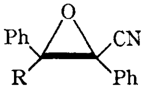
Photofragmentation of Oxirans. Precursors for Phenylcyanocarbene and Phenylmethoxycarbonylcarbene†

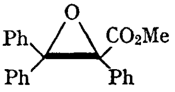
By P. C. PETRELLIS and G. W. GRIFFIN*

(*Chemistry Department, Louisiana State University in New Orleans, New Orleans, Louisiana* 70122)

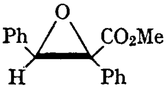
IN continuing our studies[1] on the photofragmentation of oxirans we have examined the photolysis of *trans*-2,3-dicyano-2,3-diphenyloxiran (I) and the glycidic esters 2-methoxycarbonyl-2,3,3-triphenyloxiran (II) and 2-methoxycarbonyl-2,3-diphenyloxiran (III):



(I) a; R=CN
b; R=Ph



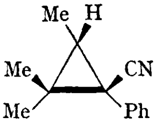
(II)



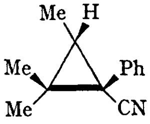
(III)

The dicyano-oxiran (Ia) was synthesized according to the method of Mukaiyaka and his coworkers[2] by addition of triethyl phosphite to a benzene solution of benzoyl cyanide at room temperature. Upon heating for 30 min. at 50° a 2 : 1 adduct of benzoyl cyanide and triethyl phosphite is formed. This adduct decomposes in refluxing xylene to (Ia), m.p. 164—165° (50—70%), (lit.[2] 162°). The ultraviolet spectrum of (Ia) exhibits a λ_{max} (EtOH) 236 mμ.

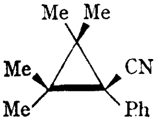
In a typical experiment a solution (0·1 M) of (Ia) upon irradiation‡ for 36 hr. in 2-methylbut-2-ene affords the 1-cyano-1-phenylcyclopropanes (IVa) and (IVb) collected by g.l.c.§ (65—70%) while in 2,3-dimethylbut-2-ene the cyclopropane (V) is obtained (m.p. 89°; 75%). The gross structures of (IVa), (IVb), and (V) were established, and the stereochemistry of (IVa) and (IVb) assigned earlier.[1d]



(IVa)



(IVb)



(V)

In view of previous e.s.r. and luminescence data obtained with related aryl-substituted oxirans,[1e] it is reasonable to assume that cyanophenylcarbene is involved in the conversion of (Ia) into (IVa), (IVb), and (V). The fate of the oxygen-containing fragment, presumably benzoyl cyanide, is currently under study.

Conversion of 2-cyano-2,3,3-triphenyloxiran (Ib) into the glycidic ester 2-methoxycarbonyl-2,3,3-triphenyloxiran (II), m.p. 109° (lit.[3] 110—111°), was accomplished according to the method of Bettinetti and Donetti.[3] The diphenylglycidic ester (III) was prepared by condensation of the methyl ester of 2-chlorophenylacetic acid with benzaldehyde,[4] m.p. 70—71° (lit.[4] 71—72°).

Photolysis‡ of the glycidic esters (II) and (III) in

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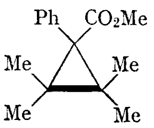
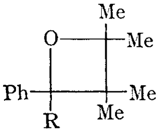
‡ All irradiations were conducted in quartz vessels fitted with an aerosol compatibility seal and valve (Fisher-Porter Co.). Samples were degassed and photolyzed at 35° using a Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with sixteen 8w low-pressure mercury lamps. Stirring was employed in those cases where solubility problems were encountered.

§ Separation of (IVa) and (IVb) was done on a 30% D. C. Hyvac on Chromosorb P column (2 m. × 8 mm.).

