
The present results, therefore, do not support those given above, which indicate a major trans elimination in ester pyrolysis. Barton[22] has given many examples of exclusive cis eliminations by the benzoates of steroid alcohols, and as proof of an ionic mechanism for a trans elimination cites[80] the pyrolysis of potassium bornyl sulphate, which yields camphene but not bornylene (trans elimination)[102], whereas the reverse holds in pyrolysis of the methyl xanthate[103].

Direction of Elimination

The results quoted above also indicate a marked preference
for elimination by the Hofmann rule.   The present results
show clearly that elimination takes place according to the
Saytzeff rule, which states that hydrogen is eliminated
preferentially from the most highly alkylated carbon atom.
Temperature of pyrolysis has also been shown to have little
or no effect on the direction of elimination.   This contrasts
with the work of Bailey and Hale[19] who found that at 400°
t-amylacetate followed the Hofmann rule, but the Saytzeff
rule at 225°.

$$AcOC(Me)_2 \cdot C_2H_5 \longrightarrow (Me)_2C:CHMe + CH_2:CMe.Et$$

	$(Me)_2C:CHMe$	$CH_2:CMe.Et$
400°	26%	74%
225°	58%	42%
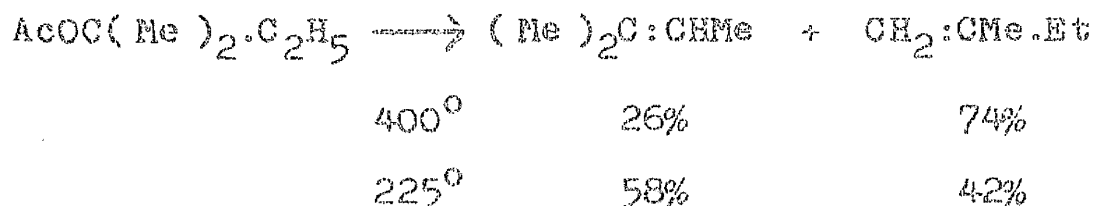
It can be seen that these results indicate a radical
change in the elimination mechanism.   Bailey has suggested
that the Saytzeff rule predominates at lower temperatures in
liquid phase pyrolyses, and that the stability of the olefin
becomes increasingly important as the temperature is lowered.
De Puy et al.[15] repeating Bailey's pyrolyses, found no such evid-
ence and concluded that the Saytzeff rule predominates at all
temperatures, with no change in the percentage composition of
the pyrolysate.   The present work, however, has shown that
the above conclusion of Bailey may be partially correct, since
a liquid phase pyrolysis of the trans isomer of 1-benzoyloxy-

1-cyano-2-methylcyclohexane at 220° showed a slight increase in favour of Saytzeff elimination from that at 500°. There was no radical change from the Saytzeff to the Hofmann rule, however, as the temperature was increased, and at 600° elimination was even more in favour of the former than at 220°.

The present results therefore, bear out the conclusions of Barton[22] that the Saytzeff rule is followed quite generally in ester pyrolysis, since preferential cis elimination takes place towards the bridgehead when this is stereochemically possible because the homolytic bond dissociation energies of C-H bonds decrease markedly in the following order:

$$-CH_3 \quad > \quad >CH_2 \quad > \quad ->CH$$
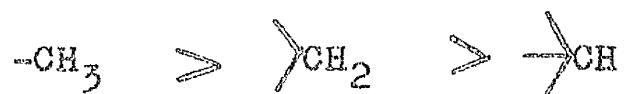
Unimolecular elimination of H-R therefore will proceed with decreasing activation energy in the following series:

$$primary \quad > \quad secondary \quad > \quad tertiary.$$
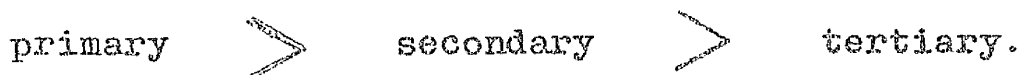
This decrease in activation energy was considered by Barton to be the principal factor in influencing the reaction velocity and causing preferential elimination towards the bridgehead. Benkeser, Hazdra and Burrows[17] have also concluded that direction of elimination does not depend on temperature of pyrolysis.

Other Products of Pyrolysis

As well as the two isomeric nitriles whose formation has already been discussed, two other products have been

identified in the pyrolysate. These are benzene and benzo-
nitrile. Benzene is an expected product produced by decarb-
oxylation of benzoic acid, while benzonitrile would be expect-
ed as a result of B^2 scission of the molecule to 2-methyl-
cyclohexanone and benzoyl cyanide, followed by decarboxylation/m
of the latter, thus:
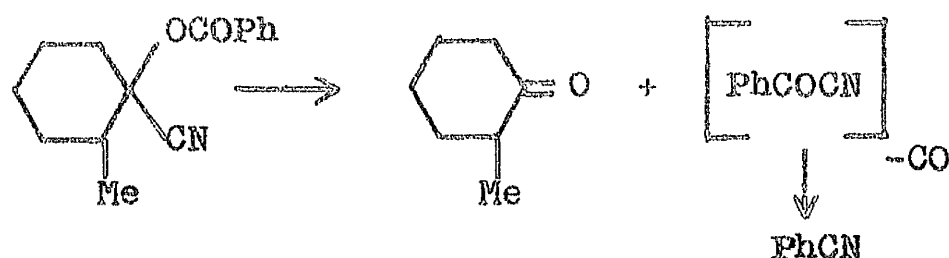
It is of interest that this is another example of a B^2
scission with transfer of a nitrile group rather than a
hydrogen atom. Surprisingly, neither 2-methylcyclohexanone
nor benzoyl cyanide could be detected in the pyrolysate.
Standard control runs with pure samples of these substances
showed that benzonitrile and the isomeric nitriles tended to
obscure their respective peaks and this was probably why they
were not observed. Analysis of the gas from pyrolysis of
the trans isomer showed the presence of 9.5% carbon dioxide
by decarboxylation of benzoic acid from A^1 scission. It is
possible that some decarboxylation of the ester might have
taken place to 1-cyano-1-phenyl-2-methylcyclohexane, thus:
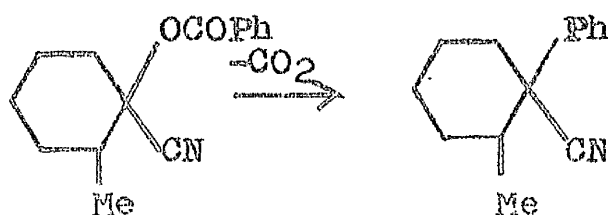
No high boiling products such as 1-cyano-1-phenyl-2-methyl-cyclohexane were observed on using gas-liquid chromatography. If present, therefore it must have been in very small quantities.

Pyrolysis of 1-Benzoyloxy-1-cyanocyclohexane

Benzoic acid and 1-cyanocyclohex-1-ene (85-90%)of the pyrolysate) were the major products of pyrolysis. Cyclo-hexanone, benzene, benzonitrile, and benzoyl cyanide were identified as present by gas-liquid chromatography. The three expected products of a $\underline{B}^2$ scission were, therefore, all found, confirming it as a minor route in the pyrolysis.
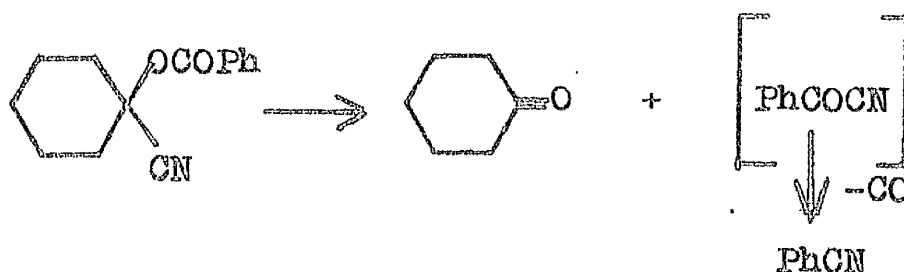
Fractional crystallisation of the solid fraction of the pyrolysate yielded only benzoic acid. There was no trace of any benzoyl cyanide dimer, α,α-dicyanobenzyl benzoate:

$$2 \text{ PhCOCN} \longrightarrow \text{PhCOOC(CN)}_2\text{Ph}$$

Source of Hydrogen Cyanide in the Pyrolyses

Pyrolysis of the isomeric benzoates has shown that only very small amounts of hydrogen cyanide are formed at 500°. Since the source of hydrogen cyanide throws fresh light on the

pyrolysis of the anilino-nitriles, cyclohex-1-enyl benzoate (the compound formed by C_1/C_2 elimination of hydrogen cyanide from 1-benzoyloxy-1-cyanocyclohexane) was carefully sought by gas-liquid chromatography, using a control sample of the ester.

