Generation of Phenylcyclopropylcarbene from 2,3-Biscyclopropylstilbene Oxide

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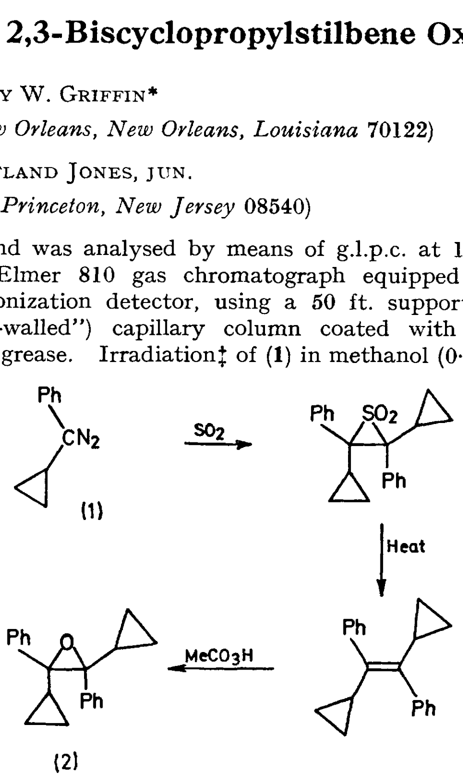
Summary The properties of phenylcyclopropylcarbene, generated from both phenylcyclopropyldiazomethane and phenylcyclopropylethylene oxide are compared.

We have shown that the photolysis of aryl-substituted oxirans leads to the generation of aryl-, diaryl-, and substituted-aryl-carbenes.[1] During our studies on the photolysis of such systems we became interested in the symmetrical phenylcyclopropylethylene oxide (**2**), as we wished to compare the properties of phenylcyclopropylcarbene from (**2**) with that obtained from a conventional diazo-precursor (**1**). Such a comparison appeared worthwhile because of the variety of competitive reactions possible when phenylcyclopropylcarbene is generated in a reactive solvent. The relative amounts of trapped and rearranged products should show how closely the carbenes compare in properties when generated from such diverse sources as (**1**) and (**2**).

The oxiran (**2**) was synthesized by peracetic acid oxidation of the parent stilbene (66%), prepared according to the method of Bennett and Bunce[2] from (**1**).†

Irradiation of (**2**) in methanol (0·2 M, 48 h) gave the methyl ether (**3**) (*ca.* 75–80%) and a small amount of phenyl cyclopropyl ketone. Aryl- and diaryl-carbenes are known to react with protic solvents such as methanol to give the corresponding ethers.[3a] The reaction mixture was clean and was analysed by means of g.l.p.c. at 150° in a Perkin-Elmer 810 gas chromatograph equipped with a flame ionization detector, using a 50 ft. support coated ("fuzzy-walled") capillary column coated with DC-550 silicone grease. Irradiation‡ of (**1**) in methanol (0·1 M, 2 h) resulted in complete discolouration of the red solution and also gave (**3**) (90%). Similar results were obtained upon decomposing an argon degassed solution of (**1**) in methanol with catalytic amounts of CuBr. The reaction proceeded to completion with vigorous evolution of nitrogen.



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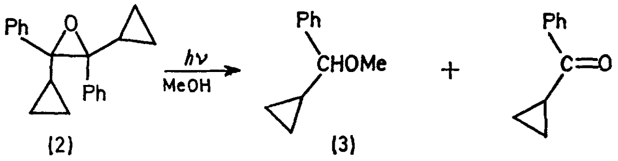
† All new compounds showed appropriate i.r. and n.m.r. spectra and satisfactory combustion analyses.

‡ At LSUNO, irradiations were conducted in quartz vessels at 40° using a Rayonet Chamber Reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 2537 Å lamps. During the preparation of (**2**) from (**1**) the diazo-compound decomposes spontaneously in the presence of CuBr. The carbene thus formed showed an affinity for oxygen and is converted into phenyl cyclopropyl ketone as the major product. All our samples were therefore degassed by bubbling argon through the solution for 30 min prior to irradiation.

