THE PHOTOLYSIS OF PHENYLBROMODIAZIRINE AND THE

GENERATION OF PHENYLBROMOCARBENE
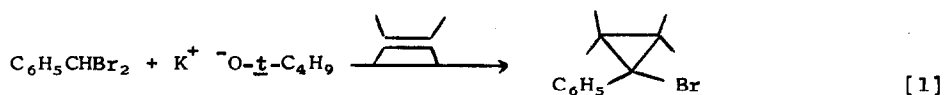
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The reaction of benzal bromide and olefinic slurries of potassium $\underline{t}$-butoxide affords phenylbromocyclopropanes, (eq. 1), (1). We suggested the possible

$$C_6H_5CHBr_2 + K^+ \ ^-O\text{-}\underline{t}\text{-}C_4H_9 \longrightarrow \underset{C_6H_5}{\diagup}\underset{Br}{\diagdown} \qquad [1]$$

intermediacy of $\underline{free}$ phenylbromocarbene, $C_6H_5\text{-}\overset{\cdot\cdot}{C}\text{-Br}$, and described its stereoselectivity and discrimination in this reaction (2).

A popular method of probing the "freeness" of a supposed carbene intermediate requires that it be generated in different ways, one of which ($\underline{e.g.}$, photolysis of a diazo compound) presumably affords a free carbene. Reactivity comparisons are then made. Such experiments have indicated that α-elimination reactions of alkyl halides, with alkyl lithiums as generative bases, involve lithium carbenoids rather than true carbene intermediates (3). In cyclopropanation reactions such as [1], however, with the generative base a sodium or potassium alkoxide, the evidence is unclear. It has been reported that the same dichlorocarbene species is produced by the action of potassium $\underline{t}$-butoxide on chloroform, the thermolysis of sodium trichloroacetate, and various decompositions of phenyl(trihalomethyl)-mercury compounds (4). Very rare, however, are investigations in which "carbene" addition to olefins via a sodium or potassium alkoxide-induced α-elimination has

been <u>quantitatively</u> contrasted to a <u>photolytic</u> α-elimination. One example is
Jones' (5) study of dichlorocarbene generation by photolysis of 1,1-dichloro-2-
phenylcyclopropane and by reaction of chloroform with potassium <u>t</u>-butoxide. Com-
parative data were limited, however, and firm conclusions about the equivalence
of the reactive intermediates could not be drawn.

    We now report a detailed comparison of the reactivities of "phenylbromocar-
bene" as produced by [1] and by photolysis of phenylbromodiazirine (6). Photo-
lyses (G.E. Sunlamp, Pyrex filter, sealed tube, 40 min.) of phenylbromodiazirine
in dilute (<u>ca</u>. 0.05M) olefinic solutions <u>afford</u> <u>essentially</u> <u>quantitative</u> <u>yields</u>
<u>of</u> <u>nearly</u> <u>pure</u> <u>phenylbromocyclopropanes</u>, I, (eq. 2). It seems likely that this
process does involve free phenylbromocarbene (7).

I
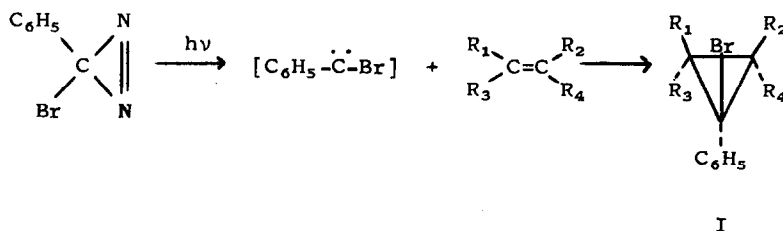
Ia; $R_1 = R_2 = R_3 = R_4 = CH_3$

Ib-<u>Syn</u>-Br; $R_1 = R_2 = R_3 = CH_3$, $R_4 = H$ Ib-<u>Anti</u>-Br; $R_1 = H$, $R_2 = R_3 = R_4 = CH_3$.

Ic; $R_1 = R_3 = CH_3$, $R_2 = R_4 = H$.

Id-<u>Syn</u>-Br; $R_1 = R_2 = CH_3$, $R_3 = R_4 = H$.   Id-<u>Anti</u>-Br; $R_1 = R_2 = H$, $R_3 = R_4 = CH_3$.

Ie; $R_1 = R_4 = CH_3$, $R_2 = R_3 = H$.

    Olefins used were tetramethylethylene, trimethylethylethylene, isobutene, <u>cis</u>-
butene, and <u>trans</u>-butene. After stripping the olefinic solvent, cyclopropanes
Ia-e were identified by comparison of their NMR spectra with published (2) auth-
entic spectra. Examination of the crude product spectra indicated that: (a)
little insertion of phenylbromocarbene into C-H bonds had occurred (from the gen-
eral absence of non-cyclopropane absorptions); (b) carbene attack on diazirine (or,
less likely, dimerization of carbene) leading to α,β-dibromostilbene was a very
minor process (since alkyl/aryl proton ratios were approximately correct for
pure cyclopropanes); (c) additions to <u>cis</u>-butene were highly stereospecific, Id
being formed to the exclusion of Ie (8).

