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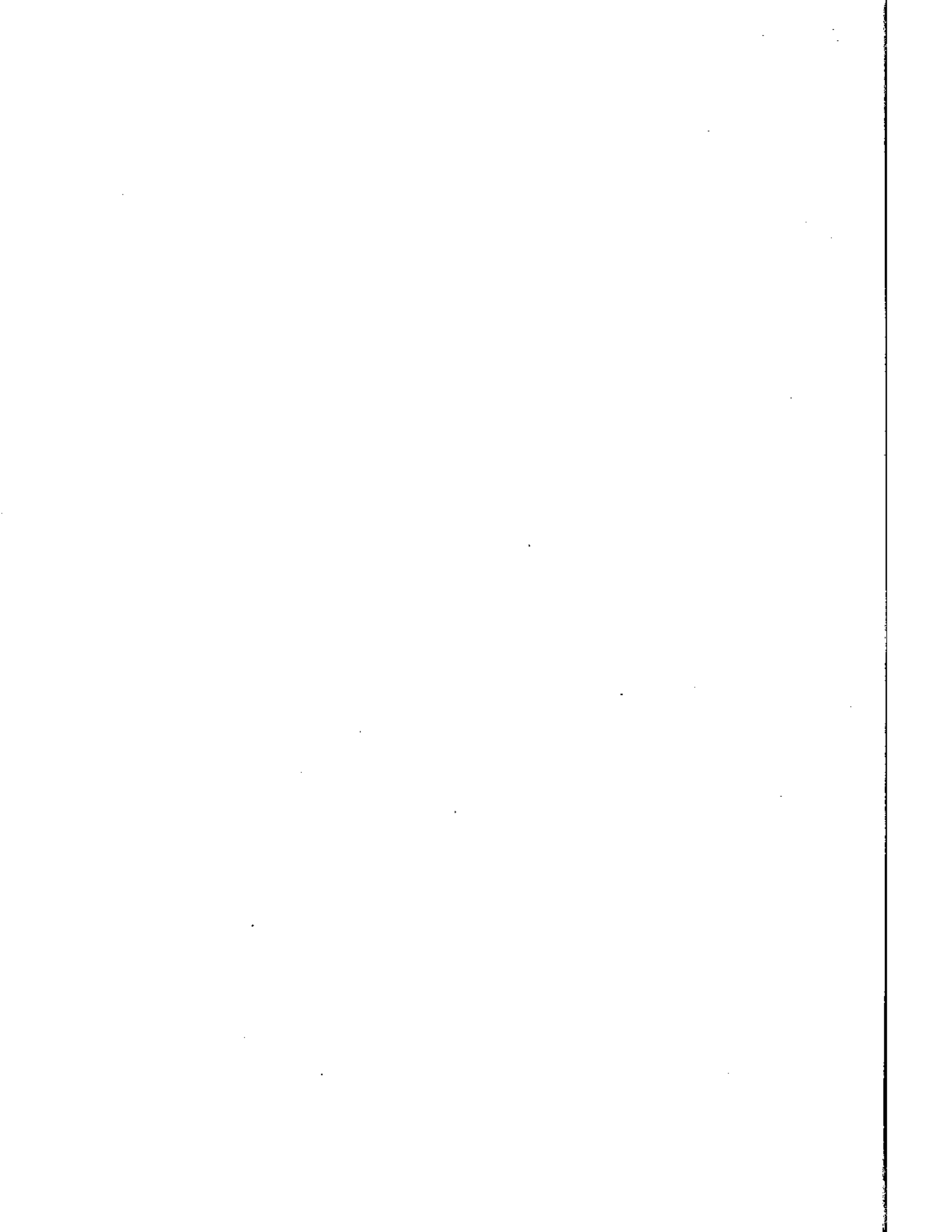
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The Thermal Decomposition of Poly(ethylene Terephthalate)

A Thesis

Submitted to the University of Glasgow in
fulfilment of the requirements for the degree
of Doctor of Philosophy.

by

H.V.R. Iengar, M.Sc.(Delhi).

Preface

The work embodied in this thesis was carried out in the Department of Technical Chemistry, The Royal Technical College, Glasgow, under the direction of Professor P.D. Ritchie, PhD., F.R.I.C., F.R.S.E. I am deeply grateful to Assam Oil Company, Ltd., for the award of a maintenance scholarship during the period of work. I thank all my colleagues for their help in many ways. I should also like to thank the staff of the Departments of Technical Chemistry, and Chemistry, of the College for their assistance at various times. Finally, I am most grateful to Professor Ritchie for the encouragement, help, and guidance he has given me at all times.

3rd Sept. 1956.

H.V.R. Iengar.
H.V.R. Iengar.

Publications

Part of the material in this thesis has been accepted for publication in the Journal of the Chemical Society in a paper entitled :- "Studies in Pyrolysis. Part VII. Model Systems for the Pyrolysis of Poly(ethylene Terephthalate): 2:2'-Dibenzoyloxydiethyl Ether, 2-Benzoyloxyethyl Vinyl Ether, and certain related Vinyl Ethers". (By M.V.R. Iengar and P.D. Ritchie).

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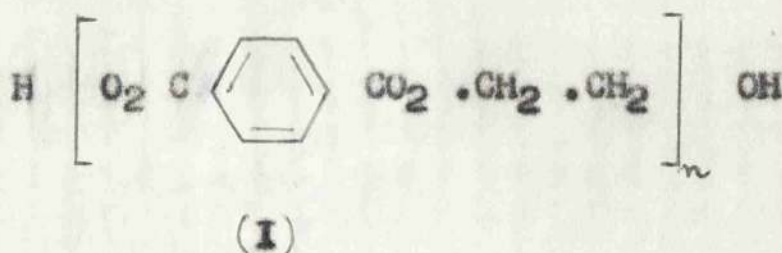
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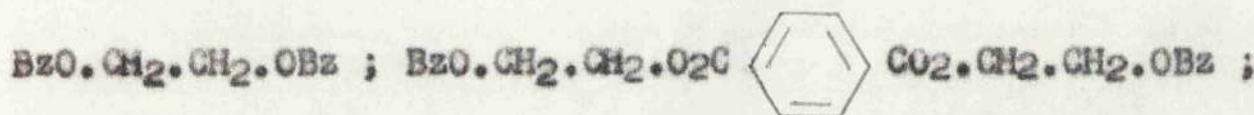
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Introduction.

The thermal stability of the polyester fibre poly(ethylene terephthalate) (I), or Terylene, is of considerable technological importance. The thermal decomposition of the polymer has been studied, but the precise mechanism of breakdown remains obscure. Pohl (1) found that the polyester undergoes random main-chain scission, with progressive reduction in molecular weight. He detected acetaldehyde, water, and carbon dioxide, as well as carboxyl and anhydride groups in the pyrolysate. Marshall and Todd (2) studied the kinetics of degradation at ca. 280-320° by following changes in melt-viscosity. They also deduced the occurrence of random chain scission. They detected terephthalic acid, a solid S (not positively identified), acetaldehyde, carbon monoxide, and carbon dioxide, and suggested that the decomposition is essentially free-radical in character. Gilchrist (3) noted the presence of high-boiling carbonyl compounds in the degraded polyester. Since the pyrolysate is obviously very complex, it therefore appeared desirable to make a full qualitative identification of the decomposition products of the polyester.

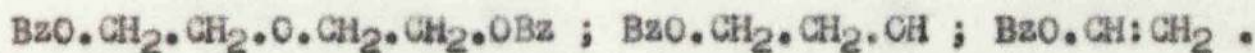


Difficulties encountered in preliminary experiments with poly(ethylene terephthalate) (I) itself, led to a study of the pyrolysis of the following model compounds, representing segments of the polyester chain:-



(II)

(III)



(IV)

(V)

(VI)

The reasons for selecting (II), (III), and (V) are evident from formula (I). (IV) represents the known incorporation of occasional ether linkages (e.g. diethylene glycol units) into the original chain during polycondensation. Vinyl benzoate (VI) was selected because ethylene dibenzoate (II) is known (4) to decompose into benzoic acid and vinyl benzoate. Owing to some ambiguous results obtained on pyrolysis of 2-benzoyloxyethyl terephthalate (III), it was found necessary to examine the behaviour of the chlorine-labelled model (VII), shown below:



(VII)

The pyrolysis of the models (II), (III), and (VI) has been described by Allan, Forman and Ritchie,^(5,6). The pyrolysis of (IV), (V), (VII), several other related compounds, and finally of the polyester (I) is described in this thesis (Chapter II). Owing to the complex results obtained in the pyrolysis of esters, and of ethers (e.g. IV), a short survey is first made of their known behaviour on pyrolysis.

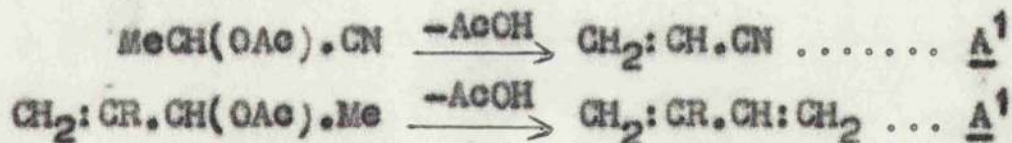
Chapter 1

1.1 The Pyrolysis of Esters.

The pyrolysis of an ester can give rise to a number of products as a result of (i) competitive primary decomposition reactions, and (ii) secondary and tertiary decomposition reactions.

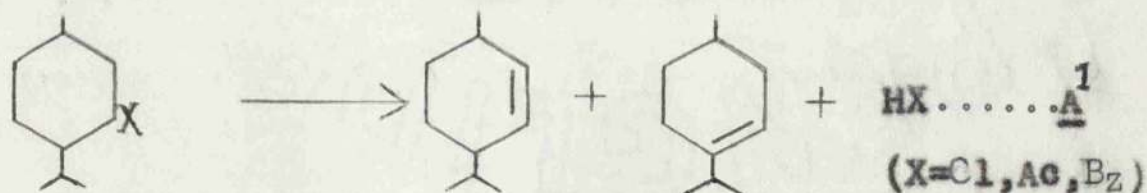
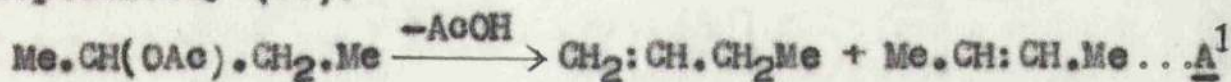
1.2. Alkyl-oxygen scission.

This takes place when a β -hydrogen atom is present, and yields an acid and olefin, thus constituting a formal reversal of the known catalysed addition of acids to olefins to form carboxylic esters. The symbols \underline{A}^1 and \underline{A}^2 have been introduced (5) to distinguish between alkyl-oxygen and alkenyl-oxygen scissions respectively. The \underline{A}^1 reaction is common, and applied very often for the synthesis of olefins, e.g. the synthesis of acrylonitrile (7) and of 2-alkyl-1,3-butadienes (8) :

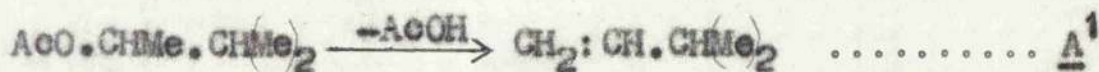


The elimination of acid from an ester of the type >CH.CH(OAc).CH< (where the two β -carbons both carry hydrogen atoms but are differently substituted) can formally give two olefins depending on the direction in which the elimination takes place. There are two rules governing

elimination reactions, and they lead to opposite predictions. The Hoffman rule (9) states that in the decomposition of a quaternary ammonium hydroxide, the major olefin will be the one having the smallest number of attached alkyl groups. According to the Saytzeff rule, (9) when an alkyl halide is converted to an olefin, the main product will be the most highly branched olefin. A mixture of products is usually obtained, with one predominating. Thus, Houtman, van Steenis, and Heertjes (10) found that the pyrolysis of sec.-butyl acetate yielded a mixture of but-1-ene and but-2-ene. Similarly, the pyrolysis of (-)-menthyl esters has been found to give (+)-p-3-menthene and (+)-p-2-menthene in the ratio of 2:1 respectively (11).

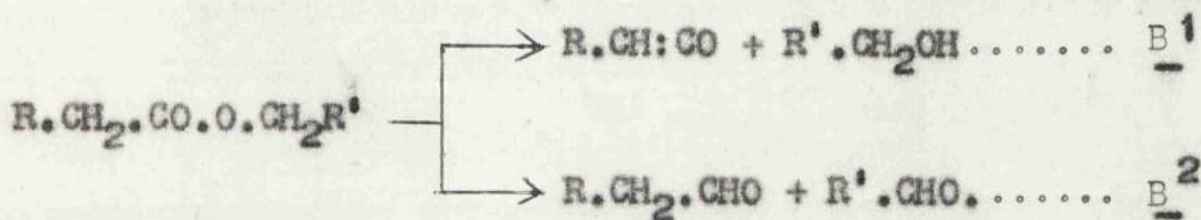


These results show that the Saytzeff rule is usually obeyed. Bailey and King (12), however, pyrolysed a number of acetates under conditions such that no carbonisation took place, and found that in each case only one olefin was formed. Their results indicated that while the corresponding alcohols were dehydrated according to the Saytzeff rule, the decomposition of the esters followed the Hoffmann rule, e.g. :

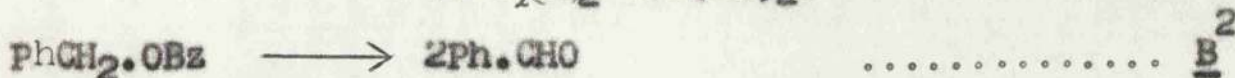
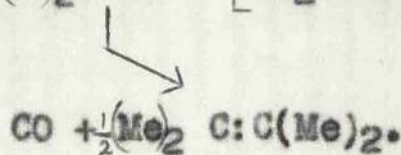
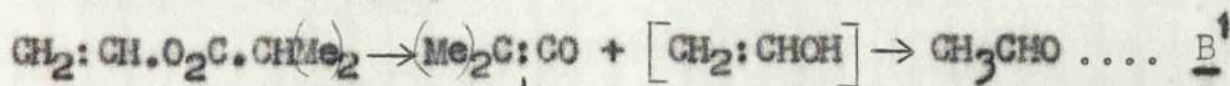


1.3. Acyl-oxygen scission.

This results in the formation of either a keten and a hydroxyl compound, or of two carbonyl compounds thus :

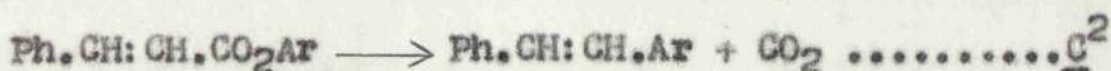


The reaction involves transfer of hydrogen from either the acyl or the alkyl group, and is designated (5) by the symbols $\underline{\text{B}^1}$ and $\underline{\text{B}^2}$ respectively. Acyl-oxygen scission is often observed with esters lacking a β -hydrogen atom. When the latter is present, however, the acyl-oxygen scission rarely predominates and the products are obtained in small amount. The formation of two carbonyl compounds from an ester constitutes a formal reversal of the Tischenko reaction (13). As examples of acyl-oxygen scission we have the decomposition of vinyl isobutyrate to acetaldehyde and secondary products attributable to dimethylketen (5) and the pyrolysis of benzyl benzoate to benzaldehyde (14) :

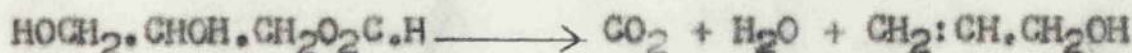


1.4. Decarboxylation.

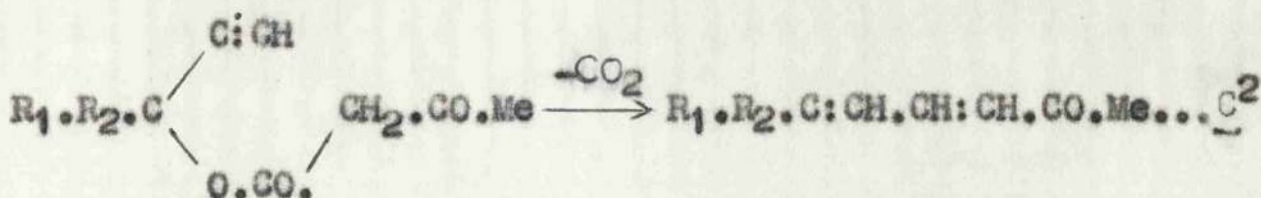
The appearance of carbon dioxide among the decomposition products of an ester does not by itself prove the primary decarboxylation of the latter, as the carbon dioxide might have arisen from secondary breakdown of a carboxylic acid formed by a primary alkyl-oxygen scission. True ester decarboxylation is, however, known to take place with certain α -unsaturated esters and with formates. Thus, aryl esters of cinnamic acid decompose to stilbene (15):



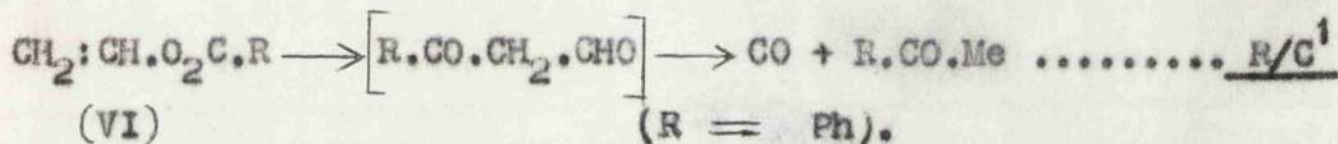
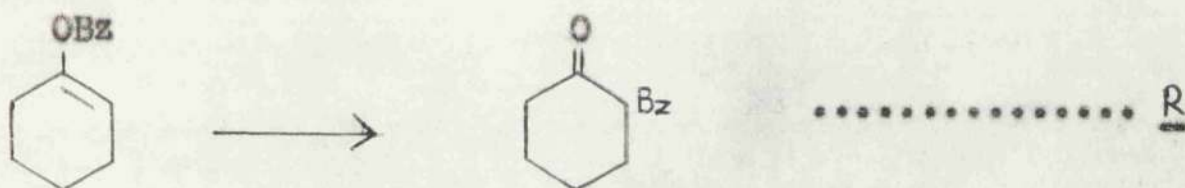
The symbol $\underline{\text{C}}^2$ is used to denote decarboxylation, while $\underline{\text{C}}^1$ is used in the case of decarbonylation, which is common with aldehydes. A well-known method for preparing allyl alcohol involves what really amounts to the thermal decomposition of glyceryl formate. The process involved is one of decarboxylation and dehydration. The method is generally applicable to the conversion of a glycol grouping -CHOH. CHOH- into an olefin -CH: CH-.



A very unusual type of ester decarboxylation was observed by Lacey (16) who showed that dienones were formed in the thermal decomposition of acetoacetates of ethynylcarbinols :

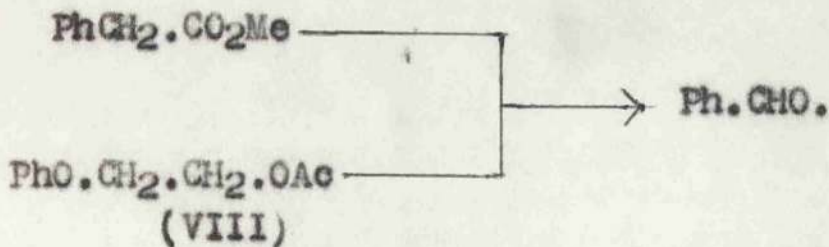


Allan and Ritchie (5) found that cyclohex-1-enyl benzoate yields 2-benzoylcyclohexanone at 480°. They found this type of reaction to be of major importance in the thermal decomposition of vinyl carboxylates. Vinyl benzoate (VI) gave mainly acetophenone on pyrolysis. It was shown ^{that} the intermediate benzoylacetaldehyde was involved, the overall reaction occurring in two stages (R/C¹).



1.7. Complex reactions.

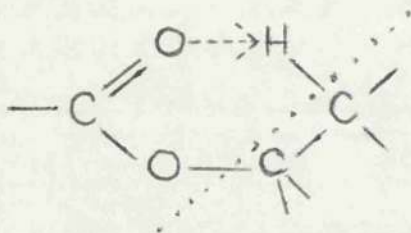
While most cases of ester pyrolysis fit into one system of classification described so far, there are a few exceptions. The formation of benzaldehyde in the pyrolysis of methyl phenylacetate (20) and of 2-phenoxyethyl acetate (21) would appear to be the result of a complicated reaction sequence:



1.8. Mechanism of pyrolysis of esters.

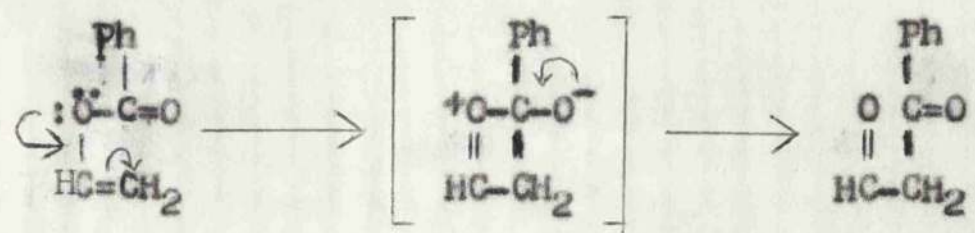
It is probable that no single mechanism accounts for all the products obtained in ester pyrolysis. A lot of

work has been done with esters possessing a β -hydrogen atom, and it seems fairly certain that the elimination of acid in such cases proceeds through a six-membered cyclic intermediate involving the cis- β -hydrogen (Hurd and Blunck, 20), thus:



Houtman, van Steenis, and Heertjes (10) have adversely criticised the Hurd and Blunck mechanism on the grounds that a hydrogen bond is usually formed between two negative elements and cannot be of much importance in an elimination reaction. This argument is not valid, because it is now known that hydrogen bonds of the type $O \rightarrow H - C$ and $N \rightarrow H - C$ are capable of formation e.g. molecular compound formation such as $Et_2O \rightarrow CHCl_3$ (22).

Young et al. (18,19) proposed an intramolecular mechanism to account for the thermal rearrangement of enol carboxylates to isomeric β -diketones, and this has been applied by Allan, Forman, and Ritchie (5) to the case of vinyl carboxylates, thus :

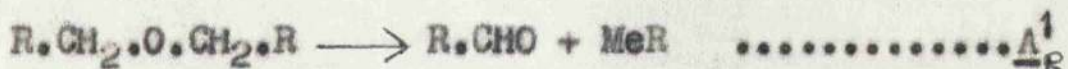


The possibility of radical intermediates in thermal reactions must always be borne in mind. Bilger and Hibbert (23) suggested that all pyrolytic reactions involve radicals, but did not have sufficient evidence. Hurd and Blunck (20) suggested that they are more likely to occur with esters lacking a β -hydrogen atom, the increased thermal stability of these esters necessitating the use of higher temperatures.

