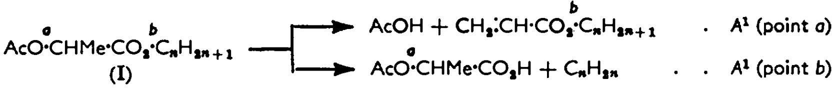
158. *Studies in Pyrolysis. Part XVII.* The Acyl Derivatives and Lactides of Some α-Hydroxy-acids.*

By A. Golomb and P. D. Ritchie.

Thermal breakdown (vapour phase: *ca.* 500°) of the lactides (dilactones) obtained from lactic and α-hydroxy-α-methylpropionic acid has been critically re-examined, with the assistance of some model compounds. The lactide of 1-hydroxycyclohexanecarboxylic acid has also been studied. The preponderating breakdown reaction of all three is a concerted double decarbonylation (yielding carbon monoxide and an aldehyde or ketone), but there are minor competing reactions. A reason is advanced for the failure of the lactides to show major alkyl–oxygen scission to the corresponding olefinic acids. Reaction mechanisms are discussed.

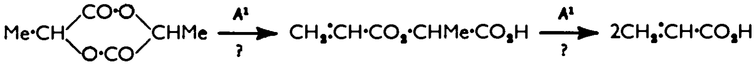
When an alkyl α-acetoxypropionate (I) is pyrolysed at *ca.* 450°, there are two points (*a*, *b*) at which alkyl–oxygen scission of the diester may formally occur. Where $n = 1$, A^1 scission is confined to point *a*, at which a β-hydrogen atom is available: any competitive elimination of ethylene by primary A° scission (nomenclature as previously defined[1]) at point *b* is negligible. Where, however, $n > 1$, and a β-hydrogen is available at two sites in the molecule, A^1 scission occurs competitively[2] at both *a* and *b*, breakdown at the latter site increasing with the value of *n*. (Secondary breakdown of primary products will be mentioned below.)



$$\mathrm{Ac\overset{a}{O}{\cdot}CHMe{\cdot}CO_2{\cdot}\overset{b}{C}_nH_{2n+1}} \rightarrow \begin{cases} \mathrm{AcOH + CH_2{:}CH{\cdot}CO_2{\cdot}\overset{b}{C}_nH_{2n+1}} & A^1 \text{ (point } a) \\ \mathrm{Ac\overset{a}{O}{\cdot}CHMe{\cdot}CO_2H + C_nH_{2n}} & A^1 \text{ (point } b) \end{cases}$$

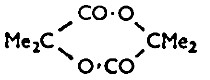
(I)

It might therefore be predicted *a priori* that lactide (II), containing as in (I) two ester groupings, each with an available β-hydrogen atom, would break down thermally at both alkyl–oxygen linkages, either consecutively as shown below, with intermediate formation of an unsaturated α-acyloxy-acid (III), or perhaps simultaneously by a concerted mechanism, yielding acrylic acid:

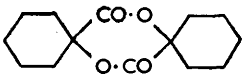


(II) (III)

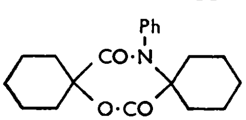
This reaction, if realised, would provide an attractive route from a cheap by-product of lactic acid to an important vinyl monomer. However, preliminary experiments[3] confirmed the earlier report by Blaise[4] that pyrolysis of lactide (II) leads simply to acetaldehyde and carbon monoxide. (For certain higher lactides,[4] the yield of aldehyde may reach 50—60%.) There is no immediately obvious reason for this failure to realise an apparently predictable A^1 scission: and further evidence on the matter has now been sought by detailed study of the pyrolysis of lactide itself, and of two higher analogues (IV, V). The Spirodilactone (V) was selected because of its formal resemblance to the lactone-lactam (VI), which had previously given unexplained results on pyrolysis.[5]



(IV)



(V)



(VI)

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* Part XVI, *J.*, 1961, 1782.

[1] Jones and Ritchie, *J.*, 1960, 4141.

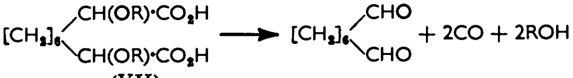
[2] Burns, Jones, and Ritchie, *J.*, 1935, 400.

[3] Ritchie, unpublished observations, 1935.

[4] Blaise, *Compt. rend.*, 1904, **138**, 697.

[5] Bain and Ritchie, *J.*, 1955, 4407.

