

PHOTOFRAGMENTATION OF OXIRANES AND CYCLOPROPANES; INSERTION REACTIONS OF
PHENYLCARBENE GENERATED FROM DIVERSE SOURCES

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We have proposed that certain aryl-substituted oxiranes¹ and cyclopropanes² photolyze to aryl- and diarylcarbenes. Direct spectroscopic evidence has been obtained for the production of di-phenylcarbene upon photolysis of geminal diaryloxiranes. In contrast the presumed phenylcarbene generated from vicinal diaryl systems has, to date, escaped spectroscopic detection.^{1f,1g}

In recent studies we have found that insertion in C-H bonds, a reaction characteristic of phenylcarbene, occurs when certain vicinal diphenyloxiranes and cyclopropanes are irradiated in n-pentane, an observation which greatly strengthens our original proposal.^{3,4} In light of these observations a rare opportunity now exists to compare quantitatively the insertion selectivity of a given carbene generated from several diverse sources including cyclopropanes, oxiranes and aryldiazomethanes (accepted phenylcarbene precursors) under virtually identical conditions in the condensed phase.

In order to measure the comparative reactivity of aliphatic CH₃- and CH₂- groups toward phenylcarbene, solutions of stilbene oxide (Ia, 0.1M) in n-pentane (10 ml.) were photolyzed⁵ for periods varying from 24 to 48 hrs. The three insertion products II, III and IV were obtained in approximate yields of 4%, 24.5% and 8.5%, respectively.^{6,7} The ratio of the combined amount of 2- and 3-benzylpentanes^{8,9} (III and IV, respectively; 2° C-H attack) to 1-phenylhexane¹⁰ (II; 1° C-H attack) as established from several determinations was 8.3 ± 0.5 (see Table 1). The selection factor for C₂-H or C₄-H over C₃-H (all 2°) was 1.4 ± 0.1 , the ratio of 2-benzyl to 3-benzylpentanes being 2.8 ± 0.2 .

This marked selectivity with respect to bond type is also characteristic of phenylcarbene produced photolytically from trans-1,2-diphenylcyclopropane (Va). In similar irradiations of trans-1,2-diphenylcyclopropane in n-pentane low yields of the same insertion products II (0.7%), III (4.8%) and IV (1.5%) were obtained. Although the principal photoreaction occurring was rearrangement to 1-phenylindane¹¹ (ca. 30%) the phenylcarbene generated behaved exactly like the phenylcarbene produced from stilbene oxide, so far as we could determine using the most sensitive methods available.⁷ The selectivity factor for secondary vs. primary C-H insertion was about 8.3 and the ratio of 2-benzyl to 3-benzylpentane near 2.8. As may be seen in the table, the results depend somewhat on the g.l.c. used and oxygen has no significant effect.

There seems to be no longer room for doubt that the same species is produced from both stilbene oxide and diphenylcyclopropane. The results obtained with triphenyloxirane (Ib), 1,2,3-triphenylcyclopropane (Vb)¹² and phenyldiazomethane complement these data.

Our figures (8.3, 8.6) for the $2^0/1^0$ C-H insertion ratio for phenylcarbene from phenyldiazomethane (VI) differ somewhat from the 6.3 ± 0.3 reported in 1962 by Gutsche and co-workers.¹³ We believe that the difference has an analytical, not a chemical, origin; the presence of numerous minor by-products makes the requisite analysis exceedingly exacting even with the great resolving power of the 50 ft. "fuzzy-walled" capillary columns which were available for the present study. It should be noted that a 0.4% yield of a by-product with the same retention time as 1-phenylhexane would be enough to change the apparent $2^0/1^0$ ratio from 8.3 to 6.3.

Certain carbenes have been found to be much less selective than phenylcarbene. Methylene for example shows almost no discrimination^{14a, 15} or only slight discrimination^{16,17} while the $2^0/1^0$ selectivity ratio for carbomethoxycarbene is 2.3.^{14b}

The data we have accumulated (Table 1) clearly establish that a common intermediate is involved for those systems delineated. Considering the data of Table 1, and notwithstanding the known and expected increase in selectivity relative to methylene due to aryl stabilization, it is startling that the selectivity ratios are virtually identical despite the widely divergent results possible (*vide supra*). It is inconceivable to us that the nascent carbene fragments generated from oxiranes, cyclopropanes and a diazo compound are isoenergetic. In view of the marked dependence of selectivity on energetics we are forced to conclude that the reactive state in each case is identical and that rapid thermal equilibration to a common vibrational level of a common state must occur prior to insertion.

Although evidence has been presented recently that triplet methylene may insert¹⁸ it is the popular belief¹⁹ that such reactions involve the singlet state. While no definitive choice can be made at this time (especially when dealing with the liquid phase) between the two possible multiplicities for the chemically significant state we are inclined to accept the usual picture of a direct single step mechanism for insertion.²⁰ Since the ground state multiplicity of phenylcarbene is triplet the excited singlet state then is implicated. Our observation that oxygen has no apparent effect on insertion selectivity lends credence to this interpretation.

