

may be found in which decay and relaxation are competitive.

Finally the results suggest that caution should be exercised in interpreting ion pair relaxation phenomena that are monitored by their electronic spectra.⁹

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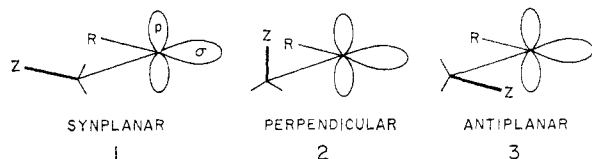
(9) E. M. Eyring, private communication.

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Stereoselectivity of 1,2-Hydrogen Shifts in Carbene Rearrangements¹

Sir:

A common and synthetically useful reaction of carbenes is intramolecular rearrangement (*i.e.*, 1,2-insertion) to give an olefin.² Such rearrangements are characteristic of singlet, rather than triplet, carbenes.³ Three extreme orientations of a migrating group (Z) with respect to the carbene center can be envisaged. These may be termed synplanar (**1**), perpendicular (**2**), and antiplanar (**3**), corresponding respectively to di-



hedral angles of 0, 90, and 180° between the C-Z and C-R bonds. Extended Hückel and MINDO/2 calculations on CH₃CH suggest a conformational barrier less than 1 kcal/mol.⁴

Our objective was to learn whether the ease of migration depends on geometry. Unlike the case of carbonium ions, prediction of stereochemical dependence in carbene rearrangements is not straightforward. Carbenes can exist in three singlet states (σ^2 , p^2 , σp), each with a different bond angle and with the two electrons paired differently in the σ and p nonbonded orbitals.^{4a} Although σ^2 is thought to be the lowest of these singlet states for CH₂, this need not be so for carbenes that are electronically or geometrically per-

(1) Supported by the National Institutes of Health (Grant GM 06304) and by the National Science Foundation.

(2) For recent reviews see (a) M. Jones, Jr., and R. A. Moss, Ed., "Carbenes," Vol. I, Wiley, New York, N. Y., 1973; (b) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971.

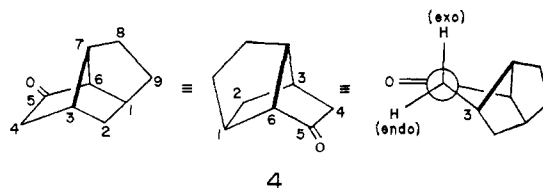
(3) (a) H. E. Zimmerman and J. H. Munch, *J. Amer. Chem. Soc.*, **90**, 187 (1968); (b) I. Moritani, Y. Yamamoto, and S. I. Murahashi, *Tetrahedron Lett.*, 5697, 5755 (1968); (c) M. B. Sohn and M. Jones, Jr., *J. Amer. Chem. Soc.*, **94**, 8280 (1972); (d) For Wolff rearrangements, see D. O. Cowan, M. M. Couch, K. R. Kopecky, and G. S. Hammond, *J. Org. Chem.*, **29**, 1922 (1964); A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965); A. M. Trozollo and S. R. Fahrenholtz, Abstracts, 151st Meeting of the American Chemical Society, March 1966, K23; M. Jones, Jr., and W. Ando, *J. Amer. Chem. Soc.*, **90**, 2200 (1968).

(4) (a) R. Hofmann, G. D. Zeiss, and G. W. Van Dine, *J. Amer. Chem. Soc.*, **90**, 1485 (1968); (b) N. Bodor and M. J. S. Dewar, *ibid.*, **94**, 9103 (1972).

turbed.^{4a,5} Furthermore, depending on the energy of the carbene when it is generated, rearrangement might occur from one of the higher energy states.^{4a} An additional complication is that the geometry and electronic configuration of the olefin initially produced on rearrangement may not correspond to those in its final ground state.^{4a,6a,c}

The stereochemical aspects have been treated by various theoretical approaches,^{4,6} but unequivocal experimental information is lacking.⁷ We now present evidence that in carbenes generated *thermally* by Bamford-Stevens reactions⁸ the ease of rearrangement does depend on geometry and, for hydrogen shifts, the perpendicular orientation (**2**) is better than the antiplanar one (**3**).