Carbene addition to trimethylethylene and cis-butene produced the antici-
pated isomeric cyclopropane mixtures. Isomer ratios observed for reaction [2]
were Ib-Syn-Br/Ib-Anti-Br = 1.31 $\pm$ 0.04$_2$ and Id-Syn-Br/Id-Anti-Br = 1.55 $\pm$
0.10$_4$. For comparison, the corresponding data obtained from reaction [1] were
1.28 $\pm$ 0.05$_3$ and 1.35 $\pm$ 0.01$_3$ (8).

Competition experiments, in which the diazirine was photolyzed in mixtures
of olefins, afforded the relative rates gathered in the Table (8). Correspond-
ing data obtained for reaction [1] are also included (2).

TABLE

Competition of Tetramethylethylene and Olefin$_i$ for
Phenylbromocarbene

Olefin$_i$ [a]	$k_{Tetramethylethylene}/k_i$	
	Reaction [2] [b]	Reaction [1] [c]
Trimethylethylene	1.74 $\pm$ 0.04	1.28 $\pm$ 0.09$_3$
Isobutene	4.44 $\pm$ 0.18	1.65 $\pm$ 0.21$_7$
cis-Butene	8.34 $\pm$ 0.04	5.79 $\pm$ 0.11$_2$
trans-Butene	17.5 $\pm$ 0.80	11.3 $\pm$ 1.58$_4$

[a] Each olefin was present in more than 20-fold excess over diazirine. Products
were photostable. [b] Average of 2 runs employing different olefin ratios.
Determined at 23 $\pm$ 5°. Controls established constancy of relative rates over
this range. [c] At ca. 25°.

The intermediates of reactions [1] and [2] are similar in that both exhibit
marked preference for addition to C=C as opposed to insertion into C-H; in that
both add stereospecifically to cis-butene, and are therefore probably singlets
(9); in that both add to trimethylethylene and cis-butene so as to produce (simi-
lar) excesses of cyclopropanes in which bromine is syn to the larger number of
alkyl groups; and in that both exhibit a similar pattern of discrimination between
different olefins. However, the data in the Table indicate that the species are
not identical. Further, the photolytic species discriminates more efficiently
and exhibits the more pronounced electrophilic character.
The simplest conclusion is that the intermediate in [1] is not a free

carbene (10). There are, however, many similarities between the intermediates of [1] and [2]; particularly striking are their nearly identical stereoselectivities. This important finding makes our previous discussion of phenylbromocarbene stereoselectivity (2) independent of the possible presence of potassium bromide in the transition state of cyclopropanation [1].

It is possible that the intermediate in [1] may closely approximate a free carbene. Its exact composition is presently a matter of speculation. It could be a weak complex of phenylbromocarbene and potassium bromide (11). On the other hand, cyclopropanation [1] could occur via a phenylbromocarbene weakly complexed to the excess potassium t-butoxide. An alternative formulation of the intermediate as α-potassio-α,α-dibromotoluene seems less acceptable (12).

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References

1. R.A. Moss and R. Gerstl, Tetrahedron Letters, 3445 (1965).

2. R.A. Moss and R. Gerstl, Tetrahedron, 22, 2637 (1966).

3. See, for example: G.L. Closs and R.A. Moss, J. Am. Chem. Soc., 86 4042 (1964); G.L. Closs and J.J. Coyle, ibid., 87, 4270 (1965). For recent reviews, see: G. Köbrich, Angew. Chem., Internat. Ed., 6, 41 (1967); W. Kirmse, ibid., 4, 1 (1965).

4. D. Seyferth, M.E. Gordon, J. Y-P. Mui, and J.M. Burlitch, J. Am. Chem. Soc., 89, 959 (1967), and references therein.

5. M. Jones, Jr., W.H. Sachs, A. Kulczycki, Jr., and F.J. Waller, ibid., 88, 3167 (1966).

6. W.H. Graham, ibid., 87, 4396 (1965). We thank Dr. Graham for detailed guidance in the preparation of this compound.

7. For a review of carbene generation via diazirine photolysis see H.M. Frey, Advances in Photochemistry, 4, 225, Interscience, New York (1966).

8. Details of NMR Analyses will be found in reference 2.

9. P.P. Gaspar and G.S. Hammond in W. Kirmse, Carbene Chemistry, chapter 12, Academic Press, New York (1964).

10. The reactivity differences probably do not derive from different multiplicities of the two intermediates (both are highly stereospecific, and therefore most likely singlets); nor can the differences be readily explained by postulating a "hot" carbene in [2], for the photo-intermediate is the more selective one. This leads us to favor the stated conclusion over the postulation of an excited diazirine (or diazo compound) as the discriminating

intermediate in [2]. As has been noted by a referee, we cannot definitely exclude the latter possibility, but intuitive considerations, such as those of Closs and Moss[3], mitigate against it. Thus, the selectivity of the photo-intermediate indicates a significant activation barrier for the addition step in [2]. The intermediate must therefore suffer numerous fruitless collisions before reacting. The considerable lifetime thus indicated should suffice to permit thermalequilibrium to be established. The above argument was originally advanced in a case where a photo-intermediate seemed less selective than the related intermediate of an α-elimination reaction[3]. It seems more potent in the present case, where the selectivity order is reversed.

11. Cf: D.F. Hoeg, D.I. Lusk, and A.L. Crumbliss, J. Am. Chem. Soc., 87, 4147 (1965).

12. Such a species, due to the strongly ionic carbon-potassium bond, would be expected to exhibit carbanion-like properties. An electrophilic selectivity toward olefins would be unexpected.