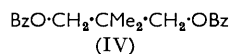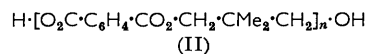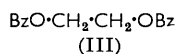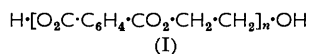## 911. *Studies in Pyrolysis. Part XIV.* The Pyrolysis of 2 : 2-Dimethyltrimethylene Dibenzoate.*

By A. GOLOMB and P. D. RITCHIE.

In the vapour phase at *ca.* 500°, 2 : 2-dimethyltrimethylene dibenzoate undergoes primary acyl–oxygen scission to benzaldehyde and an unstable ester-aldehyde, β-benzoyloxy-αα-dimethylpropionaldehyde. The latter undergoes a secondary decarbonylation to *iso*butyl benzoate, which then breaks down by the predictable alkyl–oxygen and acyl–oxygen scissions.

POHL[1] showed that poly(ethylene terephthalate) (I) is less resistant to thermal breakdown than its higher *gem.*-dimethyl analogue (II), though no detailed mechanism was suggested. Later, an interpretation for the easier breakdown of the polyester (I) was elaborated by Ritchie *et al.*[2] from a study of the model compound ethylene dibenzoate (III) and related substances, but no consideration was then given to polyester (II). However, the increasing availability of *neo*pentylene glycol (2 : 2-dimethylpropane-1 : 3-diol), which is the key raw-material for (II), has now prompted a study of the thermal stability of its esters. *neo*Pentylene dibenzoate (2 : 2-dimethyltrimethylene dibenzoate) (IV) was selected, as constituting a good model for polyester (II); the results clarify the thermal breakdown of the latter.

$$H \cdot [O_2C \cdot C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CH_2]_n \cdot OH$$
(I)

$$H \cdot [O_2C \cdot C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CMe_2 \cdot CH_2]_n \cdot OH$$
(II)

$$BzO \cdot CH_2 \cdot CH_2 \cdot OBz$$
(III)

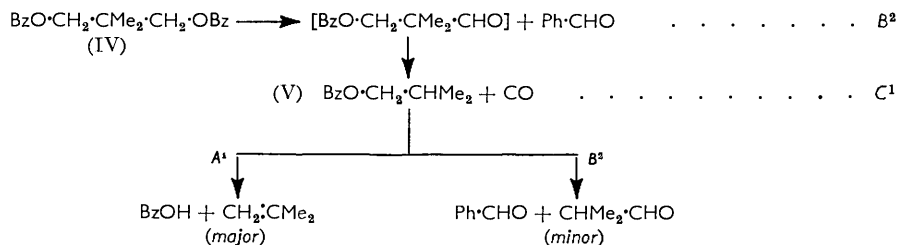$$BzO \cdot CH_2 \cdot CMe_2 \cdot CH_2 \cdot OBz$$
(IV)

The greater thermal stability of polyester (II) than of (I) finds a parallel in the behaviour of the corresponding models (IV) and (III), which under identical conditions break down at 500° (vapour phase) to the extent of *ca.* 50% and *ca.* 81% respectively (see Experimental).

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* Part XIII, preceding paper.

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

[2] Ritchie *et al.*, *J.*, 1955, 2717; 1956, 3563; 1957, 524, 2107, 2556.

The absence of a β-hydrogen atom from substances (II) and (IV) precludes the A^1 scission readily undergone by substances (I) and (III), leaving as the only readily predictable breakdown-route an acyl–oxygen scission (B^2) at higher temperatures (cf. preceding paper). The nature of the complex pyrolysate from model (IV) supports this conclusion. The major products are benzaldehyde, benzoic acid, benzene, carbon monoxide, carbon dioxide,

BzO·CH₂·CMe₂·CH₂·OBz ⟶ [BzO·CH₂·CMe₂·CHO] + Ph·CHO . . . . B²
(IV)

(V) BzO·CH₂·CHMe₂ + CO . . . . C¹

BzOH + CH₂ːCMe₂   Ph·CHO + CHMe₂·CHO
(major)   (minor)

*iso*butene, and *iso*butyl benzoate, plus traces of *iso*butyraldehyde, benzoic anhydride, and water. Other substances sought (see below), but with negative results, were formaldehyde, trimethylacetaldehyde, *iso*butylbenzene, and hydrogen. The best interpretation of the results indicates a primary non-competitive B^2 scission, followed by the secondary scissions shown in the annexed scheme (coupled with certain other simple predictable decompositions).