2,3-dimethylbut-2-ene (0·1 M, 36 hr.) affords 1-methoxycarbonyl-2,2,3,3-tetramethyl-1-phenylcyclopropane (VI) (*ca.* 40% and 20%, respectively)



(VI)

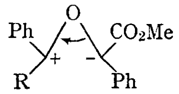


(VII) a; R=Ph
b; R=H
c; R=CO_2Me

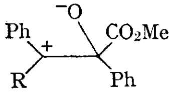
The n.m.r. spectrum of (VI) exhibits two sharp singlet signals of equal area at τ 8·76 and 9·04 (12H), the former peak is assigned to the protons of the pair of vicinal dimethyl groups of (VI) *trans* to the phenyl group while the latter peak is attributed to the two methyl groups *cis* to the phenyl and thus shielded upfield. In addition sharp singlets are apparent at τ 6·50 (3H) and 2·78 (5H) in the n.m.r. spectrum of (VI) and are assigned to the methoxy- and aryl protons, respectively. The infrared spectrum of (VI) determined in carbon tetrachloride has significant bands at 1730 (s) (ester carbonyl group), 1270 (m), 1220 (s), 1070 (m), and 700 (s) cm.$^{-1}$.

In addition to (VI), the expected oxetans of benzophenone and benzaldehyde (VIIa and VIIb) also are obtained upon photofragmentation of (II) and (III), respectively, and characterized by comparison of their infrared spectra with those of authentic samples.[1,5] The oxetan (VIIc) formed from methyl phenylglyoxylate is also obtained indicating that some fragmentation is diphenylcarbene also occurs.[6]

It is interesting that phenylmethoxycarbonylcarbene should be the major product obtained from (II) or (III) upon irradiation.¶ Earlier work with unsymmetrical precursors for phenylcyanocarbene shows that selective cleavage is also observed;[1d] while we cannot exclude a concerted or two-step homolytic fragmentation mechanism for (I), (II), and (III), we have entertained the possibility that the reaction proceeds by an ionic two-step mechanism. If indeed this is the case then initial cleavage must involve the C–C bond of the oxiran ring to give the more stable zwitterion (VIII), for preferential initial heterolytic cleavage of the C–O bond to give the stabilized zwitterion (IX) cannot account for the observed product ratio. Collapse of (VIII) to phenylmethoxycarbonylcarbene is reminiscent of typical α-elimination reactions.



(VIII) a; R=Ph
b; R=H



(IX) a; R=Ph
b; R=H

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¶ Irradiation of (II) in methanol confirms that fragmentation to diphenylcarbene also occurs to some extent. The two carbene fragments were trapped with methanol to give benzhydryl methyl ether and the methyl ether of methyl mandelate, respectively. The ratio of diphenylcarbene to phenylmethoxycarbonylcarbene determined from these ethers by g.l.c. is 3: 7.

(a) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, 1965, **77**, 859; (b) H. Kristinsson and G. W. Griffin, *J. Amer. Chem. Soc.*, 1966, **88**, 3259; (c) H. Kristinsson, *Tetrahedron Letters*, 1966, 2343; (d) P. Petrellis, H. Dietrich, E. Meyer, and G. W. Griffin, *J. Amer. Chem. Soc.*, 1967, **89**, 1967; (e) A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson, and I. Sarkar, Abstracts of Papers Presented at the 153rd Meeting of the American Chemical Society, Miami, Florida, April 10—14, 1967, 0-160.

[2] T. Mukaiyaka, I. Kuwajima, and K. Ohno, *Bull. Chem. Soc. Japan*, 1965, **38**, 1954.

[3] G. F. Bettinetti and A. Donetti, *Gazzetta*, 1966, **96**, 965.

[4] The synthesis of (III) was achieved by the method of Bliche and his co-workers for the preparation of the corresponding ethyl ester. F. F. Bliche, J. Faust, and H. Raffelson, *J. Amer. Chem. Soc.*, 1954, **76**, 3161.

[5] D. R. Arnold, R. L. Hinman, and A. Glick, *Tetrahedron Letters*, 1964, 1425.

[6] An authentic sample of the oxetan (VIIc) was obtained on irradiation‡ of methyl phenylglyoxylate in 2,3-dimethylbut-2-ene. The n.m.r. spectrum exhibits a singlet τ 9·15 (3H), three singlets at 8·76, 8·70, and 8·57 (9H), a sharp singlet 6·23 (3H), and a complex multiplet centred at 2·50 (5H).