# Studies in Pyrolysis. Part XXIV.<sup>1</sup> Competitive Routes in the Pyrolysis of Carboxylic Acid Anhydrides

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Where the open-chain anhydride of a monobasic acid contains an a-hydrogen atom, the known major primary scission is a non-radical acyl-oxygen scission, yielding a keten and a carboxylic acid as discrete molecules. If, in addition, the anhydride is αβ-unsaturated, primary intra-acyl scission competes with the above acyl-oxygen scission : however, the latter is precluded if there is no α-hydrogen atom, so that intra-acyl scission is here the only primary breakdown route. The pyrolysis of cyclic anhydrides of dibasic acids is explicable on similar lines: here, acyl-oxygen scission would yield a single open-chain 'keten-acid', terminated by a keten group (>CH·CH:CO) and a carboxyl group, the former rearranging from its cumulative to its conjugated form (>C:CH·CHO), followed by decarbonylation to >C:CH<sub>2</sub> and other competing and secondary reactions. All the observed products are explicable on this basis, coupled with the known competing formation of a cyclic ketone if the anhydride is of sufficient ring size. Cyclic transition states in the acyl-oxygen scissions are suggested. All pyrolyses were at ca. 500°.

SUCCEEDING papers <sup>2,3</sup> describe the pyrolysis of poly-(ethylene fumarate) and various model compounds, and of related industrial polymers in which the spacing of unsaturated fumaric acid residues along the chain is controlled by the incorporation of saturated dibasic acid residues, a typical chain including segments such as (A). Some of the results were surprising, notably

Scheme 1 has been presented by Davidson and Newman<sup>6</sup> to account for the overall pyrolysis of a carboxylic acid R·CH<sub>2</sub>·CO<sub>2</sub>H and its anhydride. Neunhöffer and Paschke<sup>7</sup> have shown that the ketone (IX) is formed only where the parent acid contains at least one a-hydrogen atom. They attribute its formation to a selfcondensation of the simple acid anhydride, yielding first

$$\overset{\sim}{\underbrace{\operatorname{CH}_2 \cdot \operatorname{CH}_2 \cdot \operatorname{O}_2 \operatorname{C} \cdot \operatorname{CH} \cdot \operatorname{CH}_2 \cdot \operatorname{CH}$$

the substantial absence of acrylic (I) and methacrylic (II) anhydride from the pyrolysates from certain model compounds,<sup>2</sup> although there were a priori reasons for predicting their presence: and to assist in interpreting these results a preliminary study of the thermal stability of the anhydrides of unsaturated monobasic acids and of dibasic acids was necessary. There is already a fair amount of scattered information, but it is not all consistent and there are substantial gaps in our knowledge.

$$\begin{array}{cccc} CH_2:CH \cdot CO & CH_2:CMe \cdot CO & CH_2 \cdot CO \\ & & & & & & \\ CH_2:CH \cdot CO & CH_2:CMe \cdot CO & CH_2 \cdot CO \\ & & & & & \\ (I) & & & (II) & & (III) \end{array}$$

This paper describes the pyrolysis of the unsaturated open-chain anhydrides (I) and (II), and of four cyclic anhydrides (III)--(VI) relevant to the general problem.

#### RESULTS AND DISCUSSION

General Considerations.—Vapour-phase pyrolysis of these six anhydrides at  $ca. 500^{\circ}$  gives results which are at first sight rather varied (Table 1), but a rationalised and consistent picture emerges when they are considered in the light of (i) the widely investigated pyrolysis of acetic anhydride, and (ii) the intra-acyl scission undergone  $^{4,5}$  by certain esters of  $\alpha\beta$ -unsaturated acids.

