half-life) suggests that formation of activated products arises mainly from the consequences of internal conversion and subsequent Auger electron emission (*i.e.*, ion–molecule reactions or radical–radical recombinations). If it is assumed that recoil energy is the main factor in determining the chemical fate of ^{80m}Br, it could be expected that this different nuclear origin and chemical activation would be reflected in differences in the isotopic yield.[3]

It is still unclear in what way the change from the liquid to the solid state affects the chemical consequences of a nuclear event.[2a] One of the possible interpretations would be that a truly "hot" process (that is, the result of a direct impact of an energetic atom on a molecule, or one which is followed by an extremely rapid recombination of the fragments formed) should not be greatly affected by a structural change of the surrounding "cage." Conversely, the organic yield of other processes could increase if the solidified cage were able to keep together thermalized organic fragments (that would have diffused apart in the liquid) and would only have allowed H atoms to diffuse away.

In the light of these assumptions and since the phase and isotope effect appear to be correlated, it can be tentatively concluded (thus confirming the hypothesis proposed in ref 3) that the breaking of a C–C and C–Br bond may be primarily caused by atoms having recoil energy, while H-atom substitution is caused mainly by isomeric transition activation.

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Photochemistry of Phenyloxiranes. II. New Precursor for Phenylcarbene[1]

Sir:

In an earlier communication[2] we reported our preliminary data on the photofragmentation of a variety of aryl-substituted epoxides to phenylcarbenes (or behaviorly related species) and ketones or aldehydes. The scope and synthetic utility of this reaction for the preparation of phenylcyclopropanes and -propenes as well as the stereochemical features of the observed addition processes have now been investigated. In view of the breadth of scope of this reaction and the novel stereochemical features, we now wish to supplement our previous report with further experimental details and results.

Representative compounds accessible from stilbene oxide (I) are tabulated below (Table I). Unquestionably I represents the most convenient precursor for phenylcarbene which in turn will add stereospecifically to olefins and also reacts with acetylenes and benzenes. Furthermore, the yields of phenylcyclopropanes reported herein invariably exceed those previously attainable by alternate routes using other phenylcarbene or carbenoid precursors.[3]

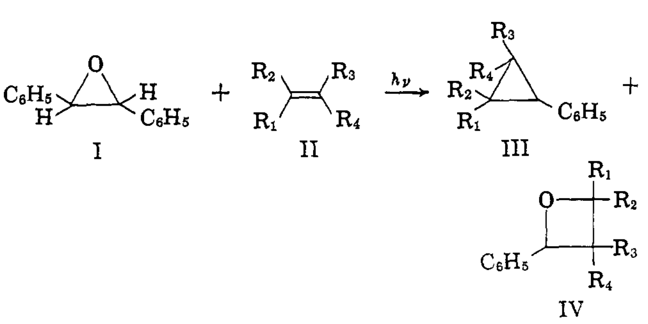

Table I

	Olefin II	R_i, II, III, and IV	Yield of III,[a] %
(a)	Isobutene	$R_1 = R_2 = H$ $R_3 = R_4 = CH_3$	60
(b)	*cis*-2-Butene	$R_1 = R_4 = H$ $R_2 = R_3 = CH_3$	65
(c)	*trans*-2-Butene	$R_1 = R_3 = H$ $R_2 = R_4 = CH_3$	65
(d)	2-Methyl-2-butene	$R_1 = H$ $R_2 = R_3 = R_4 = CH_3$	75
(e)	2-Methyl-1-butene	$R_1 = R_2 = H$ $R_3 = CH_3$; $R_4 = C_2H_5$	70
(f)	2,3-Dimethyl-2-butene	$R_1 = R_2 = R_3 = R_4 = CH_3$	60

[a] No attempt was made to maximize the yield which is based upon the initial epoxide concentration. In all irradiations (50 hr) 20–30% of the epoxide was recovered.

The simplicity of the transformation I + II → III + IV leaves little to be desired. Best results are obtained when the initial epoxide concentration is approximately 0.2–0.3 *M*. Irradiations are conducted conveniently in serum-capped quartz test tubes employing the neat olefin or acetylene as a solvent, and stirring was found advantageous.[4] In those cases where olefin or acetylene volatility precludes irradiation under these conditions a thick-walled quartz tube equipped with a commercially available pressure fitting was employed.[5] The period of irradiation was generally 50 hr. It is necessary, however, that photolysis be terminated prior to complete disappearance of epoxide; otherwise the cyclopropanes, which are unstable under these conditions, begin to absorb light and isomerize to olefins.[6] Complete separation of the cyclopropanes from the oxetanes, which also are formed, may be achieved easily by a single short-path distillation under reduced pressure. Aside from these easily separable oxetanes only trace amounts of other nonpolymeric side products were obtained. Insertion products appeared to be formed only in the case of IId (<5%).

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(1) We wish to thank the Army Research Office (Durham) for financial support of this program, and the National Science Foundation for an nmr equipment grant (NSF-GP-3674).

(2) H. Kristinsson and G. W. Griffin, *Angew. Chem.*, 77, 859 (1965).

(3) G. L. Closs and K. A. Moss, *J. Am. Chem. Soc.*, **86**, 4042 (1964).

(4) An air-cooled Rayonet Chamber Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-w germicidal lamps (2537 A) was used as a light source.

