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THE PYROLYSIS OF SOME $\alpha$-SUBSTITUTED BENZYL ESTERS
AND RELATED SUBSTANCES

THESIS

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

EDWARD JONES

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PUBLICATIONS

A part of this work has been published as follows: "Competitive Routes in the Pyrolysis of Acyl Cyanides and their Dimeric Forms", R.N. Bennett, E. Jones, and P.D. Ritchie, Journal of the Chemical Society, 1956, pages 2628–2631.


In addition, certain as yet unpublished sections of the work have been presented by the writer as a paper entitled "A Novel Reaction in the Pyrolysis of Certain $\alpha$-Substituted Esters," read before a meeting of the Glasgow and West of Scotland Section of the Chemical Society on 15th November, 1957.
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Summary

The pyrolysis of esters is exceedingly complex. It is known that most carboxylic esters decompose by two or more concurrent, competitive routes. The various breakdown routes of an ester may be predicted in advance with a fair degree of accuracy, although a novel scission is occasionally observed. Certain atoms and groups have been found to affect the thermal stability of esters and their mode of breakdown.

The present work consists of an investigation into the way in which the thermostability of benzyl benzoate is affected by the introduction of different atoms and groups into the benzyl group. Cyano, bromine and benzoyl groups were chosen to represent electrophilic substituents and the phenyl group a nucleophilic substituent. Certain other esters were also examined to facilitate the interpretation of the results obtained. While most of the breakdown routes obtained could be predicted, certain unexpected results were obtained. In the electrophilic substituted series of esters, a novel scission was recorded. This consisted of the formation of an α-diketone and the elimination of a simple molecule from the parent ester. This new scission has been examined in detail. The nucleophilic substituted esters decomposed in a complex manner giving a variety of products.
some of which were quite unexpected.

The thermal stability of diesters has also been studied and compared with that of other diesters e.g. ethylene dibenzoate, a model compound of poly (ethylene terephthalate). Attempts have been made to prepare a polyester, poly (methylene terephthalate).

Although much is known about the classes of ester breakdown little is known about the actual mechanisms involved. Preliminary investigations described in this thesis suggest the existence of charged particles during the pyrolysis of certain esters. An ionic mechanism is tentatively put forward to explain ester breakdown. A second possibility, based on free radicals, is also advanced.

Outlines for further work are indicated.
INTRODUCTION.

The Pyrolysis of Esters.

1.1. General.

A general survey of the literature on pyrolysis shows that there are many types of breakdown of alkyl esters. At moderate temperatures, around 450°C, the predominating breakdown is alkyl-oxygen scission to give an acid and an olefine. In general, esters of the type RCO₂CH₂CHR₂ pyrolyse to yield RCO₂H + CH₂:CR₂.

\[ \text{RCO}_2\text{CH}_2\text{CHR}_2 \rightarrow \text{RCO}_2\text{H} + \text{CH}_2:\text{CR}_2 \]

This scission involves the migration of a β hydrogen atom from the alkyl group on to the alkyl-oxygen atom.

If however there is no available β hydrogen atom in the alkyl group, the predominating breakdown is acyl-oxygen scission, yielding two carbonyl molecules. In general, esters of the type RCO₂CHR₂ pyrolyse to yield RCHO + R₂CO.

\[ \text{RCO}_2\text{CHR}_2 \rightarrow \text{RCHO} + \text{R}_2\text{CO} \]

Few pyrolyses of esters, however, proceed via a single scission. Competitive primary scissions take place even if only to a minor extent, giving a wide variety of products. Secondary breakdown of these products may also take place but this should not be confused with the initial primary scissions.
A general classification of the major decomposition routes is given below; the abbreviated notation (A, B, C, D) has been adopted in recent publications from these laboratories.

(i) **Alkyl-oxygen scission** (A)
This type of breakdown yields an acid and an olefine. The point of breakdown lies between the ether oxygen of the ester group and the alkyl group. Migration of a β hydrogen atom from the alkyl group occurs.

(ii) **Acyl-oxygen scission** (B)
In this type, rupture occurs between the acyl group and the ether oxygen in the carbonyl group. Migration of an α hydrogen atom occurs, either from the acyl group or from the alkyl group.

(iii) **Decarboxylation** (C)
This involves the direct elimination of carbon dioxide from the ester itself. It must not be confused with the secondary decarboxylation of acids arising from an alkyl-oxygen scission.

(iv) **Disproportionation** (D)
Two identical molecules undergo intermolecular disproportionation to give two different molecules of greater overall symmetry.
These various classes of ester breakdown are discussed in greater detail below.

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

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

**Type \( A^1 \).**

Esters containing one or more \( \beta \) hydrogen atoms in the alkyl group decompose almost quantitatively under moderate conditions by alkyl-oxygen scission to give an acid and an olefine.

\[
\text{RCO}_2\overset{\alpha}{C} - \overset{\beta}{C} - H \rightarrow \text{RCO}_2\overset{\alpha}{C} + \overset{\beta}{C} \quad (A^1)
\]

The pyrolysis proceeds in a selective manner to produce the least highly alkylated olefine according to the Hofmann rule (1). The hydrogen atom abstracted during pyrolysis comes preferentially from:

\[
\text{CH}_3 > \text{CH}_2 > \text{CH}
\]

The thermal stability of these alkyl esters decreases with an increase in the number of \( \beta \) hydrogen atoms present in the alkyl group, as in the sequence:

\[
\text{RCO}_2\text{CH}_2\text{Me} > \text{RCO}_2\text{CHMe}_2 > \text{RCO}_2\text{CMe}_3
\]

**tert-Alkyl esters** are known to decompose almost quantitatively below 300\(^\circ\)C to give an acid and olefine.
There is little or no competition by other routes. For example, tert.-amyl acetate decomposes at $155^\circ$C to give acetic acid and 2-methylbut-1-ene (2).

\[ \text{AcOCMe}_2\text{Et} \rightarrow \text{AcOH + CH}_2\text{:CMeEt} \quad (A^1) \]

tert.-Butyl acetate at 250 - 300$^\circ$C gives acetic acid and isobutene (3).

\[ \text{AcOCMe}_3 \rightarrow \text{AcOH + CH}_2\text{:CMe}_2 \quad (A^1) \]

It has been shown also that higher temperatures are needed for the decomposition of sec. and n-alkyl esters. The decomposition is more complex, although alkyl-oxygen scission predominates. This may be shown by the pyrolysis of isopropyl and ethyl acetates (3).

\[ \text{AcOCHMe}_2 \rightarrow \text{AcOH + CH}_2\text{:CHMe} \quad (A^1) \]
\[ + \text{MeCHO + COMe}_2 \quad \text{(by-products)} \]

\[ \text{AcOCH}_2\text{Me} \rightarrow \text{AcOH + CH}_2\text{:CH}_2 \quad (A^1) \]
\[ + \text{MeCHO + CH}_2\text{:C:O + CH}_4 \quad \text{(by-products)} \]

Burns, Jones, and Ritchie (4) have found that various $\alpha$-substituted esters of the type AcOCRMeX also give acid and olefine by the $A^1$ reaction.

\[ \text{AcOCRMeX} \rightarrow \text{AcOH + CH}_2\text{:CRX} \quad (A^1) \]

($R = H$ or alkyl, $X = \text{CN}$ or $\text{CO}_2\text{Me}$).
A specific example of this is the decomposition of 1-cyanoethyl acetate, which at 400-500°C gives acetic acid and acrylonitrile as the main products of decomposition.

\[
\text{AcOCHMeCN} \rightarrow \text{AcOH} + \text{CH}_2:\text{CHCN} \quad (A^1)
\]

So far, the examples of alkyl-oxygen scission given follow the Hofmann rule (1). The introduction of unsaturated electron-withdrawing groups into the β position of the alkyl group reverses the direction of elimination, however, elimination now following the Saytzeff rule (5). This rule states that in elimination reactions the most highly alkylated olefine is formed. The work of Bailey and King (6) affords examples of this, three of which are given below. The phenyl group, for example, reverses the direction of elimination.

(i) β - Phenylisopropyl acetate at 450°C produces a mixture of olefines containing 75% 1-phenylprop-1-ene and 25% allylbenzene.

\[
\text{AcOCHMeCH}_2\text{Ph} \rightarrow \begin{cases} 75\% & \text{AcOH} + \text{MeCH:CHPh} \\ 25\% & \text{AcOH} + \text{CH}_2:\text{CHCH}_2\text{Ph} \end{cases}
\]

(ii) β : β - Diphenylisopropyl acetate gives only 1:1-diphenylprop-1-ene.

\[
\text{AcOCHMeCPh}_2 \rightarrow \text{AcOH} + \text{MeCH:CPH}_2
\]
If the Hofmann rule had been followed, example (i) would have yielded only allylbenzene, and example (ii) \( \alpha \)-phenylallylbenzene. (iii) Similarly, the nitro group affects the direction of elimination.

\[ \beta \text{-Nitroisopropyl acetate gives } 1 \text{-nitroprop-1-ene, not } 1 \text{-nitroprop-2-ene.} \]

These three examples are in direct contradiction to the Hofmann rule, on which basis it would be expected that the \( \beta \) hydrogen atom would be abstracted from the methyl rather than from the methylene group.

The Hofmann rule for the formation of olefines is followed by most simple esters but may be reversed depending on the nature of the substituent attached to the \( \beta \) carbon atom in the alkyl group.

Houtman et al. (7) have found that an increase in the contact time of pyrolysis causes isomerisation of the olefine formed. Thus at 500\(^\circ\)C and long contact time, sec.-butyl acetate gives 56\% but-1-ene and 44\% but-2-ene. The former olefine is in agreement with the Hofmann rule, the latter with the Saytzeff rule.

Since alkyl-oxygen scission \( A^1 \) occurs smoothly at moderate temperatures without many perceptible side reactions,
it is commonly accepted that olefine formation occurs via a molecular mechanism rather than a radical mechanism since the latter would be likely to produce a wide variety of products. The modern concept of pyrolytic olefine formation is that propounded by Hurd and Blunck (3) and later substantiated by other workers, e.g. (8). This postulates the transient existence of a 6-membered chelate ring with hydrogen bonding.

\[
\begin{align*}
\text{R-C} & \quad \text{O} \\
\text{H} & \quad \text{CR}_2
\end{align*}
\]

This mechanism has been criticised by Houtman et al. (7), who claim that the concept of hydrogen bonding is applicable only to strongly electronegative atoms, e.g. H-O, H-F, and that there is no evidence for such bonding at high temperatures. They prefer to consider it as a mutual interaction between the acyl group and the \(\beta\) hydrogen atom, the precise mechanism not being defined.

A deposit of carbon in the pyrolysis tube has been found to have an important catalysing effect on the pyrolysis of esters. Thus Bailey and Hewitt (9) found that at 450°C 1:3-dimethyl-\(n\)-butyl acetate liberated 68% of acetic acid but that in a carbonised tube this yield was increased to 83%. These findings were supported by Houtman et al. (7) who found that carbon together with a trace of acid was necessary
for the pyrolysis of primary esters at 500°C.

**Type A^2**

This type of scission is, by definition, confined to alkenyl esters, which in part break down to give an acid and alkyne according to the general equation:

\[
\text{RCO}_2\text{C} = \text{CH} \rightarrow \text{RCO}_2\text{H} + \text{C} = \text{C} \quad (A^2)
\]

Several examples of this scission are known from the pyrolysis of various vinyl esters (10). For example, vinyl benzoate breaks down at 400-500°C by a series of competitive routes, one of which yields benzoic acid and acetylene in small amounts as shown below.

\[
\text{BzOCH}_2\text{CH} \rightarrow \text{BzOH} + \text{HC} = \text{CH} \quad (A^2)
\]

\[
\text{BzOCH}_2\text{CH} \rightarrow \text{PhCOMe} + \text{CO} \quad (R/C^1)
\]

\[
\text{PhCH}_2\text{CH}_2 + \text{CO}_2
\]

Similarly vinyl acetate gives acetic acid and acetylene in small amounts, together with other products.

\[
\text{AcOCH}_2\text{CH} \rightarrow \text{AcOH} + \text{HC} = \text{CH} \quad (A^2)
\]

The mechanism of this scission is not known, but the reaction probably proceeds via the 6-membered chelate ring structure discussed previously for the A^1 reaction.

**Type A^0**

As would be expected from the foregoing discussion, esters containing no \( \beta \) hydrogen atoms should be more
thermally stable than those with β hydrogen atoms, since the formation of the transient 6-membered chelate ring is here impossible. This prediction is confirmed by the fact that higher temperatures are needed before decomposition of such esters sets in, usually via acyl-oxygen scission (discussed later). However, under certain conditions, e.g. very high temperatures, these esters do break down in part to give an acid and an olefine, the latter presumably occurring via a transient diradical. The general equation for this type of scission is:

\[
\begin{align*}
\text{RCO}_2\text{CH} & \rightarrow \text{RCO}_2\text{H} + \left[ \right. \right. \\
& \rightarrow \text{RCO}_2\text{H} + \frac{1}{2} \right. \right. \\
& \end{align*}
\]

There are several examples in the literature showing that methylene diradicals are capable of existence and dimerise readily to ethylene. For example, methylene halides pyrolyse in the presence of sodium vapour at 300°C to give methylene which dimerises to ethylene (11). The decomposition of diazomethane, catalysed by copper stearate or boron trifluoride, gives polymethylene (12). Since such diradicals, therefore, are known to exist it is reasonable to assume their presence in ester breakdown.

The pyrolysis of methyl acetate at 1150°C gives alkyl-oxygen scission A° to a minor extent, although acyl-oxygen
Another example of this scission is provided by the pyrolysis of methyl phenylacetate (3).

1.3. Acyl-oxygen scission.

The absence of β hydrogen atoms in alkyl esters usually leads to an increase in thermal stability. At sufficiently high temperatures, however, the predominating form of decomposition is by acyl-oxygen scission. As the name implies, the point of rupture in the ester lies between the acyl group
and the ether oxygen in the carboxyl group. This is followed by the migration of a hydrogen atom either from the acyl group itself or from the α position of the alkyl group. The first type is designated B₁ scission, the second B₂ scission.

**Type B₁**

As stated above, this type of scission involves the migration of a hydrogen atom from the acyl group to yield a keten and a hydroxyl compound.

\[
\text{CHCO}^\text{\underline{OCH}} \xrightarrow{\text{B}^1} \text{C}^\text{\underline{O}} + \text{HOCH}^\text{\underline{O}}
\]

This type of scission usually occurs to a minor extent in conjunction with other primary routes. An exception to this is the decomposition of phenyl acetate which, owing to its molecular structure, decomposes entirely by a B₁ scission at 600°C to give keten and phenol (3).

\[
\text{AcOPh} \xrightarrow{\text{B}^1} \text{CH}_2:C:O + \text{HOPh}
\]

Phenyl propionate decomposes at 600°C by a variety of routes including a B₁ scission giving methylketen and phenol to the extent of ca. 5% (14).

\[
\text{MeCH}_2\text{COOPh} \xrightarrow{\text{B}^1} \text{MeCH}:C:O + \text{HOPh}
\]

**Type B₂**

The second type of acyl-oxygen scission involves the migration of a hydrogen atom from the α position in the alkyl group, to give two carbonyl molecules.
This type of scission predominates in esters possessing no \( \beta \) hydrogen atoms in the alkyl group. There are many examples showing the occurrence of this scission. Peytral (13) quotes methyl acetate at 1150°C as yielding acetaldehyde and formaldehyde.

\[
\begin{align*}
\text{AcOMe} & \rightarrow \text{AcOH} + \frac{1}{2} \text{CH}_2\text{CH}_2 \quad (A^0) \\
& \rightarrow \text{MeCHO} + \text{CH}_2\text{O} \quad (B^2)
\end{align*}
\]

Similarly, Hurd and Blunck (3) quote ethyl acetate as giving acetaldehyde to a minor extent.

\[
\begin{align*}
\text{AcOEt} & \rightarrow \text{AcOH} + \text{CH}_2\text{CH}_2 \quad (A^1) \\
& \rightarrow 2\text{MeCHO} \quad (B^2)
\end{align*}
\]

An interesting example of a \( B^2 \) scission is the decomposition of 2-phenylethyl trichloroacetate, which yields trichloroacetaldehyde and phenylacetaldehyde (15).

\[
\begin{align*}
\text{CCI}_3\text{CO}_2\text{CH}_2\text{CH}_2\text{Ph} & \rightarrow \text{CCI}_3\text{CHO} + \text{PhCH}_2\text{CHO} \quad (B^2)
\end{align*}
\]

Since the above ester possesses two available \( \beta \) hydrogen atoms, alkyl-oxygen scission \( A^1 \) might be expected as the predominating scission. This, however, is not the case. Because of the strongly electrophilic trichloromethyl group, the acyl-oxygen bond is weakened and therefore a \( B^2 \) scission
13.

There are several examples where an atom or group other than a hydrogen atom migrates during an acyl-oxygen scission. A specific example of this is the decomposition of 1-cyanoisopropyl benzoate (16) which decomposes by two competitive primary routes, the former predominating.

\[
\begin{align*}
\text{BzOCMe}_2\text{CN} & \rightarrow \text{BzOH} + \text{CH}_2:\text{CMeCN} \quad (A^1) \\
\text{BzOCMe}_2\text{CN} & \rightarrow \text{BzCN} + \text{COMe}_2 \quad (B^2)
\end{align*}
\]

The latter minor route illustrates the migration of the cyano group during pyrolysis.

The author has discovered other examples of this migration, and these will be discussed later.

Acyl-oxygen scission of the $B^2$ type may be considered as a reversal of the Tischtschenko reaction (17), which involves the self-addition of two carbonyl compounds in the presence of an aluminium alkoxide. There are different variations of this reaction, but all conform to the general overall equation:

\[
2\text{RCCX} \rightarrow \text{RCO}_2\text{CRX}_2
\]

\((R = \text{alkyl or aryl}; \quad X = \text{hydrogen or cyano})\)

All alkyl carboxylates may be formally regarded as Tischtschenko-type addition compounds (even though they may not have been prepared thus in practice). It is therefore
formally possible that reversal of this addition may occur in the complex pyrolysis of many esters: and several specific examples have already been quoted (3, 13) in conformity with this idea.

