# A Radiochemical Study of the Pyrolytic Formation of Carbon Suboxide in the Diethyl Oxaloacetate-Acetic Anhydride System : Isotopic Exchange **Between the Products**

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Diethyl [1,2-14C]-, [3-14C]-, [4-14C]-, [1,4-14C]-, [2,3-14C]-, [1',1''-14C]-, and [2',2''-14C]-oxaloacetate (1 mol.) have been pyrolysed in acetic anhydride (4 mol.) at 700°, and the position and extent of labelling in the resulting carbon suboxide traced. A radiochemical balance between the labelled esters and the carbon suboxide is not achieved; the deficiencies amount to 32-34% for the carbonyl carbons and 30% for the central carbon. Deficiencies are still more pronounced when a longer furnace is used. Pyrolysis of unlabelled diethyl oxaloacetate (1 mol.) in the presence of  $[1^{-14}C]$  acetic anhydride (4 mol.) causes transference of label (27%) to each carbonyl group of carbon suboxide but not to the central carbon; [2-14C] acetic anhydride causes no transference of label to the carbonyl groups but 29% to the central carbon of carbon suboxide. This accounts for the deficiencies. [1-14C]Propionic anhydride, when similarly pyrolysed with diethyl oxaloacetate, labels (13%) of the carbonyl groups of carbon suboxide but not the central carbon; with  $[2^{-14}C]$  propionic anhydride there is negligible labelling of all the carbon suboxide carbons. Carbon suboxide itself exchanges radioactivity with [1-14C] acetic anhydride at 700° and [1-14C]keten is implicated. A mechanism based on the reversible formation of two types of mixed dimer' is proposed.

These results indicate that earlier experimental work, which seemingly supported a cyclic heteryne intermediate in this system, was misinterpreted through failure to recognise the exchange reaction: C-1 is lost entirely during the formation of carbon suboxide from diethyl oxaloacetate. The mass spectrum of diethyl oxaloacetate is discussed.

THE pyrolysis (850-880°) of diethyl oxaloacetate (I) in the presence of an excess (ca. 14 mol.) of acetic anhydride has been recommended by Dashkevitch<sup>1,2</sup> as being superior to other hot-tube methods for preparing carbon suboxide (III). A cyclic heteryne (II), rejected in our previous Paper,<sup>3</sup> was proposed as an intermediate in the reaction, which is said to proceed as shown in Scheme 1. The evidence presented in support of (II) was that pyrolysis of 4-14C-labelled diethyl oxaloacetate resulted in the formation of carbon suboxide containing 0.55 parts of the unit molecular activity of the starting material. As this is close to one half it was considered that the hetervne (II), in which C-1 and C-4 become equivalent, was formed, and that one half of the radioactivity was lost on decarbonylation. In addition, the fact that pyrolysis of acetylene dicarboxylic ester in acetic anhydride gave 16% of carbon suboxide was used to support the idea. In view of the conclusions arrived at

<sup>1</sup> L. Dashkevitch, V. A. Buevitch, and B. E. Kubaev, J. Gen. Chem. (U.S.S.R.), 1960, 30, 1925. <sup>2</sup> L. Dashkevitch, Proc. Acad. Sci. (U.S.S.R.), 1960, 707.

in our previous Paper we have examined the pyrolysis of diethyl oxaloacetate-acetic anhydride, and formed a different opinion.



For this purpose diethyl  $[1,2-^{14}C]$ -,  $[3-^{14}C]$ -, and [4-14C]-oxaloacetate, as prepared before,<sup>3</sup> were used. In addition, diethyl [1,4-<sup>14</sup>C]- and [2,3-<sup>14</sup>C]-oxaloacetate

<sup>3</sup> L. Crombie, P. A. Gilbert, and R. P. Houghton, preceding Paper.