The Pyrolysis of Ethers.

1.9. Saturated aliphatic ethers.

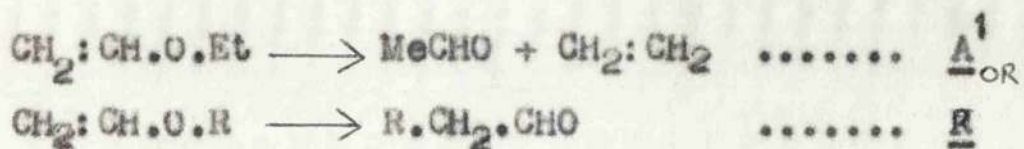
Aliphatic ethers of the type $R.CH_2.O.CH_2.R$ generally break down to an aldehyde and a hydrocarbon :



The symbol \underline{A}_R^1 indicates that hydrogen is transferred across the point of scission to the alkyl group; \underline{A}_R^2 is used when an alkenyl group is involved.

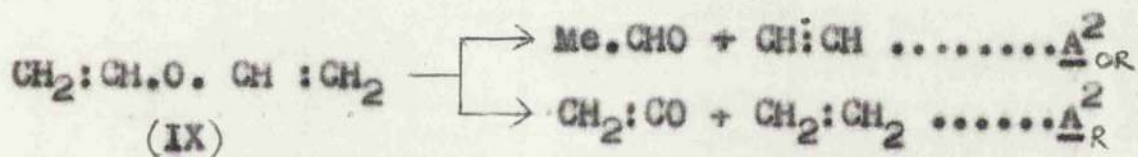
1.10. Vinyl ethers.

Vinyl alkyl ethers usually give acetaldehyde and an olefin on pyrolysis but are known to undergo rearrangement as well. Wang and Winkler (24) found that ethyl vinyl ether yields acetaldehyde and ethylene in a first-order reaction at $380-450^\circ$. Hasche and Thomson (25) found, however, that over a wide range of temperature and pressure alkyl vinyl ethers rearrange to isomeric aldehydes.



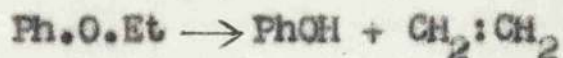
The suffix OR indicates that hydrogen is transferred to the alkoxy grouping. R is again used to represent rearrangement.

Vinyl ether (IX), being fully symmetrical and unsaturated, presents a special case. Taylor (26) has reported that it breaks down in a sealed tube at 450° to keten and ethylene ($\underline{\text{A}}^2_{\text{R}}$). It has now been found (see experimental) that in a flow-reactor it yields only acetaldehyde and acetylene by the $\underline{\text{A}}^2_{\text{OR}}$ route.

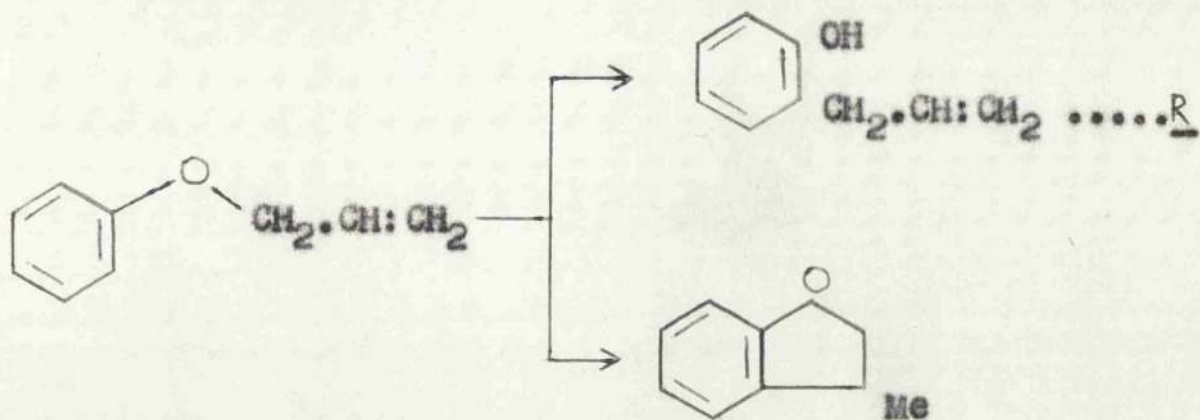


1.11. Aromatic ethers.

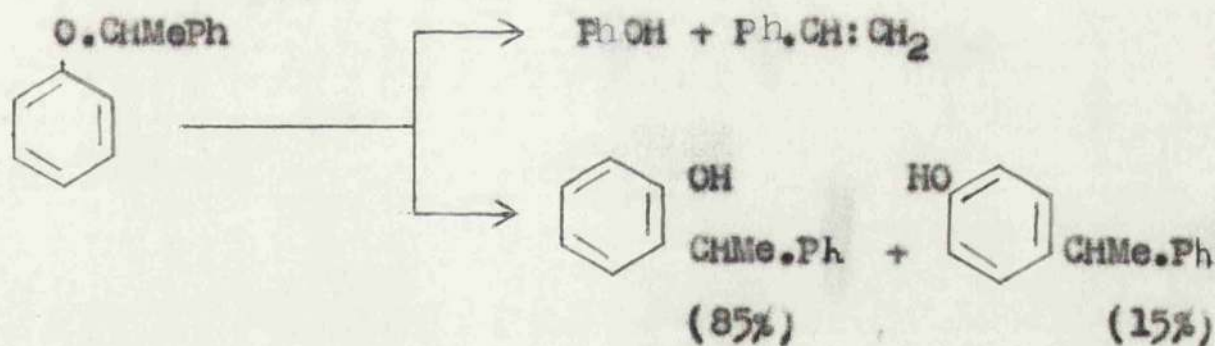
When both groups attached to the oxygen are aryl, such as in diphenyl ether, the compound is very stable and its decomposition very complex. Aryl alkyl ethers, however, decompose to a phenol and olefin, e.g. ethyl phenyl ether (27) :



Allyl aryl ethers rearrange very easily on heating (Claisen reaction). Thus, allyl phenyl ether yields o-allyl phenol on heating to its boiling point. A minor side-reaction is the cyclisation to 2-methylcoumaran (28) :

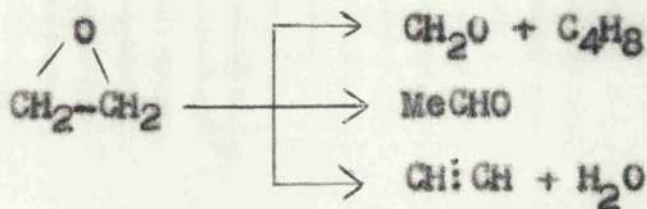


Thermal rearrangement of aryl alkyl ethers is not very common, but it has been recorded. Thus, Hart and Eleuterio (29) found that under purely thermal conditions 1-phenyl-1-phenoxyethane decomposed along two different routes, one yielding phenol and styrene, and the other mainly 1-phenyl-1-o-hydroxyphenylethane :



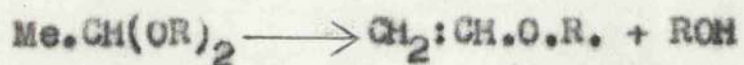
1.12. Cyclic and other ethers.

When ethylene oxide and its derivatives are cracked, carbonyl compounds are obtained. Peytral (30) found that the decomposition of ethylene oxide followed three routes :

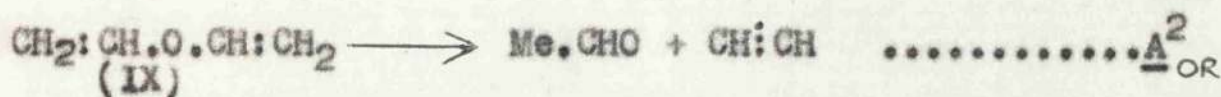
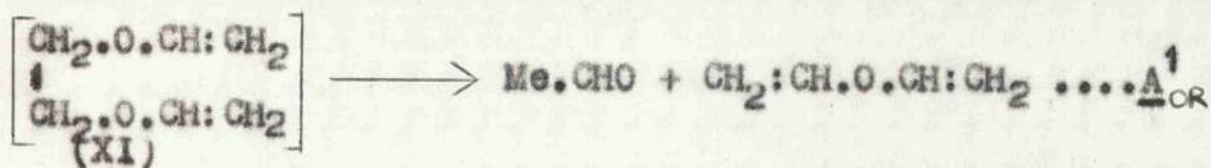


The reaction is probably complex, since Simard et al. (31) detected (among other things) keten, by infra-red analysis, in the above decomposition.

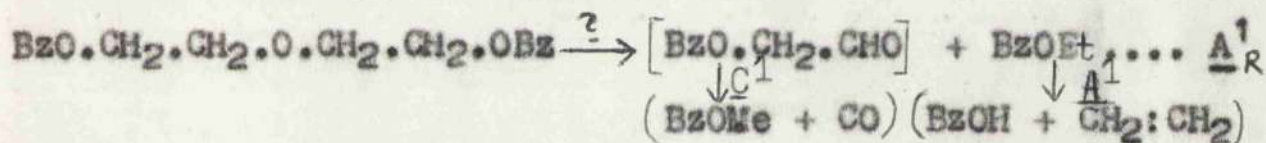
The decomposition of acetals involves elimination of alcohol. This method has been applied to the synthesis of vinyl ethers (32) :



diether (XI) by the following consecutive routes : -



The primary breakdown of the ether-diester (IV) involves alkyl-oxygen scission at one of the two identical ester groups, giving acid and olefin according to the well-known pattern. It appears that scission does not occur at the ether linkage. The latter would require the formation of methyl benzoate and ethyl benzoate, from the predictable sequence :

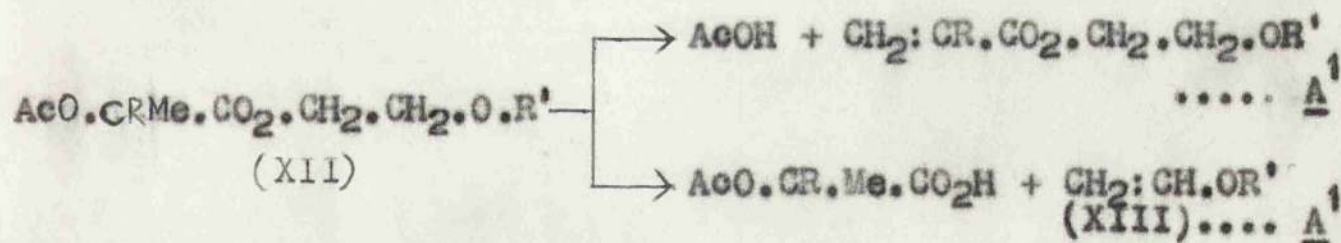


Ethyl benzoate would be destroyed to some extent at 500°, yielding benzoic acid and ethylene, both of which were identified. Since, however, vinyl benzoate itself is known (5) to give ethylene by some unknown route, the presence of ethylene cannot be taken by itself as evidence for the formation of ethyl benzoate in the pyrolysis of (IX).

Methyl benzoate, on the other hand, is a very thermostable compound (33). The pyrolysate, on hydrolysis, did not give any methanol or ethanol, which were tested for by the xanthate colour reaction (34). This proved the absence of methyl and ethyl benzoates, and hence of scission at the

ether linkage, in the pyrolysis of (IV).

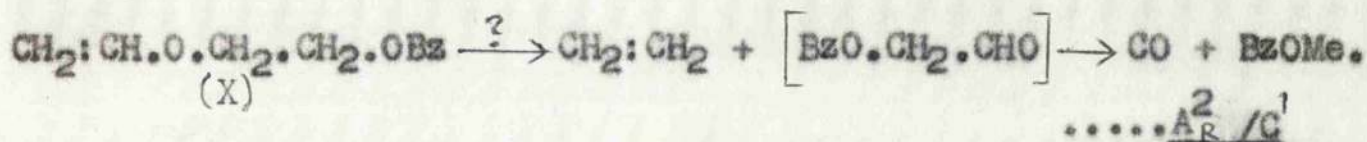
There is corroborating evidence that the pyrolysis of ether-esters involves the ester rather than the ether linkage. Burns, Jones, and Ritchie (7) found that on pyrolysis, the esters (XIIa) decompose to form substituted acrylates in good yield, while Fein, Ratchford, and Fisher (35) found that the esters (XIIb) yield acrylates as expected, though here the yields were low. The poor yield may have been due to secondary breakdown of the primary products, or there may have been competitive primary scissions. Fein et al. noted the presence of acetaldehyde in the pyrolysis of the methoxy and ethoxy esters; this might have been derived in known fashion from the vinyl ether (XIII), or from α -acetoxypropionic acid.



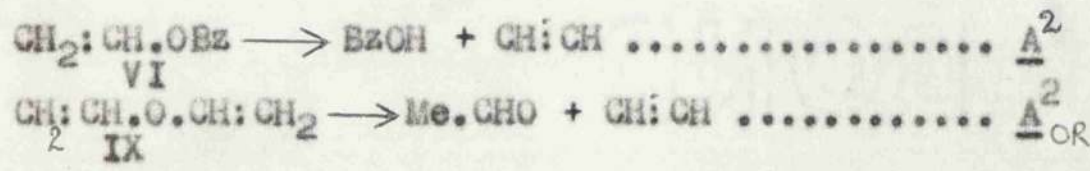
(a) R = Me; R' = Me or Ph.

(b) R = H; R' = Me, Et, Buⁿ, or tetrahydrofurfuryl.

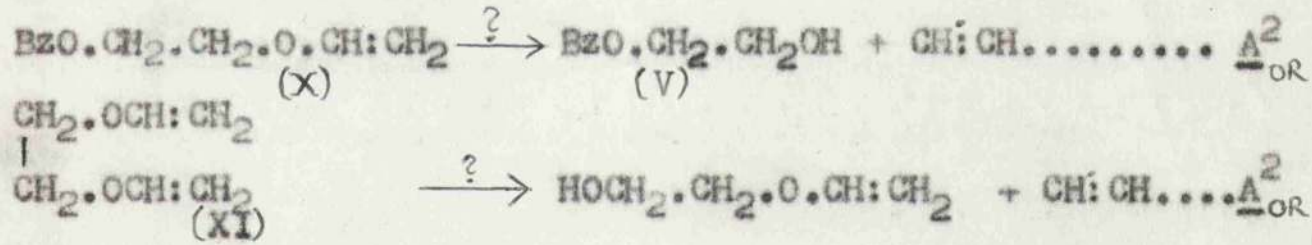
Stage 2.— The absence of methyl benzoate in the pyrolysis of (IV) precludes $\underline{\text{A}}^2_{\text{R}}$ scission of (X) to ethylene and benzoyloxyacetaldehyde, since the latter would decompose to methyl benzoate, thus:



Origin of Acetylene. This substance is attributed to (i) known alkenyl-oxygen scission (\underline{A}^2) of vinyl benzoate (VI), and (ii) the \underline{A}_{OR}^2 scission of vinyl ether (IX), thus:

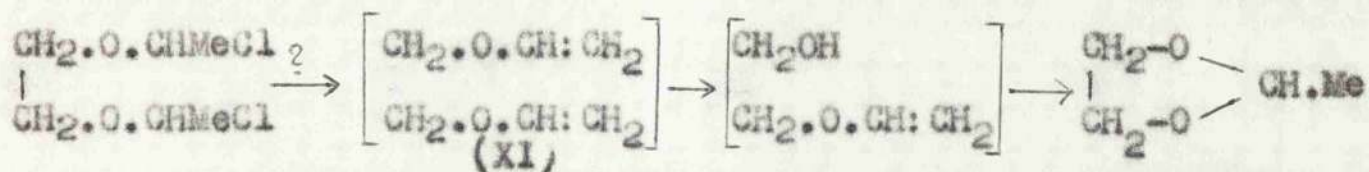


Two other possible sources can be eliminated - \underline{A}_{OR}^2 scission of the vinyl ethers (X) and (XI). If the former breaks down in this way, the accompanying product would be 2-hydroxyethyl benzoate :



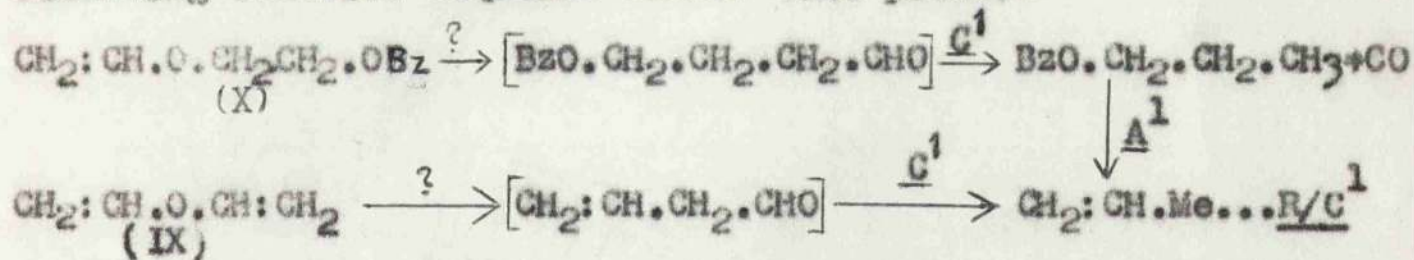
2-Hydroxyethyl benzoate (V) is known to yield water on decomposition (17); no water was found in the present instance. If the ether (XI) lost one molecule of acetylene, the resulting product would be 2-hydroxyethyl vinyl ether, a substance which is readily cyclised to ethylene acetal. Hurd and Botterton (36), in an attempt to prepare the diether (XI) by dehydrochlorination of ethylene di-1-chloroethyl ether obtained instead the cyclic ethylene acetal. This suggests the following

mechanism:



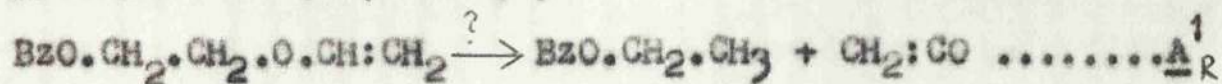
A repetition of Hurd and Botterton's experiment showed, however, that there was no liberation of acetylene; their result must therefore be attributed to some alternative mechanism.

Rearrangement of 2-benzoyloxyethyl vinyl ether (X) is an important consideration in view of previous findings on the thermal rearrangement of vinyl ethers (see 1.10). If rearrangement of (X) or vinyl ether (IX), occurs, the following reaction sequence should take place:-

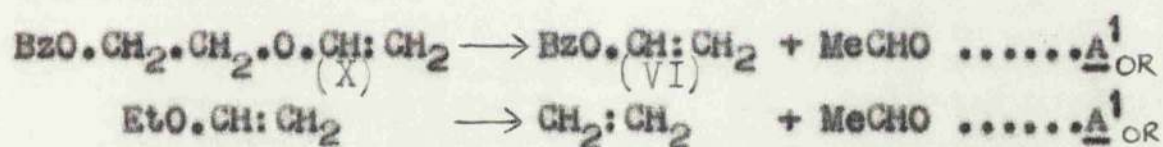


There was no sign of propene in the pyrolysates from the ether-diester (IV) from (X), or from vinyl ether itself, proving that the above rearrangement of the vinyl ether (X) does not occur.

A¹_R scission of (X) would lead to the formation of keten and ethyl benzoate. Neither of these was detected in the pyrolysis of (IV) and (X).



The intermediate ether-ester (X) in the pyrolysis of the ether-diester (IV), has not itself been identified. Its postulation is nevertheless reasonable, since it has been prepared and cracked separately, and gives the same end-products as the ether-diester(IV). It decomposes along three different routes, as indicated before. Of these, the most important is the one leading to acetaldehyde and vinyl benzoate. The latter were almost the sole products obtained in a run at 400°. The behaviour is analogous to the decomposition of ethyl vinyl ether to acetaldehyde and ethylene (24).



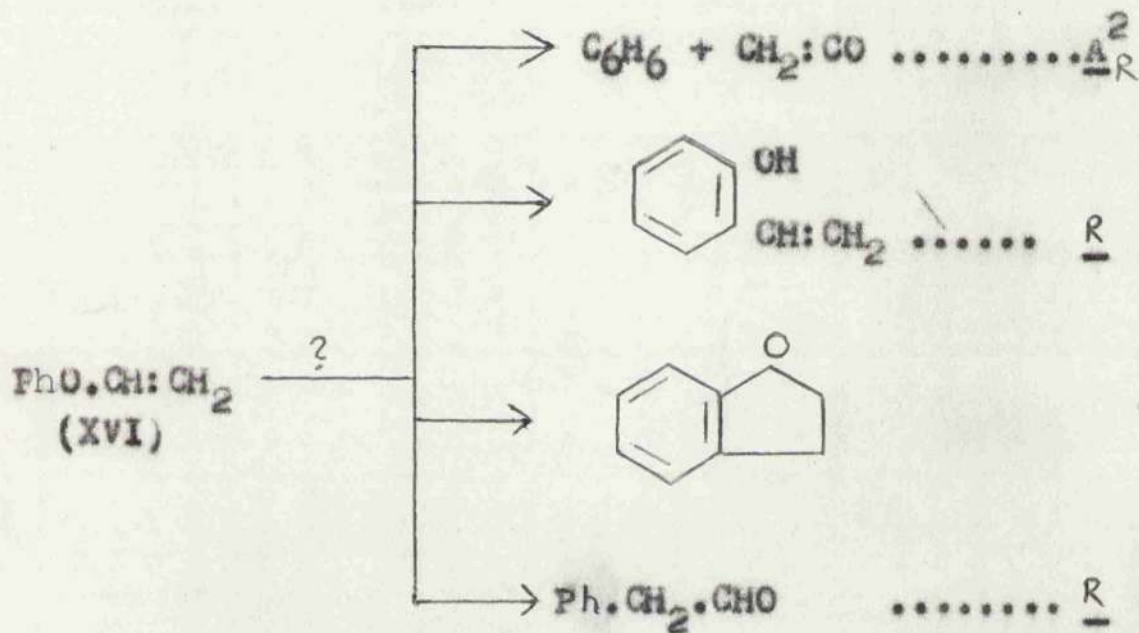
It is surprising that despite the presence of a hydrogen atom in the β -position with respect to the carboxyl grouping, alkyl-oxygen scission of the ether-ester (X) occurs only to a small degree. Vinyl ether (IX) is formed, but in amounts detectable only by infra-red spectrometry.