No formal mechanism has been propounded for this reversal of the Tischtschenko reaction, but it is felt that a molecular mechanism must be ruled out owing to the relatively high temperatures required for pyrolysis. Possible mechanisms will be discussed later.

1.4. Decarbonylation $C^1$

This type of scission is confined as a rule to those compounds which contain a carbonyl group within the molecule. As the name implies, carbon monoxide is eliminated during pyrolysis. The most common examples are found in the pyrolysis of simple aldehydes. Thus, acetaldehyde gives methane at 400°C (18).

$$\text{MeCHO} \rightarrow \text{MeH} + \text{CO} \quad (C^1)$$

Acid halides are also known to decarbonylate forming the corresponding alkyl or aryl halide. For example, acetyl bromide decomposes at 400°C by two competitive routes, the first predominating (19).

$$\text{MeCOBr} \rightarrow \text{MeBr} + \text{CO} \quad (C^1)$$

$$\text{MeCOBr} \rightarrow \text{CH}_2\text{CO} + \text{HBr} \quad (B^1)$$
In the case of benzoyl bromide, since there are no available α hydrogen atoms in the acyl group, acyl-oxygen scission $B^1$ must be precluded, and pyrolysis proceeds by the $C^1$ scission (20).

$$\text{PhCOBr} \rightarrow \text{PhBr} + \text{CO} \quad (C^1)$$

There are only a few examples of ester decarbonylation. Phenyl formate (21) decomposes quantitatively by the $C^1$ scission on heating at 550°C.

$$\text{HCO}_2\text{Ph} \rightarrow \text{HOPh} + \text{CO} \quad (C^1)$$

Methyl formate on pyrolysis at 500°C decomposes by three competitive primary routes, the first predominating (22).

$$\text{HCO}_2\text{Me} \rightarrow \text{HOMe} + \text{CO} \quad (C^1)$$

$$\text{HCO}_2\text{Me} \rightarrow 2\text{CH}_2\text{O} \quad (B^2)$$

$$\text{HCO}_2\text{Me} \rightarrow \text{CH}_4 + \text{CO}_2 \quad (C^2)$$

As discussed below, the decarbonylation of vinyl carboxylates (10) is not a direct primary reaction, but is dependent on a primary rearrangement to a β-ketoaldehyde which then loses carbon monoxide.

1.5. Decarboxylation $C^2$

Primary ester decarboxylation of the $C^2$ type must not be confused with secondary decarboxylation of acids liberated during alkyl-oxygen scission. Only a few examples of ester
Decarboxylation are recorded in the earlier literature, but it may be typified by the pyrolysis of triphenylmethyl formate at 100°C (23).

\[
\text{HCO}_2\text{OPh} \rightarrow \text{HOPh} + \text{CO}_2 \quad (C^2)
\]

Phenyl cinnamate on heating at 300°C (24) decarboxylates to trans-stilbene.

\[
\text{PhCH}_2\text{CHO}_2\text{Ph} \rightarrow \text{PhCH}_2\text{CHPh} + \text{CO}_2 \quad (C^2)
\]

Allan, Forman and Ritchie (10) have shown that vinyl esters undergo competitive breakdown on pyrolysis at 450-500°C. For example, vinyl benzoate breaks down by three competitive routes, one of these being decarboxylation to styrene. The predominating reaction, however, is a thermal rearrangement to benzoylacetaldehyde followed by decarbonylation of this latter to acetophenone.

\[
\begin{align*}
\text{BzOCH}_2\text{CH}_2 & \rightarrow \text{BzOH} + \text{CH}_2\text{CH} \quad (A^2) \\
\text{BzOCH}_2\text{CH}_2 & \rightarrow \text{PhCH}_2\text{CH}_2 + \text{CO}_2 \quad (C^2) \\
\text{BzOCH}_2\text{CH}_2 & \rightarrow \text{BzCH}_2\text{CHO} \quad (R) \\
\text{BzOCH}_2\text{CH}_2 & \rightarrow \text{PhCOMe} + \text{CO} \quad (C^1)
\end{align*}
\]

Further examples of the \( C^2 \) reaction are recorded elsewhere in this thesis.

1.6. Disproportionation D.

This reaction occurs usually between two similar
molecules which disproportionate to give two different molecules of greater overall symmetry. There are only a few examples of this type in the literature. Unsymmetrical anhydrides distil to give two symmetrical forms (25), according to the equation:

$$2R CO O . COR' \rightarrow (RCO)_{2}O + (R'CO)_{2}O$$

Examples of a D scission from the pyrolysis of esters are known. For example, ethyl hydrogen malonate (26) undergoes two competitive scissions on heating at $150^\circ C$. The first is decarboxylation giving ethyl acetate and the second is disproportionation giving diethyl malonate and malonic acid, the latter undergoing a secondary decarboxylation to acetic acid.

$$\text{CO}_2\text{Et} \rightarrow 2\text{AcOEt} + 2\text{CO}_2$$

$$2\text{CH}_2\text{CO}_2\text{H} \rightarrow \text{CH}_2(\text{CO}_2\text{Et})_2 + \left[\text{CH}_2(\text{CO}_2\text{H})_2\right]$$

$$\left[\text{CH}_2(\text{CO}_2\text{H})_2\right] \rightarrow \text{AdOH} + \text{CO}_2$$

β-Substituted ethyl esters also undergo disproportionation to the ethylene diester and the substituted ethylene derivative. For example, 2-hydroxyethyl benzoate at 450-500°C gives ethylene dibenzoate and ethylene glycol (27). A competitive disproportionation also occurs giving benzoic anhydride and the unstable diethylene glycol.
Disproportionation appears, therefore, to result in compounds of greater symmetry and stability. The actual mechanism of the reaction remains obscure but it presumably is a complex intermolecular reaction. The mechanism certainly differs from the disproportionation of esters of gem-diols. This latter reaction mechanism is likewise obscure but may, for convenience, be regarded as an intramolecular reaction to differentiate it from the previous examples of disproportionation. An example of this is the commercial preparation of acetic anhydride by the pyrolysis of ethyldiene diacetate, acetaldehyde being liberated as a by-product. A minor competitive scission which also takes place is an $A^1$ scission giving acetic acid and vinyl acetate (28). This latter reaction has been found to be reversible (section 3.12).

\[\text{MeCH(OAc)}_2 \quad \overset{\text{(D)}}{\longrightarrow} \quad \text{Ac}_2\text{O} + \text{MeCHO} \]

\[\text{AcOH} + \text{AcOCH:CH}_2 \quad \overset{\text{(A}^1\text{)}}{\longrightarrow} \]
2.1. Objects of Research

It has previously been shown that the introduction of various radicals into the \( \beta \) position of the alkyl group of an ester results in the reversal of the elimination reaction, the most highly alkylated olefine being formed according to the Saytzeff rule. There are other examples which show that an expected scission may not occur because of the introduction of a particular substituent into the ester molecule. For example, the trichloromethyl group in 2-phenylethyl trichloroacetate (15), mentioned previously, causes pyrolysis to proceed via a \( B^2 \) scission and not via the expected \( A^1 \) scission. Methyl benzoate is an ester of remarkable thermal stability (29), being undecomposed in a flow reactor at 500°C (30). Bennett and Ritchie (16), however, have shown that the introduction of a cyano group, giving cyanomethyl benzoate (discussed later), causes a marked decrease in stability. The ester is completely decomposed at 500°C.

With the above examples in mind, it was decided to investigate the way in which the thermostability of an ester is affected by the introduction of different electrophilic and nucleophilic atoms or groups into the \( \alpha \) position of the alkyl group. The parent ester selected was benzyl benzoate previously studied, by Hurd and Bennett (31), in a static reactor at 300°C. The parent ester was pyrolysed in a flow reactor at 400–550°C and the extent of decomposition noted by
measuring the amount of recovered ester. From the products obtained from the pyrolysate, the routes of decomposition were determined. An atom or group was then substituted for one of the hydrogen atoms of the benzyl group, and the effect of this substitution noted by measuring the decrease in thermal stability under similar conditions to those of the parent ester.

The $\alpha$-substituents selected for study were cyano, bromine, and benzoyl (electrophilic), and phenyl (nucleophilic).

A few related esters and other compounds were also pyrolysed in order to facilitate interpretation of the results for the above series of $\alpha$-substituted benzyl benzoates.

A preliminary study of the above problem demonstrated a new route of ester breakdown (here provisionally designated as type $B$), resulting in the formation of an $\alpha$-diketone. This route has been investigated in some detail.

The thermal stability of ethylene dibenzoate has been studied (10). This diester is a model compound for poly (ethylene terephthalate), Terylene. An analogous compound, methylene dibenzoate, has been studied and its stability compared with that of its analogue. An attempt has been made to prepare poly (methyleneterephthalate) (see Appendix III).

From the results obtained, an attempt has been made to interpret the mechanism of ester breakdown with reference to substituted benzyl esters.
### 2.2. Compounds Investigated

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<th>Formula</th>
<th>Compound No.</th>
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<td>Benzy1 benzoate</td>
<td>BzOCH₂Ph</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>α-Cyanobenzyl benzoate</td>
<td>BzOCHPhCN</td>
<td>II</td>
</tr>
<tr>
<td></td>
<td>α-Cyanobenzyl acetate</td>
<td>AcOCHPhCN</td>
<td>III</td>
</tr>
<tr>
<td></td>
<td>1-Cyanoethyl benzoate</td>
<td>BzOCHMeCN</td>
<td>IV</td>
</tr>
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<td></td>
<td>α:α-Dicyanobenzyl benzoate</td>
<td>BzOCPh(CN)₂</td>
<td>V</td>
</tr>
<tr>
<td>Br atom</td>
<td>α-Bromobenzyl benzoate</td>
<td>BzOCHPhBr</td>
<td>VI</td>
</tr>
<tr>
<td>COPh group</td>
<td>α-Benzoylbenzyl benzoate</td>
<td>BzOCHPhCOPh</td>
<td>VII</td>
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<tr>
<td></td>
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<td>AcOCHPhCOPh</td>
<td>VIII</td>
</tr>
<tr>
<td>Ph group</td>
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<td>BzOCHPh₂</td>
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</tr>
<tr>
<td></td>
<td>Triphenylmethyl benzoate</td>
<td>BzOCPH₃</td>
<td>X</td>
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### 2.2. Compounds Investigated (contd.)

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<td>Methylene dibenzoate</td>
<td>BzOCH₂OBz</td>
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<td>Ethylidene dibenzoate</td>
<td>BzOCHMeOBz</td>
<td>XIII</td>
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<td>Benzil</td>
<td>PhCOCOPh</td>
<td>XIV</td>
<td>I, II, VI, VII</td>
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<tr>
<td>Acetylbenzoyl</td>
<td>MeCOCOPh</td>
<td>XV</td>
<td>III, VIII</td>
</tr>
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<td>Acrylonitrile</td>
<td>CH₂:CHCN</td>
<td>XVI</td>
<td>IV</td>
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<td>Benzal bromide</td>
<td>PhCHBr₂</td>
<td>XVII</td>
<td>VI</td>
</tr>
<tr>
<td>Benzoic anhydride</td>
<td>BzOBz</td>
<td>XVIII</td>
<td>XII, I–VI</td>
</tr>
</tbody>
</table>
3. Discussion of Results.

3.1. The Pyrolysis of Benzyl Benzoate (I)

Benzyl benzoate (I), the parent ester for the present series of esters and related compounds, has been pyrolysed both in static and flow systems. A static pyrolysis at $300^\circ$C for 29 hours has confirmed the work of Hurd and Bennett (31). The main routes of decomposition are:

\[ \text{BzOCH}_2\text{Ph} \xrightarrow{\text{I}} 2\text{PhCHO} \quad (B^2) \]

\[ \text{I} \xrightarrow{} \frac{1}{2}\text{Bz}_2\text{O} + \frac{1}{2} \left[ \text{(PhCH}_2\text{)}_2\text{O} \right] \quad (D) \]

XVIII

Since the ester has no available $\beta$ hydrogen atoms in the alkyl group, the predominating scission, as would be expected, is acyl-oxygen scission $B^2$, producing benzaldehyde. This is a straightforward thermal reversal of the Tischtschenko reaction normally used in the preparation of this particular ester. The other identified scission is a disproportionation $D$. Hurd (32) has suggested a mechanism for this reaction which proceeds via intermolecular disproportionation to benzoic anhydride (XVIII) and the unstable dibenzyl ether.

\[ \text{BzOCH}_2\text{Ph} \xrightarrow{\text{I}} \text{Bz}_2\text{O} + \left[ \text{(PhCH}_2\text{)}_2\text{O} \right] \quad (D) \]

XVIII
Dibenzyl ether was not itself identified in the pyrolysate, but it is known to yield toluene and benzaldehyde on heating at 200°C (33), both of which were obtained in the pyrolysate from I.

\[
\text{[(PhCH}_2\text{)}_2\text{O]} \rightarrow \text{PhMe + PhCHO}
\]

Benzoic acid was obtained from the pyrolysate in large amounts. It was at first thought that this may have arisen from an A° scission, which would produce the acid and the olefine, stilbene,

\[
\text{BzOCH}_2\text{Ph} \rightarrow \text{BzOH + } \frac{1}{2}\text{PhCH:CHPh} \quad (A°)
\]

However, the absence of stilbene (which is very stable) shows that this reaction does not take place. It will be shown later (section 3.12) that benzoic acid arises from the secondary decomposition of benzoic anhydride itself (34), presumably via a highly complex radical mechanism.

Benzyl benzoate (I) is unaffected on heating at 420°C in a flow reactor, and only 20% is decomposed at 500°C. At 550°C, however, 70% of the ester has reacted. As would be expected, the higher the temperature the more complex was the pyrolysate. No benzoic anhydride was found at 550°C, and only a trace of benzoic acid. Toluene and benzaldehyde were detected, together with large amounts of benzene and diphenyl. There was, however, sufficient evidence to prove that the two
competitive scissions B² and D, mentioned above, did occur. A third competitive scission was unexpectedly detected, occurring to a minor extent. This was α-diketone formation, here designated an E type scission, in which hydrogen was eliminated from the molecule with the liberation of the α-diketone, benzil XIV. This novel reaction is discussed more fully later (section 3.11).

\[
\begin{align*}
\text{BzOCH}_2\text{Ph} & \rightarrow \text{PhCOCOPh} + H_2 \\
\text{I} & \quad \text{XIV}
\end{align*}
\]

Having determined the thermal stability of benzyl benzoate in a flow reactor and its mode of decomposition via three competitive routes, it was decided to study the way in which the thermal stability of an α-substituted or α:α-disubstituted benzyl benzoate is affected by the nature of the α-substituent. Both electrophilic and nucleophilic substituents were studied.

**The Effect of Electrophilic Groups**

**The introduction of one cyano group**

3.2. **α-Cyanobenzyl Benzoate (II)**

The introduction of a cyano group into the α position of the alkyl group of an ester has been found to increase the rate of decomposition of the ester. α-Cyanobenzyl benzoate (II), a monosubstituted benzyl benzoate, is decomposed to the
extent of ca. 80% in a flow reactor at 420°C. The routes of decomposition are:

\[
\begin{align*}
\text{BzOCHPhCN} & \rightarrow [\text{BzCN}] + \text{PhCHO} & \text{(B)}^2 \\
\text{II} & \rightarrow \text{PhCOCOPh} + \text{HCN} & \text{(E)}
\end{align*}
\]

XIV

The principal route of decomposition is acyl-oxygen scission, B^2, producing benzaldehyde and the thermally unstable benzoyl cyanide. Benzoyl cyanide itself was not detected, but it is known to decarbonylate (35) to benzonitrile, which was obtained in large quantities. It will be shown later that in general the cyano group rather than the hydrogen atom migrates during this type of scission. Hydrogen cyanide and benzil (XIV), produced by an E type scission, occurred to the extent of ca. 11% at 420°C and ca. 15% at 500°C. XIV on pyrolysis at 500°C was found to produce benzophenone and diphenyl, produced by successive decarbonylations of the diketone.

\[
\begin{align*}
\text{PhCOCOPh} & \rightarrow \text{CO} + \text{PhCOPh} & \rightarrow \text{CO} + \text{PhPh} & \text{(C)}^3
\end{align*}
\]

XIV

Large amounts of benzoic acid and some trans- \(\alpha : \alpha'\)-dicyanostilbene were also obtained in the pyrolysate. It was at first considered that these products could arise from a competitive A^0 scission.
The absence of this route, however, in the breakdown of benzyl benzoate (I) suggests that the route does not occur in the pyrolysis of II; and the above-mentioned products may in fact arise from a competitive disproportionation D producing benzoic anhydride (XVIII) and, presumably, the transitory $\alpha:\alpha'$-dicyanodibenzyl ether.

$$2\text{BzOCHPhCN} \rightarrow \text{Bz}_2\text{O} + [(\text{PhCHCN})_2\text{O}]$$

Benzoic anhydride was not detected on pyrolysis of $\alpha$-cyanobenzyl benzoate (II) at 420$^\circ$C, but it is known to produce benzoic acid and benzene on pyrolysis (34), both of which were identified in the pyrolysate from II. A further confirmation that disproportionation does occur is the formation of XVIII on heating II for 24 hours at 160$^\circ$C.

The decomposition of ethers has been discussed previously by Iengar and Ritchie (36). On the basis of this work, therefore, $\alpha:\alpha'$-dicyanodibenzyl ether would be expected to decompose by two competitive primary routes. The predominating scission would be the migration of the cyano group to give benzaldehyde and the unstable benzal cyanide, the latter eliminating hydrogen cyanide by an intermolecular reaction to yield $\alpha:\alpha'$-dicyanostilbene. A second
competitive scission would involve the migration of the hydrogen atom to produce benzoyl cyanide and benzyl cyanide, the former decarbonylating to benzonitrile.

\[
\begin{align*}
(\text{PhCHCN})_2O & \xrightarrow{\text{CN migration}} \text{PhCHO} + \left[\text{PhCH(CN)}_2\right]_A^R \\
& \xrightarrow{\text{H migration}} \text{PhCOCN} + \text{PhCH}_2\text{CN} \quad A_R^I
\end{align*}
\]

2 \left[\text{PhCH(CN)}_2\right] \rightarrow 2\text{HCN} + \text{PhCCN:CPhCN}

This suggested mechanism is similar to the decomposition of \(\alpha\)-bromobenzyl benzoate (VI), discussed later (section 3.6).

