ratio of 41 : 59 is in excellent agreement with the experimentally determined 40 : 60 steady state. The quantum yields for the 1,3-aminoboryl shift are only slightly lower than those measured for the formally analogous 1,3-acyl shifts of β,γ-unsaturated ketones.[16] That the 1,3-shift quantum yields are not higher can probably be attributed to efficient deactivation by the invisible photochemical geometrical isomerization about the boron–nitrogen bond, recently demonstrated to be an important photochemical process in similar aminoboranes.[17]

Attempts to sensitize the 1,3-aminoboryl shift with fluorene (E_T = 68 kcal mol^{-1})[18] failed. However, irradiation of **2** in chlorobenzene (E_T = 82 kcal mol^{-1})[19] at 254 nm (chlorobenzene absorbing *ca.* 85% of incident light) resulted in formation of very small amounts of **1** and a new photoproduct not yet identified. These experiments indicate that the 1,3-aminoboryl shift, like the analogous 1,3 shift in β,γ-unsaturated ketones, is a singlet-state process.

The fact that allyl(amino)boranes, which are isoelectronic with 1,4-dienes, undergo a 1,3 shift that is analogous to the reactivity of β,γ-unsaturated ketones (among others) rather than of 1,4-dienes suggests some interesting inferences about the relative importance of various factors determining photochemical reaction mechanisms. Extended Hückel and *ab initio* calculations indicate the B–N bond in aminoboranes has a net polarization in the sense $B^{\delta+}$–$N^{\delta-}$,[20,21] paralleling the charge distribution in a carbonyl. Photochemical aminoboron–carbon cleavage in the 1,3 shift thus closely resembles the carbonyl–carbon α-cleavage step of a β,γ-unsaturated ketone, despite the absence of strictly nonbonding electrons and n–π^* states in the aminoborane. Although it is thus clear that the aminoborane excited singlet in the 1,3 shift is surely not n–π^*, both π–π^* and σ–π^* singlets are compatible with present data. Calculations on simple aminoboranes in fact predict S_1 to be σ–π^*.[20,21] The corresponding σ-HOMO in allyl(amino)borane would be largely B–C bonding so that α cleavage (α to boron) and a 1,3 shift would be probable in the σ–π^* state. Thus, a general reactivity parallel may exist between ketone n–π^* singlets and σ–π^* aminoborane singlets.[22] Alternatively, mixing of the B–N π system with the π systems of the allyl and/or phenyl moieties may cause the π–π^* state to drop below σ–π^* in allyl(amino)boranes.[23] In this case, the difference in reactivity between a π–π^* 1,4-diene singlet and an allyl(amino)borane π–π^* singlet seems most likely due to the known preference of olefinic π–π^* singlets for a 90°-twisted geometry, an arrangement expected to favor the 1,2 bonding (di-π-methane reaction) observed in 1,4-dienes over the nonobserved 1,3 bonding. In contrast, calculations on aminoboranes predict no such predilection for excited-state twisting.[20,21]

At the moment, we lean toward the hypothesis that the reordering of energy levels occasioned by the electronegativity effects in the B–N bond makes aminoboranes more analogous to ketones than to olefins. However, we are presently exploring the full scope of allylborane photochemistry, including identification of excited states.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 5860-AC3), and from the Research Corporation is gratefully acknowledged.

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[16] See, for example, K. G. Hancock and R. O. Grider, *Tetrahedron Lett.*, 1367 (1972).

[17] K. G. Hancock and D. A. Dickinson, *J. Amer. Chem. Soc.*, **94**, 4396 (1972).

[18] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

[19] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

[20] R. Hoffmann, *J. Chem. Phys.*, **40**, 2474 (1964).

[21] D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

[22] Another example of the σ–π^* aminoborane–n–π^* ketone analogy may be found in comparing biacetyl and bis(amino)diborane(4) photochemistry.[7]

[23] Conjugation of an aminoborane with a carbon π system has been shown to cause raising of a π-MO energy and lowering of the B-σ-HOMO energy. With strong interaction, inversion of σ and π levels will occur.[24]

[24] A. K. Uriarte and K. G. Hancock, *Inorg. Chem.*, in press.