The amount of phenyl cyclopropyl ketone generated from (**2**) upon photolysis§ in methanol appears substantially less than that expected on a theoretical basis. That this observation is not due to a differential g.l.p.c. response factor was proved by mixing equimolar amounts of (**3**) and phenyl cyclopropyl ketone and analysing the resulting mixture under conditions simulating those used for the analysis of the photoproducts. Higher molecular weight materials were formed when (**2**) was irradiated and perhaps the nascent carbonyl fragment is photolabile. It is possible that photolysis of (**2**) may generate an excited state of phenyl cyclopropyl ketone which subsquently undergoes photoreactions with solvent.

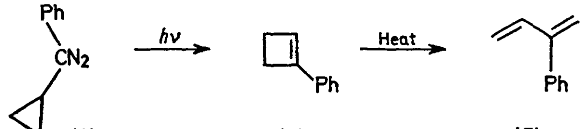


(2) (3)

In both of the photoreactions of (**1**) and (**2**) performed in methanol, the amount of 1-phenylcyclobutene (**4**) formed was negligible, indicating that the reaction of phenylcyclopropylcarbene with methanol is faster than the well known ring expansion of cyclopropylcarbenes.[3b]

Photolysis of (**1**) in benzene,§ hexafluorobenzene,‡ or saturated§ and unsaturated hydrocarbons§ resulted in nearly quantitative conversion into (**4**). The cyclobutene (**4**) was readily converted into (**5**) on either incautious gas chromatography or by passage through an evacuated (0·15 torr) Pyrex tube maintained at 350°. In the latter reaction, traces of phenylacetylene also appeared.

Both (**4**) and (**5**) were isolated by g.l.p.c. and their n.m.r. and i.r. spectra shown to be identical to those of authentic samples. Phenylcyclobutene (**4**) was prepared from cyclobutanone virtually as described by Burger and Bennett.[4] 2-Phenylbuta-1,3-diene (**5**) was obtained by dehydration (30% hydrogen bromide) of the alcohol obtained from vinylmagnesium bromide and acetophenone. Only traces of (**4**) were formed upon irradiation of (**2**) in hexafluorobenzene (0·2 M, 48 h). Substantial amounts of polymer are deposited as a film on the walls of the irradiation tube, however. The difference in behaviour of (**1**) and (**2**) in perfluorobenzene may occur because in the case of (**1**) the cyclobutene (**4**) is shielded by the precursor diazo-compound from further photoreactions and therefore survives. In the case of (**2**), the product (**4**) may undergo secondary reactions, perhaps to give (**5**) and polymers thereof, because of inefficient shielding by (**2**).



(1) (4) (5)

Attempts to inhibit the rearrangement to (**4**) by photosensitization of the decomposition of (**2**) were unsuccessful. However, phenylcarbenes generally show properties independent of method of generation.[5] We were also unable to trap phenylcyclopropylcarbene by the sensitized irradiation of (**1**) in 2-methylbut-2-ene.

The number and distribution of products obtained from phenylcyclopropylcarbene generated from (**1**) and (**2**) (at least under the conditions studied) were less than expected, but the oxiran (**2**), unlike the diazo-compound, has the advantage of being a stable precursor for the carbene. Therefore, while we have so far been unable to show clearly that phenylcyclopropylcarbene generated from (**2**) is identical in reactivity to that obtained from (**1**), the latter is a superior precursor.

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§ At Princeton, degassed solutions were sealed under nitrogen and irradiated with G. E. Sunlamps at room temperature.

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[3] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971; (a) p. 424 ff; (b) p. 467.
[4] A. Burger and R. Bennett, *J. Medicin. Pharm. Chem.*, 1960, **2**, 687.
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