813. *Studies in Pyrolysis. Part XV.* Competitive Routes in the Pyrolysis of Various α-Substituted Benzyl Esters: A Novel Route to α-Diketones.*

By E. Jones and P. D. Ritchie.

Benzyl benzoate, and its derivatives containing an electrophilic α-substituent (*e.g.*, CN, Br, COPh), break down pyrolytically (vapour phase, *ca.* 500°) by two competitive primary reactions: (i) a predominating acyl–oxygen scission by what is essentially a retro-Tishchenko reaction, and (ii) disproportionation to benzoic anhydride and a labile ether; also there is (iii) a novel reaction yielding an α-diketone. If the α-substituent is nucleophilic (*e.g.*, a further Ph group), reactions (i) and (iii) do not occur. Other analogous pyrolyses are described, and possible reaction mechanisms are discussed.

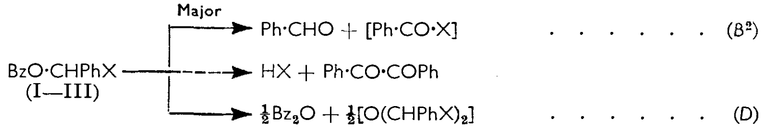
It was shown previously[1] that pyrolysis of alkyl carboxylates in which the alkyl group lacks an α-hydrogen atom leads in general to competition between alkyl–oxygen (A^1) and acyl–oxygen (B^2) scission, unless these are precluded structurally. Other breakdown routes may also compete (*e.g.*, decarboxylation such as that undergone by αα-dicyanobenzyl benzoate[2]). It is now shown that where the alkyl group contains an α-hydrogen atom the novel formation of an α-diketone may compete in the overall breakdown, benzil being obtained from esters (I—IV) and acetylbenzoyl from esters (V—VII). A study of the conditions promoting this reaction, and of the breakdown of three esters (VIII—X) which do not undergo it, provides a further step towards a fully generalised picture of the pyrolytic breakdown of esters.

BzO·CH$_2$Ph (I)	BzO·CHPh·CN (II)	BzO·CHPhBr (III)	BzO·CHPh·COPh (IV)
AcO·CHPh·CN (V)	AcO·CHPh·COPh (VI)	BzO·CHMe·CN (VII)	
BzO·CH$_2$·CN (VIII)	BzO·CHPh$_2$ (IX)	BzO·CPh$_3$ (X)	

Like most methyl esters, methyl benzoate is highly thermostable.[3] Under the vapour-phase conditions now employed, it is unchanged at *ca.* 500°; but introduction of a phenyl group reduces the thermostability, and benzyl benzoate (I) was selected as a suitable starting point for this investigation. Introduction of further α-substituents (electrophilic, such as cyano, bromo, and benzoyl; nucleophilic, such as phenyl) provided a varied range of pyrolysands for study.

Effect of Electrophilic Substituents in Ester (I).—*Benzyl benzoate* (I), *α-cyanobenzyl benzoate* (II), *and α-bromobenzyl benzoate* (III). The thermal breakdown of these three esters can be represented by the annexed common scheme (X = H, CN, or Br respectively), which is simplified at this stage by the omission of a number of secondary products.

The second of these reactions (indicated by a broken arrow) is probably a primary thermal scission, proceeding by an ionic mechanism *via* a rearrangement product: alternatively, the simple equation may represent the overall summation of several



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* Part XIV, *J.*, 1958, 4515.

[1] Bennett, Deans, Harris, Ritchie, and Shim, *J.*, 1958, 4508.

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

[3] Hurd, "The Pyrolysis of Carbon Compounds," Chemical Catalog Co., New York, 1929, p. 537.

secondary reactions in which benzaldehyde from the B^2 scission plays a part. These alternatives are discussed later.

Hurd and Bennett[4] found that static pyrolysis of benzyl benzoate (I) at *ca.* 300° led to competition between B^2 (preponderating) and D reactions. Although dibenzyl ether was not actually observed, disproportionation (D) was inferred from the formation of benzoic anhydride and toluene, since the latter is formed[5] from the ether, along with further benzaldehyde, by A_R^1 scission (nomenclature as previously defined[6]). These results have now been confirmed; in addition, benzoic acid is a minor product. However, at higher temperatures (*ca.* 500°), a surprising minor route appears in the overall reaction, yielding hydrogen and benzil. Unexpectedly, no benzoic anhydride is observed in the high-temperature pyrolysate, though formed at *ca.* 300°; but a separate pyrolysis of ester (I) containing 1% of added benzoic anhydride showed that the latter (when originally present in only such small amount) is destroyed under the conditions used.

By-products include benzoic acid, benzene, benzophenone, and biphenyl. A separate pyrolysis of benzil (*ca.* 500°) indicated that the last two by-products are due to successive decarbonylations of the α-diketone: and partial decarboxylation of benzoic acid can account for the benzene. Formally, the acid itself might originate *via* the special type of alkyl–oxygen scission (hereafter designated by the symbol $A°$) undergone at high temperatures by certain alkyl esters lacking a β-hydrogen atom (*e.g.*, methyl acetate,[7] phenylacetate,[8] and carbonate[9]). Here an alkene is formed (presumably by dimerisation of an alkylidene diradical: cf. pyrolysis of methylene dihalides[10]); but stilbene, the alkene corresponding to $A°$ scission of benzyl benzoate, could not be identified in the pyrolysate. Hence, the benzoic acid (and at least part of the benzene) is more probably a breakdown product of benzoic anhydride itself, which yields these products, *inter alia*, on pyrolysis at *ca.* 550° in a flow system,[11] and might be expected to behave similarly at *ca.* 300° in the static system, with its longer residence time.

The complex pyrolysates from the α-cyano- and the α-bromo-ester (II, III) at *ca.* 400—500° are again best interpreted by the foregoing competition between three routes. Secondary products in each pyrolysate include benzene, benzoic acid, and benzophenone (explicable as in the case of benzyl benzoate); carbon monoxide and PhX (the known breakdown products[2,12] of Ph·COX); and *trans*-αα′-di-X-stilbene. This stilbene is believed to originate in the following A_R^1 breakdown of the labile ether [O(CHPhX)$_2$], with migration of X, thus:

$$\begin{tikzcd}{[\mathrm{O(CHPhX)_2}]} \arrow[r] & \mathrm{Ph{\cdot}CHO} + {[\mathrm{Ph{\cdot}CHX_2}]} \arrow[d] & \cdots\cdots\cdots (A_R^1) \\ & \mathrm{HX} + \tfrac{1}{2}\mathrm{CPhX{:}CPhX} & \end{tikzcd}$$

All the end-products corresponding to this scheme occur in the complex pyrolysates from esters (II) and (III). Further, benzylidene bromide itself is found in the latter pyrolysate, and a separate pyrolysis of this intermediate showed that it breaks down smoothly at *ca.* 425° as follows (cf. the reported analogous breakdown of benzylidene chloride over a red-hot wire[13]):

$$\mathrm{Ph{\cdot}CHBr_2} \longrightarrow \mathrm{HBr} + \tfrac{1}{2}\mathrm{CPhBr{:}CPhBr}\ (\textit{trans})$$

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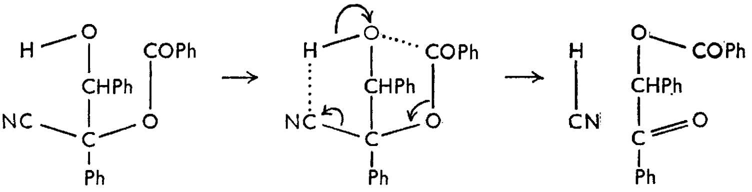
[4] Hurd and Bennett, *J. Amer. Chem. Soc.*, 1929, **51**, 1197.
[5] Lowe, *Annalen*, 1887, **241**, 374.
[6] Iengar and Ritchie, *J.*, 1957, 3563.
[7] Peytral, *Bull. Soc. chim. France*, 1920, **27**, 34.
[8] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.
[9] Ritchie, *J.*, 1935, 1054.
[10] Bawn and Milsted, *Trans. Faraday Soc.*, 1939, **35**, 889.
[11] Allan, Jones, and Ritchie, *J.*, 1957, 524.
[12] Ladacki, Leigh, and Szwarc, *Proc. Roy. Soc.*, 1952, *A*, **214**, 273.
[13] Löb, *Ber.*, 1903, **36**, 3069; cf. Hurd, ref. 3, pp. 136—138.