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Participation of an sp Hybrid Center in the Di-π-methane Rearrangement[1]

Sir:

In an extension of our studies on the di-π-methane rearrangement[2] we have investigated *cis*- and *trans*-1,5-diphenyl-3-methyl-3-methoxy-1-penten-4-yne (**1**), in which the di-π moieties bound to the sp^3 center are styryl and phenylethynyl groups. Our objective was to assess the migratory potential of an sp center and to evaluate the effect of C-1 stereochemistry on the reaction course.[3]

The enyne **1b** was prepared by addition of phenylethynylmagnesium bromide to benzalacetone and subsequent etherification of the resulting alcohol.[4] The cis isomer **1a** was obtained from **1b** by acetophenone-sensitized photoisomerization (at 350 nm).[5a] The assignment of cis and trans stereochemistry is based upon infrared and 100-MHz pmr data.[5b] A 10.30-μ band characteristic of trans 1,2-disubstituted alkenes appears in the infrared spectrum of **1b** and is absent in that of **1a**.[6a] Trans vicinal coupling constants for vinyl protons in isomeric 1,2-disubstituted alkenes are generally larger than their cis counterparts as is the case for **1a** and

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[1] Presented in part by J. Perreten and G. W. Griffin at the 27th Southwestern Regional Meeting of the American Chemical Society, San Antonio, Tex., Dec 1–3, 1971, Abstract No. 238.

[2] B. Halton, M. Kulig, M. A. Battiste, J. Perreten, D, M. Gibson, and G. W. Griffin, *J. Amer. Chem. Soc.*, **93**, 2327 (1971).

[3] An independent investigation of the effect of stereochemistry of a methyl group at C-1 on the rearrangement was recently reported. See H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **92**, 6267 (1970).

[4] Satisfactory analyses and mass spectra were obtained on all compounds with the exception of **2b**.

[5] (a) Irradiations were conducted in a Rayonet RPR-100 reactor (The Southern New England Ultraviolet Co., Middletown, Conn.) equipped with 16 8-W 254- or 350-nm lamps; (b) pmr spectra were recorded on a Varian HA-100 instrument.

[6] (a) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 25; (b) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, Oxford, England, 1969, p 301; (c) *ibid.*, p 286.