A static pyrolysis of II at 300\(^\circ\)C for 5\(\frac{1}{2}\) hours produces the compounds mentioned previously, together with a small quantity of benzoylbenzoin (\(\alpha\)-benzoylbenzyl benzoate) (VII). Greene and Robinson (37) have shown that \(\alpha\)-cyanobenzyl benzoate (II) and benzaldehyde interact in the presence of sodium ethoxide to produce benzoylbenzoin, with the elimination of hydrogen cyanide. These authors suggest that the benzaldehyde forms with the cyano ester an addition compound of the aldol type. This aldol then rearranges to form the cyanohydrin of benzoylbenzoin, which eliminates hydrogen cyanide to give benzoylbenzoin (VII).
In view of this concept, it is important to note that benzoylbenzoin has, in fact, been identified in the pyrolysate from α-cyanobenzyl benzoate. Presumably this reaction may also occur thermally, in the absence of a catalyst.

The author considered that a co-pyrolysis of II with benzaldehyde should induce an increase in breakdown of II by the above route. The experiment, however, was not successful; on the contrary, it was found that the aldehyde had an inhibiting rather than a promoting effect on the breakdown of II.

It will be shown later that benzoylbenzoin (VII) yields benzil (XIV) via acyl-oxygen scission $B^2$, on pyrolysis.

The main formation of α-diketone from II may well proceed in four distinct steps via the intermediate VII. An alternative mechanism is also discussed later.
3.3. α-Cyanobenzyl Acetate (III)

α-Cyanobenzyl acetate (III) has been studied in order to determine whether α-diketone formation occurs with acetates as well as with benzoates, and also whether the hydrogen atom or the cyano group migrates during an acyl-oxygen scission. If the former migrates, the expected products will be acetaldehyde and benzoyl cyanide; if the latter, acetyl cyanide and benzaldehyde. The formal possible decomposition routes are:

\[ \text{AcOCHPhCN} \rightarrow \begin{align*}
&\text{MeCHO} + [\text{BzCN}] \quad (B^2) \\
&[\text{AcCN}] + \text{PhCHO} \quad (B^2) \\
&\text{PhCOCOMe} + \text{HCN} \quad (E) \\
&\text{CH}_2:CO + [\text{PhCH(OH)CN}] \quad (B^1) \\
&\frac{1}{2}\text{Ac}_2O + \frac{1}{3}[(\text{PhCHCN})_2O] \quad (D)
\end{align*} \]

The principal scission is again acyl-oxygen scission. From the products identified in the pyrolysate, it can be seen that the cyano group migrates preferentially during acyl-oxygen scission. Acetyl cyanide was not itself identified, but its breakdown products are known and these are identified in the pyrolysate from III.

\[ \text{AcCN} \rightarrow \begin{align*}
&\text{MeCN} + \text{CO} \quad (C^1) \\
&\text{CH}_2:CO + \text{HCN} \quad (B^1)
\end{align*} \]
A competitive primary scission is \( \alpha \)-diketone formation, type E, giving hydrogen cyanide and acetylbenzoin XV. This is analogous to the benzil formation from \( \alpha \)-cyanobenzyl benzoate. At 550\(^\circ\)C this scission occurs to the extent of ca. 10%.

It was considered that XV should decompose by two competitive primary routes (the first being a straightforward decarboxylation to acetophenone; the second, the formation of keten and benzaldehyde). The present work shows, however, that at 500\(^\circ\)C XV decarbonylates in part to acetophenone; the second route does not occur. This explains, therefore, the presence of acetophenone in the pyrolysate from III.

\[
\begin{align*}
\text{PhCOCOMe} & \rightarrow \text{PhCOMe} + \text{CO} & (C^1) \\
\text{PhCOCOMe} & \rightarrow \text{CH}_2:\text{CO} + \text{PhCHO} & (B^1)
\end{align*}
\]

Owing to the complexity of the results, it is almost impossible to state specifically whether or not disproportionation D or acyl-oxygen scission B\(^1\) occurs on pyrolysis of III. Disproportionation of the ester would yield acetic anhydride and the labile \( \alpha: \alpha' \)-dicyanodibenzyl ether. The former compound was identified in the pyrolysate from III. The latter should decompose, as mentioned previously (section 3.2) to produce \( \alpha: \alpha' \)-dicyanostilbene; but this was not detected in the pyrolysate, possibly being dissolved in unreacted ester (III). A trace of benzonitrile, however,
identified in the pyrolysate, may emanate from the cyano ester. An acyl-oxygen scission $B^1$ would produce keten and mandelonitrile. The latter compound is known to decompose at $170^\circ C$ to benzaldehyde and hydrogen cyanide (38).

$$\text{PhCH(OH)CN} \rightarrow \text{PhCHO} + \text{HCN}$$

The products corresponding to a $B^1$ scission can, however, arise from other sources, e.g. benzaldehyde from a $B^2$ scission, and hydrogen cyanide from $B^2$ and $E$ type scissions. Keten may arise from the secondary decomposition of acetic anhydride (39).

$$\text{Ac}_2\text{O} \rightarrow \text{AcOH} + \text{CH}_2:\text{CO}$$

This secondary breakdown can also account for the acetic acid obtained in the pyrolysate from III.

$\alpha$-Cyanobenzyl acetate is more thermostable than its benzoate analogue. A temperature of $550^\circ C$ is necessary before any appreciable breakdown occurs in the flow system used.

3.4. $l$-Cyanoeethyl Benzoate (IV)

By way of comparison, $l$-cyanoethyl benzoate (IV), isomeric with $\alpha$-cyanobenzyl acetate, has been pyrolysed in a flow reactor under similar conditions ($550^\circ C$). Since this ester possesses $\beta$ hydrogen atoms in the alkyl group, the predominating scission (ca. 85%) is alkyl-oxygen scission $A^1$ to benzoic acid and acrylonitrile. A competitive scission is
the $B^2$ type involving the migration of the cyano group. This produces acetaldehyde and the unstable benzoyl cyanide, the latter decarbonylating to benzonitrile. It has also been found that $\alpha$-diketone formation, type E, giving hydrogen cyanide and acetylbenzoyl, occurs to the extent of ca. 0.2\% (this figure being based on the estimation of hydrogen cyanide only). The routes of decomposition of IV at 550°C are thus:

$$
\begin{align*}
\text{IV} & \rightarrow \text{BzOH} + \text{CH}_2:\text{CHCN} \quad (A^1) \\
& \rightarrow \text{BzCN} + \text{MeCHO} \quad (B^2) \\
& \rightarrow \text{PhCOCOMe} + \text{HCN} \quad (E)
\end{align*}
$$

It was considered that hydrogen cyanide might arise from the secondary decomposition of acrylonitrile produced by the $A^1$ scission. However, it has been found that acrylonitrile is thermostable up to 650°C, at which temperature only 0.2\% of hydrogen cyanide and acetylene are evolved.

$$
\text{CH}_2:\text{CHCN} \rightarrow \text{CH}:\text{CH} + \text{HCN}
$$

The introduction of two cyano groups

3.5. $\alpha:\alpha$-Dicyanobenzyl Benzoate (V)

The introduction of two cyano groups into benzyl benzoate, producing benzoyl cyanide dimer ($\alpha:\alpha$-dicyanobenzyl benzoate), has been found to decrease the stability still further and also produces a highly complex pyrolysate.

A comparison between the pyrolysis of V and that of its
analogue acetyl cyanide dimer, previously pyrolysed by Ardis et al. (40), shows that both esters undergo a thermal reversal of the Tischtschenko-type addition undergone during the esters' preparation, although other reactions predominate.

Acetyl cyanide can dimerise under certain conditions to acetyl cyanide dimer, which is known to be the ester 1:1-dicyanoethyl acetate and which decomposes at 600–650°C (40) producing mainly acetic acid and vinylidene cyanide. The writer considered that a minor competitive B\(^2\) scission was also a possibility, producing acetyl cyanide and its breakdown products. A private communication from Dr. Ardis (41) confirmed that minor by-products supporting this prediction had, in fact, been observed. The routes of breakdown are thus:–

\[
\begin{align*}
\text{AcOCMe(CN)}_2 & \rightarrow \text{AcOH} + \text{CH}_2: \text{C(CN)}_2 \quad (A^1) \\
\text{AcOCMe(CN)}_2 & \rightarrow 2\text{AcCN} \quad (B^2)
\end{align*}
\]

It is possible that the acetyl cyanide and its secondary products can arise by either or both of two acyl-oxygen scissions, either a B\(^2\) type shown above or a B\(^1\) type giving keten and a hydroxyl compound thus:–

\[
\text{AcOCMe(CN)}_2 \rightarrow \text{CH}_2: \text{CO} + [\text{HOOCMe(CN)}_2] \quad (B^1)
\]

The resulting transient 1:1 dicyanoethanol, the cyanohydrin
of acetyl cyanide, should readily lose hydrogen cyanide and yield acetyl cyanide.

On the above evidence alone is is not possible to discriminate between the \( B^1 \) and \( B^2 \) scissions, each of which explains all of the possible products. However, the results obtained from the pyrolysis of benzoyl cyanide dimer (V) support the \( B^2 \) rather than the \( B^1 \) route.

At the commencement of this work, the only predictable route of decomposition of benzoyl cyanide dimer, \( \alpha : \alpha \)-dicyanobenzyl benzoate, based on the pyrolysis of acetyl cyanide dimer, was reversion to benzoyl cyanide by a \( B^2 \) scission. The present work shows that at 500\(^\circ\)C, V is completely destroyed, highly complex scissions taking place. The \( B^2 \) scission occurs to the extent of 10%; benzoyl cyanide itself was not identified but its decomposition products were detected. A competitive scission is decarboxylation \( C^2 \) giving diphenylmalononitrile. Hydrogen cyanide, benzene, benzoic acid and a large amount of tar were also obtained, indicative of a highly complex radical reaction and accounting for some 70\% of the ester decomposition.
36. **α-Bromobenzyl Benzoate (VI)**

The present work shows that the introduction of the strongly electronegative atom, bromine, into benzyl benzoate to give α-bromobenzyl benzoate (VI) causes a marked decrease in thermal stability. VI is prepared by the addition of benzoyl bromide to benzaldehyde in a sealed flask. No catalyst nor heating is required. The ester is unstable and must be stored under air-free conditions (42), otherwise it reverts to the original reactants.

\[ \text{BzBr} + \text{PhCHO} \rightarrow \text{BzOCHPhBr} \]

VI

VI is completely decomposed during a static pyrolysis at 225°C for three hours. The routes of decomposition are:

\[ \text{BzOCHPhBr} \rightarrow \begin{array}{c} \text{BzOH} + \frac{1}{2}\text{PhCHO: CPhBr} \quad (A^0) \\ \frac{1}{2}\text{Bz}_2\text{O} + \frac{1}{2}[(\text{PhCHBr})_2\text{O}] \quad (D) \end{array} \]

\[ \rightarrow \text{PhCOBr} + \text{PhCHO} \quad (B^2) \]

The predominating route, as would be expected, is acyl-oxygen scission $B^2$ to give benzoyl bromide and benzaldehyde. A little bromobenzene, also obtained, arises from the
decarbonylation of benzoyl bromide (20).

\[
\text{PhCOBr} \rightarrow \text{PhBr} + \text{CO} \quad (c^1)
\]

The remaining products of decomposition can be explained by a competitive disproportionation D to benzoic anhydride and the presumably unstable \(\alpha: \alpha'\)-dibromodibenzyl ether. The anhydride was readily detected but there was no evidence for the ether. However, in the light of the work of Iengar and Ritchie (36) on the decomposition of ethers, the latter may have decomposed by two possible routes. These both involve scission at the C-O bond and the migration of either a bromine atom to give benzal bromide or a hydrogen atom to give benzyl bromide, and the formation of a carbonyl compound. A third possibility is the direct elimination of water with the formation of \(\alpha: \alpha'\)-dibromostilbene.

\[
\begin{align*}
(\text{PhCHBr})_2\text{O} & \rightarrow \text{PhCHO} + \text{PhCHBr}_2 \\
 & \rightarrow \text{PhCOBr} + \text{PhCH}_2\text{Br} \\
 & \rightarrow \text{PhCBr: CPhBr} + \text{H}_2\text{O}
\end{align*}
\]

With the exception of water, the above products were identified. The first of these three routes predominated. It is improbable that the third route actually takes place as there is no evidence (36, 43) for the dehydration of ethers on pyrolysis. Furthermore, the presence of \(\text{trans-\(\alpha: \alpha'\)}\)-dibromostilbene can be alternatively explained, by the decomposition of benzal bromide which has now been found to
decompose almost quantitatively, in a flow reactor at 425°C, to this substituted stilbene and hydrogen bromide.

\[ 2\text{PhCHBr}_2 \rightarrow \text{PhCBr: CPhBr} + 2\text{HBr} \]

Benzoic acid, also detected in the pyrolysate from VI, arises from the secondary decomposition of benzoic anhydride (34).

It is considered that disproportionation D, with subsequent decomposition of the products thereof, affords a more reasonable explanation for the existence of benzoic acid and \( \alpha : \alpha ' \)-dibromostilbene than would alkyl-oxygen scission \( A^0 \) involving the transitory existence of an \( \alpha \)-bromobenzylidene diradical (PhCBr\( \angle \)). Although diradicals of the methylene type are known to exist (II), there is as yet no proof for their existence in the pyrolysis of esters. For example, in the pyrolysis of benzyl benzoate the absence of stilbene indicates the non-occurrence of the transitory benzylidene diradical (PhCH\( \angle \)).

In conclusion it seems probable that the products, acid and substituted stilbene, arise from the secondary decomposition of the products from the D type scission and not directly from the \( A^0 \) type.

The above results were confirmed by the pyrolysis of the ester VI in a flow reactor at 425°C. A further primary decomposition route was observed, namely, \( \alpha \)-diketone.
formation E, producing benzil and hydrogen bromide.

\[
\text{BzOCHPhBr} \rightarrow \text{PhCOCOPh + HBr} \quad (E)
\]

Since hydrogen bromide was obtained in any case from another source, viz the decomposition of benzal bromide, it is not possible to estimate the extent to which this route occurred.

The introduction of the benzoyl group.

3.7. Benzoylbenzoin (VII) and Acetylbenzoin (VIII)

It was decided to investigate the decomposition of benzoylbenzoin (VII) (α-benzoylbenzyl benzoate) since this compound had been discovered in the pyrolysate from α-cyanobenzyl benzoate (II). The mechanism previously suggested to explain the presence of VII included, as one step, the elimination of hydrogen cyanide. Since II had already been found to eliminate hydrogen cyanide and form the α-diketone, benzil, it was thought that this elimination might proceed via the formation of VII which would decompose by acyl-oxygen scission \( B^2 \) to benzil and benzaldehyde.

\[
\text{BzOCHPhCOPh} \rightarrow \text{PhCOCOPh + PhCHO} \quad (B^2)
\]

VII is relatively less stable than its parent, benzyl benzoate, about 70% being decomposed at 500\(^\circ\)C. The main route of decomposition is the predicted \( B^2 \) scission. Minor components of the pyrolysis are benzene, benzoic acid and
diphenyl.

It is difficult here to visualise a simple scission other than acyl-oxygen scission $B^2$. The initial break must occur at the acyl-oxygen bond in the ester group; but it is possible that either the hydrogen atom or the benzoyl group might thereupon migrate to the acyl group. To determine which of the two migrated, the writer decided to pyrolyse the analogue, acetylbenzoin (VIII) ($\alpha$-benzoylbenzyl acetate). This compound should also be formed from III in a similar manner to the formation of VII from II. It has now been found that acetylbenzoin decomposes at 480°C to give acetylbenzoyl and benzaldehyde, showing that the acyl group migrates during the $B^2$ scission. By-products of this pyrolysis are benzene and acetic acid.

\[
\begin{align*}
\text{AcOCHPhCOPh} & \quad \rightarrow \quad \text{PhCOCOMe + PhCHO} \\
\text{VIII} & \\
\text{AcOCHPhCOPh} & \quad \rightarrow \quad \text{PhCOCOPh + MeCHO}
\end{align*}
\]

Acetoxyacetone, the only other $\alpha$-ketoalkyl ester recorded in the literature, decomposes (44) at 430-450°C to give acetaldehyde. This is in direct contradiction to the present results for the above esters (VII, VIII), since it would be expected that the acetyl group would migrate to give diacetyl and formaldehyde.
It is concluded that the phenyl group in the α position of esters VII and VIII must exhibit a directional influence favouring the migration of the acyl group.

The Effect of Nucleophilic Groups

The nucleophilic substituent selected for study was phenyl. It was preferred to an alkyl group (although the latter is also nucleophilic), since a group such as methyl or ethyl would introduce a β hydrogen atom into the ester structure, and thus promote breakdown by A¹ scission.

The introduction of one phenyl group

3.8. Benzhydryl Benzoate (IX)

Benzhydryl benzoate may be prepared by heating an equimolar mixture of benzoic acid and benzhydrol, water being eliminated. By-products of this reaction are benzoic anhydride and tetraphenylethane (45). The present work shows that the ester itself pyrolyses in a flow reactor at 420–500°C. The presence of a second phenyl group has been found to eliminate acyl-oxygen scission B², the sole route of decomposition proceeding via disproportionation D.
The dibenzhydryl ether was not detected but it is known (46) to decompose readily to benzophenone, diphenylmethane and tetraphenylethane. These products were all identified in the pyrolysate from the ester IX. The first two products arise from an alkyl-oxygen scission of the ether (cf. 36), but the presence of the tetraphenylethane is more difficult to explain.

\[
\begin{align*}
(\text{Ph}_2\text{CH})_2\text{O} & \quad \rightarrow \quad \text{Ph}_2\text{CO} + \text{Ph}_2\text{CH}_2 \quad (A^1_R) \\
& \quad (+ \text{Ph}_2\text{CH} \cdot \text{CHPh}_2)
\end{align*}
\]

The absence of benzaldehyde in the pyrolysate of the ester shows that a $B^2$ scission does not take place during the pyrolysis of IX.