All the known facts, therefore, support the generalised reaction scheme advanced for the pyrolysis of esters (I—III). In each competition the ketone-producing route is only a minor one, though more marked when there is an electrophilic α-substituent (particularly the cyano-group) than for benzyl benzoate itself. However, although it is presented in the foregoing scheme as a single-stage process, this is clearly an over-simplification: for there must, at some stage, be a structural change in which two oxygen atoms, originally attached to a single carbon atom, become redistributed between two adjacent carbons. One possible mechanism is discussed in the following section, as a first approach to the problem.

O-Benzoylbenzoin (IV) *and O-acetylbenzoin* (VI). A static pyrolysis of α-cyanobenzyl benzoate (*ca.* 300°) confirmed the foregoing results, but gave in addition traces of an unexpected product, benzoylbenzoin (IV). Greene and Robinson[14] have shown this α-keto-alkyl ester to be formed, along with hydrogen cyanide, on condensation of α-cyanobenzyl benzoate (II) with benzaldehyde in presence of sodium ethxoide. They suggested the initial formation of an aldol-like intermediate (XI), and that this breaks down to hydrogen cyanide and benzoylbenzoin (IV) *via* a cyclic transition state which may be represented as (XII):



(XI) (XII) (IV)

This concept suggests that the same sequence may be followed during pyrolysis of ester (II), part of the ester combining initially with benzaldehyde (one of its own primary B^2 scission products) under the influence of heat instead of a catalyst: and a separate pyrolysis of benzoylbenzoin (*ca.* 500°) has shown that it does, in fact, break down mainly by the following B^2 scission and might hence be the true precursor of benzil in the pyrolysis of ester (II):

$$\underset{\text{(IV)}}{\text{BzO·CHPh·COPh}} \longrightarrow \text{Ph·CHO} + \text{Ph·CO·COPh} \quad . \; . \; . \; . \; . \; . \; . \quad (B^2)$$

A little benzoic anhydride is also formed, presumably by the predictable *D* reaction.

The concept of a cyclic transition state is difficult to apply in full as an explanation of the formation of hydrogen and benzil from benzyl benzoate itself. However, the initial aldol-like intermediate (XIII), if formed in this case, would be expected to break down thermally largely as a secondary alcohol, by dehydrogenation,[15] again yielding benzoylbenzoin (IV) as the possible precursor of benzil, thus:

$$\underset{\text{(XIII)}}{\text{BzO·CHPh·CHPh·OH}} \longrightarrow \text{H}_2 + \underset{\text{(IV)}}{\text{BzO·CHPh·COPh}}$$

The aldehyde and α-diketone formed during pyrolysis of ester (IV) can be accounted for by acyl–oxygen scission (B^2), either with orthodox migration of the α-hydrogen atom or with migration of the α-benzoyl group. The identity of their end-products renders these two routes indistinguishable for ester (IV); but the latter type of migration is supported by the fact that the analogous compound acetylbenzoin (VI) breaks down mainly as follows (*ca.* 480°), a little benzene and acetic acid also being formed:

$$\underset{\text{(VI)}}{\text{AcO·CHPh·COPh}} \longrightarrow \text{Ph·CHO} + \text{Me·CO·COPh} \quad . \; . \; . \; . \; . \; . \; . \quad (B^2)$$

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[14] Greene and Robinson, *J.*, 1922, **121**, 2186.
[15] Hurd, ref. 3, p. 160.

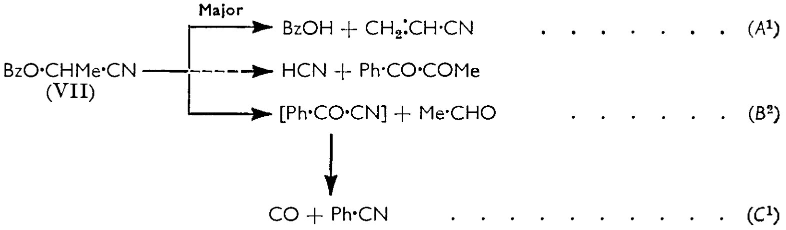
α-Cyanobenzyl acetate (V) *and* 1-*cyanoethyl benzoate* (VII). These esters are isomeric, their phenyl and methyl groups simply being interchanged; but ester (VII), which unlike ester (V) possesses a β-hydrogen atom, should break down mainly by A^1 scission, and the chief purpose in pyrolysing both esters was to determine whether the same α-diketone (acetylbenzoyl) is a minor product in each case.

The acetate (V) undergoes the same basic type of breakdown as the corresponding benzoate (II), namely, a competition between B^2 and D scissions, and the diketone-producing reaction. The principal products are benzaldehyde, acetylbenzoyl, hydrogen cyanide, and acetic anhydride: secondary products include benzene, acetophenone, acetic acid, and the four known scission products [2] of acetyl cyanide.

A separate pyrolysis of acetylbenzoyl showed that the observed acetophenone can be accounted for by a secondary semidecarbonylation of the α-diketone; and the acetic acid is most probably formed by scission of acetic anhydride to keten and acid.[16] Of the various end-products from route B^2, only one (acetonitrile) is diagnostic of this route alone: all the others have a probable alternative origin.

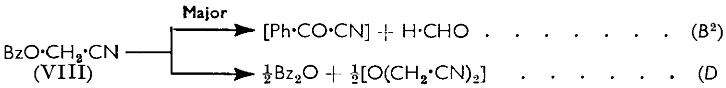
Like benzoylbenzoin (IV), the acetate (V) offers two formally possible acyl–oxygen scission routes. Migration of the α-cyano-group (with formation of acetyl cyanide and benzaldehyde) is supported by the formation of all the end-products corresponding to this route, rather than to its alternative (migration of the α-hydrogen). The benzonitrile formed (trace) is a predictable [6] scission-product of the labile cyano-ether.

In the corresponding pyrolysis of 1-cyanoethyl benzoate (VII), the expected A^1 scission preponderates strongly (*ca.* 85%). The overall products are best interpreted by the following scheme, no detectable disproportionation (D) occurring in this case:



Formation of acetylbenzoyl from esters (V) and (VII) can, like formation of benzil from esters (I—III), be explained by invoking the Greene and Robinson concept; however, reasons are advanced later (p. 4146) in support of an alternative ionic mechanism.

Cyanomethyl benzoate (VIII). Here the breakdown products seem to indicate that the principal primary reaction is a B^2 scission with migration of the cyano-group (yielding benzoyl cyanide and formaldehyde), in competition with a minor disproportionation (D) on the usual lines, thus:

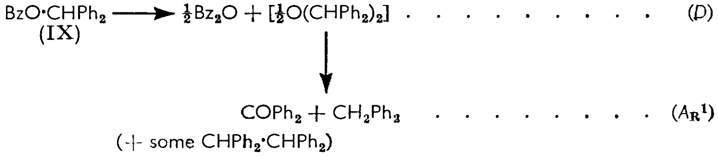


The pyrolysate (*ca.* 500°: vapour phase) contains carbon monoxide and dioxide, hydrogen, hydrogen cyanide, benzonitrile, benzoic acid, benzene, benzaldehyde, and possible traces of acetonitrile: at lower temperatures (*ca.* 200°: liquid phase) the last three products are not observed, though formaldehyde appears (as paraformaldehyde). The D reaction is inferred from the formation of acetonitrile, most probably *via* secondary $A_R{}^1$ scission of the labile cyano-ether, the accompanying product (the very unstable " formyl cyanide ") breaking down to carbon monoxide and hydrogen cyanide; and, although the expected anhydride could not be detected, its two known major breakdown products (benzoic acid and benzene [11]) are formed in fair quantity.