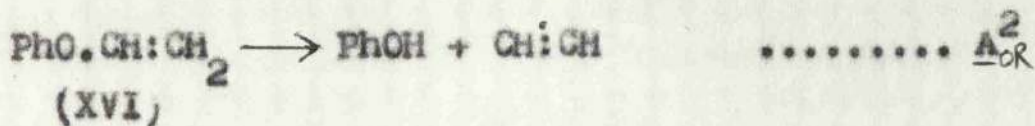
The disproportionation of the ether-ester (X) is again not easily predicted. Ethylene dibenzoate (II) was obtained from (X) at 450-70°; it was also obtained

from the ether-diester (IV) at 450°. It was not formed at higher temperatures, owing possibly to some catalytic effect of the carbon deposit on the walls, or to decomposition of the ethylene dibenzoate at higher temperatures. The decomposition of the diether (XI), which would be expected to accompany ethylene dibenzoate, and of the latter substance itself, yields acetaldehyde and vinyl benzoate. These again can be attributed to alternative routes. In one run at 500°, the pyrolysis of the ether-ester (X) gave vinyl ether (IX) and benzoic acid when no ethylene dibenzoate was observed, proving the A^1 route. This variation between the results of two similar runs may be due to different degrees of carbonisation on the walls of the reactor. The possible effect of a carbon deposit on the course of reaction can be seen from the observation of Houtman, van Steenis, and Heertjes (10) that the absence of carbonisation practically inhibits reaction. Bailey and his co-workers have shown (37) that by carrying out a pyrolysis in such a manner that substantially no carbonisation occurs, some side-reactions are avoided. The A^1_{-OR} route of decomposition of the ether-ester (X) is strongly supported by the known A^1_{-OR} breakdown of alkyl vinyl ethers. Benzoic anhydride is obtained in small amounts in the pyrolysis of both the

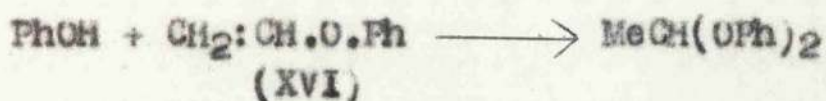
Phenyl vinyl ether (XVI) provides a case where A_{-OR}^1 scission is structurally precluded. Its decomposition has previously been studied (38), but the results were indefinite. The following possibilities have been considered at present and ruled out because the required products were not identified though carefully sought.



According to the present studies, phenyl vinyl ether yields a pyrolysate containing phenol and acetylene. The reaction is not simple, however, as a lot of carbonisation takes place, and the phenol and acetylene are not isolated in equivalent amounts. The latter was identified by infra-red spectroscopy. It is reasonable, nevertheless, to regard the primary breakdown, thus:



Phenol can add on to phenyl vinyl ether to give diphenyl acetal when the decomposition is effected in a sealed tube (Lauer & Spielman, 38).



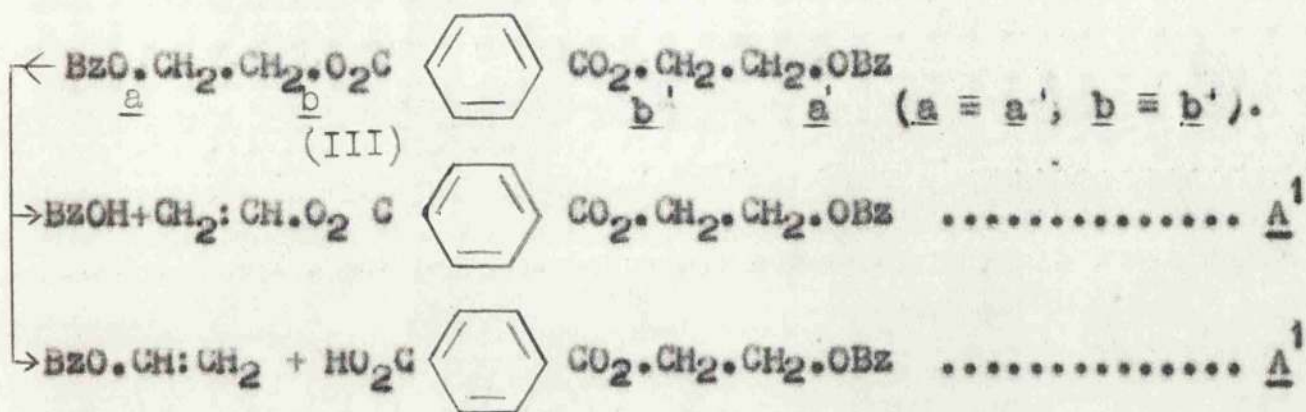
This reaction does not, however, take place in a vapour-phase pyrolysis; there was no evidence for diphenyl acetal in the pyrolysate.

The behaviour of the two butyl vinyl ethers, and of vinyl ether (IX) is in agreement with that of the ether-ester (X), the intermediate in the pyrolysis of 2:2'-dibenzoyloxydiethyl ether (IV); $\underline{A}^1_{\text{OR}}$ scission is the principal reaction involved. Another constant feature of the pyrolysis of the various vinyl ethers and esters is the formation of ethylene. There is no simple explanation of its presence; the occurrence of some form of radical reaction suggests itself.

2.3. The Pyrolysis of 2-Benzoyloxyethyl Terephthalate (VII).

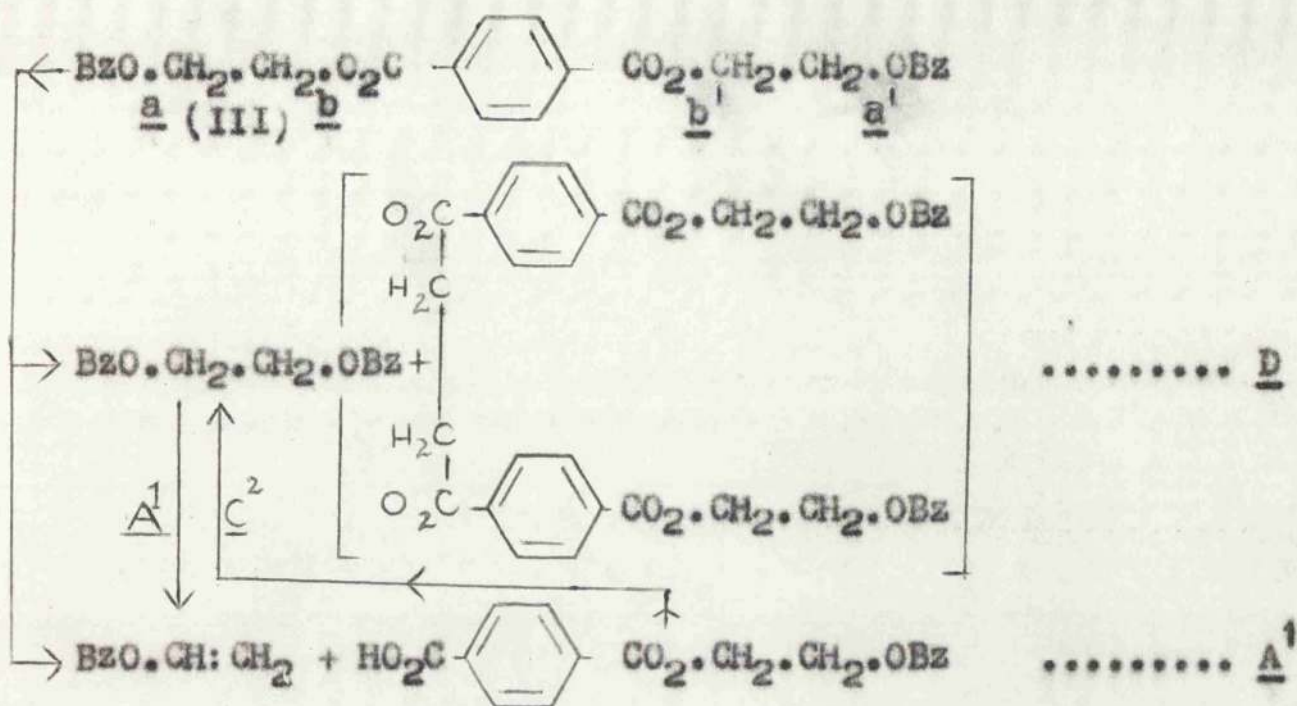
The pyrolysis of the unchlorinated model, 2-benzoyloxyethyl terephthalate (III) has been described by Allan (6), and it is convenient to discuss his results here. Because of the presence of several β -hydrogen atoms (see formula below), it is to be expected that the primary reaction will be alkyl-oxygen scission(\underline{A}^1) at the ester linkages. It is possible that the following primary breaks

will occur at the points a and b, giving different vinyl esters:



Further reaction sequence is difficult to predict, because the various formal possibilities all lead to the same end-products (which were identified), viz., terephthalic acid, benzoic acid, 4-acetylbenzoic acid (XVII), ethylene dibenzoate, vinyl benzoate, acetophenone, acetaldehyde, benzoic anhydride, carbon monoxide and dioxide, methane, acetylene, and ethylene. The latter is a known decomposition product of vinyl benzoate (5) though its precise origin remains uncertain.

The important features of the pyrolysis are the formation (i) of ethylene dibenzoate, (ii) of vinyl benzoate and its decomposition products, and (iii) of acetaldehyde and benzoic anhydride. Ethylene dibenzoate (II) can arise either by disproportionation at the 'end' of the molecule, or by alkyl-oxygen scission at the point b followed by decarboxylation, thus:



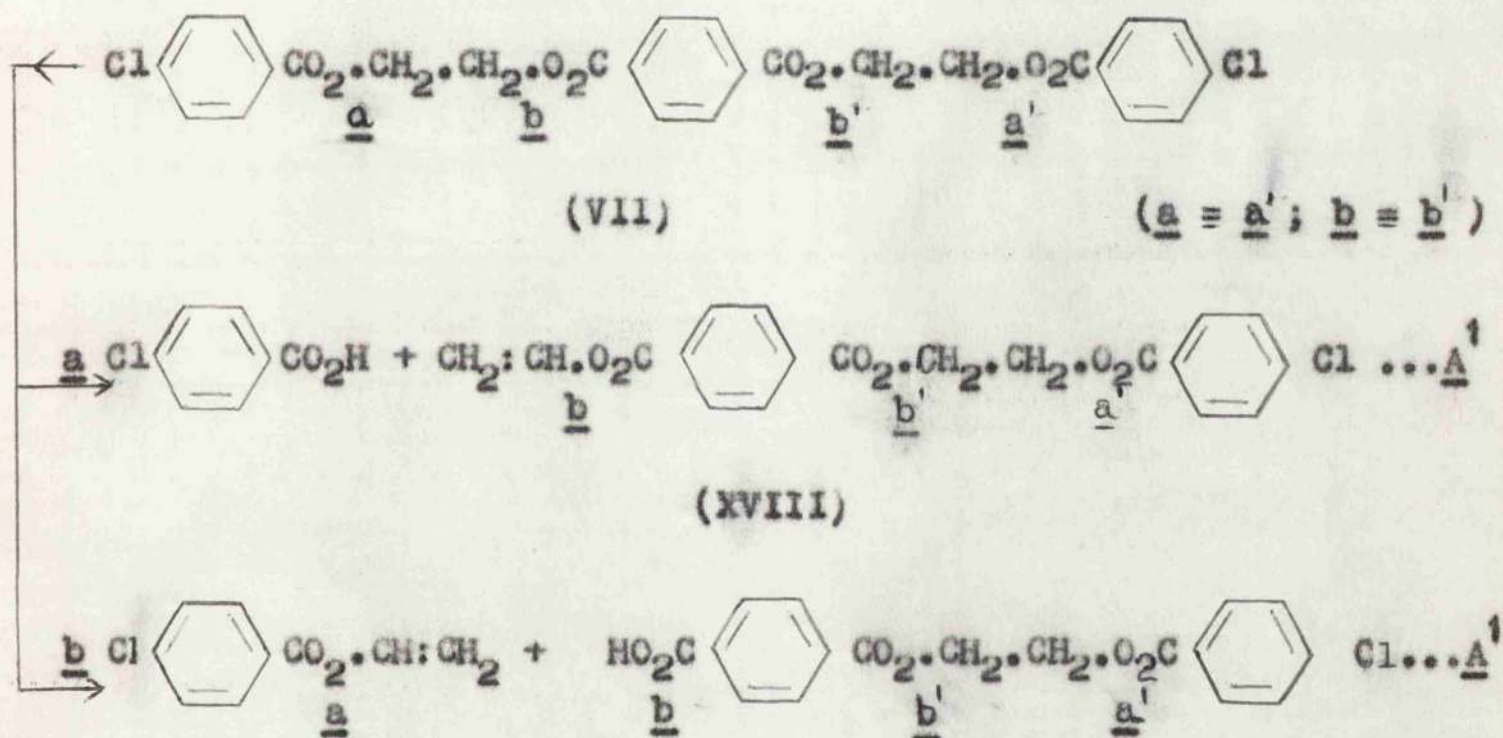
By labelling the terminal benzoyloxy groups with a 4-chloro substituent (see Section 2.4.), it is possible (i) to distinguish between the A¹ / C² and D routes in the pyrolysis of (III) leading to ethylene dibenzoate, and (ii) to determine how much of the benzoic acid from (III) is obtained by A¹ scission at the point a, and how much is derived from a semi-decarboxylation of terephthalic acid.

2.4. The Pyrolysis of 2-(4-Chlorobenzoyloxy) ethyl Terephthalate (VII).

The results obtained with the chlorine-labelled compound (VII) are in good agreement with those obtained with (III). The products obtained at 500° were as follows:- (i) terephthalic acid, (ii) 4-chlorobenzoic acid, (iii) benzoic acid, (iv) 4-acetylbenzoic acid (XVII), (v) 'anhydrides', (vi) acetaldehyde, (vii) ethylene di-4-

-chlorobenzoate, (viii) acetophenone, (ix) 4-chloroacetophenone, (x) carbon monoxide, (xi) carbon dioxide, (xii) methane, (xiii) acetylene, and (xiv) ethylene.

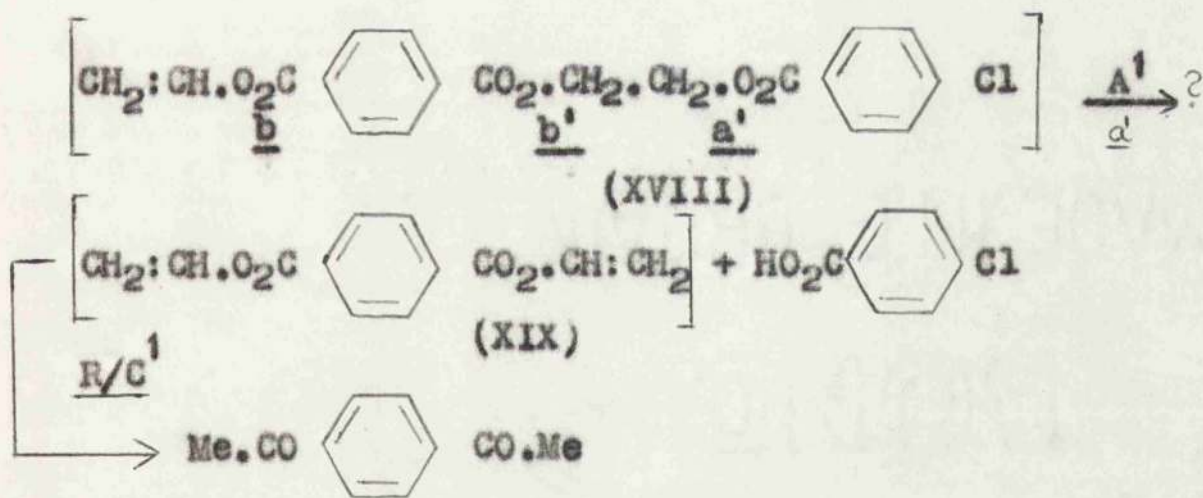
Again, because of the presence of several β -hydrogen atoms, the primary reaction will be A^1 scission at the points a and b, leading to the following pairs of products: -



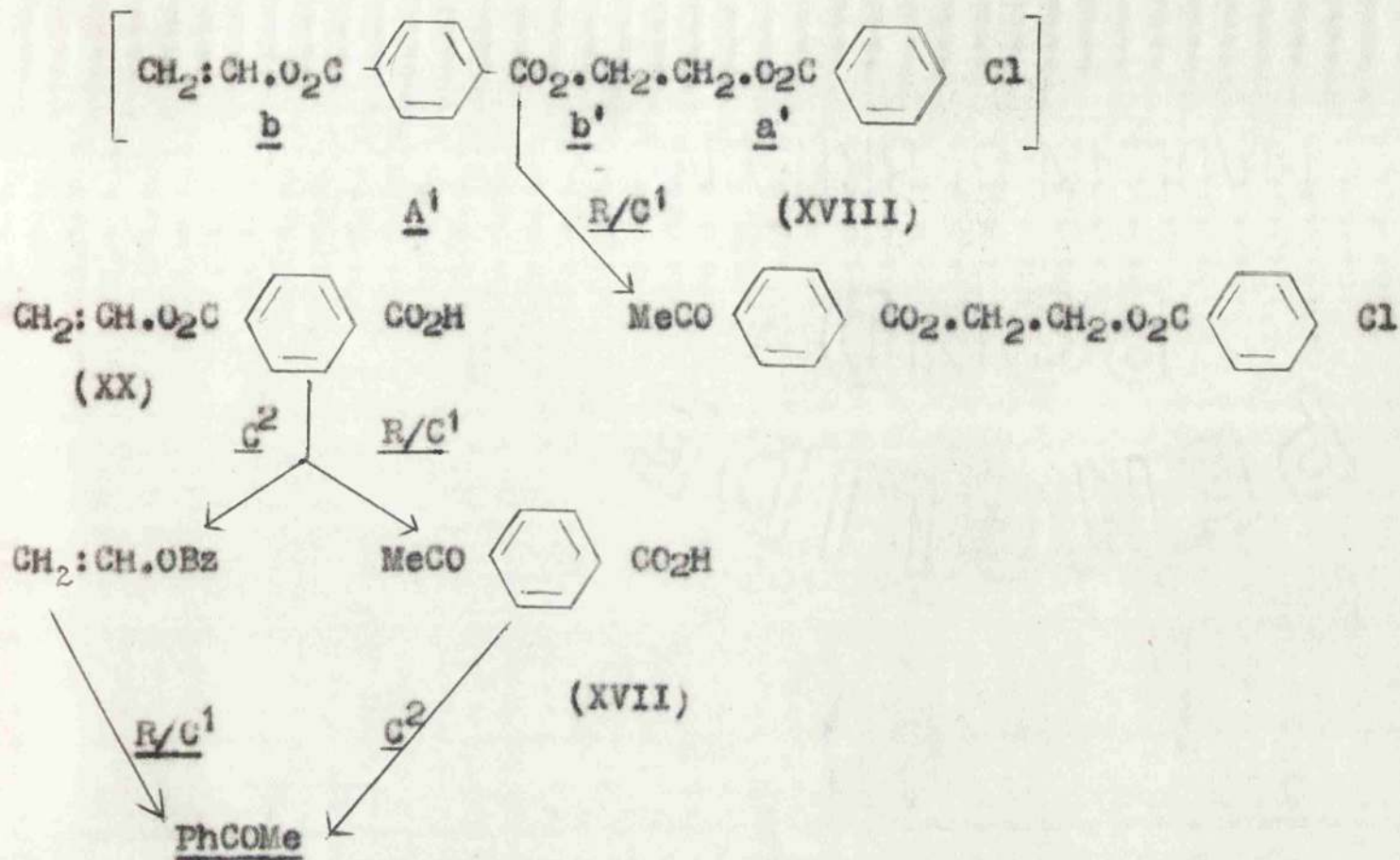
The formation of both terephthalic acid and 4-chlorobenzoic acid shows that scission does in fact occur at the points a and b. The former compound is probably derived from (VII) by A^1 scission at the point b'. Since the amount of benzoic acid obtained in the pyrolysis of the labelled compound

(VII) is very small, the semi-decarboxylation of terephthalic acid must be only a minor reaction. The benzoic acid obtained in the pyrolysis of the unlabelled model (III), is therefore formed at the point a.

The decomposition of the intermediate (XVIII) will involve the A¹ and R / C¹ reactions; the exact sequence is not easily predicted. A¹ scission at the point a['] leads to vinyl terephthalate (XIX), which by analogy with vinyl benzoate (5) would be expected to give 1:4-diacetylbenzene. The latter was not found, though carefully sought.



A combination of the A¹ and R / C¹ reactions, with scission at the point b['] leads however, to 4-acetylbenzoic acid, which was found in small amounts.



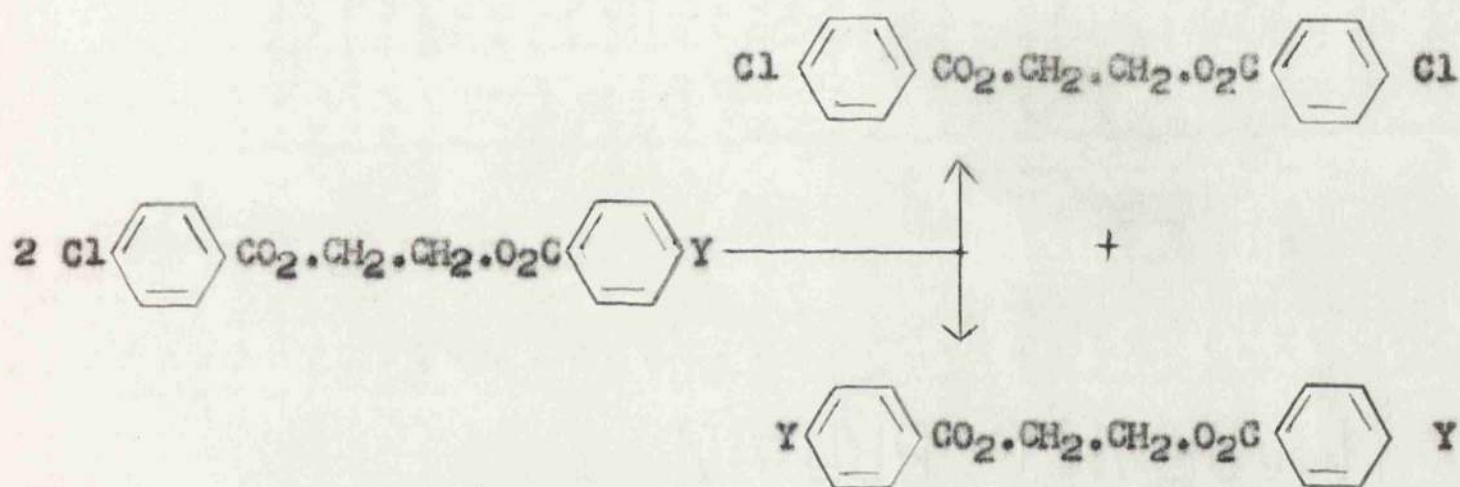
4-Acetylbenzoic acid has been shown by Allan (6) to yield acetophenone on pyrolysis. The latter can also be obtained from vinyl hydrogen terephthalate (XX) by decarboxylation to vinyl benzoate, which then decomposes by the known R / C¹ route to acetophenone. Since the pyrolysis of (VII) would be expected to give vinyl 4-chlorobenzoate, the pyrolysate should contain 4-chloroacetophenone, formed by R / C¹ decomposition of vinyl 4-chlorobenzoate.

