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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(11) G. Büchi, J. T. Kofron, E. Koller, and D. Rosenthal, *J. Am. Chem. Soc.*, **78**, 876 (1956).

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

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(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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(1) For 2H-benzothiete precursors see L. A. Paquette and T. R. Phillips, *J. Org. Chem.*, 30, 3883 (1965), and D. C. Dittmer and N. Takashina, *Tetrahedron Letters*, **50**, 3809 (1964).

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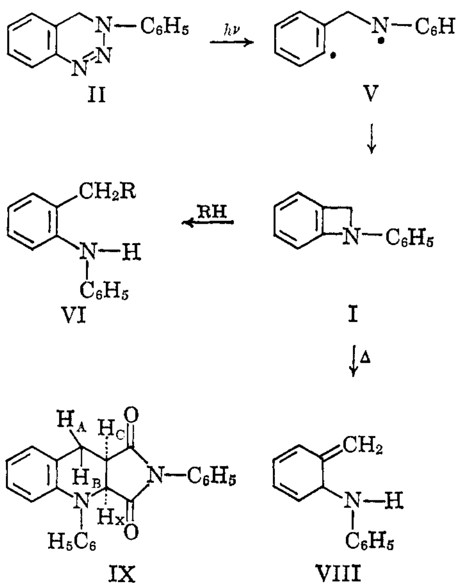
(3) J. A. Moore in "Heterocyclic Compounds with Three- and Four-Membered Rings," Part II, Interscience Publishers, Inc., New York, N. Y., 1964, pp 885–977.

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

(5) K. R. Henery-Logan and J. V. Rodricks, *J. Am. Chem. Soc.*, **85**, 3524 (1963).

wish to report the isolation and characterization of the stable N-phenylbenzoazetine (I).

3-Phenyl-4H-benzo-1,2,3-triazine (λ_{max} 360 mμ) (II), derived from the nitrosation of N-(*o*-aminobenzyl)-aniline,[6] was irradiated in benzene solution with ultraviolet light (Hanovia A 450-w lamp, Pyrex filter) for 30 min at 30° to afford, after chromatography on basic alumina, crystallization from hexane, and sublimation (60°, 10^{-3} mm), a 50% yield of I, mp 104° dec. *Anal.* Calcd for $C_{13}H_{11}N$: C, 86.19; H, 6.08; N, 7.73; mol wt, 181. Found: C, 85.90; H, 6.02; N, 7.61; mol wt, 170 (cryoscopic in benzene). The ultraviolet absorption occurred with a maxima at 280 mμ. The nmr spectrum of I (CCl_4, 60 Mc) displayed a low-field methylene singlet at τ 5.22 and a nine-proton multiplet from τ 2.7 to 3.4. As anticipated these signals are within the normal aromatic proton envelope and indicate an undisturbed benzenoid ring current.

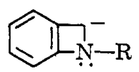


In addition to I the photolyzed solutions of II provided benzalaniline (10%) (III) and 9,10H-phenanthridine (25%) (IV) identified by mixture melting point comparison with authentic samples. The appearance of these products suggests the interposition of a common 1,4-diradical, V, which subsequently undergoes cyclization to I or IV and hydrogen migration to afford III, the reported[6] product from the thermolysis of II. The long wavelength transition of II may be presumed to arise from the promotion of an antibonding 1,2-aza electron in the higher nonbonding molecular orbital to the π^* configuration.[7] If the observed transformation occurs in the singlet state, then overlap of the odd electron, coplanar n-orbital with the 2,3-σ bond leads to the generation of an amino and azo radical pair which after loss of nitrogen gives V.[4]

The increased nucleophilic reactivity (*cf.* azetidine[3]) imposed by the geometry in the base, I, and the corresponding conjugate acid is evident from the following observations. Treatment of I with aniline in benzene at 30° (or more rapidly at 80°) affords in high yield VI (R = NHC_6H_5), mp 80–81°.[8] Likewise I with acetic acid and sodium acetate in refluxing benzene provided VII (R = OAc), mp 57–58°.[9]

N-Phenylbenzoazetine upon thermal or photochemical excitation is rapidly converted to a reactive species which we propose is the valence tautomer VIII. Photoexcitation (unfiltered radiation from the previously described lamp) in aqueous dimethoxyethane at 30° for 1 hr affords VI (R = OH) isolated as the previously described acetate.[10] This behavior is analogous to the characteristic high nucleophilic reactivity of the related *o*- and *p*-quinone methides. Further evidence for the thermal (200°) production of VIII was provided by its interception with N-phenylmaleimide to yield a 1:1 adduct IX, mp 155–156°.[11] The nmr spectrum ($CDCl_3$, 60 Mc) of IX displayed an ABCX pattern as a doublet at τ 5.05 for H_X and an octet at τ 6.37 for H_C, reflecting J_{CX} = 9.5 cps in agreement with the *cis* relationship of these two protons. A two-proton multiplet at τ 6.97 was assigned to the H_{AB} methylene group and was coupled with H_C in the order J_{cis} = 6.5 cps and J_{trans} = 2.5 cps.

A study of the chemistry of VIII and the conversion of I or its derivatives to the possibly aromatic anion, X,



X

is continuing.

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[6] M. Busch, *Chem. Ber.*, **25**, 445 (1892); *J. Prakt. Chem.*, **51**, 257 (1895).

[7] S. F. Mason, *J. Chem. Soc.*, 1240 (1959).

(8) An authentic sample for comparison was prepared by the lithium aluminum hydride reduction of N,N′-diphenylanthranilamide. *Anal.* Calcd for $C_{19}H_{18}N_2$: C, 83.16; H, 6.62; N, 10.22. Found: C, 82.93; H, 6.65; N, 10.02.

(9) Lithium aluminum hydride reduction of N-phenylanthranilic acid followed by O-acetylation gave an authentic sample of the acetate. *Anal.* Calcd for $C_{15}H_{15}NO_2$: C, 74.65; H, 6.27; N, 5.81. Found: C, 74.31; H, 6.35; N, 5.79.

(10) It may be noted that I fails to react nonphotochemically with water at 100°.

(11) *Anal.* Calcd for $C_{23}H_{18}N_2O_2$: C, 77.97; H, 5.08; N, 7.91. Found: C, 77.70; H, 5.10; N, 7.80.

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Reductive Cleavage of Toluenesulfonates with Sodium Naphthalene[1]

Sir:

We wish to report that treatment of alkyl toluenesulfonates with sodium naphthalene anion radical in tetrahydrofuran solution constitutes an almost ideal procedure for regenerating the corresponding alcohols. Reconversion of toluenesulfonates to alcohols (O–S cleavage), often a necessary tool for the detailed study of solvolysis reactions, is also important in steroid and carbohydrate chemistry where sulfonate esters are

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