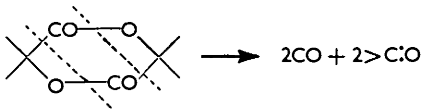
Some recorded pyrolyses of α-hydroxy- and α-acyloxy-acids are pertinent to the present study. Dry distillation of α-hydroxy-acids[6] yields a complex pyrolysate which may contain a lactide (arising *via* a linear hemilactide formed by intermolecular dehydration), an olefinic acid (by intramolecular dehydration), water, carbon monoxide, and an aldehyde or ketone. The size and number of α-substituents in the hydroxy-acid strongly influence the product: the yield of a lactide may reach 30%, but declines rapidly (with increasing formation of olefinic acid) as the molecular weight of the α-hydroxy-acid is increased, and falls to zero when there are two large alkyl α-substituents (a structure which, of course, also yields a ketone rather than an aldehyde). A similar overall result is noted[7] on pyrolysis of certain αα′-dihydroxy-dicarboxylic acids (*e.g.*, VII; R = H), thus:



$$[CH_2]_6\left\langle\begin{matrix}CH(OR)\cdot CO_2H\\ CH(OR)\cdot CO_2H\end{matrix}\right. \longrightarrow [CH_2]_6\left\langle\begin{matrix}CHO\\ CHO\end{matrix}\right. + 2CO + 2ROH$$

(VII)

Just as dry distillation of the appropriate lactide yields an aldehyde,[4] so also an α-hydroxy-acid may yield[8] carbon monoxide, water, and a lower aldehyde (one of the classical descents of a homologous series): and if pyrolysis is arrested before completion a lactide may be isolated, which on continued pyrolysis also yields the same aldehyde. Hurd[9] concluded from all these results that " it is reasonable to infer that loss of carbon monoxide [from α-hydroxy-acids] is more properly a function of the lactide than of the α-hydroxy-acid ": but he suggested no mechanism for this peculiar double decarbonylation, simply representing it thus:



A more precise formulation of this idea is discussed later in this paper.

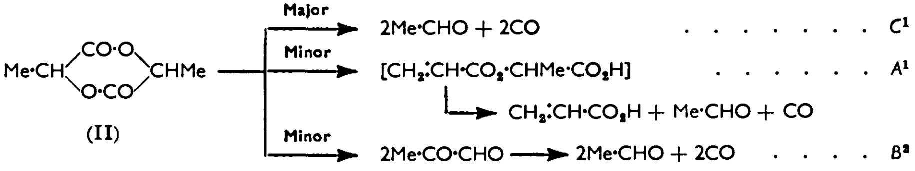
Somewhat analogous results are observed[8] on pyrolysis of simple α-acyloxy-acids, thus:

$$R\cdot CO_2\cdot CHR'\cdot CO_2H \longrightarrow R\cdot CO_2H + R'\cdot CHO + CO$$

Similarly, the dicarboxylic acid (VII; R = Ac) breaks down[7] as represented previously for (VII; R = H).

This breakdown of α-acyloxy-acids contrasts sharply with that of their alkyl esters. It is consistent with the observation[2] that the pyrolysate from ester (I; $n > 1$) contains much carbon monoxide and acetaldehyde, which may have arisen partly from an α-acyloxy-acid formed by primary A^1 scission at point *b*, and partly *via* a minor primary acyl–oxygen scission.[10]

Pyrolysis of Lactide (II).—In a Pyrex glass flow-reactor (*ca.* 500°), lactide (II) decomposes to the extent of *ca.* 50%. The major products, as expected from earlier work,[3,4] are acetaldehyde and carbon monoxide; but the pyrolysate also contains ethylene and carbon dioxide (minor), and methylglyoxal and acrylic acid (traces). These results are best represented by the following scheme of competitive breakdowns.



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[6] Blaise and Bagard, *Ann. Chim. Phys.*, 1907, **11**, 111.

[7] Le Sueur, *J.*, 1907, **91**, 1365.

[8] Bagard, *Bull. Soc. chim. France*, 1907, **1**, 307.

[9] Hurd, " The Pyrolysis of Carbon Compounds," Chemical Catalog Co. Inc., New York, 1929, p. 426.

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

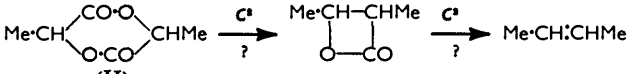
Pyrolysis by the A^1 route should yield acrylic acid, acetaldehyde, and carbon monoxide in equimolar amounts: but the observed ratio of acrylic acid to carbon monoxide was very much lower than this, so that the A^1 route can make only a small contribution to formation of carbon monoxide. Also, the B^2 route should yield equimolar amounts of acetaldehyde and carbon monoxide: but although a separate pyrolysis of methylglyoxal confirmed this route qualitatively, decarbonylation occurred to the extent of only *ca.* 50%, and the mere trace of methylglyoxal observed in the pyrolysate from (II) thus makes it clear that the B^2 route, like the A^1 route, yields little of the total carbon monoxide formed. It thus appears that the main breakdown of (II) occurs directly by a double decarbonylation to acetaldehyde and carbon monoxide.

The very small yield of acrylic acid might be due either to its secondary breakdown to carbon dioxide and ethylene,[11] or to its polymerisation during the working-up of the pyrolysate. The former idea is refuted by the very low ratio of ethylene to carbon dioxide in the pyrolysate, and by a control experiment in which a small amount of acrylic acid intentionally added to (II) before pyrolysis largely survived unchanged; also, although no acrylic acid could be detected when the pyrolysate was directly fractionated, a small amount (*ca.* 1%) was noted when quinol was added before distillation to inhibit polymerisation.