the mixed carboxylic  $\beta$ -ketocarboxylic anhydride (VII) and R·CH<sub>2</sub>·CO<sub>2</sub>H, followed by disproportionation to  $(R \cdot CH_2 \cdot CO)_2O$  and  $\beta$ -ketocarboxylic acid (VIII), the latter then yielding ketone (IX) by decarboxylation. [That mixed anhydrides of type (VII) can exist has been shown<sup>8</sup> by their formation on addition of carboxylic acids to diketen.] If no  $\alpha$ -hydrogen atom is present. the anhydride has an enhanced thermal stability, and breaks down in a different way: for example, benzoic

$$\begin{array}{cccc} \mathrm{CHMe}\text{-}\mathrm{CO} & \mathrm{CH}_2\text{-}\mathrm{CH}_2\text{-}\mathrm{CO} & \mathrm{CH}\text{-}\mathrm{CO} \\ | & & & \\ \mathrm{CH}_2\text{-}\mathrm{CO} & | & & \\ \mathrm{CH}_2\text{-}\mathrm{CO} & \mathrm{CH}_2\text{-}\mathrm{CO} & | & & \\ \mathrm{(IV)} & & & (\mathrm{V}) & & \\ \mathrm{(V)} & & & (\mathrm{V}) & & \\ \end{array}$$

anhydride is very stable in the vapour phase up to ca. 500°, but at ca. 550° undergoes a complex pyrolysis in which at least some of the steps are free-radical in character.9 This is in marked contrast to the above self-condensation of the anhydride (R·CH<sub>2</sub>·CO)<sub>2</sub>O, which requires no free-radical stage, and to the very important competing scission to carboxylic acid and a keten, which for acetic anhydride (R = H) has been shown by Szwarc and Murawski<sup>10</sup> to be a non-radical unimolecular dissociation. (It does not necessarily

<sup>&</sup>lt;sup>1</sup> Part XXIII, W. C. Bain, P. D. Ritchie, and A. E. Wright, J. Chem. Soc. (C), 1968, 554. <sup>2</sup> Part XXV, R. L. Forman, H. M. Mackinnon, and P. D.

Ritchie, following paper. <sup>3</sup> Part XXVI, R. L. Forman, H. M. Mackinnon, and P. D.

Ritchie, J. Chem. Soc. (C), 1968, 2016.

<sup>&</sup>lt;sup>4</sup> H. M. Mackinnon and P. D. Ritchie, J. Chem. Soc., 1957, 2564.

<sup>&</sup>lt;sup>5</sup> P. E. Reininger, P. D. Ritchie, and D. Ferguson, J. Chem. Soc., 1963, 2688. <sup>6</sup> D. Davidson and P. Newman, J. Amer. Chem. Soc., 1952,

<sup>74, 1515.</sup> 

<sup>7</sup> O. Neunhöffer and P. Paschke, Ber., 1939, 72, 919.

 <sup>&</sup>lt;sup>8</sup> H. J. Hagemeyer, U.S.P. 2,476,859/1949.
 <sup>9</sup> R. J. P. Allan, E. Jones, and P. D. Ritchie, *J. Chem. Soc.*, 1957, 524.

<sup>&</sup>lt;sup>10</sup> M. Szwarc and J. Murawski, Trans. Faraday Soc., 1951, 47. 267.

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follow that this also applies to the pyrolysis of unsaturated anhydrides, described below.) As these authors pointed out, molecular models demonstrate that the anhydride molecule can readily assume the quasi-six-membered cyclic transition state (X), which can account for the observed acyl-oxygen  $(B^1)$  scission products, keten and acetic acid, and is closely analogous molecule. It is, however, clear that although the cyclic transition states (X) and (XII) could formally be assumed by the open-chain acetic anhydride and acrylic anhydride (I) respectively, the corresponding structure (XIII) involves far too much strain for it to intervene in the pyrolysis of the cyclic anhydride (III); the same consideration applies to other cyclic anhydrides such as



to the transition state (XI) which has been suggested <sup>11</sup> and latterly quite widely accepted <sup>12</sup> as intervening in the alkyl-oxygen  $(A^1)$  scission of alkyl carboxylates containing a  $\beta$ -hydrogen atom.