[16] Szwarc and Murawski, *Trans. Faraday Soc.*, 1951, **47**, 269.

The diketone-producing reactions of esters (I—VII) suggest that ester (VIII) should by a similar mechanism yield the α-keto-aldehyde, phenylglyoxal: but no firm evidence for such a scission could be obtained, though the possibility is not excluded. If ester (VIII) forms an aldol-like intermediate by condensation with either (i) formaldehyde or (ii) benzaldehyde, again followed by the Greene and Robinson sequence, the predictable product would be either (i) $BzO\cdot CH_2\cdot CHO$ or (ii) $BzO\cdot CH_2\cdot COPh$, respectively. The former should yield methyl benzoate by decarbonylation: the latter, either formaldehyde (observed) and benzil by B^2 scission with migration of benzoyl (cf. the analogous breakdown of acetylbenzoin), or benzaldehyde (observed) and phenylglyoxal by B^2 scission with migration of hydrogen. Neither methyl benzoate nor benzil could be detected; nor was phenylglyoxal observed, though this is hardly surprising, for, even if initially formed, this very labile α-keto-aldehyde should undergo ready decarbonylation at *ca.* 500° (like its analogue methylglyoxal[17]). The conclusion must be either that the diketone-producing reaction has no parallel in the pyrolysis of ester (VIII), or that phenylglyoxal is formed by B^2 scission of the intermediate $BzO\cdot CH_2\cdot COPh$ although its positive detection is precluded by the possibility of other reactions with identical end-products.

Effect of Nucleophilic Substituents.—Diphenylmethyl benzoate (IX). Breakdown appears here to follow a single primary route (*ca.* 500°), with various secondary reactions, thus:



$$\underset{\text{(IX)}}{BzO\cdot CHPh_2} \longrightarrow \tfrac{1}{2}Bz_2O + [\tfrac{1}{2}O(CHPh_2)_2] \quad \ldots\ldots\ldots\ldots \quad (D)$$

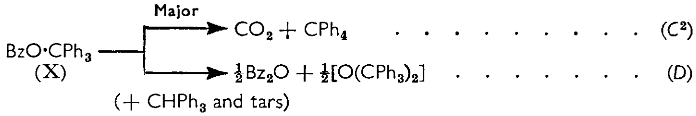
$$\downarrow$$

$$COPh_2 + CH_2Ph_2 \quad \ldots\ldots\ldots\ldots \quad (A_R{}^1)$$

$$(+\ \text{some } CHPh_2\cdot CHPh_2)$$

Bisdiphenylmethyl ether, though not detected, has been shown by Nef[18] to yield the above $A_R{}^1$ scission-products, together with the less readily explicable *s*-tetraphenylethane. Some benzoic acid is formed, again probably from the primary benzoic anhydride.[11] There is no evidence for benzaldehyde, which rules out competition by B^2 scission.

Triphenylmethyl benzoate (X). Here the effect of the nucleophilic α-phenyl groups reaches its cumulative maximum in weakening the alkyl–oxygen and acyl–oxygen bonds: and it is not surprising that ester (X) is completely decomposed under relatively mild conditions (*ca.* 225°: 24 hr.). Hurd,[19] in discussing esters (IX) and (X), predicted that the latter should break down by the disproportionation (*D*) shown below: but this, though observed, proves to be a minor reaction, the preponderating route being a decarboxylation (C^2) to tetraphenylmethane, with triphenylmethane as an unexpected major by-product.



$$\underset{\text{(X)}}{BzO\cdot CPh_3} \xrightarrow{\text{Major}} CO_2 + CPh_4 \quad \ldots\ldots\ldots\ldots \quad (C^2)$$

$$\underset{\text{(X)}}{BzO\cdot CPh_3} \longrightarrow \tfrac{1}{2}Bz_2O + \tfrac{1}{2}[O(CPh_3)_2] \quad \ldots\ldots\ldots \quad (D)$$

$$(+\ CHPh_3 \text{ and tars})$$

Bistriphenylmethyl ether, which decomposes at its melting point,[20] is not itself observed. Minor by-products include benzoic acid and benzene: presumably they arise from the primary benzoic anhydride, and here the alternative origin *via* A° scission is completely excluded structurally. The reaction temperature is much lower than that normally required[11] for breakdown of benzoic anhydride: however, the formation of triphenylmethane strongly suggests that free radicals are present in the reaction system, and it has previously been shown that certain free radicals (*e.g.*, those derived from carbon tetrachloride) assist in thermal breakdown of the anhydride.[11]

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[17] Golomb and Ritchie, unpublished observations, 1959.

[18] Nef, *Annalen*, 1897, **298**, 374, where is also described the corresponding pyrolysis of diphenylmethyl acetate; cf. Bacon, *Amer. Chem. J.*, 1905, **33**, 90; Anschütz, *Annalen*, 1897, **298**, 374.

[19] Hurd, ref. 3, p. 539.

[20] Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 205.

The origin of the triphenylmethane is uncertain. This substance is formed in various analogous pyrolyses (*e.g.*, from triphenylmethyl acetate and ketone [21]): and for the present it is sufficient to note this tendency of various compounds containing the triphenylmethyl group to yield triphenylmethane at relatively low temperatures, probably by some kind of free-radical mechanism.

General Conclusions.—The foregoing results may be summarised as follows.

(i) Electrophilic α-substituents decrease the thermostability of benzyl benzoate. The amount of BzO•CHPhX destroyed under standard conditions increases as the electronegativity of X follows the sequence: $H < COPh < CN < Br$. B^2 scission predominates over the minor ketonic and D reactions: where α-hydrogen and an electrophilic α-substituent are both present, only the latter migrates during the B^2 reaction. The B^2 and D reactions can occur at relatively low temperatures (*ca.* 250—300°): but a temperature of *ca.* 400—500° is required for onset of diketone formation, which is most noticeable where $X = CN$, but does not occur at all if there is no α-hydrogen atom.

(ii) Nucleophilic α-substituents (*e.g.*, phenyl) decrease the stability of methyl benzoate, though less markedly than electrophilic. The amount of pyrolysand destroyed under standard conditions follows the sequence: $Me < CH_2Ph < CHPh_2 \ll CPh_3$. Introduction of α-phenyl groups into benzyl benzoate suppresses the B^2 and diketone-forming reactions: but decarboxylation (C^2) appears and predominates in the competition on complete α-phenylation (*i.e.*, for triphenylmethyl benzoate).

Possible Reaction Mechanisms.—Hurd and Blunck [8] have suggested both molecular and free-radical mechanisms to explain specific examples of ester pyrolysis. It was for long quite widely accepted that A^1 scission of an alkyl ester involves an intermediate six-membered cyclic transition stage,[8,22] and that it occurs by a molecular mechanism. Lately, however, the idea of a polar or heterolytic mechanism in vapour-phase eliminations has been gaining ground; and Maccoll [23] has shown that the mechanism is heterolytic and unimolecular for s- and t-alkyl esters, but free-radical and chain for n-alkyl esters.