The detection of acetophenone and 4-chloroacetophenone in the pyrolysate from (VII) was thus of great importance. The complete separation of a mixture of vinyl benzoate, vinyl 4-chlorobenzoate, acetophenone, and 4-chloroacetophenone is a matter of some difficulty, since they all possess closely related boiling points. The

detection of vinyl benzoate and acetophenone in a mixture of vinyl 4-chlorobenzoate and 4-chloroacetophenone by infra-red spectroscopy is impracticable owing to the presence of similar functional groups. Attention was therefore focussed on the identification of the two acetophenones alone. This has been done by a chromatographic analysis of their 2:4-dinitrophenylhydrazones (which will henceforward be DNPs). The two derivatives have a small difference in R_f values for a number of solvent systems. However, they showed some streaking, which was unavoidable, and made the characterisation of the spot with the smaller R_f value somewhat open to question; but identification was made more rigorous, by chromatographing the mixture of DNPs on a column of bentonite / kieselguhr by the method of Elvidge and Whalley (39), and then spotting the separate fractions on paper. The results are given in Fig. 3 (p. 98). The separate DNP fractions were obtained from the column by elution with chloroform / acetone in 10 ml. amounts. Five fractions were obtained, as shown by plotting the optical density of the fractions against fraction number. The last three fractions were obtained in quick succession and were therefore collected in 2 ml. lots. The optical density shown in the graph is one-fifth of that actually measured; the smaller value is convenient to plot. The

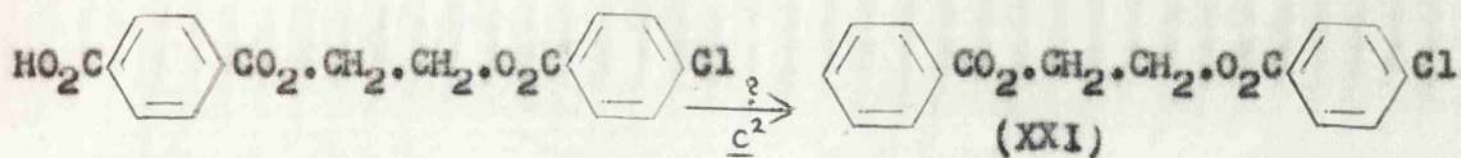
first two fractions corresponded to the two acetophenones (Fig. 4). The other three have not been identified owing to lack of time. They are probably the DNPs of carbonyl compounds of higher molecular weight than the two acetophenones identified.

The formation of ethylene di-4-chlorobenzoate in the pyrolysis of (VII) shows that disproportionation takes place at some stage. It may involve either the original molecule, or one of its decomposition products, thus:

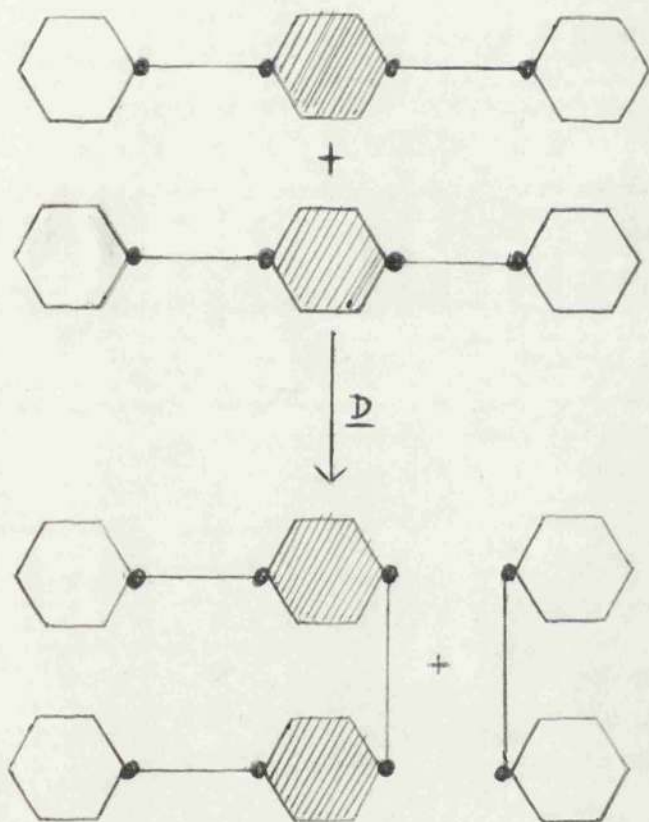


(where Y = CO₂H, CO₂CH:CH₂, or CO₂·CH₂·CH₂·O₂C Cl)

The product accompanying ethylene di-4-chlorobenzoate (see above) will in all probability decompose further; no such material has been found in the pyrolysate. The formation of ethylene di-4-chlorobenzoate and not of 2-benzoyloxyethyl 4-chlorobenzoate (XXI) is significant.



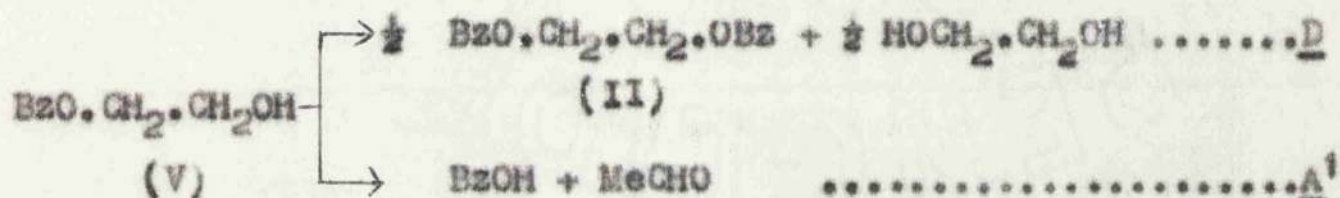
It shows that the formation of ethylene dibenzoate in the pyrolysis of (III) (Section 2.3.) is due to a disproportionation reaction, probably involving the original molecule itself.



The formation of acetaldehyde in the pyrolysis of (III) and the labelled compound (VII) is important. By analogy with the formation of acetaldehyde from ethylene dibenzoate (5, 6), it is possibly obtained by the following reaction sequence:-



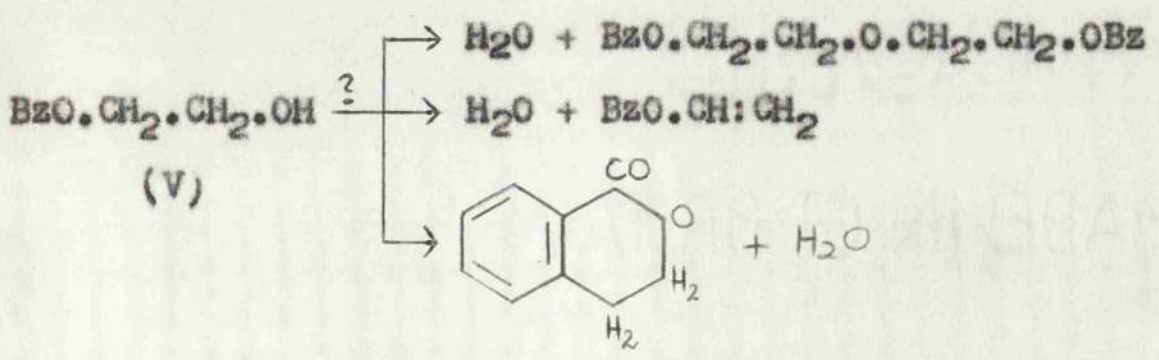
compounds as well as benzoic anhydride. At 500°, however, benzoic acid is obtained in addition, but not vinyl benzoate (VI). This can only be interpreted by assuming that at the higher temperature, alkyl-oxygen scission (A¹) takes place, giving benzoic acid and vinyl alcohol, which isomerises at once to acetaldehyde. This shows that 2-hydroxyethyl benzoate (V) decomposes along two different primary routes at higher temperatures, but at lower temperatures undergoes only a disproportionation.



The extremely easy formation of water requires an explanation. On heating 2-hydroxyethyl benzoate in a flask, the temperature rises gradually to 100° when a small amount of water distills over. At high temperatures, it is possible to attribute the water to a secondary breakdown of ethylene glycol, which is known to be stable up to 400° and to start decomposing above 500° (40). Ethylene glycol has now been cracked at 370-80°, and found to lose water in traces. A Karl Fisher estimation of the water content of ethylene glycol (See Appendix III) before and after pyrolysis showed a significant difference in titre value, which

amounted, however, to only a very small increase in water content. Since formation of water was detected only by the application of extremely sensitive tests, the experiment showed that the comparatively large amount of water formed during the decomposition of 2-hydroxyethyl benzoate (V) by mere distillation or at 375° cannot have been obtained entirely from ethylene glycol.

The possibility of intermolecular dehydration (see scheme below) must be ruled out, since 2:2'-dibenzoyloxydiethyl ether is not obtained. For a similar reason, dehydration involving cyclisation cannot be considered. An intramolecular dehydration is formally possible, since such a reaction is observed with alcohols; but the absence of vinyl benzoate eliminates this possibility. In any case, if vinyl benzoate were obtained in the pyrolysis of 2-hydroxyethyl benzoate, it would be more reasonable to ascribe it to an alkyl-oxygen scission (A¹) of the ethylene dibenzoate (II) which is obtained in large amounts.



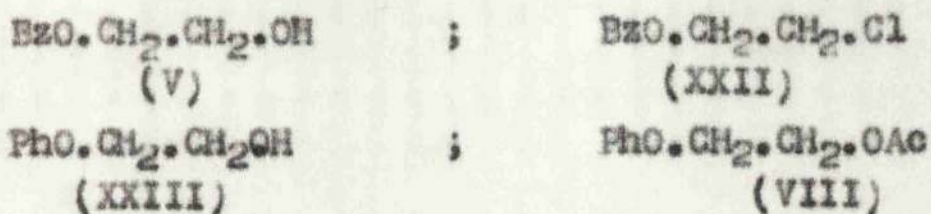
There exists, finally, the possibility that

The presence of the hydroxyl group causes the β -hydrogen atom to be more firmly bound to the carbon. This explains the occurrence of alkyl-oxygen scission at high temperatures only (higher energy of activation); but it does not provide a mechanism for the disproportionation reaction.

2.6. Selection of models related to 2-hydroxyethyl benzoate.

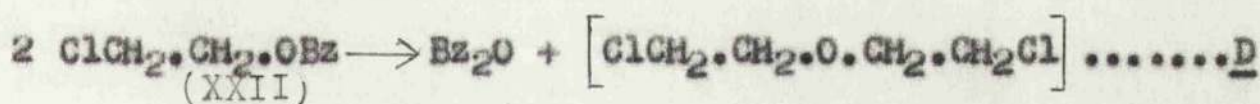
The model compounds discussed so far have all been related to poly (ethylene terephthalate). The remaining compounds that are now discussed are not directly connected with poly (ethylene terephthalate) but were studied in order to discover more about the thermal disproportionation of 1:2- disubstituted ethanes of the type $X.CH_2.CH_2.Y$ (see also Section 2.10), and for reasons that will become apparent in the following sections.

The results obtained with 2-hydroxyethyl benzoate showed that further investigation of the disproportionation reaction was necessary. For this reason, the pyrolysis of compounds related to 2-hydroxyethyl benzoate has been studied. The compounds selected for this purpose are related to (V), but with various modifications of its terminal groupings. Thus, 2-chloroethyl benzoate (XXII), 2-phenoxyethanol (XXIII), and 2-phenoxyethyl acetate (VIII) were chosen.

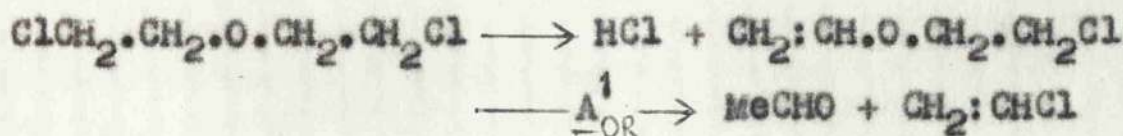


Hydrogen chloride and vinyl benzoate are formed in smaller amount, the latter being detected by infra-red spectroscopy. In one run at 400°, the main reaction was, however, the formation of ethylene dibenzoate; in this case, no benzoic acid was detected. This apparent anomaly may be due to surface effects at the carbonised walls of the reactor. The tendency of 2-chloroethyl benzoate to undergo disproportionation is shown by the fact that it yields ethylene dibenzoate after a few hours of refluxing. In comparison with 2-hydroxyethyl benzoate (V), (XXII) shows a lesser tendency to disproportionate.

Benzoic anhydride has also been detected in the pyrolysate from 2-chloroethyl benzoate (XXII), but in small amount. Its presence suggests the occurrence of a fourth mode of scission of (XXII) (see also p. 36).



The accompanying product would be 2:2'-dichlorodiethyl ether which might be expected to yield hydrogen chloride and 2-chloroethyl vinyl ether, the latter then breaking down to acetaldehyde and vinyl chloride.

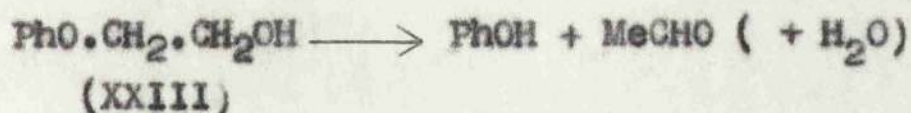


There is no definite evidence as yet for this sort of

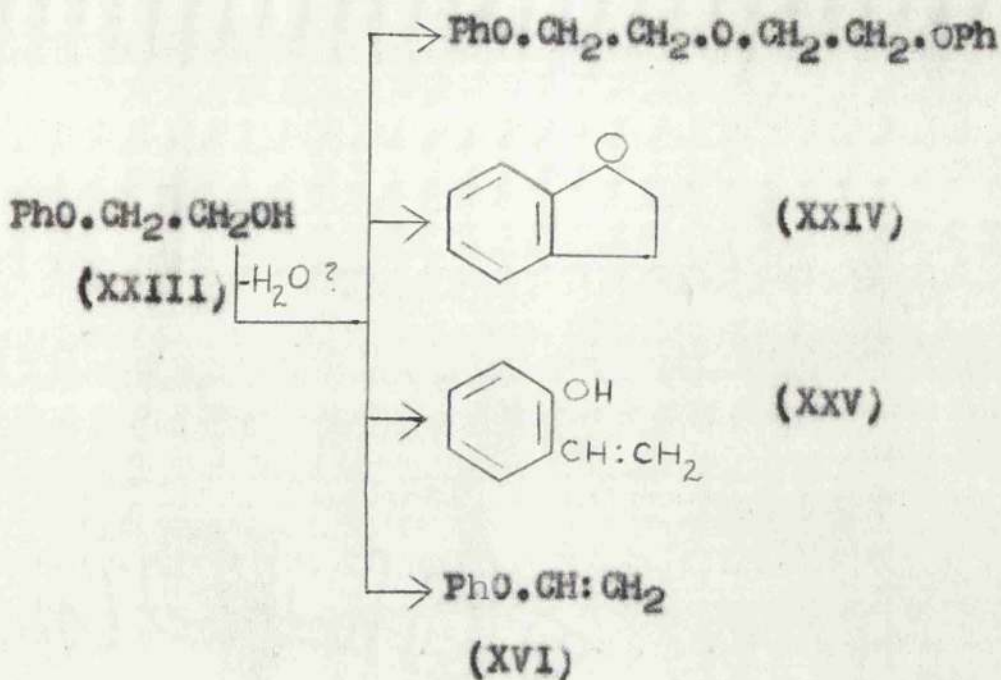
bimolecular disproportionation reaction, as acetaldehyde has not been positively identified among the decomposition products of (XXII). A minute amount of a volatile carbonyl compound was found to be present, giving only a minute yield of DNP. The latter could not unfortunately be characterised.

2.8. The Pyrolysis of 2-Phenoxyethanol (XXIII):

Replacement of the ester carboxyl group in a molecule of the type X.CH₂.CH₂.O.CO.R by an ether grouping has a very noticeable effect. Thus, 2-phenoxyethanol (XXIII) shows no tendency to disproportionate on pyrolysis (contrast behaviour of 2-hydroxyethyl benzoate). At 500°, it yields phenol and acetaldehyde, and also a small amount of water. The formation of phenol is to be expected of a phenyl alkyl ether. The elimination of water recalls the behaviour of alcohols on pyrolysis.



2:2'-Diphenoxydiethyl ether and coumaran (see scheme below) were absent in the pyrolysate from (XXIII), and phenyl vinyl ether (XVI) could not be positively identified, but Knights has found that (XVI) is formed in the pyrolysis of 2-phenoxyethanol (42). Phenyl vinyl ether decomposes to phenol and acetylene (see Section 2.2); but no acetylene was found in the pyrolysate from (XXIII).



Smith and Niederl (43) reported that dehydration of 2-phenoxyethanol with cold concentrated sulphuric acid gave not the expected phenyl vinyl ether, but the isomeric o-vinyl phenol (see above). On the other hand, Rindfus et al. (44) found that dehydration of (XXIII) with zinc chloride or phosphorus pentoxide yielded coumaran (XXIV). However, in the present work, neither o-vinyl phenol (XXV) nor coumaran was found in the pyrolysate from (XXIII).

An extension of the above work led to a study of the dehydration of 2-phenoxyethanol (XXIII) by chemical as distinct from thermal means. A repetition of Smith and Niederl's work (43) using cold concentrated sulphuric acid showed that dehydration is not easily effected; no o-vinyl phenol was obtained. Knights and Cooper (21) were also unable to duplicate the results of

Smith and Niederl. Heating (XXIII) with concentrated sulphuric acid for a few hours at 100° has now produced a white, ether-insoluble solid which was extremely soluble in water; it was not examined further, but was certainly not o-vinyl phenol (XXV). Similarly the results of Rindfusz et al. could not be reproduced. These workers claimed good yields of coumaran (XXIV) on treating 2-phenoxyethanol with phosphorus pentoxide; but the product obtained in the present work was simply 2-phenoxyethyl phosphate. Similarly, attempted dehydration of (XXIII) with glacial acetic acid /zinc chloride, and acetic anhydride / pyridine simply yielded 2-phenoxyethyl acetate (VIII).

Summing up, it is clear that the foregoing experiments on compounds analogous to 2-hydroxyethyl benzoate suggest no simple mode by which water can arise on pyrolysis of the latter ester.

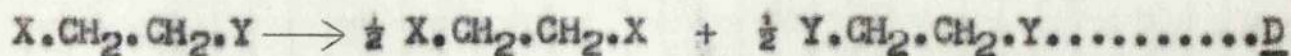
2.9. The Pyrolysis of 2-Phenoxyethyl Acetate (VIII):

Knights and Cooper (21), in an attempt to prepare phenyl vinyl ether (XVI) from 2-phenoxyethanol (XXIII), cracked the acetate of the latter, and obtained acetic acid, phenol, and benzaldehyde, but no phenyl vinyl ether. Pyrolysis of the acetate (VIII) has now been studied in some detail, partly to verify these results, since the formation of benzaldehyde is very surprising, and also to complete the work on disproportionation, and on the dehydration of 2-phenoxyethanol.

does not yield any phenylacetaldehyde on pyrolysis (see Section 2.2). The presence of anisole (b.p. 154°) was proved by the preparation of its dinitro derivative; this was obtained in poor yield, because the pyrolysate fraction also contained phenyl vinyl ether (b.p. 156°), and the action of a nitrating mixture led to considerable resinification. Phenol is obtained in small amounts; it may arise in part from phenyl vinyl ether (Section 2.2.) but the presence of acetone indicates that (VIII) undergoes scission directly to phenol and vinyl acetate, the latter being known to yield much acetone on pyrolysis (4,5). The only product for which no simple explanation is apparent is benzaldehyde. The formation of acetic acid and phenyl vinyl ether suggests by analogy that pyrolytic dehydration of 2-phenoxyethanol (XXIII) leads to water accompanied by phenyl vinyl ether.

2.10. Effect of structure on disproportionation.

The foregoing results confirm that (as might be expected) the occurrence of the following disproportionation is markedly affected by the nature of the groups X and Y:



Thus, where X = BzO and Y = OH, Cl, or O.CH:CH₂, pyrolysis yields ethylene dibenzoate; but when X = AcO and Y = OPh,

neither ethylene diacetate nor ethylene diphenyl ether is obtained. It is not very likely that they will be entirely consumed in secondary reactions.

2.11. The Liquid-phase Pyrolysis of Poly(ethylene Terephthalate)

(I), Terylene.

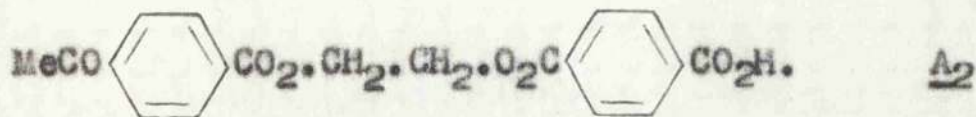
Poly(ethylene terephthalate) (I) is stable up to ca. 200° , but above 210° it begins to decompose. 10g. and 20g. samples of Terylene chips were heated in an open conical flask immersed in a bath of Wood's metal. The following preliminary observations were made:-

<u>Run.</u>	<u>Bath Temperature.</u>	<u>Duration</u>	<u>Decomposition.</u>
1.	100°	2hr.	Nil.
2.	145°	2hr.	Nil.
3.	190°	2hr.	Nil.
4.	$230-40^{\circ}$ (Temp. $^{\circ}$ in flask: $210-20^{\circ}$)	2hr.	White sublimate.

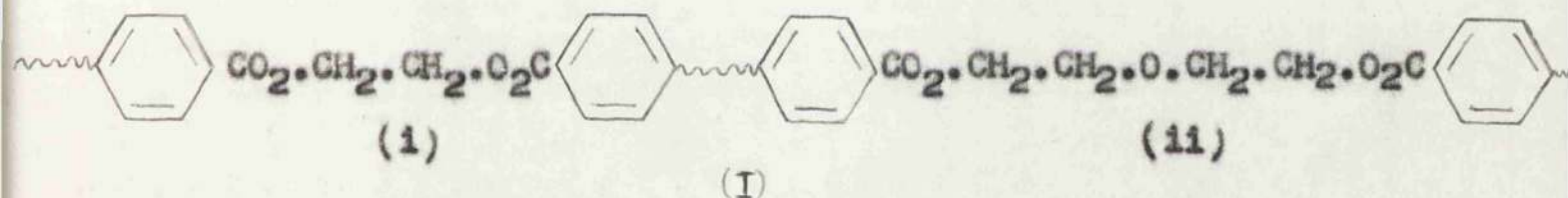
A sublimate was also formed when the experiment was performed under nitrogen ($230-40^{\circ}$). Thus, decomposition appears to set in just below the melting point of poly(ethylene terephthalate) (ca. 260°).

