104. *Studies in Pyrolysis. Part VIII.* Competitive Routes in the Pyrolysis of Esters: Alkylene and Alkylidene Dibenzoates and Some Related Substances.*

By R. J. P. ALLAN, E. JONES, and P. D. RITCHIE.

Methylene dibenzoate at *ca.* 500—550° undergoes a primary disproportionation (*D*) to benzoic anhydride and formaldehyde; but trimethylene and propylene dibenzoate at *ca.* 400—500° undergo a primary alkyl–oxygen scission (A^1) to benzoic acid and allyl benzoate only. From these and supporting results it is concluded that the known A^1 and D scissions of ethylene dibenzoate [1] are consecutive rather than competitive, with formation of ethylidene dibenzoate as an intermediate. Competitive routes in the pyrolysis of allyl benzoate and acetate, and of benzoic anhydride, are described and discussed.

ETHYLENE DIBENZOATE, in the vapour phase at *ca.* 400—550°, yields two major pairs of products: (i) benzoic acid and vinyl benzoate (A^1 scission), and (ii) benzoic anhydride and acetaldehyde, corresponding to a disproportionation (D); and Allan, Forman, and Ritchie [1] visualised these A^1 and D reactions as concurrent and competitive (followed by secondary breakdowns). A modified and more precise interpretation of this "disproportionation" is now advanced, based upon studies of the pyrolysis of alkylene and alkylidene dibenzoates (I—IV) and of certain related substances.

$$\begin{array}{ll} \text{(I)}\ \ \mathrm{BzO{\cdot}CH_2{\cdot}OBz} & \mathrm{BzO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OBz}\ \ \text{(II)} \\ \text{(III)}\ \mathrm{BzO{\cdot}CHMe{\cdot}OBz} & \mathrm{BzO{\cdot}CH_2{\cdot}CHMe{\cdot}OBz}\ \ \text{(IV)} \end{array}$$

Methylene (I) *and Trimethylene Dibenzoate* (II).—Methylene dibenzoate, lacking a β-hydrogen atom, is much more thermostable than its ethylene homologue, and is not appreciably decomposed below *ca.* 500—550°. At this temperature, it breaks down by one detectable primary route (D) only:

$$\text{(I)}\ \mathrm{BzO{\cdot}CH_2{\cdot}OBz} \longrightarrow \mathrm{Bz_2O + CH_2O} \quad \dots\dots\dots \quad D$$

Other minor products observed (hydrogen, carbon monoxide and dioxide, benzoic acid, benzaldehyde, benzophenone, and diphenyl, the last three appearing only at *ca.* 550°) can all be accounted for as secondary products, some from formaldehyde and some (see below) from benzoic anhydride, though a number might also formally arise from other competitive primary scissions, such as the following:

$$\text{(I)}\ \mathrm{BzO{\cdot}CH_2{\cdot}OBz} \longrightarrow \begin{cases} \xrightarrow{?} \mathrm{Ph{\cdot}CHO + [BzO{\cdot}CHO]} \quad \dots\dots \quad B^2 \\ \xrightarrow{?} \mathrm{CO_2 + BzO{\cdot}CH_2Ph} \quad \dots\dots \quad C^2 \end{cases}$$

On secondary breakdown, the labile intermediate from route B^2 should undergo either decarbonylation (*i.e.*, behaving as an aldehyde) or disproportionation (*i.e.*, behaving as the mixed benzoic formic anhydride [2]); but in either case all the predictable end-products, though observed, can equally well be explained by other known scissions, so that there is no firm evidence either to confirm or to exclude the B^2 route. However, as shown below, ethylidene dibenzoate (III) yields *inter alia* a minor amount of benzaldehyde (*ca.* 500°); and here, though again the B^2 route might formally be responsible, there is no evidence for the acetic anhydride (or its scission products) which would be formed by disproportionation [2] of the mixed acetic benzoic anhydride arising concurrently with benzaldehyde by a B^2 scission. Indirectly, therefore, this evidence is an argument against competition

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* Part VII, *J.*, 1956, 3563.