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were made by converting labelled tartaric acid into diacetyltartaric anhydride, and proceeding to diethyl oxaloacetate by way of the pyridinium salt of oxaloacetic anhydride.<sup>4</sup> The [2,3-14C]tartaric acid was prepared by hydroxylation of [2,3-14C]fumaric acid. Ester labelled diethyl oxaloacetate was made from [1-14C]- and from [2-14C]-ethanol. The general procedure in the investigation followed the lines of the previous Paper, and results from pyrolysis carried out in a 30 cm. furnace with an ester to anhydride molar ratio of 1 to 4 are shown in Table 1. In contrast to the results obtained with

# TABLE 1

Distribution of <sup>14</sup>C label in diethyl oxaloacetate and carbon suboxide formed by pyrolysis in the presence of unlabelled acetic anhydride

	$\begin{array}{c} 2 & 1 & 1' & 2' \\ O = C - C O \cdot O \cdot C H_2 \cdot C H_3 \\ \downarrow \\ H_2 C - C O \cdot O \cdot C H_3 \cdot C H_3 \end{array}$						-	0=c=c=c=o		
		3	4	1"	· <sup>-</sup> 2''					
1	<b>2</b>	3	4	1′	1‴	2'	$2^{\prime\prime}$	×	Ţ	×
1	1	-		-			_	0.32	0.00	0.32
		1						0.00	0.70	0.00
_	_	_	1		_			0.34	0.00	0.34
1			1				_	0.36	0.00	0.36
				1	1	-		0.00	0.00	0.00
	—					1	1	0.00	0.00	0.00
								$\Sigma 0.66$	0.70	0.66
								0.68		0.68

diacetyltartaric anhydride and acetoxymaleic anhydride where results were very sharp, an apparently diffuse picture is presented. In particular, only 66-68% of the radioactivity of the terminal carbon atoms, and 70% of that in the central carbon atom, can be accounted for. With all the carbon atoms in the precursor traced, this cannot be due to a dilution effect, for it was checked by independent experimentation that pyrolysis of acetic anhydride under the reaction conditions gives no trace of carbon suboxide.

Clearly, radioactivity is being withdrawn from the system studied, and acetic anhydride appears to be implicated. Suspicions that an exchange reaction was taking place were raised by the observation that when a longer pyrolysis furnace (60 cm.) was used, *i.e.*, longer contact time, the radioactivity deficiency increased still more (Table 2). Unlabelled diethyl oxaloacetate was therefore pyrolysed in the presence of [1,1'-14C]- and  $[2,2'-{}^{14}C]$ -acetic anhydride. The results are summarised in Table 3. Carbonyl labelling (one unit in each carbonyl group) of acetic anhydride causes 0.27 parts of each unit to be transferred to each carbonyl group of carbon suboxide; none is incorporated into the central carbon of the latter. On the other hand the use of methyllabelled acetic anhydride results in no transference of radioactive label to the carbonyls of carbon suboxide, but 0.29 parts of a unit are transferred to the central carbon atom. Addition of the summations from Tables 1 and 3 now accounts for 93-95% of the radioactivity for the flanking carbonyls and 99% of the radioactivity for the

central carbon atom of carbon suboxide. Taking into account the fact that special measures to effect complete standardisation were not taken in the five significant runs involved, this seems fully acceptable. Whereas in the

TABLE 2

Distribution of <sup>14</sup>C label in diethyl oxaloacetate and carbon suboxide formed by pyrolysis in the presence of unlabelled acetic anhydride (60 cm. furnace)



pyrolysis of pure diacetyltartaric anhydride or acetoxymaleic anhydride we were concerned with breakdown of a single species,<sup>3</sup> we now have a more complicated situation which involves bimolecular exchange.

Acetic anhydride is readily reversibly cracked to acetic acid and keten when passed through a hot tube,<sup>5</sup> and exchange between carbon suboxide and keten seems an attractive possibility. In a separate experiment we have shown that pyrolysis of unlabelled carbon suboxide in a solution of  $[1,1'-{}^{14}C]$  acetic anhydride results in carbon suboxide in which the terminal carbonyl groups are now <sup>14</sup>C labelled, though the central carbon atom remains unlabelled. [1,1'-14C]Propionic anhydride, like [1,1'-14C]acetic anhydride, causes radiochemical labelling of the carbonyl groups (but not the central carbon) of carbon suboxide when pyrolysed with unlabelled diethyl oxalo-acetate (Table 3). [2,2'-14C]Propionic anhydride used in a similar experiment, unlike [2,2'-14C]acetic anhydride, brought about labelling of neither the central nor terminal carbon atoms of carbon suboxide. At least on a qualitative basis, the reversible formation of crossed dimers' between ketens and carbon suboxide would provide an understanding of the exchanges.