Ionic mechanisms have been invoked [24] to explain reactions of the Cannizzaro and Tischchenko types: and, to take ester (III) as an example, its formation [25] from benzaldehyde and benzoyl bromide may be explained thus:

$$\begin{aligned}
\mathrm{Ph{\cdot}COBr} &\longrightarrow \mathrm{Ph{\cdot}\overset{+}{C}O} + \overset{-}{\mathrm{Br}}\\
\mathrm{Ph{\cdot}CHO} &\longleftrightarrow \mathrm{Ph{\cdot}\overset{+}{C}H{-}\overset{-}{O}}\\
\mathrm{Ph{\cdot}\overset{+}{C}H{-}\overset{-}{O}} + \overset{-}{\mathrm{Br}} &\longrightarrow \mathrm{Br{\cdot}CHPh{\cdot}\overset{-}{O}}\\
\mathrm{Br{\cdot}CHPh{\cdot}\overset{-}{O}} + \mathrm{Ph{\cdot}\overset{+}{C}O} &\longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPhBr}\ \text{(III)}
\end{aligned}$$

Ester (III) tends to revert to its original constituents, even at room temperature; and it may well be that the above type of ionic sequence is responsible not only for this liquid-phase retro-Tishchenko reaction but also for the vapour-phase B^2 scission of esters (II, III) and analogous compounds. (It is known that acetyl chloride dissociates ionically in nitromethane solution; [26] and it is now found that benzoyl bromide, chloride, and cyanide dissociate similarly in benzonitrile solution.) The known weakness of the C–Br bond might lead to preferential dissociation of ester (III) to a bromide anion and the cation $\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}\overset{+}{C}HPh}$; but it is difficult to see how the latter could thereafter lead to the observed products. Also, the acyl–oxygen bond energy will be lowered by the presence of

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[21] Norris and Young, *J. Amer. Chem. Soc.*, 1924, **46**, 2581; Declaré, *Bull. Soc. chim.*, 1909, **5**, 1144.

[22] DePuy, King, and Froemsdorf, *Tetrahedron*, 1959, **7**, 123.

[23] Maccoll, *J.*, 1958, 3398. For a general survey, see Ingold, Pedler Lecture, *Proc. Chem. Soc.*, 1957, 279.

[24] For summary, see Dewar, " Electronic Theories of Organic Chemistry," Bell, London, 1953, p. 707.

[25] Adams and Vollweiler, *J. Amer. Chem. Soc.*, 1918, **40**, 1732.

[26] Burton and Praill, *J.*, 1950, 1203, 2034.

the bromo-group, and also to a lesser extent by the α-phenyl group, though the latter is only weakly electron-attracting: hence, scission of the acyl–oxygen bond seems the preferred mode of heterolysis.

Homolysis of this bond is also a formal possibility, the initiation and propagation steps being visualised thus:

$$\begin{array}{l}
\textit{Initiation}\text{: } \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPhBr} + \mathrm{R}\cdot \longrightarrow \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPh}\cdot + \mathrm{RBr} \\
\textit{Propagation}\text{: } \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPh}\cdot \longrightarrow \mathrm{Ph{\cdot}CO}\cdot + \mathrm{Ph{\cdot}CHO} \\
\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPhBr} + \mathrm{Ph{\cdot}CO}\cdot \longrightarrow \mathrm{Ph{\cdot}COBr} + \mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPh}\cdot
\end{array}$$

However, the variety of possible termination steps suggests a wider range of end-products than has so far been observed, an additional argument for the preferred heterolytic mechanism.

With regard to the diketone-producing reaction, there is again reason for suggesting an ionic mechanism. The Greene and Robinson [14] concept can be invoked to explain formation of an α-diketone from esters (I), (II), (III), (V), and (VII); but there is no clear evidence that the same mechanism operates for cyanomethyl benzoate (VIII), nor can it explain the minor formation of biacetyl on pyrolysis of certain aryl α-acetoxypropionates (XIV) (see p. 4148). A moregenerally applicable ionic mechanism is therefore proposed: with ester (III) as an example once more, this involves rearrangement of the α-bromobenzyloxy-anion to a hydrin anion:

$$\begin{array}{rcl}
\mathrm{Ph{\cdot}CO{\cdot}O{\cdot}CHPhBr} & \longrightarrow & \mathrm{Ph{\cdot}}\overset{+}{\mathrm{C}}\mathrm{O} + \overset{-}{\mathrm{O}}\mathrm{{\cdot}CHPhBr} \\
\overset{-}{\mathrm{O}}\mathrm{{\cdot}CHPhBr} & \longrightarrow & \mathrm{HO{\cdot}}\overset{-}{\mathrm{C}}\mathrm{PhBr} \\
\mathrm{Ph{\cdot}}\overset{+}{\mathrm{C}}\mathrm{O} + \mathrm{HO{\cdot}}\overset{-}{\mathrm{C}}\mathrm{PhBr} & \longrightarrow & [\mathrm{Ph{\cdot}CO{\cdot}CPh(OH)Br}] \\
 & & \Big\downarrow \\
 & & \mathrm{HBr} + \mathrm{Ph{\cdot}CO{\cdot}COPh}
\end{array}$$

This rearrangement can occur only if there is an electrophilic α-substituent. Hence, esters such as (II) and (III) should yield an α-diketone readily, and esters such as (IX) and (XI) not at all; benzyl benzoate will occupy an intermediate position. The greater observed yield of benzil from ester (II) than from ester (III) agrees with the fact that a cyanohydrin is more stable than a bromohydrin.

No mechanism is yet advanced for the disproportionation (D); but the decarboxylation (C^2) undergone by ester (X) is probably free-radical in character (though apparently not a chain reaction [27]). This ester, and the various other esters now known [2,28,29] to undergo C^2 scission, all have at least one unsaturated grouping (aryl or alkenyl) directly attached to the –CO·O– grouping, which favours resonance stabilisation.

Aryl α-Acetoxypropionates (XIV).—Filachione, Lengel, and Ratchford [30] found that various aryl α-acetoxypropionates (XIV) broke down mainly by the predictable A^1 scission, but also yielded a number of minor unexplained by-products. Some of these have recently been shown [29] to occur *via* secondary breakdown of the aryl acrylate formed by A^1 scission; and biacetyl, which was reported [30] in small amount when Ar = *m*-tolyl or

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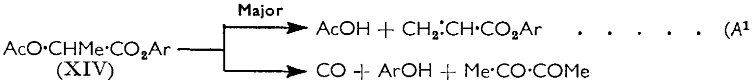
[27] See Steedman, Ph.D. Thesis, Glasgow University, 1959, p. 85, for decarboxylation mechanism of vinyl benzoate.

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

[29] Mackinnon and Ritchie, *J.*, 1957, 2564; for earlier results, see Anschütz, *Ber.*, 1885, **18**, 1945; Anschütz and Wirtz, *Ber.*, 1885, **18**, 1947; Bischoff and von Hedenström, *Ber.*, 1902, **35**, 4084; Anschütz, *Ber.*, 1927, **60**, 1320.

[30] Filachione, Lengel, and Ratchford, *J. Amer. Chem. Soc.*, 1950, **72**, 839; cf. Filachione, Lengel, and Fisher, *ibid.*, 1944, **66**, 494.

p-chlorophenyl, can now be explained by assuming that ester (XIV) breaks down by competition between at least the following two routes:



The second of these routes is here expressed without details of any intermediate stages: but on the basis of the foregoing ionic mechnism, ester (XIV) would first rearrange to the complex intermediate Me·CO·CMe(OH)·CO_2Ar. This substance is unknown: but it might be expected to yield biacetyl by either (i) intermolecular elimination of a phenol, with cyclisation to a lactide (which should then break down on predictable lines [31] to carbon monoxide and biacetyl), or (ii) intramolecular elimination of an aryl formate (which would then break down [29] to carbon monoxide and a phenol, both noted in certain cases [30]), with formation of biacetyl. The ionic concept can thus be applied to explain the results of Filachione *et al.*,[30] whereas the Greene and Robinson concept [14] offers no simple explanation.