It is believed, though positive evidence is lacking, that the small amount of acrylic acid is formed by primary A^1 scission of the ring, followed by secondary breakdown of the resulting α-acyloxy-acid (III) (α-acryloyloxypropionic acid) on known lines,[8] rather than by concerted double A^1 ring-scission. Other secondary breakdowns of the acid (III) are formally possible—B^2 scission to pyruvic acid and acraldehyde, and decarboxylation (C^2) to α-vinylpropionic acid and/or ethyl acrylate—but none of these products could be detected.

On the other hand, it seems that the observed methylglyoxal is formed by concerted double B^2 ring-scission, rather than by two successive B^2 scissions. The latter process should give the aldehydo-pyruvate $Me{\cdot}CO{\cdot}CO_2{\cdot}CHMe{\cdot}CHO$ as an intermediate, which in view of the known ready thermal decarbonylation of alkyl pyruvates [12] should in turn yield some α-acetoxypropionaldehyde: but no sign of the latter could be detected.

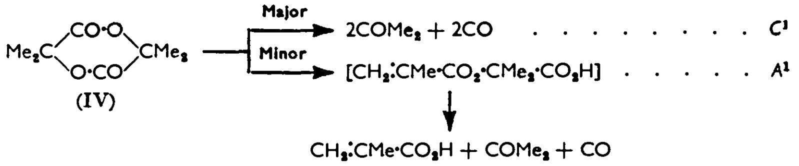
The origin of the observed carbon dioxide cannot be positively attributed to any of the decarboxylations mentioned above. Since lactide (II) is a dilactone, there is a possibility that it might exhibit the thermal decarboxylation already observed [13,14] for β-lactones, thus:



(II)

However, no but-2-ene could be detected: and the origin of the carbon dioxide remains for the present uncertain.

Pyrolysis of the Lactide (IV).—This decomposes under the same conditions to the extent of *ca.* 69%, yielding mainly acetone and carbon monoxide, with minor amounts of methacrylic acid, propene, and carbon dioxide. The results are best represented by the following reaction scheme.



(IV)

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[11] Mackinnon, Ph.D. Thesis, Glasgow University, 1959, p. 31.

[12] Calvin and Lemmon, *J. Amer. Chem. Soc.*, 1947, **69**, 1232.

[13] Staudinger, *Annalen*, 1907, **356**, 51: Staudinger and Kon, *ibid.*, 1911, **384**, 38.

[14] Hurd, *op. cit.*, ref. 9, p. 448.

B^2 scission, observed in the breakdown of (II), is here precluded by the absence of an α-hydrogen atom: on the other hand, A^1 scission is more important than in the pyrolysis of (II), though still only a minor route.

There is at first sight a possibility that acetone and carbon monoxide can be accounted for (without having to postulate the major concerted double C^1 ring-scission) by formation of α-methacryloyl-α-methylpropionic acid (VIII) by primary A^1 scission, followed by feasible secondary reactions, thus:

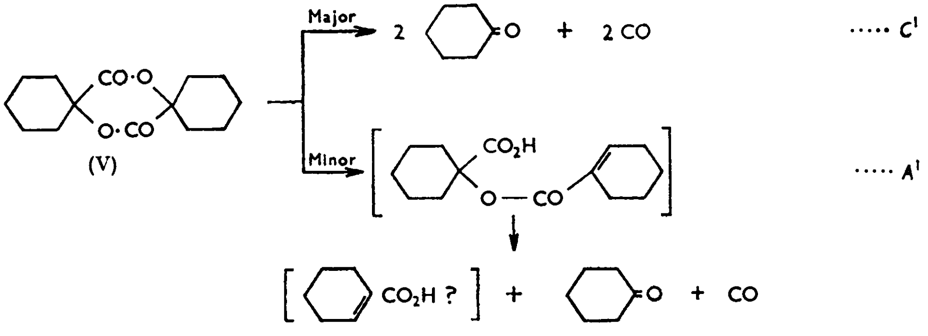
$$\underset{\text{(VIII)}}{[\mathrm{CH_2{:}CMe{\cdot}CO_2{\cdot}CMe_2{\cdot}CO_2H}]} \xrightarrow[?]{C^1} \underset{\text{(IX)}}{[\mathrm{CH_2{:}CMe{\cdot}CO_2{\cdot}CHMe_2}]}$$

$$\xrightarrow[?]{B^2} \begin{array}{c}[\mathrm{CH_2{:}CMe{\cdot}CHO}] + \mathrm{COMe_2} \\ \downarrow \\ \mathrm{CO} + \mathrm{CH_2{:}CHMe}\end{array}$$

Methacraldehyde is known [15] to break down (*ca.* 79%) to carbon monoxide and propene on pyrolysis under the same conditions, in equimolar amounts: but here the carbon monoxide preponderates greatly. Also, although a control run showed that isopropyl methacrylate breaks down mainly by the predictable A^1 scission, and also forms a minor amount of acetone by B^2 scission, it yields no detectable methacraldehyde. Hence, the concerted double C^1 scission of (IV) is preferred as the origin of the bulk of the carbon monoxide and acetone.

