497. *Studies in Pyrolysis. Part X.* Model Systems for the Pyrolysis of Poly(ethylene Terephthalate): 2-Hydroxyethyl Benzoate and Related Substances.*

By H. V. R. Iengar and P. D. Ritchie.

2-Hydroxyethyl (or 2-chloroethyl) benzoate breaks down thermally in the vapour phase by three competitive primary reactions: (i) disproportionation to ethylene dibenzoate and ethylene glycol (or 1 : 2-dichloroethane): (ii) disproportionation to benzoic anhydride and diethylene glycol (or 2 : 2′-dichlorodiethyl ether); and (iii) alkyl–oxygen scission to benzoic acid and acetaldehyde (or vinyl chloride). These reactions are compared with analogous competitive scissions of 2-phenoxyethanol and 2-phenoxyethyl acetate; the pyrolysis of phenyl vinyl ether is also described. The results assist in interpreting the thermal breakdown of poly(ethylene terephthalate)

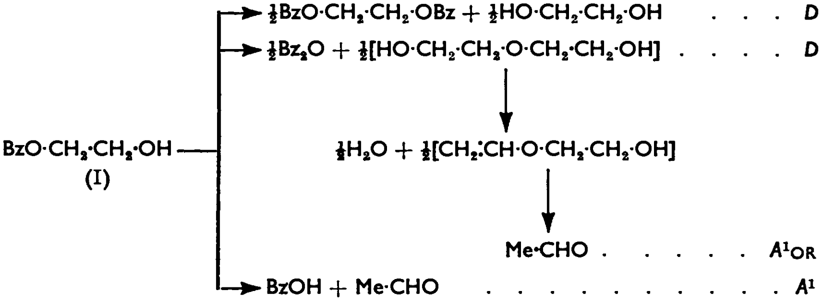
2-Hydroxyethyl benzoate (I), previously suggested [1] as a suitable model compound for studying the thermal breakdown of a terminal chain-segment of poly(ethylene terephthalate) (II), has now been pyrolysed under various conditions, and its behaviour compared with that of a number of analogous compounds.

(I) $BzO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (II) $H{\cdot}[p\text{-}O_2C{\cdot}C_6H_4{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2]_n{\cdot}OH$

2-Hydroxyethyl Benzoate (I).—The work has confirmed and considerably extended Cretcher and Pittenger's observation [2] that 2-hydroxyethyl esters of aromatic acids disproportionate on distillation as follows with concurrent formation of some water:

$$Ar{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \longrightarrow \tfrac{1}{2}Ar{\cdot}CO_2{\cdot}CH_2{\cdot}CH_2{\cdot}O_2C{\cdot}Ar + \tfrac{1}{2}HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

It has been found that although 2-hydroxyethyl benzoate can be distilled unchanged under reduced pressure, at higher temperatures it yields a range of products (including the key substance acetaldehyde, not recorded by Cretcher and Pittenger [2]) best interpreted by the following scheme of concurrent competitive reactions:



(The symbols *D*, A^1_{OR}, and A^1 have been defined previously.[1,3])

Disproportionation (*D*) of two types predominates at lower temperatures (*e.g.*, during distillation, or in the vapour phase at *ca.* 375°), though it still occurs to some extent at higher temperatures; but at *ca.* 500° alkyl–oxygen scission (A^1), which does not occur measurably at *ca.* 375°, predominates strongly, with formation of much benzoic acid (not accompanied by vinyl benzoate or its scission products, and hence not arising by the known A^1 scission of ethylene dibenzoate [1]). This effect of temperature is at first sight

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* Part IX, *J.*, 1957, 2107.

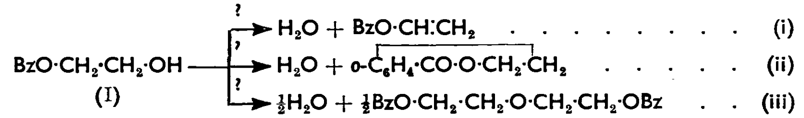
[1] Allan, Forman, and Ritchie, *J.*, 1955, 2717.

[2] Cretcher and Pittenger, *J. Amer. Chem. Soc.*, 1925, **47**, 2560.

[3] Iengar and Ritchie, *J.*, 1956, 3563.

surprising, since the hydroxy-ester (I) possesses the structural feature so frequently associated with an easy A^1 scission, namely, the presence of one or more β-hydrogen atoms. It may be that the polar β-hydroxyl substituent causes the β-hydrogen atoms to be more strongly bonded to carbon, so that A^1 scission here requires a high activation energy.