Our substrate was the rigidly locked, brexan-5-one (**4**),



which contains a norbornyl ketone somewhat distorted by an additional two-carbon bridge (C-8 and C-9). Molecular models show that this distortion increases the dihedral angle between the carbonyl group and the exo-H at C-4 and decreases the angle for the endo-H at C-4 relative to a normal norbornyl system. The carbonyl carbon becomes the carbene site in a Bamford-Stevens sequence and so the exo and endo C-H bonds in **4** simulate to some degree the perpendicular and antiplanar arrays.

For synthesis of **4** and the required D analogs (**9c** and **9e**), brexan-4-one⁹ (**5**) was converted to brex-4-ene (**6a**; C₉H₁₂, ir 1615, 1585 cm⁻¹; nmr δ 6.01 (C-4), 5.77 (C-5), $J_{4,5} = 5.7$ Hz) by monobromination with pyridine·HBr₃ followed by reduction with NaBH₄ and treatment with zinc.¹⁰ Brex-4-ene-4-*d* (**6b**; nmr δ 5.76 (C-5)), 6% *d*₀, 94% *d*₁, was prepared by use of NaBD₄ in place of NaBH₄. Conventional deuteration (B₂D₆)¹¹ of **6a** followed by acetylation of the alcohol mixture gave a 35:65 ratio of known acetate **7c**⁹ and **8c**. Cleavage of **8c** with LiAlH₄ gave alcohol **8d**, which was oxidized with Brown's reagent¹² to *exo*-brexan-5-one-4-*d* (**9c**; 11% *d*₀, 89% *d*₁) and converted to the tosylhydrazide **9d**. A similar sequence that used B₂H₆ on

(5) (a) R. Gleiter and R. Hofmann, *J. Amer. Chem. Soc.*, **90**, 5457 (1968); (b) N. Bodor, M. J. S. Dewar, and J. S. Wasson, *ibid.*, **94**, 9095 (1972).

(6) (a) O. S. Tee and K. Yates, *J. Amer. Chem. Soc.*, **94**, 3074 (1972); (b) H. E. Zimmerman, *Accounts Chem. Res.*, **5**, 393 (1972); (c) J. A. Altmann, I. G. Csizmadia, and K. Yates, *J. Amer. Chem. Soc.*, **96**, 4196 (1974).

(7) Y. Yamamoto and I. Moritani, *Tetrahedron*, **26**, 1235 (1970).