The present results, dealt with individually below, can all be explained by the general concept that where an  $\alpha$ -hydrogen atom is present the first stage in the pyrolysis is  $B^1$  scission of an acyl-oxygen linkage. For open-chain anhydrides of monobasic acids, this yields <sup>10</sup> a keten and a carboxylic acid as two discrete molecules, whereas for cyclic anhydrides of dibasic acids  $B^1$  scission would yield an intermediate open-chain 'keten-acid' terminated by a keten group >CH·CH:CO and a carboxyl group, undergoing further reaction as a single <sup>11</sup> C. D. Hurd and F. H. Blunck, J. Amer. Chem. Soc., 1938, **60**, 2419. (IV) and (V). Further, even for the open-chain methacrylic anhydride (II), a cyclic transition state of type (XII) is impossible (quite apart from any question of strain) because unlike acrylic anhydride it contains no  $\alpha$ -hydrogen atom; here, at least, breakdown must involve some other kind of transition state.

In explaining the  $A^1$  scission of alkyl esters, the concept of the transition state (XI) has been so simple and attractive that there is a danger of its too uncritical acceptance as a proven fact, despite the absence of specific experimental evidence for its correctness. Other transition states have been suggested, equally feasible and equally unproven, such as the quasi-fourmembered system (XIV).<sup>13</sup> Something like (XIV) must, it seems, be visualised as the transition state in the pyrolytic  $B^1$  scission of various esters which lack an  $\alpha$ -hydrogen atom and are structurally precluded from assuming a six-membered cyclic arrangement resembling (X), for example, phenyl acetate<sup>11</sup> (XV; R = Ph) and isopropenyl acetate <sup>14</sup> (XV;  $R = \cdot CMe:CH_2$ ). It seems likely that their breakdown is molecular or ionic, involving a cyclic transition state such as (XVI), which may be compared with the transition state (XVII) suggested 15 for the unimolecular pyrolysis of alkyl

<sup>&</sup>lt;sup>12</sup> See e.g., D. J. Cram, 'Steric Effects in Organic Chemistry,' ed. M. Newman, Wiley, New York, 1956, chap. 6.

 <sup>&</sup>lt;sup>13</sup> E. Warrick and P. Fugassi, J. Phys. Colloid Chem., 1948, 52, 1314.
 <sup>14</sup> R. J. P. Allan, J. McGee, and P. D. Ritchie, J. Chem. Soc.,

<sup>&</sup>lt;sup>14</sup> R. J. P. Allan, J. McGee, and P. D. Ritchie, J. Chem. Soc., 1957, 4700.

<sup>&</sup>lt;sup>15</sup> D. H. R. Barton, A. J. Head, and R. J. Williams, J. Chem. Soc., 1952, 453; cf. A. Maccoll, J. Chem. Soc., 1958, 3398.

 $C^1$ 

halides. Such a concept may be applicable to the  $A^1$ scission of anhydrides as well as of esters: this possibility is further considered later.

even though self-condensation *cum* decarboxylation is formally possible.

Methacrylic Anhydride (II).-Since the absence of



Acrylic Anhydride (I).—The pyrolysis products from this anhydride (Table 1) are best accounted for by Scheme 2. All the competing reactions are predictable on the basis of previous work.  $B^1$  Scission would here yield methyleneketen [CH<sub>2</sub>:C:CO], possibly via a cyclic transition state. This keten is apparently unknown, but should be highly labile and reactive, and would most

an  $\alpha$ -hydrogen atom here precludes the formation of a keten, primary  $B^1$  scission cannot occur, and the main observed product, methacrylic acid (Table 1), can therefore only arise via a primary E scission (Scheme 3). On this basis, methylacetylene should be formed along with the mixed formic methacrylic anhydride in equimolar amount. The fact that only a trace is formed