A more puzzling feature of the pyrolysis of 2-hydroxyethyl benzoate is the very ready evolution of small quantities of water (even in the early stages of a simple distillation). There are various formally possible sources of this water, such as the three following direct dehydrations, of which (i) and (ii) are intramolecular, and (iii) intermolecular :



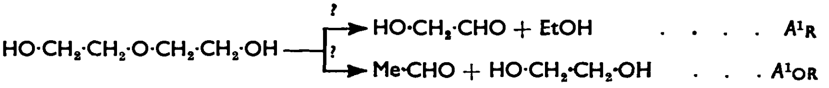
$$\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}OH}\ (\mathrm{I}) \begin{cases} \xrightarrow{?} \mathrm{H_2O + BzO{\cdot}CH{:}CH_2} & \text{(i)} \\ \xrightarrow{?} \mathrm{H_2O + \textit{o}\text{-}C_6H_4{\cdot}CO{\cdot}O{\cdot}CH_2{\cdot}CH_2} & \text{(ii)} \\ \xrightarrow{?} \tfrac{1}{2}\mathrm{H_2O} + \tfrac{1}{2}\mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OBz} & \text{(iii)} \end{cases}$$

Reaction (i) at first seems likely, in view of Vaughn's claim[4] that the analogous ester 2-hydroxyethyl acetate yields, *inter alia*, water and vinyl acetate on pyrolysis; but all three reactions are here ruled out by the absence of the appropriate scission product from the low-temperature pyrolysate.

Two other possible sources of the water remain, and merit fuller consideration. In the first place, disproportionation of the benzoate (I) yields ethylene dibenzoate and ethylene glycol, and it is known[5] that at *ca.* 500° the latter yields water and acetaldehyde. However, it has been found that at *ca.* 375°, in the vapour phase, the glycol is largely unchanged, yielding only a very small amount of water (much less than that formed from 2-hydroxyethyl benzoate at this temperature).

The only reasonable alternative is a disproportionation of 2-hydroxyethyl benzoate to benzoic anhydride and diethylene glycol, followed by breakdown of the latter. This is suggested by the fact that at *ca.* 375° the ester (I) yields benzoic anhydride, but not the benzoic acid which would be expected to accompany the anhydride if the latter arose from ethylene dibenzoate by the A^1/D sequence described by Allan, Jones, and Ritchie.[6] The concept is further supported by the observation that diethylene glycol is markedly less thermostable than ethylene glycol, yielding water and acetaldehyde quite readily in the vapour phase at *ca.* 375°.

The latter observation is surprising, for it is known[7] that, in general, saturated aliphatic ethers break down thermally by $A^1{}_\mathrm{R}$ scission; and neither this nor the alternative type of alkyl–oxygen scission $A^1{}_\mathrm{OR}$ (which in any case is not known to occur for such ethers) can satisfactorily account for the observed products from diethylene glycol, as is clear from the following scheme :



$$\mathrm{HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}OH} \begin{cases} \xrightarrow{?} \mathrm{HO{\cdot}CH_2{\cdot}CHO + EtOH} & A^1{}_\mathrm{R} \\ \xrightarrow{?} \mathrm{Me{\cdot}CHO + HO{\cdot}CH_2{\cdot}CH_2{\cdot}OH} & A^1{}_\mathrm{OR} \end{cases}$$

It can only be supposed that the presence of negative 2 : 2′ substituents X in an aliphatic ether (III) induces thermal breakdown as shown below, the second stage being supported by previous observations[3] on the pyrolysis of alkyl vinyl ethers :

$$\text{(III)}\quad \mathrm{X{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}X} \longrightarrow \mathrm{HX} + [\mathrm{CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}X}]$$

$$[\mathrm{CH_2{:}CH{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}X}] \longrightarrow \mathrm{Me{\cdot}CHO + CH_2{:}CHX} \quad . \; . \; . \quad A^1{}_\mathrm{OR}$$

This sequence has been confirmed experimentally (*ca.* 375°) for 2 : 2′-dichlorodiethyl ether (III; X = Cl). This explains the present results, where X = OH; here the substituted olefin $\mathrm{CH_2{:}CHX}$ is the enol of acetaldehyde.