Cyclohex-1-enyl benzoate was not detected in the pyrolysate, though 1.67% of hydrogen cyanide was given off. Further pyrolysis of the isomeric nitrile mixture from pyrolysis of the trans isomer gave a small amount of hydrogen cyanide, though the residence time was less than for the ester. It would appear, therefore, that the hydrogen cyanide is formed mainly if not entirely by secondary breakdown of the nitriles formed by primary scission of the ester.

Two unidentified compounds, present in small amount in the pyrolysate of the trans isomer were probably the above breakdown products.

Pyrolysis of 1-Cyano-6-methylcyclohex-1-ene

Pyrolysis of this compound has shown that for a residence time similar to that of the trans isomer, no isomerisation to 1-cyano-2-methylcyclohex-1-ene takes place. The proportion of isomers in the pyrolysate of the trans isomer will, therefore,

be that as actually formed by primary scission and not by an interconversion between the nitriles after breakdown has taken place.

EXPERIMENTAL

Experimental Section

Preparation of trans-1-Anilino-1-cyano-2-methylcyclohexane from trans-2-Methylcyclohexanone cyanohydrin

2-Methylcyclohexanone cyanohydrin (m.p.56-59°) (2 g.) and aniline (1.8 g.) were maintained at 50-60° for 72 hr. On cooling the reaction mixture, a dark brown solid separated: which recrystallised twice from benzene, had m.p.126-126.5°. (Mixed m.p. with trans isomer, 126-126.5°).

Preparation of trans-1-Benzoyloxy-1-cyano-2-methylcyclohexane from 2-Methylcyclohexanone cyanohydrin

Cyanohydrin (2.8 g.) was dissolved in dry pyridine (5 ml.) and cooled to 0°C: benzoyl chloride (2.8 g.) was then added and the whole heated to 130° for 2 hr. The reaction mixture was then cooled and poured on to a mixture of conc. hydrochloric acid and ice, followed by extraction with ether (25 ml.). The ethereal extract was washed with dilute hydrochloric acid, 10% sodium bicarbonate solution, and water, in that order, and then dried overnight over magnesium sulphate. After removal of the ether a light brown solid (5.1 g.) was left, m.p.92-92.5° (from 95% ethanol). (Mixed m.p. with trans isomer, 91-92°).

Preparation of cis and trans 1-Anilino-1-cyano-2-methyl-cyclohexane

The isomers were prepared by the method of Bukhsh et al.[104] from 2-methylcyclohexanone, aniline, potassium cyanide, and mineral acid and separated by the method of Bain[2] by fractional crystallisation from benzene and light petroleum.

Potassium cyanide (140 g.) in water (400 ml.) was added to a stirred solution of 2-methylcyclohexanone (224 g.), aniline (184 g.) and glacial acetic acid (1,000 ml.). After 1½ hr. stirring, the mixture solidified in the flask. The material was left standing overnight, filtered off and washed with water: yield 262 g. (61%). The crude product was then dried before fractional crystallisation. Final yield of isomers: trans form - 155 g. (65%) m.p.126-126.5°

cis   form - 107 g. (35%) m.p. 86-88°.

Subsequent work with pyrolysates containing mixtures of the isomers has shown that they can be more easily separated from light petroleum (b.p.60-80°). If the isomer mixture is dissolved in the minimum of solvent, the trans isomer crystallises first as large crystals on the walls of the containing vessel; on further cooling, the cis isomer starts to crystallise, shown by the appearance of milkiness in the solution. The solution is then warmed slightly, the trans isomer filtered off and pure uncontaminated cis isomer is finally obtained from the filtrate as fluffy white crystals.

1-Anilino-1-cyanocyclohexane : This was prepared in the same way as the anilino-nitriles above; obtained as colourless prisms m.p.74-75° (from ethanol): yield 66%; lit.[71] m.p.75°.

1-Anilino-1-cyanocycloheptane: Prepared in the same way; colourless prisms m.p.74-75° from ethanol; yield 67%, lit.[2] m.p.85-86°.

Preparation of Anils

These were prepared by pyrolysis of the corresponding anilino-nitriles in a static reactor similar to that described by Bain[2]. The anils prepared in this way were:

2-Methylcyclohexylideneaniline: Yield 83%, b.p.110-114°/3 mm., n_D^{20} 1.5503; lit.[105,2] b.p.143-146°/12 mm., n_D^{25} 1.5481, n_D^{20} 1.5504.

Cyclohexylideneaniline: Yield 87%, b.p.106°/2 mm., n_D^{20} 1.5451; lit. Reddelien and Meyn[88] give b.p.138-142°/19 mm.

Cycloheptylideneaniline: Yield 86%, b.p.108-110 /2-3 mm., n_D^{20} 1.5258; (not quoted in lit.).

The anils were all colourless compounds when freshly distilled, turning yellow within a few hours in contact with air and finally after several weeks a dark yellow-red colour.

The anils were pyrolysed immediately after being distilled and tested for their purity by gas-liquid chromatography since a pure sample of cyclohexylideneaniline analysed at regular intervals over a period of weeks slowly formed aniline by self-condensation to 2-cyclohex-1-enylcyclohexylidene-aniline.   It is of interest that cycloheptylideneaniline (shown to be the most unreactive anil) which had been kept for 5 years in a sealed tube was found on distillation, to have decomposed entirely by self-condensation.

Preparation of the Condensation Products of the Anils

2-Cyclohex-1-enylcyclohexylideneaniline

Cyclohexylideneaniline (4.5 g.) was heated with aniline hydro-chloride (0.5 g.) (200°: 5 min.).   The reaction mixture was then distilled giving 2 fractions: (i) 1.4 g., b.p.180-190°, (ii) 1.5 g., b.p.160-170°/1 mm.   Fraction (i) was identified as aniline;   fraction (ii) was identified as the required product by hydrolysis to the corresponding ketone and prepara-tion of solid derivatives.   The anil is a viscous yellow liquid which darkens rapidly on contact with air;   lit.Sapiro and P'eng[89] b.p.200-210°/15 mm.: Reddelien and Meyn[88] 212-214°/18mm.

2-Methyl-6,2'-methylcyclohex-1-enylcyclohexylideneaniline

This was prepared similarly.   A viscous yellow liquid b.p.

b.p. 160-170°/4 mm. was obtained (not quoted in lit.)

Condensation took place much more slowly.

Preparation of the Corresponding Ketones

These were prepared in known fashion[97].

2-Cyclohex-1-enylcyclohexanone: b.p.138-140°/12 mm., n_D^{20} 1.5061; lit., Brown and Ritter[106], b.p.137-139°/14 mm., n_D^{20} 1.515: Kon and Nutland[107], b.p.145°/17 mm., n_D^{15} 1.50692. The ketone formed a semicarbazone, m.p.179-181°; lit. m.p. 178-180°[88], m.p.175-177°[92]; and an oxime m.p.142-143°; lit.[92], 146-148°.

2-Methyl-6,2'-methylcyclohex-1-enylcyclohexanone: b.p.140-142° /2 mm., n_D^{20} 1.5000. The compound did not form any solid derivatives.

Preparation of 2-Methylcyclohexanone cyanohydrin

Most of the workers who have prepared this compound have obtained liquid mixtures of isomers, which were difficult to separate. Since it was desired to prepare at least the pure solid isomer in fairly large quantities, several methods of preparation were tried in order to find the most convenient.