ACKNOWLEDGMENTS

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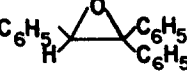
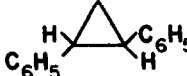
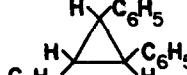
PHENYLCARBENE PRECURSOR	% INSERTION	$C_2-H + C_3-H$ TO C_1-H INSERTION RATIO ^{21a}	C_2-H TO C_3-H INSERTION RATIO ^{21a}
Ia 	37%	8.3 ± 0.5	1.4 ± 0.1
Ib 	10%	8.45 ± 0.3	1.5 ± 0.1
V 	7-8% ^{21b}	8.6 ± 0.4 ^{7c} 8.2 ± 0.2 ^{21b, 7a} 8.6 ± 0.5 ^{21b, 7c} 7.7 ± 0.4	1.39 ± 0.04 1.41 ± 0.05 1.3 ± 0.1
Vb 	ca. 5%	ca. 8.7	ca. 1.4
VI $C_6H_5CHN_2$	9% ^{21c}	ca. 8.6 ^{5c} ca. 8.3 ^{5b}	ca. 1.4 ca. 1.3

TABLE 1

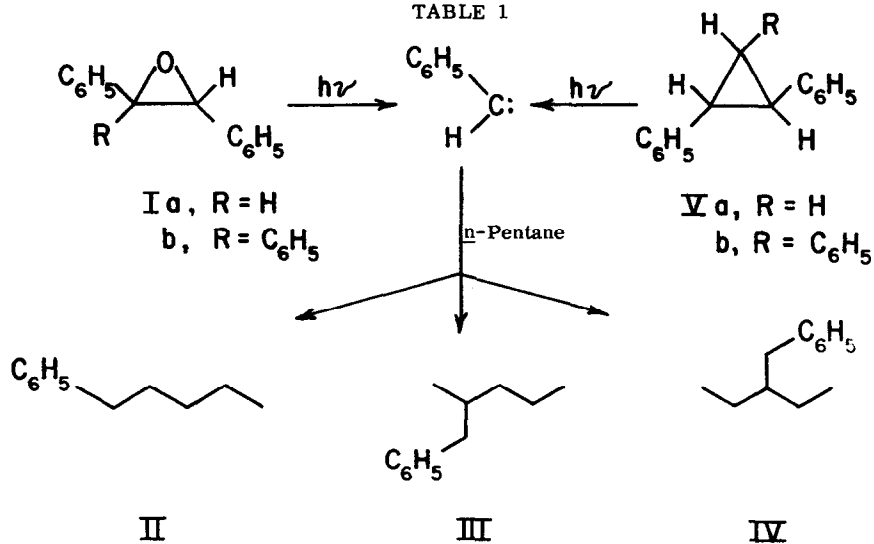


FIGURE 1

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* Author to whom inquiries regarding this paper should be addressed.

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3. (a) We have already reported that these precursors also give typical phenylcarbene adducts upon irradiation in olefins and alcohols; ¹³C, ² (b) See W. Kirmse, Carbene Chemistry, p. 86, Academic Press, Inc., New York, N. Y. (1964).
4. The syn anti ratios for the cyclopropanes obtained from Ia by photolysis in cis-2-butene or 2-methyl-2-butene (1.17 ± 0.03 and 1.12 ± 0.03, respectively) correspond closely to the values obtained by Closs and Moss using phenyldiazomethane as the carbene precursor (1.1 and 1.1, respectively). See G. L. Closs and K. A. Moss, J. Am. Chem. Soc., 86, 4042 (1964). In our original report ¹³C values of 0.60 - 0.65 and 0.95 - 1.0 were given and must be corrected in light of improvements in our analytical techniques. P. Petrellis and G. W. Griffin, unpublished results.
5. Irradiations were conducted in serum-capped 15 cm. x 13 mm. O.D. quartz tubes using three different light sources: (a) A Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 G8T5 8-w low pressure mercury lamps (2537A) at 30-35°; (b) the same reactor as (a) but fitted with F8T5 8-w lamps (3500A) at 35°; and (c) a quartz Hanovia probe employing a 450-w high pressure mercury lamp (Type 79A36) at 10°. The solutions were sparged with nitrogen prior to irradiation with one exception. See Table 1.
6. Separation was achieved by g.l.c. using a column (2 m x 8 mm O.D.) packed with 25% DC-Hyvac grease on Chromosorb P at 215°.
7. The yields as well as the ratios of insertion products were determined by g.l.c. using internal standards with a Perkin-Elmer 810 gas chromatograph equipped with a flame ionization detector. Satisfactory resolution of the benzylpentanes was obtained on the following 50 ft. support-coated ("fuzzy-walled") capillary columns: (a) Silicone DC-550 (150°); (b) Carbowax 20M (170°); (c) Apiezon L (145°).
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of pure III and IV which were used for direct comparison with photolysis products.

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21. (a) Limits of error are standard deviations; (b) Not deoxygenated; (c) Yield reported in reference 13.