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[4] Vaughn, U.S.P. 2,415,378/1947.

[5] Nef, *Annalen*, 1904, **335**, 200.

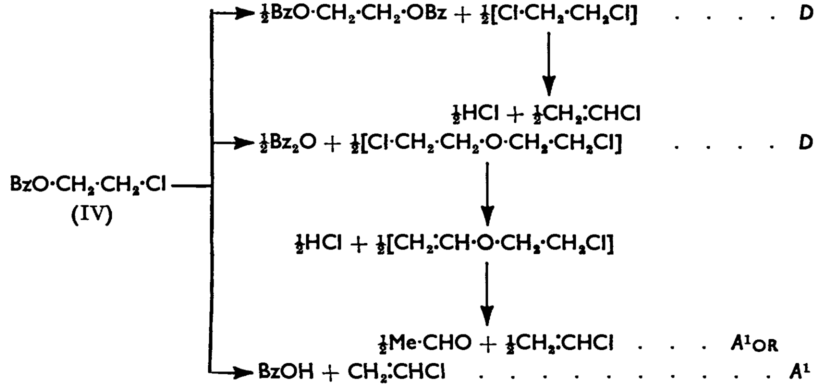
[6] Allan, Jones, and Ritchie, *J.*, 1957, 524.

[7] Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, Chap. 8.

In view of the frequency with which disproportionation has been observed in this and cognate work,[1,3,8] various analogues of 2-hydroxyethyl benzoate have been studied, partly to determine some of the structural features promoting disproportionation, and partly to confirm that the foregoing interpretation of its pyrolysis is correct. The compounds studied were the ester 2-chloroethyl benzoate (IV), the ether 2-phenoxyethanol (V), and the ether-ester 2-phenoxyethyl acetate (VI); in these the terminal groups of 2-hydroxyethyl benzoate are replaced by other simple groups of similar polarity. Phenyl vinyl ether (VII), which is related to 2-phenoxyethanol (V) and its acetate (VI), has also been studied.

$BzO{\cdot}CH_2{\cdot}CH_2{\cdot}Cl$ (IV) $PhO{\cdot}CH_2{\cdot}CH_2{\cdot}OH$ (V) $AcO{\cdot}CH_2{\cdot}CH_2{\cdot}OPh$ (VI) $PhO{\cdot}CH{:}CH_2$ (VII)

2-*Chloroethyl Benzoate* (IV).—Bilger and Hibbert[9] have shown that 2-chloroethyl acetate yields acetic acid and vinyl chloride on pyrolysis, and it has now been found that the analogous benzoic ester (IV) also undergoes A^1 scission as one of several competitive breakdown routes at 450—500°, thus :



As in several other related pyrolyses studied recently,[3,8] the pyrolysate is complex, and more than one formally possible reaction scheme can be devised to account for it; the above scheme, based partly on the present results and partly on their correlation with other analogous pyrolyses, is probably the most reliable interpretation. It is precisely parallel to the scheme proposed above for 2-hydroxyethyl benzoate. Ethylene dibenzoate was obtained in one run at *ca.* 400° (thus confirming the first *D* route), though it could not be detected in subsequent runs; 1 : 2-dichloroethane, which should have accompanied it, was not detected, though its known pyrolysis products[10] hydrogen chloride and vinyl chloride were identified. (The scheme suggests other possible sources of these, however; and 1 : 2-dichloroethane, pyrolysed under the same conditions, was observed to break down only to the extent of *ca.* 7%.) Benzoic anhydride is most probably attributable to the second *D* route, just as was deduced for the ester (I).

2-*Phenoxyethanol* (V).—This compound at *ca.* 500° yielded phenol, acetaldehyde, and water; these products were also obtained at *ca.* 600° by Knights and Cooper,[11] who in addition observed traces of phenyl vinyl ether. The normal $A^1{}_{OR}$ scission of an alkyl phenyl ether to phenol and olefin[12] here accounts for the formation from 2-phenoxyethanol

[8] Allan, Iengar, and Ritchie, *J.*, 1957, 2107.

[9] Bilger and Hibbert, *J. Amer. Chem. Soc.*, 1936, **58**, 823.

[10] Barton and Howlett, *J.*, 1949, 155; Howlett, *Trans. Faraday Soc.*, 1952, **48**, 25.