The best method was that of Bockelheide and Schelling.[108] 2-Methylcyclohexanone (50 g.), methanol (500 ml.), and potassium cyanide (75 g.) were mixed, cooled to 0°C and glacial acetic acid (150 ml.) was added dropwise. The mixture was

then refluxed for 1 hr., cooled and poured into water (1500 ml.). The above authors state that the cyanohydrin separated at this stage. None separated out in this instance. The watery mixture was therefore extracted twice with ether. The ethereal extract was dried over magnesium sulphate and the ether distilled off. The crude residue (51 g., 82% yield) after removal of the ether slowly crystallised in 48 hr., yielding 22 g. of solid isomer which separated from methanol as colourless crystals, m.p. 56-59°; lit., Bain[2] gives 56-59°. The liquid residue slowly deposited crystals over a period of weeks. The final product of the reaction was 26 g. of solid isomer and 25 g. of a liquid product, shown by gas-liquid chromatography to contain the cis and trans cyanohydrin isomers in about equal proportions: The reaction produces, therefore, 76% of solid isomer and 24% of liquid isomer.

Dehydration of trans-2-Methylcyclohexanone cyanohydrin

The cyanohydrin was dehydrated in pyridine solution with phosphorus oxychloride by standard methods. The product obtained was a colourless liquid b.p. 80°/10 mm., n_D^{20} 1.4783, lit., Braude and Wheeler[77] give b.p. 78°/10 mm., n_D^{21} 1.4782. Gas-liquid chromatography showed that the product was pure, uncontaminated by any isomeric products. The product was identified as 1-cyano-6-methylcyclohex-1-ene by hydrolysis with sulphuric acid/glacial acetic acid to 6-methylcyclohex-1-ene carboxylic acid m.p. 106-106.5°, lit.[77], m.p. 106-106.5°.

Isomerisation of 1-Cyano-6-methylcyclohex-1-ene to 1-Cyano-2-methylcyclohex-1-ene

The nitrile (2 g.) was added to a hot solution of sodium isopropoxide (0.25 g. sodium/11 ml. dry isopropyl alcohol) and the resulting solution refluxed for 24 hr. The mixture was poured on to ice, neutralised with 6 N-sulphuric acid and extracted with ether. The ethereal solution was dried over magnesium sulphate. The residue left after removal of the ether had b.p.80-83°/10 mm. Gas-liquid chromatography showed that the product contained 5% of 1-cyano-2-methylcyclohex-1-ene. A 56 hr. reflux yielded the olefin in 40% yield.

Dehydration of Liquid Cyanohydrin Isomers.

Dehydration by the same method used for the solid isomers yielded a mixture of the olefinic nitriles in the ratio 1,6 : 1,2 isomer, 79 : 21, b.p.85-86°/11 mm.

Hydrolysis of the Mixture of Olefinic Nitriles

Hydrolysis of the nitrile mixture (1 g.) for 96 hr. with sulphuric acid/glacial acetic acid (2 g.) yielded an ethereal extract and a sodium carbonate extract which on acidification yielded an impure solid m.p.92-98° separated by fractional crystallisation into 6-methylcyclohex-1-ene carboxylic acid m.p.105.5-106° and 2-methylcyclohex-1-ene carboxylic acid m.p.86-87°; lit.[109], m.p.88°. The ethereal extract, on

reduction deposited a solid which formed fine colourless
needles m.p.139-140° from benzene/light petroleum. (Found:
C, 69.04; H, 9.6; N, 21.45% . Calc. for $C_8H_{13}ON$: C, 69.1;
H, 9.3; N, 27.6%). Hydrolysis of this compound to its
corresponding acid identified it as 2-methylcyclohex-1-ene
carboxamide (not quoted in lit.). A similar hydrolysis for
only 18 hr. gave a high yield of an amide m.p.147-148° and a
trace of acid m.p.105.5-106°. The amide was identified as
6-methylcyclohex-1-ene carboxamide by hydrolysis to its acid.
Rapson and Shuttleworth[110] obtained two amides on hydrolysis
of a mixture of the nitriles, m.p.128° and m.p.146°. Grund-
mann and Low[111] give 6-methylcyclohex-1-ene carboxamide as
m.p.142°. It is considered that the low-melting amide of
Rapson and Shuttleworth was a mixture of the two amide isomers
and the amide of Grundmann and Low a slightly impure version
of the high-melting compound.

A partial hydrolysis of the nitrile mixture to the
amides alone with hydrogen peroxide/potassium hydroxide by
the method of Radziozewski[112] and Buck and Ide[113] yielded only
the high melting amide. It can be seen therefore that the
1,6-nitrile is much more readily hydrolysable than its 1,2-
isomer. This is in agreement with McElvain[114] who states that
completely substituted olefins are very difficult to hydrolyse
(particularly those bearing electronegative substituents) and
also resistant to permanganate oxidation. It is not surpris-
ing therefore that an attempt to verify the structure of the

1,2-nitrile by permanganate oxidation failed.   Price[115]
similarly failed to oxidise 1-methylcyclohex-2-ene.

Preparation of 1-Benzoyloxy-1-cyanocyclohexane and the cis-trans isomers of 1-Benzoyloxy-1-cyano-2-methylcyclohexane

1-Benzoyloxycyanocyclohexanes are readily prepared from the
corresponding ketones by reaction with potassium cyanide and
benzoyl chloride by the method of Aloy and Rabaut[116].

Potassium cyanide (100 g.) in water (2 ml.) and
cyclohexanone (130 g.) were cooled to 6° with constant stirr-
ing in a 3 litre flask;   freshly distilled benzoyl chloride
(70 g.) was then added dropwise.   After 30 min. stirring a
white pasty material was precipitated.   The addition of
benzoyl chloride was then continued for a further 6 hr.
followed by stirring for another 2.   The organic layer in the
flask was then extracted with ether and the ethereal solution
shaken with sodium carbonate solution followed by washing with
water.   Removal of the ether yielded 50 g. of the ester,
obtained as colourless plates, m.p.77-77.5°, from ethanol;
lit.[72], m.p.73-74°.

Preparation of cis and trans 1-Benzoyloxy-1-cyano-2-methylcyclohexane

Preparation of the cis isomer proved rather difficult. Aloy
and Rabaut[116] prepared the esters from 3-and 4-methylcyclo-

hexanone but reported only one compound from each ketone though two would be expected. Ritchie and Shim[72] successfully prepared the _trans_ ester from 2-methylcyclohexanone but did not isolate any other material from the reaction mixture.

Initial attempts to prepare the isomers by the above method yielded only the _trans_ isomer m.p. 92-92.5° and a liquid mixture of the isomers of 2-methylcyclohexanone cyanohydrin which made fractional crystallisation of the product very difficult. Variation of the proportions of the reactants with cooling to -15° and raising the final temperature to 40° gave similar results. When the preparation was attempted without cooling the reaction mixture in any way, large quantities of benzoic anhydride were formed and very little of the _trans_ isomer.

Attempted Separation of the Benzoate and Cyanohydrin Isomers by Chromatography

By means of column chromatography it was hoped to separate either the benzoates themselves, or the corresponding cyanohydrins from which they can be easily prepared. The semisolid high-boiling fraction from the benzoate preparation, and the liquid residue from the cyanohydrin preparations were used for the separations.

In both instances 1 g. of isomer mixture was dissolved

in 25 ml. of benzene/light petroleum (b.p.60-80°), 1:10 mixture and introduced on to a 2 cm. column, containing 30 g. alumina. The column was elutriated with benzene/light petroleum (b.p.60-80°), 1:50 mixture followed by 1:20 and 1:10 mixtures. The main product of the benzoate separation was the trans isomer, m.p.92-92.5°, but a small quantity (7 mg.) of a colourless crystalline substance m.p.84-85° was obtained, but the small amount available made positive identification impossible. The cyanohydrins could not be separated possibly because of hydrolysis on the column.

Final Preparation of cis and trans Isomers

The cis isomer was finally prepared by benzoylation of the cyanohydrin isomers in pyridine solution followed by fractional crystallisation of the product from ethanol.