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

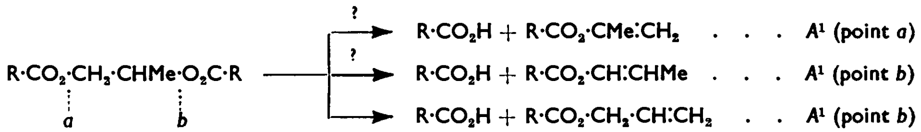
[2] Autenrieth, *Ber.*, 1901, **34**, 168.

by B^2 acyl–oxygen scission in the pyrolysis of diester (I). Likewise, the C^2 reaction does not appear to compete; for the pyrolysate from diester (I) contains neither benzyl benzoate nor the key breakdown-product, toluene, which is formed when the benzyl ester is pyrolysed in a sealed tube (*ca.* 340°)[3] or in the vapour phase (*ca.* 500°).[4]

The observed D reaction of methylene dibenzoate, coupled with the known A^1 and D reactions of ethylene dibenzoate,[1] suggests that the trimethylene homologue (II) should undergo both alkyl–oxygen scission (to benzoic acid and allyl benzoate) and disproportionation (to benzoic anhydride and propionaldehyde); but only the former primary reaction is observed (*ca.* 400—500°). An explanation of this apparent anomaly is given later.

$$\text{(II) BzO·CH}_2\text{·CH}_2\text{·CH}_2\text{·OBz} \longrightarrow \text{BzOH} + \text{BzO·CH}_2\text{·CH:CH}_2 \quad \ldots\ldots\ldots \quad A^1$$

Propylene Dibenzoate (IV) *and Diacetate.*—These diesters, each containing three β-carbon atoms showing different degrees of substitution, offer the formal possibility of three competitive A^1 scissions:



$$\text{R·CO}_2\text{·CH}_2\text{·CHMe·O}_2\text{C·R} \begin{cases} \xrightarrow{?} \text{R·CO}_2\text{H} + \text{R·CO}_2\text{·CMe:CH}_2 & \ldots\ A^1 \text{ (point } a) \\ \xrightarrow{?} \text{R·CO}_2\text{H} + \text{R·CO}_2\text{·CH:CHMe} & \ldots\ A^1 \text{ (point } b) \\ \longrightarrow \text{R·CO}_2\text{H} + \text{R·CO}_2\text{·CH}_2\text{·CH:CH}_2 & \ldots\ A^1 \text{ (point } b) \end{cases}$$

The views of Bailey *et al.*[5] on analogous systems suggest that only the last of these three primary routes will be followed; and pyrolysis of the rigorously purified dibenzoate and diacetate at *ca.* 500° now confirms that carboxylic acid and allyl ester are the only primary products, with no evidence for disproportionation (to acid anhydride and propionaldehyde) or for competitive A^1 routes.

The patent literature contains several claims[6-9] in apparent conflict with the above completely selective reaction. Thus, Chitwood[6] claims that propylene diacetate at *ca.* 470° yields propionaldehyde (*ca.* 22%) in addition to acetic acid and allyl acetate; and Ash *et al.*[7] and Burchfield[8] claim that the last two products are accompanied, at *ca.* 455—500°, by propenyl acetate, though they report it in widely differing amounts (*ca.* 2% and *ca.* 25% respectively). Similarly, Vaughn[9] claims that both allyl and propenyl acetate are formed, *inter alia,* during pyrolysis of a mixture of the 1- and the 2-monoacetate of propylene glycol at *ca.* 525°.

Some of these anomalies have a simple explanation. It has now been found that propylene diacetate is exceptionally difficult to free from unchanged diol, and that when the crude diester is pyrolysed the product contains propionaldehyde (a known breakdown product of the glycol[10]). None of the above four workers[6-9] mentions any criterion of the purity of the pyrolysand; and, in default of this evidence, it must be concluded that in each case the pyrolysate contained propionaldehyde arising from free propylene glycol and not necessarily, as suggested by Chitwood[6] and Vaughn,[9] from an ester. In addition, the system studied by Vaughn[9] offers yet a further source of aldehyde *via* the glycol; for the two monoacetates, even if originally rigorously pure (which is improbable), must have undergone at least in part a disproportionation of the type described by Cretcher and Pittenger.[11] This reaction would here yield propylene glycol and its diacetate; and a little of the latter was actually observed by Vaughn[9] in the pyrolysate, though admittedly it might have been present in the original pyrolysand.

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[3] Hurd and Bennett, *J. Amer. Chem. Soc.*, 1929, **51**, 1197.

[4] Jones and Ritchie, unpublished observation, 1956.

[5] Bailey and Rosenberg, *J. Amer. Chem. Soc.*, 1955, **77**, 73; Bailey and King, *ibid.*, p. 75; Bailey, Hewitt, and King, *ibid.*, p. 357.

[6] Chitwood, U.S.P. 2,251,983/1941.

[7] Ash, Carlson, Koslin, and Vaughn, U.S.P. 2,441,540/1948.

[8] Burchfield, U.S.P. 2,485,694/1949.

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

[10] Nef, *Annalen*, 1904, **335**, 191.