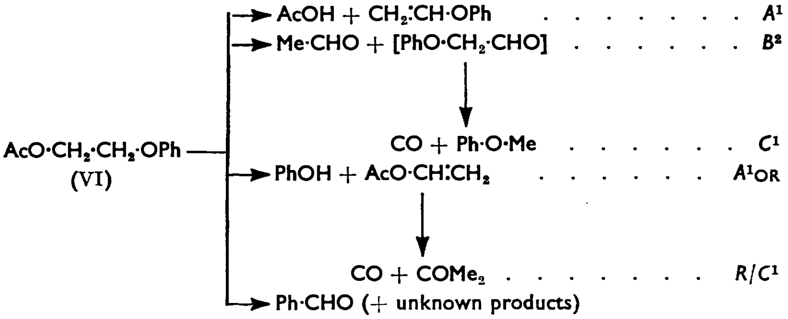
[11] Knights, personal communication, 1956.

[12] Bamberger, *Ber.*, 1896, **19**, 1818; Hart and Eleuterio, *J. Amer. Chem. Soc.*, 1954, **76**, 519; cf. Skraup and Beifuss, *Ber.*, 1927, **60**, 1070.

of phenol and (*via* its enol) acetaldehyde; but, as in the pyrolysis of 2-hydroxyethyl benzoate, the origin of water is less obvious. It cannot arise by intramolecular cyclodehydration to coumaran, or by intermolecular dehydration to 2 : 2′-diphenoxydiethyl ether, since neither of these substances was present in the pyrolysate, though both should be fairly thermostable. Direct intramolecular dehydration to water and phenyl vinyl ether remains as a possibility, though somewhat unexpected; the fact that only a trace of the ether was noted [11] may be accounted for by its secondary breakdown, discussed later.

Some of these conclusions conflict with the reported ready dehydration of 2-phenoxyethanol by chemical reagents, but it has not been possible to confirm these claims. For example, it has been stated [13] that it is cyclodehydrated to coumaran by treatment with phosphoric oxide or zinc chloride; several attempts to repeat this have failed, the former reagent yielding only tri-2-phenoxyethyl phosphate. Similarly, it could not be confirmed that 2-phenoxyethanol, treated with concentrated sulphuric acid, yields *o*-vinylphenol, as claimed by Smith and Niederl; [14] a similar negative result has recently been reported by Bader [15] and Knights and Cooper.[16]

2-*Phenoxyethyl Acetate* (VI).—Knights and Cooper [11, 16] have found that pyrolysis of the acetate (VI) at *ca.* 600° yields acetic acid (33%), benzaldehyde (17%), phenol (11%), and a little vinyl acetate, but no phenyl vinyl ether or *o*-vinylphenol; *ca.* 30% of the material was lost as gases. The present work agrees with this in the main, but has shown in addition the formation of carbon monoxide and a little anisole, acetone, and phenyl vinyl ether. The whole complex breakdown is best interpreted by the following scheme of concurrent competitive scissions, which accounts for everything except the very unexpected formation of benzaldehyde:



The breakdown of the ether-ester (VI) predominantly as an ester (by the A^1 route, with a little acyl–oxygen scission, B^2), but also concurrently as an ether (by the $A^1{}_{\mathrm{OR}}$ route), agrees with previous conclusions.[3] Phenoxyacetaldehyde itself was not found in the pyrolysate, but anisole and carbon monoxide, its predictable decarbonylation (C^1) products, were identified, as was acetone, a predictable scission product of vinyl acetate by the major R/C^1 sequence.[1] Benzaldehyde is the only product for which no obvious precursor suggests itself; clearly, its formation entails a step where the phenoxy-group is ruptured at the very stable phenyl–oxygen bond, and probably occurs by a radical reaction.

Phenyl Vinyl Ether (VII).—As a check on some of the foregoing views, phenyl vinyl ether was pyrolysed. Its thermal breakdown has been described previously, but the results are inconclusive and somewhat conflicting. Claisen [17] reported that it rearranges thermally, but Powell and Adams [18] reported that in a sealed tube at 260—280° there is

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[13] Rindfusz, *J. Amer. Chem. Soc.*, 1919, **41**, 665; Rindfusz, Ginnings, and Harnack, *ibid.*, 1920, **42**, 157.
[14] Smith and Niederl, *ibid.*, 1931, **53**, 806.
[15] Bader, *ibid.*, 1955, **77**, 4155.
[16] Knights and Cooper, *Chem. and Ind.*, 1955, 1558.
[17] Claisen, G.P. 268,099/1913.
[18] Powell and Adams, *J. Amer. Chem. Soc.*, 1920, **42**, 646.