A liquid mixture of cyanohydrin isomers (30 g.) was benzoylated by standard methods. The reaction mixture was initially kept at 0° for 30 min. and then at 80° for 6 hr. followed by cooling to room temperature; water (150 ml.) was then added dropwise to destroy excess of benzoyl chloride (dropwise addition was intended to prevent formation of benzoic anhydride at this stage which had been troublesome in several previous preparations). The mixture was then extracted with ether and the ethereal extract washed with dilute hydrochloric acid, sodium carbonate solution and water before drying over magnesium sulphate. Removal of the ether left

a dark brown semi-solid (39.5 g.) which on crystallisation from ethanol (100 ml.) gave the following fractions:(i) 7 g., m.p.92-93°, (ii) 7.5 g.,m.p.92-93° on reduction to 75 ml., (iii) 5 g.,m.p.120-121° on reduction to 50 ml. Fractions (i) and (ii) were the trans isomer, fraction (iii) was benzoic acid. Progressive removal of solvent yielded no more solid. On distillation the liquid residue gave two fractions (i) 10 g., b.p.70-90°/2 mm., liquid and (ii) 7.3 g., b.p.168°/2 mm. Fraction (i) was shown by infrared spectroscopy to be unchanged starting material. Fraction (ii) was dissolved in ethanol (20 ml.) yielding a crystalline solid (3.7 g.) m.p.70-80°. This solid was much more soluble in ethanol than the pure trans-isomer: recrystallised from ethanol (5 ml.) two crystalline forms were obtained (i) hexagonal colourless plates m.p.92-93°, trans-isomer; (ii) large colourless needles m.p.85-86°; cis-isomer. Since further separation by fractional crystallisation yielded a mixture of the isomers, the cis-isomer was separated from the trans-isomer using tweezers and recrystallised again from ethanol: 0.75 g. of the cis-isomer were finally obtained. A mixed m.p. determination with the trans-isomer showed a depression to 65-80°. The cis-isomer is considerably more soluble in all solvents than the trans-isomer and was found to be identical to that previously obtained by chromatography (mixed m.p.). (Found: C, 73.98; H, 7.11; N, 5.49%. $C_{15}H_{17}O_2N$ requires C, 74.09; H, 6.99; N, 5.79%); M (cryoscopic in benzene 251; theory 257. The infrared spectrum

of the cis-isomer was very similar to that of the trans-
isomer.

Preparation of Reference Compounds

Benzoyl Cyanide

This was prepared by the method of Oakwood and Weisberger[117]
by refluxing cuprous cyanide and benzoyl chloride for 1½ hr.
at 220-230°. Crystallisation of the product from light
petroleum (b.p.60-80°) yielded colourless crystals m.p.32-32.5°.
(Oakwood and Weisberger give 32-33°).

Cyclohex-1-enyl Benzoate

This ester was prepared by the method of Nesmeyanov et al.[118]
with certain modifications[35]. A colourless liquid was
obtained b.p.140-142°/5 mm.; lit., 140-147°/6. mm[118].

Apparatus and Procedure

Flow Reactor   *Fig 1.*

Both pairs of isomers were pyrolysed in the standard flow
reactor already described. During pyrolysis of the anilino-
nitriles a stream of nitrogen was passed continuously through
the reactor to remove any hydrogen cyanide formed, the latter
being absorbed in two wash bottles each containing 100 ml. of

30% sodium hydroxide. After pyrolysis had ceased, the nitrogen flow was continued for 10 min. to remove all traces of hydrogen cyanide from the system; the hydrogen cyanide absorbed was then estimated by titrating the alkaline wash liquors against standard silver nitrate[119]. Nitrogen flow was adjusted by means of a flow meter and needle valve to 15 cc./min.

Static Reactor

The apparatus consisted of a 100 ml. 3-necked flask immersed in a Wood's metal bath. The bath was heated by an electric hot plate controlled by a "Simmerstat" to $\pm 5^{\circ}$. The apparatus was assembled as a reflux unit, the gaseous pyrolysis products being collected as for the flow reactor. Before each run, the reactor was flushed and evacuated with nitrogen several times.

Semi-Micro Reactor

2 see over

This apparatus is shown in fig(3) and is described elsewhere[69]. This reactor is very useful for the investigation of small amounts of valuable material, used in conjunction with gas-liquid chromatography. The pyrolysand (100-300 mg.) was placed in bulb A and bulb B filled with glass beads up to a constriction at C. The system was then evacuated and flushed with nitrogen several times via D and E. Furnaces G and F were heated to the desired temperature and furnace G slowly

POSITION 1   POSITION 2
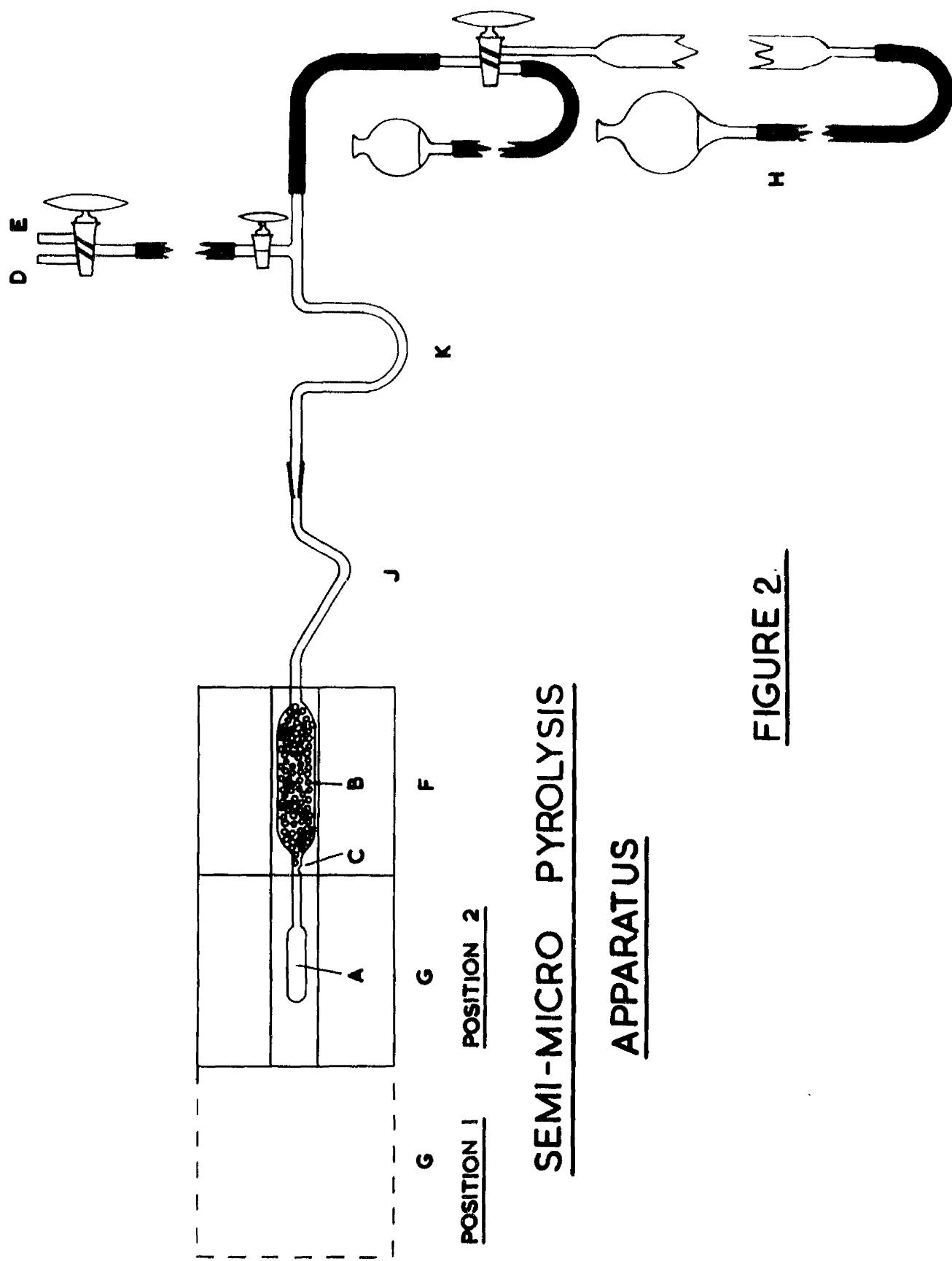
SEMI-MICRO PYROLYSIS
APPARATUS

FIGURE 2.

moved from position 1 to position 2, enclosing A.   The
barometric leg H was adjusted during the pyrolysis to keep the
system at atmospheric pressure and collect any gas evolved.
The solid and liquid pyrolysate was collected in the cold trap
K.   After pyrolysis the reactor was lowered to position 1 and
the system allowed to cool for 20 min.   Any gas evolved was
measured in the gas burette H.

