

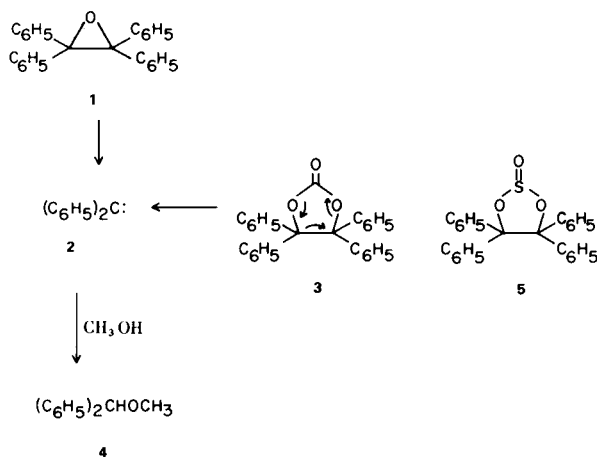
Photofragmentation of Cyclic Carbonates and Sulfites: A New Route to Diphenylmethylene (1)

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Sir:

Our previous studies on the photolysis of oxiranes, (3a) dioxoles (3b) and phosphoranes (3c) leaves no doubt that many aryl-substituted members of these heterocyclic systems photolyze to give arylcarbenes. For example tetraphenyloxirane (1) upon photolysis (4) gives benzophenone and diphenylmethylene (2) which may be intercepted conveniently with methanol and detected as benzhydryl methyl ether (4) (5,6).



We report here that benzpinacol carbonate (3) (7) (0.1 M) fragments upon irradiation (4) (14 hours) in methanol (5 ml.) to give benzophenone (10%) and diphenylcarbene detected as benzhydryl methyl ether (60%). Under these conditions no residual carbonate could be detected by thin layer chromatography. That carbon dioxide is a photoproduct of 2 was demonstrated by mass spectroscopy (8). It is noteworthy that no tetraphenyloxirane (1) could be detected among the photoproducts of 3. This result does not preclude the possibility that the epoxide is an intermediate in the conversion of 3 to 2. However, if such a two-step mechanism were operative under the conditions of low conversion one would

anticipate that effective shielding of 1 by 3 should occur and 1 would have been observed. Such a stepwise process appeared to be an attractive alternative in view of the reported thermal conversions of carbonates to epoxides (9). Our preliminary competitive rate studies on the photofragmentation of 1 and 3 employing an internal standard (hexadecane) indicate that 4 is formed at a faster rate from 3 than 1, thus excluding the intervention of 3 in its ground state as an intermediate. In the absence of further data and for the sake of convenience we write a concerted collapse of 3 to 2, carbon dioxide and benzophenone.

The benzpinacol sulfite (5) (10) also affords 4 in high yield upon irradiation (12 hours) in methanol (0.25 M). A more detailed description of our work on cyclic sulfites and carbonates including those of hydrobenzoin which fragment to phenylcarbene will be the subject of a future communication.

REFERENCES

- (1) We gratefully acknowledge financial support from the Army Research Office (Durham) and the National Institutes of Health.
- (2) Inquiries regarding this Communication should be addressed to: Dr. G. W. Griffin, Department of Chemistry, Louisiana State University in New Orleans, Lake Front, New Orleans, Louisiana 70122 (U.S.A.).
- (3a) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, **77**, 859 (1965); (b) R. M. G. Nair, E. Meyer and G. W. Griffin, *ibid.*, **80**, 442 (1968); (c) P. Petrellis and G. W. Griffin, *Chem. Commun.*, **18**, 1099 (1968).
- (4) The solutions were degassed by nitrogen sparging and irradiated in sealed quartz vessels at 40°. The radiation source was an air-cooled Rayonet RPR-100 Chamber Reactor (from The Southern New England Ultraviolet Co., Middletown, Conn., U.S.A.) containing sixteen 8-watt low-pressure mercury lamps, or the larger preparative RPR-208 model. The yields reported are based on reactions performed in the former unit.
- (5) ESR spectroscopy was used to demonstrate conclusively that the transient species obtained upon photofragmentation of

1 is identical to that obtained from diphenyldiazomethane, the conventional precursor for **2**. See A. M. Trozzolo, W. A. Yager, H. Kristinsson, I. Sarkar and G. W. Griffin, *J. Am. Chem. Soc.*, **90**, 3292 (1968).

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(8) The mass spectrometer (Hitachi Perkin-Elmer RMU-6E) was calibrated against air prior to analysis of the effluent gasses from the reaction mixture.

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(10) The sulfite (**5**) (m.p. 137-138°) was prepared using essentially the same technique applied by Price and Berti (11) for the preparation of a variety of other symmetrical sulfites.

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