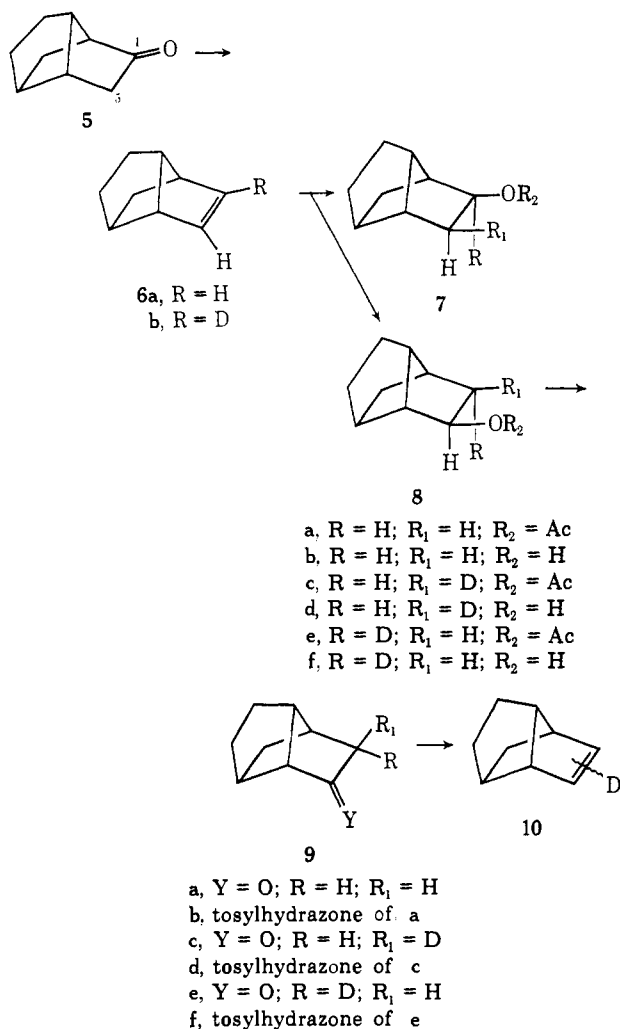
(8) (a) J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 168 (1961); L. Friedman and H. Shechter, *J. Amer. Chem. Soc.*, **83**, 3159 (1961). For leading references see A. Nickon and N. H. Werstiuk, *ibid.*, **94**, 7081 (1972). (b) J. H. Robson and H. Shechter, *ibid.*, **89**, 7112 (1967), have presented kinetic evidence that rearrangement and nitrogen loss from the intermediate diazohydrocarbon are not concerted (at least when the migrating group is SCH₂CH₃).

(9) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Amer. Chem. Soc.*, **87**, 1615 (1965).

(10) Unless noted otherwise nmr (100 MHz) and ir spectra refer to CCl₄ and agreed with proposed structures. Compounds indicated by empirical formula gave satisfactory C and H analyses and are liquids if no melting point is given.

(11) F. Y. Edamura and A. Nickon, *J. Org. Chem.*, **35**, 1509 (1970).

(12) H. C. Brown and C. Carg, *J. Amer. Chem. Soc.*, **83**, 2951 (1961).



brex-4-ene-4-d (6b) gave (via 8e and 8f) the endo 4-d ketone 9e (6% d_0 , 94% d_1) and then its tosylhydrazone 9f.¹³

For carbene generation by Bamford-Stevens reaction the tosylhydrazones were converted with NaOCH₃ to their salts, which were thoroughly dried and pyrolyzed at 170–200° to produce deuterated brex-4-ene (54–58%; >99% pure by glpc). The extent of deuterium loss (e.g., by enolization during preparation and pyrolysis of the tosylhydrazone salts) was revealed by mass spectral analysis. The deuterium at each olefinic site was determined by quantitative pmr (100 MHz with CAT integration) and subtraction of the proportion of d_0 olefin, whose presence therefore does not interfere with the deuterium distribution in the d_1 product. The ratio of D shift vs H shift from both epimers allows calculation of the primary isotope effect (k_H/k_D)¹⁴ and determination of the inherent exo-H/endo-H migration ratio. The first two entries in Table I show that the fractional per cent D loss was low (2–11%) and that for each substrate migration of the exo group (H or D) was strongly preferred. After correction for the isotope effect ($k_H/k_D = 1.30$) the exo/endo migration ratio was 138.

In view of the rigidity in the brexyl skeleton, we conclude that for migration to a carbene center a perpen-

(13) Authentic natural abundance samples: 8a C₁₁H₁₆O₂, ir 1740, 1250 cm⁻¹; nmr δ 4.79 ($J_{cis4,5} = 7.2$ $J_{trans4,5} = 4.0$ Hz); 8b C₉H₁₄O, ir 3605, 1068, 1012 cm⁻¹; nmr δ 3.95, ($J_{cis4,5} = 7.0$ $J_{trans4,5} = 4.0$ Hz); 9a, C₉H₁₂O, ir 1749 cm⁻¹; 9b, C₁₁H₂₀O₂N₂S, mp 214–215° dec.
(14) W. Kirmse and K. Horn, *Chem. Ber.*, 100, 2698 (1967).

dicular orientation of the hydrogen is preferred over an antiplanar orientation. The preference is not reasonably accounted for on steric hindrance grounds because the two hydrogens have comparable steric environments and are free of serious nonbonded interactions.