Secondary decarboxylation of methacrylic acid, previously noted,[15] is regarded as the origin of propene and part of the carbon dioxide: but, as in the breakdown of (II), there is a large excess of carbon dioxide. Again, this product remains partly unaccounted for; two successive decarboxylations of the dilactone (IV), on the lines discussed for (II), must be excluded, since there was no sign of the appropriate accompanying olefin, tetramethylethylene.

Pyrolysis of the Spirodilactone (V).—This decomposes under the same conditions to the extent of *ca.* 44%, yielding cyclohexanone and carbon monoxide, together with some carbon dioxide, and a trace of unidentified carboxylic acid. Here, again, B^2 scission is precluded by the absence of an α-hydrogen atom: and the results are best represented by the following reaction scheme:



Here the concerted double C^1 ring-scission seems to predominate very markedly. There is, in fact, no conclusive evidence for competition by the A^1 reaction and its secondary consequences, as established in the breakdown of (II) and (IV): for neither cyclohex-1-enecarboxylic acid not its decarboxylation product cyclohexene could be detected, although a trace of an acidic product was noted. Once more, the origin of the observed carbon dioxide is obscure: two successive decarboxylations of the spirodilactone (V) are

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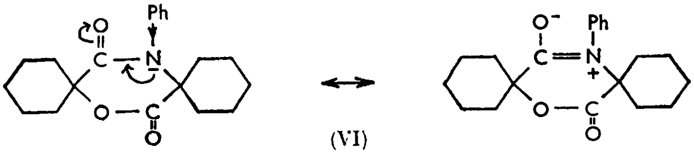
[15] Forman, Ph.D. Thesis, Glasgow University, 1958, pp. 47, 50.

excluded because of the absence of the predictable accompanying olefin, cyclohexylidenecyclohexane.

Pyrolysis of α-Acetoxypropionic Acid.—In the vapour phase at *ca.* 500°, this breaks down completely, yielding mainly acetic acid, acetaldehyde, and carbon monoxide (in agreement with Bagard's work[8] at lower temperatures), together with traces of acetic anhydride and water, presumably arising from the acetic acid.[16] However, no acrylic acid, the expected product of A^1 scission, could be detected. It had been thought likely that lactide (II) would be formed as an intermediate, by ester-interchange, thus providing an origin for the observed acetaldehyde and carbon monoxide: but no (II) could be detected in the pyrolysate from the α-acyloxy-acid. Hence, it seems that the reaction proceeds as follows, without intermediate formation of lactide (II) itself.

$$\mathrm{AcO{\cdot}CHMe{\cdot}CO_2H \longrightarrow AcOH + Me{\cdot}CHO + CO}$$

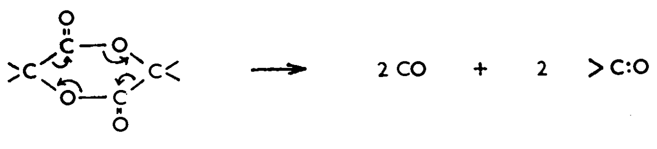
Like the lactides, the spiro-lactone-lactam (VI) also yields carbon monoxide[5] on pyrolysis (*ca.* 540°): yet, despite its formal resemblance to lactide (V), its decarbonylation must be due to some unknown reaction other than the foregoing type of concerted decarbonylation, since the two other main predictable products (cyclohexanone and its anil) are absent from the pyrolysate from (VI).[5] To account for the failure of the central ring in (VI) to undergo the same kind of electronic rearrangement as in (V), it is suggested that in the former the C–N bond of the CO·NPh group is strengthened jointly by the electron-repelling effect of the phenyl group and the electron-attracting effect of the carbonyl group. In this way, the resonating system illustrated may be set up, in which the concerted decarbonylation is strongly disfavoured if the second canonical form contributes markedly.


(VI)

Reaction Mechanisms.—*Major decarbonylation of lactides.* This reaction provides an almost unique example of C^1 scission in carboxylic esters. (In the few other recorded examples, such as pyruvic[12] and formic[17,18] esters, the reaction is dictated by some specific extraneous structural feature.) The breakdown is possibly partly free-radical in character, since in some cases it can be reduced, though not completely suppressed (contrast the intra-acyl scission of phenyl acrylate and methacrylate[17]), by addition of quinol (1%) as an inhibitor before pyrolysis under the standard gas-phase conditions at *ca.* 500°, as follows:

Lactide	(II)	(IV)	(V)
Destroyed (%) without quinol	50	69	44
Destroyed (%) with quinol	50	53	28