Two types of reaction involving crossed ' dimer ' can be considered. In the first type, the cyclobutanedione (IV) can decompose in one of two ways; the first regenerates the original components and the second gives an exchange of carbonyl groups. In the second type the 'dimer' (V), familiar as keten dimer itself, could form and then decompose as suggested, with incorporation of both the 1,1'- and 2,2'-labels of acetic anhydride into carbon suboxide. Roughly equally matched pathways by way of dimers (IV; R = H) and (V; R = H) would account for the results obtained with labelled acetic anhydride. The carbonyl exchange with  $[1,1'-{}^{14}C]$ methylketen from [1,1'-14C]propionic anhydride is acommodated by formation and decomposition of the 'dimer'

<sup>4</sup> J. C. Roberts, *J. Chem. Soc.*, 1952, 3315. <sup>5</sup> G. T. Fisher, A. F. MacLean, and A. W. Schrizer, *J. Org.* Chem., 1953, 18, 1055.

(IV; R = Me), but a process involving breakdown of (V; R = Me) by way of (VI; R = Me) would involve an alkyl shift and, as found experimentally, this does not occur. Other more complex pathways for radiochemical exchange have been considered, and are not excluded,

#### TABLE 3

Distribution of <sup>14</sup>C label in diethyl oxaloacetate and carbon suboxide formed by pyrolysis in the presence of  $[1,1'-^{14}C]$ - and  $[2,2'-^{14}C]$ -acetic anhydride or propionic anhydride



but in the absence of more experimental evidence it is unnecessary to discuss them further here; our main purpose is to illustrate that suitable mechanisms are available to account for exchanges of the kind observed.



It is clear that Dashkevitch's radiochemical experiment, although we do not contest its correctness, is unacceptable evidence for the cyclic heteryne (II) and that his figure for carbon suboxide is low not because the 1- and 4-positions have become equivalent, but because of exchange in the acetic anhydride-containing system (cf. Table 2). Taking into account this factor, the data in Table 1 show that C-1 is lost completely, and C-4 forms one of the carbonyl groups of carbon suboxide (*i.e.*, two halves) and C-2 the other. The 3carbon of diethyl oxaloacetate forms the entire central carbon atom only of carbon suboxide.

The radiochemical labelling position is thus analogous to that for acetoxymaleic anhydride.<sup>3</sup> The mechanistic situation, however, is still more complex. Carbon suboxide can be produced from diethyl oxaloacetate, malonic ester formed by decarbonylation,<sup>6</sup> or acetoxymaleic or fumaric ester formed by enol acetylation. In all these cases a similar radiochemical labelling pattern is expected. Dashkevitch's observation that acetylenedicarboxylic acid and acetic anhydride give carbon suboxide on pyrolysis may involve formation of acetoxymaleic anhydride.



The mass spectrum of diethyl oxaloacetate  $(m/e \ 188)$ shows fragments due to loss of OEt (-45) formulated as (VII), and additional loss of CO (-28) (VIII). Loss of ethanol from the ion (VIII) can account for the characteristic m/e 69 ion (IX) which occurs together with the carbon suboxide ion m/e 68; the latter is much less intense. Loss of CO from the ion (VIII) gives (X), metastable m/e 65.8, and loss of vinyl radical (-27) could give an ion m/e 88. Mass measurement shows it to contain only a little  $C_3H_4O_3$  (XI): it is mainly (XIV)  $C_4H_8O_2$ . For comparison (see ref. 8), diethyl malonate  $(m/e \ 160)$  gives the ion  $m/e \ 115$  by loss of  $\cdot OEt \ (-45)$ which can give rise to (IX); again the carbon suboxide peak m/e 68 is small relative to the latter. Loss of vinyl radical (-27) accounts for (XIII) m/e 133, and the ion (VIII) may also result from loss of water from this. Further loss of CO gives (X).



The ion m/e 115 is strong and the ion (XIV) is present.

<sup>6</sup> K. Banholzer and H. Schmid, *Helv. Chim. Acta*, 1959, 42, 2584.

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There are metastable ions at 110.8 (160  $\longrightarrow$  133), 99.4 (133  $\longrightarrow$  115), and 55.6 (88  $\longrightarrow$  70).