Photic Bamford-Stevens reactions¹⁵ are being used increasingly in synthetic work as putative carbene sources,¹⁶ and it is presumed, often tacitly, that such irradiations involve diazohydrocarbons and carbenes analogous to the situation for thermal Bamford-Stevens processes.^{15,16} To compare stereoselectivity, we irradiated the tosylhydrazone salt of 9c (suspended in dry pentane in a quartz tube) at 0° for 1 hr with a 450-W medium-pressure Hg lamp and found the migration ratio reduced to 4.8 (last entry Table I). Lower stereo-

Table I. 1,2-Shifts in Thermal and Photic Bamford-Stevens Reactions

Ketone (D config)	Method	Fractional % D loss	Relative amount of shift		Migration ratio exo-H/ endo-H
			D	H	
9c (exo-D)	Thermal	11	106	1	138 ^a
9e (endo-D)	Thermal	2	1	180	
9c (exo-D)	Photic	5	4.8	1	4.8 ^b

^a Corrected for the observed isotope effect of $k_H/k_D = 1.30$ (170–200°). ^b Uncorrected for isotope effect because only one epimer was irradiated. Primary isotope effects of 1.16–1.36 have been reported for H shifts by carbenes from irradiation of diazohydrocarbons.¹⁴

selectivity in the photic Bamford-Stevens suggests a higher energy for the derived "carbene" or, perhaps, that rearrangement occurs from a noncarbene intermediate.

(15) (a) W. G. Dauben and F. G. Willey, *J. Amer. Chem. Soc.*, 84, 1498 (1962); (b) S. Cristol and J. K. Harrington, *J. Org. Chem.*, 28, 1413 (1963); (c) G. L. Closs, L. E. Closs, and W. Böll, *J. Amer. Chem. Soc.*, 85, 3796 (1963).

(16) (a) G. Büchi and J. D. White, *J. Amer. Chem. Soc.*, 86, 2884 (1964); (b) D. M. Lemal and A. J. Fry, *J. Org. Chem.*, 29, 1673 (1964); (c) J. R. Chapman, *Tetrahedron Lett.*, 113 (1966); (d) S. Masamune, K. Fukumoto, Y. Yasunari, and D. Darwish, *ibid.*, 193 (1966); (e) W. Kirmse and K.-H. Pook, *Angew. Chem., Int. Ed. Engl.*, 5, 594 (1966); (f) S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, 89, 4808 (1967); (g) R. E. Moser, J. M. Fritsch, T. L. Westman, R. M. Kliss, and C. N. Mathews, *ibid.*, 89, 5673 (1967); (h) W. M. Jones and C. L. Ennis, *ibid.*, 91, 6391 (1969); (i) K. Kondo and I. Ojima, *J. Chem. Soc., Chem. Commun.*, 62, 63, 860 (1972); (j) I. Ojima and K. Kondo, *Bull. Chem. Soc. Jap.*, 46, 1539 (1973).

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Reaction of Pyridine 1-Oxides with Benzyne.

β -Hydroxyarylation of Pyridines via $[\sigma 2_s + \pi 2_a + \pi 4_s]$ Rearrangements

Sir:

In the reaction of six-membered heteroaromatic *N*-oxides with suitable acetylenes, β -alkylated products^{1,2}

(1) R. A. Abramovitch, G. Grins, R. B. Rogers, J. L. Atwood, M. D. Williams, and S. Crider, *J. Org. Chem.*, 37, 3383 (1972).

(2) R. A. Abramovitch and I. Shinkai, *J. Chem. Soc., Chem. Commun.*, 569 (1973).