$$[CH_2:CCO] + CH_2:CH \cdot CO_2H$$

$$R$$

$$B^1$$

[CH:C·CHO] → CH:CH + CO

$$\begin{array}{c} CH_2:CMe \cdot CO \\ CH_2:CMe \cdot CO \\ CH_2:CMe \cdot CO \\ CH_2:CMe \cdot CO_2H \\ CH_2:CMe \cdot CH_2 \\ CH_2:CMe \cdot CH_2 \\ CH_2:CMe \cdot CH_2 \\$$

$$\begin{array}{c} \text{CH}_{2}:\text{CMe}\cdot\text{CO} & -\text{CH}_{1}:\text{CMe} & \text{CH}_{2}:\text{CMe}\cdot\text{CO} & \text{CO}_{2} + \text{CH}_{2}:\text{CMe}\cdot\text{CHO} & C^{2} \\ (\text{II}) & & & \\ \end{array}$$



probably undergo rearrangement (R) from the cumulative to the conjugated isomer, propiolaldehyde, which very readily breaks down to acetylene and carbon monoxide on pyrolysis (Run 7, Table 2). The intra-acyl scission (E) undergone by aryl acrylates and methacrylates 4would be expected to compete with primary  $B^1$  scission, vielding acetylene and mixed formic acrylic anhydride (XVIII). Mixed anhydrides can, as shown by Autenrieth,<sup>16</sup> undergo thermal disproportionation to two simple anhydrides; but this is a slow reaction, and the predictable major breakdown of (XVIII) is ready decarbonylation of the formyl group, yielding further acrylic acid, in competition with decarboxylation of the acrylyloxy-group, yielding acraldehyde. (This competing  $C^2$  scission is analogous to that occurring in the breakdown of aryl acrylates and methacrylates.<sup>4</sup> It is of interest that decarboxylation also occurs, at only ca. 150-170°, in the pyrolysis <sup>17</sup> of certain mixed carboxylic carbonic anhydrides, Ph·CO·O·CO·OR.) Partial  $C^1$  scission of acraldehyde and  $C^2$  scission of acrylic acid account for the observed ethylene. There is here no evidence for the formation of a ketone (divinyl ketone),

<sup>16</sup> W. Autenrieth, Ber., 1901, 34, 168; W. Autenrieth and G. Thomae, Ber., 1924, 57, 423.

(Runs 3 and 4, Table 2) is not, however, surprising. A similar alkyne-deficiency has been noted in the pyrolysis of phenyl acrylate and methacrylate<sup>4</sup> and phenyl vinyl ether,<sup>18</sup> attributable to secondary high-temperature reactions of the alkyne, with formation of tar. [There is also an alkyne-deficiency in the pyrolysate from acrylic anhydride (cf. Runs 1 and 2, Table 2), though it is not so marked.] The observed alkene (propene) can be accounted for by partial  $C^1$  and  $C^2$  scission of methacraldehyde and methacrylic acid respectively.

Methacrylic anhydride (II) is markedly more thermostable than acrylic (I) (cf. Runs 1 and 2 with Runs 3 and 4, Table 2). This is presumably because intraacyl scission requires a higher temperature<sup>4</sup> than does acyl-oxygen scission via a cyclic transition state; the latter is possible (whether six-or four-membered) for anhydride (I) but structurally precluded for (II), which lacks an  $\alpha$ -hydrogen atom.

The formation of a ketone (di-isopropenyl ketone) is here precluded <sup>7</sup> by the absence of an  $\alpha$ -hydrogen atom.