## EXPERIMENTAL

General Pyrolysis Conditions.—Unless specified otherwise, the compound (1 mol.) in acetic anhydride (ca. 4 mol.) was introduced slowly through a sloping heat-resisting (M.J.V.) glass tube maintained at 700° by a controllable electric furnace (tube length 40 cm.; hot zone  $30 \times 1$  cm.). Workup, degradation, and counting procedures were as described previously.<sup>3</sup>

Under these conditions, acetic anhydride itself (400 ml.) gave no detectable amount of carbon suboxide (as malonic acid) when pyrolysed.

Pyrolysis of Diethyl  $[1,2^{-14}C]Oxaloacetate$  in Acetic Anhydride.—Diethyl  $[1,2^{-14}C]Oxaloacetate$  in Acetic Anhydride.—Diethyl  $[1,2^{-14}C]Oxaloacetate (28 g.)$  diluted with unlabelled ester (80 g.) was converted into diethyl  $[1,2^{-14}C]$ oxaloacetate (43 g.). The latter (35 g.; counts/100 sec. as barium carbonate 105.9, 108.1) was pyrolysed in acetic anhydride as above (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 90.4; AF 0.32), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/ 100 sec. 131.7 (AF 0.155). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 131.9; AF 0.155) and from the methyl group (counts/100 sec. 0.0).

In a similar experiment, with a 60 cm. furnace zone, diethyl  $[1,2^{-14}C]$ oxaloacetate (40 g.) (counts/100 sec. as barium carbonate 144·0, 144·6) was pyrolysed in acetic anhydride (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 113·7; AF 0·296), which was decarboxylated. The resultant carbon dioxide, as barium carbonate, had counts/100 sec. 179·5 (AF 0·155). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 172·4; AF 0·150) and from the methyl group (counts/100 sec. 1·6; AF 0·014).

Pyrolysis of Diethyl [ $3^{-14}$ C]Oxaloacetate in Acetic Anhydride. --Ethyl [ $2^{-14}$ C]acetate was used to prepare diethyl [ $3^{-14}$ C]oxaloacetate. The latter (37 g., counts/100 as barium carbonate 32.0, 31.8) was pyrolysed in acetic anhydride (delivery period 5 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 59.3; AF 0.701), which was decarboxylated. The resultant carbon dioxide, as barium carbonate, had counts/100 sec. 0.0. Degradation of the acetic acid gave barium carbonate from the carboxygroup (counts/100 sec. 0.6; AF 0.002) and from the methyl group (counts/100 sec. 178.7; AF 0.699).

In a similar experiment using a 60 cm. furnace, diethyl [3-14C]oxaloacetate (45 g., counts/100 sec. 81.5) was pyrolysed in acetic anhydride (delivery period 5 hr.). Corresponding data are: malonic acid, counts/100 sec. 110.4 (AF 0.509); carbon dioxide by decarboxylation, counts/100 sec. 0.0; carboxy-group of sodium acetate, counts/100 sec. 6 (AF 0.009); and methyl, counts/100 sec. 323.8 (AF 0.496).

Pyrolysis of Diethyl [4-14C]Oxaloacetate in Acetic Anhydride. —Ethyl [1-14C]acetate was used to prepare diethyl [1-14C]oxaloacetate. The latter (40 g.; counts/100 sec. 41.4, 38.9) was pyrolysed in acetic anhydride (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 73.2; AF 0.686), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/100 sec. 106.7 (AF 0.333). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 110.5; AF 0.343) and from the methyl group (counts/100 sec. 0.00).

In a similar experiment with a 60 cm. furnace diethyl  $[4^{-14}C]$ oxaloacetate (36 g.; counts/100 sec. 72.5) was pyrolysed in acetic acid (delivery period 6 hr.). Corresponding data are: malonic acid, counts/100 sec. 101.4 (AF 0.524); carbon dioxide by decarboxylation, counts/100 sec. 154.2 (AF 0.265); carboxy-group of sodium acetate, counts/100 sec. 151.8 (AF 0.262); and methyl, counts/100 sec. 13.6 (AF 0.02).