EXPERIMENTAL

Apparatus and Procedure.—The flow-reactor, receiver, traps, and general mode of operation have been described previously.[28] Five different Pyrex-glass reaction vessels were used, each packed with Pyrex-glass tubing; they are denoted in the Tables by the symbols P/20, P/30, P/50, P/80, and P/200, the number indicating the free unpacked space (ml.). Appropriate choice of reaction vessel assisted in varying the residence (contact) time, which was calculated as previously.[11] The above flow-reactor system was used for most pyrolyses. In addition, the semimicro-reaction vessel described by Bain and Ritchie [32] was used for run 24; while for runs 2, 5, 9, 16, and 22 the pyrolysand was refluxed in a static reaction vessel consisting of a 3-necked Quickfit flask, fitted with thermocouple-pocket, nitrogen-inlet, and lead-off for the exit gases, by way of the condenser, to the traps and receiver, the whole being thoroughly flushed with nitrogen before each run.

Analytical Methods.—The non-gaseous pyrolysates (*a*) were examined after fractional distillation. Acid anhydrides were detected by the Davidson–Newman [33] colour test; benzonitrile was characterised by conversion [34] into benzamide by means of alkaline hydrogen peroxide; unless otherwise stated, aromatic hydrocarbons were characterised by conversion into an appropriate solid nitro-derivative. All solid derivatives and pyrolysate components were identified by mixed m. p. Carbonyl compounds were characterised by conversion into 2,4-dinitrophenylhydrazones, mixtures of these being separated by column chromatography on bentonite–kieselguhr [35] and identified by paper chromatography.[36] Hydrogen cyanide was removed from the exit gases by an alkali trap, and hydrogen bromide by a water trap, both acids then being determined volumetrically; keten was removed by an aniline–ether trap, and characterised by conversion into acetanilide. In some difficult cases, standard chemical tests were supplemented by infrared spectrometry.

Results.—Tables 1—3 summarise the general experimental conditions and results for 23 of the 25 pyrolyses reported. Apparent overall losses in weight are due to carbonisation and/or hold-up in the packed reaction vessel. The preparation of pyrolysands, and the detailed analytical results for each run, are summarised below.

Methyl Benzoate.—Pure ester, from British Drug Houses Ltd., was used.

Pyrolysis 1. No breakdown whatever was detected. The refractive index remained unchanged after passage of the ester through the flow-reactor at *ca.* 500°, and no gases were liberated.

Benzyl Benzoate (I).—Pure ester, from British Drug Houses Ltd., was used.

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[31] Blaise, *Compt. rend.*, 1904, **138**, 697; Hurd, ref. 3, p. 426.
[32] Bain and Ritchie, *J.*, 1955, 4411.
[33] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.
[34] Radziszewski, *Ber.*, 1885, **18**, 355.
[35] Elvidge and Whalley, *Chem. and Ind.*, 1955, 589.
[36] Burton, *Chem. and Ind.*, 1954, 576.

Pyrolysis 2. The ester was heated in the static reaction vessel (*ca.* 300°; 29 hr.); the liquid pyrolysate (*a*) yielded: 1·75 g., b. p. 104—112° (toluene); 0·75 g., b. p. 118—120° (toluene and benzaldehyde); 1·8 g., b. p. 76—80°/20 mm. (benzaldehyde); 4·75 g., b. p. 160—184°/20 mm.

TABLE 1. *Pyrolysis of methyl benzoate, benzyl benzoate* (I), *and α-cyanobenzyl benzoate* (II).

Pyrolysand	BzOMe	(I)			(II)		
Run no.	1	2	3	4	5	6	7
Reaction vessel	P/200	*	P/200	P/200	†	P/200	P/50
Temp.	500°	300°	500°	550°	300°	420°	500°
Feed-rate (g./min.)	0·30	*	0·40	0·30	†	0·60	0·27
Residence time (sec.)	86	*	95	125	†	92	42
Wt. pyrolysed (g.)	30·0	50·0	50·0	50·0	50·0	125·0	110·0
(*a*) Non-gaseous pyrolysate (g.)	30·0	49·0	48·0	40·0	42·0	95·0	91·5
(*b*) Gaseous pyrolysate (l.)	Nil	1·25	1·25	8·0	2·5	2·0	8·0
Composition (%) of (*b*) (approx.):							
CO	—	77	61	63	80	Pres.	Pres.
CO_2	—	23	18	24	20 ‡	Pres.	Pres.
H_2	—	Nil	21	13	Nil	Nil	Nil

* Static pyrolysis: 29 hr. † Static pyrolysis: 5¼ hr. ‡ Part of the CO_2 removed by alkali trap during determination of hydrogen cyanide.

TABLE 2. *Pyrolysis of α-bromobenzyl benzoate* (III), *benzoylbenzoin* (IV), *acetylbenzoin* (VI), *α-cyanobenzyl acetate* (V), 1-*cyanoethyl benzoate* (VII), *and cyanomethyl benzoate* (VIII).

Pyrolysand	(III)		(IV)	(VI)	(V)		(VII)	(VIII)	
Run no.	9	10	11	12	13	14	15	16	17
Reaction vessel	*	P/200	P/200	P/20	P/200	P/200	P/30	*	P/80
Temp.	225°	425°	500°	480°	550°	500°	550°	205°	500°
Feed-rate (g./min.)	*	0·42	0·40	0·29	0·48	0·30	0·64	*	0·29
Residence time (sec.)	*	156	149	17	103	110	75	*	41
Wt. pyrolysed (g.)	40·0	40·0	30·0	20·0	46·3	43·0	38·0	37·5	43·0
(*a*) Non-gaseous pyrolysate (g.)	39·5	31·0	23·5	19·5	38·0	—	28·5	36·9	40·5
(*b*) Gaseous pyrolysate (l.)	1·0	3·25	3·0	1·25	6·25	6·0	0·8	1·75	2·0
Composition (%) of (*b*) (approx.):									
CO	95	100	86	94	77	—	Pres.†	—	80
CO_2	5	Nil	14	6	23	—	Pres.†	—	2
H_2	Nil	Nil	Nil	Nil	Nil	—	—	—	18
Unsatd. hydrocarbons	Nil	Nil	Nil	Nil	Nil	—	Pres.†	—	—
Satd. hydrocarbons	Nil	Nil	Nil	Nil	Nil	—	—	—	—

* Static pyrolysis (Run 9, 3 hr.: Run 16, 36 hr.). † Detected by infrared spectrometry. — Not observed.

TABLE 3. *Pyrolysis of diphenylmethyl benzoate* (IX), *triphenylmethyl benzoate* (X), *benzil, acetylbenzoyl, and benzylidene bromide.*

Pyrolysand	(IX)		(X)		Bz_2	AcBz	$Ph{\cdot}CHBr_2$
Run no.	18	19	21	22	23	24	25
Reaction vessel	P/200	P/20	P/50	*	P/200	†	P/200
Temp.	500°	425°	500°	225°	500°	500°	425°
Feed-rate (g./min.)	0·30	0·30	0·60	*	0·30	†	0·33
Residence time (sec.)	183	21	29	*	133	†	161
Wt. pyrolysed (g.)	25·0	30·0	20·0	20·0	110·0	0·30	20·0
(*a*) Non-gaseous pyrolysate (g.)	21·5	27·0	15·3	19·8	85·0	—	10·5
(*b*) Gaseous pyrolysate (l.)	0·8	0·4	0·5	0·1	9·75	0·04	0·7 ‡
Composition (%) of (*b*) (approx.):							
CO	51	77	8	—	97	74	Nil
CO_2	49	23	92	—	3	26 §	Nil

* Static pyrolysis: 24 hr. † Pyrolysed in semimicro-reaction vessel: 10 min. ‡ (*b*) consisted of hydrogen bromide, with about 11% of displaced nitrogen. — Not observed. § During this run there was a slight leakage of air into the system which probably accounts for the unexpectedly high CO_2 content.