slow decomposition to phenol, with no concurrent formation of acetylene, and a similar result was noted for *p*-tolyl vinyl ether. Lauer and Spielman [19] found that under similar conditions only a small amount of phenol was formed, together with diphenylacetal, $CHMe(OPh)_2$, and a tar with *M ca.* 800, but no acetylene : further, a mixture of the ether with phenol yielded more phenol than was present (free) in the mixed pyrolysand, with complete destruction of the ether. We have found that in a flow reaction vessel (*i.e.*, with a contact time very much less than in pyrolysis in a sealed tube) the ether (VII) breaks down primarily to phenol and acetylene at *ca.* 500°. There is a marked molar deficiency of the latter, and much tar is retained in the vessel : there is no evidence of any primary reaction other than this $A^1{}_{OR}$ scission (*e.g.*, rearrangement to *o*-vinylphenol), or for formation of benzaldehyde (cf. pyrolysis of 2-phenoxyethyl acetate).

No clear-cut conclusion is possible, from the limited number of pyrolyses considered here, as to the factors promoting disproportionation. The *D* reaction undergone by substances (I) and (IV) suggests that the ester group common to both may be a promoting structure : and the failure of substances (V) and (VI) to disproportionate suggests that the phenoxy-group may be an inhibiting structure, even, in the latter example, to the extent of overcoming the effect of the ester group also present. The formation of 1 : 2-diphenoxyethane by a side reaction when the ether (VII) is prepared by heating 2-bromoethyl phenyl ether with solid alkali (see Experimental) appears to constitute disproportionation of a compound containing a phenoxy-group (this by-product was not recorded by Chalmers,[20] although he noted a somewhat analogous side-reaction of alkyl 2-bromoethyl ethers), but this example is inconclusive because reactions other than disproportionation may formally be responsible for the diphenoxy-compound (*e.g.*, interaction of the starting material, in presence of alkali, with phenol produced by its own decomposition, or by that of phenyl vinyl ether).

Poly(*ethylene Terephthalate*) (II).—Application of the foregoing results to the pyrolysis of the polyester (II) leads to some interesting conclusions, subject to the usual proviso that caution is necessary in extrapolating results from vapour-phase to liquid-phase conditions. Since the initial concentration of 2-hydroxyethyl end-groups in the polyester (II) is low, disproportionation by their mutual intermolecular reaction will contribute only slightly to the initial pyrolytic changes. As the breakdown proceeds, however, and the molecules in the molten pyrolysand become smaller and more mobile, conditions will increasingly favour the continual interaction (disproportionation) of surviving 2-hydroxyethyl end-groups, just as they favour the continual ester-interchange (within the chain) described previously.[8] This *D* reaction will temporarily unite small molecules into longer chains, simultaneously producing water and assisting in the production of acetaldehyde and anhydride groupings, though the last two products are formed mainly by chain scission *via* the A^1/D mechanism.[6] At higher temperatures, A^1 scission of the 2-hydroxyethyl end-groups will compete more strongly with their *D* reaction, forming new carboxyl end-groups and at the same time providing a further route to acetaldehyde.

None of the various other models previously studied [1,3,8] as a guide to interpreting the thermal breakdown of poly(ethylene terephthalate) has yielded water on pyrolysis. The present work on model (I) suggests, therefore, that the small amount of water given by the polyester on pyrolysis [21] arises solely by way of 2-hydroxyethyl end-groups.

EXPERIMENTAL

Apparatus.—The arrangement of reaction vessel, furnace, traps, and receivers has been described.[1,3] Several vessels, of slightly different dimensions, were used; they were evacuated and thoroughly flushed with nitrogen before each run.

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[19] Lauer and Spielman, *J. Amer. Chem. Soc.*, 1933, **55**, 1572.

[20] Chalmers, *Canad. J. Res.*, 1932, **7**, 464, 472.

[21] Pohl, *J. Amer. Chem. Soc.*, 1951, **73**, 5660.

Results.—Tables 1 and 2 summarise the general experimental results for 13 pyrolyses. The detailed examination of each liquid pyrolysate (*a*) is summarised below; the composition of gaseous pyrolysates (*b*) is reported on a nitrogen-free basis. The considerable overall losses recorded for several pyrolyses (*e.g.*, pyrolysis 10) are due to carbonisation and/or hold-up in the reaction vessel.