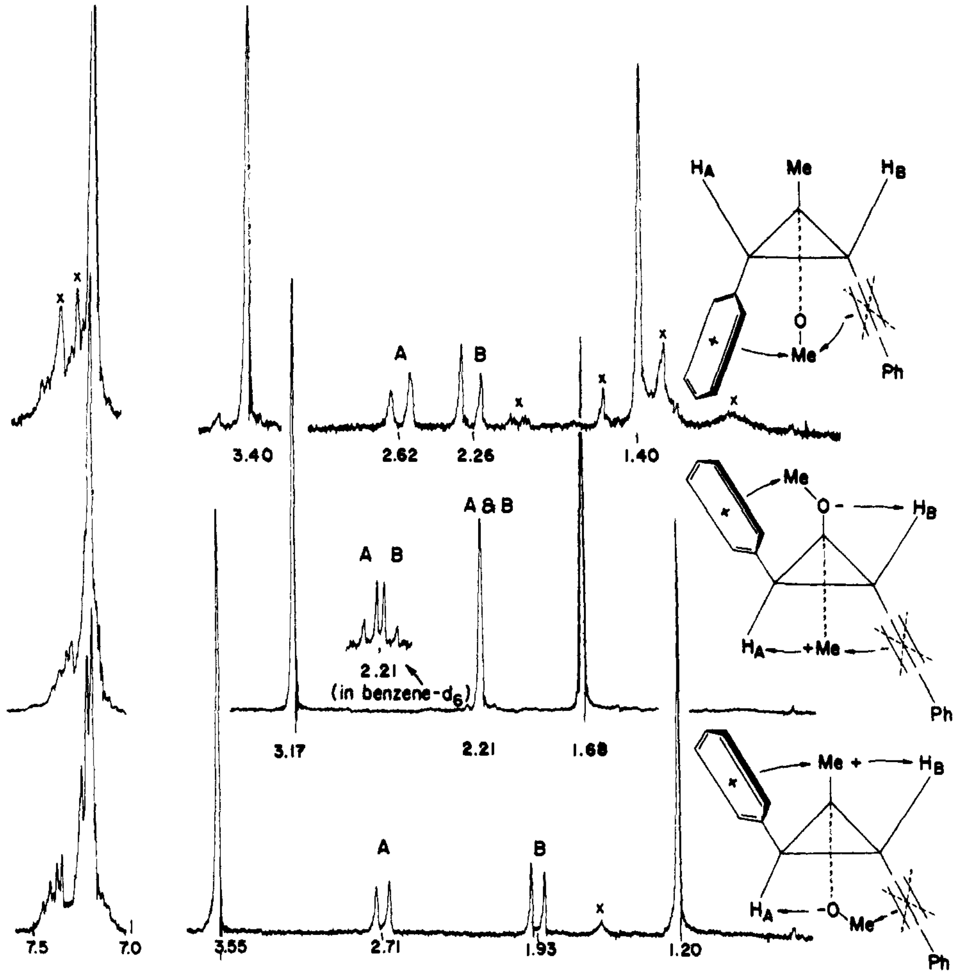
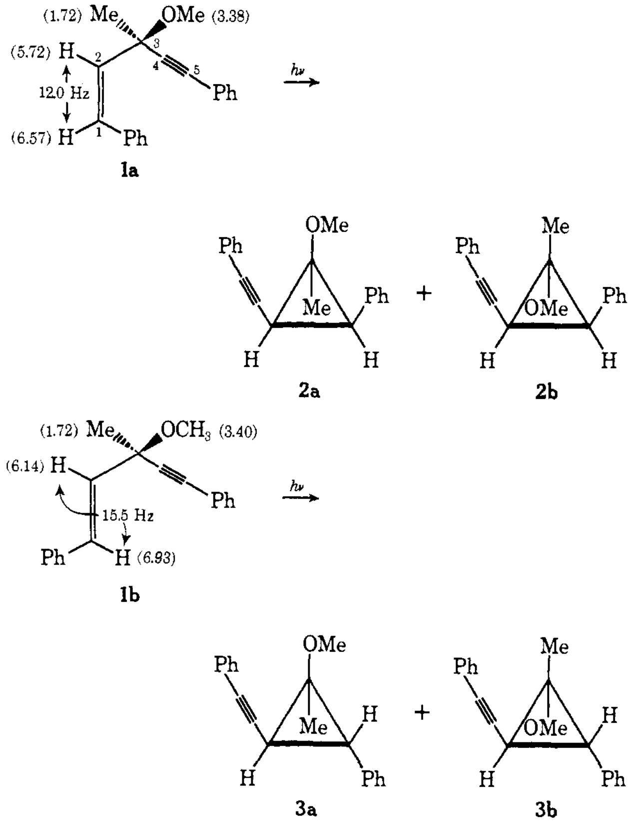


Figure 1. 100-MHz spectra of cyclopropyl derivatives in $CDCl_3$ and benzene-d_6; x = impurities.



1b.[6b] The significant pmr chemical-shift data (δ, CCl_4) and coupling constants (hertz) for **1a** and **1b** are indicated on their respective structures.

Direct irradiation (at 254 nm)[5a] of **1b** for 30 min (~10% conversion) in *tert*-butyl alcohol (5×10^{-2} *M*) afforded two main photoproducts, **3a** (mp 36–37°) and **3b** (mp 68–69°), in a 2:1 ratio.[7] Irradiation of **1a** under similar conditions gave **2a** (mp 48–49°) and **2b**[4] in addition to lesser amounts of **3a** and **3b**. The presence of **3a** and **3b** among the photoproducts obtained from **1a** is attributed to prior photoisomerization of **1a** to **1b**.