It is considered likely that the double decarbonylation occurs mainly by a concerted molecular mechanism, with rearrangement of electrons, thus:



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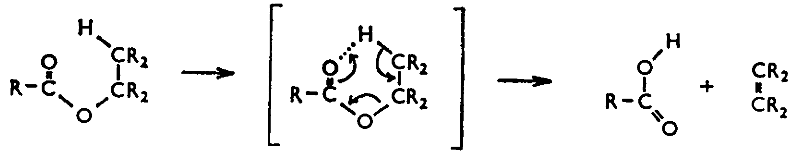
[16] Davidson and Newman, *J. Amer. Chem. Soc.*, 1952, **74**, 1515.
[17] Mackinnon and Ritchie, *J.*, 1957, 2564.
[18] Adickes, Brunnert, and Lücker, *J. prakt. Chem.*, 1931, **130**, 163.

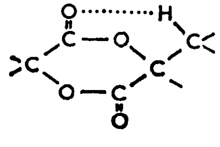
This requires no migration of atoms or groupings, and should be favoured energetically, according to the " principle of least motion." [19] It depends on the existence of a regular cyclic system such as the above, and would not occur for simple open-chain carboxylic esters (see also below).

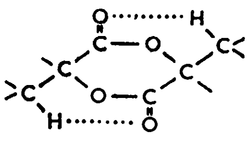
Minor alkyl–oxygen scission of lactides. The very minor occurrence of A^1 scission in the pyrolysis of all three lactides is probably due to their inability to fulfil readily the steric requirements of the mechanism first proposed by Hurd and Blunck [20] for alkyl-oxygen scission of esters, and now quite widely accepted as a concerted process involving a quasi-six-membered ring as the transition state: [21]



...... A^1

(X)





(XI)

In an open-chain alkyl ester, the necessary close proximity of a β-hydrogen atom and the carbonyl oxygen involves no strain: but, as structure (X) shows, great distortion of the rather rigid lactide ring would have to occur to permit a single A^1 scission, and still further distortion, as in (XI), for double scission. In the spirodilactone (V), all four bonds of each spiro-carbon atom are rigidly held in space, offering a maximum energy barrier to the approach of β-hydrogen atoms to carbonyl oxygen: and here, as already noted, A^1 scission is extremely minor, if indeed it occurs at all.

The idea of steric resistance to A^1 scission of esters applies in the independent work of Bird [22] on the pyrolysis of monolactones. Thus, γ-butyrolactone and γ-valerolactone do not undergo A^1 scission at *ca.* 590°, whereas this breakdown occurs smoothly, with formation of the isomeric terminally unsaturated acid, when the ring is larger, as in 6-hexanolactone (52% at *ca.* 580°). Bird's work suggests that a lactone ring must be at least seven- or eight-membered if there is to be sufficient flexibility to permit A^1 scission.

Recent work by Huisgen and Ott [23] seems to support these ideas. In a series of ω-lactones, the physical constants fall into two groups corresponding to *cis*- and *trans*-configurations about the single C–O bond of the ester group. Four- to seven-membered rings are forced into the energetically less favoured *cis*-configuration: eight- and nine-membered rings are intermediate in character: ten- to sixteen-membered rings readily adopt the more favoured planar *trans*-configuration inherent in open-chain esters.

Stuart models show that for eight-membered lactone rings the Hurd and Blunck cyclic system is most readily achieved when the lactone adopts the *trans*-configuration, which accords with the above ideas.

When these observations are related to the present work, it is clear that lactides are double *cis*-esters, which explains their reluctance to undergo double A^1 scission. Bird did not observe any decarbonylation (C^1) to accompany the A^1 scission of large lactone rings, nor has it been reported for simple open-chain alkyl esters: and this is consistent with the concerted double C^1 mechanism suggested above for lactides (dilactones), which

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[19] Peytral, *Bull. Soc. chim. France*, 1920, **27**, 34.

[20] Hurd and Blunck, *J. Amer. Chem. Soc.*, 1938, **60**, 2419.

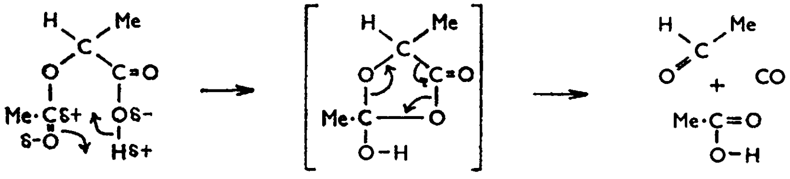
[21] Cram, " Steric Effects in Organic Chemistry " (ed. Newman), Wiley, New York, 1956, Chap. 6.

[22] Bird, Ph.D. Thesis, Maryland University, 1957.

[23] Huisgen and Ott, *Tetrahedron*, 1959, **6**, 253.

alone possess the regular ring-system necessary for the electron shifts. The free energy of the *cis*-ester configuration exceeds that of the *trans* by *ca.* 3·6 kcal./mole:[23] hence, the energy of activation for decarbonylation of a lactide molecule should be compensated by *ca.* 7·2 kcal./mole, and the reaction thus facilitated.