Analysis.—Aldehydes and ketones were characterised as their 2 : 4-dinitrophenylhydrazones (paper chromatography [22] and/or mixed m. p.); all other solids were identified by mixed m. p. Acid anhydrides were detected by the Davidson and Newman colour reaction,[23] and water by the anhydrous copper sulphate test. The normal chemical examination of fractions was in some cases supplemented by infrared spectrometry and vapour-phase chromatography.

TABLE 1. *Pyrolysis of 2-hydroxyethyl benzoate* (I), *2-chloroethyl benzoate* (IV), *and 2-phenoxyethanol* (V).

Pyrolysand	(I)	(I)	(IV)	(IV)	(IV)	(IV)	(V)
Pyrolysis no.	1	2	3	4	5	6	7
Temperature	375°	500°	400°	400°	450°	500°	500°
Feed-rate (g./min.)	0·34	0·54	0·43	0·48	0·51	0·57	0·39
Wt. pyrolysed (g.)	20·0	99·0	49·3	30·0	83·3	57·4	40·0
(*a*) Liquid pyrolysate (g.)	17·0	76·0	43·1	29·3	67·8	41·0	39·7
(*b*) Gaseous pyrolysate (l.)	Negl.	8·0	1·5	Negl.	2·0	Negl.	1·0
Composition (%) of (*b*) :							
CO	—	49·5	32·0	—	29·2	—	35·9
CO_2	—	1·8	23·3	—	55·4	—	Nil
CH_4	—	45·9	Nil	—	Nil	—	34·6
Unsat. hydrocarbons	—	2·8	44·7	—	15·4	—	29·5

— Not observed.

TABLE 2. *Pyrolysis of 2-phenoxyethyl acetate* (VI), *phenyl vinyl ether* (VII), *diethylene glycol* (III; X = OH), *2 : 2′-dichlorodiethyl ether* (III; X = Cl), *ethylene glycol* (VIII), *and 1 : 2-dichloroethane* (IX).

Pyrolysand	(VI)	(VI)	(VII)	(III : X = OH)	(III : X = Cl)	(VIII)	(IX)
Pyrolysis no.	8	9	10	11	12	13	14
Temperature	400°	500°	500°	375°	375°	375°	400°
Feed-rate (g./min.)	0·27	0·37	0·73	0·55	0·38	1·00	0·36
Wt. pyrolysed (g.)	65·4	96·0	22·0	50·0	50·0	25·0	10·3
(*a*) Liquid pyrolysate (g.)	63·3	89·0	10·0 *	46·0	34·0	23·2	7·6
(*b*) Gaseous pyrolysate (l.)	Negl.	14·0	1·0	Negl.	2·3	Negl.	†
Composition (%) of (*b*) :							
CO	—	34·9	—	—	—	—	—
CO_2	—	37·6	—	—	—	—	—
Unsat. hydrocarbons	—	27·5	‡	—	—	—	—

* Much carbonisation. ‡ Mainly acetylene.
† Contained hydrogen chloride (7·2% of theory). — Not observed.

2-Hydroxyethyl Benzoate (I).—*Preparation.* The pure benzoate (I), prepared (92%) by heating sodium benzoate with excess of ethylene chlorohydrin and a little diethylamine (140°; 4 hr.), had m. p. 37° (lit.,[24] 45°) and b. p. 146°/3 mm. (lit.,[2] b. p. 173°/21 mm.) (Found: C, 65·4; H, 6·1. Calc. for $C_9H_{10}O_3$: C, 65·1; H, 6·0%).

Pyrolysis 1. Acetaldehyde vapour was detected in the gaseous pyrolysate (*b*) by a 2 : 4-dinitrophenylhydrazine trap. Distillation of the liquid pyrolysate (*a*) yielded water (0·6 g.) and a residue which, when dissolved in ether and extracted with water and then with dilute alkali, yielded ethylene dibenzoate (major portion of pyrolysate), ethylene glycol (characterised as its dibenzoate), and only a trace of benzoic acid.

Pyrolysis 2. Distillation of (*a*) yielded acetaldehyde, 0·4 g. of a liquid, b. p. 80° (probably

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[22] Burton, *Chem. and Ind.*, 1954, 576.

[23] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.