Methods of Analysis

Aniline was determined by the method of Siggia[120].   Liquid
products were identified by conversion to known solid deriv-
atives followed by a mixed m.p.   Infrared spectrometry and
gas-liquid chromatography were used extensively as supplement-
ary methods of analysis.   The light petroleum used for
crystallisations and extractions was the fraction b.p.60-80°,
unless otherwise stated.

Gas-Liquid Chromatography

The unit used was a Griffin and George Mark II model with
columns of either silicone grease or Apiezon M grease on
kieselguhr using nitrogen as the carrier gas.   Care must be
taken when evaluating the results of gas-liquid chromatography
since the results may vary considerably from run to run
because of the large number of variables.   Certain compounds
have a tendency to give peaks which "drift" across the

recorder chart which makes for large variations in their
retention times from run to run; others are not separated
and show as one peak eg. benzonitrile and aniline. 2-Methyl-
cyclohexylideneaniline gave a very small peak which was
difficult to detect.   Whenever possible, therefore, gas-
liquid chromatography has been used as a preliminary means of
analysis followed by positive identification of pyrolysis
products as solid derivatives.

Details of Pyrolyses

Pyrolysis of trans-1-Anilino-1-cyano-2-methylcyclohexane

Run 1.

40 g. of the anilino-nitrile was pyrolysed at 400° yielding
hydrogen cyanide (22.5% of theory).   The semi-solid
pyrolysate (37.4 g.) was dissolved in light petroleum (100
ml.) yielding by fractional crystallisation 6.5 g. of trans-
and 14.2 g. of cis-isomer.   The liquid residue from the
crystallisation on distillation yielded the following
fractions: (i) 3 g., 200-220°, (ii) 4.5 g., 220-260°
(iii) 4 g., 260° and (iv) 2 g. a dark red residual tar.   All
liquid fractions were first investigated by gas-liquid
chromatography.   Fraction (i) contained two compounds.
Redistillation yielded a few drops of liquid identified as
aniline by conversion to acetanilide (m.p. and mixed m.p.
113-114°) and aniline hydrochloride (m.p. and mixed m.p.

196.5-198°).   Fractions (ii) and (iii) were 2-methylcyclo-

hexylideneaniline (the other component of fraction (i)) along

with traces of aniline.   2-Methylcyclohexylideneaniline was

identified by hydrolysis with 2N hydrochloric acid to 2-methyl-

cyclohexanone and aniline.   The 2-methylcyclohexanone was

identified as its 2,4-dinitrophenylhydrazone (m.p. and mixed

m.p.134-135°) and the aniline as acetanilide (m.p. and mixed

m.p.113-114°).

Run 2

This run was very similar to run 1.   The anilino-nitrile

(40 g.) was pyrolysed at 500° yielding hydrogen cyanide 29.7%

of theory and a pyrolysate (37.5 g.) from which was obtained

5.9 g. of trans and 13.8 g. of cis isomer.   The liquid residue

on distillation yielded four fractions: (i) 1 g., 170-190°,

(ii) 5.3 g., 190-240°,   (iii) 6 g., 240-280° and (iv) 2.4 g.,

a sticky black tar.   Fractions (i), (ii) and (iii) corres-

ponded to the same fractions from run 1.   Fraction (iv) was

not investigated further at this stage.

Run 3

Pyrolysis of the trans-isomer (40 g.) at 600° gave a dark

brown pyrolysate (30 g.) with much carbonisation in the

pyrolysis tube.   No solid crystallised out after 2 days.

The pyrolysate was distilled giving the fractions (i) 0.2 g.,

60°, (ii) 1 g., 60-100°, (iii) 2.3 g., 100-120°, (iv) 1.4 g.,

120-170°, (v) 2.5 g., 175-180°, (vi) 1.6 g., 180-260°,

(vii) 15 g., 260°, (viii) 6 g., a black glassy residue.

Fractions (i) - (vi) investigated by gas-liquid chromatography

proved to be an exceedingly complex mixture of about fourteen

compounds in varying proportions corresponding to a complete

breakdown of the molecule at the high temperature used,

probably by dehydrogenation and free radical reactions. Only

aniline was identified in the mixture. Surprisingly/neither /

1-cyano-2-methylcyclohex-1-ene nor 1-cyano-6-methylcyclohex-1-

ene could be detected since at the high temperature used some

decomposition to aniline and nitrile might have been expected.

The low boiling products were not further studied because of

their complexity. Fraction (vii) was the anil- 2-methylcyclo-

hexylideneaniline.

Pyrolysis of cis-1-Anilino-1-cyano-2-methylcyclohexane

Run 4

Pyrolysis of the cis isomer (20 g.) at 400° gave hydrogen

cyanide (17% of theory). The liquid fraction of the

pyrolysate contained aniline, 2-methylcyclohexylideneaniline

and a tarry residue: the solid fraction contained 0.4 g. of

trans isomer and 14.5 g. of cis isomer.

Run 5

Pyrolysis at 500° gave very similar results for the same

amount of material pyrolysed. Hydrogen cyanide (23% of

theory) was given off and the pyrolysate was of similar composition to run 4: 0.6 g. of trans isomer and 13.8 g. of cis isomer were identified in the pyrolysate.

Run 6

As with the high temperature pyrolysis of the trans-isomer, pyrolysis at 600° of the cis-isomer (20 g.) yielded an exceedingly complex pyrolysate in which only aniline and 2-methylcyclohexylideneaniline were identified. There was a large amount of tarry residue. Hydrogen cyanide (38.5% of theory) and 0.2 g. of the trans-isomer were also identified.

Large-scale Pyrolyses of trans-1-Anilino-1-cyano-2-methylcyclohexane

Run 7

A large scale pyrolysis of the trans-isomer was now undertaken in order to investigate further the high boiling fraction of the pyrolysate. The trans-isomer (100 g.) was pyrolysed at 500° eliminating hydrogen cyanide (26.4% of theory). Fractional crystallisation of the solid portion of the pyrolysate yielded 18 g. of trans-isomer and 31.5 g. of cis isomer. Distillation of the liquid pyrolysate yielded five fractions: (i) 5 g., 108-110°/2 mm., (ii) 0.25 g., 110-115°/2mm., (iii) 0.5 g., 145-180°/2 mm., (iv) 0.5 g., 180°/2 mm., A preliminary distillation at atmospheric pressure yielded only aniline and 2-methylcyclohexylideneaniline. Fractions (i),

(ii) and (iii) were 2-methylcyclohexylideneaniline with traces of aniline. Fraction (iv) was a thick yellow liquid which darkened rapidly on contact with air. A preliminary investigation showed that it had functional groups similar to those of 2-methylcyclohexylideneaniline (infrared) and an additional double bond (ultraviolet).

Run 8

This was very similar to run 7. The isomer (80 g.) produced hydrogen cyanide (21.5% of theory); 13.3 g. of trans-isomer and 27.1 g. of cis-isomer formed the solid portion of the pyrolysate. Distillation again yielded a very high boiling fraction b.p. 180-190°/2-3 mm. Hydrolysis of this fraction with 2N hydrochloric acid yielded aniline and a ketone which did not form solid derivatives but was identified as 2-methyl-6- 2'-methylcyclohex-1-enylcyclohexanone (infrared). Estimation of the aniline gave: 102.5%, 103.4% calculated for 1 mole aniline equivalent to 1 mole of 2-methyl-6, 2'-methyl-cyclohex-1-enylcyclohexylideneaniline. The deviation from 100% was probably caused by traces of 2-methylcyclohexyl-ideneaniline.