<sup>&</sup>lt;sup>17</sup> D. S. Tarbell and E. J. Longosz, J. Org. Chem., 1959, 24,

<sup>774.</sup> <sup>18</sup> H. V. R. Iengar and P. D. Ritchie, J. Chem. Soc., 1957,

### J. Chem. Soc. (C), 1968

Succinic Anhydride (III).—The pyrolysis of this compound has previously been studied, at two widely different temperatures and with widely different results. Volhard <sup>19</sup> found that on prolonged refluxing at 250— 280° the anhydride eliminated carbon dioxide and yielded the spiro-dilactone (XX), and he suggested a complicated reaction mechanism. (It has been observed <sup>20</sup> that the decarboxylation temperature of succinic acid under somewhat different conditions is  $ca. 300-330^{\circ}$ ). This curious result was confirmed by Hurd and Bennett,<sup>21</sup> who advanced a perhaps deceptively simple explanation: primary decarboxylation, followed by addition of the resulting fragment (XIX) to a carbonyl group in

of (III) at ca. 500°, gives results quite different from those at the higher and lower extremes of temperature. The products (Table 1) are readily accounted for by an extension of the foregoing principles, in which the primary acyl-oxygen scission yields the single intermediate 'keten-acid' (XXI) instead of two separate molecules (a keten and a carboxylic acid) as shown in Scheme 5. The observed ethylene is accounted for by partial  $C^2$  scission of acrylic acid and  $C^1$  scission of acraldehyde, reactions which might well be complete at the higher temperature used by Rice and Murphy.<sup>22</sup>

The mechanism of  $B^1$  scission of cyclic anhydrides such as (III) requires comment. As pointed out earlier,

TABLE 2	2
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Pyrolysis of anhydrides (I) and (II), acetic anhydride, and propiolaldehyde

Pyrolysand	(	I)	(]	I)	Acetic a:	nhydride	Propiol- aldehyde
Run no.	1	2	3	4	<b>5</b>	6	7
Temperature	$500^{\circ}$	500°	500°	$500^{\circ}$	500°	$500^{\circ}$	500°
Reaction vessel	P/20	P/20	P/20	P/20	P/220	P/220	P/20
Feed-rate (g./min.)	0.12	0.42	Ó•63	0.22	<b>0</b> ·21	0.47	0.15
Residence time (sec.)	<b>24</b>	6	6	<b>24</b>	127	58	6
Wt. pyrolysed (g.)	15.0	14.5	12.7	16.6	41.5	56.0	11.4
(a) Liquid pyrolysate (g.)	$7 \cdot 3$	9.5	10.4	10.3	31.5	50.2	6.0
(b) Gaseous pyrolysate (l.)	<b>4</b> ·7	$3 \cdot 8$	1.5	$3 \cdot 4$	4.3	$3 \cdot 8$	$2 \cdot 3$
Composition (%) of $(b)$ (approx.):							
CO	58	55	62	56	39	42	86.5
CO,	15.5	14	26	35	47.5	37	5
Alkyne	18	<b>26</b>	1	t	t	t	2.5
Alkene	8.5	<b>5</b>	11	9	13.5	13	5
Alkane	Nil	Nil	Nil	Nil	t	8	Nil
Decomposition (%)	88	73	<b>45</b>	56	47	35	50
Carbonisation in vessel	1	1	1	1	m	m	h

t = Trace, l = light, m = medium, h = heavy.

 $\overset{\mathrm{CH}_2 \cdot \mathrm{CO}}{\longrightarrow} [-\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CO}_-] \overset{+}{\longrightarrow}$  $\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}{|} \overset{\mathrm{O} - - \mathrm{CO}}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2}}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2}}}{\overset{\mathrm{CH}_2 \cdot \mathrm{CH}_2 \cdot \mathrm{CH}_2}}{\overset{\mathrm{CH}_2 \cdot$ сн₃∙сб (III) (XIX) (XX)SCHEME 4

$$\begin{array}{c} CH_2 \cdot CO \\ CH_2 \cdot CO \\ (III) \end{array} \xrightarrow{P} \begin{bmatrix} CH:CO \\ CH_2 \cdot CO_2H \end{bmatrix} \xrightarrow{R} \begin{bmatrix} CH:CHO \\ CH:CO_2H \end{bmatrix} \xrightarrow{P} CO + CH_2:CH \cdot CO_2H \qquad C^1 \\ CH:CO_2H \end{bmatrix} \xrightarrow{CO} CO_2 + CH_2:CH \cdot CHO CO_2H \qquad C^2 \\ SCHEME 5 \end{array}$$