Benzoic acid, obtained in the pyrolysate from IX, is produced by the secondary decomposition of benzoic anhydride.

An interesting comparison can be drawn between the decomposition of IX and that of the corresponding acetate. Benzhydryl acetate is reported (46) to decompose to acetic acid, tetraphenylethane and tetraphenylethylene. This work was repeated by Bacon (47) who pyrolysed the ester at 300°C. The products obtained were acetic acid, benzophenone,
diphenylmethane and tetraphenyethylene, but no
tetraphenylethane. By analogy with IX, the writer interprets
the mechanism as:–

\[
\text{AcOCHPh}_2 \rightarrow \frac{1}{2} \text{Ac}_2\text{O} + \frac{1}{2} \left[ (\text{Ph}_2\text{CH})_2\text{O} \right] \quad (D)
\]

Dibenzhydryl ether, as mentioned previously, is a known
source of benzophenone and diphenylmethane. Acetic anhydride
decomposes at 500°C (39) to acetic acid and keten; however,
it is probable that the reaction will also occur at lower
temperatures.

\[
\text{Ac}_2\text{O} \rightarrow \text{AcOH} + \text{CH}_2\text{CO}
\]

Neither acetic anhydride nor keten was specifically sought by
Bacon although both products were probably present in the
ester pyrolysate.

Further work is necessary to explain why benzhydryl
benzoate produces tetraphenylethane and benzhydryl acetate
tetraphenyethylene.

The absence of acetaldehyde shows that a B² scission
does not take place.

\[
\text{AcOCHPh}_2 \rightarrow \text{MeCHO} + \text{COPh}_2 \quad (B^2)
\]

A third competitive reaction may be a B¹ scission
involving the migration of a hydrogen atom from the acyl
group to give keten and benzhydrol

\[
\text{AcOCHPh}_2 \rightarrow \text{CH}_2\text{CO} + \text{HOCHPh}_2 \quad (B^1)
\]
Benzhydrol decomposes at 300°C (48) by two competitive routes, dehydration and dehydrogenation. The first of these routes is an intermolecular elimination of water with the formation of dibenzhydryl ether. In theory, the water may either hydrolyse the acetic anhydride, formed by the D scission, or combine with the keten from the B\(^1\) scission, both processes giving acetic acid. The second competitive scission is dehydrogenation to benzophenone.

\[
\begin{align*}
2\text{Ph}_2\text{CHOH} & \xrightarrow{\text{H}_2\text{O} + (\text{Ph}_2\text{CH})_2\text{O}} \\
& \xrightarrow{2\text{H}_2 + 2\text{Ph}_2\text{CO}}
\end{align*}
\]

Since the above products can arise from the secondary decomposition of the products of the D scission, it is difficult to discriminate between the B\(^1\) and D scissions. However, a comparison with benzhydryl benzoate favours the D route with subsequent secondary breakdown.

In conclusion, a comparison of the pyrolyses of benzhydryl acetate and benzoate shows that disproportionation, yielding the anhydride and the unstable dibenzhydryl ether, is common to both. The acetate affords the possibility of a competitive B\(^1\) scission yielding keten and the unstable benzhydrol. B\(^2\) scission, although a possibility with both esters, does not take place. It is difficult to explain the formation of tetraphenylethylene in the acetate
and tetraphenylethane in the benzoate.

The introduction of two phenyl groups.

3.9. Triphenylmethyl Benzoate (X)

In triphenylmethyl benzoate (X), the nucleophilic effect of the phenyl groups is at a maximum. This nucleophilic repulsion will considerably weaken the alkyl-oxygen and the acyl-oxygen bonds. Furthermore the triphenylmethyl group can exist as a stable entity, viz as a stable free radical (49). The ester, therefore, should prove to be the most unstable of the nucleophilic substituted esters studied.

X decomposes on heating for 24 hours at 225°C. Disproportionation and decarboxylation are the only two identifiable routes of decomposition. A complex reaction (presumably free radical) also occurs producing benzene, benzoic acid and large amounts of triphenylmethane.

\[ \frac{1}{3} \text{Bz}_2\text{O} + \frac{1}{3} \left[ (\text{Ph}_3\text{C})_2\text{O} \right] \quad (D) \]

\[ \text{BzOCPh}_3 \quad \rightarrow \quad \text{CPh}_4 + \text{CO}_2 \quad (c^2) \]

\[ \rightarrow \text{PhH + BzOH + CHPh}_3 \]

Disproportionation produces benzoic anhydride and the unstable bistriphenylmethyl ether. Benzene and benzoic acid are secondary products arising from the decomposition of the benzoic anhydride. The ether is known (50) to decompose at its melting point but its breakdown products are unknown.
Decarboxylation of $X$ produces tetraphenylethane. This is another of the rare examples of true ester decarboxylation (for a review of which see MacKinnon & Ritchie (21).

The formation of triphenylethane, present in the pyrolysate in large quantities, is difficult to explain. Phenyl triphenylmethyl ketone, analogous to the ester $X$ except that it has a carbonyl instead of a carboxyl group, is known to decompose on distillation to produce large amounts of triphenylethane (51). Other products obtained from the ketone are 4-benzoyltriphenylethane, tetraphenylethylene, benzene, benzoaldehyde, benzophenone and 9-phenylfluorene.

\[
\text{Ph}_3\text{CCOPh} \rightarrow \text{CHPh}_3, \text{BzC}_6\text{H}_4\text{CHPh}_2, \text{Ph}_2\text{C:CPh}_2, \\
\text{PhH, PhCHO, Ph}_2\text{CO}, (\text{C}_6\text{H}_4)_2\text{CHPh}
\]

It can be seen that the decomposition of phenyl triphenylmethyl ketone is exceedingly complex. The formation of benzoaldehyde and 9-phenylfluorene is analogous to the formation of hydrogen chloride and the fluorene on pyrolysis of triphenylmethyl chloride at 200°C (52).

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{Cl} & \quad \text{C}_6\text{H}_5 \\
\text{Cl} & \quad - & \quad \text{C}_6\text{H}_5 \\
\text{C}_6\text{H}_5 & \quad \text{Cl} & \quad \text{H} & \quad \text{C}_6\text{H}_5 + \text{HCl}
\end{align*}
\]

On the above evidence it might seem reasonable to expect triphenylmethyl benzoate to follow a similar course, forming
benzoic acid and 9-phenylfluorene. The absence, however, of
the latter compound in the pyrolysate of the ester shows
that this route is not followed.

Triphenylmethyl acetate also produces large amounts of
triphenylmethane on heating (53) but this ester has not been
investigated fully.

A further product identified in the pyrolysate of X was
a crystalline material with a melting point (169°) almost
identical with that of the original ester (168°). Although
the micro-analyses of the two substances gave concordant
results, a mixed melting point was depressed by ca. 10°C.
To eliminate any personal error the melting point and mixed
melting point were checked by an independent worker who
obtained concordant results. Hydrolysis of both substances
yielded triphenylmethyl carbinol and benzoic acid. In many
respects the i.r. spectra were identical.

The relationship between the two substances is still
obscure; but a study of Stuart models suggests a possible
explanation which is here advanced tentatively as a basis for
future studies.
Figures 1 and 2 indicate that the ester may display a novel type of isomerism. In both figures, the triphenylmethyl group constitutes the base of the models with the benzoyloxy group raised above it, the relative positions of the triphenylmethyl group being identical. Model (A) represents the unhindered and presumably normal state of the molecule, with the benzoyloxy group upright and free to rotate; (B) represents the hindered structure of a possible isomer, with the benzoyloxy group locked between two of the phenyl groups of the triphenylmethyl group, and thus not free to rotate.
3.10. **General Assessment of Results.**

The introduction of an electrophilic atom or group into the alkyl group of an ester leads to a marked decrease in thermal stability. This has been shown already, prior to the present investigation, by the introduction of a cyano group to methyl benzoate giving cyanomethyl benzoate (16), which unlike its parent is highly unstable (see section 3.11). The addition of electrophilic radicals to benzyl benzoate confirms this decrease in stability.

The electronegative substituent X in the structure PhCO$_2$CH$_2$X causes an electronic displacement towards the benzyl group and in consequence weakens the alkyl-oxygen and acyl-oxygen bonds. The ester must, therefore, be less thermostable than its parent, PhCO$_2$CH$_2$Ph.

\[
\text{PhCO}_2\text{C-} \xrightarrow{\text{X}} \text{PhC-} \xrightarrow{\text{O}} \text{C-} \xrightarrow{\text{X}} \text{Ph}
\]

\((X = \text{Br, CN or Bz})\)

As might be predicted, the decrease in thermal stability is apparently connected with an increase in the electronegativity of the substituent as in the series:

\(H < \text{COPh} < \text{CN} < \text{Br}\)

This decrease in stability is measured by the amount of ester recovered after pyrolysis at 400-500°C.
The predominating route of breakdown for these electrophilic-substituted benzyl esters is acyl-oxygen scission $B^2$, the migrating group being the electronegative substituent. A minor competitive scission is disproportionation to the anhydride and the unstable substituted ether. It is unlikely that alkyl-oxygen scission $A^0$ to an acid and a substituted stilbene occurs, since these two compounds can be readily explained by the secondary decomposition of the disproportionation products.

A moderately high temperature (400-500°C) is required before a competitive scission $E$ takes place, giving an $\alpha$-diketone and $HX$ ($X$ being the electronegative radical). This particular scission takes place more readily with the cyano group, presumably owing to the ease of formation of a transitory cyanohydrin (cf. Robinson mechanism, section 3.2). If there is no available $\alpha$ hydrogen atom (e.g. $\alpha$: $\alpha$-dicyanobenzyl benzoate) this scission does not take place.

A comprehensive mechanism for the pyrolysis of esters is difficult to formulate, but two possibilities, one ionic and the other free radical, will be discussed later (section 4).

It has been found that the introduction of a nucleophilic grouping into the alkyl group of an ester causes a decrease in thermal stability, although this is less
marked than the introduction of an electrophilic grouping. It is useful to consider, as an example, methyl benzoate (XI), an ester of remarkable thermal stability (29), being unaffected in a flow reactor at 500°C (30). The substitution of one of the hydrogens in the methyl group by phenyl, giving benzyl benzoate, causes a slight decrease in thermal stability, some 20% of the ester decomposing at 500°C. The introduction of two and three phenyl groups, giving benzhydryl and triphenylmethyl benzoates respectively, decreases the stability still further.

Generally speaking, the instability brought about by the introduction of phenyl groups increases with an increase in the number of phenyl groups in the alkyl group, as in the series:

\[
\text{Me} < \text{CH}_2\text{Ph} < \text{CHPh}_2 < \text{CPh}_3
\]

If methyl benzoate is considered as the parent ester for the series the methyl group is "dormant", i.e. the three hydrogen atoms of the methyl group exert no directional influence on the alkyl-oxygen bond. The substitution of one of the hydrogens of the methyl group by phenyl, giving benzyl benzoate, introduces a slight repelling influence on the alkyl group and this in turn will be transferred to the electrons of the alkyl-group and thence to the acyl-oxygen bond. This repulsion will weaken the bonds and the ester
will be less thermally stable.

As more phenyl groups are introduced into the alkyl group, this repelling force will be increased, the alkyl-oxygen and acyl-oxygen bonds will be weakened still further and the esters will be less thermally stable.

There is a further factor to be considered. As more phenyl groups are introduced into the molecule, the greater will be the stability of the substituted benzyl group itself. For example, if three phenyl groups are introduced, giving triphenylmethyl benzoate, the triphenylmethyl group can exist as a stable free radical. The benzhydryl group behaves similarly (54) but to a lesser extent.

Since the pyrolysates of benzhydryl and triphenylmethyl benzoates are complex (more so than that from benzyl benzoate) the increasing introduction of phenyl groups into the alkyl group of an ester would appear to favour free radical breakdown. Acyl-oxygen scission $B^2$ and $\alpha$-diketone formation $E$ are suppressed entirely. Disproportionation is the main primary route of decomposition. Decarboxylation occurs in the breakdown of triphenylmethyl benzoate. Many of the products obtained, however, cannot be explained by
any of the known decomposition routes. It must be concluded that the introduction of nucleophilic groups (other than alkyl) into an ester favours a free radical breakdown.
3.11. \( \alpha \)-Diketone Formation.

There have been several examples in recent years of the formation of diketones from the pyrolysis of various esters. However, these are confined to the formation of \( \beta \)-diketones from the rearrangement of an isomeric enol carboxylate at ca. 500°C (55). For example, isopropenyl esters are known to isomerise to \( \beta \)-diketones.

\[
\text{RCO}_2\text{CMe}_2\text{CH}_2 \rightarrow \text{RCOCH}_2\text{COMe}
\]

This is a simple ester rearrangement involving no elimination from the parent ester. Young et al. (55) suggest that the mechanism involves a 1:3 shift through the intermediate formation of a 4-membered ring.

\[
\begin{align*}
\text{MeC-OH} & \quad \text{MeC-CH} \\
\text{MeC-} & \quad \text{MeCOCH}_2\text{COR}
\end{align*}
\]

Although the above reaction can also occur at ordinary temperatures catalysed by boron trifluoride, it is in this latter case an intermolecular reaction, not a rearrangement.

Allan, Forman, and Ritchie (10) have shown that vinyl esters also undergo amongst other competitive reactions, a thermal rearrangement yielding unstable \( \beta \)-ketoaldehydes which decarbonylate readily to ketones. Vinyl benzoate, for example, rearranges to benzoylacetaldehyde which decarbonylates to acetophenone.
BzOCH:CH₂ ⇌ PhCOCH₂CHO ⇌ PhCOMe + CO

The present work has, however, brought to light a real novelty in the pyrolytic formation of α-diketones from certain α-substituted esters. This is, of course, not simply a rearrangement, since the original ester and the diketone are not isomeric (as in the examples quoted above); the elimination of a simple molecule must occur in the process. Only in one previous publication does this novel reaction appear to be mentioned, though without comment or details. The pyrolytic A¹ scission of certain aryl α-acetoxypropionates (56) is accompanied by the formation of a little diacetyl. There appears to be no evidence for a B² scission. The present work suggests that the overall primary reaction is as follows:

\[
\begin{align*}
\text{AcOH} + \text{CH₂:CHCO₂Ar} & \quad (A¹) \\
\text{AcOCHMeCO₂Ar} & \quad \text{MeCOCOMe} + \text{HCO₂Ar} \quad (E)
\end{align*}
\]

(Ar = m-tolyl or p-chlorophenyl)

A¹ scission, giving acetic acid and aryl acrylate, predominates. The minor competitive scission E, should give the α-diketone, diacetyl, and the unstable aryl formate; the latter was not identified, but its key decomposition product (a phenol) was recorded (cf. section 1.4).
From the present results, several examples of α-diketone formation have now been obtained. For example, the pyrolysis of α-cyanobenzyl benzoate gives benzil, hydrogen cyanide being eliminated.

\[
\text{BzOCHPhCN} \rightarrow \text{PhCOCOPh + HCN} \quad (E)
\]

The E scission may be used to explain certain unexpected products from the pyrolysis of cyanomethyl benzoate. Bennett and Ritchie (16) investigated the pyrolysis of cyanomethyl benzoate and found that it decomposed entirely at 500°C. They interpreted the decomposition routes as:

\[
\begin{align*}
\text{BzOCH}_2\text{CN} & \rightarrow \text{BzCN + CH}_2\text{O} \quad (B^2) \\
& \quad \text{PhCHO + [HOCN]} \quad (B^2) \\
& \quad \text{BzOH + [CHCN]} \quad (A^0) \\
\end{align*}
\]

\[
\text{[HOCN]} \rightarrow \text{HCN + CO}
\]

The expected \( B^2 \) scission involving the migration of the cyano group, giving benzoyl cyanide and formaldehyde, predominated. The products of the \( A^0 \) scission (in the light of the present work) may be alternatively explained by the secondary decomposition of disproportionation products. The important reaction, however, (and unexpected to the above authors) was the formation of benzaldehyde, hydrogen cyanide and carbon monoxide. The authors envisaged a second type of competitive \( B^2 \) scission involving the migration of a hydrogen atom, benzaldehyde and the labile formyl cyanide.
being formed.

The present work shows that where the \( \alpha \) carbon atom in the alkyl group carries both a hydrogen atom and an electrophilic group (e.g. CN), only the latter group migrates during a B\(^2\) scission. In view of the pyrolytic formation of \( \alpha \)-diketones, the writer considers that the unusual products obtained by Bennett and Ritchie are more satisfactorily explained by an E scission, giving phenylglyoxal and hydrogen cyanide, the former decarbonylating to benzaldehyde, thus:

\[
\text{PhCOCHO} \longrightarrow \text{PhCHO + CO} \quad (\text{C}^1)
\]

\[
\text{PhCOCHO} \longrightarrow \text{PhCHO + CO} \quad (\text{C}^1)
\]

The following conditions appear necessary before an E scission can occur.

(i) It is preferable that there are no \( \rho \) hydrogen atoms in the alkyl group of the ester because such an ester would decompose almost quantitatively by alkyl-oxygen scission A\(^1\).

(ii) There must be at least one available hydrogen atom in the \( \alpha \) position of the alkyl group to facilitate the elimination of the electronegative substituent. If there is no available \( \alpha \) hydrogen atom, e.g. \( \alpha : \alpha \)-dicyanobenzyl benzoate (V), \( \alpha \)-diketone formation cannot take place.

(iii) All the observed examples of \( \alpha \)-diketone formation
occur with those esters possessing an electrophilic substituent (e.g. Br, CN) in the α position of the alkyl group. This substituent is eliminated from the molecule together with the α hydrogen atom, the rest of the ester fragment rearranging to the diketone. The best yields of diketone occur with α-cyanosubstituted esters, presumably owing to the ease of formation of a stable transitory cyanoxydrin.

(iv) If there is more than one nucleophilic substituent (e.g. Ph) in the α position of the alkyl group (e.g. benzhydryl benzoate) the α-diketone reaction is suppressed.

(v) Moderately high temperatures (400-500°C) appear to be a necessary condition for the reaction.