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

These considerations can readily account for the propionaldehyde observed by Chitwood;[6] and they invalidate the proof advanced by Vaughn[9] for the presence of propenyl acetate (namely, detection of propionaldehyde in the hydrolysate from low-boiling pyrolysate fractions), since the pyrolysate must have contained this aldehyde even before hydrolysis. No evidence is recorded by Ash *et al.*[7] or Burchfield[8] in support of their claim that propenyl acetate is formed.

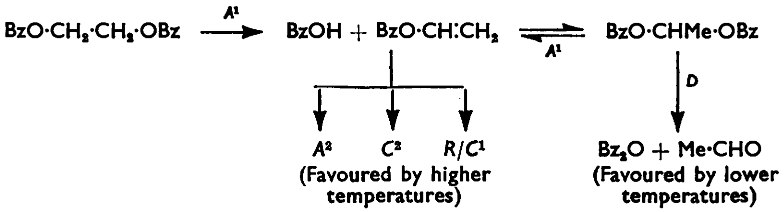
Mechanism of Disproportionation.—In view of the foregoing results, it is necessary to seek a mechanism for the *D* reaction which will permit disproportionation of ethylene dibenzoate[1] but not of its trimethylene and propylene homologues. A convincing explanation emerges from the following three experiments:

(i) Copyrolysis of benzoic acid and vinyl benzoate (equimolar mixture: *ca.* 500°) gives a much higher yield of benzoic anhydride than does pyrolysis of ethylene dibenzoate itself.[12] Since benzoic acid undergoes negligible conversion into anhydride under the same conditions,[1] the latter must be produced in the actual copyrolysis of the acid and its vinyl ester.

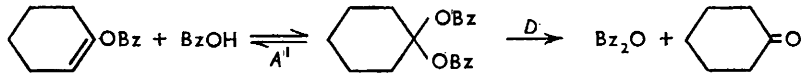
(ii) Vinyl benzoate, refluxed gently with a molar equivalent of benzoic acid (bath *ca.* 280°), yields benzoic anhydride almost quantitatively,[12] presumably because here the much lower temperature minimises competitive destruction of vinyl benzoate by the R/C^1 breakdown (threshold temperature *ca.* 190°).[1]

(iii) Ethylidene dibenzoate (*ca.* 500°) undergoes two competitive scissions: (*a*) a major disproportionation to benzoic anhydride and acetaldehyde, and (*b*) a minor A^1 scission to benzoic acid and vinyl benzoate. This agrees with Matheson's claim[13] that the analogous compound ethylidene diacetate (at *ca.* 410°) yields mainly acetic anhydride and acetaldehyde, with a small amount of acetic acid and vinyl acetate.

These results clearly indicate that the overall breakdown of ethylene dibenzoate is best represented thus:



This concept is supported by the fact that at *ca.* 480° *cyclo*hex-1-enyl benzoate yields a negligible amount of benzoic acid, and no anhydride; whereas, gently refluxed with a molar equivalent of benzoic acid, it gives the anhydride and *cyclo*hexanone in fair yield,[12] a result now best interpreted thus:



It appears, therefore, that "disproportionation" of a 1 : 2-alkylene diester is preceded by thermal re-addition of the primary A^1 scission products to give a 1 : 1-alkylidene diester, the true precursor of the *D* reaction. This explains very simply the failure of trimethylene (II) and propylene dibenzoate (IV) to disproportionate, since here the A^1 scission products, benzoic acid and allyl benzoate, cannot yield a 1 : 1-diester by re-addition (cf. the known interaction of acetic acid and allyl acetate to yield a 1 : 2-diester, propylene diacetate[14]).

The formation of an alkylidene diester by the *catalysed* addition of a carboxylic acid to its

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[12] Allan, Ph.D. Thesis, Glasgow University, 1956.

[13] Matheson, B.P. 368,835/1930; U.S.P. 1,872,479/1932; cf. Geuther, *Annalen*, 1858, **106**, 249.

[14] von Béhal and Desgrez, *Compt. rend.*, 1892, **114**, 676.

own [15] (or another [16]) vinyl ester is, of course, well known; but the above *uncatalysed* thermal additions, in the liquid or vapour phase, do not appear to have been recorded previously.