an unchanged anhydride molecule, as in Scheme 4. It is not clear, however, whether they regarded (XIX) as a biradical, though radical formation seems unlikely at the low reaction temperature involved. However, totally different behaviour of (III) at 800-900° was observed by Rice and Murphy,<sup>22</sup> who reported theoretical conversion into an equimolar gaseous mixture of carbon monoxide, carbon dioxide, and ethylene, in agreement with the 'principle of least motion' advanced by Rice and Teller.<sup>23</sup> The present work, involving breakdown

even if the transition state (XI) be accepted as occurring in the  $A^1$  scission of alkyl esters (and there is no positive evidence that it does so), it need not follow that the analogous states (X) and (XII) occur in the  $B^1$  scission of the corresponding open-chain anhydrides, though they are formally possible: in any event, for a cyclic anhydride such as (III), the transition state (XIII) is too highly strained to exist. However, an anhydride exists in equilibrium with its enolic form, and in (XXII), the enol of (III), the hydroxylic hydrogen can without strain approach much more closely to the anhydride oxygen >0 than to the remaining >CO group, so that

J. Volhard, Annalen, 1889, 253, 206.
 V. V. Korshak and S. V. Rogozhin, Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk, 1952, 531; 1954, 541; P. E. Reininger, Ph.D. Thesis, Glasgow University, 1961, p. 135.

<sup>&</sup>lt;sup>21</sup> C. D. Hurd and C. W. Bennett, unpublished results, quoted by C. D. Hurd, 'The Pyrolysis of Carbon Compounds,' Chemical Catalog Co., New York, 1929, pp. 404, 579.

<sup>22</sup> F. O. Rice and M. T. Murphy, J. Amer. Chem. Soc., 1947,

<sup>64, 896.</sup> <sup>23</sup> F. O. Rice and E. Teller, J. Chem. Phys., 1938, 6, 489; Pointral Compt. rend., 1917, 165, 703; 1939, 7, 199; cf. also E. Peytral, Compt. rend., 1917, 165, 703; 1924, 179, 831.

the quasi-four-membered transition state (XXIII) becomes a formal possibility. We shall not pursue these speculations further: they are mentioned simply to indicate that acyl-oxygen scission of cyclic anhydrides is an acceptable concept, and that there is a possible

is almost theoretical, the key-product being allylacetic acid. But-1-ene is present, and can arise by partial  $C^2$ scission of the acid. In addition, cyclopentanone appears as a major product, predictable on the basis of Blanc's rule, and previously observed 6,7 (cf. Scheme 1): this



mechanism equally applicable to both open-chain and cyclic anhydrides.

Methylsuccinic Anhydride (IV).—The presence of the  $\alpha$ -methyl group in this unsymmetrical anhydride leads to complications. There are now two different points at which acyl-oxygen scission of (IV) can formally occur, and two different ways in which one of the resulting

ketone also yields but-1-ene on pyrolysis, along with carbon monoxide and ethylene.<sup>24</sup>

Maleic Anhydride (VI).—Rice and Murphy<sup>22</sup> guote as an example of the 'principle of least motion' the total breakdown of maleic anhydride at 800-900° to an equimolar gaseous mixture of carbon monoxide, carbon dioxide, and acetylene. They envisaged that



'keten-acids' (XXIV) can rearrange. The foregoing principles suggest that Scheme 6 represents the overall breakdown. The presence of much methacrylic acid and a little crotonaldehyde in the pyrolysate (Table 1) points strongly to the route proceeding via the aldoketen intermediate (XXV): transfer of hydrogen from the unsubstituted CH<sub>2</sub> group rather than the CHMe group would be favoured by the inductive effect of the methyl group. No vinylacetic acid or crotonic acid could be detected, which would have provided evidence for competing breakdown via the keto-keten intermediate (XXIV), but a little methacraldehyde was found, and there seems to be no other route by which this could have been produced. The evidence, then, indicates a major decomposition via (XXV), with a minor competitive breakdown via (XXIV).