[24] Heim and Poe, *J. Org. Chem.*, 1944, **9**, 299; cf. also G.P. 245,532/1910.

benzene), and 2·3 g. of water. Treatment of the residue with alkali removed benzoic acid (26·8 g.), leaving ethylene dibenzoate (24·1 g.) containing a little benzoic anhydride. Vinyl benzoate and acetophenone were not detected.

2-*Chloroethyl Benzoate* (IV).—*Preparation.* Prepared (85%) by heating benzoyl chloride (slight excess) with ethylene chlorohydrin (100°; 2 hr.), the pure benzoate had b. p. 152°/15 mm. (lit.,[25] b. p. 118—120°/2 mm.).

Pyrolysis 3. Hydrogen chloride was removed from (*b*) by a water trap (silver nitrate), and vinyl chloride (*ca.* 1·5 ml.) by the cold trap (infrared); a 2 : 4-dinitrophenylhydrazine trap showed only a trace of precipitate. Distillation of (*a*) yielded 12·9 g. of unchanged 2-chloroethyl benzoate, b. p. 160—180°/26 mm. (containing a little vinyl benzoate; infrared), and 17·5 g. of ethylene dibenzoate containing a trace of benzoic anhydride. Benzoic acid and 1 : 2-dichloroethane were not detected.

Pyrolysis 4. Hydrogen chloride and vinyl chloride were detected in (*b*) as before. Distillation of (*a*) yielded unchanged benzoate (IV) (24 g.), benzoic acid (3 g.), and a trace of ethylene dibenzoate.

Pyrolysis 5. Hydrogen chloride and vinyl chloride were detected in (*b*); a 2 : 3-dinitrophenylhydrazine trap showed a trace of precipitate. Distillation of (*a*) yielded unchanged benzoate (IV) (41 g.), benzoic acid (15 g.), and a liquid (*ca.* 1 g.), b. p. 215°/15 mm., which partly solidified, and which contained a little benzoic anhydride.

Pyrolysis 6. Hydrogen chloride and vinyl chloride were detected in (*b*); the cold trap contained a large condensate (*ca.* 25 ml.), in which vinyl chloride was detected by conversion into 1 : 2-dibromo-1-chloroethane, b. p. 163° (lit.,[9] b. p. 162·5—163°). Distillation of (*a*) yielded unchanged benzoate (IV) (12·3 g.), benzoic acid (23·0 g.), and a trace of liquid (*ca.* 0·1 g.), b. p. >280°, which partially solidified. Benzoic anhydride was present in (*a*).

2-*Phenoxyethanol* (V).—Pure material, from British Drug Houses Ltd., was used.

Pyrolysis 7. Acetaldehyde vapour was detected in (*b*) (2 : 4-dinitrophenylhydrazine trap). Distillation of (*a*) yielded water (2·7 g.); the residue, when dissolved in ether and washed with water, yielded no ethylene glycol; an alkali-soluble fraction (5 g.) was removed, which on acidification, extraction with ether, and distillation, yielded phenol (characterised as its benzoate) and unchanged 2-phenoxyethanol (V), b. p. 190—232° (infrared). No evidence could be found for the presence of phenyl vinyl ether (VII), diphenyl ether, diphenylacetal, or coumaran.

2-*Phenoxyethyl Acetate* (VI).—*Preparation.* Prepared (81%) by heating (V) with excess of acetic anhydride and a little pyridine (100°; 4 hr.), the pure acetate had b. p. 252—256° and n_D^{22} 1·504 (lit.,[26] b. p. 241—243°).

Pyrolysis 8. Acetaldehyde vapour (2 : 4-dinitrophenylhydrazine trap) was detected in (*b*), but no keten. Distillation of (*a*) yielded fractions (i)—(iv), b. p. 100—130°, 150—170°, *ca.* 180°, and 200° respectively, and a residue. Fraction (ii) contained anisole (characterised as 2 : 4-dinitroanisole) and on hydrolysis yielded acetaldehyde (indicating the presence of a vinyl ester and/or ether); fraction (iii) contained benzaldehyde, but gave a negative reaction (ferric chloride) for phenol; fraction (iv) was unchanged 2-phenoxyethyl acetate.

