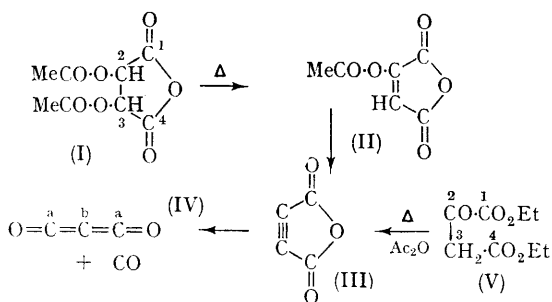


## Isotope Distribution in the Formation of Carbon Suboxide by Pyrolysis at 700°

By L. CROMBIE,\* P. A. GILBERT, and R. P. HOUGHTON

[Department of Chemistry, University College (University of Wales), Cathays Park, Cardiff]

CARBON suboxide (IV) is frequently prepared by pyrolysis of diacetyltartaric anhydride (I). The suggested<sup>1-3</sup> reaction mechanism proceeds *via* acetoxymaleic anhydride (II): a second pyrolytic elimination of acetic acid then gives the cyclic heteryne (III) which collapses to carbon suboxide with elimination of carbon monoxide. Such a heteryne invites preparative attention by the methods of aryne chemistry, and the possibility of its intervention has therefore been examined.



Yields of carbon suboxide are modest (usually < 35%)<sup>4</sup> and there is opportunity for side-reactions and for thermal decomposition of the carbon suboxide;<sup>5,6</sup> carbon is deposited in the pyrolysis tube and the reaction may be classed as "dirty". For this reason the pyrolysis (700°) was investigated by an isotopic approach to isolate the reaction or reactions of diacetyltartaric anhydride and acetoxymaleic anhydride which lead to carbon suboxide; the position and extent of labelling in the atoms of the pyrogenitor were related to those of the product being examined. The carbon suboxide formed was converted into malonic acid

and C-a isolated by decarboxylation. Schmidt degradation of the acetic acid then gave C-a' and C-b was obtained by permanganate oxidation of the methylamine formed; all three atoms were thus counted as barium carbonate. The pyrogenitor was similarly counted, after combustion. Results are summarized in Table 1: they are well defined with no evidence of "scrambling". It is apparent that C-1 and C-4 do not become equivalent as required by intervention of the intermediate (III).† C-1 is lost entirely: C-3 is the sole source of the central carbon atom of carbon suboxide C-b, and C-2 and C-4 provide the two carbonyl carbons.

Pyrolysis of diethyl oxaloacetate in the presence of an excess of acetic anhydride, reported to be a superior method for making carbon suboxide, is claimed to involve (III) as [4-<sup>14</sup>C]-unit labelled ester gives carbon suboxide containing 0.55 parts of label *i.e.*, C-1 and C-4 become equivalent before one is lost.<sup>3,7</sup> Our results (Table 2) show that an acceptable balance sheet for radioactivity is not attained, and this must mean that radioactivity is being withdrawn from the carbon suboxide producing system by acetic anhydride (the latter cracks to keten and acetic acid;<sup>8</sup> no carbon suboxide is formed). Table 3 confirms this, and a more reasonable balance sheet (C-a and C-a' 93—95%, C-b 99%) is attained on addition of the two sets of figures. Examination of Table 2 now shows that C-1 of diethyl oxaloacetate is lost, C-3 forms the central carbon atom of carbon suboxide, and C-2 and C-4 the two carbonyl carbons. Present evidence indicates that the exchange reaction involves crossed dimerisation between carbon suboxide and ketene. The cyclobutanedione type (VI) leads to carbonyl exchange, whilst the

† Diacetyltartaric anhydride with unit [<sup>18</sup>O] labelling of each ester-ether atom gives carbon suboxide containing 0.78 atom of [<sup>18</sup>O]: this too is not in agreement with intervention of (III).

TABLE 1

Distribution and extent of [ $^{14}\text{C}$ ]labelling in carbon suboxide formed by pyrolysis of [ $^{14}\text{C}$ ]labelled diacetyl tartaric anhydride and acetoxymaleic anhydride at  $700^\circ$

				Labelling in pyrogenerator				Labelling in carbon suboxide (IV)		
				C-1	C-2	C-3	C-4	C-a	C-b	C-a'
(I)	..	..	..	1	-	-	1	0.50	0.00	0.50
(I)	..	..	..	-	1	1	-	0.50	1.01	0.50
(II)	..	..	..	1	1	-	-	0.50	0.00	0.50
(II)	..	..	..	-	-	1	-	0.00	0.99	0.00
(III)	..	..	..	-	-	-	1	0.50	0.00	0.50

TABLE 2

Distribution and extent of [ $^{14}\text{C}$ ]labelling in carbon suboxide formed by pyrolysis of [ $^{14}\text{C}$ ]labelled diethyl oxaloacetate (1 mol.) in the presence of acetic anhydride (approx. 4 mol.)

	Labelling in pyrogenerator (V)‡				Labelling in carbon suboxide		
	C-1	C-2	C-3	C-4	C-a	C-b	C-a'
	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
					$\Sigma 0.66-0.68$	0.70	0.66-0.68

‡ Labelled ester groups contribute no radioactivity to  $\text{C}_3\text{O}_2$ .

TABLE 3

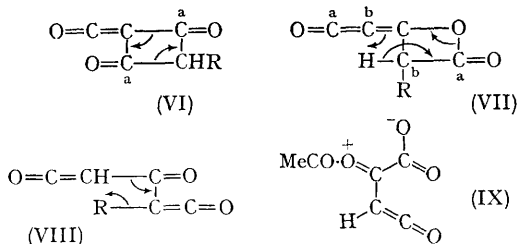
Distribution and extent of [ $^{14}\text{C}$ ]labelling in carbon suboxide formed by pyrolysis of unlabelled diethyl oxaloacetate (1 mol.) in the presence of [ $^{14}\text{C}$ ]labelled acetic anhydride (approx. 4 mol.)

	Labelling in acetic anhydride				Labelling in carbon suboxide		
	C-1	C-1'	C-2	C-2'	C-a	C-b	C-a'
	1	1	-	-	0.27	0.00	0.27
	-	-	1	1	0.00	0.29	0.00

$\beta$ -lactone type (VII) leads to C-a and C-b exchange (VIII): both mechanisms are available when keten is involved ( $\text{R} = \text{H}$ ), but only the former, leading to carbonyl exchange, when methylketen

( $\text{R} = \text{Me}$ ) from propionic anhydride is concerned; this agrees with the [ $^{14}\text{C}$ ]labelling results.

Since (III) is not involved, an attractive explanation for the specific loss of C-1 from acetoxymaleic anhydride is bond-breaking at the C-4-anhydride oxygen bond assisted by electron release from the acetoxy-group to form an ion-paired gas-phase intermediate (IX) for which various resonance contributors can be written. The ways in which the latter might break down, and the comparative mass-spectral data obtained, will be discussed in full elsewhere.



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