Pyrolysis of 1-Anilino-1-cyanocyclohexane

Run 9

1-Anilino-1-cyanocyclohexane (40 g.) was pyrolysed at 500° producing hydrogen cyanide (21.5% of theory). The pyrolysate -

a sticky yellow solid - was extracted with warm light petroleum and filtered.   Distillation of the filtrate residue after removal of the light petroleum yielded four fractions: (i) 1 g., 60-100°/2 mm., (ii) 6.5 g., 106°/2 mm., (iii) 1.3 g., 106-180°/2 mm., (iv) 1 g., 180-186°/2 mm. Fractions (i), (ii) and (iii) contained cyclohexylidene-aniline with traces of aniline.   Fraction (iv) was identi-fied as 2-cyclohex-1-enylcyclohexylideneaniline by hydrolysis to aniline and the corresponding ketone, identified as 2-cyclo-hex-1-enylcyclohexanone (semicarbazone and oxime: mixed m.p.). There was also 2-3 g. of a hard glassy residue from the distillation which could not be crystallised, probably a further condensation product.

Pyrolysis of Anils

Run 10

Cyclohexylideneaniline (6 g.) was pyrolysed at 500°.   The pyrolysate, investigated by gas-liquid chromatography showed three main peaks corresponding to aniline, cyclohexylidene-aniline and 2-cyclohex-1-enylcyclohexylideneaniline.   A comparison with the results from run 9 showed that these com-pounds were in approximately the same proportions in both pyrolysates.

Run 11.

2-Methylcyclohexylideneaniline (10 g.) was pyrolysed at 500°.

Both aniline and 2-methyl-6, 2'-methylcyclohex-1-enylcyclo-hexylideneaniline were identified in the pyrolysate by gas-liquid chromatography.

Run 12

Cycloheptylideneaniline (10 g.) pyrolysed at 500° was almost unchanged after pyrolysis. The pyrolysate contained only a trace of aniline, the remainder being unchanged starting material.

Pyrolysis of trans-1-Benzoyloxy-1-cyano-2-methylcyclohexane

Run 13

The ester (50 g.) was pyrolysed at 500° producing hydrogen cyanide (0.87% of theory), 1.2 litres of gas and a semi-liquid pyrolysate (49.1 g.) which was left overnight and filtered yielding benzoic acid (m.p. and mixed m.p.). The liquid residue was then distilled giving the fractions: (i) 5.7 g., 60-200°, (ii) 10.7 g., 200-208°, (iii) 2.2 g., 208-215°, (iv) 8 g., a solid brown residue. Fraction (i) contained the isomeric nitriles, 1-cyano-2-methylcyclohex-1-ene and 1-cyano-6-methylcyclohex-1-ene with small amounts of benzene and benzonitrile. Gas-liquid chromatography also indicated the presence of two other low boiling compounds, not identi-fied. Fractions (ii) and (iii) were mixtures of the unsaturated nitriles. Their presence was confirmed by hydrolysis of fraction (ii) to the corresponding acids which

were then identified (m.p. and mixed m.p.). Fraction (iv)
was benzoic acid (m.p. and mixed m.p.). Fractional
crystallisation of this fraction from light petroleum yielded
no other product. No starting material was found in the
pyrolysate: 21.5 g. of benzoic acid equivalent to an 83%
breakdown by an $\underline{A}^1$ scission were finally obtained.

Run 14

The trans-isomer (2 g.) was pyrolysed at 500° in the small
reactor in order to determine the exact proportions of the
unsaturated nitriles in the pyrolysate. Gas-liquid chroma-
tography showed them to be present in the ratio 1,6 : 1,2
33 : 67.

Pyrolysis of cis-1-Benzoyloxy-1-cyano-2-methylcyclohexane

Run 15

The cis-isomer (0.1784 g.) was pyrolysed at 500° in the semi-
micro reactor. The pyrolysate was extracted from the reactor
with ether and submitted undistilled to gas-liquid chromato-
graphy. Benzene and benzonitrile were detected as minor
components. The unsaturated nitriles were present in the
proportions 1,2 : 1,6 , 96.5 : 3.5 . The hydrogen cyanide
given off was too small in quantity to be detected.

Run 16

1-Benzoyloxy-1-cyanocyclohexane (4 g.) pyrolysed at 500° in
the small reactor gave off hydrogen cyanide (1.67% of theory).

As well as large quantities of 1-cyanocyclohexene and benzoic acid, cyclohexanone, benzoyl cyanide and benzonitrile were detected in the pyrolysate by gas-liquid chromatography. Cyclohex-1-enyl benzoate though carefully sought for was not detected.

Runs 17, 18, and 19

These three pyrolyses were all very similar. The mixture of isomeric nitriles from the pyrolysis of the trans-isomer was repyrolysed at 500, 550, and 600° in the small reactor in order to determine the quantity of hydrogen cyanide evolved and to compare it with the quantity from the ester itself. The results were as follows: run 17, 500°, 0.54%; run 18, 550°, 0.8%; run 19, 600°, 1.93%.

Runs 20, 21, 22, and 23

These pyrolyses were undertaken to see whether the distribution of isomers from the trans benzoate changed with temperature. The benzoate (2 g.) was pyrolysed in the small reactor and the pyrolysate dissolved in ether and submitted to gas-liquid chromatography.

	T^{o}C	Hydrogen cyanide (% of theory)	Isomers 1,2	1,6
Run 20	300	-	-	-
Run 21	400	0.63	62.7%	37.3%
Run 22	500	1.29	59.2%	40.7%
Run 23	600	2.13	75.2%	24.8%

Run 24

The trans-isomer was pyrolysed at 220° for 22 hr. in a static reactor. No gas was given off. The pyrolysate had a definite nitrile-like odour. Gas-liquid chromatography showed that the proportion of nitriles in the pyrolysate was similar to the proportions from previous pyrolyses: 1,2 : 1,6

69.5 : 30.5

Runs 25 and 26

In these pyrolyses 1-cyano-6-methylcyclohex-1-ene was pyrolysed at 500 and 550° to see whether there was any equilibrium between the nitrile and its 1,2-isomer of the type:
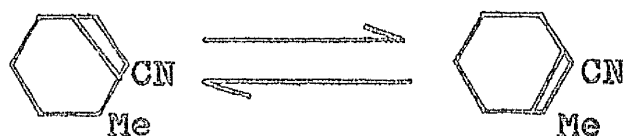
No 1-cyano-2-methylcyclohex-1-ene was found in the pyrolysate, however.

New Infrared Data

The following are the principal infrared absorption bands of the compounds studied.

2-Cyclohex-1-enylcyclohexylideneaniline

3210 w, 2930 w (shoulder), 2820 s, 2780 s (shoulder), 2580 w, 1680 s, 1635 m (shoulder), 1605 s, 1580 s, 1480 s, 1430 s, 1400 s, 1379 m, 1300 m, 1265 m, 1240 m, 1190 w, 1160 w, 1110 w, 1060 w, 1020 w, 985 w,

950 w,   920 w,   905 w,   870 w,   820 w,   748 s,   690 s, cm.$^{-1}$

Assignments

3210 cm.$^{-1}$ nitrogen NH

1680 cm.$^{-1}$ C:C or C:N

1605 cm.$^{-1}$ } anilino   NHPh

1580 cm.$^{-1}$

2-Methyl-6-(2'-methylcyclohex-1-enyl)-cyclohexylideneaniline

3300 w,   3150 w (shoulder),   3000 w (shoulder),

2900 s,   2820 m (shoulder),   1900 w,   1690 m,   1650 m, 1610 m,

1590 m,   1485 s,   1445 m,   1410 m (shoulder),   1330 w (shoulder), 1300 m,   1230 w,   1200 w,   1145 w,   1075 w,   1050 w,

780 m,   750 s,   693 s. cm.$^{-1}$

Assignments

3300 cm.$^{-1}$ nitrogen NH

1690 cm.$^{-1}$ C:C or C:N

1610 cm.$^{-1}$ } anilino NHPh

1590 cm.$^{-1}$

2-Cyclohept-1-enylcycloheptylideneaniline

3500 m (shoulder),   3420 s,   3280 m (shoulder)