It is possible that this concept may have other applications. The well-known efficiency of enol carboxylates (*e.g.*, *iso*propenyl acetate) as acylating agents is usually attributed to ester interchange. However, although an equimolar mixture of vinyl benzoate and benzyl alcohol yields benzyl benzoate and acetaldehyde almost quantitatively when simply refluxed (5 hr.; bath 240°), an equimolar mixture of allyl benzoate and benzyl alcohol remains virtually unchanged under the same conditions.[4] This suggests that the "ester interchange" may be, in fact, an addition–disproportionation sequence of the general type discussed above:

$$\begin{array}{ccccc} \text{BzO·CH:CH}_2 & & & & \text{BzO·CH}_2\text{Ph} \\ + & \longrightarrow & [\text{BzO·CHMe·O·CH}_2\text{Ph}] & \xrightarrow{D} & + \\ \text{Ph·CH}_2\text{·OH} & & \text{1 : 1-Addition product ?} & & \text{Me·CHO} \end{array}$$

Allyl Benzoate and Acetate.—Pyrolysis of these esters was studied, to assist in interpreting minor secondary products obtained from diesters (II) and (IV). The two allyl esters break down, at *ca.* 450—500°, by the following competitive routes:

$$\text{R·CO}_2\text{·CH}_2\text{·CH:CH}_2 \longrightarrow \begin{cases} \longrightarrow \text{R·CHO} + \text{CH}_2\text{:CH·CHO} \quad . \; . \; . \; . \; . \; . \quad B^2 \\ \longrightarrow \text{CO}_2 + \text{CH}_2\text{:CH·CH}_2\text{R} \quad . \; . \; . \; . \; . \; . \quad C^2 \end{cases}$$

There was no evidence for the further formal possibility that both allyl esters might undergo A^1 scission to carboxylic acid and allene (and/or methylacetylene), and that the acetate might yield keten and allyl alcohol by B^1 scission.

Both allyl esters yield the known scission-products of the aldehyde R·CHO, and of acraldehyde; but, while the latter aldehyde can readily be detected in the pyrolysate, it is unexpectedly difficult to demonstrate directly the formation of benzaldehyde from allyl benzoate by reaction B^2. Pure benzaldehyde largely survives passage through the reaction vessel under the same conditions; yet allyl benzoate containing 5% of added benzaldehyde yields a pyrolysate containing only a trace of the latter. Possibly some unexpected type of free-radical attack is responsible for this enhanced destruction of benzaldehyde during the copyrolysis.

Benzoic Anhydride.—This substance was studied to assist in accounting for minor by-products in the pyrolysate from methylene dibenzoate. The anhydride, like the diester, is remarkably thermostable; but at *ca.* 550° it yields a complex pyrolysate containing benzoic acid and benzene (predominating), together with carbon monoxide and dioxide, benzophenone, diphenyl, and benzaldehyde. Some of these products can be tentatively but reasonably explained thus:

$$\text{Bz}_2\text{O} \longrightarrow \text{CO}_2 + \text{COPh}_2 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad C^2$$

$$\text{COPh}_2 \longrightarrow \text{CO} + \text{Ph}_2 \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad C^1$$

The others, however, are more surprising; and the formation of benzoic acid (which is one possible precursor of the observed benzene) may be compared to the unexpected formation of traces of this substance in the pyrolysis of αα-dicyanobenzyl benzoate,[17] which like the anhydride possesses no β(or α)-hydrogen atom.

For most of the observed products, more than one possible origin can be visualised, by way of high-temperature radical reactions. That such radical reactions do, in fact, occur is demonstrated by the formation of chlorobenzene and, rather surprisingly, hexachlorobenzene during the copyrolysis, at *ca.* 550°, of an equimolar mixture of benzoic anhydride and carbon tetrachloride (cf. the analogous use of carbon tetraiodide [18]).

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[15] Chem. Fab. Griesheim-Elektron, G.P. 271,381/1914.

[16] *Idem*, G.P. 313,696/1919; Hermann and Haenel, G.P. 753,039/1952.

[17] Bennett, Jones, and Ritchie, *J.*, 1956, 2628.

[18] Simon and Dull, *J. Amer. Chem. Soc.*, **1933**, **55**, 2696.

EXPERIMENTAL

Apparatus.—The arrangement of reaction vessel, furnace, traps, and receivers has previously been described.[1]

Results.—The Table summarises the general experimental results for 17 pyrolyses. The composition of each gaseous pyrolysate (*c*) is reported on a nitrogen-free basis. Several reaction vessels, of different dimensions, were used (all of Pyrex glass, packed with Pyrex helices); and to bring all results on to a common basis, a contact time (t_c sec.) is calculated for each run from the usual type of formula, $t_c = 273pV/22{\cdot}4TN$, where p = pressure in reaction vessel (atm.); V = free unpacked space therein (l.); T = temp. of reaction zone (°K); N = feed rate of pyrolysand (mole/sec.). In the present work, where $p = 1$ atm. (approx.), $t_c = 12{\cdot}2V/TN$. This expression is, of course, an over-simplification (it assumes that T is uniform over the whole contact-volume V, and that the gaseous pyrolysand undergoes no volume change other than that due to thermal expansion), but it gives a useful common comparative measure of contact time.

