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THE REACTION OF DICARBOMETHOXYCARBENE WITH DIETHYL ETHER. THE MECHANISM OF THE FORMATION OF CLEAVAGE PRODUCTS.[1]

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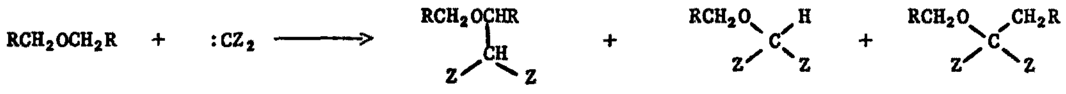
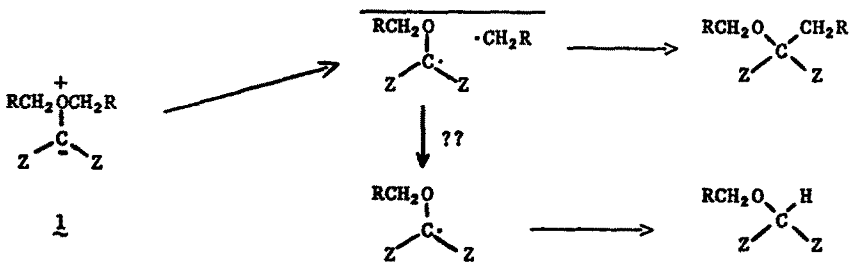
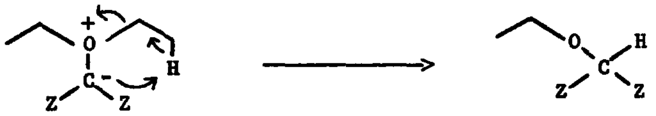
Carbenes react with ethers by three major pathways; carbon-hydrogen insertion, carbon-oxygen "insertion" and cleavage of one of the groups originally attached to the ether oxygen.[2] The carbon-hydrogen insertion reaction is commonplace in carbene chemistry and a combination of experiment and theory has contributed to our current appreciation of the complexities of this subtle process.[3] The other two reactions have received comparatively little attention and consequently our understanding of their mechanisms is considerably more primitive. Speculation centers upon the role of the ylide 1 as an intermediate central to the formation of both carbon-oxygen "insertion" and cleavage products. For instance, the



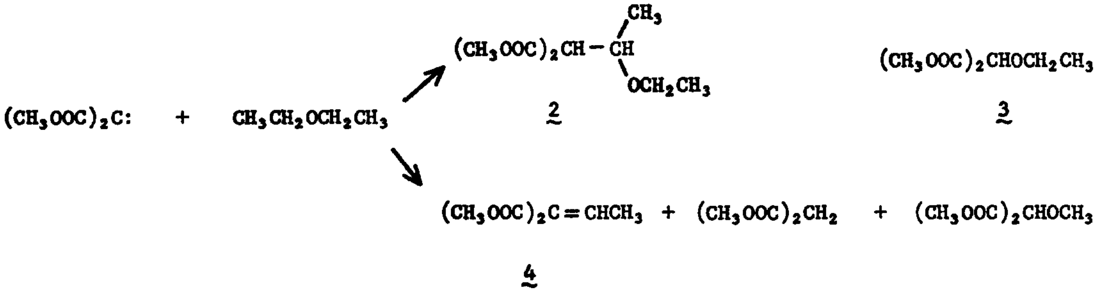


analogous sulfur ylide can be prepared and shown to rearrange, at 160°, to a cleavage product.[4] Very recently, Iwamura, Imahashi and Kushida[5] have shown through CIDNP studies of benzyl ethers that the rearrangement to the carbon-oxygen "insertion" product occurred via radical pairs and thus that this reaction was quite analogous to the Stevens and Wittig rearrangements.[6]

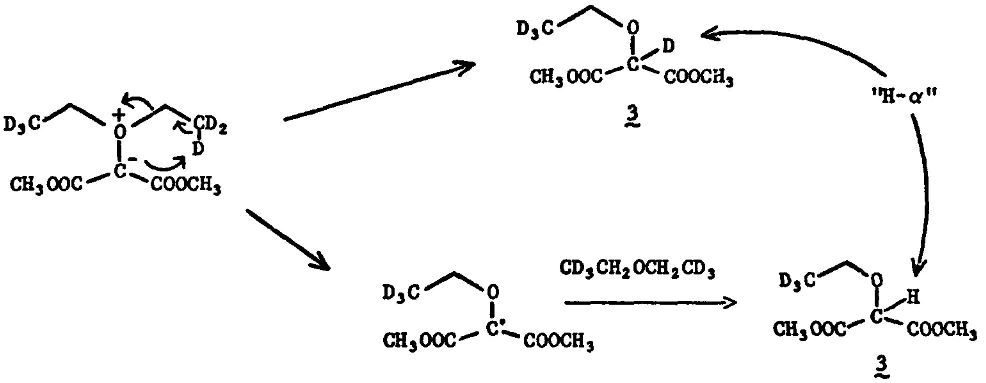
It is tempting to presume that the cleavage products result from escape of the radicals from the cage followed by hydrogen abstraction. However, Iwamura *et al.* presented indirect evidence against such a mechanism and an attractive alternative exists in which the ylide rearranges intramolecularly to product with loss of olefin. Although the intramolecular mechanism suffers the deficiency that methyl ethers are known to undergo efficient cleavage,[2] a test seemed in order.



We have examined the products of the reaction of dicarbomethoxycarbene with diethyl ether. We find the product of insertion into the α position of diethyl ether (**2**,40%), the cleavage product (**3**,40%), dimethyl malonate (7%) and methoxymalonic ester[7] (7%). Products of unknown structure account for the remaining 6% and on occasion ethylidene malonate (**4**) also appeared. Control experiments established that **4** was generated from **2** on gas chromatography.



The use of ether specifically deuterated in the β position allows a firm choice to be made between the intramolecular and intermolecular mechanisms for formation of 3. Direct rearrangement of an ylide inevitably places a deuterium in the position adjacent to the two esters (Hα). To the extent that this product is formed by abstraction of hydrogen by an escaped radical, hydrogen from the α position of the ether must appear in the Hα position in 3.



The required deuterated ether was made after the procedure of Vogel[8] and was at least 93% deuterated in the β position. Authentic deuterated 3 was made through the reaction of dicarbomethoxycarbene with CH_3CH_2OD. It soon became clear that deuterated 3 underwent partial exchange under all gas chromatographic conditions. Thus examination of pure 3 for deuterium content was not possible. However, the crude reaction mixture, never exposed to gas chromatography, could be examined. This procedure reduces the accuracy of the determination, but a conservative value for the amount of deuterium at Hα is ca.95%. The product 3 is formed overwhelmingly through the direct, intramolecular mechanism and not by the escape of a radical from the cage.

Problems remain - what is the mechanism of the cleavage of methyl ethers for instance? but the evidence is clear that the cleavage reaction in more substituted simple ethers is intramolecular in nature.

REFERENCES AND NOTES

1. This work was supported by the National Science Foundation Grant MPS74-05690 (MJ,Jr) and by a Grant in Aid of Research from Sigma Xi (DWB).

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7. This compound is probably formed through a Wolff rearrangement followed by capture of the resulting ketene.

8. A. I. Vogel, "Practical Organic Chemistry," 3rd ed., Wiley, New York, 1957, p 310.