(benzoic acid and a little benzaldehyde); 30·0 g., b. p. 184—194°/20 mm. [unchanged (I) containing benzoic anhydride]; and 3·6 g. of high-boiling tars.

Pyrolysis 3. There was little breakdown in the flow-reactor at *ca.* 500°; the liquid pyrolysate (*a*) yielded: 2·3 g., b. p. 74—105° (benzene and toluene; infrared); 1·3 g., b. p. 80—110°/16 mm. (benzaldehyde and a trace of benzoic acid); 41·8 g., b. p. 170—204°/16 mm. (unchanged pyrolysand); and 2·6 g. of high-boiling tars.

Pyrolysis 4. Breakdown was greater at *ca.* 550°; the liquid pyrolysate (*a*) yielded: 6·0 g., b. p. 80—86° (benzene); 1·3 g., b. p. 86—96° (benzene and toluene); 1·5 g., b. p. 98—108° (benzene and toluene); 5·0 g., b. p. 108—120° (toluene and benzaldehyde); 2·0 g., b. p. 85—120°/22 mm. (benzaldehyde); 5·3 g., b. p. 140—170°/22 mm. (biphenyl and a trace of benzoic acid); 9·5 g., b. p. 170—200°/22 mm. [unchanged (I), benzil, and benzophenone]; and 4·0 g., b. p. 200—258°/22 mm. [unchanged (I) and a trace of unidentified solid, m. p. 209°]. (*Note.*—Pyrolyses 3 and 4 showed no evidence for formation of benzoic anhydride; but the pyrolysate from a control run at *ca.* 550°, using ester (I) containing 1% of added benzoic anhydride, gave a similar negative result.)

α-Cyanobenzyl Benzoate (II).—*Preparation.* Francis and Davis's method [37] gave the ester (68%), m. p. 58° (from ethanol) (lit.,[37] m. p. 60°).

Pyrolysis 5. The ester was heated in the static reaction vessel (*ca.* 300°: 5¼ hr.). The pyrolysate (*a*) yielded: 6·5 g., b. p. 42—44°/2 mm. (benzaldehyde and benzonitrile); 4·5 g., b. p. 120—160°/2 mm. (benzaldehyde, benzonitrile, and benzoic acid); 2·3 g., b. p. 164—200°/2 mm. (benzoic acid, benzil, and unchanged pyrolysand); 3·5 g., b. p. 200—250°/2 mm. (benzil and a trace of unchanged pyrolysand); 1·8 g., b. p. 165—200°/1 mm. (benzil and a trace of pyrolysand); 6·0 g., b. p. 200—236°/1 mm. (high-boiling tars, containing solid); and 10·8 g. of high-boiling tars. The solid from the penultimate fraction, recrystallised from ethanol, yielded benzoylbenzoin, m. p. and mixed m. p. 124·5° (Found: C, 80·4; H, 5·4. Calc. for $C_{21}H_{16}O_3$: C, 79·8; H, 5·1%). Hydrogen cyanide (9·6% of theory) was removed from the exit gases by an alkali-trap.

Pyrolysis 6. The pyrolysate (*a*) yielded: 0·9 g., b. p. 22—50° (hydrogen cyanide); 12·0 g., b. p. 55—85°/5 mm., 3·0 g., b. p. 85—122°/5 mm., and 12·0 g., b. p. 122—155°/5 mm. (all containing benzaldehyde, benzonitrile, and benzoic acid); 11·5 g., b. p. 160—180°/5 mm. (benzil and unchanged pyrolysand); 10·0 g., b. p. 160—184°/2·5 mm. (unchanged pyrolysand and a trace of benzil); and 11·5 g., b. p. 184—205°/2·5 mm. (unchanged pyrolysand containing solid). The solid from the last fraction, recrystallised from methanol, yielded *trans*-αα′-dicyanostilbene, m. p. 160° (lit.,[38] m. p. 160°) (Found: C, 83·6; H, 4·2; N, 12·2. Calc. for $C_{16}H_{10}N_2$: C, 83·5; H, 4·4; N, 12·2%). The total hydrogen cyanide formed (first fraction, above, plus material retained by alkali trap) was 11·3% of theory.

Pyrolysis 7. The pyrolysate (*a*) yielded: 10·0 g., b. p. 80—81° (benzene); 12·7 g., b. p. 66—100°/2·5 mm. (benzaldehyde and benzonitrile); 6·8 g., b. p. 100—158°/2·5 mm. (benzaldehyde, benzonitrile, benzoic acid, and a trace of unchanged pyrolysand); 16·0 g., b. p. 162—195°/5 mm. (mainly tars, with benzoic acid and a trace of unchanged pyrolysand); 9·3 g., b. p. 195—250°/5 mm. (high-boiling tars); and 15·0 g. of residual tars.

Pyrolysis 8. A small amount of ester (II) was heated at *ca.* 160° for 24 hr. There was little decomposition and charring; the pyrolysate contained benzoic anhydride.

α-Bromobenzyl Benzoate (III).—*Preparation.* Condensation of benzaldehyde with benzoyl bromide by Adams and Vollweiler's method [25] gave a practically theoretical yield of ester (III), m. p. 68—69° (from light petroleum) (lit.,[25] m. p. 69—70°). The ester is unstable in air, reverting readily to benzaldehyde and benzoyl bromide. It was stored in light petroleum, in a well-stoppered flask; immediately before use, it was dried *in vacuo* and transferred as quickly as possible to the oxygen-free conditions of the nitrogen-filled reaction vessel.

Pyrolysis 9. The ester was heated in the static reaction vessel (*ca.* 225°: 3 hr.). The pyrolysate (*a*) yielded: 18·3 g., b. p. 89—109°/10 mm. (benzaldehyde, benzoyl bromide, and traces of bromobenzene, benzyl bromide, benzylidene bromide, and benzoic acid; infrared); 3·5 g., b. p. 109—120°/10 mm. (benzoyl bromide, benzylidene bromide, benzoic acid, and a trace of benzoic anhydride; infrared); 10·3 g., b. p. 194—198°/10 mm. (benzoyl bromide, benzylidene bromide, and benzoic anhydride; infrared); and 4·8 g. of high-boiling tars. There

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[37] Francis and Davis, *J.*, 1909, **95**, 1403.

[38] von Braun, *Ber.*, 1903, **36**, 2652. For proof of *trans*-configuration of this isomer, see Coe, Gale, Garnish, and Timmons, *Chem. and Ind.*, 1957, 665.

was a little solid in the penultimate fraction, which on recrystallisation from glacial acetic acid yielded *trans*-αα′-dibromostilbene, m. p. 205° (lit.,[39] m. p. 206°); the mother-liquors contained no benzaldehyde (infrared), but the presence of benzylidene bromide was confirmed by its hydrolysis to benzaldehyde. Hydrogen bromide (2·3%) was removed from the exit gases by an alkali trap.

Pyrolysis 10. The pyrolysate (*a*) yielded: 7·5 g., b. p. 76—86° (benzene); 10·3 g., b. p. 54—100°/12 mm. (benzoyl bromide and bromobenzene; infrared); 1·0 g., b. p. 124—144°/7 mm. (benzoic acid and a trace of benzoyl bromide); and 5·3 g., b. p. 185—200°/7 mm. This last fraction contained *trans*-αα′-dibromostilbene (mixed m. p.); benzil and benzophenone (infrared; paper chromatography); and benzoic anhydride. Hydrogen bromide (7·6%) was removed from the exit gases by an alkali trap.