Pyrolysand	(I)		(II)		(III)	(IV)	Propylene diacetate	
Pyrolysis no.	1	2	3 *	4	5	6	7	8
Temp.	500°	550°	400°	500°	500°	500°	500°	500°
Feed rate (g./min.)	0·38	0·33	0·85	0·50	0·20	0·36	0·56	0·57
Contact time (sec.)	19	147	18	16	250	22	8	13
Weight pyrolysed (g.)	45·5	52	104	60	10	79	50	80
Pyrolysate:								
(*a*) in cold trap (g.)	—	3·5	Trace	Trace	Nil	Trace	Trace	‡
(*b*) in main receiver (g.)	37	42·5	99·5	52·5	9·3	72	40	48
(*c*) gaseous (l.)	2·5	12	1·5	4	1·5	3	5 †	17
Composition (%) of (*c*):								
Carbon monoxide	40·0	58·6	40·5	38·6	66·5	45·7	35·0	—
Carbon dioxide	14·8	27·8	46·8	48·5	20·5	45·3	22·2	—
Hydrogen	42·0	12·9	Nil	Nil	Nil	Nil	Nil	—
Sat. hydrocarbons	*ca.* 3·0	Trace	Nil	Nil	12·2	Nil	33·5	—
Unsat. hydrocarbons	Trace?	Nil	12·7	12·9	0·8	9·0	9·3	—

Pyrolysand	Allyl benzoate		Acraldehyde	Benzaldehyde	Allyl acetate		Benzoic anhydride		
Pyrolysis no.	9	10	11	12	13	14	15	16	17
Temp.	455°	500°	480°	500°	500°	500°	525°	550°	565°
Feed rate (g./min.)	0·75	0·33	0·50	0·50	1·00	0·62	0·34	0·60	0·60
Contact time (sec.)	6	14	34	10	5	5	122	67	66
Weight pyrolysed (g.)	50	40	30	50	60	50	76	60	80
Pyrolysate:									
(*a*) in cold trap (g.)	Nil	<1	Nil	Nil	10	—	—	—	0·8
(*b*) in main receiver (g.)	49	37	27	46	40·5	42·5	65·5	53	65·5
(*c*) gaseous (l.)	1	2	3	1	7	4·5	3·3	3·8	6·5
Composition (%) of (*c*):									
Carbon monoxide	—	47·4	77·5	96·0	43·0	47·0	80·9	58·5	49·5
Carbon dioxide	—	40·4	3·5	Nil	51·0	43·7	19·1	41·5	50·5
Hydrogen	—	Nil	Nil	Nil	Nil	Nil	Trace?	Nil	Nil
Sat. hydrocarbons	—	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Unsat. hydrocarbons	—	12·2	19·0	4·0	6·0	9·3	Nil	Nil	Nil

* Pyrolysand introduced in pellet form. † Including 0·5 l. obtained on evaporation of (*a*).
‡ Cold trap omitted. — Not examined.

Analytical Methods.—The detailed examination of each pyrolysate is summarised below. All aldehydes and ketones were characterised as their 2 : 4-dinitrophenylhydrazones (paper chromatography [19] or mixed m. p.); benzene was characterised as *m*-dinitrobenzene (mixed m. p.); all other solids mentioned were identified by mixed m. p. Acid anhydrides were also detected by the Davidson–Newman [20] colour reaction. The normal chemical examination of fractions was in many cases supplemented by infrared spectrometry.

Methylene Dibenzoate (I).—*Preparation.* The diester, prepared by the action of benzoyl

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[19] Burton, *Chem. and Ind.*, 1954, 576.
[20] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.

chloride on paraformaldehyde in presence of zinc chloride,[21] and crystallised from ethanol, had m. p. 99° (Staudinger and Lüthy,[21] m. p. 99°) (Found: C, 70·3; H, 4·9. Calc. for $C_{15}H_{12}O_4$: C, 70·3; H, 4·7%).

Pyrolysis 1. The exit gases (*c*) contained formaldehyde (2 : 4-dinitrophenylhydrazine trap); the cold trap (*a*) contained polyoxymethylene (yielding formaldehyde on heating). Product (*b*), treated with ether, gave an insoluble residue of polyoxymethylene; the extract, distilled, yielded benzoic acid (b. p. 120—138°/10 mm). and benzoic anhydride (b. p. 192—198°/6 mm.).