Although the α-diketones obtained from acetyl and benzoylbenzoins may arise from an E reaction, the writer considers it more likely that they occur directly from a B2 scission since this latter route predominates in the other electrophilic substituted esters studied.

Poly (ethylene terephthalate), Terylene, is a polyester of considerable commercial value as a synthetic fibre. It is 'melt-drawn' into fibre form at 280°C (57). The temperature is critical, since decomposition sets in at ca. 300°C (58) producing a low molecular weight polymer of little commercial use. The thermal decomposition of this polyester has been studied in the last few years in these laboratories by means of model systems (59). Each model represents an important repeating or terminal unit in the polymer chain. One of the models studied is ethylene dibenzoate, which represents the ethylene linkage between the carboxyl groups in the polymer.

Ethylene dibenzoate decomposes at 400-500°C by a single primary route of decomposition, viz alkyl-oxygen scission $A^1$ giving benzoic acid and vinyl benzoate (10, 34).

$$\text{BzOCH}_2\text{CH}_2\text{OBz} \rightarrow \text{BzOH} + \text{BzOCH}:\text{CH}_2 \quad (A^1)$$

There are secondary breakdown products. Vinyl benzoate decomposes via three competitive scissions (section 1.5). It will be shown later that the primary $A^1$ scission products undergo thermal readdition to ethyldiene dibenzoate which in turn disproportionates to benzoic anhydride and acetaldehyde, the last two products also being identified in the pyrolysate from ethylene dibenzoate.
Methylene dibenzoate (XII) has been studied by Allan, Jones and Ritchie (34); see also Jones (60). This ester, which is similar to ethylene dibenzoate except that it possesses a single methylene group, has no available \( \beta \) hydrogen atoms and, therefore, is more thermally stable than its higher homologue. It is not appreciably decomposed below 500–550\(^\circ\)C but at this temperature it undergoes disproportionation.

\[
\text{BzOCH}_2\text{OBz} \longrightarrow \text{Bz}_2\text{O} + \text{CH}_2\text{O} \quad (D)
\]

Minor products observed were hydrogen and carbon monoxide (from formaldehyde), and carbon dioxide, benzene, benzoic acid, benzaldehyde, benzophenone and diphenyl (from benzoic anhydride). The last three products only occur at 550\(^\circ\)C.

Two other routes of decomposition remain formal possibilities, \( B^2 \) scission and decarboxylation.

\[
\begin{align*}
\text{BzOCH}_2\text{OBz} & \longrightarrow \text{PhCHO} + \begin{bmatrix} \text{BzOCHO} \end{bmatrix} \quad (B^2) \\
& \longrightarrow \text{BzOCH}_2\text{Ph} + \text{CO}_2 \quad (C^2)
\end{align*}
\]

Acyl-oxygen scission \( B^2 \) would give benzaldehyde and the labile compound XIX. This latter could undergo decarbonylation (as an aldehyde) or behave as a mixed benzoic formic anhydride which would give benzoic and formic anhydrides in accordance with the observation that mixed anhydrides disproportionate to two simple anhydrides (25).
Formic anhydride is unknown, presumably decomposing as it is formed to carbon monoxide, carbon dioxide and hydrogen.

Since the end products can also arise from other sources, there is no evidence to support the B^2 route specifically. Ethylidene dibenzoate (discussed later) also gives a little benzaldehyde at ca. 500°C and here again a B^2 route is a possibility, but there is no evidence for acetic anhydride (or its breakdown products) which would be formed by disproportionation of the mixed benzoic acetic anhydride. This, therefore, affords indirect evidence against a B^2 route in methylene dibenzoate.

Similarly, decarboxylation should yield benzyl benzoate or its key breakdown product toluene, neither of which was detected.

Alkylidene diesters may be prepared by the catalysed addition of an acid to a vinyl ester (61). This addition may also take place thermally and without a catalyst (34). Thus, the refluxing of vinyl benzoate and benzoic acid will initially give ethylidene dibenzoate (XIII), which then decomposes by a D scission to benzoic anhydride and
acetaldehyde.

Ethylidene dibenzoate (XIII), on pyrolysis at 500°C, undergoes two competitive reactions, (a) a major disproportionation D to benzoic anhydride and acetaldehyde, and (b) a minor alkyl-oxygen scission A¹ to benzoic acid and vinyl benzoate.

\[
\begin{align*}
BzOCHMeOBz & \quad \longrightarrow \quad Bz_2O + MeCHO \\
XIII & \quad \longrightarrow \quad BzOH + BzOCH:CH_2
\end{align*}
\]

A by-product of pyrolysis is acetophenone, originating from the vinyl benzoate which rearranges to benzoylacetaldehyde, the latter then decarbonylating (see section 3.11).

By analogy with the dibenzoate, ethylidene diacetate decomposes via two competitive routes (a) a major disproportionation D to acetic anhydride and acetaldehyde, and (b) a minor alkyl-oxygen scission A¹ to acetic acid and vinyl acetate (28).

\[
\begin{align*}
AcOCHMeOAc & \quad \longrightarrow \quad Ac_2O + MeCHO \\
& \quad \longrightarrow \quad AcOH + AcOCH:CH_2
\end{align*}
\]

In conclusion, the primary decomposition of ethylene dibenzoate (a 1:2-alkylene ester) proceeds solely through alkyl-oxygen-scission A¹ to benzoic acid and vinyl benzoate.
These two products add thermally to form ethylidene dibenzoate (a 1:1-alkylidene diester), isomeric with the original ester. This in turn disproportionates to benzoic anhydride and acetaldehyde.

\[
\begin{align*}
\text{BzOCH}_2\text{CH}_2\text{OBz} & \xrightarrow{\text{A}} \text{BzOH} + \text{BzOCH}\text{CH}_2 & \xrightarrow{\text{A}} \text{BzOCHMeOBz} \\
& \xrightarrow{D} \text{Bz}_2\text{O} + \text{MeCHO}
\end{align*}
\]

The pyrolysis of benzoic anhydride has been investigated to assist in the interpretation of the decomposition of methylene dibenzoate and the substituted benzyl benzoates. The present work shows that the anhydride is remarkably thermostable. It breaks down in part at 550°C yielding a complex pyrolysate containing mainly benzene and benzoic acid. Other products identified are carbon monoxide, carbon dioxide, diphenyl, benzaldehyde and benzophenone.

This is broadly in line with the work of Sabatier (62) who passed the anhydride vapours over calcium carbonate at 550°C and identified the above products. However, Sabatier also identified anthraquinone, which was not detected in the present work, and may have been due to catalysis by the calcium salt.

Obviously the decomposition of benzoic anhydride is exceedingly complex. Prior to the present investigations, it was considered that there would be two routes decomposition.
(a) decarboxylation $C^2$, and (b) decarbonylation $C^1$.

\[
\text{BzOBz} \quad \xrightarrow{\text{PhCO}^+ \text{Ph} + \text{CO}} \quad \text{PhCO}_2^+ \text{Ph} + \text{CO} \\
\text{(C}^2\text{)} \quad \text{(C}^1\text{)}
\]

It has now been found that decarboxylation occurs only to a slight extent and there is no evidence for decarbonylation.

The large amounts of benzene and benzoic acid observed are not readily explained. There must be a very complex free radical breakdown. That such radical reactions occur has been demonstrated by the formation of chlorobenzene and hexachlorobenzene during a co-pyrolysis at 550°C of an equimolar mixture of benzoic anhydride and carbon tetrachloride. Since carbon tetrachloride itself is thermostable up to 600°C (63), the free radicals must be generated by the benzoic anhydride. The use of carbon tetrachloride as a radical detector is similar to that of carbon tetraiodide (64) used to detect alkyl radicals in the thermal breakdown of lead alkyls.

**Conclusions**

The introduction of the benzoyloxy group into methyl benzoate, giving methylene dibenzoate (XII), causes a decrease in thermal stability. This is due in part to the electrophilic character of the group but it is also due to the fact that two ester groups are attached to a single
carbon atom, presumably facilitating disproportionation. This instability is confirmed by the breakdown of ethylidene dibenzoate (XIII) which, although possessing \( \beta \) hydrogen atoms, decomposes mainly by disproportionation.

On the other hand, the lack of \( \beta \) hydrogen atoms in methylene dibenzoate gives an ester relatively more stable than ethylene dibenzoate, a model compound of "Terylene". This is of considerable importance since if poly (methylene terephthalate) can be prepared, it should theoretically be more thermostable than poly (ethylene terephthalate), although it is difficult to predict whether the former polymer would have useful fibre-forming characteristics.

Two attempts in the present investigations to prepare poly (methylene terephthalate) have not met with any success (see Appendix III).
4. **Interpretations of ester breakdown**

It is evident from the results that the mechanism of ester breakdown is exceedingly complex. Apart, perhaps, from the molecular mechanism for the alkyl-oxygen scission $A^1$ involving an intermediate 6-membered chelate ring, there is no agreed mechanism for ester breakdown. Two tentative mechanisms are discussed below, which attempt to explain breakdown with particular reference to substituted benzyl esters. The first of these mechanisms is ionic, the second free radical.

4.1. **Ionic Mechanism**

**Introduction**

All reactions in organic chemistry are explained by some application of electronic theories. These theories are based on electronic displacements brought about by differences in the electronegativity of the different atoms in the molecule. Reactions, in which these displacements occur, are said to be "heterolytic" or "polar" reactions, terms which signify that the transition state carries electric charges. Ionic character is, therefore, not confined entirely to inorganic chemistry.

A single bond may behave either as a covalent or as an electrovalent bond. A double bond may react as if it consisted of a covalency and an electrovalency. The reactivity
of such compounds is based on the ease of conversion of a covalency to an electrovalency. This conversion is termed "heterolysis" and involves the breaking of a covalent bond so that the electron pair is retained by one of the separating fragments. An example of this is provided by methyl iodide (65):-

\[ \text{Me:} \text{I} \xrightarrow{\text{Me}^+ + \text{I}^-} \]

(Iodine has a high electronegativity; the methyl group has a low electronegativity).

Aldehydes and ketones are considered to resonate between the two canonical structures (a) and (b) (66):-

\[ \begin{array}{cc}
\text{R}_2\text{C} : \ddot{\text{O}} & \xrightarrow{\text{R}_2\text{C}^+ : \ddot{\text{O}}^-} \\
\text{(a)} & \text{(b)}
\end{array} \]

The characteristic addition reactions of aldehydes and ketones are attributed (67) to this polar activation of the carbonyl group, \( \text{C} - \ddot{\text{O}} \xrightarrow{\text{C}^+ - \ddot{\text{O}}^-} \). The carbon atom is the centre of attack in an addition reaction, e.g. cyanohydrin formation from carbonyl compounds is considered (68) to proceed:

\[ \text{R}_2\text{C} = \ddot{\text{O}} \xrightarrow{\text{R}_2\text{C}^+ - \ddot{\text{O}}^-} \]
These electronic theories have been used as a basis to explain certain reactions which are important in pyrolysis work, e.g. Tischtschenko and Cannizzato reactions (69).

**Application of theory.**

The various schemes outlined below are shown for convenience as ionic dissociations rather than as ionisations. It is impossible at present to decide which of the two is the correct interpretation.

The preparation of α-bromobenzyl benzoate from benzaldehyde and benzoyl bromide proceeds via a Tischtschenko-type addition. The reaction is one of self-addition. No catalyst is present and heat is not required. It is unlikely, therefore, that free radicals are present.

On the basis of the polar activation of the carbonyl group, benzaldehyde will resonate between two forms:

\[
\begin{align*}
\text{Ph:C::O} & \leftrightarrow \text{Ph:C:O:} \\
\text{H} & \text{H}
\end{align*}
\]

Owing to the strong electron attraction of the bromine atom, benzoyl bromide will tend to ionise into the benzoyl
cation and the bromide anion, rather than resonate between two forms as does benzaldehyde (see Appendix I).

\[
\begin{align*}
\text{Ph}:\text{C}:\text{O} & \quad \text{Ph}:\text{C}:\text{O} + \text{Br} \\
\text{Br} & \quad \text{Ph}:\text{C}:\text{O} + \text{Br}
\end{align*}
\]

Evidence for the ionisation of benzoyl bromide is based on its ease of hydrolysis to benzoic acid and hydrogen bromide in the presence of a trace of moisture. Halogen atoms attached to a carbon atom may separate as ions in suitable solvents. For example, acetyl chloride dissociates in nitromethane into acetyl cations and chloride anions (70). Benzoyl cations have similarly been shown to exist (see Appendix I).

This concept of ionisation of the acid halide is of considerable interest. Benzoyl chloride, by analogy, would give benzoyl and chloride ions. The alkaline hydrolysis, therefore, of this acid chloride would proceed as follows:

\[
\begin{align*}
\text{PhCOCl} & \quad \text{PhCO} + \text{Cl} - \text{OH} \rightarrow \text{PhCOOH} + \text{Cl} - \rightarrow \text{PhCOO} - \text{HCl} \\
\end{align*}
\]

This offers an alternative explanation to the mechanism postulated by Remec (71).

\[
\begin{align*}
\text{PhCOCl} + \text{OH} & \quad \text{PhC} - \text{O} + \text{OH} \rightarrow \text{PhC} - \text{OH} \rightarrow \text{PhCOO} - \text{HCl} \\
\end{align*}
\]

In the preparation, therefore, of \(\alpha\)-bromobenzyl benzoate from benzoyl bromide and benzaldehyde, the original
benzoyl bromide will ionise to benzoyl and bromide ions and the benzaldehyde will exist in an activated state. It has been mentioned previously that the carbonium ion is the centre of attack in addition reactions (68). The bromide anion produced from the ionisation of benzoyl bromide will unite with benzaldehyde to form an unstable anion, which will combine with the benzoyl cation to form α-bromobenzyl benzoate.

\[
\begin{align*}
\text{Ph-C}=\overset{\cdot}{\text{O}} & \text{H} & \text{Ph-C}=\overset{\cdot}{\text{O}} & \text{H} \\
+ \text{Br} & \text{Ph-C}=\overset{\cdot}{\text{O}} & \text{H} & \text{PhC}=\overset{\cdot}{\text{O}} \text{C-Ph} \\
\text{Ph-C}=\overset{\cdot}{\text{O}} \text{H} & + \text{Ph-C}=\overset{\cdot}{\text{O}} \text{H} & \text{PhC}=\overset{\cdot}{\text{O}} \text{C-Ph}
\end{align*}
\]

**Routes of Decomposition.**

**Acyl-oxygen scission B²**

This class of scission has been shown to be general for esters containing no \( \beta \) hydrogen atoms in the alkyl group, the ease of scission being dependent on the nature of the electrophilic substituent in the α position. If there is a nucleophilic instead of an electrophilic substituent, the scission tends to be suppressed.
Consider as an example, $\alpha$-bromobenzyl benzoate. Two possibilities can occur on pyrolysis; either the mechanism will involve the initial loss of the bromide anion and the subsequent decomposition of the cationic intermediate, or the mechanism will be a simple reversal of the Tischtschenko-type preparation of the ester.

The first possibility involves the initial loss of the bromine atom, the cationic intermediate subsequently decomposing. This is based on a study of the table of bond energies (72) which shows that the C-Br bond is the weakest in the ester and therefore the bromine atom will be more readily lost from the molecule.

\[
\begin{align*}
\text{Ph-C-O-C-Ph} & \quad \rightarrow \quad \text{Ph-C-O-C-Ph} + \text{Br} \\
\text{Ph-C-O-C-Ph} & \quad \rightarrow \quad \text{Ph-C} + \text{C-Ph} \\
\text{Ph-C} + \text{Br} & \quad \rightarrow \quad \text{Ph-CBr}
\end{align*}
\]

This mechanism is considered unlikely since the intermediate cation would be relatively stable. It is more likely that the mechanism is a reversal of the Tischtschenko-type ester preparation.

The relative electron attractions of the different atoms and groups (73) show that bromine has a strong and
phenyl a weak electron attraction. The carbonyl group is also known to be electrophilic. Hence, α-bromobenzyl benzoate (i) may be considered to exist as:

$$\begin{align*}
\text{Ph-C} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\end{align*}$$

(i)

If it is assumed that, because of the combination of the different electron attractions of the atoms and groups in the molecule, the acyl-oxygen bond has a lower bond energy than the C-Br bond, then scission will be a reversal of the postulated self-addition reaction for the ester preparation. Scission, therefore, takes place at the acyl-oxygen bond, producing a benzoyl cation (ii) and the α-bromobenzyloxy anion (iii). This latter loses bromine giving benzaldehyde. The bromine unites with (ii) to form benzoyl bromide.

$$\begin{align*}
\text{Ph-C} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\end{align*}$$

(i) (ii) (iii)

$$\begin{align*}
\text{Ph-C} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\end{align*}$$

(iii)

$$\begin{align*}
\text{Ph-C} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\text{Br} & \equiv \text{O} \equiv \text{C-Ph} \\
\end{align*}$$

(ii)
\( \alpha \)-Diketone formation E

Benzoyl benzoin (VII) was identified in the pyrolysate from \( \alpha \)-cyanobenzyl benzoate (II). VII was considered to be the prime source of \( \alpha \)-diketone from the ester II. Since the Robinson mechanism, discussed in section 3.2, requires four distinct steps to produce the \( \alpha \)-diketone, a simpler mechanism has been sought.