Breakdown of α-acyloxy-acids. Here, on the other hand, there is no apparent obstacle to formation of the Hurd and Blunck ring, and an alternative reason must be sought for the complete failure to undergo A^1 scission. Maccoll[24] has shown that for simple esters the Hurd and Blunck mechanism is quasi-heterolytic, ease of occurrence depending on the inductive effect of any α-alkyl substituents. Since carbonyl and methoxycarbonyl groups have similar electron-attracting properties, it is unlikely that any very slight differences are responsible for the widely different thermal behaviour of, for example, α-acetoxypropionic acid[8] and its methyl ester.[2] An obvious special feature which might dictate the specific breakdown of the former, by facilitating some preferred configuration, is the high mobility of the carboxylic proton. It is now suggested that, for example, α-acetoxypropionic acid breaks down thermally by a concerted mechanism as illustrated, being activated by relatively strong electrostatic forces. At lower temperatures, this does not occur, since the α-acyloxy-acid distils almost unchanged at 127°/11 mm., but proton migration is probably facilitated by higher temperatures.



EXPERIMENTAL

General Methods.—Flow-reactors, both large[25] and semi-micro,[5] were used as described previously. All pyrolyses were run at *ca.* 500°. Aldehydes and ketones in the pyrolysates were characterised as their 2,4-dinitrophenylhydrazones: these and all other solid derivatives or pyrolysate components were identified by mixed m. p., except the bis-2,4-dinitrophenylhydrazone of methylglyoxal, where paper chromatography was preferred. Free acids (liquid) were identified by gas–liquid chromatography, and gaseous products by infrared spectrometry.

Preparation of Pyrolysands.—*Lactide* (II). Slow distillation[26] of lactic acid at 120—140° under reduced pressure gave the lactide (II) as colourless plates (34%) (from ethanol), m. p. 124° (lit.,[26] m. p. 124·5°).

Lactide (IV). Slow distillation[6] of α-hydroxy-α-methylpropionic acid at 190—220° gave this lactide as colourless prisms (12%) (from light petroleum), m. p. 79° (lit.,[6] yield 30%, m. p. 79°).

Lactide (V). Cyclohexanone cyanohydrin was hydrolysed[27] to 1-hydroxycyclohexanecarboxylic acid, and the latter converted in poor yield into the lactide (V), by heating batches of 20 g. at 150° for 5 hr. (the yield was approximately halved when larger batches were used). A mixture of water and cyclohexanone distilled (*ca.* 2·5%): further distillation then yielded a mixture (b. p. 125—160°/6 mm.) of undecomposed acid, cyclohex-1-enecarboxylic acid, and lactide (V). The acids were removed by potassium hydrogen carbonate; the residue gave *bis-1-hydroxycyclohexanecarboxylic acid dilactone* (V) as colourless needles (9·5%) (from ethanol), m. p. 176° [Found: C, 67·0; H, 8·2; *M* (cryoscopic in benzene), 254. $C_{14}H_{20}O_4$ requires C, 66·7; H, 7·9%; *M*, 252]. It had the following principal infrared absorption bands: *ca.* 2867s, 1728s, 1454s, 1375m, 1266s, 1247s, 1159m, 1084s, 984s, 930m, 917w, 881m, 847w, and 727w cm.$^{-1}$. Attempts to show whether it had the true lactide structure or the isomeric ether-anhydride structure (cf. the corresponding derivatives of 1-hydroxycyclobutanecarboxylic

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[24] Maccoll, *J.*, 1958, 3398.
[25] Allan, Forman, and Ritchie, *J.*, 1955, 2717.
[26] Carothers, Dorough, and Van Natta, *J. Amer. Chem. Soc.*, 1932, **54**, 761.
[27] Boeseken and Lutgerhorst, *Rec. Trav. chim.*, 1932, **51**, 159.

acid [28]) by stepwise two-stage hydrolysis, or by reduction with lithium aluminium hydride, were unsuccessful: but its pyrolysis (runs 6 and 7) is analogous to that of lactides (II) and (IV), where the constitution is not in doubt, and it is therefore believed to have the lactide structure.

Methylglyoxal. Oxidation of acetone by selenium dioxide [29] yielded this keto-aldehyde as a mobile yellow liquid, distilling at room temperature under a high vacuum (vapour condensed in liquid nitrogen).

Isopropyl methacrylate. Commercial ester (from Polymer Consultants Ltd.) was purified by distillation (b. p. 105°/760 mm., 25—26°/14 mm.).

α-Acetoxypropionic acid. Lactic acid was treated with a mixture of acetic acid and acetic anhydride containing 4% of hydrogen chloride: [30] fractionation yielded the α-acetoxy-acid (65%) as a colourless liquid, b. p. 126—130°/11 mm. (lit.,[30] b. p. 127°/11 mm.). Cooling in carbon dioxide–acetone did not induce crystallisation, although in two earlier papers [31,32] the compound is described as a solid (m. p. 57—60° and 39—40°).