Pyrolysis 2. The exit gases (*c*) contained formaldehyde (2 : 4-dinitrophenylhydrazine trap); the cold trap (*a*) contained benzene (*ca.* 2 g.) and polyoxymethylene (*ca.* 1·5 g.). Distillation of (*b*) yielded (i) 10·25 g., b. p. 78—82° (benzene), (ii) 2·25 g., b. p. 60—87°/6 mm. [diphenyl (characterised as 4 : 4′-dinitrodiphenyl), benzaldehyde, and a trace of benzoic acid] (iii) 2·5 g., b. p. 87—120°/6 mm. (diphenyl, benzoic acid, and trace of benzoic anhydride), and (iv) 12·0 g., b. p. 148—164°/6 mm. (benzoic anhydride and trace of benzophenone).

Trimethylene Dibenzoate (II).—*Preparation.* Trimethylene glycol was benzoylated in acetone solution, and the product precipitated with alkali. Recrystallisation from benzene–light petroleum gave the pure dibenzoate, m. p. 57—59° (Gabriel,[22] m. p. 57·5°).

Pyrolysis 3. In this run, the solid pyrolysand was introduced in pellet form by a solenoid-operated feed. Distillation of (*b*) yielded (i) 2 g., b. p. 50—72°, (ii) 2 g., b. p. 50—82°/1 mm., (iii) 20 g., b. p. 78—81°/0·5 mm., (iv) 4 g., b. p. 86°/0·5 mm., and (v) 71·5 g. of high-boiling material. No carbonyl compound other than acraldehyde was detectable in fractions (i) and (ii); fractions (ii)—(iv) were mixtures of allyl benzoate and allylbenzene (cf. Pyrolysis 4); fraction (v) yielded benzoic acid (22 g.) and unchanged diester (38·5 g.), and gave the colour reaction [20] of an acid anhydride. The gaseous pyrolysate (*c*) contained ethylene, acetylene, and possible traces of methane (infrared).

Pyrolysis 4. The exit gases (*c*) and the contents of the cold trap (*a*) contained acraldehyde. Distillation of (*b*) yielded (i) 1·5 g., b. p. 40—70°/7 mm. (160° by capillary tube method), (ii) 7 g., b. p. 90—98°/6 mm., (iii) 16 g., b. p. 100—109°/6 mm., and (iv) 27 g. of residue. Fraction (i) contained traces of acraldehyde; the main constituent (unidentified) showed infrared absorption bands tentatively correlated with vinyl and hydroxyl groups. Fractions (ii) and (iii) were mainly allyl benzoate; the combined fractions had b. p. 228—230°, and an alkaline hydrolysis yielded benzoic acid, allyl alcohol (phenylurethane), and a non-saponifiable fraction, allylbenzene (infrared spectrum identical with that of a specimen prepared by the Friedel–Crafts method [23]). The residue (iv) yielded benzoic acid (20 g.) and charred material (7 g.).

Ethylidene Dibenzoate (III).—*Preparation.* The diester was prepared[24] by heating ethylidene diacetate with benzoic anhydride and a trace of concentrated sulphuric acid (100°); it formed crystals [from light petroleum (b. p. 100—120°)], m. p. 70° (Wegscheider and Späth,[24] m. p. 72°).

Pyrolysis 5. The exit gases (*c*) contained acetaldehyde. Distillation of (*b*) yielded (i) 0·2 g., b. p. 70—120°/2 mm., (ii) 1·3 g., b. p. 120—170°/2 mm., (iii) 3·5 g., b. p. 170—180°/2 mm., and (iv) 1·5 g., residual tars (overall loss 3·5 g.). Fraction (i) was vinyl benzoate (infrared), benzaldehyde, acetophenone (chromatography), and (trace) benzoic acid; fractions (ii) and (iii) were benzoic acid, benzoic anhydride, and acetophenone. (In a repetition of Pyrolysis 5, keten and acetic anhydride were carefully sought, but were absent.)

Propylene Dibenzoate (IV).—*Preparation.* Propylene glycol was benzoylated with a 20% excess of benzoyl chloride, and the product carefully fractionated. The pure ester (IV) had b. p. 202—203°/4 mm. (Heim and Poe,[25] b. p. 232°/12 mm.) (Found: C, 71·8; H, 5·8. Calc. for $C_{17}H_{16}O_4$: C, 71·8; H, 5·7%).

Pyrolysis 6. Distillation of (*b*) yielded (i) 1 g., b. p. 45—80°, (ii) 22 g., b. p. 40—90°/5 mm., (iii) 3 g., b. p. 82—92°/0·5 mm., (iv) 1 g., b. p. 92—180°/0·5 mm., (v) 6 g., b. p. 180—195°/0·5 mm., and (vi) 14 g. of residue. Fraction (i), and a trace of liquid in the cold trap (*a*), consisted of acraldehyde, with no evidence for propionaldehyde; fractions (ii) and (iii) were mainly allyl benzoate (infrared; no bands present attributable to propenyl or *iso*propenyl benzoate); fractions (iv) and (v) were mainly unchanged ester (IV). Benzoic acid (31 g.) was recovered

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[21] Staudinger and Lüthy, *Helv. Chim. Acta*, 1925, **8**, 57.