Pyrolysis of Diethyl  $[2,3-^{14}C]Oxaloacetate$  in Acetic Anhydride.— $[2,3-^{14}C]$ Fumaric acid  $(0\cdot1 \text{ mc})$  was added to unlabelled fumaric acid  $(1\cdot4 \text{ g.})$ , and the mixture was used to prepare  $[2,3-^{14}C]$ tartaric acid  $(1\cdot2 \text{ g.})$ , which was further diluted with unlabelled tartaric acid (50 g.) and used to make  $[2,3-^{14}C]$ diacetyl tartaric anhydride  $(57\cdot2 \text{ g.}).^3$  The anhydride (20 g.) was converted into the pyridinium salt of oxaloacetic anhydride and the latter was added to dry ethanol (50 ml.), saturated with hydrogen chloride, and kept overnight. Work-up as above gave diethyl  $[2,3-^{14}C]$ oxaloacetate, which was diluted to 50 g. with unlabelled ester.

Diethyl [2,3-14C]oxaloacetate (45 g.; counts/100 sec. as barium carbonate 21.5, 22.1) was pyrolysed (60 cm. furnace) in acetic anhydride (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 36.2; AF 0.622), which was decarboxylated. The resulting carbon dioxide (barium carbonate) had counts/100 sec. 28.2 (AF 0.162). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 29.2; AF 0.168) and from the methyl group (counts/100 sec. 51.7; AF 0.297).

Pyrolysis of Diethyl [1,4-14C]Oxaloacetate in Acetic Anhydride.-[1,4-14C]Tartaric acid (0.1 mc) was added to unlabelled tartaric acid (50 g.) and the mixture was used to prepare [1,4-14C]diacetyltartaric anhydride (58.8 g.). The anhydride (20 g.) was added to pyridine (40 ml.) and shaken until a pale green colour developed. After the addition of glacial acetic acid (12 ml.) the mixture was kept at 40° for 20 sec. and then cooled in ice. Ether (45 ml., at 0°) was added, and the brown solid was filtered off and washed with dry ethanol  $(3 \times 8 \text{ ml.})$  and dry ether  $(3 \times 8 \text{ ml.})$  to give the pyridinium salt of oxaloacetic anhydride (12.8 g.).4 This anhydride (12 g.) was added to dry ethanol (50 ml.), and the mixture was saturated with hydrogen chloride at  $0^{\circ}$ and set aside overnight. The ethanol was then evaporated, water (50 ml.) was added, and the mixture was extracted with ether (3 imes 50 ml.). The ethereal extracts were washed with sodium hydrogen carbonate solution and water, and then dried  $(MgSO_4)$ . Distillation gave diethyl oxaloacetate (6.5 g.) which was diluted to 50 g. with unlabelled ester.

Diethyl [1,4-14C]oxaloacetate (45 g.; counts/100 sec. as barium carbonate 44.2, 43.9) was pyrolysed in acetic anhydride (delivery period 5 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 42.4; AF 0.360), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/100 sec. 65.6 (AF 0.186). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 65.0; AF 0.184) and from the methyl group (counts/100 sec. 0.002).

Pyrolysis of Diethyl  $[1'-{}^{14}C]Oxaloacetate$  in Acetic Anhydride.— $[1-{}^{14}C]E$ thanol (0·1 mc) was diluted with unlabelled ethanol to 20 ml. and then saturated with dry hydrogen chloride. The pyridinium salt of oxaloacetic anhydride (see above) (13 g.) was added and, after work-up and purification the diethyl [1'-14C]oxaloacetate was diluted with unlabelled ester. A solution of diethyl [1'-14C]oxaloacetate (35 g.; counts/100 sec. as barium carbonate 40.2, 40.0) in acetic anhydride was pyrolysed (delivery period 5 hr.). The carbon suboxide was converted into malonic acid (counts/100 sec. 0.0).

Pyrolysis of Diethyl [2'-14C]Oxaloacetate in Acetic Anhydride.-[2-14C]Ethanol (0.1 mc) was converted into diethyl [2'-14C]oxaloacetate as before. The ester (45 g.; counts/100 sec. as barium carbonate 51.6, 51.3) in acetic anhydride was pyrolysed (delivery period 5 hr.). The carbon suboxide was converted into malonic acid (counts/ 100 sec. 0.8 as barium carbonate; AF 0.002).

Pyrolysis of Diethyl Oxaloacetate in [1-14C] Acetic Anhydride. -Sodium [1-14C]acetate (0.1 mc) was added to acetic anhydride, and the mixture was heated under reflux (3 hr.) and then distilled to give [1-14C] acetic anhydride. Diethyl oxaloacetate (45 g.) in [1-14C]acetic anhydride (counts/100 sec. as barium carbonate 131.2, 130.5) was pyrolysed (delivery period 7 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 47.5; AF 0.272), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/100 sec. 71.4 (AF 0.136). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 70.2; AF 0.134) and from the methyl group (counts/100 sec. 0.5; AF 0.001).