Results of Pyrolysis.—The general conditions for 15 runs are summarised in Tables 1 and 2.

TABLE 1.

Pyrolysis of lactides (II, IV, V) at 500°.

Pyrolysand	(II)			(IV)		(V)	
Run no.	1	2	3	4	5	6	7
Feed-rate (g./min.)	0·32	0·29	0·34	0·41	0·39	0·23	*
Residence time (sec.)	134	148	142	125	131	328	*
Wt. pyrolysed (g.)	35	35	27·5 †	35	30	28	0·374
(*a*) Pyrolysate in main receiver (g.)	21·0	16·0	16·0	25·1	21·4	23·5	0·2
(*b*) Pyrolysate in cold trap (g.)	Nil	Nil	Nil	Nil	Nil	Nil	Nil
(*c*) Gaseous pyrolysate (l.)	7·8	10·9	4·9	3·6	3·8	1·8	0·055
Composition (%) of (*c*) (approx.):							
CO	89	92	80	91	86	90	98
CO_2	9	7	18	7	11	10	2
Unsat. hydrocarbons	2	1	2	2	3	Nil	Nil

* In semimicro-reactor: Runs 1—6 in normal flow-reactor.
† 25·0 g. of (II) + 2·5 g. of acrylic acid.

TABLE 2.

Pyrolysis of lactides (II, IV, V) in presence of quinol (1%), and of related model compounds, at 500°.

Pyrolysand	(IV) + quinol	(IV) + quinol	(V) + quinol	Methyl-glyoxal	Isopropyl methacrylate		α-Acetoxy-propionic acid	
Run no.	8	9	10	11	12	13	14	15
Feed-rate (g./min.)	0·29	0·44	0·17	*	0·38	0·45	0·39	0·35
Residence time (sec.)	148	117	447	*	100	85	101	112
Wt. pyrolysed (g.)	35	35	17	0·411	35	30	35	35
(*a*) Pyrolysate in main receiver (g.)	17·5	27·0	14·7	0·2	28·1	23·5	18·1	19·0
(*b*) Pyrolysate in cold trap (g.)	Nil	Nil	Nil	0·1	2·0	1·5	Nil	Nil
(*c*) Gaseous pyrolysate (l.)	8·8	2·6	0·4	0·088	1·4	1·2	8·5	8·7
Composition (%) of (*c*) (approx.):								
CO	86	86	89	70	34	52	98	98
CO_2	9	11	11	30 †	17	18	2	2
Unsat. hydrocarbons	5	3	Nil	Nil	49	30	Nil	Nil

* In semimicro-reactor: runs 8—10, 12—15 in normal flow-reactor.
† Figure probably also includes some acetaldehyde vapour.

Detailed results are given below: where two runs are quoted for a single pyrolysand, the details refer to the first of these, those for the second being closely parallel and concordant.

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[28] Demjanow and Dajarenko, *Ber.*, 1922, **55**, 2737.

[29] Riley, Morley, and Friend, *J.*, 1932, 1875; Moulds and Riley, *J.*, 1938, 621.

[30] Filachione and Fisher, U.S.P. 2,399,595/1946.

[31] Anschütz and Bertram, *Ber.*, 1904, **37**, 3972.

[32] Auger, *Compt. rend.*, 1905, **140**, 938.

Pyrolysis of Lactide (II).—*Runs* 1 *and* 2. Liquid (*a*), distilled, yielded (i) 0·05 g., b. p 45—60°/15 mm., (ii) 0·7 g., b. p. 60—80°/15 mm., (iii) 11·5 g., b. p. 70—150°/8 mm., and (iv) 6·0 g. of tarry residue. Fractions (i—iii) solidified, and were largely unchanged lactide (II): none contained any detectable carboxylic acid, although (*a*) itself had effervesced slightly on treatment with sodium hydrogen carbonate (for reason, see run 3). A trap containing 2,4-dinitrophenylhydrazine, placed between the main receiver and the cold trap, gave the appropriate derivative of acetaldehyde: the nitrobenzene-soluble portion of the total crude precipitate from the trap contained methylglyoxal bis-2,4-dinitrophenylhydrazone. Gas (*c*) contained ethylene but no but-2-ene. Products sought in the pyrolysate, with negative results, were pyruvic acid, acraldehyde, α-vinylpropionic acid, and α-acetoxypropionaldehyde.

Run 3. Acrylic acid (10%) was added to the pyrolysand before the run. Liquid (*a*), distilled, yielded (i) 0·5 g., b. p. 40—60°/15 mm. (mainly acrylic acid), (ii) 1·5 g., b. p. 60—80°/15 mm. (mainly acrylic acid and unchanged lactide), (iii) 6·9 g., b. p. 70—150°/8 mm. (mainly unchanged lactide), and (iv) 6·0 g. of tarry residue. Acetaldehyde was detected as in run 1. It appears from these results that the absence of acrylic acid from the products of runs 1 and 2 is due, not to its secondary breakdown, but probably to polymerisation during distillation of liquid (*a*).