[22] Gabriel, *Ber.*, 1905, **38**, 2406.

[23] Huston and Sager, *J. Amer. Chem. Soc.*, 1926, **48**, 1956.

[24] Wegscheider and Späth, *Monatsh.*, 1909, **30**, 860.

[25] Heim and Poe, *J. Org. Chem.*, 1944, **9**, 299.

from the residue. A sub-fraction (b. p. 34—48°/0·7 mm.) from fraction (ii) contained allylbenzene (infrared).

Propylene Diacetate.—Preparation. Propylene glycol was acetylated in presence of zinc chloride (violent reaction);[14] the product was dissolved in ether and very carefully washed, to remove free glycol, and fractionally distilled several times. The purified diester had b. p. 188—191° (von Béhal and Desgrez,[14] b. p. 191°) (Found : C, 52·4; H, 7·8. Calc. for $C_7H_{12}O_4$: C, 52·5; H, 7·6%).

Pyrolysis 7. Slightly impure propylene diacetate was used, to demonstrate the effect of propylene glycol in the pyrolysand. Distillation of (*b*) yielded (i) 1 g., b. p. 50—99° (mainly propionaldehyde), (ii) 14 g., b. p. 99—110° (allyl acetate) (refractive index), giving allyl alcohol (phenylurethane) on hydrolysis, (iii) 15 g., b. p. 110—130° (containing acetic acid), (iv) 8 g., b. p. 130—186° (unchanged diester), and (v) 2 g. of residue. Fractions (iii) and (iv) contained no acid anhydride (colour test[20]).

Pyrolysis 8. Highly purified propylene diacetate was used for this run. Distillation of (*b*) yielded (i) 3 g., b. p. 48—105°, (ii) 13 g., b. p. 105—113°, (iii) 16 g., b. p. 113—118°, (iv) 7 g., b. p. *ca.* 118°, and (v) 7 g. of residue. Fraction (i) contained acraldehyde and traces of allyl acetate (refractive index); fractions (iii) and (iv) were acetic acid (refractive index). Fractions (ii), (iii), and (iv) were combined, washed free from acid, and carefully fractionated, yielding 3 g. of pure allyl acetate, b. p. 100—104° (infrared); hydrolysis of this yielded only acetic acid and allyl alcohol, and there was no evidence (infrared) for propenyl or *iso*propenyl acetate. The exit gases (*c*) contained acraldehyde, and a vanishingly small trace of propionaldehyde (2 : 4-dinitrophenylhydrazine trap; paper chromatography[19]).

Allyl Benzoate.—Preparation. Benzoylation of allyl alcohol,[26] followed by careful fractionation, yielded the pure ester, b. p. 78—80°/2 mm. (Perkin,[26] b. p. 80°/1 mm.).

Pyrolysis 9. Distillation of (*b*) yielded (i) a few drops, b. p. 52—120° (mainly acraldehyde), (ii) 1 g., b. p. 40—80°/7 mm. (containing acraldehyde), (iii) 34 g., b. p. 77—80°/2 mm. (unchanged allyl benzoate), and (iv) 14 g. of residue. No benzaldehyde could be detected, but its breakdown product, benzene, was identified.

Pyrolysis 10. The pyrolysand was a mixture of allyl benzoate (95%) and benzaldehyde (5%). The cold trap contained a trace of unidentified liquid (*a*) having the same infrared spectrum as fraction (i) from Pyrolysis 4. Distillation of (*b*) yielded (i) 1·5 g., b. p. 60—82° (acraldehyde and benzene : infrared), (ii) 1 g., b. p. 40—80°/10 mm. (unchanged allyl benzoate, with trace of benzaldehyde : infrared), (iii) 26 g.; b. p. 80—90°/5 mm. (unchanged allyl benzoate), (iv) 1 g., b. p. 92°/4 mm. (containing benzoic acid), and (v) 7·5 g. of residue (benzoic acid and charred material).

Pyrolysis 11. Acraldehyde was pyrolysed as a check on the infrared spectrum of (*c*) from Pyrolyses 3 and 9. Distillation of (*b*) yielded (i) 1 g., b. p. 20—51°, (ii) 25 g., b. p. 52—56°, and (iii) 1 g., b. p. 56—58°. All three consisted almost wholly of unchanged acraldehyde; no material was obtained corresponding to the unidentified liquid from Pyrolyses 4 and 10.