The structural assignments **2a**, **2b**, **3a**, and **3b** rest on 100-MHz pmr spectral data and nuclear Overhauser effect results. The disappearance of the two olefinic proton doublets, emergence of the AB doublet of doublets, and retention of the aromatic proton resonance pattern characteristic of the phenylethynyl and phenyl protons indicate that **1a** and **1b** are converted to isomeric cyclopropanes at the expense of the styrenyl rather than the phenylethynyl group, which was verified by infrared spectroscopy. The cis and trans isomeric cyclopropanes were differentiated by the magnitude of vicinal spin–spin interactions of the cyclopropyl protons. J_{cis} (7.0–12.6 Hz) is nearly always larger than J_{trans} (4.0–9.6 Hz)[6c] and the presence of an 11.0-Hz vicinal proton coupling in **2a** and a 9.5-Hz

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[7] Analytical data were obtained on product mixtures by integration of 100-MHz pmr spectra using the methyl and methoxy protons.

coupling in **2b** attests to their cis geometry. Correspondingly, trans configurations were assigned to **3a** and **3b** on the basis of a vicinal coupling of 6.5 Hz observed for both (Figure 1).

The stereochemistry of each product was deduced utilizing long-range anisotropic shielding and deshielding effects. The results of this self-consistent correlation are depicted in Figure 1. Appropriate nuclear Overhauser effect experiments were also performed to verify the assignments. Although a pure sample of **2b** was not obtained, pmr data obtained on mixtures enriched with **2b** are consistent with the cis structure advanced.

The efficiency with which the acetylenic function participates as the migrating moiety in the rearrangement is intriguing. Relative migratory aptitudes for sp and sp^2 centers cannot be inferred from the fact that PhC≡C migrates to the exclusion of PhCH=CH since the alternate and undetected rearrangement path available for **1a** and **1b** would consist of cyclization with ultimate incorporation of the sp-hybridized atoms 4 and 5 into a cyclopropene ring, which may be inherently less favorable than the observed process involving inclusion of the sp^2 centers 1 and 2 into a cyclopropane ring.

The stereochemical outcome also represents a novel feature of the di-π-methane rearrangement observed for **1a** and **1b**. Such stereospecificity is assumed to be associated with a high degree of concertedness for the bond cleavage and bond formation processes required for atom reorganization of the di-π-methane type. The photorearrangement of **1b** may be formulated as a 4q system as proposed by Woodward and Hoffmann[8] in which a single bond (3–4) adds to a π bond (1–2), *i.e.*, a $[_\pi 2_a + {}_\sigma 2_a]$ cycloaddition. The results of the analysis using all of the $[_\pi 2_s + {}_\sigma 2_s]$ and $[_\pi 2_a + {}_\sigma 2_a]$ combinations of orbitals and two nearly isoenergetic conformations of **1b** confirm that all four possible stereochemically distinct π-cyclopropanes **2a**, **2b**, **3a**, and **3b** may be formed through symmetry-allowed photochemical routes. Presumably additional structural and/or electronic factors determine the lowest energy pathways leading to the preferred products observed.

Neglect of the acetylenic orbitals is at best qualitative since a second π bond is apparently required for facile rearrangement to occur. While there are reported examples of related rearrangements in which a hydrogen or alkyl group migrates, efficiencies of such reactions are lower than that observed for **1a** and **1b**.[9,10] It is noteworthy, however, that overall predictions based upon analysis of the reaction as a $[_\pi 2 + {}_\sigma 2 + {}_\pi 2]$ cycloaddition are identical with those reached above.[11]

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[8] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970, p 97.