The liquid-phase pyrolysis of poly(ethylene terephthalate) was then carried out at 340° for five hours. The products included the following compounds: - (i) terephthalic acid, (ii) benzoic acid, (iii) 4-acetylbenzoic acid, (iv) acetaldehyde, (v) acetophenone, and (vi) a

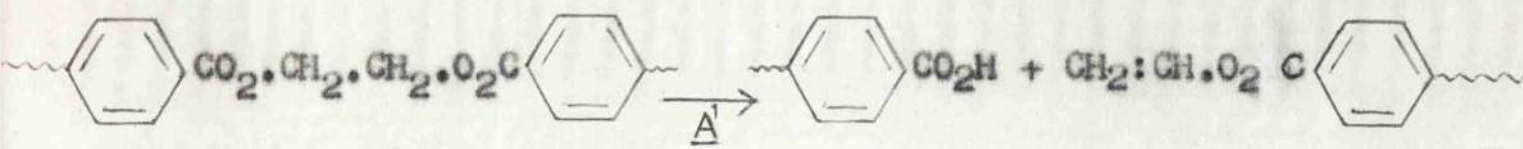
compound A₂ (see experimental section) that has been tentatively assigned the following formula:-



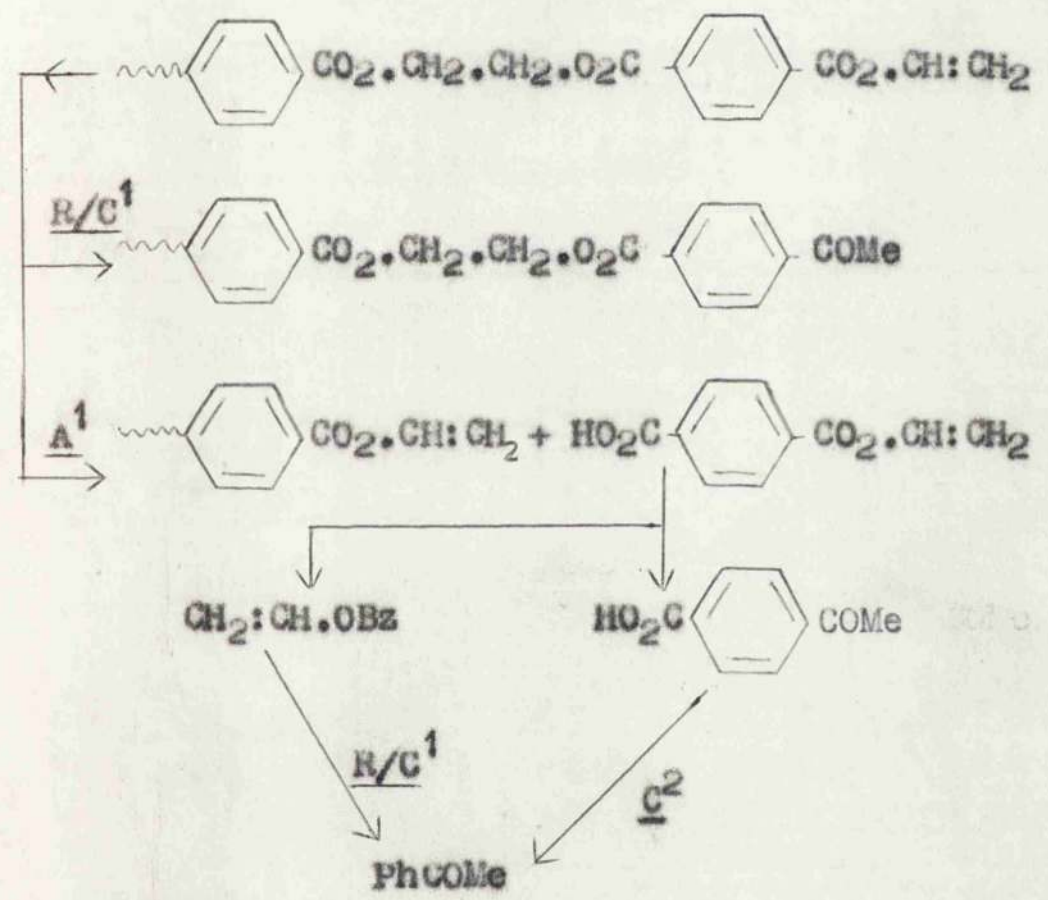
There was a residue (dark solid) (A₃), which is believed to be poly (ethylene terephthalate) of lower molecular weight than the initial value. There was no indication of the presence of (i) water, (ii) ethylene dibenzoate, (iii) a compound S having the properties described by Marshall and Todd (2) in their pyrolysis of Terylene at ca. 300° (mp. 150° decomp.)



A consideration of the formula of (technical) Terylene (above) suggests that the most important primary reaction in the degradation will probably be alkyl-oxygen scission at the predominating ethylene glycol units (i) and/or the subordinate diethylene glycol units (ii). On this basis, terephthalic acid should be an important primary decomposition product, and has been found by the previous workers; in addition, benzoic acid is formed by the well-known semi-decarboxylation of terephthalic acid. This A¹ scission gives rise concurrently to vinyl carboxylic esters, thus:



The secondary decomposition of the vinyl ester end-groups leads to the formation of methyl ketones by the known R/C¹ route. It is not possible to determine precisely the stages leading to acetophenone; but the following chart shows the various possibilities:-

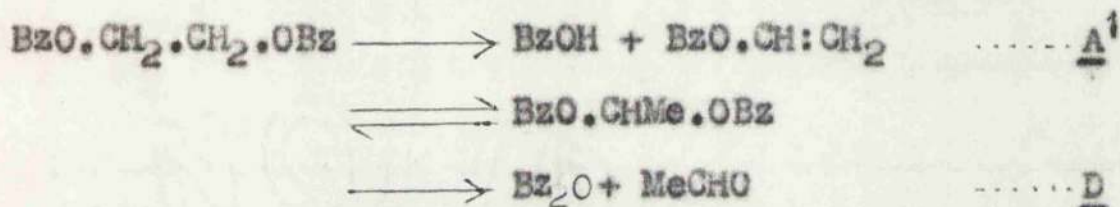


1:4-diacetylbenzene is a likely decomposition product of poly(ethylene terephthalate), but it was not found. This may have been due to the fact it is not formed at all, or more likely, is formed in such small amounts as to escape detection.

The formation of acetaldehyde in the decomposition of poly(ethylene terephthalate) has been reported before by Pohl(1)

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and Marshall and Todd (2). The two principal sources of acetaldehyde are, on the basis of results obtained with the model compounds, (i) a disproportionation reaction occurring at various points of the polyester chain, (ii) the ether linkages in the polyester chain, which yield first of all vinyl ethers by \underline{A}^1 scission and then acetaldehyde by \underline{A}^1 scission, OR It has already been shown by Allan (6) that consecutive \underline{A}^1 and \underline{D} reactions are responsible for the formation of benzoic anhydride and acetaldehyde in the pyrolysis of ethylene dibenzoate, thus:

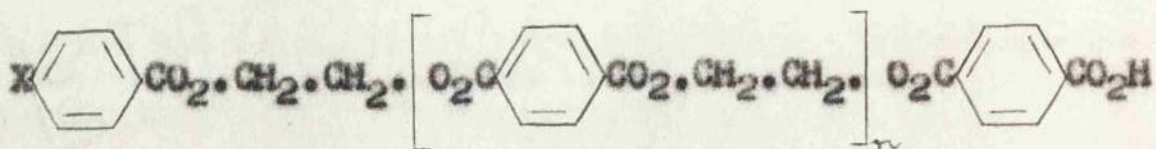


Precisely the same $\underline{A}^1/\underline{D}$ mechanism can explain the formation of acetaldehyde and acid anhydrides from poly(ethylene terephthalate). As random chain scission of the polyester chain proceeds, collision and interaction between carboxyl and vinyl ester end-groups will occur more frequently as the individual molecules become smaller.

2.12. Detection of a low molecular weight intermediate.

The identification of the compound \underline{A}_2 is based on various analytical figures. \underline{A}_2 was obtained from the pyrolysis residue by extraction with boiling acetone. It was, however, a sparingly soluble solid, the best solvent being glacial acetic acid. It was a carboxylic acid, dissolving in sodium hydrogen carbonate solution on warming and more readily in caustic alkali, and was reprecipitated

Table 1



n	X	E _{acid}	E _{CO₂⁻}	C (%)	H (%)	Glycol (%)
0	H	314	104.7	64.9	4.5	19.8
	CO ₂ H	179	89.5	60.3	3.9	17.3
	MeCO	356	118.7	63.9	4.5	17.4
1	H	506	101.2	64.0	4.3	24.5
	CO ₂ H	275	91.7	61.1	4.0	22.5
	MeCO	548	109.6	63.6	4.4	22.6
2	H	698	99.7	63.6	4.3	26.7
	CO ₂ H	371	92.8	61.5	4.0	25.0
	MeCO	740	105.7	63.2	4.3	25.1
3	H	890	98.9	63.4	4.3	27.9
	CO ₂ H	467	93.4	61.6	4.0	26.6
	MeCO	932	103.6	63.1	4.3	26.6

The formula of A_2 must be regarded as tentative, until it has been synthesised and compared with the original material. The formation of a compound such as A_2 is, however, compatible with previous results.

The residue A_3 from the pyrolysate was in all probability poly(ethylene terephthalate) of lower molecular weight than the initial value. It dissolved more readily in phenol than the starting material. Marshall and Todd (2) have shown that the molecular weight of the polyester decreases gradually on heating, and the liquid-phase pyrolysis at 340° (five hours) may therefore be expected to yield a polyester having a smaller molecular weight than the original material. A_3 on hydrolysis gave ethylene glycol and terephthalic acid. A compound having the formula, $-\left[CH_2 \cdot CH_2 \cdot O_2C \cdot C_6H_4 \cdot CO_2\right]_n-$ gives on hydrolysis 86.4% of terephthalic acid (by weight), whereas 87.9% of this acid was liberated on hydrolysis of A_3 . The slight excess is probably due to the presence of random anhydride linkages.

2.13. Pyrolysis of poly(ethylene terephthalate) in a flow-reactor.

The "vapour-phase" pyrolysis of poly(ethylene terephthalate) (I) was carried out by allowing molten Terylene (commercial material, chips) to drip into a glass reactor, modified for this purpose (Fig. 2) by fusing the

dropping funnel on to the reactor so as to dispense with a joint. Instead of a tap, a wide glass tube was used and the rate of flow was controlled by regulating the heating of the Terylene, and thereby its viscosity.

The results obtained in the vapour-phase at 450-75° are in good agreement with those obtained with the model compounds and with the results of the liquid-phase pyrolysis. The substituted ethylene dibenzoate (A₂) and the high-molecular-weight residue obtained in the liquid-phase pyrolysis were, however, absent. The products identified were (i) terephthalic acid, (ii) benzoic acid, (iii) 4-acetylbenzoic acid, (iv) vinyl benzoate, (v) acetophenone, (vi) acetaldehyde, (vii) an anhydride, (viii) carbon monoxide, (ix) carbon dioxide (x) methane, (xi) acetylene, and (xii) ethylene. The absence of the higher molecular-weight compounds obtained in the liquid-phase pyrolysis is probably due to the higher temperature involved in the present case. The results obtained in the flow-reactor show that the decomposition of poly(ethylene terephthalate) follows the same pattern essentially as before.

2.14 Conclusions.

An important aspect of the study of the thermal decomposition of poly(ethylene terephthalate) has been the detailed examination of the pyrolysis of several simple model compounds. The information derived from them, taken

together with previous knowledge, has made it possible to interpret more accurately the results obtained with the polyester. The important features of the decomposition of poly(ethylene terephthalate) may be summarised as follows:-

(1) The formation of terephthalic acid (by alkyl-oxygen scission), accompanied by the appearance of vinyl ester end-groups, (2) The formation of methyl ketones by R/C¹ conversion of a vinyl ester, the natural end-product being acetophenone, (3) The formation of acetaldehyde and anhydrides by a two-stage disproportionation reaction; the aldehyde can also be formed at ether linkages (diethylene glycol units) via vinyl ether intermediates, (4) Onset of decomposition of the polyester near its melting-point.

The elimination of acid in the pyrolysis of an ester probably takes place via a quasi six-membered ring intermediate. The conversion of a vinyl ester to a methyl ketone has been shown by Allan (5,6) to involve the formation of a β -ketoaldehyde. There appears, therefore, to be some justification for on a molecular basis, explaining the results obtained. Considering, however, the formation of ethylene from vinyl ethers and esters, and of benzaldehyde from the model compound 2-phenoxyethyl acetate, it is clear that no single mechanism accounts for all the facts. A very desirable corollary to the foregoing work would be a kinetic study of the various competitive routes observed, with a

view to deciding whether each one is molecular or radical
in nature, and a study on these lines has now been commenced
in these laboratories.

Chapter III - (Experimental)

3.1 Apparatus. (a) Flow-reactor:

The cracking unit consisted of a vertically supported Pyrex-glass tube represented diagrammatically in Fig. 1. It was filled with short lengths (ca. 1") of Pyrex-glass tubing, and had a contact volume of ca. 250 ml. It was heated electrically in a furnace whose silica tube was 18" long, and had a diameter of 2". The temperature of the furnace was controlled by a 'Sunvic' energy regulator. The temperature of the reactor was measured at approximately its middle, by means of a chromel-alumel thermocouple, encased in a glass sheath to prevent any catalysis by the metal. It probably represents the maximum temperature in the reactor, there being some variation due to radiation and convection effects.

(b) Static reactor:

This consisted of an ordinary round-bottomed 'Quickfit' flask with three necks, heated in an 'Electrothermal' heating mantle. The temperature was measured by an ordinary thermometer, using a 'Quickfit' thermometer pocket.

3.2 Method of Pyrolysis.

Most of the compounds mentioned in this dissertation were pyrolysed in the flow-reactor. Terylene

was cracked in the flow-reactor as well as in the static reactor. The pyrolysis was carried out by dropping the material from a funnel fitted with a side arm (see Fig. 1) to equalise pressure above and below. Solid compounds were melted, using a heating tape wrapped on the outside of the dropping funnel. For the pyrolysis of vinyl ether (IX), a triple-walled condenser was converted into a dropping funnel, and the ether was cooled during the run to prevent undue evaporation. The reactor was slightly modified for the vapour-phase pyrolysis of Terylene, and is shown in Fig. 2.

The pyrolysate, as it came out of the reactor, was divided into various fractions by fractional condensation. An outlet from the first receiver (high-boiling fractions and solids) led to a second receiver cooled in acetone-'Drikold', and thence to a 20-litre aspirator where the gas was collected at atmospheric pressure (constant level device) over water with an overlying paraffin layer. In many cases, appropriate chemical traps were placed between the first receiver and the aspirator. An aniline trap was used for keten (acetanilide). A solution of 2:4-dinitrophenylhydrazine in dilute hydrochloric acid / ethanol was used to collect volatile aldehydes - to give DNPs.

The pyrolyses were conducted in an atmosphere of nitrogen. The whole system was evacuated first, and then nitrogen passed through for several minutes before starting

a run. The evacuation was not carried out for every pyrolysis; in such cases the system was flushed with nitrogen for a longer period before commencing. Caution is necessary in evacuating the system, since the application of a vacuum to a well-heated glass tube may cause the latter to buckle. The passage of nitrogen was in general discontinued once the pyrolysis had begun. At the end of the run, the system was flushed with nitrogen to expel all pyrolysis gases.

3.3. Temperature and Contact Time:

As mentioned in the introduction to this thesis, the object of the work was a full qualitative study of the thermal decomposition of poly(ethylene terephthalate) or Terylene. There being no set conditions of temperature and contact time which had to be followed, the pyrolyses of the model and related compounds were carried out in the region of 350-550°, using a rate of flow of ca. 0.3-1.0g/min. The pyrolysis of Terylene was effected in the static reactor at 340°. Previous workers had employed slightly lower temperatures. It has been found that in the range employed, an increase in temperature or contact time leads only to increased decomposition, and perhaps to greater carbonisation. The latter appears to be a constant feature of the thermal decompositions studied, the amount of carbonisation being variable. The procedure with regard to carbonisation was as follows. When the reactor was used successively for the

pyrolysis of the same compound, it was freed from soluble matter, before a run, using ordinary solvents. When the amount of carbonisation was such that it might have caused blocking during a run, the reactor was cleaned thoroughly before starting. The carbon deposit was removed very simply by heating to a sufficiently high temperature in the furnace.

3.4. Methods of Analysis.

Pyrolysate fractions were divided where possible into different groups by chemical methods of separation. This applied in particular to the removal of carboxylic acids. The neutral fractions were usually liquid and fractionally distilled. Caution is necessary in employing fractionating columns, because the longer periods of heating that are then necessary sometimes cause further chemical changes to take place, and in any case lead to slight loss of material. The examination of the various fractions obtained from a pyrolysis was done by established procedures. The knowledge derived from boiling points was useful, in that some possible constituents could be eliminated straightaway. Solid materials were confirmed by mixed melting points. Gases were analysed by the standard Hempel method.

3.5. Use of infra-red spectrometry:

The normal chemical methods of examination of pyrolysate fractions were in many cases supplemented

by (a) infra-red spectroscopy, and (b) chromatography, and (c) colour tests.

The infra-red analyses were done in a double beam spectrometer, described by Brownlie (58). Solid samples were done as a Nujol mull. Liquids were determined either in capillary films or in standard cells. Gases were examined in a 10 cm. cell. The windows were all of sodium chloride. The identification of pyrolysate fractions involved comparison of their infra-red spectra with standard compounds. This method of proving the identity of a compound, viz., the obtaining of two identical spectra, one of the unknown and one of a known, is very accurate, and in many cases rapid.

3.6. Chromatography:

The technique of paper chromatography consists of applying a very small amount of substance on one side of a sheet of filter-paper, and then feeding the paper with a developing solvent in a tank saturated with vapour of the solvent. The spot of material travels along the paper (upwards or downwards) and is located visually, by means of a spray, or by means of ultra-violet light or some such means. For a given set of conditions of paper, temperature, and solvent, the ratio of the distance travelled by a spot to the distance travelled by the solvent is constant, and is called the R_f value.

$$\frac{\text{Distance travelled by substance}}{\text{Distance travelled by solvent}} = \frac{R_F}{}$$

The identification of an unknown is very simply accomplished by spotting several suspected standards along with it and then developing with one or more sets of solvents. Two samples which are the same give spots at similar positions for any solvent system.

The paper chromatographic method of analysis has been applied in the present instance chiefly to aldehydes and ketones, and also to an acid. Aldehydes and ketones have been identified by their 2:4-dinitrophenylhydrazones, or DNPs. The mixed melting point method is satisfactory in many cases, but the application of the chromatographic method enables very small amounts of material to be detected. The latter is one of the very special merits of paper chromatographic method of analysis.

The method of Burton (45) has been employed for the analysis of DNPs obtained from pyrolysate fractions. Whatman No. 1 paper was treated with either 70% aq. ethyl lactate, or ethyl tartrate in aqueous methanol (ethyl tartrate: water: methanol = 1:3:12) and dried until surface wetness had just disappeared. The degree of drying has a profound effect on R_F values, and so standard compounds were used in all cases for identification. It was found after trial, that by using slightly over-dried paper, the time required could be

- 01 -

considerably reduced without affecting the identification of the spots. The latter were in many cases visible as pale yellow spots, but always showed up in ultra-violet light as dark spots. There was not much difference between ethyl lactate and ethyl tartrate as stationary phases, and their use was somewhat arbitrary. When using the DNP of 4-acetylbenzoic acid, however, the latter was employed. The solvent used for irrigation was 1.75 or 2% solution of carbon tetrachloride in light petroleum (60-80°). For identifying 4-acetylbenzoic acid DNP, a 20% solution of acetone in light petroleum (60-80°) was found to be effective. The carbon tetrachloride/light petroleum mixture was inadequate to distinguish between benzaldehyde and acetaldehyde, and this was overcome by using untreated paper and a 5% solution of ether in light petroleum (60-80°) (46).

The occurrence of streaking was found to be unavoidable in some cases, without using a more powerful solvent system which prejudiced the separation. For the identification of some constituents, however, this did not matter. To distinguish between the DNPs of acetophenone and 4-chloroacetophenone proved very difficult. Both have nearly the same R_f values, and with the presence of some streaking, the separation between the two in a mixture was not very obvious. To make the identification more rigorous, the DNP mixture was first chromatographed on a column of

bentonite /kieselguhr (39) using chloroform as eluting solvent, and finally working upto 100% acetone. The eluate was collected in 10 ml. fractions and the various constituents identified by plotting optical density against fraction number. The fractions containing one constituent were collected and concentrated to small volume. The latter were then analysed on paper in the usual way. Using single compounds thus, the identification of the DNPs of acetophenone and 4-chloroacetophenone was accomplished.

The paper chromatography of substituted benzoic acids has not been done to any great extent in the past. The pyrolysis of 2-(4-chlorobenzoyloxy)ethyl terephthalate (VII) involved the identification of benzoic acid in the presence of 4-chlorobenzoic acid. This has been done by the method of paper chromatography. For this purpose, Whatman No. 1 paper was used with 40% aqueous acetone as developer, and bromophenol blue as spray indicator. The spots were revealed as yellow spots against a blue background.

3.7. Colour tests:

The colour reaction test was used (1) for the examination of methyl and ethyl benzoates in one of the pyrolyses of 2:2'-dibenzoyloxyethyl diethyl ether (IV). For this purpose, the total pyrolysate was hydrolysed and

distilled. The low boiling material so obtained was used to test for the presence of an alcohol by the xanthate colour test (34). No alcohol was found. A blank with a trace of methanol was carried out at the same time. (ii) Several of the compounds examined gave rise on pyrolysis to small amounts of anhydride the identification of which in traces is a matter of some difficulty. Hurd and Bennet identified benzoic anhydride formed in the pyrolysis of benzyl benzoate, by the absorption of a small amount of bromine without the evolution of hydrogen bromide (14). A more elegant test for linear anhydrides was described by Davidson and Newman (47) using α -4-nitrobenzamidophenylacetic acid. The test is done in pyridine solution, and a blue colour is obtained almost immediately, the colour soon fading away. By applying this delicate test, the presence of anhydride has been revealed, which may otherwise have escaped detection.

3.8. Synthesis.

The synthesis of the model compounds, and the other compounds relevant to this work, is described. The gift of the following chemicals by Imperial Chemical Industries, Ltd. is acknowledged gratefully. (i) 2-hydroxyethyl terephthalate, and (ii) poly(ethylene terephthalate), or Terylene, chips.

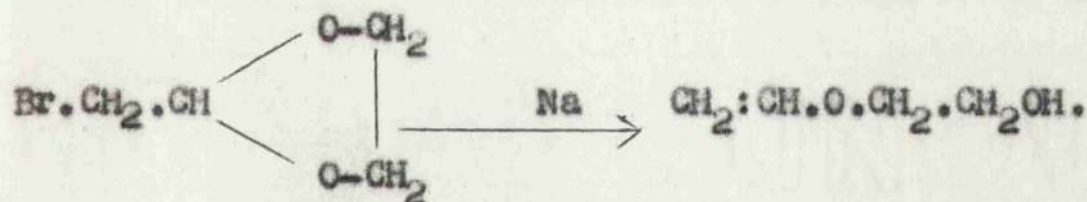
(1) 2:2'-Dibenzoyloxydiethyl Ether (IV) (48).