Pyrolysis 9. The cold trap contained some acetone. Liquid (*a*) was washed free from acetic acid, dried, and distilled, yielding fractions (i)—(vi), b. p. 145°, 150—160°, 170—180°, 180—200°, 200—220°, and 220—270° respectively, and a residue. Fraction (ii), treated with bromine–carbon tetrachloride, yielded 1 : 2-dibromoethyl phenyl ether (16 g.), b. p. 120°/6 mm., n_D^8 1·585 (lit.,[27] b. p. 140—145°/18 mm., n_D^{20} 1·5845), and was hence largely starting material; fraction (iv) contained carbon monoxide and dioxide, methane, ethylene, and acetylene (infrared).

Phenyl Vinyl Ether (VII).—*Preparation.* 2-Bromoethyl phenyl ether (400 g.) was refluxed (5 hr.) with solid sodium hydroxide (400 g.). Distillation yielded a liquid, b. p. *ca.* 100° (probably an azeotrope: separated into two layers), followed by 120 g. (56%) of 1 : 2-diphenoxyethane, b. p. 292—295°/6 mm., m. p. 98° (from ethanol), mixed m. p. 98°. The low-boiling fraction, on extraction with ether and distillation, yielded crude phenyl vinyl ether; refractionation yielded 22 g. (18%) of pure ether (VII), b. p. 155—158° (lit.,[18, 19] b. p. 155—156°).

Pyrolysis 10. Treatment with alkali divided (*a*) into phenol (6 g.; characterised as its

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[25] Kirner, *J. Amer. Chem. Soc.*, 1926, **48**, 2745.

[26] Roithner, *Monatsh.*, 1894, **15**, 675.

[27] McElvain and Fajardo-Pinzón, *J. Amer. Chem. Soc.*, 1945, **67**, 650.

benzoate; vapour-phase chromatography demonstrated the absence of *o*-cresol and *o*-vinylphenol) and an unidentified alkali-insoluble fraction (4 g.; b. p. 120—135°) which decolorised bromine–carbon tetrachloride and gave no 2 : 4-dinitrophenylhydrazone. The gaseous pyrolysate (*b*) was mainly acetylene (infrared).

Diethylene Glycol (III; X = OH).—Purified material, from British Drug Houses Ltd., was used.

Pyrolysis 11. Distillation of (*a*) yielded water (<1 g.; anhydrous copper sulphate test). Acetaldehyde was readily detected (chromatography of 2 : 4-dinitrophenylhydrazone).

2 : 2′-*Dichlorodiethyl Ether* (III; X = Cl).—Purified material, from British Drug Houses Ltd., was used.

Pyrolysis 12. The gaseous pyrolysate contained hydrogen chloride (water trap; silver nitrate) and acetaldehyde (2 : 4-dinitrophenylhydrazine trap). The cold trap collected *ca.* 1·8 g. of volatile liquid, containing vinyl chloride (infrared) and acetaldehyde.

Ethylene Glycol.—Purified material, from British Drug Houses Ltd., was used. Its water content was 0·26% (Karl Fischer method).

Pyrolysis 13. The liquid (*a*) was essentially unchanged ethylene glycol, containing no diethylene glycol (infrared), but with a water content of 2·10% (*i.e.*, about eight times the original value). No measurable amount of acetaldehyde was detected.

1 : 2-*Dichloroethane.*—Purified material, from British Drug Houses Ltd., was used.

Pyrolysis 14. The extent of decomposition was determined by passing the gaseous pyrolysate (*b*) through a water trap and titrating the dissolved hydrogen chloride (7·2% of theory).

Attempted Dehydrations (*Non-pyrolytic*) *of* 2-*Phenoxyethanol* (V).—The following reagents were applied:

(i) *Phosphoric oxide.* 2-Phenoxyethanol (excess) was slowly added to a suspension of phosphoric oxide in benzene; after refluxing (2 hr.), removal of solvent yielded tri-2-phenoxyethyl phosphate, m. p. 142° (from acetone), mixed m. p. 140°. Distillation of 2-phenoxyethanol over phosphoric oxide led to profound decomposition.

(ii) *Acetic acid and anhydride.* Treatment of 2-phenoxyethanol with glacial acetic acid and fused zinc chloride, or with acetic anhydride and pyridine, led only to formation of its acetate (VI).

(iii) *Sulphuric acid.* Treatment of 2-phenoxyethanol with cold concentrated or fuming sulphuric acid (7 days) caused little or no change; treatment at 100° (4 hr.) yielded an unidentified white solid, insoluble in ether but extremely soluble in water, which was certainly not *o*-vinylphenol (cf. Smith and Niederl [14]).

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