Benzoylbenzoin (IV).—*Preparation.* Zinin's method [40] yielded the ester (67%), m. p. 124° (from ethanol–water) (lit.,[40] m. p. 124—125°).

Pyrolysis 11. The pyrolysate (*a*) yielded: 3·0 g., b. p. 78—84° (benzene); 3·5 g., b. p. 130—150°/15 mm. (benzaldehyde, benzoic acid, and biphenyl); 1·5 g., b. p. 150—180°/15 mm. (benzaldehyde, benzoic acid, and a trace of benzil); 5·0 g., b. p. 180—210°/15 mm. (benzil and a trace of benzoic acid); and 2·8 g., b. p. 210—250°/15 mm. (benzil and tars). There was a tarry residue, which yielded: 2·0 g., b. p. 220—250°/1·5 mm. (unchanged pyrolysand and tars); 1·0 g., b. p. 250—280°/1·5 mm. (mainly tar, with a trace of unchanged pyrolysand); and 2·5 g. of carbonised residue.

Acetylbenzoin (VI).—*Preparation.* Corson and Saliani's method [41] yielded the ester (70%), m. p. 85° (from ethanol–water) (lit.,[41] m. p. 83°).

Pyrolysis 12. The pyrolysate (*a*) yielded: 1·0 g., b. p. 90—120° (acetic acid; infrared); 0·3 g., b. p. 80—100°/2 mm. (benzoic acid and acetylbenzoyl; infrared); 1·5 g., b. p. 115—150°/2 mm. (benzaldehyde, acetylbenzoyl, and unchanged pyrolysand); 7·3 g., b. p. 160—180°/2 mm. (unchanged pyrolysand); 5·0 g., b. p. 180—198°/2 mm. (tars; not examined); and 2·5 g. of carbonised residue.

α-*Cyanobenzyl Acetate* (V).—*Preparation.* Michael and Jeanprêtre's method [42] yielded the ester (76%), b. p. 152°/25 mm. (lit.,[42] b. p. 152°/25 mm.).

Pyrolysis 13. The pyrolysate (*a*) yielded: 3·3 g., b. p. 76—86° (acetonitrile and a trace of benzene; infrared); 2·0 g., b. p. 88—110° (acetonitrile and acetic acid); 1·0 g., b. p. 110—124° (acetic acid and acetic anhydride); 3·5 g., b. p. 180—200° (benzaldehyde); 5·0 g., b. p. 70—100°/3 mm., and 6·7 g., b. p. 100—130°/3 mm. (both fractions contained benzaldehyde, acetylbenzoyl, acetophenone, and benzonitrile; infrared and paper chromatography); 4·0 g., b. p. 130—160°/3 mm. (unchanged pyrolysand); and 12·6 g. of high-boiling tars. Hydrogen cyanide (10·4%) was removed from the exit gases by an alkali trap.

Pyrolysis 14. The presence of keten in the exit gases was proved by the isolation of acetanilide from the aniline–ether trap.

1-*Cyanoethyl Benzoate* (VII).—*Preparation.* Davis's method [43] yielded the ester (65%), b. p. 269—270° (lit.,[43] b. p. 269—270°).

Pyrolysis 15. The pyrolysate (*a*) yielded: 8·3 g., b. p. 64—74° (acrylonitrile and benzene; infrared); 1·0 g., b. p. 40—44°/4 mm. (benzonitrile); 0·3 g., b. p. 60—70°/4 mm. (benzonitrile and benzoic acid); 4·0 g., b. p. 88—140°/4 mm. (benzoic acid); and 5·3 g., b. p. 140—180°/4 mm. (benzoic acid, acetylbenzoyl, and acetophenone). Hydrogen cyanide (0·3%) was removed from the exit gases by an alkali trap: the unabsorbed gases contained carbon monoxide, carbon dioxide, and acetylene (infrared) (cf. previously recorded pyrolysis of acrylonitrile [1]).

Cyanomethyl Benzoate (VIII).—*Preparation.* A modification of Aloy and Rabaut's method [44] was used, the equimolar aqueous solution of potassium cyanide and formaldehyde being kept at *ca.* 0° during the slow addition of benzoyl chloride (1 mole), with stirring. The resulting ester (89%) had b. p. 163—166°/25 mm., m. p. 25—26° (lit.,[44] b. p. 165°/25 mm., m. p. 26—27°).

Pyrolysis 16. The ester was heated in the static reaction vessel (*ca.* 205°: 36 hr.): the

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[39] Staudinger, *Ber.*, 1916, **49**, 1972.
[40] Zinin, *Annalen*, 1857, **104**, 116.
[41] Corson and Saliani, *Org. Synth.*, 1932, **12**, 1.
[42] Michael and Jeanprêtre, *Ber.*, 1892, **25**, 1681.
[43] Davis, *J.*, 1910, **97**, 950.
[44] Aloy and Rabaut, *Bull. Soc. chim. France*, 1913, **13**, 457.

pyrolysate (*a*) yielded: 3·5 g., b. p. 90—150°/23 mm. (contained benzonitrile, but no benzaldehyde); 14·8 g., b. p. 150—188°/23 mm. (benzonitrile, unchanged pyrolysand, and a trace of suspended benzoic acid); 5·3 g., b. p. >188°/23 mm. (benzoic acid and unidentified tars); and 13·3 g. of residual tars. (Overall loss, 0·6 g.) Methyl benzoate and benzoic anhydride could not be identified in (*a*). The gaseous pyrolysate (*b*) contained a trace of hydrogen cyanide; some paraformaldehyde was deposited in the condenser.

Pyrolysis 17. For this run, the cold trap was replaced by an alkali trap (which absorbed 0·1 g. of hydrogen cyanide: 1·4%) followed by a 2,4-dinitrophenylhydrazine trap (which yielded no aldehydic or ketonic derivative). The pyrolysate (*a*) yielded: 1·0 g., b. p. 58—93°/760 mm. [contained hydrogen cyanide (0·05 g.; 0·7%) and benzene: also probable trace of acetonitrile, though the infrared spectrum of the fraction was not quite conclusive]; 4·5 g., b. p. 120—152°/20 mm. (benzonitrile and benzaldehyde); 14·5 g., b. p. 152—168°/20 mm. (unchange pyrolysand, with a little benzonitrile and benzaldehyde); 15·4 g., b. p. 168—196°/20 mm. (mostly unchanged pyrolysand, with some suspended benzoic acid); 2·6 g., b. p. 196—214°/20 mm. (benzoic acid and unidentified tars); and 0·5 g. of residual tars. (Overall loss, 4·0 g.). Methyl benzoate and benzoic anhydride could not be identified in (*a*).

Diphenylmethyl Benzoate (IX).—*Preparation.* Linnemann's method [45] yielded the ester (46%), m. p. 86° (from ethanol) (lit.,[45] m. p. 88°).

Pyrolysis 18. The pyrolysate (*a*) yielded: (i) 0·7 g., b. p. 78—81° (benzene); (ii) 8·0 g., b. p. 106—130°/2 mm. (benzoic acid, benzophenone, and diphenylmethane); (iii) 2·0 g., b. p. 130—148°/2 mm. (benzophenone and diphenylmethane); (iv) 6·0 g., b. p. 194—215°/2 mm.; and (v) 4·3 g. of residual tars. Fraction (iv) contained a solid, which on extraction with ether yielded (iv*a*) a soluble fraction and (iv*b*) an insoluble residue. Residue (iv*b*), recrystallised from glacial acetic acid, yielded *s*-tetraphenylethane as needles, m. p. 210° (lit.,[46] m. p. 211°) (Found: C, 93·3; H, 6·9. Calc. for $C_{26}H_{22}$: C, 93·4; H, 6·6%): the mother-liquors, concentrated, deposited a solid, which on recrystallisation from methanol yielded fine white crystals, m. p. 90—91°. This product was not identified; but a mixed m. p. showed that it was not simply unchanged pyrolysand, despite a similar analysis (Found: C, 83·4; H, 6·0. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·6%). The soluble fraction (iv*a*) consisted of tar and a little solid: the latter (unidentified) gave crystals, m. p. 89—90°, from methanol; again, a mixed m. p. showed that this was not simply unchanged (IX).