(a) Dry sodium benzoate (50g.), 2:2'-dichlorodiethyl ether (100g.) and a few drops of diethylamine, heated at 200° (6 hr.), yielded 2-chloro-2'-benzoyloxydiethyl ether, b.p. 166°/8mm. (lit. b.p. 191°/25mm.) (Found: C, 58.1 ; H, 6.0. Calc. for C₁₈H₁₈O₅Cl: C, 57.8 ; H, 5.7%) and the ether-diester (IV) (10g.; 18% of theory), m.p. 33.5°, b.p. 250°/3mm. (lit: b.p. 279-81°/24 mm.; no m.p. recorded previously).

(b) 2:2'-Dihydroxydiethyl ether (diethylene glycol), on benzylation (Schotten-Baumann), yielded the ether-diester (IV) smoothly (47% of theory) (Found: C, 68.6; H, 6.0. Calc. for C₁₈ H₁₈ O₅: C, 68.8; H, 5.7%).

(ii) Ethylene bromoacetal (49)

This is a starting material for making 2-hydroxyethyl vinyl ether, thus:



125g. of paraldehyde were brominated at -10°, with 315g. bromine as described by Hill and Pidgeon (49); after 10 hours, 135g. ethylene glycol were added slowly, to prevent heating. After six hours at room temperature, the mixture was taken up in ether, and washed successively

with concentrated sodium bisulphite solution, 10% alkali, water, and dried over potassium carbonate. Distillation afforded 185g. of material, b.p. $62^{\circ}/4.5$ mm. Lit: b.p. $68-71^{\circ}/15$ mm.

(iii) 2-Hydroxyethyl vinyl ether:

75g. bromoethylidene ethylene glycol were gently warmed with 20g. sodium in 150 ml. anhydrous ether for 7 hours. The brown deposit obtained was decomposed with water (150ml.), taken up in ether, and dried (potassium carbonate). Distillation gave ca. 10g. of 2-hydroxyethyl vinyl ether, b.p. $44-5^{\circ}/10$ mm., used without further purification in the next step.

(iv) 2-Benzoyloxyethyl vinyl ether (X).

(a) 2-Hydroxyethyl vinyl ether (10g.), treated with 10ml. benzoyl chloride in pyridine (20ml.) in the usual way, gave 5.7g. (X), b.p., $130-40^{\circ}/9$ mm. Lit: b.p. $133^{\circ}/9$ mm.

(b) Attempts to prepare (X) by dehydrochlorination of 2-chloro-2'-benzoyloxydiethyl ether with pyridine, quinoline, or collidine were unsatisfactory on account of low yields. Heating in an autoclave led to total resinification.

(c) The best results were obtained as follows. Dry sodium benzoate (60g.), 2-chloroethyl vinyl ether (200g.) and triethylamine (3g.) (found to be a better catalyst than diethylamine), refluxed gently for 24 hours and filtered,

gave 70g. (87% theory) of the ether-ester (X), b.p. 138-40°/15mm. Lit: b.p. 133°/9mm.

(v) 2-Hydroxyethyl benzoate (V) (17):

Sodium benzoate (200g.), ethylene chlorhydrin (400ml.) and a few drops of diethylamine, heated for four hours at 140° and filtered, gave 415g. (V), b.p. 146°/3mm. and m.p. 37°. Lit: b.p. 173°/21mm. It has been described as a solid (50) m.p. 45°. (Found : C, 65.7; H, 6.1; Calc. for $C_9H_{10}O_3$: C, 65.1 ; H, 6.0%).

(vi) 2-Hydroxyethyl terephthalate:

Sodium terephthalate (8g.) was heated with ethylene chlorhydrin (20ml.) and a few drops of diethylamine for 24hr. at 140°. After the sodium salts had been filtered off, the filtrate slowly yielded a white solid. Yield : 1.3g. It crystallised from acetone as shining plates, m.p. 112°, and did not depress the melting point of a sample of 2-hydroxyethyl terephthalate, supplied by Imperial Chemical Industries, Ltd.

(vii) 2-Chloroethyl 4-Chlorobenzoate:

Ethylene chlorhydrin (20g.) was heated with 4-chlorobenzoyl chloride (45g.) for two hours on a boiling water bath, and left overnight, when a white solid was obtained. It was dissolved in ether, washed twice with dilute alkali, then with water and dried over $CaCl_2$. Distillation afforded 42g. of pure 2-chloroethyl

4-chlorobenzoate, b.p. 145°/5mm. and m.p. 40°.

(viii) 2-(4-Chlorobenzoyloxy)ethyl terephthalate(VII):

(a) 2-Chloroethyl 4-chlorobenzoate (21g.), sodium terephthalate (10g.), and a few drops of diethylamine were heated in tetralin (25ml.) for 6 hr. at 200°. The mixture was poured into 200ml. water, and extracted repeatedly with chloroform (CaCl₂). Evaporation of solvent gave a dark-brown liquid with a solid suspension. The latter was filtered off and recrystallised from methanol several times (Norit). (VII) was obtained as a finely divided solid, m.p. 140°. (Found : C,59.1; H,4.1%;

C₂₆ H₂₀ O₈ Cl₂ requires C, 58.8 ; H,3.8%).

(b) 2-Hydroxyethyl terephthalate (10g.) was treated in pyridine solution (20ml.) with 4-chlorobenzoyl chloride (14g.), warmed for a short while and poured into 100ml cold water. The yellow solid obtained was filtered, and washed successively with dilute hydrochloric acid, sodium hydrogen carbonate solution, and water. It was then recrystallised thrice from ethanol: m.p. 138-40°. (Found : C,59.0;H,4.3; Cl,13.7; C₂₆ H₂₀ O₈ Cl₂ requires C,58.8; H,3.8; Cl,13.4 %). A mixed melting point with a sample prepared as in (a) was 139°. Yield: Quantitative.

(ix) Ethylene di-4-chlorobenzoate:

This was made by treating ethylene glycol with an equivalent amount of 4-chlorobenzoyl chloride in

pyridine solution. It was recrystallised from ethanol, m.p. 142-3° Heim and Poe (50) give the m.p. as 140°.

(x) 2-Benzoyloxyethyl 4-chlorobenzoate (XXI)

2-Hydroxyethyl benzoate (10g.) was treated with 4-chlorobenzoyl chloride (10.5g) and pyridine (10ml.), and after a short period of reaction, the mixture was poured into water. The solid precipitate crystallised from ethanol as needles m.p. 188°.

(xi) 4-Ethylacetophenone (51)

Ethylbenzene (100g.) was dissolved in carbon tetrachloride (600ml.) and treated with acetic anhydride (112g.) and anhydrous aluminium chloride (146g.) After 4 hr. the mixture was poured into a large excess of water, the decomposition of the complex being completed by the addition of hydrochloric acid. The carbon tetrachloride layer was separated, dried over potassium carbonate, and distilled. The fraction boiling at 210-45° (30g.) was taken as the required substance and used without further purification for the next stage. Lit: b.p. 235°, 236°.

(xii) 1:4-Diacetylbenzene (XIX):

4-Ethylacetophenone (28g.) was partially oxidised by heating at 150° for 24 hr. while dry air was blown through, using a mixture of chromium sesquioxide (0.3g.) and cadmium carbonate (0.1g.) as catalyst. On cooling, the

mass solidified. It was dissolved in ether (250ml.), and washed with sodium carbonate solution. After drying over CaCl_2 , ether was removed, and the residue distilled at reduced pressure. The solid distillate was the required 1:4-diacetylbenzene. It was obtained in rather poor yield, mainly because of loss of 4-ethylacetophenone when air was passed through. A crude sample melted at 103° . Lit: m.p. $111-12^\circ$.

The DNP of 1:4-diacetylbenzene was made by reacting the ketone with a large excess of reagent. In spite of this however, the derivative, after crystallisation from glacial acetic acid, showed two spots when analysed chromatographically on filter paper. The two spots are probably due to the mono- and di- DNPs of 1.4 diacetylbenzene. The mixture was used without resolution, when used as reference material for the testing of unknown DNPs for the presence of 1:4-diacetylbenzene.

(xiii) 2-Chloroethyl benzoate (XXII) (52):

Ethylene chlorhydrin (100g.) was heated with benzoyl chloride (192g.) on a water bath, brought gradually to boiling. After 2 hr., the mixture was set aside overnight. The mixture was poured into a separating funnel containing 200ml. water and solid sodium hydrogen carbonate added till all acid was neutralised. The oily layer was taken up in

ether (100ml.), washed with water, and dried over CaCl_2 . Distillation afforded (XXII) as a colourless liquid, b.p. $152^\circ/15\text{mm.}$ (Lit: $118-20^\circ/2\text{mm.}$). Yield: 194g. (84.5% of theory).

(xiv) 2-Phenoxyethyl acetate (VIII) :

2-Phenoxyethanol (27.6g.) was refluxed gently for 4 hr. with acetic anhydride (50ml.) and a few drops of pyridine. The product was worked up as usual, and amounted to 29g. of a colourless liquid, b.p. $252-6^\circ$. (Found : C, 67.1; H, 6.9; Calc. for $\text{C}_{10}\text{H}_{12}\text{O}_3$, C, 66.7; H, 6.7%). (n_D^{22} : 1.504). Yield : 80.6% of theory.

(xv) Phenoxyacetaldehyde (53):

2-Phenoxyethanol (30g.) was oxidised using potassium dichromate (20g.), conc. sulphuric acid (25ml.) and water (200ml.). After half an hour at room temperature, the product was dissolved in ether, and washed with sodium carbonate solution, and dried over sodium sulphate. Distillation afforded phenoxyacetaldehyde as an oily liquid, $130^\circ/15\text{mm.}$ The distillate was freed from 2-phenoxyethanol by shaking with alkali, from ether solution. Phenoxyacetaldehyde gave a brownish DNP, crystallising from ethanol as fine needles, m.p. 128° . It gave a single, clear spot, when analysed chromatographically on filter paper.

(xvi) 2-Bromoethyl phenyl ether :

Phenol (188g.) was heated with ethylene dibromide (376g.) and 800ml. 10% sodium hydroxide solution, for 5 hr. The product was cooled, extracted with ether, washed well with water, and dried (CaCl_2). Removal of ether gave 350g. of crude 2-bromoethyl phenyl ether, which was a mass of shiny white plates, m.p. 30° (Lit: 35°). It was not distilled further, as it decomposes easily.

(xvii) Phenyl vinyl ether (XVI) (54) :

2-Bromoethyl phenyl ether (400g.) was gently refluxed over solid sodium hydroxide (400g.) for 5 hr. whereby a fraction (b.p. ca. 100°) was obtained, separating into two layers. When the residue showed no sign of distilling any further, suction was carefully applied. 120g. of a colourless liquid was thus obtained (b.p. $292-5^\circ/6\text{mm.}$), solidifying immediately. It recrystallised from ethanol as white leaflets, and was identical with ethylene diphenyl ether, m.p. and mixed m.p. 98° . The low boiling emulsion was extracted with ether, dried, and distilled twice. Pure phenyl vinyl ether free from halogen compounds was thus obtained. Yield: 22g. Boiling point : $155-8^\circ$. The low yield was due to the unexpected formation of ethylene diphenyl ether. Allowing for the presence of small amounts of it in the 2-bromoethyl phenyl ether, it is apparent that most of it arose out of

a disproportionation of the latter. Its formation has not been reported before; it may be a general reaction since it was formed by heating (refluxing) a pure sample of 2-chloroethyl phenyl ether.

(xviii) Ethylene glycol diphenyl ether :

A solution of phenol (9.4g.) in 8% sodium hydroxide (50ml.) was refluxed with ethylene dibromide (9.4g.) for a few hours, cooled and filtered. The solid that separated crystallised from ethanol as plates, m.p. 98°.

(xix) α -Aminophenylacetic acid (55):

Sodium cyanide (25g.) was dissolved in water (100ml.), and then 26.5g. ammonium chloride added. When all had dissolved, a solution of benzaldehyde (53g.) in ethanol (100ml.) was added. The mixture was shaken thoroughly and allowed to stand for 1½ hr. water (250ml.) was then added, causing an oil to separate. This was collected in benzene (250ml.) and washed with water. The amino nitrile so obtained was extracted from benzene solution by shaking it twice with 150ml. hydrochloric acid solution (1:1). The aqueous solution was refluxed for two hours, cooled, and filtered from small amounts of tarry material. The free amino acid was precipitated with ammonium hydroxide, filtered, washed with water, and some

ethanol, and dried. Yield : 15.1g. m.p. : 264°.

(xx) ~~α-(4-Nitrobenzamid)~~phenylacetic acid (55) :

A solution of pure α-aminophenylacetic acid (15.1g.) was dissolved in 120 ml. 10% sodium hydroxide solution and made up to 250 ml. with water. 16g. of sodium hydrogen carbonate were then added, causing a part of the amino acid to precipitate. Finally, 20g. finely divided 4-nitrobenzoyl chloride was added, and the mixture vigorously stirred for 50 min., maintaining the temperature below 20°. At the end of the time, the acid and acid chloride had gone into solution (deep purple). The solution was filtered, and acidified with an excess of 10% hydrochloric acid. The pink sticky solid obtained soon turned into a flocculent white solid. It was filtered, and recrystallised from ethanol. Yield: 13.8g. m.p. : 184°. Lit: m.p. 184°. Its solution in pyridine gave a deep blue colour with acetic and benzoic anhydrides, which gradually faded away.

Details of Pyrolysis of Various Compounds:

3.9. 2:2'-Dibenzoyloxydiethyl ether (IV).

Pyrolysis I. - Distillation of (IV) at atmospheric pressure led to some decomposition. From the distillate, benzoic acid was removed by sodium hydrogen carbonate. The neutral fraction afforded a DNP, which was identical with acetophenone DNP (m.p. and mixed m.p. 238-9°).

Pyrolysis 2. The details of this pyrolysis are given in Table 2. Distillation of (a) yielded acetaldehyde, followed by (i) 6g. 80-90° (mainly benzene, characterised as m-dinitrobenzene, m.p. and mixed m.p. 90°), (ii) 2.6g., b.p. 90-120°, and (iii) 1.6g., b.p. 120-160° (containing styrene; infra-red). Benzoic acid was removed from the residue, by sodium hydrogen carbonate; further distillation then yielded (iv) 1.4g., b.p. 160-210° (containing acetophenone, DNP, m.p. and mixed m.p. 240°), (v) 4g., b.p. 210-80°, and (vi) 8.5g., high boiling residue. The gaseous pyrolysate (b) contained carbon monoxide and dioxide, methane, ethylene, and acetylene, but no propene (infra-red). As in previous pyrolyses (5), the infra-red spectrum of (b) showed a strong unallocated band at 1140 cm^{-1} . This band was not found in the present case when the pyrolysis temperature was below 550°. Keten was absent.

Pyrolysis 3. Vinyl ether (IX) was identified in the 'Drikold' trap (infra-red). The total pyrolysate (a) was refluxed (1 hr.) with 10% aqueous sodium hydroxide (100ml.); a distillation of the hydrolysate (water-bath) yielded no alcohols (xanthate colour test) (34). A control test with methanol gave a positive result.

Pyrolysis 4. The liquid pyrolysate (a) contained benzoic anhydride (colour reaction) (47). Distillation of (a) then

yielded 7.1g., b.p. 190-240^o/15 mm., which was found to contain ethylene dibenzoate, m.p. and mixed m.p. 73^o.

3.10. 2-Benzoyloxyethyl vinyl ether (X)

Pyrolysis 5. The 'Drikold' trap contained vinyl ether (IX) (infra-red) and acetaldehyde. Distillation of the main liquid pyrolysate yielded a fraction containing benzoic acid, but no ethylene dibenzoate (contrast Pyrolysis 6). The gaseous pyrolysate (b) contained carbon monoxide and dioxide, methane, ethylene, and acetylene, but no propene (infra-red). Keten was absent (aniline trap).

Pyrolysis 6. The 'Drikold' trap contained acetaldehyde and an unsaturated liquid (not positively identified, but probably vinyl ether). Distillation of (a) yielded benzoic acid, and the following liquid fractions: (i) b.p. 20-60^o, (ii) b.p. 60-130^o, (iii) b.p. 130-160^o, (iv) b.p. 100-110^o/15mm., (v) 110-40^o/15 mm., and (vi) b.p. above 200^o/15 mm. Fraction (iv) contained acetophenone (paper chromatography of DNP) ; fraction (vi) consisted of ethylene dibenzoate, m.p. and mixed m.p. 73^o.

Pyrolysis 7. The 'Drikold' trap contained acetaldehyde. Distillation of (a) yielded 3.7g., b.p. 94^o/15 mm. (vinyl benzoate ; infra-red), a trace of benzoic acid, and unchanged 2-benzoyloxyethyl vinyl ether.

3.11. Vinyl ether (IX).

The material was obtained commercially

(anaesthetic quality ; ex- May and Baker Ltd.). Before use, it was freed from inhibitor by distillation, b.p. 28-34°.

Pyrolysis 8. The liquid pyrolysate (a) consisted of unchanged vinyl ether (infra-red) and acetaldehyde. Liquid (a) yielded an immediate precipitate of acetaldehyde DNP, whereas pure vinyl ether yields this substance only very slowly, as a result of gradual hydrolysis of the ether. The gaseous pyrolysate contained carbon monoxide, methane, ethylene, and acetylene, but no propene (infra-red).

3.12 n-Butyl vinyl ether (XIV).

The ether (ex. Light & Co.) was carefully redistilled before use, b.p. 92-94°.

Pyrolysis 9. Acetaldehyde was identified as in Pyrolysis 8. The 'Drikold' trap contained an olefinic liquid; treated with bromine, this yielded 1:2-dibromobutane, b.p. 162-67° (lit. 166°). The main liquid pyrolysate (a) had b.p. 92-97°, and was unchanged.(XIV). There was no evidence of keten (aniline trap), n-butyraldehyde, or any other breakdown product. The gaseous fraction (b) contained carbon monoxide, methane, and ethylene (infra-red).

3.13. iso-Butyl vinyl ether (XV).

The ether was obtained commercially ex. Light & Co.), and was carefully redistilled before use, b.p. 82°.

Pyrolysis 10. Acetaldehyde was identified as in Pyrolysis 8. The 'Drikold' trap contained an olefinic liquid; treated with bromine, this yielded 1:2-dibromoisobutane (9g.), b.p. 149° , n_D^{10} : 1.513 (lit. b.p. $149-51^{\circ}$, n_D^{20} : 1.512). The main liquid pyrolysate (a) had b.p. 83° , and was unchanged (XV). There was no evidence of keten (aniline trap), isobutyraldehyde, or any other breakdown product.

3.14. Phenyl vinyl ether (XVI).

Pyrolysis II. The liquid pyrolysate (a) was divided into a phenolic (6g.) and a non-phenolic fraction (4g.) by means of alkali. The former consisted of phenol (b.p. $60-75^{\circ}$ / 6mm.; benzoate m.p. 64° , mixed m.p. with pure phenyl benzoate (m.p. 68°) was $64-8^{\circ}$. The redistilled material was examined by gas-liquid chromatography and shown to contain phenol, and no o-cresol, or o-vinyl phenol. The neutral fraction on redistillation from a micro-distillation flask showed a b.p. $120-35^{\circ}$; yield: ca. 2g. From its boiling point, the presence of diphenyl acetal (b.p. 256°) can be ruled out. The infra-red spectrum showed the absence of benzene. Since, the substance did not give a DNP, the possibility of phenylacetaldehyde and benzaldehyde can be eliminated. It decolorised bromine/carbon tetrachloride, and neutral permanganate.

3.15. 2-Hydroxyethyl benzoate (V).

Pyrolysis I2. Acetaldehyde was identified from a DNP trap

(m.p. and mixed m.p. of derivative : 161°). Distillation of (a) yielded water (0.6g.) (copper sulphate test). The material was cooled, dissolved in ether (100ml.), and extracted with 100ml. water, and then with a saturated solution of sodium hydrogen carbonate (250ml.). The neutral, ether soluble material remaining, was ethylene dibenzoate (major portion of pyrolysate collected; m.p. and mixed m.p. 73°). The aqueous extract on benzoylation gave ethylene dibenzoate. The sodium hydrogen carbonate extract on acidification turned a little cloudy, showing that the amount of acid present was negligible.

Pyrolysis 13. Distillation of (a) gave (i) acetaldehyde, (ii) a liquid (emulsion) b.p. 80° (0.4g.), probably benzene, and (iii) water (2.3g.). Treatment with alkali removed benzoic acid (26.8g.). The final fraction was ethylene dibenzoate (24.1g.), containing small amounts of benzoic anhydride (colour test). The gaseous pyrolysate contained no hydrogen. There was no evidence for vinyl benzoate, or acetophenone.

3.16. Ethylene glycol.

Pyrolysis 14. No acetaldehyde was detectable by means of a DNP trap. The liquid (a) was unchanged ethylene glycol, containing no 2-hydroxyethyl ether (infra-red). It contained, however, a trace of water. This was proved by a

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Karl Fisher estimation of the amount of water present in the ethylene glycol before and after pyrolysis (see Appendix III). This is done by estimating the amount of water per ml. of substance. 1 ml. of material was dissolved in 10ml. absolute methanol, and titrated against the reagent in the standard apparatus. The titre values are given below: -

Standard solution (0.5% methanolic solution of water) — 3.5, 3.3ml.
Ethylene glycol (before pyrolysis) — 1.7, 1.9, 1.8ml.
Pyrolysate (ethylene glycol after pyrolysis). — 14.1, 14.5ml.

3.17. 2-Hydroxyethyl ether.

Pyrolysis 15. Acetaldehyde was detected in the usual way (DNP, chromatography). Distillation of (a) afforded water (copper sulphate test, Karl Fisher reagent) (ca. $\frac{1}{2}$ lg.).

3.18. 2-Chloroethyl benzoate (XXII).

Pyrolysis 16. Hydrogen chloride was detected by means of a water trap (reaction with sodium hydrogen carbonate, and silver nitrate). A DNP trap was found to contain a precipitate, which was, however, too small to identify. It showed nevertheless the presence of a trace of a volatile carbonyl compound, probably acetaldehyde. A 'Drikold' trap contained vinyl chloride (infra-red) (1-2 ml., 'Drikold' trap).

The liquid (a) on distillation gave (i) b.p. 160-80°/26 mm. (12.9g.), unchanged (XXII), and (ii)

ethylene dibenzoate (17.5g.), m.p. and mixed m.p. 73°.

The latter contained a trace of benzoic anhydride (colour test). Neither ethylene dichloride nor benzoic acid were found.