Again, consider \( \alpha \)-bromobenzyl benzoate (i) as an example. The ester decomposes, as mentioned above, to a benzoyl cation (ii) and the \( \alpha \)-bromobenzylxyloxy anion (iii). It is assumed that this latter can rearrange to a "hydrid" anion (iv) which can combine with (ii) to form the monobromohydrin of benzil (v) which will readily lose hydrogen bromide and form benzil.

\[
\begin{align*}
\text{(i)} & : \text{O} & \text{H} & \text{Ph-C-} & \text{O-} & \text{Ph} \\
& & & \text{Br} & & \\
\text{(ii)} & : \text{O} & \text{H} & \text{Ph-C}^+ & \text{Ph} & \text{Br} \\
& & & \text{Br} & & \\
\text{(iii)} & : \text{O} & \text{Br} & \text{Ph-C-O}^{-} & \text{Ph} & \text{Br} \\
\text{(iv)} & : \text{O} & \text{Br} & \text{Ph-C-OH} & \text{Br} & \\
\text{(v)} & : \text{O} & \text{OH} & \text{Ph-C}^- & \text{Ph} & \text{PhCO}^- & \text{OH} & + \text{HBr}
\end{align*}
\]
Unless there is an electrophilic group in the $\alpha$ position of the alkyl group in the ester, $\alpha$-diketone formation does not take place because rearrangement of the anion cannot take place. Thus $\alpha$-bromo- and $\alpha$-cyanobenzyl benzoates readily produce the $\alpha$-diketone on pyrolysis. Benzhydryl and triphenylmethyl benzoates do not. Benzyl benzoate itself occupies an intermediate position. Furthermore, the extent of formation of $\alpha$-diketone will be dependent on the stability of the "hydrin" ion. Thus a cyanohydrin anion would be expected to be more stable than a bromohydrin. More $\alpha$-diketone, therefore, would be expected from $\alpha$-cyanobenzyl benzoate than from $\alpha$-bromobenzyl benzoate. This has been found to be so.

Disproportionation D

The esters under consideration are known to undergo disproportionation, and, therefore, it is probable that dissociation takes place at the ether-alkyl bond.

\[
\text{Ph-C-O-C-Ph} \quad \rightarrow \quad \text{Ph-C-0-} + \text{C-Ph} \\
\text{(i)} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \q
There are two possibilities which can explain the formation of benzal bromide, which decomposes to $\alpha : \alpha^1$-dibromostilbene. The first involves the union of the $\alpha$-bromobenzyl cation (vii) with a bromide ion to give benzal bromide.

The second possibility involves combination of the $\alpha$-bromobenzyl cation (vii) with the $\alpha$-bromobenzyloxy anion (iii), the latter produced by an acyl-oxygen scission, to form the unstable $\alpha : \alpha^1$-dibromobenzyl ether which is a probable source of benzal bromide.

Conclusions.

If the above tentative picture is correct, acyl-oxygen scission $B^2$ should predominate, other scissions e.g. disproportionation $D$, occurring to a relatively minor extent, with esters containing an electrophilic atom or group in the
α position of the alkyl group. A typical example of this is α-bromobenzyl benzoate which decomposes to a large extent by the B2 route, the D route occurring to a minor extent.

Nucleophilic atoms or groups in the α position of the alkyl group, e.g. phenyl, should suppress acyl-oxygen scission, although disproportionation can still occur to a minor extent. Examples of this are benzhydryl and triphenylmethyl benzoates.

α-Diketone formation is dependent on the nature of the substituent in the α-position and on the stability of the "hydrin" ion. There must be at least one α hydrogen atom. If there is none (e.g. α:α-dicyanobenzyl benzoate) α-diketone formation does not take place.

The concept of polar gaseous reactions finds support in a recent lecture by Ingold (74). Maccoll (75) has found that the elimination of hydrogen bromide during pyrolysis of sec. and tert.-alkyl bromides follows a heterolytic unimolecular mechanism. Similarly, the elimination of acids from the pyrolysis of sec. and tert.-alkyl esters has been shown (76) to be a heterolytic unimolecular reaction; primary alkyl esters, on the other hand, decompose by a free radical chain mechanism.

4.2. Free Radical Mechanism

Free radicals offer an alternative basis, now to be
discussed, for a mechanism explaining the thermal decomposition of esters. There are numerous examples in the literature showing the formation of radicals in the pyrolysis of organic compounds (77), e.g. aldehydes, ketones, acid halides, alkyl halides. On the above evidence, therefore, it seems reasonable to expect radicals to be present during pyrolytic ester breakdown. A reaction mechanism based on free radicals can be drawn up as follows to explain the decomposition of substituted benzyl esters.

**Application.**

As with all free radical reactions, the mechanism under discussion involves initiation, propagation and termination steps. In the initiation step, the ester collides with a free radical. The ester used as an example is again α-bromobenzyl benzoate (i). It has been mentioned previously that in ester (i), the C-Br bond appears to be the weakest in the molecule. It is reasonable, therefore, to expect the bromine atom to be removed initially if the ester (i) collides with a radical. The resulting radical (ii) will probably be unstable and rearrange to a more stable form, giving the benzoyl radical (iii) and benzaldehyde.
Initiation step.

\[
\begin{align*}
\text{PhC-OCHPhBr} + R^* & \rightarrow \text{PhC-O-CHPh} + \text{RBr} \\
\text{(i)} & \rightarrow \text{(ii)} \\
\text{PhC-O-CHPh} & \rightarrow \text{Ph-C}^* + \text{PhCHO} \\
\text{(ii)} & \rightarrow \text{(iii)}
\end{align*}
\]

The propagation step involves the transfer of the unpaired electron on (iii) to another ester molecule. The benzoyl radical (iii) will collide with a second molecule of (i) to form benzoyl bromide and the ester radical (ii).

Propagation step.

\[
\begin{align*}
\text{PhCO}^* + \text{PhCO.OCHPhBr} & \rightarrow \text{PhCOBr} + \text{PhCO.OCHPh}^* \\
\text{(iii)} & \rightarrow \text{(i)} \\
\text{PhCO.OCHPh}^* & \rightarrow \text{PhCO}^* + \text{PhCHO} \\
\text{(ii)} & \rightarrow \text{(iii)}
\end{align*}
\]

Acyl-oxygen scission $B^2$, producing benzoyl bromide and benzaldehyde, may be regarded as a chain reaction. The length of the chain will determine the extent to which the reaction occurs, and this in turn is dependent on the termination step.

Termination Step.

Several different possibilities may lead to termination of the chain reaction. All of these will produce by-products
of acyl-oxygen scission.

Two like radicals may collide, e.g. benzoyl radicals may produce benzil.

\[ 2 \text{PhCO}^* \rightarrow \text{PhCO} \cdot \text{COPh} \]

A collision of two like radicals is improbable since it is more usual for like to combine with unlike.

It is possible that the ester may dissociate at the ether-alkyl bond to produce two radicals

\[ \text{PhCOO}^* \cdot \text{CHPhBr} \rightarrow \text{PhCOO}^* + \text{*CHPhBr} \]

(i) (iv) (v)

The benzoyloxy radical (iv) can combine with (iii) to produce benzoic anhydride.

\[ \text{PhCO}^* + \text{*OCOPh} \rightarrow \text{PhCOOCOPh} \]

(iii) (iv)

If dissociation occurs at the acyl-oxygen bond, two further radicals will be produced.

\[ \text{PhCOOCCHPhBr} \rightarrow \text{PhCO}^* + \text{*OCPhBr} \]

(i) (iii) (vi)

The \( \alpha \)-bromobenzyloxy radical (vi) may unite with (v) to form \( \alpha : \alpha^1 \)-dibromodibenzyl ether.

\[ \text{PhCHBrO}^* + \text{*CHPhBr} \rightarrow \text{PhCHBrOCHPhBr} \]

(vi) (v)

There are various other theoretical termination steps which could produce a wide variety of products not identified in the ester pyrolysate, e.g. (iii) with (v), (ii) with (vi).
Decarboxylation.

All the examples of ester decarboxylation come from those esters which decompose in a highly complex manner, e.g. vinyl benzoate, triphenylmethyl benzoate, \( \alpha: \alpha \)-dicyanobenzyl benzoate. In all these examples the carboxyl group of the ester is immediately attached to an unsaturated group or groups, e.g. phenyl, alkenyl group. These esters very probably decompose via a free radical mechanism. All the recorded examples of decarboxylation have the maximum number of unsaturated groups in the \( \alpha \) position of the alkyl group (e.g. three in a substituted methyl group). This unsaturation presumably leads to resonance of the unpaired electron within the radical and so produces stability. For example, the triphenylmethyl group is extremely stable owing to this resonance effect (49). Other esters, e.g. benzyl benzoate, cannot stabilise a radical and therefore decarboxylation is considered unlikely.

4.3. Conclusions.

From the foregoing discussion it may be seen that a single mechanism cannot explain ester breakdown completely. There is evidence to show that free radicals are present during the pyrolysis of esters and they must be used to explain, e.g. the secondary breakdown of benzoic anhydride and the formation of triphenylmethane from triphenylmethyl
benzoate. On the other hand there is no evidence as yet to show that these radicals are involved in primary ester breakdown, although it is almost certain that decarboxylation, at least, proceeds via a free radical mechanism. The decomposition of benzhydryl and triphenylmethyl benzoates is probably free radical.

A free radical mechanism should yield a wide variety of products, not identified in the pyrolysates from the various esters. It does not explain the Tischtschenko-type reaction for the preparation of \( \text{\( \alpha\)} \)-bromobenzyl benzoate, nor does it explain satisfactorily \( \text{\( \alpha\)} \)-diketone formation.

An ionic mechanism, on the other hand, can explain the preparation of \( \text{\( \alpha\)} \)-bromobenzyl benzoate and the primary routes of decomposition of the electrophilic-substituted benzyl esters, except decarboxylation. The mechanism should not produce such a wide variety of products, explains all the primary products obtained, but does not explain secondary breakdown, e.g. of benzoic anhydride.

In conclusion, it is impossible to postulate a single mechanism which explains completely the overall breakdown of an ester. It is possible that both the mechanisms discussed above occur simultaneously or consecutively. It is also possible that other mechanisms are involved. There is, as yet, insufficient information available to prove or disprove
any single mechanism.

The field of investigation is so open that a short series of experiments would be inadequate to explain the mechanism of ester breakdown. However, a continuation of the preliminary investigations described in Appendix II, using an ionisation detector, is suggested. This should determine conclusively whether ions are present and perhaps even detect which ions are present. The addition of suitable inhibitors, e.g. benzoquinone, prior to pyrolysis may prevent certain ester scissions and so decide if the mechanisms are free radical or not.
Apparatus and Analytical Methods

5.1. Apparatus

The apparatus used (Figure 3) was of the type described by Allan, Forman, and Ritchie (10). It consisted of a Pyrex tube, packed with small lengths of Pyrex tubing, supported vertically inside an electric furnace which was maintained at the desired temperature by means of a variable resistance and a "Simmerstat" energy control. The temperature was measured by a chromel-alumel thermocouple situated within the furnace. Various reaction vessels were used, the dimensions of these being given below. The difference in volumes between the unpacked tube and the actual packing itself gives the free volume of the reaction vessels.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Heated Length (cm)</th>
<th>Bore (cm)</th>
<th>Free Volume (ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Pyrex, large</td>
<td>40</td>
<td>3.0</td>
<td>200</td>
</tr>
<tr>
<td>2. Pyrex, medium</td>
<td>30</td>
<td>2.3</td>
<td>50</td>
</tr>
<tr>
<td>3. Pyrex, small</td>
<td>18</td>
<td>2.0 inlet</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0 outlet</td>
<td></td>
</tr>
<tr>
<td>4. Pyrex, micro</td>
<td>12</td>
<td>2.5 inlet</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5 outlet</td>
<td></td>
</tr>
</tbody>
</table>

Before every run, the system was evacuated and flushed several times with nitrogen in order to remove oxygen and prevent combustion of the vapours. The system, however, was not rigorously oxygen-free because the nitrogen added
contained a trace of oxygen (ca. 0.05-0.1%). The material to be pyrolysed was added by means of a dropping funnel equipped with a side arm for the equalisation of the pressure on the feed. Liquids were added dropwise from the funnel. Low-melting solids were first melted in the funnel by means of an electric heating jacket and then added as liquids. Liquid and solid pyrolysates were collected in a receiver via an inclined air condenser; low boiling liquids and gases were then passed through a water condenser to a second receiver cooled in a Drikold-acetone bath. The exit gases were collected in a 20-litre aspirator over water with an overlying layer of liquid paraffin and equipped with a constant pressure device.

In the case of triphenylmethyl benzoate, a high melting solid, the pyrolysand was introduced in the form of pellets. The pellets (each ca. 0.25g) were contained in an inclined tube, which replaced the dropping funnel, and moved gradually by means of an iron rod activated by a slowly moving solenoid. By controlling the speed of the solenoid, the pellets were allowed to drop into the reactor singly and at any required rate.

The rate of addition of the pyrolysand was kept arbitrarily within the limits 0.3 - 0.6g/min. From this, it was possible to determine the contact time from the formula
devised by Smith et al. (78).

In certain cases it was found necessary to supplement or replace the Drikold trap by appropriate chemical traps. Thus, hydrogen cyanide from the cyano esters was removed from the gaseous pyrolysate by a 30% caustic potash solution, hydrogen bromide from VI by water. Volatile aldehydes were removed as 2,4-DNPs by a solution of 2:4-dinitrophenylhydrazine in dilute hydrochloric acid. Keten was removed as acetanilide by an aniline/ether trap.

**Static reactor (5)**

The apparatus consisted of a 3-necked Quickfit flask, with a thermocouple pocket and nitrogen inlet, and heated by an "Electrothermal" heating mantle. It was assembled as a reflux apparatus, the exit gases being led off via a water condenser, receiver, and Drikold trap to the gas aspirator. As with the flow reactors, the system was evacuated and flushed several times with nitrogen before each run.
Semi-micro reactor (6)

The apparatus (Figure 4) was of the type described by Bain and Ritchie (79). Its chief usefulness is in the analysis of gases and in the investigation of small amounts of valuable material. The pyrolysand (300mg.) was placed in bulb C, and bulb D filled with glass beads, constriction E preventing their entry into C. The whole was evacuated and filled with nitrogen via F and G. Furnaces A and B were heated to the desired temperature and A slowly raised over a period of five minutes from position 1 to position 2 to enclose C. The barometric leg H was adjusted throughout the run to collect the gases evolved and to keep the system at atmospheric pressure. Non-gaseous material was collected in a cold trap cooled by Drikold-acetone.

After pyrolysis (10 mins.) A was lowered to position 1 and the system allowed to stand for 15 minutes. The gas evolved during pyrolysis was measured from readings on the gas burette J. About 80% of the gas in the system was then collected for analysis by adjusting the barometric leg so as to evacuate the system partially. The gas analysis was conducted by the Sleigh method (80).

5.2. Methods of Analysis

Chemical Analysis

The pyrolysates were separated into fractions by
fractional distillation. The fractions were then examined by standard chemical methods. Unless otherwise stated, aromatic hydrocarbons were characterised as their nitration products. Thus benzene was characterised as $m$-dinitrobenzene, m.p. 80°C; toluene as 2:4-dinitrotoluene, m.p. 72°C; diphenyl as 4:4\textsuperscript{1}-dinitrodiphenyl m.p. 234°C; diphenylmethane, as 2:4:2\textsuperscript{1}:4\textsuperscript{1}-dinitrodiphenylmethane, m.p. 172°C. Aldehydes and ketones were characterised by their conversion to 2:4-DNPs, mixtures being separated by column chromatography and identified by paper chromatography. Benzonitrile was converted to benzamide by alkaline hydrogen peroxide (81). All solid products were identified by mixed m.ps.

Anhydrides were detected by the Davidson–Newman colour test (82).

Hydrogen cyanide collected in the chemical traps was estimated volumetrically by the silver nitrate method (83). Hydrogen bromide was likewise estimated by titration against a standard silver nitrate solution (84). Except when reactor 6 was used, all gases were estimated by the Hempel method.

**Infra-red spectrometry**

In many cases the chemical methods of analysis were supplemented by i.r. spectrometry. The instrument used was the double-beam type described by Brownlie (85). Liquids
were examined either in a capillary or in a standard cell. Solids were made into a mull with Nujol and examined in a capillary. Gases were examined in a 10 cm. gas cell. The vessels used were all faced with rock salt. The various samples examined were compared with standards so that their identities were established by obtaining two identical spectra.

**Chromatography.**

This section is divided into (a) column and (b) paper chromatography.

(a) Column Chromatography.

The use of column chromatography was confined to the separation into distinct fractions of mixtures of 2:4-DNPs. The column used was bentonite/kieselguhr (86) with chloroform as the eluting solvent. The eluate was collected in 5 ml fractions. Distinct concentrations of material in the fraction were obtained by plotting optical density against fraction number. The various fractions were concentrated and identification established by paper chromatography.

(b) Paper Chromatography.

The method employed for paper chromatography was that described by Burton (87). Whatman No. 1 paper was treated with either ethyl lactate-water (70:30) or ethyl tartarate,
water, methanol (5, 15 and 60 ml respectively) and the paper carefully dried. The 2:4-DNPs were dissolved in chloroform and spotted onto the paper which was then developed in a tank saturated with solvent vapour. The most satisfactory solvent was found to be 2% carbon tetrachloride in light petroleum (60–80°).  

The unknown 2:4-DNPs were run against standard samples. The distances travelled by the unknown materials were noted at the end of every run and compared with the standards. Ultra-violet light facilitated the analysis of the chromatogram, the pale yellow spots showing up as dark spots. The exact position of the centre of concentration of material could be readily ascertained.  

Instead of moving as distinct spots, aromatic derivatives tended to give long streaks, despite the care taken in the preparation of the paper. It was found that upward development, instead of the downward development prescribed by Burton (87), partially overcame this streaking effect, although taking a little longer.
Preparation of Compounds for Pyrolysis.

6.1. \( \alpha \)-Cyanobenzyl benzoate.

The reaction of benzaldehyde and aqueous potassium cyanide produced mandelonitrile which on treatment with benzoyl chloride gave \( \alpha \)-cyanobenzyl benzoate (88). The ester was crystallised from ethanol, m.p. 58\(^\circ\)C (lit. 60\(^\circ\)C). Yield 68%.

6.2. \( \alpha \)-Cyanobenzyl acetate.

Mandelonitrile was prepared by the reaction of benzaldehyde and aqueous potassium cyanide. The product was acetylated with acetic anhydride giving \( \alpha \)-cyanobenzyl acetate (89). The ester was a yellow oil, b.p. 152\(^\circ\)/25 mm. (lit. 152\(^\circ\)/25 mm).

6.3. \( l \)-Cyanoethyl benzoate.

The reaction of aqueous potassium cyanide with acetaldehyde gave lactonitrile which on benzoylation yielded \( l \)-cyanoethyl benzoate (90). The ester was a colourless oil, b.p. 269–270\(^\circ\)C. Yield 65%.

