PHOTOFRAGMENTATION OF CYCLIC CARBONATES AND SULFITES: INSERTION REACTIONS OF PHENYLCARBENE GENERATED FROM DIVERSE SOURCES

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In a preliminary communication[1] we reported that photofragmentation of tetraaryl cyclic carbonates and sulfites gives diarylcarbenes which are conveniently trapped as benzhydrylmethyl ethers.[2] Our investigations have now been extended to vicinal diaryl cyclic carbonates and sulfites. Phenylcarbene produced photochemically from these vicinal diaryl systems has to date escaped spectroscopic (optical and esr) detection although our efforts in this area are continuing.[3]

In recent chemical studies we have found that insertion into C–H bonds, a reaction characteristic of phenylcarbene, occurs when vicinal diaryl cyclic carbonates and sulfites are irradiated in n-pentane. In this communication we wish to describe the results of a quantitative study in which the insertion selectivity of the transients generated from dl- and meso-hydrobenzoin carbonates and sulfites are compared with those obtained from the accepted phenylcarbene precursors, trans-stilbene oxide (1) and phenyldiazomethane (4).

In order to measure the comparative selectivity of phenylcarbene toward aliphatic 1° and 2° C–H bond types, equimolar solutions of the compounds under study in n-pentane were photolyzed under similar conditions.[5,6] Yields as well as insertion product ratios were determined gas chromatographically employing n-amylbenzene as an internal standard.[7] To ensure that the results obtained reflect initial insertion rates relatively short irradiation times (25 min) were employed.

In a typical case the three insertion products, 5, 6, and 7 were obtained from dl-hydrobenzoin carbonate (2a) in the ratio of 1.00:6.12:2.16, respectively. The ratio of the combined amount of 2- and 3-benzylpentanes[8,9] (6 and 7, respectively; 2° C–H attack) to 1-phenylhexane[10] (5; 1° C–H attack) was established from several determinations as 8.27 ± 0.23 (see Table I). The selectivity factor for C_2-H or C_4-H over C_3-H (all 2°) was found to be 1.42 ± .03, the ratio of 2-benzyl to 3-benzylpentanes being 2.84 ± 0.06.
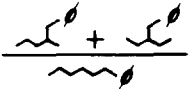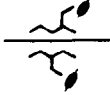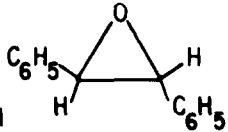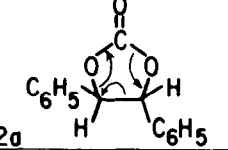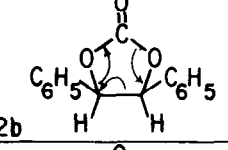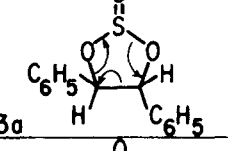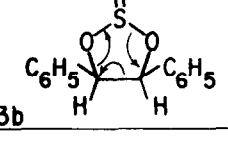
The results obtained in all cases substantiate our original proposal that photolysis of aryl cyclic carbonates and sulfites do in fact give rise to species similar if not identical to those produced from

accepted carbene precursors such as stilbene oxide (1) and phenyldiazomethane (4). The higher yields observed with the oxirane 1 and the diazo precursor 4 are indicative of faster initial reaction rates which are possibly due to the higher extinction coefficients exhibited by these molecules at $2537\overset{o}{A}$. The carbonates and sulfites presently under examination do give significantly higher yields of insertion products upon prolonged irradiation; however, preservation of the initial selectivity factors was of paramount importance in this study.

The stereochemistry of the cyclic carbonate or sulfite apparently has little or no effect on the selectivity, although the initial fragmentation rates for the dl-isomers 2a and 3a appear to be slightly higher. This is not unexpected in view of the higher extinction coefficients observed for the dl-diastereomers. Analyses of reaction mixtures (tlc, nmr) at low conversions (10%) where shielding of the alternate isomer, if formed, should be effective indicates that no interconversion of the diastereomers occurs under the reaction conditions. Furthermore no fragmentation was observed when the carbonates and sulfites were irradiated in pentane at $3500\overset{o}{A}$ for extended periods. The presence of oxygen has no apparent effect on the selectivity factors exhibited by the hydrobenzoin carbonates and sulfites under study. Whether a concerted or stepwise mechanism, perhaps involving the oxiranes, is operative remains to be established, although the latter appears unlikely since neither cis- nor trans-stilbene oxides could be detected by tlc among the reaction products in any of those cases studied.