(5) The quartz tubes were easily adapted to fit a Fisher-Porter Co. (Lab Crest Scientific Division, Warminster, Pa.) aerosol compatibility coupling equipped with a needle valve.

(6) H. Kristinsson and G. W. Griffin, unpublished results.

According to expectations two epimeric cyclopropanes were obtained from the addition reactions of phenylcarbene generated from I to the noncentrosymmetric olefins IIb, IId, and IIe. We shall employ the Closs convention[3] of designating that isomer as *syn* which has the largest number of alkyl groups (or more complex substituent) *cis* to the aromatic ring and the alternate configuration as *anti*. The isomers were separated by glpc and identified by comparison to nmr data previously reported by Closs and Moss.[3]

As demonstrated convincingly by Closs the minimization of nonbonding interactions in the transition state is not invariably the product-controlling feature in carbene or carbenoid addition reactions; *e.g.*, the more sterically crowded isomer is formed in greater amount when the carbenoid generated from benzal bromide or the carbene from phenyldiazomethane adds to olefins.[3] Although the *syn* adduct (more sterically crowded cyclopropane) is the predominant product obtained from both sources, a significant difference in stereoselectivity was reported by Closs with the carbenoid species exhibiting greater specificity. In contrast the reactive intermediate generated upon photolysis of I exhibits a marked preference for formation of the *least* hindered (*anti*) isomer with IIb and IIe (Table II). The ratios of the epimeric cyclopropanes tabulated in Table II were determined by glpc and nmr. The irradiations for these studies were conducted under conditions which preclude significant photoisomerization subsequent to addition. The irradiation times varied from 15 to 60 min and the initial epoxide concentration was 0.3–0.4 *M*. It should be stressed that even after irradiation of I in IIb for a period exceeding 30 hr the *syn*:*anti* ratio did not change. Furthermore it is significant that no *trans* isomer (IIIc) was formed, and it is unlikely that selective epimerization of the phenyl group could occur without affecting the relative orientation of the methyl groups. In the case of IId photoequilibration subsequent to addition cannot be responsible for the observed *syn*:*anti* ratio since the photostationary state has been shown to favor the *syn* isomer.

Table II

Olefin	*syn*:*anti*
cis-2-Butene (IIb)	0.60–0.65
2-Methyl-2-butene (IId)	0.95–1.0
2-Methyl-1-butene (IIe)	0.65–0.75

The carbene produced from I adds entirely stereospecifically to IIb and IIc. This stereospecificity suggests that a singlet carbene is involved.[7] The validity of such assignments of spin multiplicity, however, have been the subject of controversy.[3,8a] Preliminary attempts to observe triplet phenylcarbene by esr upon photolysis of I in three different matrices have been unsuccessful.[9] In previous esr studies it has been demonstrated that the ground states of arylcarbenes, including phenyl- and diphenylcarbene as well as fluorenylidene, generated from diazomethanes are triplet in character.[10]

Phenylcarbene generated from I (50 hr, 0.3 *M*) will also add to 2-butyne to give 1,2-dimethyl-3-phenylcyclopropene in surprisingly high yield (65%). In this case the benzaldehyde moiety upon reaction with acetylene gives an unstable oxetene which undergoes valence isomerization to *cis*- and *trans*-3-methyl-4-phenylbutenone.[11] The cyclopropene, like the cyclopropanes, cannot be subjected to irradiation in the absence of epoxide or isomerization occurs in this case to 1,2- and 2,3-dimethylindene.[12]

Photolysis of I in benzene in the absence of other more reactive materials gives phenylcycloheptatriene which was characterized as its reduction product, phenylcycloheptane.[13] If methyl alcohol is present, however, a reaction similar to that described for diphenylcarbene occurs to give benzyl methyl ether in high yield.[8a]

Structural changes in the precursor epoxide may affect the reaction course. Although tri- and tetraphenylethylene oxide,[2] methyl- and dimethylstilbene oxide, and bisdiphenylene oxide,[14] as well as stilbene oxide, fragment to carbenes, styrene oxide (V) behaves atypically. The photoisomerization of styrene oxide must proceed with initial fission of the α-carbon–oxygen bond of the oxirane ring, followed by hydrogen transfer, to give phenylacetaldehyde. In benzene the hydrogen shift must be followed by a novel decarbonylation step since carbon monoxide and bibenzyl are produced efficiently.

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[9] We wish to thank Dr. A. M. Trozzolo of the Bell Telephone Laboratories for attempting these measurements.

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[12] Thermal isomerizations of this type have been observed by Dr. M. Battiste, personal communication.

[13] C. D. Gutsche, G. L. Bachman, and R. S. Coffey, *Tetrahedron Letters*, No. 18, 617 (1962).

[14] H. Kristinsson and G. W. Griffin, unpublished results.

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N-Phenylbenzoazetine

Sir:

The recent interest[1] in the construction of benzo-fused four-membered heterocycles has grown from consideration of the potential aromatic properties of the derived naphthalene isoelectronic anion, the possibility of benzenoid bond fixation resulting from the small ring fusion,[2] and the ease of valence tautomerization. Past efforts[3] to obtain a stable azetine have proved unsuccessful although the benzoazetinone[4] and azetinone[5] systems appear to be documented. We now

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[4] E. M. Burgess and G. Milne, *Tetrahedron Letters*, 1, 93 (1966).

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