Pyrolysis 12. Redistilled benzaldehyde was pyrolysed as a check on Pyrolysis 10, in which benzaldehyde was almost wholly destroyed. Distillation of (*b*) yielded (i) 1 g., b. p. 84—160° (containing benzene: characterised as *m*-dinitrobenzene), (ii) 41 g., b. p. 176—180° (unchanged benzaldehyde), and (iii) 4 g., b. p. 180° (benzaldehyde, with a little benzoic acid, the latter being a pyrolysis product previously reported by Lachman[27]).

Allyl Acetate.—Preparation. Pure ester, b. p. 103—104°, from British Drug Houses Ltd., was used.

Pyrolysis 13. Evaporation of (*a*) at room temperature yielded mostly but-1-ene (infrared), with some acraldehyde, but no keten (aniline–ether trap); distillation of the less volatile residue from (*a*) then gave acraldehyde (1 g., b. p. 45—70°) and allyl acetate (2 g.; b. p. 70—102°). Distillation of (*b*) yielded (i) 6 g., b. p. 70—100°, (ii) 32·5 g., b. p. 100—108°, and (iii) 4 g. of residue. Fraction (i) contained no allyl alcohol (alkali alkyl xanthate test,[18] with control tests on pure allyl alcohol); fractions (ii) and (iii) were mainly unchanged allyl acetate, and contained no acid anhydride (colour reaction[20]).

Pyrolysis 14. The gaseous pyrolysate (*c*) only was examined, in two portions. Olefins were removed from the first by bromine–chloroform; the residue contained methane (trace)

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[26] Perkin, *J.*, 1896, **69**, 1226.

[27] Lachman, *J. Amer. Chem. Soc.*, 1924, **46**, 720.

[28] Feigl, " Spot Tests," Elsevier, Amsterdam, 4th Edn. (revised), 1954, p. 129.

and ethylene. The second contained acraldehyde but no acetaldehyde (fractional crystallisation of product from 2 : 4-dinitrophenylhydrazine trap).

Benzoic Anhydride.—Preparation. Pure anhydride was prepared by treatment of benzoic acid with acetic anhydride; [29] crystallised from light petroleum, it had m. p. 42·5° (Anschütz,[29] m. p. 42·5°).

Pyrolyses 15—17. The analyses of the gaseous pyrolysates (*c*) show a diminishing $CO : CO_2$ molar ratio with increasing temperature. In Pyrolysis 17, the cold trap (*a*) contained benzene (0·8 g.); distillation of (*b*) yielded (i) 7·5 g., b. p. 78—82° (benzene), (ii) 6·5 g., b. p. 100—130°/10 mm. [diphenyl (characterised as 4 : 4′-dinitrodiphenyl), benzaldehyde, and benzoic acid], (iii) 4·25 g., b. p. 130—160°/10 mm. (benzoic acid and trace of diphenyl), (iv) 32·5 g., b. p. 160—170°/10 mm. (benzoic anhydride and a trace of benzophenone), (v) 2·0 g., b. p. 170—210°/10 mm. (benzoic anhydride and tar), and (vi) 5·75 g. of high-boiling tars.

Copyrolysis of Benzoic Anhydride and Carbon Tetrachloride.—A mixture of benzoic anhydride (22·3 g.) and " AnalaR " carbon tetrachloride (23·2 g.), pyrolysed at 550° (feed rate, 0·25 g./min.; contact time, 119 sec.) gave a gaseous pyrolysate (10·0 l.) containing 51·5% of displaced nitrogen; the nitrogen-free fraction consisted of carbon monoxide (41·7%), carbon dioxide (32·8%), and hydrogen chloride (25·5%). On distillation, the liquid pyrolysate (23·0 g.) yielded (i) 2·5 g., b. p. 97—115°, (ii) 2·0 g., b. p. 115—130°, (iii) 2·5 g., b. p. 130—146°, (iv) 3·0 g., b. p. 54—74°/4 mm., (v) 1·0 g., b. p. 75—100°/4 mm., (vi) 3·5 g., b. p. 100—150°/4 mm., and (vii) 8·25 g. of high-boiling tars. Fractions (i)—(iii) consisted of carbon tetrachloride and chlorobenzene; fraction (iv) was chlorobenzene (characterised as 1-chloro-2 : 4-dinitrobenzene); fraction (v) was benzoic anhydride and (trace) chlorobenzene; fraction (vi) was hexachlorobenzene, m. p. and mixed m. p. 227°.

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[29] Anschütz, *Annalen*, 1885, **226**, 12.