6.4. \( \alpha : \alpha \)-Dicyanobenzyl benzoate.

This ester was prepared by the reaction of benzoyl chloride with aqueous potassium cyanide in the presence of a trace of alcohol. The reaction mixture was kept at -10\(^\circ\)C (91) for one hour, the ester then separating out. The ester
was crystallised from ethanol, m.p. 97°C (lit., 99°C) (Found: C, 73.1; H, 3.9; N, 10.9. Calc. for $\text{C}_16\text{H}^{10}\text{O}_2\text{N}_2$: C, 73.3; H, 3.8; N, 10.7%). Yield 20%.

6.5. $\alpha$-Bromobenzyl benzoate.

Equimolar quantities of benzaldehyde and benzoyl bromide were allowed to stand in a well-stoppered flask for 12 hours (42). The mixture solidified to $\alpha$-bromobenzyl benzoate and was crystallised from petroleum, m.p. 68-69°C (lit. 69-70°C). Yield was theoretical.

$\alpha$-Bromobenzyl benzoate was unstable in air, decomposing to give benzaldehyde and benzoyl bromide. It was found necessary to store the ester in petroleum and keep in a well-stoppered flask. Before use the ester was dried in vacuo and quickly put under air-free conditions.


Benzaldehyde was refluxed in the presence of phosphorus pentabromide for 2 hours (92) to give benzal bromide, b.p. 126°/23 mms.; 115°/15 mms. (lit., 156°/23 mms.; 105-107°/12 mms.). It is thought that the quoted figure of 156° is a mis-print for 126°. Yield 60%.

6.7. Benzoylbenzoin.

Benzoin was heated with benzoyl chloride for 15 minutes at 180°C and the whole allowed to solidify (93). The product
was crystallised from 70% ethanol, m.p. 124°C (lit., 124-
125°C) (Found: C, 80.2; H, 5.1. Calc. for C\textsubscript{21}H\textsubscript{16}O\textsubscript{3}: C, 79.8;
H, 5.1%). Yield 67%.

6.8. **Acetylbenzoin.**

Benzoin was added to a well-stirred mixture of acetic acid and acetic anhydride. A little concentrated sulphuric acid was added and the whole heated to 100°C for 20 minutes before being poured into excess cold water (94). The ester solidified out and was crystallised from 90% ethanol, m.p. 85°C. (lit., 83°C). (Found: C, 76.0; H, 5.8. Calc. for C\textsubscript{16}H\textsubscript{14}O\textsubscript{3}: C, 75.6; H, 5.5%). Yield 70%.

6.9. **Benzhydryl benzoate.**

A mixture of benzhydrol and benzoic acid was heated to 180°C, at which temperature water was evolved (45). After the evolution had ceased, the whole was cooled and excess of benzoic acid removed by sodium carbonate solution. The residue was crystallised from alcohol, m.p. 86°C (lit., 88°C). Yield 46%.

6.10. **Triphenylmethyl benzoate.**

Equimolar amounts of triphenylmethyl chloride and sodium benzoate in dry acetone were refluxed for 7 hours on a water bath (95). After filtering free from sodium chloride and unreacted sodium benzoate, the solution was concentrated.
The ester crystallised out and was recrystallised from ethyl acetate, m.p. 168°C (lit., 169°C) (Found: C, 85.8; H, 5.8. Calc. for $C_{26}H_{20}O_2$: C, 85.7; H, 5.5%). Yield 41%.

6.11. Methylene dibenzoate.

The diester was prepared by the action of benzoyl chloride on paraformaldehyde in the presence of zinc chloride (96). It was crystallised from ethanol, m.p. 99°C (lit., 99°C) (Found: C, 70.3; H, 4.9. Calc. for $C_{15}H_{12}O_4$: C, 70.3; H, 4.7%).


The diester was prepared (97) by heating ethylidene diacetate with benzoic anhydride and a trace of concentrated sulphuric acid at 100°C. It was crystallised from petroleum, m.p. 70°C (lit., 72°C) (Found: C, 70.0; H, 5.4. Calc. for $C_{16}H_{14}O_4$: C, 71.0; H, 5.2%). Yield 16%.


The pure anhydride was prepared by treatment of benzoic acid with acetic anhydride (98). It was crystallised from petroleum, m.p. 42.5°C (lit., 42.5°C). Yield 64%.


All the other compounds pyrolysed were obtained by purchase. The melting points of the solid compounds obtained by purchase were determined and compared with the
values quoted in the literature. All liquids are redistilled before use.
Experimental Details of Pyrolysis.

The experimental data for the pyrolysis are given separately in tables I-V.

7.1. Benzyl benzoate (I).

Pyrolysis 1.

The ester was heated for 29 hours at 300° C. The liquid pyrolysate yielded (i) 1.75g., b.p. 104-112° (toluene), (ii) 0.75g., b.p. 118-120° (a mixture of toluene and benzaldehyde), (iii) 1.8g., b.p. 76-80°/20mms. (benzaldehyde), (iv) 4.75g., b.p. 160-184°/20mms. (benzoic acid with a little benzaldehyde), (v) 30.0g., b.p. 184-194°/20mms. (unreacted ester with benzoic anhydride, colour test), (vi) 3.6g. high boiling tars.

Pyrolysis 2.

The pyrolysis of I in a flow reactor at 500° did not produce much breakdown. From 50.0g. of ester, the liquid pyrolysate yielded (i) 2.3g., b.p. 74-105° (benzene and toluene, i.r.), (ii) 1.3g., b.p. 80-110°/16mms. (benzaldehyde with a trace of benzoic acid), (iii) 41.8g., b.p. 170-204°/16 mms. (unreacted ester), (iv) 2.6g. high boiling tars.

Pyrolysis 3.

This was a repeat of pyrolysis 2 with temperature at 550° C. 50.0g. of ester yielded (i) 6.0g., b.p. 80-86° (benzene), (ii) 1.3g., b.p. 86-96° and (iii) 1.5g., b.p. 98-108° (both
fractions contained benzene and toluene) (iv) 5.0g., b.p. 108-120° (toluene and benzaldehyde), (v) 2.0g., b.p. 85-120°/22mms. (benzaldehyde) (vi) 5.25g., b.p. 140-170°/22mms. (diphenyl and a trace of benzoic acid), (vii) 9.5g., b.p. 170-200° C (unreacted ester and benzil and benzophenone, the last two being identified by paper chromatography of 2:4-DNPs.), (viii) 4.0g., b.p. 200-258°/22mms. (unreacted ester and trace of solid m.p. 209° C).

There was no evidence in pyrolysis 2 and 3 for the presence of benzoic anhydride. That benzoic anhydride decomposed under the experimental conditions was proved by a co-pyrolysis of benzyl benzoate and 1% of benzoic anhydride, no anhydride being detected in the pyrolysate.

7.2. α-Cyanobenzyl benzoate (II)

Pyrolysis 4.

A static pyrolysis of the ester gave (i) 6.5g., b.p. 42-44°/2mms. (benzaldehyde and benzonitrile) (ii) 4.5g., b.p. 120-160°/2mms. (benzonitrile, benzaldehyde and benzoic acid) (iii) 2.3g., b.p. 164-200°/2mms. (benzoic acid, benzil and unreacted ester), (iv) 3.5g., b.p. 200-250°/2mms. and (v) 1.8g., b.p. 165-200°/1mm. (benzil with a trace of ester), (vi) 6.0g., b.p. 200-236°/1mm. (high boiling tar with solid) (vii) 10.8g. high boiling tars.

Fraction (vi) was examined in detail. The solid was
recrystallised from alcohol m.p. 124.5°C. A mixed m.p. with benzoylbenzoin showed no depression. (Found; C, 80.4; H, 5.4. Calc. for C_{21}H_{16}O_{3}; C, 79.8; H, 5.1%). Alkaline hydrolysis gave benzoic and benzilic acids, the expected products from benzoylbenzoin. The solid, therefore, was benzoylbenzoin VII.

Hydrogen cyanide (9.6% of theory) was present in the pyrolysis gases. This was removed by an alkaline trap and estimated volumetrically against silver nitrate solution.

**Pyrolysis 5.**

Pyrolysis of ester II in a flow reactor at 420°C gave (i) 0.89g., b.p. 22-50° (hydrogen cyanide), (ii) 12.0g., 55-85°/5mms. (iii) 3.0g., b.p. 85-122°/5mms. and (iv) 12.0g., b.p. 122-155°/5mms. (these three fractions consisted of mixtures of benzaldehyde, benzonitrile and benzoic acid). (v) 11.5g., b.p. 160-180°/5mms. (benzil and recovered ester), (vi) 10.0g., b.p. 160-184°/2.5mms. (unreacted ester and a trace of benzil), (vii) 11.5g., b.p. 184-205°/2.5mms. (unchanged ester and trans-\(\alpha:\alpha^1\)-dicyanostilbene). The latter was isolated as needles from methanol, m.p. 160°C, lit., 160°C (99). (Found; C, 83.6; H, 4.2; N, 12.2. Calc. for C_{16}H_{10}N_{2}; C, 83.5; H, 4.4; N, 12.2%). Coe et al. (100) have shown that this compound is the trans form of the substituted stilbene.
The total hydrogen cyanide evolved from pyrolysis gases and fraction (i) was 11.3%.

**Pyrolysis 6.**

Pyrolysis at 500°C of ester II gave (i) 10.0g., b.p. 80-81° (benzene), (ii) 12.7g., b.p. 66-100°/2.5mms. (benzaldehyde and benzonitrile), (iii) 6.8g., b.p. 100-158°/2.5mms. (benzaldehyde, benzonitrile, benzoic acid and trace of ester. (iv) 16.0g., 162-195°/5mms. (benzoic acid trace of ester, mainly tars), (v) 9.3g., b.p. 195-250°/5mms. (high boiling oils). 15.0g. tars.

**Pyrolysis 7.**

In previous pyrolysis 4-6, there was no evidence for the presence of benzoic anhydride which would be produced by a disproportionation D reaction. A small amount of the ester was heated for 24 hours at 160°C. There was little charring and practically no decomposition but the presence of benzoic anhydride was established by the colour test.

7.3. Benzil (XIV).

**Pyrolysis 8.**

The α-diketone benzil was examined to facilitate the interpretation of the results from II. At 500°C it gave (i) 3.0g., b.p. 65-85° (benzene), (ii) 7.0g., b.p. 120-150°/3mms. (benzaldehyde and diphenyl), (iii) 7.0g., b.p. 150-180°/3mms. 
(benzophenone and a trace of diphenyl), (iv) 36.0g., b.p. 194-198°/3mms. (benzil). High boiling tars 33.0g.

7.4. \( \alpha \)-Cyanobenzyl acetate (III)

Pyrolysis 9

The liquid pyrolysate gave (i) 3.25g., b.p. 76-86°, (acetonitrile with a trace of benzene, i.r.), (ii) 2.0g., b.p. 88-110° (acetonitrile and acetic acid), (iii) 1.0g., b.p. 110-124° (acetic acid and acetic anhydride, the latter by the colour test), (iv) 3.5g., b.p. 180-200° (benzaldehyde), (v) 5.0g., b.p. 70-100°/3mms. and (vi) 6.7g., b.p. 100-130°/3mms. (benzaldehyde, acetylbenzoyl, acetophenone and benzonitrile; analysis confirmed by i.r.), (vii) 4.0g., b.p. 130-160°/3mms. (unchanged ester). High boiling tars, 12.6g.

10.4% of hydrogen cyanide was obtained in the alkali trap.

Pyrolysis 10.

The pyrolysis of ester III was repeated at 500°C to determine whether keten was evolved during pyrolysis. The aniline trap was examined and found to contain acetanilide, m.p. 111°C, mixed m.p. 114°C. This showed therefore, that keten was evolved during pyrolysis.
7.5. **Acetylbenzoyl (XV)**

Pyrolysis 11.

Pyrolysis of acetylbenzoyl at 500°C shows that the diketone is the source of the acetophenone obtained from the pyrolysate of ester III. 300 m.g. of diketone in reactor 6 at 500°C gave acetophenone and unreacted XV (i.r. and paper chromatography). There was no evidence for keten or benzaldehyde.

7.6. **1-Cyanoethyl benzoate (IV).**

Pyrolysis 12.

The ester on pyrolysis gave (i) 8.25 g., b.p. 64-74°C (acrylonitrile and benzene, i.r.), (ii) 1.0 g., b.p. 40-44°C/4 mms. (benzonitrile), (iii) 0.25 g., b.p. 60-70°C/4 mms. (benzonitrile and benzoic acid), (iv) 4.0 g., b.p. 88-140°C/4 mms. (benzoic acid) (v) 5.25 g., b.p. 140-180°C/4 mms. (benzoic acid and carbonyl compounds; chromatography indicates that the latter was a mixture of acetylbenzoyl and acetophenone).

The pyrolysis gases contained carbon dioxide, carbon monoxide, methane and acetylene (i.r.). The alkali trap yielded 0.3% of hydrogen cyanide.

7.7. **Acrylonitrile (XVI)**

Pyrolysis 13.

A series of tests was carried out between 500°C and 650°C. The acrylonitrile was found to be very thermostable. At
650°C, 20g. of nitrile yielded 17.3g. unchanged material and 2.0g high boiling tars. 0.2% of hydrogen cyanide was removed from the pyrolysis gas which consisted of acetylene (i.r.) and displaced nitrogen.

7.8. α:α-Dicyanobenzyl benzoate (V)

Pyrolysis 14.

30.0g. molten ester was fed into the flow reactor at 500°C. The liquid pyrolysate contained (i) hydrogen cyanide (trace), b.p. 23–30°, (ii) 1.25g., b.p. 78–80° (benzene), (iii) 1.25g., b.p. 180–200° and (iv) 0.25g., b.p. 70–140°/10mms. (benzonitrile with a trace of benzoic acid), (v) 4.0g., b.p. 140–170°/10mms. (vi) 2.0g., b.p. 180–210°/10mms. High boiling tars 8.25g.

Fraction (v) contained benzonitrile, benzoic acid and diphenylmalononitrile. The latter compound was isolated from aqueous methanol or ethanol as colourless needles, m.p. 87.5°C. It was insoluble in water and soluble in methanol, ethanol, acetone, ether, benzene and acetic acid [Found: C, 82.5; H, 4.7; N, 12.8%; M.W. (Rast camphor method) 217. Calc. for C_{15}H_{10}N_{2}: C, 82.6; H, 4.6; N, 12.8%; M.W. 218].

Acid hydrolysis of the nitrile for 48 hours yielded not the readily decarboxylated diphenylmalonic acid (I01) but its breakdown product diphenylacetic acid, m.p. and mixed m.p. 147°C [Found: C, 79.2; H, 5.8. Calc. for C_{14}H_{12}O_{2}: C, 79.2; H, 5.8%].
Fraction (vi) also contained a little diphenylmalononitrile and high boiling tars.

11.0% of hydrogen cyanide was removed from the gaseous pyrolysate.

7.9. \( \alpha \)-Bromobenzyl benzoate (VI)

Pyrolysis 15.

The ester VI was most unstable, decomposing at 225° on heating for 3 hours to give (i) 18.3g., b.p. 89-109°/10mms. (benzaldehyde, benzoyl bromide with traces of bromobenzene, benzyl bromide and benzel bromide, i.r. spectrum; benzoic acid was also present), (ii) 3.5g., b.p. 109-120°/10mms. (benzoyl bromide, benzal bromide, benzoic acid and a trace of benzoic anhydride i.r.), (iii) 10.3g., b.p. 194-198°/10mms. (benzoic anhydride, benzoyl bromide and benzal bromide, i.r.), (iv) 4.8g., high boiling tars.

Fraction (iii) containing a little solid which was crystallised from glacial acetic acid. It was found to be trans.-\( \alpha : \alpha \)\(^{1}\)-dibromostilbene m.p. 205°C, lit., 206°C(102). The filtrate contained no benzaldehyde (i.r.). The presence of benzal bromide was confirmed by its hydrolysis to benzaldehyde and the formation of the 2:4-DNP.

2.3% hydrogen bromide was removed from the pyrolysis gases.
Pyrolysis 16.

The ester in a flow reactor yielded (i) 7.5g., b.p. 76-86° (benzene), (ii) 10.3g., b.p. 54-100°/12mms. (benzoyl bromide and bromobenzene, i.r.), (iii) 1.0g., b.p. 124-144°/7mms. (benzoic acid and a trace of benzoyl bromide), (iv) 5.3g., b.p. 185-200°/7mms. (trans-α:α'-dibromostilbene, m.p. 204°C, mixed m.p. 206°C; also benzoic anhydride, benzil and benzophenone, the last two being identified by i.r. and confirmed by paper chromatography of their 2:4-DNPs).

Owing to possible ambiguities in purely chemical analysis, i.r. was used to a large extent in identifying the products of pyrolyses 15 and 16.

7.6% hydrogen bromide was removed from the gaseous pyrolysate.

7.10. Benzal bromide XVII

Pyrolysis 17.

Benzal bromide, a by-product of pyrolyses 15 and 16, was pyrolysed at 425°C. It gave (i) 0.8g., b.p. 90-125°/8 mms. (benzal bromide, confirmed by its conversion to benzaldehyde; no evidence for bromobenzene), (ii) 5.8g., b.p. 125-160°/8mms. (trans-α:α'-dibromostilbene, crystallised from glacial acetic acid, m.p. 208°C, lit. 206°C (102) [Found; C, 49.11; H, 3.2; Br, 47.3. Calc. for C_{14}H_{10}Br_{2}; C, 49.4; H, 3.5; Br, 47.0%]), (iii) 3.3g., b.p. 160-200°/8mms.
(trans.- $\alpha: \alpha^1$-dibromostilbene and tars). 0.5g. of high boiling tars were also obtained.

The gaseous pyrolysate contained 88.5% hydrogen bromide, the residual gas being displaced nitrogen.

7.11. $\alpha$-Benzoylbenzyl benzoate (VII) Benzoylbenzoin.

Pyrolysis 18.