Adipic Anhydride (V).—Here the results (Table 1) are again quite simply explained (Scheme 7). Decomposition

24 E. R. Johnson and W. D. Walters, J. Amer. Chem. Soc., 1954, 76, 6266.

concerted bond-breaking and bond-making occurred by a cyclic transition state, with minimum change in electronic configuration and maximum gain in resonance energy. This view is in line with later work 25 on the high-temperature pyrolysis of phthalic anhydride (ca. 690°), where the pyrolysate contained products indicating the primary formation (1) of a transient alkyne, benzyne,



along with carbon dioxide and monoxide. Nevertheless. although such a transition state is attractively simple. the present work suggests that the mechanism may be

<sup>&</sup>lt;sup>25</sup> E. K. Fields and S. Myerson, Chem. Comm., 1965, 474; cf. S. Myerson and E. K. Fields, ibid., 1966, 275, and R. F. C. Brown, D. V. Gardner, J. F. W. McOmie, and R. K. Solly, ibid., 1966, 407.

15

 $500^{\circ}$ 

P/220

0.13

rather more complex (Runs 13-15, Table 3). Decomposition of anhydride (VI) is negligible in the vapour phase at ca. 350°; at ca. 430° there is ca. 9% decomposition, and the  $CO: CO_2: C_2H_2$  ratio is 28: 52: 20; and it is only at ca. 500°, with ca. 50% decomposition, that the ratio becomes equimolar. On the basis of the consistent picture developed above to explain the

CH·CO

to the reaction vessel at ca. 500° was accompanied by a flash of light, suggesting a highly exothermic breakdown.

Acetic Anhydride.-Runs 5 and 6, Table 2, gave results in agreement with published work, but in addition vielded a trace of acetaldehyde, which does not seem to have been recorded previously. It is not easy to explain this surprising product without invoking a minor

 $CO_2 + [CH:C\cdot CHO]$  $C^2$ С•СНО CO + CH**:**CH CO + [CH**:**C·CO₂H] └║ С∙со₂н\_  $C^1$  $C^1$ 



TABLE 3

		Pyrolysis of	f anhydrid	les (III)(V	7I)		
Pyrolysand	(III)		(IV)		(V)		(VI)
Run no.	8	9	10	11	12	13	14
Temperature	$500^{\circ}$	$500^{\circ}$	550°	600°	500°	350°	430°
Reaction vessel	P/220	P/4	P/4	P/4	P/20	P/H	P/H
Fee-rate (g./min.)	0.39	0.09	0.05	0.03	0.11	0.35	0.27
Residence time (sec.)	69	5	8	11	22.5	14	14.5
Wt. pyrolysed (g.)	<b>40</b> ·0	$8 \cdot 2$	$5 \cdot 4$	3.0	8.6	53.8	37.0
(a) Solid pyrolysate (g.)	18.0		1	t	Nil	52.0	33.7
(b) Liquid pyrolysate (g)	4.5	1.8	<u>{</u> 4·0 }	1.4	6.7	NO	NT:1