3080 w,   2950 s,   2880 m,   1690 s,   1620 m,   1600 s,   1575 w,

1495 s,   1450 m,   1440 m,   1400 w,   1340 m,   1310 m,   1275 m,

1250 m,   1170 m,   1027 m,   941 m,   859 w,   752 s,   694 s. cm.$^{-1}$

Assignments

3420 cm.$^{-1}$ nitrogen   NH

1690 cm.$^{-1}$ C:C   or   C:N

1620 cm.$^{-1}$ }
1600 cm.$^{-1}$ }   aniline   NHPh

1-Cyano-6-methylcyclohex-1-ene

3300 w,   2900 s,   2850 m (shoulder),   2225 m,   1700 w,
1680 w,   1620 m,   1580 w,   1450 s,   1420 m,   1373 w,   1340 w,
1335 w,   1300 w,   1252 w,   1222 w,   1170 w,   1160 w,   1137 w,
1098 w,   1077 w,   1002 m,   978 w,   935 w, 893 m,   875 w,
866 w,   812 m,   745 w. cm.$^{-1}$

Assignments

2225 cm.$^{-1}$ nitrile   CN

1450 cm.$^{-1}$ C:C

trans-2-Methylcyclohexanone cyanohydrin

3350 s,   2900 s,   2820 s (shoulder),   2210 w,   1710 w,
1600 w,   1450 s,   1380 s (shoulder),   1470 s,   1340 m (should-
er),   1320 m,   1255 m,   1210 m,   1160 m,   1128 m,   1087 s,
1070 s,   1055 m (shoulder) cm.$^{-1}$.

Assignments

3350 cm.$^{-1}$ hydroxyl   OH

2210 cm.$^{-1}$ nitrile   CN

1-Benzoyloxy-1-cyanocyclohexane

2880 s,   1715 m,   1600 w,   1580 w,   1450 s,   1375 m,
1322 w,   1276 m,   1250 m,   1165 w,   1110 m,   1072 m,   1042 m

(shoulder), 1028 w, 964 m (shoulder), 952 w, 909 w, 851 w, 814 w, 708 s, 688 w, cm.$^{-1}$

Assignments

1715 cm.$^{-1}$	ester C:O
1650 cm.$^{-1}$ 1580 cm.$^{-1}$	phenyl

trans-1-Benzoyloxy-1-cyano-2-methylcyclohexane

3330 w, 2905 s, 2860 m (shoulder), 1720 s, 1590 m, 1575 w, 1445 s, 1365 m, 1303 m, 1265 s, 1240 s, 1224 m (shoulder), 1172 w, 1160 w, 1090 s, 1065 s, 1058 m (shoulder), 1028 s, 992 m, 982 m, 952 m, 921 m, 895 m, 870 w, 850 w, 825 w, 805 w, 710 s, cm.$^{-1}$.

Assignments

1720 cm.$^{-1}$	ester C:O
1590 cm.$^{-1}$ 1575 cm.$^{-1}$	phenyl

cis-1-Benzoyloxy-1-cyano-2-methylcyclohexane

2880 s, 1720 s, 1595 w, 1450 m, 1370 w, 1355 w, 1310 w, 1280 m, 1250 m, 1225 m, 1172 w, 1148 w, 1100 m, 1092 m, 1068 m, 1000 w, 944 m, 922 w, 710 s, cm.$^{-1}$

Assignments

1720 cm.$^{-1}$	ester C:O
1595 cm.$^{-1}$	phenyl

It is notable that for the three cyanobenzoates there is no characteristic peak for the nitrile group.

Tabulated Results

Table 1

Pyrolysand	trans-1-Anilino-1-cyano-2-methylcyclohexane		
Run No.	1	2	3
Temperature	400^0	500^0	600^0
Feed Rate (g./min.)	0.588	0.506	0.494
Contact Time (sec.)	30	30.5	27.5
Wt. pyrolysed (g.)	40	40	40
(a) In main receiver (g.)	37.4	37.5	30
Hydrogen cyanide (% of theory)	22.5	29.7	48
Gaseous pyrolysate (l.)	--	--	1.9
Trans isomer in pyrolysate (g.)	6.5	5.7	--
Cis isomer in pyrolysate (g.)	14.2	13.8	--

Table 2

Pyrolysand	cis-1-Anilino-1-cyano-2-methylcyclohexane		
Run No.	4	5	6
Temperature	400^0	500^0	600^0
Feed Rate (g./min.)	0.48	0.5	0.385
Contact time (sec.)	37	31	35
Wt. pyrolysed (g.)	20	20	20
(a) In main receiver (g.)	19.5	19.3	16.4
(b) Gaseous pyrolysate (l.)	--	--	2.
Hydrogen cyanide evolved (% of theory)	17	23	38.5
Trans isomer in pyrolysate (g.)	0.4	0.6	0.15
Cis isomer in pyrolysate (g.)	14.5	13.8	--

Table 3

Pyrolysand	trans-Anilino-nitrile		1-Anilino-1-cyano-cyclohexane
Run No.	7	8	9
Temperature	500°	500°	500°
Feed Rate (g./min.)	0.636	0.526	0.25
Contact time (sec.)	24	29	22.5
Wt. pyrolysed (g.)	100	80	10
(a) In main receiver (g.)	92.5	75.3	8.8
(b) Gaseous pyrolysate (l.)	--	--	--
Hydrogen cyanide (% of theory)	26.4	27.2	21.5
Trans isomer in pyrolysate (g.)	18	13.3	--
Cis isomer in pyrolysate (g.)	31.5	27.1	--

Table 4

These three pyrolyses cover the three cyclic anils
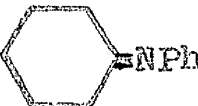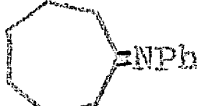
Pyrolysand	=NPh	=NPh Me	=NPh
Run No.	10	11	12
Temperature	500°	500°	500°
Feed Rate (g./min.)	0.226	0.25	0.25
Contact time (sec.)	21.5	21	21
Wt. pyrolysed (g.)	6	10	10
(a) In main receiver (g.)	5.8	9.7	9.8
(b) Gaseous pyrolysate (l.)	--	--	--

Table 5

Pyrolysands   **The Isomers of 1-Benzoyloxy-1-cyano-2-methylcyclohexane**

	trans isomer		cis isomer
Run No.	13	14	15
Temperature	500°	500°	500°
Feed Rate (g./min.)	0.455	0.455	—
Contact time (sec.)	38.5	15.5	
Wt. pyrolysed (g.)	50	2	0.1784
(a)In main receiver (g.)	49.1	1.9	0.165
(b) Gaseous pyrolysate(l.)	1.2	*	*
Composition of (b) approx.			
CO	79	*	*
CO_2	9.5	*	*
Unsat. hydrocarbons	11.5	*	*
Hydrogen cyanide (% of theory)	0.87	1.35	*

*   not measured

Table 6

Pyrolysands   1-Benzoyloxy-1-cyanocyclohexane   1-Cyano-2-methyl-cyclohex-1-ene + 1-Cyano-6-methyl-cyclohex-1-ene.

Rune No.	16	17	18	19
Temperature	500°	500°	550°	600°
Feed rate (g./min.)	0.47	0.26	0.254	0.273
Contact time (sec.)	0.123	13.2	12.7	11
Wt. pyrolysed (g.)	4	2	2	2
(a) In main receiver (g.)	3.85	1.9	1.9	1.8
Hydrogen cyanide (% of theory)	1.67	0.54	0.8	1.93

Table 7

Pyrolysand   trans-1-Benzoyloxy-1-cyano-2-methylcyclohexane

Run No.	20	21	22	23
Temperature	300°	400°	500°	600°
Feed Rate (g./min.)	0.2	0.266	0.25	0.23
Contact time (sec.)	44	28	26	25
Wt. pyrolysed (g.)	2	2	2	2
(a) In main receiver (g.)	1.98	1.95	1.84	1.7
Hydrogen cyanide (% of theory)	0	0.63	1.29	2.13

Table 8

Pyrolysand   trans-1-Benzoyloxy-1-cyano-   1-Cyano-6-methylcyclo-
            2-methylcyclohexane   hex-1-ene

Run No.	24	25	26
Temperature	220°	500°	550°
Feed Rate (g./min.)	*	0.31	0.28
Contact time (sec.)	22 hr.	11	11.5
Wt. pyrolysed (g.)	5	2	2
(a) In main receiver(g.)	4.95	1.9	1.9
Hydrogen cyanide (% of theory)	-	0.61	0.73

*   Static   pyrolysis

The Pyrolysis of Racemic 2-Butanol over Optically Active Quartz.