[9] (a) G. W. Griffin, A. F. Marcantonio, H, Kristinsson, R. C. Petterson, and C. S, Irving, *Tetrahedron Lett.*, 2951 (1965); (b) H. Kristinsson and G, W. Griffin, *J. Amer. Chem. Soc.*, **88**, 378 (1966); (c) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *J. Amer. Chem. Soc.*, **84**, 2268 (1962); (d) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966); (e) O. L. Chapman, T. A. Rettig, A. A. Griswold, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

[10] The role of this second π bond has recently been evaluated and it was concluded that the di-π-methane rearrangement is best described as a $[_\sigma 2_a + {}_\sigma 2_a + {}_\pi 2_a]$ process: H. E. Zimmerman and R. D. Little, *J. Amer. Chem. Soc.*, **94**, 8256 (1972).

[11] Analysis of this photoconversion as a $4n + 2$ system from the Zimmerman Möbius-Hückel perspective leads to equivalent results: H. E. Zimmerman, *J. Amer. Chem. Soc.*, **88**, 1564, 1566 (1966); *Accounts Chem. Res.*, **4**, 272 (1971).

Conversion of Ketones to Epoxides *via* β-Hydroxy Sulfides[1]

Sir:

Nucleophilic alkylidene transfer from a sulfur ylide to a carbonyl group is the standard method for achieving the conversion of an aldehyde or ketone to an oxirane.[2] Such reactions are quite general, but in some instances the reactions fail. The two most prevalent reasons for failure are (1) enolization of the substrate[3] and (2) steric hindrance.[4] It appeared to us that one might be able to circumvent these difficulties by use of a simple multistep sequence for the transformation, the first step of which would employ a reagent of amplified nucleophilicity. The model reagent which we chose for this purpose was phenylthiomethyllithium, which is readily prepared by reaction of *n*-butyllithium and thioanisole in the presence of 1,4-diazabicyclo[2.2.2]octane (Dabco).[5] This reagent readily adds to aldehydes and ketones to yield β-hydroxy sulfides[5,6] which, in turn, can be transformed to oxiranes by alkylation at sulfur followed by treatment with base (Scheme I). Note that the intermediate betaine generated by this method[7] is identical with that which would be produced by addition of an alkylphenylsulfonium methylide to the carbonyl compound.

Both dimethylsulfonium and dimethyloxosulfonium methylide fail to produce epoxide when allowed to react with deoxybenzoin, presumably because of the ease of enolization of this material by basic reagents. Using the method just described we have been able to convert deoxybenzoin to 2-benzyl-2-phenyloxirane in 79% yield. Utilizing methylthiomethyllithium,[8] a like method applied to the highly hindered 2,2,6,6-tetramethylcyclohexanone resulted in the formation of 4,4,8,8-tetramethyl-1-oxaspiro[2.5]octane in 80% yield. Other examples are summarized in Table I.

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[1] Part XLIII in the series "Chemistry of Sulfoxides and Related Compounds."

[2] For a review see A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966.

[3] E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

[4] E. J. Corey and W. Oppolzer, *ibid.*, **86**, 1899 (1964); W. E. Parham and L. J. Czuba, *ibid.*, **90**, 4030 (1968).

[5] E. J. Corey and D. Seebach, *J. Org. Chem.*, **31**, 4097 (1966).

[6] These same intermediates may be converted to olefins by reductive elimination of their acyl derivatives: R. L. Sowerby and R. M. Coates, *J. Amer. Chem. Soc.*, **94**, 4758 (1972).

[7] For previous examples of generation of betaines by this method see M. Yashimini and M. J. Hatch, *ibid.*, **89**, 5831 (1967); C. R. Johnson and C. W. Schroeck, *ibid.*, **93**, 5303 (1971); T. Durst, R. Viau, and M. R. McCloy, *ibid.*, **93**, 3077 (1971); T. Durst, R. Viau, R. VanDen Elzen, and C. H. Nguyen, *Chem. Commun.*, 1334 (1971); J. M. Townsend and K. B. Sharpless, *Tetrahedron Lett.*, 3313 (1972).

[8] D. J. Peterson, *J. Org. Chem.*, **32**, 1717 (1967).