Discussion.—The key to the above interpretation of the analytical results is the identification of *iso*butyl benzoate (V). This can hardly originate otherwise than by decarbonylation of the ester-aldehyde β-benzoyloxy- αα-dimethylpropionaldehyde, which, though not identified, can therefore confidently be postulated as the intermediate product accompanying benzaldehyde on primary B^2 scission of ester (IV). No evidence was found that this ester-aldehyde also breaks down by other competitive routes, such as a further secondary scission to two aldehydes, benzaldehyde and dimethylmalondialdehyde. The latter is likely to be very unstable thermally, like its lower monomethyl homologue,[3] and at 500° could well yield *iso*butyraldehyde by semidecarbonylation; but, though a trace of the latter aldehyde occurs in the pyrolysate from ester (IV), it can be accounted for alternatively and with greater certainty. A separate pyrolysis of *iso*butyl benzoate (Table, Run 4) showed, as expected, predominating A^1 scission accompanied by a minor B^2 scission to benzaldehyde and *iso*butyraldehyde, a result in agreement with the by-products recorded by Hurd and Blunck [4] in the analogous pyrolysis of *iso*butyl acetate.

Certain other constituents of the pyrolysate may formally arise *via* more than one route. For example, A^1 scission of *iso*butyl benzoate is certainly responsible for most of the *iso*butene (which corresponds roughly in molar amount to the observed benzoic acid and its decarboxylation product, benzene), but part of the alkene may conceivably be formed in another way. Other work [5] has shown that for many esters the competitive pyrolytic routes include a disproportionation to acid anhydride plus an unstable ether; on this basis the ester (IV) might yield benzoic anhydride and the cyclic ether 2 : 2-dimethyltrimethylene oxide (VI). The present results, however, suggest that this does not occur. The pyrolytic properties of ether (VI) are not known, but its simplet analogue trimethylene oxide (VII) breaks down [6] at *ca.* 450° to formaldehyde and ethylene (with no evidence for rearrangement to propionaldehyde), which suggests that ether (VI), if formed initially at *ca.* 500°, should similarly yield formaldehyde (or its breakdown products, including hydrogen) and *iso*butene, but probably not trimethylacetaldehyde.

Formaldehyde, hydrogen, and trimethylacetaldehyde could not be detected; also, the observed trace of acid anhydride is apparently formed by direct dehydration of benzoic

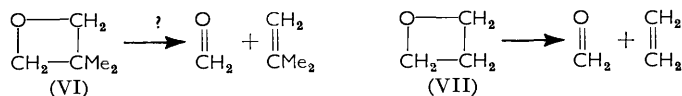[3] Pummerer, Hahn, Johne, and Kahlen, *Ber.*, 1942, **75**, 867.
[4] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.
[5] Jones and Ritchie, unpublished observations.
[6] Bittker and Walters, *J. Amer. Chem. Soc.*, 1955, **77**, 1429.

acid (cf. Davidson and Newman [7]), since a little water is also found. Hence, it seems that no significant amount of the observed *iso*butene arises *via* such a disproportionation.

No products attributable to primary decarboxylation of ester (IV) could be detected; for example, there was no *iso*butylbenzene, which should result from a C^2–B^2–C^1 sequence. Benzene is the only decarboxylation-product observed, though part of it is also probably formed by decarbonylation of benzaldehyde.

$$\begin{array}{ccc}
\overset{O\text{---}CH_2}{\underset{CH_2\text{---}CMe_2}{|\quad\quad|}} & \overset{?}{\longrightarrow} & \overset{O}{\underset{CH_2}{\|}} + \overset{CH_2}{\underset{CMe_2}{\|}} \\
\text{(VI)} & &
\end{array}
\qquad
\begin{array}{ccc}
\overset{O\text{---}CH_2}{\underset{CH_2\text{---}CH_2}{|\quad\quad|}} & \longrightarrow & \overset{O}{\underset{CH_2}{\|}} + \overset{CH_2}{\underset{CH_2}{\|}} \\
\text{(VII)} & &
\end{array}$$

It thus appears that the pyrolysis of ester (IV) is adequately represented by the relatively simple breakdown-scheme given above, which can also be applied to elucidate the thermal breakdown of the polyester (II) studied by Pohl.[1]

EXPERIMENTAL

General.—The apparatus and procedure have been described.[2] The Table summarises the general conditions; the temperature was 500°; detailed analyses are given below. Aldehydes were characterised as their 2 : 4-dinitrophenylhydrazones, and benzene as *m*-dinitrobenzene; all solid derivatives or pyrolysis products were identified by mixed m. p., except in Run 4, where paper chromotography was preferred. Hydrogen and saturated hydrocarbons were absent.