Pyrolysis of Diethyl Oxaloacetate in [2-14C] Acetic Anhydride. -Sodium [2-14C]acetate (0.1 mc) was added to acetic anhydride (150 ml.), and the mixture was heated under reflux (2 hr.) and then distilled to give [2-14C]acetic anhydride. Diethyl oxaloacetate (40 g.) in [2-14C]acetic anhydride (counts/100 sec. as barium carbonate 203.5, 199.7) was pyrolysed (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 40.1; AF 0.148), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/100 sec. 0.0. Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 0.0) and from the methyl group (counts/100 sec. 116.8; AF 0.144). Acetic anhydride cracks reversibly to acetic acid and keten so both labels are assumed to be available in the keten-carbon suboxide exchange.

Pyrolysis of Diethyl Oxaloacetate in [1-14C]Propionic Anhydride.—Sodium [1-14C]propionate (0.1 mc) was added to propionic anhydride (150 ml.) and heated under reflux (3 hr.); the [1-14C] propionic anhydride was then distilled off. Diethyl oxaloacetate (45 g.) in [1-14C]propionic anhydride (counts/100 sec. as barium carbonate 201.3, 202.8) was pyrolysed (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 54.6; AF 0.135), which was decarboxylated. The resulting carbon dioxide as barium carbonate had counts/100 sec. 78.7 (AF 0.065). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 80.8; AF 0.067) and from the methyl group (counts/100 sec. 0.0).

Pyrolysis of Diethyl Oxaloacetate in [2-14C]Propionic Anhydride.-Sodium [2-14C] propionate (0.1 mc) was converted into [2-14C]propionic anhydride (150 ml.) as above. Diethyl oxaloacetate (40 g.) in [1-14C]propionic anhydride (counts/100 sec. as barium carbonate 244.6, 248.7) was pyrolysed (delivery period 6 hr.). The carbon suboxide gave malonic acid (counts/100 sec. as barium carbonate 1.3; AF 0.001).

Pyrolysis of Carbon Suboxide in [1-14C] Acetic Anhydride.---Carbon suboxide (4.8 g.) in [1-14C]acetic anhydride (50 ml.; counts/100 sec. as barium carbonate 247.5, 251.1) was pyrolysed (delivery period 2.5 hr.). The carbon suboxide (18% recovery) was converted into malonic acid (counts/100 sec. as barium carbonate 18.4; AF 0.056) and decarboxylated. The resulting carbon dioxide had counts/100 sec. 28.6 (AF 0.029). Degradation of the acetic acid gave barium carbonate from the carboxy-group (counts/100 sec. 27.6; AF 0.028) and from the methyl group (counts/100 sec. 0.0)

Pyrolysis of Diethyl Acetonedicarboxylate and Diethyl Diacetoxyfumarate in Acetic Anhydride.-Diethyl acetonedicarboxylate (20 g.) in acetic anhydride (50 ml.) was pyrolysed (delivery time 5 hr.) to give carbon suboxide (14%; as malonic acid). Similar pyrolysis of the acid caused rapid blockage of the tube though some carbon suboxide was formed. Diethyl diacetoxyfumarate (14 g.)7 in acetic anhydride (15 ml.) gave carbon suboxide (14%; as malonic acid).

Pyrolysis of Diacetyltartaric Anhydride in Acetic Acid.-The warm solution was introduced to the furnace at an even rate by means of a pressure-equalised dropping funnel. Carbon suboxide was determined gravimetrically as malonic acid.

Weight of anhydride (g.)	30	50	50
Vol. of acetic anhydride (ml.)	75	150	100
Pyrolysis time (hr.)	21/2	6	6
Yield $C_3O_2$ (%)	$3\bar{7}$	17	14

This suggests that lengthened residence time diminishes vields of carbon suboxide (see also the losses in the pyrolysis of carbon suboxide with [1-14C]acetic anhydride above).

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 <sup>7</sup> J. U. Nef, Annalen, 1893, 276, 200.
<sup>8</sup> J. H. Bowie, D. H. Williams, S. O. Lawesson, and G. Schroll, J. Org. Chem., 1966, 31, 1792.