The data we have accumulated (Table I) clearly indicate a common species is generated in the photolysis of the systems studied. The fact that the selectivity ratios obtained from such widely diverse sources are virtually identical leads us to believe that rapid thermal equilibration to a common vibrational level of the same state occurs prior to insertion. It is generally conceded that phenylcarbene insertion reactions involve the singlet state which reacts with the substrate more rapidly than it interconverts to the triplet ground state. It appears that the phenylcarbene produced by photodecomposition of 4 using a $2537\overset{o}{A}$ source has lower selectivity. The reason(s) for this lower selectivity remains to be established. The results reported here on the insertion selectivity of phenylcarbene generated from 4 differ slightly from those reported previously by Gutsche (6.0 ± 0.3)[11], and we believe that this disparity is analytical rather than chemical in origin.[12]

PHENYLCARBENE PRECURSOR	YIELDS (25 MIN.; 8 LAMPS)	INSERTION RATIO	INSERTION RATIO
C_6H_5 ... H / H ... C_6H_5 (epoxide) **1**	45.4 %	$8.33 \pm .14$[a]	$1.35 \pm .04$[a]
C_6H_5 ... H / H ... C_6H_5 **2a**	5.2	8.27 ± 0.23	$1.42 \pm .03$
C_6H_5 ... C_6H_5 / H ... H **2b**	3.8	8.47 ± 0.20	$1.42 \pm .03$
C_6H_5 ... H / H ... C_6H_5 **3a**	6.6	8.00 ± 0.18	1.45 ± 0.02
C_6H_5 ... C_6H_5 / H ... H **3b**	5.5	8.48 ± 0.24	1.41 ± 0.05
$C_6H_5CHN_2$ **4**	31.5 / 18.3[b]	7.14 ± 0.14 / 8.38 ± 0.19	$1.31 \pm .09$ / $1.33 \pm .09$

(a) Limits of error in all cases are standard deviations

(b) 3500 Å; 16 lamps; 4 hrs.

TABLE I

FIGURE I

2a, R = C$_6$H$_5$, R' = H

b, R = H, R'= C$_6$H$_5$

n-Pentane

3a, R = C$_6$H$_5$, R'= H

b, R = H, R'= C$_6$H$_5$

5

7

6

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

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(2)   W. Kirmse, L. Horner, and H. Hoffmann, Liebigs Ann., 614, 19 (1958).

(3)   A. M. Trozzolo, T. DoMinh, R. L. Smith, and G. W. Griffin, unpublished results.

(4)   For an earlier analysis of oxiranes and cyclopropanes as phenylcarbene precursors see H. Dietrich and G. W. Griffin, Tetrahedron Lett., 153 (1968).

(5)   The insertion reactions were conducted in reagent grade n-pentane (Columbia Organic Chemicals Co., Inc., Columbia, S. C.) (3.30 x 10^{-3} M; 10 ml) and were degassed by nitrogen sparging prior to irradiation in serum-capped 15 cm x 12.6 mm ID quartz tubes.

(6)   A Rayonet chamber reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) fitted with a Rayonet MGR-1 Merry-Go-Round apparatus equipped with 8 G8T5 8-w low pressure mercury lamps (2537Å) or 16 F8T5 8-w lamps (3500Å) was used as a light source in all photolyses.

(7)   The yields as well as the ratios of insertion products were determined by capillary gas chromatography on a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. Satisfactory resolution of the benzylpentanes was obtained on a 50 ft x 0.020 in support-coated ("fuzzy-walled") silicone DC-550 column utilizing an appropriate temperature program.

(8)   E. Bjelouss, Ber., 45, 625 (1912).

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(11)   C. D. Gutsche, G. L. Bachman, and R. S. Coffey, Tetrahedron, 18, 617 (1962).

(12)   As reported previously (see Reference 4) a 0.4% yield of a by-product possessing an identical retention time as 1-phenylhexane would be sufficient to change the apparent 2°/1° ratio from 8.3 to 6.3.