Pyrolysis 19. The pyrolysate (*a*) yielded: 5·0 g., b. p. 88—120°/2 mm., and 2·0 g., b. p. 120—164°/2 mm. (both fractions contained benzoic acid, benzophenone, and diphenylmethane); 12·2 g., b. p. 164—202°/2 mm. (benzoic acid, benzophenone, diphenylmethane, *s*-tetraphenylethane, and the same unidentified solid as in the previous run, m. p. 89—90°); and 3·3 g. of residual tars.

Pyrolysis 20. Formation of benzoic anhydride was not detectable in the two previous runs; but a further sample of ester (IX), heated at *ca.* 200° for 2 hr., showed the colour reaction of the anhydride.

Triphenylmethyl Benzoate (X).—*Preparation.* Hammond and Rudeshill's method [47] yielded the ester (41%), m. p. 168° (from ethyl acetate) (lit.,[47] m. p. 169°) (Found: C, 85·8; H, 5·8. Calc. for $C_{26}H_{20}O_2$: C, 85·7; H, 5·5%).

Pyrolysis 21. The pyrolysate (*a*) yielded: (i) a trace of benzene; (ii) 2·0 g., b. p. 145—162°/1·5 mm. (benzoic acid and triphenylmethane); (iii) 5·0 g., b. p. 162—192°/1·5 mm. (benzoic acid, triphenylmethane, and tetraphenylmethane); (iv) 2·5 g., b. p. 260—280°/1·5 mm. (mainly tar, with traces of benzoic acid and triphenylmethane); and (v) 2·0 g. of residual tars. Benzoic anhydride was detected in fractions (ii) and (iii). The hydrocarbons in fraction (iii) were separated by ether into a more soluble fraction (iii*a*) and an undissolved residue (iii*b*). Fraction (iii*a*), freed from benzoic acid by aqueous sodium carbonate, yielded triphenylmethane as plates (from methanol), m. p. 91° (lit.,[48] m. p. 91°) (Found: C, 93·5; H, 6·8. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%). The residue (iii*b*), recrystallised from benzene, yielded tetraphenylmethane, m. p. 282° (lit.,[49] m. p. 282°) (Found: C, 93·4; H, 6·6. Calc. for $C_{25}H_{20}$: C, 93·8; H, 6·2%). No carbonyl compounds could be detected in the pyrolysate.

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[45] Linnemann, *Annalen*, 1865, **133**, 20.

[46] Heilbron, " Dictionary of Organic Compounds," Eyre & Spottiswoode, London, 1934, Vol. III, p. 736.

[47] Hammond and Rudeshill, *J. Amer. Chem. Soc.*, 1950, **72**, 2770.

[48] Heilbron, ref. 46, p. 886.

[49] Gomberg and Kamm, *J. Amer. Chem. Soc.*, 1917, **39**, 2009.

Pyrolysis 22. The ester was heated in the static reaction vessel (225°: 24 hr.): the pyrolysate (*a*) yielded: (i) 3·3 g., b. p. 110—140°/2 mm. (benzoic acid and triphenylmethane); (ii) 5·5 g., b. p. 184—215°/2 mm.; (iii) 6·3 g., b. p. 215—245°/2 mm.; (iv) 1·7 g., b. p. 245—255°/2 mm.; and (v) 3·2 g. of residual tars. Fractions (ii) and (iii), extracted with ether and freed from benzoic acid by aqueous sodium carbonate, yielded a solid, m. p. 169° from benzene-light petroleum. A mixed m. p. test (depression *ca.* 10°) showed that this was not simply unchanged (X) (m. p. 168°), despite the closely similar m. p. and elementary analysis (Found: C, 86·1; H, 5·9. Calc. for $C_{26}H_{20}O_2$: C, 85·7; H, 5·5%). This unidentified substance is being studied further.

Benzil.—Pure α-diketone, from British Drug Houses Ltd., was used.

Pyrolysis 23. The pyrolysate (*a*) yielded: 3·0 g., b. p. 65—85° (benzene); 7·0 g., b. p. 120—150°/3 mm. (benzaldehyde and biphenyl); 7·0 g., b. p. 150—180°/3 mm. (benzophenone and a trace of biphenyl); 36·0 g., b. p. 194—198°/3 mm. (unchanged pyrolysand); and 33·0 g. of high-boiling tars.

Acetylbenzoyl.—Pure α-diketone, from British Drug Houses Ltd., was used.

Pyrolysis 24. The α-diketone was pyrolysed in the semimicro-reaction vessel described by Bain and Ritchie [32] (*ca.* 500°; 10 min.); the pyrolysate contained acetophenone and unchanged pyrolysand, with no evidence for keten or benzaldehyde.

Benzylidene Bromide.—Preparation. Curtius and Quedenfeldt's method [50] yielded this bromide (60%), b. p. 115°/15 mm., 126°/23 mm. (lit.,[50] b. p. 105—107°/12 mm., 156°/23 mm.). The b. p. was checked carefully several times, with concordant results; and it is thought that the published figure of 156° is a mis-print for 126°.

Pyrolysis 25. The pyrolysate (*a*) yielded: 0·8 g., b. p. 90—125°/8 mm. (benzylidene bromide, characterised by hydrolysis to benzaldehyde; no evidence for bromobenzene); 5·8 g., b. p. 125—160°/8 mm. (*trans*-αα′-dibromostilbene, m. p. 208°, from acetic acid; lit.,[39] m. p. 206°) (Found: C, 49·1; H, 3·2; Br, 47·3. Calc. for $C_{14}H_{10}Br_2$: C, 49·4; H, 3·5; Br, 47·0%); 3·3 g., b. p. 160—200°/8 mm. (*trans*-αα′-dibromostilbene and tars); and 0·5 g. of high-boiling tars. The gaseous pyrolysate (*b*) was hydrogen bromide, containing *ca.* 11% of displaced nitrogen.

Detection of Ionic Dissociation of Benzoyl Chloride, Bromide, and Cyanide in the Liquid Phase.—Silver nitrate dissolved very readily in benzonitrile, no precipitate of silver cyanide being formed. To three portions of this solution were added (separately) pure benzoyl chloride, bromide, and cyanide: in each case, the appropriate silver salt was precipitated.

New Derivatives of Benzil and Acetylbenzoyl.—During the preparation of reference derivatives for chromatography, the following new compounds were obtained (the former by treatment of the α-diketone with a large excess of 2,4-dinitrophenylhydrazine): (i) *Benzil bis*-2,4-*dinitrophenylhydrazone*, orange powder (from ethanol), m. p. 316° (Found: C, 54·6; H, 3·0; N, 19·7. $C_{26}H_{18}O_8N_8$ requires C, 54·7; H, 3·2; N, 19·7%). (ii) *Acetylbenzoyl* 2,4-*dinitrophenylhydrazone*, yellow-orange needles (from ethanol), m. p. 185° (Found: C, 54·7; H, 3·7; N, 17·0. $C_{15}H_{12}O_5N_4$ requires C, 54·8; H, 3·7; N, 17·1%). It is not known whether the mono-derivative (ii) is substituted in the acetyl or in the benzoyl moiety.

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[50] Curtius and Quedenfeldt, *J. prakt. Chem.*, 1898, **58**, 390.