Westdence time (sec.)         Wt. pyrolysed (g.)         (a) Solid pyrolysate (g.)         (b) Liquid pyrolysate (g.)         (c) Gaseous pyrolysate (l.)	$\begin{array}{c} 69 \\ 40 \cdot 0 \\ 18 \cdot 0 \\ 4 \cdot 5 \\ 10 \cdot 5 \end{array}$	5 8·2 7·8	8 5·4 4·0	$ \begin{cases} 11 \\ 3 \cdot 0 \\ t \\ 1 \cdot 4 \\ 1 \cdot 2 \end{cases} $	22.5 8.6 Nil 6.7	14 53·8 52·0 Nil	14.5 37.0 33.7 Nil 1.9	195 20·0 10·0 Nil
Composition (%) of (c) (approx.):	60		63	51	10	1111	00	94
CO <sub>2</sub> Alkyne	29 t		19 t	31 1	83 Nil		52 $20$	34 33 32
Alkene Decomposition (%) Carbonisation in vessel	$11 \\ 55 \\ 1$	t t	18 58 t	17 95 m	7 95 +	t t	$\overset{t}{\overset{9}{1}}$	0·5 50
Decomposition (%) Carbonisation in vessel		t t	58 t	95 m	95 t	t t	9	1

pyrolysis of anhydrides (I)—(V), it is considered that at ca.  $400-500^{\circ}$  the complex conversion of maleic anhydride into gases proceeds on similar lines, with formation of the 'keten-acid' (XXVI) by primary  $B^1$ scission, and, because of the unsaturation of anhydride (VI), a competitive intra-acyl (E) scission leading to the labile formic propiolic anhydride (XXVII) (Scheme 8). Propiolic acid is readily decarboxylated at its b.p.,<sup>26</sup> and it is now shown (Run 7, Table 2) that propiolaldehyde readily undergoes decarbonylation, so that completion of all the above stages could lead to the simple gas-ratio observed (800-900°) by Rice and Murphy,<sup>22</sup> whereas incomplete breakdown at lower temperatures could give a different ratio. The composition of the gas eliminated from propiolaldehyde (Run 7, Table 2) indicates that its  $C^1$  scission is not quite simple. A little carbon dioxide and ethylene are produced, and there is again a marked alkyne-deficiency (cf. acrylic and methacrylic anhydride), presumably owing to drastic secondary decomposition of acetylene. It is interesting that during Run 7, which showed heavy carbonisation, the entry of each drop of propiolaldehyde

free-radical reaction, such as proton capture by an acetyl radical.

### EXPERIMENTAL

Apparatus and Procedure .- Pyrolyses were run as described previously.9 Four different reaction vessels were used, all of Pyrex and packed with broken Pyrex: they are indicated in Tables 2 and 3 by the notation P/4, P/20, P/220(where the number indicates the free unpacked space in ml.), and P/H. In the first three, the pyrolysand was run into the vertical heated vessel under gravity: the fourth was used horizontally, the pyrolysand being distilled into one end of it from a separate evaporator. The reaction vessels were cleaned before each run by heating in a current of air (ca. 500°) and then flushing the whole system thoroughly with nitrogen before starting the run. Hydrocarbons in each pyrolysate were identified by i.r. spectrometry, and carbonyl compounds by their 2,4-dinitrophenylhydrazones (paper chromatography or mixed m.p.). Table I summarises the qualitative composition of each pyrolysate, and Tables 2 and 3 the general experimental conditions

<sup>26</sup> E. Baudrowski, Ber., 1882, 66, 2698.

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Materials Pyrolysed.-Anhydrides (III), (IV), and (VI) were pure materials obtained from British Drug Houses Ltd. The other pyrolysands were prepared in known fashion, as follows: (I),<sup>27</sup> b.p. 97°/38 mm.; (II),<sup>28</sup> b.p.

- <sup>27</sup> C. Moureu, Ann. chim. phys., 1894, [7], 2, 167.
  <sup>28</sup> L. Rubenstein, U.S.P. 2,134,924/1939.

84°/11 mm.; monomeric adipic anhydride (V),29 b.p. 97°/1-3 mm.; propiolaldehyde,30 b.p. 49-50°.

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- <sup>29</sup> J. W. Hill, J. Amer. Chem. Soc., 1930, 51, 4110.
   <sup>30</sup> J. C. Sauer, Org. Synth., 1956, 36, 66.