Pyrolysis of Lactide (IV).—*Runs* 4 *and* 5. The semi-solid product (*a*), filtered off, yielded 3·5 g. of unchanged lactide (IV): the filtrate, distilled, yielded (i) 3·2 g., b. p. 56—60° (mainly acetone), (ii) 4·2 g., b. p. 60—80° (acetone and some methacrylic acid), (iii) 5·4 g., b. p. 60—82°/25 mm. (mainly methacrylic acid), and (iv) 7·5 g. of tarry residue which deposited crystals of unchanged lactide (IV) on cooling. Acetone was detected as in run 1, with no evidence for methacraldehyde. Gas (*c*) contained propene. There was no evidence of tetramethylethylene in (ii), or of isopropyl methacrylate in (iii).

Pyrolysis of Lactide (V).—*Runs* 6 *and* 7. The semi-solid product (*a*), filtered off, yielded 15·7 g. of solid, which effervesced faintly on treatment with sodium hydrogen carbonate, but was mainly unchanged lactide (V). Distillation of the filtrate gave a fraction (b. p. 140—168°) containing mainly cyclohexanone, with no evidence for cyclohexene or cyclohexylidenecyclohexane (gas–liquid chromatography). There was a small tarry residue (0·2 g.). Run 7 (semi-micro-reactor [5]) was made to check the composition of gas (*c*).

Pyrolysis of Lactide (II) *containing Quinol* (1%).—*Run* 8. Product (*a*), distilled, yielded (i) 0·3 g., b. p. 40—60°/15 mm. (containing acrylic acid), (ii) 0·6 g., b. p. 60—80°/15 mm. (acrylic acid and unchanged lactide), (iii) 10·2 g., b. p. 60—170°/8 mm. (mainly unchanged lactide), and (iv) *ca.* 5 g. of tarry residue. Acetaldehyde and methylglyoxal were detected as in Run 1.

Pyrolysis of Lactide (IV) *containing Quinol* (1%).—*Run* 9. The semi-solid product (*a*), filtered off, yielded 5·6 g. of unchanged lactide: the filtrate, distilled, yielded (i) 3·8 g., 56—69° (mainly acetone), (ii) 4·8 g., b. p. 70—100°/14 mm. (containing methacrylic acid), and (iii) *ca.* 11 g. of tarry residue which deposited crystals of unchanged lactide on cooling.

Pyrolysis of Lactide (V) *containing Quinol* (1%).—*Run* 10. The semi-solid product (*a*), filtered off, yielded 12·2 g. of solid, which effervesced faintly on treatment with sodium hydrogen carbonate, but was mainly unchanged lactide (V). Distillation of the filtrate gave a fraction (b. p. 135—165°) containing mainly cyclohexanone, with no evidence for cyclohexene (gas–liquid chromatography). There was a small tarry residue (*ca.* 0·2 g.).

Pyrolysis of Methylglyoxal.—*Run* 11. Liquid (*a*) was mainly unchanged pyrolysand, and liquid (*b*) a mixture of acetaldehyde and methylglyoxal. Gas (*c*) was mainly carbon monoxide: the apparent content of carbon dioxide was artificially enhanced by acetaldehyde vapour swept through the solid carbon dioxide–acetone trap by the rapid gas-flow.

Pyrolysis of Isopropyl Methacrylate.—*Runs* 12 *and* 13. Liquid (*a*) gave a positive reaction to the Davidson–Newman colour test [16] for acid anhydride, and to the anhydrous copper sulphate test for water. It contained nothing boiling below 90°: further fractionation yielded (i) 18 g., b. p. 25—40°/14 mm. (mainly unchanged ester), (ii) 3·4 g., b. p. 40—57°/14 mm. (unchanged ester and methacrylic acid), (iii) 3·1 g., b. p. 60—83°/14 mm. (mainly methacrylic acid), and (iv) *ca.* 1 g. of tarry residue. Acetone was detected as in run 1, with no evidence for other carbonyl compounds. Liquid (*b*), raised to room temperature, gave 0·24 l. of propene (infrared).

Pyrolysis of α-Acetoxypropionic Acid.—*Runs* 14 *and* 15. Liquid (*a*), when distilled, yielded (i) 5·0 g., b. p. 16—100° (mainly acetaldehyde and acetic acid), (ii) 8·3 g., b. p. 100—130°, (iii) 2·1 g., b. p. 90—100°/15 mm. (both mainly acetic acid and acetic anhydride), and (iv) a small tarry residue. Acetaldehyde was detected as in run 1, with no evidence for methylglyoxal. No acrylic acid was detected in any fraction.

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CHEMICAL TECHNOLOGY DEPARTMENT, ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW.

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