Pyrolysis 17. Hydrogen chloride and vinyl chloride were identified as in Pyrolysis 16. From (a) was obtained this time, 3g. benzoic acid, (ii) unchanged (XXII) (24g.), and (iii) a minute amount of a white crystalline solid. It could not be crystallised satisfactorily but since its m.p. was raised on admixture with ethylene dibenzoate (m.p. 73°) from 60° to 69°, it was in all probability ethylene dibenzoate.

Pyrolysis 18. Hydrogen chloride and vinyl chloride were identified as before. A DNP trap showed the presence of a volatile aldehyde or ketone, from a small amount of precipitate. From (a) was obtained 15g. benzoic acid, 4lg. pure unchanged (XXII), and ca. 1 g. of material b.p. 215°/15mm. which solidified partially. The latter could not be identified positively as ethylene dibenzoate. It contained traces of benzoic anhydride (colour test).

Pyrolysis 19. Hydrogen chloride and vinyl chloride (ca. 25 ml., 'Drikold' trap) were identified as before. The DNP trap again showed a minute amount of precipitate. From (a) was obtained 23.0 g. benzoic acid, and 12.3 g. unchanged

2-chloroethyl benzoate. Benzoic anhydride was found as before. ca. 0.1g. of liquid boiling above 280° was obtained and appeared to solidify partially. It could not be identified positively as ethylene dibenzoate.

3.19. Ethylene dichloride.

Pyrolysis 20. The hydrogen chloride formed in the reaction was collected in 100 ml. distilled water, and the solution titrated against standard alkali. From the amount of hydrogen chloride formed, the extent of ethylene dichloride decomposed was found to be 7.2%.

3.20. 2-Phenoxyethanol (XXIII).

Pyrolysis 21. Acetaldehyde was identified from a DNP trap. Distillation of (a) yielded water (2.7g.). The residue was dissolved in ether (100ml.) and extracted with water (2 x 50 ml.) (A) and then with 10% sodium hydroxide (2 x 50 ml.) (B), and finally washed with water. The ether residues were dried over CaCl_2 (C). A on benzylation did not give ethylene dibenzoate, showing the absence of ethylene glycol. B was acidified to litmus and extracted with ether. Distillation of the residue (5g.) yielded (i) b.p. $180-90^{\circ}$, (ii) b.p. $190-210^{\circ}$, (iii) b.p. $210-32^{\circ}$. Fraction (i) was phenol (benzoate, m.p. 65° ; mixed m.p. 68°). Fractions (ii) and (iii) were found by infra-red analysis to be unchanged 2-phenoxyethanol. There was no positive

evidence for phenyl vinyl ether (b.p. 156°), diphenyl ether (m.p. 98°), (iii) diphenyl acetal (b.p. 256°), or (iv) coumaran (b.p. 188°).

3.21. 2-Phenoxyethyl acetate (VIII).

Pyrolysis 22. Acetaldehyde was identified from a DNP trap. An aniline trap showed the absence of keten. Distillation of (a) yielded (i) b.p. 100-30°, (ii) b.p. 150-70°, (iii) ca. 180°, (iv) b.p. 200°, and (v) a distillation residue. From (ii) was obtained a nitro derivative, mixed m.p. with 2:4-dinitroanisole: 85° (original sample m.p. 90°). The presence of anisole is therefore inferred. Hydrolysis of (ii) yielded acetaldehyde (DNP, chromatography) showing also that a vinyl ether/ester is present. Fraction (iii) gave a negative ferric reaction but yielded a DNP readily. This was found to be that of benzaldehyde by paper chromatography using two solvent systems (45, 46). Fraction (iv) was unchanged ester (VIII).

Pyrolysis 23. Acetone was detected in the 'Drikold' trap by its DNP (m.p. and mixed m.p. 126°; paper chromatography). The liquid (a) was washed with water to remove acetic acid. After drying, distillation afforded (i) b.p. 145°, (ii) b.p. 150-60°, (iii) b.p. 170-80°, (iv) b.p. 180-200°, (v) b.p. 200-20°, (vi) b.p. 220-70°, (vii) residue. 9g. Fraction (ii) treated with bromine /carbon tetrachloride gave ca. 16g. 1:2-dibromoethyl phenyl ether, b.p. 120° /6mm.

and n_D^{20} : 1.585 (lit. b.p. $141^\circ/18$ mm, n_D^{20} : 1.5845). Fraction (ii) consisted largely of phenyl vinyl ether. Fraction (iv) gave a DNP corresponding to that of benzaldehyde (m.p. and mixed m.p. 239°). It also contained phenol (ferric reaction). The other fractions were unchanged 2-phenoxyethyl acetate. The gaseous pyrolysate (b) contained carbon monoxide and dioxide, methane, acetylene and ethylene (infra-red).

3.22. 2-(4-chlorobenzoyloxy)ethyl terephthalate (VII).

Pyrolysis 24. This was intended as a trial run. The pyrolysate was found to contain 4-chlorobenzoic acid, a neutral solid, anhydride and a suggestion of acetaldehyde. The total pyrolysate gave a DNP which was chromatographed (circular paper) on Whatman No. 3mm. paper, using aqueous ethanol as developer. Four bands developed, showing the presence of four carbonyl compounds other than acetaldehyde.

Pyrolysis 25. Acetaldehyde was identified by chromatographic analysis of its DNP. The total pyrolysate (a) was triturated with aq. alkali and extracted with ether. Three layers were obtained. The ether layer was removed and filtered (A). The same was done with the alkaline layer. An insoluble solid was obtained from the interface (B). The alkaline solution on acidification furnished a pale yellow precipitate (C).

From the total acid fraction (C) a DNP was

obtained which was analysed by paper chromatography. It corresponded to the DNP of 4-acetylbenzoic acid. 5g. of the acid fraction when treated with 100 ml. boiling chloroform and 100 ml. cold chloroform left a residue of 1g. The infra-red spectrum of this was identical with that of a synthetic mixture of 4-chlorobenzoic and terephthalic acids. The chloroform solution obtained above was filtered and the solvent removed. The residue was analysed on filter paper, and found to be a mixture of benzoic and 4-chlorobenzoic acids.

The ether solution A yielded 22.7g of a neutral liquid which solidified overnight. 5g of it were macerated with 20 ml. petroleum ether (b.p. 80-100°) and then warmed with another 20 ml. petroleum ether. A separation took place into two layers. The upper petroleum ether layer was decanted off from an insoluble oil. On cooling, the petroleum ether solution afforded a white solid (0.6g.) which was recrystallised from 10 ml. methanol. Prismatic rods were obtained melting at 133°.

Mixed m.p. with starting material (VII) (m.p. 140°)	: 116-31°
Mixed m.p. with 2-benzoyloxyethyl 4-chlorobenzoate (XXI) (m.p. 188-9°)	: 126-32°
Mixed m.p. with ethylene di-4-chlorobenzoate (m.p. 143°)	: 136-40°

It was recrystallised from ethanol : m.p. 133-9°. A mixed melting point with ethylene di-4-chlorobenzoate was 140°. The infra-red spectrum was identical with of ethylene di-4-chlorobenzoate.

A also furnished a bright red DNP. This was chromatographed on a column of bentonite / kieselguhr (4:1) (39), using chloroform as developer at first and then working upto 100% acetone. The eluate was collected in 10ml. samples, and the separation followed by plotting optical density against fraction number. The former was measured in a Spekker colorimeter using a blue filter. The last three fractions were collected in 2 ml. amounts because they were washed down in quick succession. The optical density plotted is one-fifth of the values actually obtained, and is more convenient for the purpose.

The presence of five carbonyl compounds was deduced, since five maxima were obtained (Fig. 3). Two of these (Nos. 1 and 2) were found by paper chromatography to be the DNPs of acetophenone and 4-chloroacetophenone. (Fig.4). The other three remain for the present unidentified. They had smaller R_f values than the acetophenones and might possibly be higher molecular weight compounds.

3.23. Poly(ethylene terephthalate)(I).

Pyrolysis 26. The object of this was to determine approximately when poly(ethylene terephthalate) or Terylene

begins to decompose. 10g. and 20g. samples of Terylene chips were heated in an open conical flask immersed in a bath of Wood's metal. The following observations were made:-

	<u>Temperature.</u>	<u>Time.</u>	<u>Decomposition.</u>
1.	100°	2 hr.	Nil.
2.	145°	2 hr.	Nil.
3.	190°	2 hr.	Nil.
4.	230-40° (temp. in flask : 210-20°)	2 hr.	White sublimate.

The sublimate was also obtained when the experiment was performed under nitrogen. The sublimate was acidic to litmus and was in all probability terephthalic acid.

Pyrolysis 27. This was a liquid-phase pyrolysis and was carried out at 340° for 5 hr. The 'Drikold' receiver contained ca. 5 g. of acetaldehyde. It formed a DNP, m.p. 153-6°, mixed m.p. 158-9°. It was examined in the gas phase by infra-red, when no indication of vinyl ether (IX) was found. The pyrolysate consisted of a sublimate (14.2g.) and a very dark, rather intractable solid (70g.) which remained at the bottom of the flask.

The sublimate was boiled with 100 ml. water and filtered - A. The residue was warmed with 100 ml. ethanol, and filtered - B. The residue C was shown by infra-red to consist of terephthalic acid. 64g. of the tarry residue at

the bottom of the flask was separated by 400 ml. boiling acetone into two fractions - A₃ and A₁. The latter (the soluble fraction) was now separated by cold alkali into two fractions A₁ and A₂. A₁ proved to be terephthalic acid.

A on cooling gave a solid m.p. 108°. It was identical with benzoic acid (mixed m.p. 116°).

B formed a DNP. On paper, it gave two spots corresponding to acetophenone and an unknown. Evaporation of the alcohol caused the separation of a white solid, which was filtered off. From the filtrate was obtained a DNP corresponding now to acetophenone only. The total pyrolysate yielded a DNP from which the presence of acetophenone and 4-acetylbenzoic acid was inferred. The solid obtained from B above, melted above 360° (Found : C, 63.9 ; H, 4.7%). It yielded a DNP; owing to lack of material, it was not possible to characterise the solid. A paper-chromatographic examination of the DNP also did not yield any positive evidence, as to its formula. It was found to be contaminated with traces of 4-acetylbenzoic acid (chromatography). The micro-analytical values must therefore be regarded with reserve.

Although A₂ was obtained from acetone solution, it was actually a very insoluble solid. The only satisfactory

solvent was glacial acetic acid. When heated alone, a cloud of white material was observed; carbon monoxide was evolved. A₂ is insoluble in cold alkali, but dissolves in warm alkali and hot sodium hydrogen carbonate solution, showing that it is a carboxylic acid. A small portion of it on crystallisation from ethanol had m.p. > 350°; it was probably identical with the solid from B. In the absence of a reliable molecular weight (the camphor method was tried, but hopelessly inconsistent values were obtained), the further examination of A₂ involved quantitative hydrolysis. The ethylene glycol liberated on hydrolysis was estimated by heating a known weight of A₂ with excess alkali (heat for 1 hr.) followed by neutralisation and addition of a known amount of standard periodic acid. After standing for half an hour, the excess periodic acid was determined by reduction to iodine and titrating the latter against standard sodium thiosulphate solution. The glycol is represented as the percentage by weight of material liberated. The following constants were obtained for A₂: -

Acid equivalent	: 361.9
Total CO ₂ -equivalent	: 121.6; 123.8.
% Glycol liberated	: 17.1.

The solid A₃ on hydrolysis gave a water soluble material, which on benzoylation yielded ethylene

dibenzoate, m.p. and mixed m.p. 73°. A₃ is thus a polyester of ethylene glycol. The acid obtained on hydrolysis is a very dark solid and this is probably what gives to A₃ its very deep colour. The acid contained terephthalic acid. Quantitative hydrolysis of A₃ showed that the percentage acid obtained on hydrolysis was 87.9%. A polyester of the type $\left[\text{CH}_2.\text{CH}_2.\text{O}_2\text{C} \text{---} \text{C}_6\text{H}_4 \text{---} \text{CO}_2 \right]_n$ gives on hydrolysis 86.4%

acid. The slightly higher value obtained from A₃ may be due to the presence of random anhydride groups.

Pyrolysis 28. The reactor was slightly modified for the vapour-phase pyrolysis of Terylene, and is shown in Fig. 2 (p. 96). The thermocouple wires were placed between the reactor and furnace. The main portion of the pyrolysate (a) on refluxing with ca. 100ml. ether yielded 2g. insoluble solid. The latter was found to be terephthalic acid (infra-red). The ether solution was washed with water to remove any acetaldehyde and then with alkali to remove acids, and finally dried (anhydrous sodium sulphate). The aqueous extract on acidification gave 10g. of a yellowish solid (A). The ether on evaporation left ca. 1 g. of a yellow liquid containing a trace of solid in suspension (B).

The 'Drikold' product gave a DNP corresponding to acetaldehyde (m.p. and mixed m.p. 164°). The total

pyrolysate gave a positive test for anhydride.

A was separated into a hot-water-soluble (A₁), ethanol-soluble (A₂), and insoluble fractions (A₃). A₁ gave a trace of DNP. It was mostly benzoic acid (infra-red). From A₂ was obtained a DNP which was proved to be that of 4-acetylbenzoic acid. A₃ was terephthalic acid (infra-red).

B yielded a DNP shown by paper chromatography to be identical with that of acetophenone. B consisted mostly of vinyl benzoate (infra-red). The gaseous fraction of the pyrolysate (b) contained carbon monoxide and dioxide, methane, acetylene and ethylene.

Compounds listed in Tables 2, 3, and 4.

Table 2.

2:2'-Dibenzoyloxydiethyl Ether	(IV)
2-Benzoyloxyethyl Vinyl Ether	(X)
Vinyl Ether	(IX)
<u>n</u> -Butyl Vinyl Ether	(XIV)
<u>iso</u> -Butyl Vinyl Ether	(XV)

Table 3.

2-Hydroxyethyl Benzoate	(V)
Ethylene Glycol	
2 -Hydroxyethyl Ether	
2-Phenoxyethanol	(XXIII)
2-Phenoxyethyl Acetate	(VIII)
Phenyl Vinyl Ether	(XVI)

Table 4.

2-Chloroethyl Benzoate	(XXII)
2-(4-Chlorobenzoyloxy)ethyl Terephthalate	(VII)
Poly (ethylene Terephthalate)	(I)

Table 2.

Pyrolysis of Compounds (IV), (X), (IX), (XIV)
and (XV).

Pyrolysand	(IV)	(IV)	(IV)	(X)	(X)	(X)	(IX)	(XIV)	(XV)
Pyrolysis No.	2	3	4	5	6	7	8	9	10
Temperature(°C)	550	500	450	500	470	400	500	500	500
Feed rate (g./min.)	0.30	0.54	0.70	0.53	0.53	0.44	0.34	0.30	0.34
Weight pyrolysed (g.)	64.0	35.0	73.1	70.0	20.0	28.0	32.5	47.0	30.0
(a) Liquid pyrolysate(g)	23.3*	23.6*	52.6*	57.8*	13.3*	22.2*	†	‡	‡
(b) Gaseous pyrolysate(l.)	16.0	7.5	9.7	8.0	3.1	3.1	9.0	5.7	4.0
Composition (%) of (b) :-									
Carbon monoxide	41.0	44.5	39.5	59§	53§	43.5	48.2	33.9	39.1
Carbon dioxide	25.5	22.3	16.5	19§	22§	30.9	Nil	Nil	Nil
Methane	23.9	22.8	31.4	Nil	Nil	Nil	27.4	46.3	49.0
Unsat. Hydrocarbons	9.6	10.4	12.6	22§	25§	25.6	24.4	19.8	11.9

* Excluding minor amounts of volatile material in 'Drikold' trap.

† Large volatile fraction in 'Drikold' trap not weighed.

‡ Acetaldehyde (DNP trap) and olefin ('Drikold' trap) not weighed.

§ Figures only approximate.

Table 3.

Pyrolysis of Compounds (V), (XXIII), (VIII), Ethylene glycol
and 2-Hydroxyethyl ether.

Pyrolysand	(V)	(V)	Ethylene glycol	2-Hydroxy-ethyl ether	(XXII)	(VIII)	(VIII)	(XVI)
Pyrolysis No.	12	13	14	15	21	22	23	11
Temperature (°C)	375	500	370-85	370-80	500	400	500	500
Feed rate (g./min.)	0.34	0.54	1.0	0.55	0.39	0.27	0.37	0.73
Weight pyrolysed (g.)	20.0	99.0	25.0	50.0	40.0	65.4	96.0	22.0
Liquid pyrolysate (g.) (a)	17.1	76.0	23.2	46.0	39.7	63.3	89.0	10.0
Gaseous pyrolysate (l.) (b). ±	±	8.0	Nil	±	1.0	±	14.0	1.0
Composition (%) of (b):-								
Carbon monoxide	-	49.5	-	-	35.9	-	34.9	±
Carbon dioxide	-	1.8	-	-	-	-	37.6	±
Methane	-	45.9	-	-	34.5	-	-	±
Unsat. hydrocarbons	-	2.8	-	-	29.4	-	27.5	±

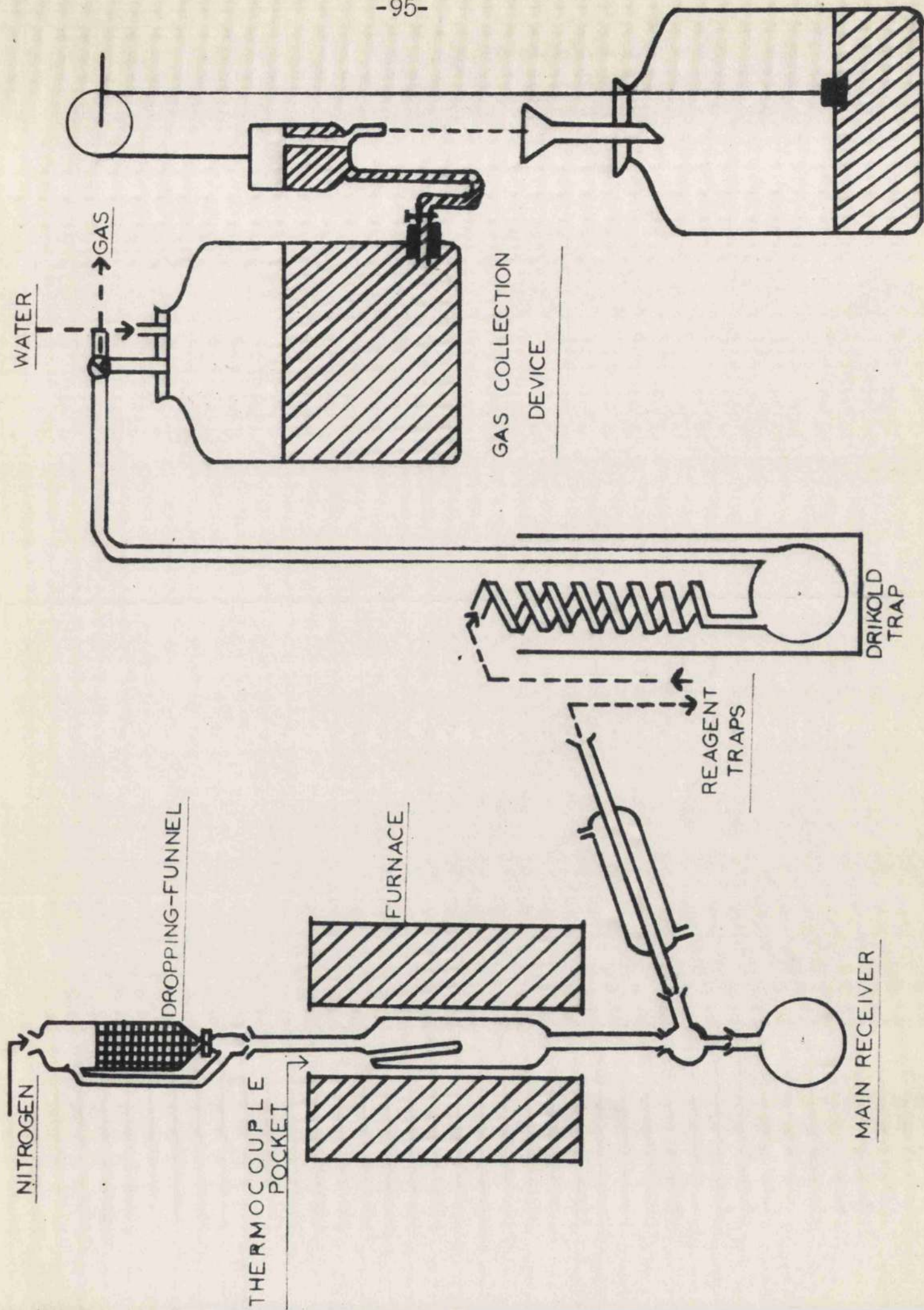
± Negligible.

Table 4.

Pyrolysis of Compounds (XXII), (VII), and (I).

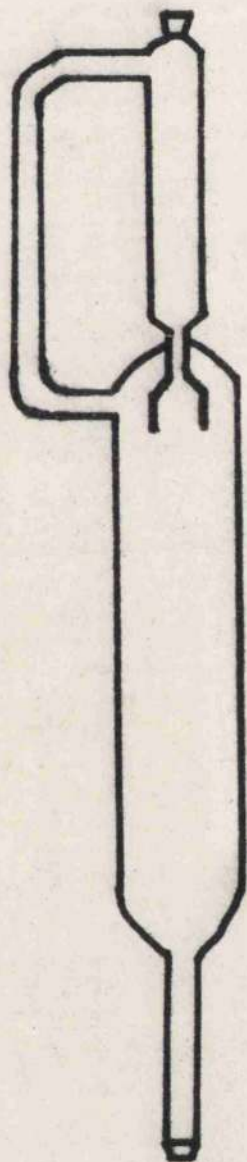
Pyrolysand	(XXII)	(XXII)	(XXII)	(XXII)	(VII)	(VII)	(I)
Pyrolysis No.	16	17	18	19	25	24	28
Temperature (°C)	400	400	450	500	500	525-50	450-75
Feed rate (g./min.)	0.43	0.48	0.51	0.57	1.03	1.03	ca. 0.67
Weight pyrolysed (g.)	49.3	30.0	83.3	57.4	65.0	51.4	50.0
Liquid pyrolysate (g.) (a)	43.1	29.3	67.8	41.0	47.0	24.9	17.0
Gaseous pyrolysate (l) (b)	1.5	±	2.0	±	4.0	6.9	9.0
Composition of (b) (%) :-							
Carbon monoxide	32.0	-	29.2	-	65.6	54.0	45.6
Carbon dioxide	23.3	-	55.4	-	27.7	44.7	47.8
Methane	-	-	-	-	-	-	±
Unsat. hydrocarbons	44.7	-	15.4	-	6.7	1.3	6.6

± Negligible.