Introduction.

For some years there has been an apparent discrepancy between the experimental results summarised in sections A and B (below). This Appendix outlines a preliminary investigation into the reason for this discrepancy. For lack of time this work had to be broken off before conclusive evidence was obtained: but the interim results seem worthy of record.

(A). During a study of the solubility of silicious dusts[121,122], the existence of a highly soluble non-crystalline layer on the dust particle surface was deduced. Further investigation[123] showed that the apparent quartz content of the dust as shown by differential thermal analysis (which detects crystalline but not amorphous silica) fell off rapidly as the particle size decreased (that is to say as the proportion of non-crystalline material increased) but was restored to 100% by etching the dusts with hydrofluoric acid. A further investigation[124] by electron optical methods indicated that the surface layer (produced automatically by the grinding process) was amorphous, though there was some evidence of very minute crystallites between the amorphous and the crystalline layers. It would appear from this that any surface reactions of finely-ground quartz should be governed by the properties

of amorphous rather than crystalline silica.

(B)   Schwab and Rudolph[125] found that racemic 2-butanol,
pyrolysed by refluxing for several hours over copper
coated L-quartz in a nitrogen atmosphere, yielded an opti-
cally active liquid product having a slight dextro rotation.
Similarly, pyrolysis over D-quartz gave rise to a laevo-
rotation.   In a more detailed study of the reaction,
Terent'ev, Klabunovskii and Patrikeev[126] obtained similar
results, and it was suggested[127] that the reaction took place
by a stereo-selective asymmetric adsorption of the D-antipode
on the L-quartz surface (already known to be possible[128])
followed by the catalysed breakdown of the adsorbate at the
copper/quartz boundary, thus giving a greater concentration
of the L-antipode in the product.   An alternative explana-
tion was suggested by Burnwell[129] who observed racemisation
of D-2-butanol during its pyrolysis at 150-200°/360 mm. over
L-quartz coated with copper or zinc chromite.   He suggested
that the reaction mechanism was a racemisation of the
adsorbed D-alcohol rather than its preferential breakdown.

The results in section B have been explained on the
assumption that adsorption occurred on the surface of
crystalline quartz which has an asymmetric structure;   and
they /therefore_ conflict with the view[121,122] that finely-
ground quartz becomes coated with an amorphous layer which
because of the loss of asymmetric structure would not be

expected to have any stereo-selective effect on surface reactions with racemic compounds.   It was, therefore, decided to reinvestigate the pyrolysis of racemic 2-butanol over copper-coated D- and L-quartz, and in particular the effect of washing the quartz in hydrofluoric acid before pyrolysis to ensure that all amorphous quartz was removed from the surface.

Discussion of Results.

The results were inconsistent and difficult to interpret.   Preliminary results agreed with those of previous workers, in which the alcohol after pyrolysis over copper-coated L-quartz showed laevo-rotation.   These results however, were not reproducible.   Indeed in the great majority of runs no optical rotation was observed, although the racemic alcohol was pyrolysed over the copper coated quartz under a wide variety of conditions.   Analysis of the results showed that the reaction was more complicated than at first thought and demonstrated the need for a closer investigation of the nature of the quartz/copper surface and of the copper catalyst itself.   This further investigation was precluded through lack of time, and the work had to be left unfinished.

A curious feature of the few positive results obtained was that after 16-24 hr. the sign of rotation had changed from negative to positive.   This phenomenon was observed several times but from the results obtained it was impossible to deduce

a mechanism for this reaction.

The copper catalyst deposit on the quartz surface was obtained by reduction of a copper oxide deposit with hydrogen at 500°. A curious feature of this deposit was that it turned a bright green when exposed to air but after being submitted to a vacuum for 6 hr. no green colour appeared. It is possible that this effect was caused by adsorbed hydrogen on the copper surface. Adsorbed hydrogen may interfere with the breakdown reaction, since one of the two possible breakdown routes is a dehydrogenation to ethyl methyl ketone, thus:

$$\text{Et.CH(OH).Me} \xrightarrow{-H_2} \text{Et.COMe}$$
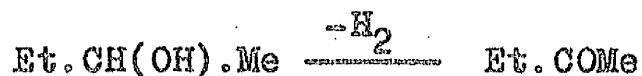
Preliminary washing of the quartz with hydrofluoric acid increased the volume of pyrolysis gas evolved, although it is not known whether this was due to cleaning the surface of amorphous quartz or to some catalytic effect of adsorbed hydrogen fluoride. The evolution of gas fell off very rapidly as the pyrolysis progressed, indicating that some kind of catalyst poisoning was taking place.

Conclusions.

The results obtained contrast markedly with those of previous workers who obtained reproducible constant rotations. This may be due to differences in the nature of the surface of the quartz or of the copper catalyst. The results do not show any positive evidence for the existence of a crystalline

layer on the quartz.   Physical methods of analysis are likely to be a more accurate method of determining the nature of the quartz surface.

Apparatus and Procedure.

The pyrolysis unit used was a modification of the static unit already described (page 108).   The alcohol was boiled in a 3-necked flask and its vapour passed through the pyrolysis tube in the furnace.   The liquid pyrolysate issuing from the furnace was either recycled to the flask or collected in a receiving tube as required.   During this work it was found that expansion of the quartz during the heating-up period caused the pyrolysis tube to crack.   The apparatus was successfully modified by using a horizontal pyrolysis tube. Pyrolysis gases were collected by the method previously described (page 33).

The 2-butanol used, supplied by British Drug Houses was dried over magnesium sulphate and distilled twice before use.   The quartz used was of the size $\frac{1}{2} - \frac{1}{4}$ in. produced by the shattering by impact of large pieces of quartz with a hammer.   Copper was deposited on the quartz by wetting the latter with a 5% solution of copper nitrate, followed by heating to 150° for 1 hr. and to 500° for 2 hr.   The cuprous oxide deposit left was reduced to copper by hydrogen at 500°. Optical activity was measured in a 10 cm. cell with a Hilger-Watts polarimeter reading to $\pm 0.02^{\circ}$.

Summary of Runs

Run No.	Temp. °C	Reactor	Wt. Pyrolysed (g.)	Gas Vol. (l.)	Coating	Pretreatment of Quartz	Observed Rotation
1.	500	Medium	30	1.9	Copper	—	—
2.	500	Medium	40	3.33	Copper	Hydrofluoric acid	—
3.	500	Medium	40	2.5	Copper	10% Sodium Hydroxide	—
4.	500	Medium	50	6.33	Copper	Hydrofluoric acid	—
5.	500	Medium	50	16.75	Copper	Hydrofluoric acid	—
6.	500	Medium	50	2	Copper	Hydrofluoric acid	$-.085°$
7.	500	Medium	40	1.66	Copper	Same as run 6	$-.06°$
8.	500	Medium	40	3	Copper	Hydrofluoric acid	$-.04°$
9.	500	Medium	50	5	Copper	Same as run 8	$-.13°$
10.	300	Small	40	0.97	Copper	—	—
11.	400	Small	30	0.3	Copper	—	—
12.	500	Small	30	0.45	Copper	—	—
13.	500	Small	40	4	Copper	—	—
14.	500	Small	40	2	Copper	Hydrofluoric acid	$-.02$
15.	500	Small	40	3.1	Copper	—	—
16.	500	Small	40	0.86	Copper	Hydrofluoric acid	—
17.	500	Small	40	0.56	Copper	Hydrofluoric acid	—

⊞ + .05 after 24 hr.

⊬ +0.24 after 72 hr.

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