Benzoylbenzoin, $\alpha$-benzoylbenzyl benzoate (VII), pyrolysed in a flow reactor at 500°C, gave (i) 3.0g., 78-84° (benzene), (ii) 3.5g., b.p. 130-150°/15mms. (benzaldehyde, benzoic acid and diphenyl), (iii) 1.5g., b.p. 150-180°/15mms. (benzoic acid, benzaldehyde and a trace of benzil), (iv) 5.0g., b.p. 180-210°/15mms. (benzil with trace of benzoic acid), (v) 2.8g., b.p. 210-250°/15mms. (benzil and tars). The residual tar was distilled in vacuo to yield (vi) 2.0g., b.p. 220-250°/1.5mms. (unchanged ester and tar), (vii) 1.0g., b.p. 250-280°/1.5mms. (mainly tar but with a trace of unchanged ester). Weight of carbonaceous residue 2.5g.

7.12. $\alpha$-Benzoylbenzyl Acetate (VIII) Acetylbenzoin.

Pyrolysis 19.

Acetylbenzoin, $\alpha$-benzoylbenzyl acetate (VIII), on pyrolysis at 480°C, gave (i) 1.0g., b.p. 90-120° (acetic acid, i.r.), (ii) 0.3g., b.p. 80-100°/2mms. (benzaldehyde and acetylbenzoyl, i.r.), (iii) 1.5g., b.p. 115-150°/2mms. (benzaldehyde, acetylbenzoyl and unchanged ester), (iv) 7.3g., b.p. 160-180°/2mms. (unchanged ester), (v) 5.0g., 180-198°/
2 mms. (tarry residue; not examined). Carbonaceous residue 2.5 g.

7.13. Benzhydryl benzoate (IX)

Pyrolysis 20

Pyrolysis of the ester in a flow reactor at 500°C gave
(i) 0.7 g., b.p. 78-81°C (benzene), (ii) 8.0 g., b.p. 106-130°C/
2 mms. (benzoic acid, benzophenone and diphenylmethane), (iii)
2.0 g., b.p. 130-148°C/2 mms. (benzophenone and diphenylmethane),
(iv) 6.0 g., b.p. 194-215°C/2 mms. Weight of residual tar was
4.3 g.

Fraction (iv) consisted of tar and a solid. The solid
was extracted with ether. The ether-insoluble residue was
tetraphenylethane, crystallised as needles from glacial
acetic acid, m.p. 210°C, lit., 211°C (103) [Found: C, 93.3;
H, 6.9. Calc. for C_{26}H_{22}: C, 93.4; H, 6.6%]. The mother
liquor from the above crystallisation on concentration gave
a solid which on crystallisation from methanol gave fine
white crystals m.p. 90-91°C. It was thought that this
might be the original ester (Found: C, 83.4; H, 6.0. Calc.
for C_{20}H_{16}O_{2}: C, 83.3; H, 5.6%). A mixed m.p. was depressed.
There was little similarity between the i.r. spectra. There
was insufficient material for a complete chemical analysis.

The ether-soluble fraction consisted of a tar and a
little solid which on crystallisation from methanol had a
m.p. 89-90°C. A mixed m.p. with the original ester was depressed.

There was no evidence for the presence of benzoic anhydride.

**Pyrolysis 21.**

This experiment was a repeat of pyrolysis 20 but done at a lower temperature (425°C). The liquid pyrolysate gave (i) 5.0g., b.p. 88-120°/2mms. (diphenylmethane, benzophenone and benzoic acid), (ii) 2.0g., b.p. 120-164°/2mms. (diphenylmethane, benzophenone and benzoic acid) (iii) 12.2g., b.p. 164-202°C (diphenylmethane, benzophenone, benzoic acid, tetraphenylethene and unidentified solid m.p. 89-90°C). Weight of residual tar 3.3g.

**Pyrolysis 22.**

There was no evidence for benzoic anhydride from pyrolysis 20 and 21. The ester, therefore, was heated for two hours at 200°C. Benzoic anhydride was detected by the colour test.

**7.14. Triphenylmethyl benzoate (X)**

**Pyrolysis 23.**

The pyrolysate of ester X gave on fractional distillation (i) trace of benzene, (ii) 2.0g., b.p. 145-162°/1.5mms. (benzoic acid and triphenylmethane), (iii) 5.0g.,
b.p. 162-192°/1.5mms. (benzoic acid, triphenylmethane and
tetraphenylmethane), (iv) 2.5g., b.p. 260-280°/1.5mms.
(mainly tar but containing traces of benzoic acid and
triphenylmethane). Weight of residual tar 2.0g.

Benzoic anhydride was identified in fractions (ii) and
(iii) by the colour test. The hydrocarbons in fraction (iii)
were separated by ether extraction. The residual solid was
tetraphenylmethane, crystallised from benzene, m.p. 282°C,
lit. 282° (104) [Found: C, 93.4; H, 6.6. Calc. for C_{25}H_{20}:
C, 93.8; H, 6.2%]. The ether extract was washed with
sodium carbonate solution to remove benzoic acid and the
ether evaporated off leaving a solid. This solid was
triphenylmethane, crystallised as white plates from methanol,
for C_{19}H_{16}: C, 93.4; H, 6.6%].

Carbonyl compounds were not detected in the pyrolysate.

Pyrolysis 24.

This was a repeat of pyrolysis 23, but in a static
system at 225°C instead of a flow system. The fractions
obtained were, (i) 3.3g., b.p. 110-140°/2mms. (triphenyl-
methane and benzoic acid), (ii) 5.5g., b.p. 184-215°/2mms.
and (iii) 6.3g., b.p. 215-245°/2mms., (iv) 1.7g., b.p.
245-255°/2mms. Weight of residual tar was 3.2g.

Fractions (ii) and (iii) were extracted with ether and
washed with sodium carbonate solution to remove benzoic acid. The ethereal extract was concentrated to produce a solid which on crystallisation from benzene/petroleum had a m.p. 169°C. It was at first thought that this was recovered original ester m.p. 168°C (Found: C, 86.1; H, 5.9. Calc. for C_{26}H_{20}O_{2}; C, 85.7; H, 5.5%). However a mixed m.p. was depressed by ca. 10°C. To eliminate any personal error the m.p. and mixed m.p. were checked by an independent worker who obtained concordant results. Differences in crystalline forms could arise from the purification of the materials from different solvents. To obviate this, the unknown and the original ester were crystallised from the same solvent (ethyl acetate), but again a mixed m.p. was depressed. The i.r. spectra (Figure 6) of the unknown and the original ester were, similar in many respects. An alkaline hydrolysis for 24 hours gave benzoic acid and triphenylcarbinol, products expected from ester X. It is tentitively concluded that this solid, m.p. 169°C, is an isomer of the original triphenylmethyl benzoate. A possible structure for this isomer has been discussed previously in section 3.9.

7.15. **Methyl benzoate (XI)**

**Pyrolysis 25.**

An attempted pyrolysis of methyl benzoate in a flow reactor at 500°C produced no breakdown whatsoever. No gases
were evolved and no breakdown products detected in the pyrolysate. Indeed, the refractive indices of the original ester and the pyrolysate remained the same.

7.16. Methylene dibenzoate (XII)

Pyrolysis 26.

The pyrolysate was extracted with ether. The insoluble residue was polyoxymethylene (yielding formaldehyde on heating). The ether extract on distillation yielded benzoic acid (b.p. 120-138°/10mms.) and benzoic anhydride (b.p. 192-198°/6mms., m.p. 42.5°C).

Formaldehyde was removed as a 2:4-DNP from the gaseous pyrolysate by passing through 2:4-dinitrophenylhydrazine solution.

Pyrolysis 27.

Distillation of the pyrolysate gave (i) 10.25g., b.p. 78-82° (benzene), (ii) 2.25g., b.p. 60-87°/6mms. (diphenyl, benzaldehyde and a trace of benzoic acid), (iii) 2.5g., b.p. 87-120°/6mms. (diphenyl, benzoic acid and a trace of benzoic anhydride), (iv) 12.0g., b.p. 148-164°/6mms. (benzoic anhydride and a trace of benzophenone).

The Drikold trap contained ca. 2.0g. of benzene and ca. 1.5g. polyoxymethylene. The exit gases contained formaldehyde identified in the usual way.
7.17. Ethylidene dibenzoate (XIII)

Pyrolysis 28.

The liquid pyrolysate gave (i) 0.2g., b.p. 70-120°/2mms. (vinyl benzoate, benzaldehyde, acetophenone and benzoic acid; the first compound was identified by i.r., the carbonyl compounds by chromatography), (ii) 1.3g., b.p. 120-170°/2mms., and (iii) 3.5g., b.p. 170-180°/2mms. (benzoic acid, benzoic anhydride and acetophenone).

Keten and acetic anhydride, possible products arising from a secondary B² scission, were not detected.

The pyrolysis gases contained acetaldehyde vapour.

7.18. Benzoic anhydride (XVIII)

Pyrolysis 29.

The pyrolysate on distillation gave (i) 1.0g., b.p. 78-80°C (benzene), (ii) 6.0g., b.p. 128-160°/2mms. (diphenyl, benzoic acid and benzoic anhydride, trace of benzaldehyde), (iii) 2.5g., b.p. 160-182°/2mms. (benzoic acid, diphenyl and benzoic anhydride), (iv) 37.5g., 197-204°/2mms. (benzoic acid and unchanged benzoic anhydride), (v) 8.0g., b.p. 204-209°/2mms. (recovered benzoic anhydride). Weight of tar 7.0g.

Pyrolysis 30.

This was a repeat of pyrolysis 29. The increase in temperature caused a decrease in the CO:CO₂ ratio.
Pyrolysis 31.

With the further increase in temperature, the extent of decomposition was increased still further. The pyrolysate gave (i) 7.5g., b.p. 78-82° (benzene), (ii) 6.5g., b.p. 100-130°/10mms. (diphenyl, benzaldehyde and benzoic acid), (iii) 4.25g., b.p. 130-160°/10mms. (benzoic acid and a trace of diphenyl), (iv) 32.5g., b.p. 160-170°/10mms. (benzoic anhydride and a trace of benzophenone), (v) 2.0g., b.p. 170-210°/10mms. (benzoic anhydride and tar). 5.75g. of high boiling tars.

The DriKold trap contained 0.8g. benzene.

Pyrolysis 32.

A co-pyrolysis of benzoic anhydride (22.3g.) and "AnalaR" carbon tetrachloride (23.2g.) at 550°C (rate of addition 0.25g/min.) contact time 119 secs.) gave a gaseous pyrosate (10.0 l) containing 51.5% displaced nitrogen: the nitrogen-free fraction consisted of 41.7% carbon dioxide, 32.8% carbon monoxide and 25.5% of hydrogen chloride. The liquid pyrolysate (23.0g.) gave (i) 2.5g., b.p. 97-115°C, (ii) 2.0g., b.p. 115-130°, (iii) 2.5g., b.p. 130-146°, (iv) 3.0g., b.p. 54-74°/4mms., (v) 1.0g., b.p. 75-100°/4mms., (vi) 3.5g., b.p. 100-150°/4mms. High boiling tars 8.25g. Fractions (i)-(iii) consisted of carbon tetrachloride and chlorobenzene: (iv) was chlorobenzene (characterised as
116.

2:4-dinitrochlorobenzene, m.p. 52°C), (v) was benzoic anhydride with a trace of chlorobenzene, (vi) was hexachlorobenzene, m.p. and mixed m.p. 227°C.
FIGURE 5.

INFRARED SPECTRA

ABSORPTION (cm⁻¹)

INFRARED SPECTRA
**FIGURE 6.**

**INFRARED SPECTRA**

- **BENZHYDRYL BENZOATE**
- **SOLID M.R 89°C FROM BENZHYDRYL BENZOATE**
- **TRIPHENYL METHYL BENZOATE**
- **SOLID M.R. 169°C FROM TRIPHENYL METHYL BENZOATE**

Absorption (cm⁻¹)
### Table I.

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<td>II</td>
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<td>50.0</td>
<td>50.0</td>
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For the list of compounds pyrolysed, see section 2.2

*Carbon dioxide mostly removed in alkali trap.*
### Table II.

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<td>%</td>
<td>%*</td>
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* Gases examined by i.r.
Table III.

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<th>X</th>
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| **$B^2$-type scission** |   |    |     |    |   |    |      |       |    |   |       |
| $\text{RCOX} + R^{1}\text{COR}^{11}$ | X | X | X | X | X | X | X(2) | X(2)  | 0  | 0 | 0     |

| **Decarboxylation $C^2$** |   |    |     |    |   |    |      |       |    |   |       |
| $\text{CO}_2 + \text{RCR}^{1}\text{R}^{11}X$ | 0 | 0 | 0 | 0 | 0 | X  | 0    | 0     | 0  | 0 | X     |

| **Disproportionation $D$** |   |    |     |    |   |    |      |       |    |   |       |
| $\frac{1}{2}(\text{RCO}_2)_2O + \frac{1}{2}[\text{ether}]$ | X | X | X | 0 | 0 | X  | 0    | 0     | 0  | X | X     |

| **$\alpha$-diketone reaction $E$** |   |    |     |    |   |    |      |       |    |   |       |
| $\alpha$-diketone + HX | X | X | X | X | 0 | X | (2)  | (2)   | 0  | 0 | 0     |
(1) Products of possible $A^0$ scission best explained by the secondary decomposition of disproportionation $D$ products.

(2) $\alpha$-Diketone formed by acyl-oxygen scission $E^2$ although an $E$ type scission is a formal possibility.

(3) Methyl benzoate is thermostable at 500°C.
APPENDIX I

Notes on ionisation of organic compounds

Aromatic acylation, as with nitration and chlorination processes, is a form of electrophilic substitution in which the substituting agent is simply the introduced group in a free cationic form. A typical acylating agent is acetyl chloride which has been shown by MacKenzie and Winter (106) to be ionisable and that acetylation is carried out by the free acetyl cation MeCO⁺. This work has been extended by Burton and Praill (70) using a modified technique. These authors found that when acetyl chloride and silver perchlorate are allowed to interact in nitromethane, a precipitate of silver chloride is formed and that the solution contains a powerful acetylating agent capable of almost quantitative conversion of anisole to p-methoxyacetophenone. The acetylating agent can only have been the acetyl cation. In the liquid state, therefore, acetyl chloride can exist as acetyl and chloride ions.

\[ \text{MeCOCl} \quad \rightarrow \quad \text{MeCO}^+ + \text{Cl}^- \]

Similar work by the present writer has been carried out and these give more examples of ionisation.

Silver nitrate is extremely soluble in benzonitrile, no precipitate of silver cyanide being obtained. The addition of benzoyl chloride, bromide or cyanide to this
FIGURE 7.

IONISATION DETECTOR TUBE

GLASS SHEATHES

TUNGSTEN WIRES

MOLYBDENUM FOIL

PYREX TUBE

+VE

-VE
solution precipitates the appropriate silver salt. This shows that these three compounds ionise in the liquid state. It also supports the idea that benzoyl bromide ionises as shown in 4.1.

**APPENDIX II**

The use of an ionisation detector

Benzoyl bromide was formed in the pyrolysis of α-bromobenzyl benzoate. Benzoyl cyanide, although not isolated, was an intermediate in the pyrolysis of α-cyanobenzyl benzoate. Since both these compounds in solution have been shown to be capable of ionisation (Appendix I), it is possible that ions are also present during the pyrolysis of the respective esters. An attempt has, therefore, been made to detect such ions in the vaporised ester during its pyrolysis.

The apparatus used was the standard flow reactor described previously. The pyrolysis tube, however, was slightly modified; see Figure 7. The tube used was 75 cms. in length, 4.3 cms. diameter. In the centre of the tube was a coaxial cylinder of molybdenum foil 9 cms. long x 4.2 cms. diameter x 0.13 mm. thick. A tungsten wire
sheathed in pyrex tubing was led from the foil along the wall of the tube and out at the top. A second tungsten wire was held centrally within the metal foil. This wire was sheathed entirely in glass, except that portion which lay within the foil, sealed into the bottom of the tube and led out at the top. The wires were connected to an electrical circuit with a 2.5 kV supply, and the whole apparatus earthed. Current between the cylinder and wire was measured on a sensitive milliammeter.

The apparatus was tested under nitrogen at 400°C. A steady current of 10 μA was obtained. The temperature was increased further but this only resulted in an increase in current. This was a "stray" current and could not be eliminated. The operating temperature was kept at 380-400°C with a stray current of 10 μA.

If any charged particles were present when the pyrolysis vapours were passed through the tube, these would be detected in the electrostatic field by a deflection on the milliammeter scale.

α-Bromo- and α-cyanobenzyl benzoates were pyrolysed in the usual way and deflections were obtained on the milliammeter. The former ester gave a deflection, allowing for the stray current, of ca. 70 μA; the latter, ca. 25 μA. Triphenylmethyl benzoate gave a slight deflection. Benzene, a
compound expected to remain non-polar under the conditions used, was run as a blank to determine whether the foregoing effects were a result of conductance across the vapours. No deflection was obtained and, therefore, there was no conductance. Benzoic acid and benzyl benzoate likewise gave no deflections.

These experiments are to be regarded as merely preliminary, and as an indication of further possible lines of study. Nevertheless, even the few results obtained indicate that charged particles are present during pyrolysis of certain esters. A fuller investigation is, however, necessary to confirm these results and to determine which ions are present. The stray current will need to be eliminated to enable the apparatus to be worked at higher temperatures and a sensitive galvanometer incorporated into the circuit. These refinements are essential if the apparatus is to be used at temperatures at which most compounds decompose (ca. 450-550°C).
ATTEMPTED PREPARATION OF POLY (METHYLENE TEREPHTHALATE)

Two attempts have been made to prepare poly (methylene terephthalate).

\((-\text{OCH}_2\text{OCOC}_6\text{H}_5\text{CO-})_n\)

These experiments were carried out to determine whether this polyester was capable of existence and, if so, to compare its properties with those of poly (ethylene terephthalate).

(i) 1 mol. of sodium terephthalate and 2 mol. of methylene bromide were heated in the presence of a trace of triethylamine for five days at 100\(^\circ\)C. No reaction took place, the reactants being recovered.

(ii) By analogy with the preparation of methylene dibenzoate (97) (see section 6.11.), 1 mol. of terephthaloyl chloride and 2 mol. of paraformaldehyde were heated under reflux for two days in the presence of zinc chloride. Apart from some charring, no reaction took place.
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