(NOT TO SCALE)

FIG 1



MODIFIED FLOW-REACTOR
WITH SPECIAL FEEDER
FOR PYROLYSIS OF
POLY(ETHYLENE TEREPHTHALATE)

(NOT TO SCALE)

FIG. 2

Fig. 3

Graphical representation of the separation of DNPs of
pyrolysate from 2-(4-chlorobenzoyloxy)ethyl terephthalate,
by passing through a bentonite-kieselguhr (4:1) column.

Colorimeter- 'Spekker' colorimeter (blue
filter).

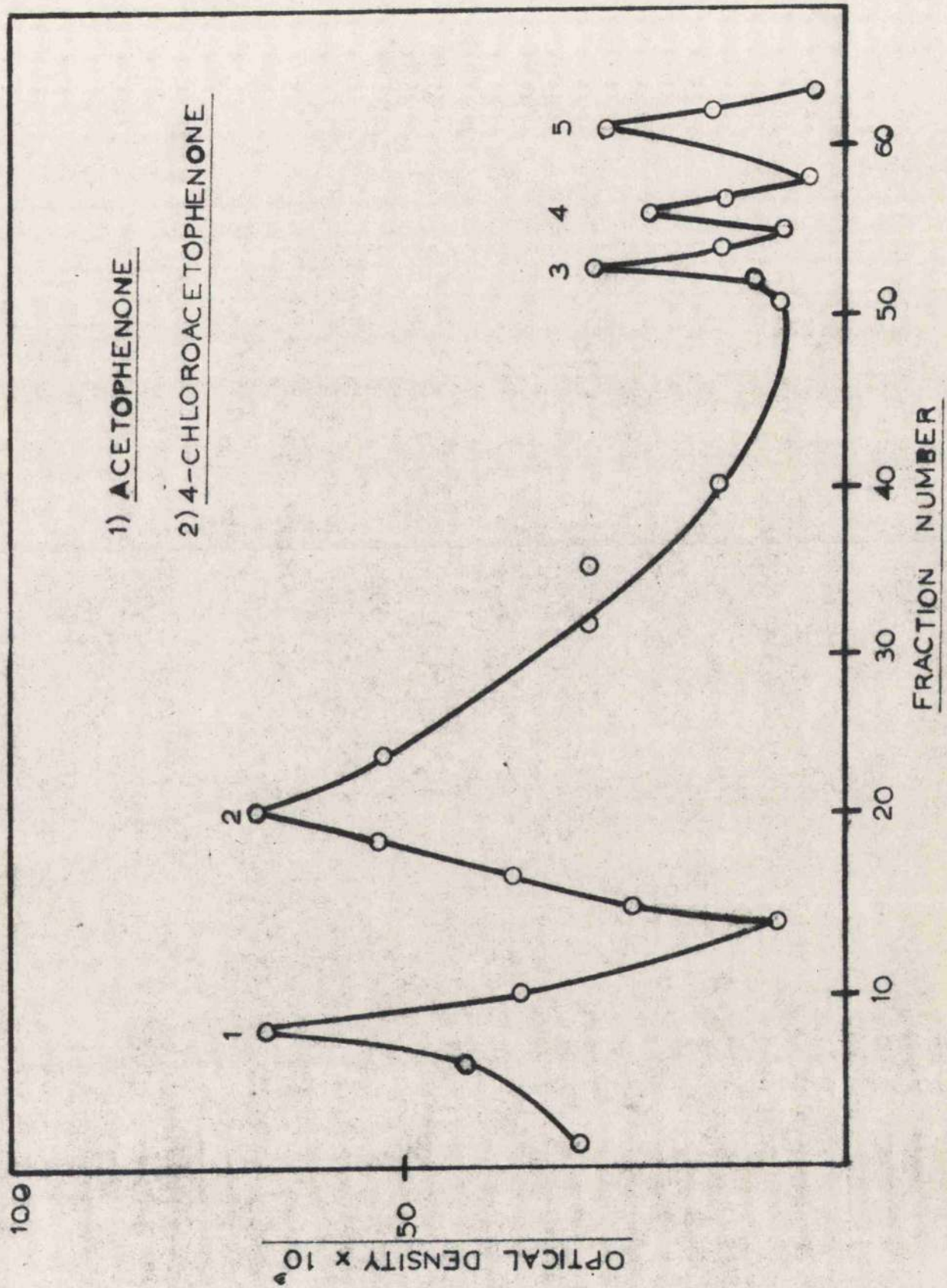


FIG. 3

77
49170
Fig. 4

Paper chromatography of fractions (Nos. 1-5) obtained by passing DNPs of pyrolysate from 2-(4-chlorobenzoyloxy)ethyl terephthalate through a bentonite-kieselguhr (4:1) column.

Paper- Whatman No. 1 impregnated with ethyl lactate.

Developer- 2% Carbon tetrachloride in light petroleum (60-80°).

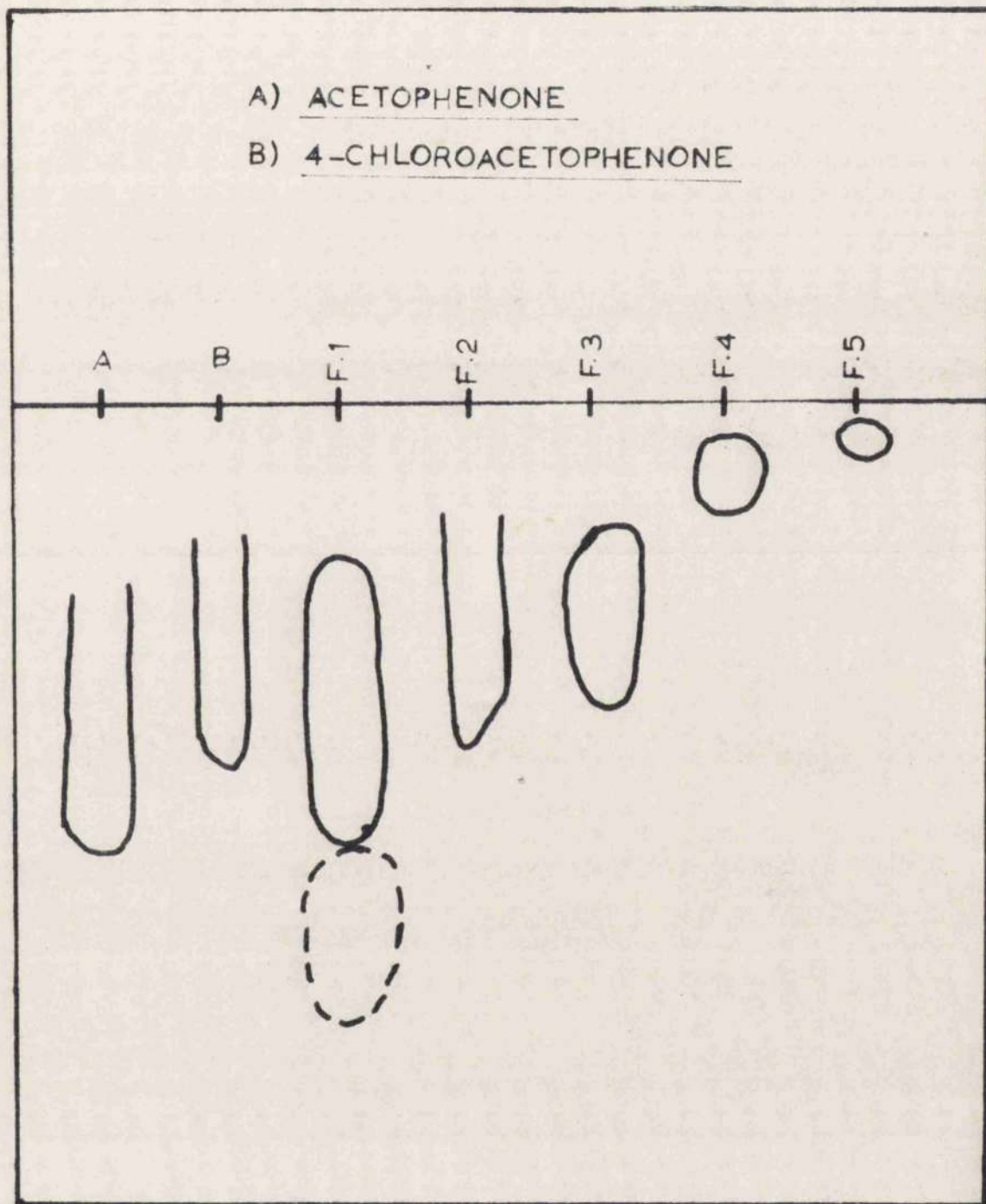


FIG. 4

Fig. 5

Paper chromatography showing the presence of benzoic and 4-chlorobenzoic acids in the pyrolysis of 2-(4-chlorobenzoyloxy)ethyl terephthalate.

Paper- Whatman No. 1
Developer- 40% Aq. acetone.
Indicator- Bromophenol blue.

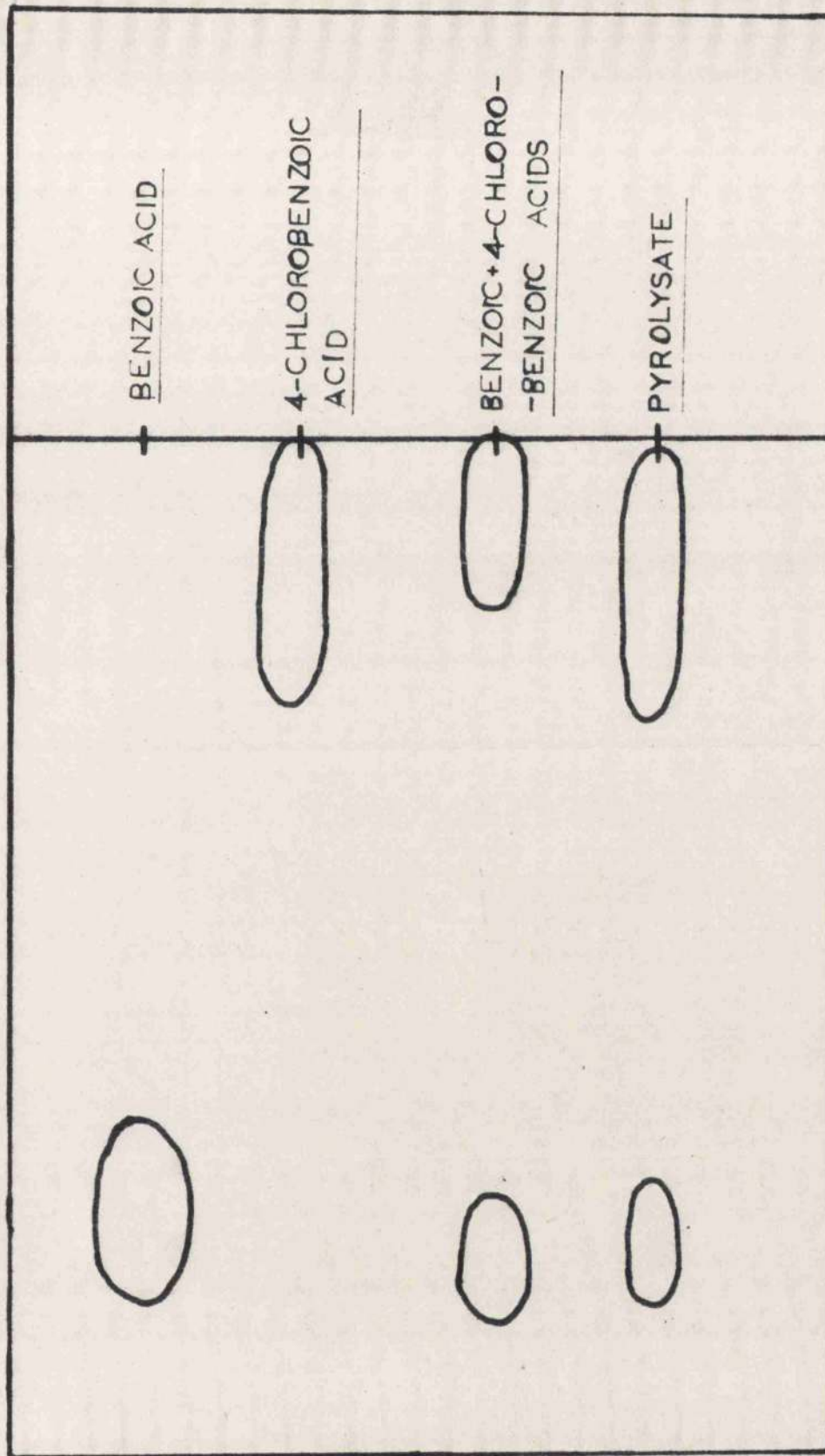


FIG. 5

Fig. 6

Paper chromatography (DNPs) showing the presence of acetophenone and 4-acetylbenzoic acid in the pyrolysis of 2-(4-chlorobenzoyloxy)ethyl terephthalate.

<u>Paper-</u>	Whatman No. 1 impregnated with ethyl tartrate.
<u>Developer-</u>	20% Acetone in light petroleum (60-80°).

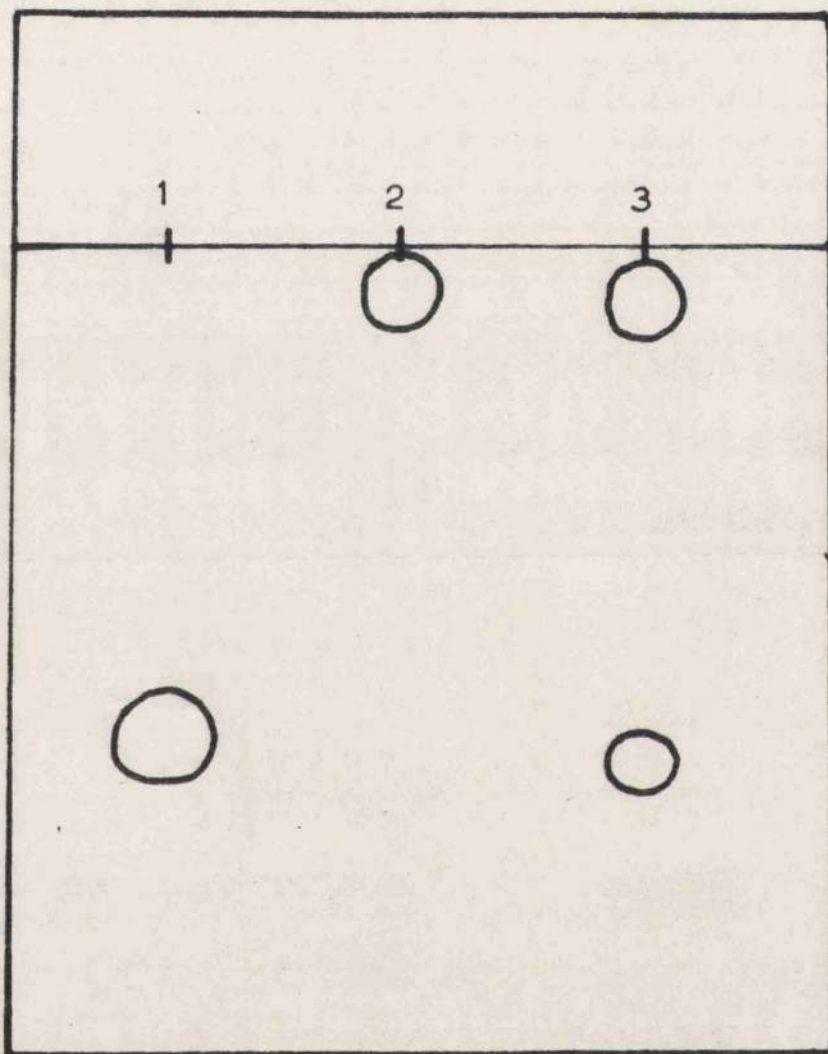


FIG-6

- 1) ACETOPHENONE
- 2) 4-ACETYLBENZOIC ACID
- 3) PYROLYSATE

Fig. 7

Paper chromatography showing the presence of acetophenone and 4-acetylbenzoic acid in the liquid-phase pyrolysis of Poly(ethylene terephthalate).

Paper- Whatman No. 1 impregnated with ethyl lactate.

Developer- 20% Acetone in light petroleum (60-80°).

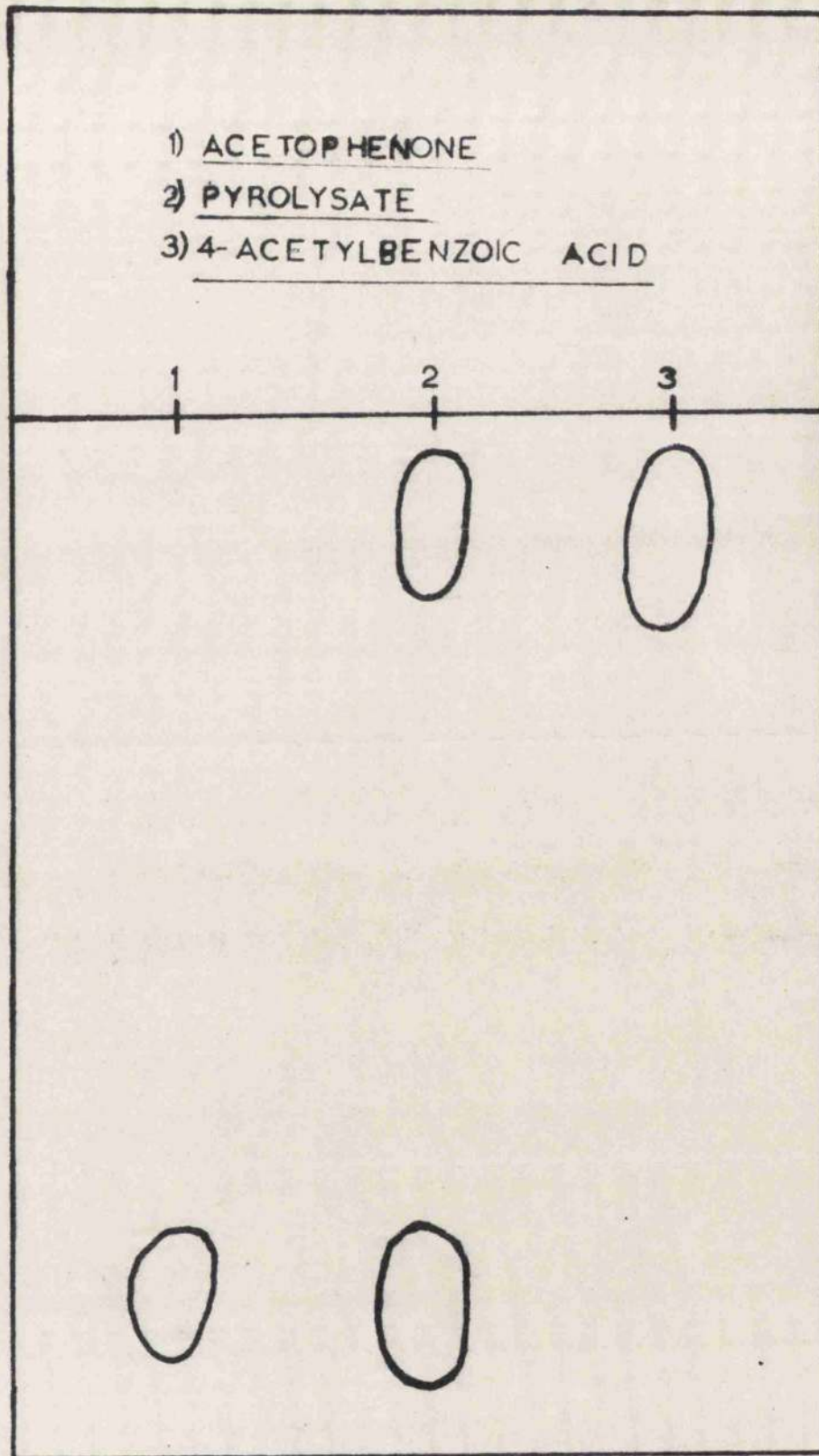


FIG. 7

Appendix I

The dehydrochlorination of ethylene di-1-chloroethyl ether with pyridine yields ethylene acetal (Hurd and Botterton, 36). There is no liberation of acetylene (see p. 18)

Ethylene di-1-chloroethyl ether :

A mixture of 120 ml. paraldehyde and 63 ml. ethylene glycol was saturated with dry hydrogen chloride at 0° in the course of 5 hr. The upper layer was dried over calcium chloride overnight and distilled twice. Yield : 46.5g. B.p., 84-6° / 6 mm.

Reaction of ethylene di-1-chloroethyl ether with pyridine.

A mixture of 12.5g. ethylene di-1-chloroethyl ether and 12 ml. pyridine was carefully distilled with the exit tube of the system connected to an infra-red gas cell. No acetylene was found in the latter.

Appendix II.

The dehydration of 2-phenoxyethanol with a number of chemical reagents failed to produce either phenyl vinyl ether or coumaran.

2-Phenoxyethyl phosphate (56):

(a) 2-phenoxyethanol (34g.) was heated with phosphorus oxychloride (3g.) on a water bath for 2 hr. The flask was cooled and ether added. A white solid was obtained,

m.p. 138° . (lit. m.p. 142°).

(b) 2-Phenoxyethanol (26.6g.) was added slowly to a suspension of phosphorus pentoxide (9.5g.) in benzene (100 ml.). The mixture was refluxed gently for 2 hr. and solvent removed. A white solid was obtained on cooling, and was crystallised twice from acetone. M.p. and mixed m.p. with solid obtained in (a) : 142° , 140° .

Distillation of 2-Phenoxyethanol over Phosphorus pentoxide:

This led to profound decomposition.

2-Phenoxyethyl acetate:

(a) Reaction of 2-phenoxyethanol with acetic anhydride / pyridine afforded only 2-phenoxyethyl acetate (see p. 70).

(b) 2-Phenoxyethanol (20g.) was refluxed vigorously for 4 hr. with fused zinc chloride (18g.) and glacial acetic acid (50ml.). The product when worked up in the usual manner was identical with the acetate obtained in (a).

Saponification regenerated 2-phenoxyethanol.

Treatment of 2-Phenoxyethanol with sulphuric acid:

(a) Treatment with cold concentrated sulphuric acid for one week according to the method of Smith and Niederl (43) did not cause any dehydration. Unchanged material was obtained on distillation.

(b) 2-Phenoxyethanol (10g.) was heated on a steam bath for 4 hr. with conc. sulphuric acid (5g.) and left overnight. A white solid was obtained, insoluble in ether, but extremely

soluble in water.

(c) Treatment with fuming sulphuric acid as in (a) again yielded only unchanged material. There was no evidence for o-vinyl phenol, which was obtained by Smith and Niederl (43).

Appendix III.

The Karl Fisher estimation of water (57) was performed in a standard apparatus (direct titration) (ex. Messrs. Townson and Mercer Ltd., Croydon, Surrey), using Karl Fisher reagent (ex. British Drug Houses, Ltd.) which was standardised against a standard solution of water in methanol.

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