2 : 2-Dimethyltrimethylene Dibenzoate (IV).—Prepared from 2 : 2-dimethylpropane-1 : 3-diol, benzoyl chloride, and pyridine in standard fashion (77% yield), this had m. p. 51—53° (lit.,[8] m. p. 52—54°) and b. p. 225°/9 mm., 271°/40 mm.

Pyrolysis of Ester (IV).—Runs 1 and 2 gave concordant results; those of Run 1 are given here. Liquid (*a*) from the cold trap, raised to room temperature, evolved 0·34 l. of gas, identified as *iso*butene (infrared spectrometry); benzene remained (*ca.* 2 ml.). Distillation of (*b*) yielded four primary fractions (i—iv) and a residue (v). Fraction (i) (b. p. 30—110°/40 mm.), redistilled, yielded 2·8 g. of colourless liquid, b. p. 60—90°, containing benzene and *iso*-butyraldehyde, and 1·5 g. of colourless liquid, b. p. 90—150°, containing benzene and water (anhydrous copper sulphate test). Fraction (ii) (b. p. 110—160°/40 mm.), redistilled, yielded 0·5 g. of yellowish liquid, b. p. 155—175° (in which no *iso*butylbenzene could be detected by attempted Friedel–Crafts aroylation with phthalic anhydride), and 2·7 g. of yellowish liquid, b. p. 175—220°, containing mainly benzaldehyde. (No further aldehydes could be detected in the total pyrolysate.)

Pyrolysand, run no.	(IV), 1	(IV), 2	(III), 3	(V), 4
Feed-rate (g./min.)	0·42	0·38	0·42	0·45
Contact time (sec.)	140	150	135	82
Wt. pyrolysed (g.)	50·0	50·0	50·0	50·0
(*a*) In cold trap (ml.)	3·0	3·0	X	X
(*b*) In main receiver (g.)	38·1	36·6	44·5	34·0
(*c*) Gaseous pyrolysate (l.) *	4·8 { CO 70% CO₂ 25% Uns 5%	4·2 { 68% 28% 4%	3·0 { — — —	— { — — —

	(IV), 1	(IV), 2	(III), 3	(V), 4
(*c*) Gaseous pyrolysate (l.) *	4·8 $\left\{\begin{array}{l}\text{CO } 70\%\\ \text{CO}_2\ 25\%\\ \text{Uns } 5\%\end{array}\right.$	4·2 $\left\{\begin{array}{l}68\%\\ 28\%\\ 4\%\end{array}\right.$	3·0 $\left\{\begin{array}{l}-\\ -\\ -\end{array}\right.$	$\left\{\begin{array}{l}-\\ -\\ -\end{array}\right.$

* With approximate percentages (v/v); uns = unsaturated hydrocarbons.
X = No cold trap used.
— = Not observed. Overall losses in weight are due to carbonisation and hold-up in the vessel.

Fraction (iii) (b. p. 160—200°/40 mm.), redistilled, yielded 2·5 g. of yellow semi-solid product, b. p. 220—280°, from which hot water extracted benzoic acid; the residue, freed from benzoic acid by treatment in ethereal solution with dilute aqueous sodium carbonate, followed by removal of ether, was an oil which on hydrolysis with aqueous alkali yielded *iso*butyl alcohol (characterised as its 3 : 5-dinitrobenzoate) and benzoic acid, thus proving the presence of *iso*butyl benzoate. Fraction (iv) (b. p. 200—260°/40 mm.), redistilled, yielded 0·3 g. of crude benzoic acid, b. p. 280—300°; attempts to detect 2 : 2-dimethyl-1 : 3-diphenylpropane (b. p.

[7] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.
[8] Bincer and Hess, *Ber.*, 1928, **61**, 537.

273°) gave negative results. The residue (v) was mainly unchanged pyrolysand (*ca.* 25 g.; 50%): a portion, tested by the Davidson–Newman reagent,[7] gave a slight positive reaction for acid anhydride.

Pyrolysis of Ethylene Dibenzoate (III).—The ester was prepared as previously described:[2] under the same conditions as for ester (IV), only *ca.* 19% of the pyrolysand remained unchanged (Run 3).

Pyrolysis of iso*Butyl Benzoate* (V).—Under the same conditions (Run 4), the carefully purified ester yielded chiefly benzoic acid and *iso*butene; but the liquid pyrolysate yielded a trace of a mixture of crude 2 : 4-dinitrophenylhydrazones, shown by paper chromotography to consist of those of benzaldehyde and *iso*butyraldehyde.

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