Although **8** is not known and its thermal behavior is uncertain, one can assume that it may undergo ring opening under the reaction conditions to produce the highly stabilized pentadienyl radical **9**[12] which could then close under the formation of **5**.[13]

We are currently engaged in a series of experiments to gain further insight into the detailed mechanism of this system.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support of this research.

References and Notes

(1) (a) Brown, J. M.; Golding, B. T.; Stofko, J. J., Jr. *J. Chem. Soc., Chem. Commun.* **1973,** 319. (b) Schneider, M.; Rebell, J. *ibid.*, **1975,** 283. (c) Schneider, M. *Angew. Chem., Int. Ed. Engl.* **1975,** *14*, 707.

(2) (a) Stogryn, E. L.; Gianni, M. H.; Passanante, A. J. *J. Org. Chem.* **1964,** *29*, 1275. (b) Braun, R. A. *ibid.* **1963,** *28*, 1383. (c) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* **1967,** *6*, 385. (d) Pommelet, J. C.; Manisse, N.; Chuche, J. *Tetrahedron.* **1972,** *28*, 3929.

(3) (a) Stogryn, E. L.; Brois, S. J. *J. Org. Chem.* **1965,** *30*, 88. (b) Pommelet, J. C.; Chuche, J. *Tetrahedron Lett.* **1974,** 3897.

(4) (a) Doering, W. E.; Roth, W. R. *Tetrahedron.* **1963,** *19*, 715. (b) Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1963,** *2*, 1. (c) Arai, M.; Crawford, R. J. *Can. J. Chem.* **1972,** *50*, 2158. (d) Ullenius, C.; Ford, P. W.; Baldwin, J. E. *J. Am. Chem. Soc.* **1972,** *94*, 5910. (e) Stogryn, E. L.; Brois, S. J. *ibid.* **1967,** *89*, 605.

(5) This is probably due to an observed predominance of sulfur extrusion leading to the corresponding olefins. Loss of sulfur occurs readily in a large number of thiiranes with electron-withdrawing and conjugated substituents. (a) Braslavsky, S.; Heicklen, J. *Chem. Rev.* **1977,** *77*, 473. (b) Sander, M. *ibid.* **1965,** *65*, 297. The synthesis of **1c** was claimed in a footnote,[3a] but no details were ever published.

(6) (a) Mock, W. L.; *J. Chem. Soc., Chem. Commun.* **1970,** 1254. (b) Paquette, L. A.; Maiorana, S. *ibid.* **1971**, 313. We thank Professor Paquette for copies of the NMR spectra.

(7) All new compounds gave satisfactory analytical data and all spectroscopic properties were in good agreement with the proposed structures.

(8) NMR data were readily interpreted by comparison with the derivative obtained from cyclohepta-1,3-diene, accounting for the sulfur bridge.

(9) One referee suggested that **1t** could be a precursor for **5** in the thermolysis of **1c.** While our control experiments gave no evidence for such an interconversion, the possibility cannot be ruled out completely.

(10) **7a** and **7b** are stabilized by allylic delocalization; similarly, S radicals are known to be quite stable.[5a]

(11) This process is well established in the vinylcyclopropane–cyclopentene rearrangement.

(12) Pentadienyl radicals are stabilized by between 4 and 9 kcal/mol (depending on the source) over allylic radicals and could well account for a lowering of the activation enthalpy for the reaction **8** → **9:** Pettus, J. A. Jr.; Moore, R. E. *J. Am. Chem. Soc.* **1971,** *93*, 3037.

(13) Alternatively, conrotatory opening for the C–C bond in **1c** and **1t,** a process well documented in the thermolysis of oxiranes,[2d] would lead to isomeric thiocarbonyl ylides.[14] Their disrotatory ring closure would lead to 2-vinyl-2,3-dihydrothiopene, which could, via a similar sequence of diradicals, provide another route to **5**.

(14) For formation and reactions of thiocarbonyl ylides, see Buter, J.; Wassenar, S.; Kellogg, R. M. *J. Org. Chem.* **1972,** *37*, 4045.

Manfred P. Schneider,* Margit Schnaithmann
Institut für Chemie, Universität Hohenheim
D-7000 Stuttgart-70, West Germany

Received August 17, 1978

Photolysis of Aryldiazo Compounds in Rigid Matrices. Temperature and Matrix Effects on the Selectivities of Insertion of Arylcarbenes into Carbon–Hydrogen Bonds

Sir:

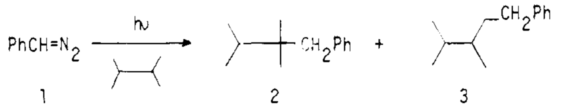
Recent reports from this[1] and other[2] laboratories have demonstrated that the low-temperature photolysis of aryldiazo compounds in rigid matrices can be a unique and widely applicable method for detecting triplet arylcarbene chemistry, especially in the systems in which competitive singlet and triplet reactions occur. The C–H "insertion" products derived from triplet carbene in rigid matrices of olefins and alcohols, which apparently arise via an abstraction-recombination mechanism, are in many cases entirely different from those observed[3] in liquid phase experiments. The difference may be explained mainly in terms of a difference in diffusibility between two reaction phases. In order to obtain more precise insight into the mechanism by which the matrix controls C–H insertion processes within it, we have investigated carbene processes in matrices of alkane which are, unlike other systems thus far reported,[1,2] not able to lead to *multiplicity-specific* products. We find that the matrix not only selects the multiplicity of arylcarbenes, but it also imposes a severe steric demand on carbene processes within it.

Table I. Temperature and Matrix Effects on C–H Insertion Selectivity of Phenylcarbene[a]

substrate	ratio	rel ratio[b] 0 °C	rel ratio[b] −196 °C
isobutane	tertiary:primary	118	4.1
2,3-dimethylbutane	tertiary:primary	69	6.5
isopropyl ether	tertiary:primary	194	4.3
isopropyl alcohol[c]	tertiary:primary	194	26
n-butane	secondary:primary	9.6	2.7
n-pentane	secondary:primary	9.0	4.9
	d	1.4	0.3
ethyl ether[e]	secondary:primary	148	17
ethyl alcohol[c]	secondary:primary	150	20

[a] All products were identified by GC comparisons with authentic samples and GC-mass spectral techniques. Other minor products detected in each experimental condition were toluene, bibenzil, benzaldehyde, benzaldazine, and stilbenes. [b] Corrected for number of hydrogens. Averages of triplicate runs are tabulated; reproducibility was <±3%. [c] The O–H insertion product was main one (>73%) in 0 °C photolysis and C–H insertion became dominant (>70%) in the solid run.[1a] [d] Ratio of 2- to 3-benzylpentanes. [e] Benzyl ethyl ether was formed in 30% yield of total products at 0 °C, but was not detected in −196 °C photolysis.

Direct irradiation of phenyldiazomethane (**1**) in degassed 2,3-dimethylbutane in a sealed Pyrex tube at 20 °C was carried out by a 300-W high-pressure mercury arc without filter until all of the diazo compound was destroyed. GC analysis of the resulting mixture showed that two C–H insertion products (**2** and **3**) were formed (~75%) in a ratio of 11.5:1.0. In contrast,



1 2 3

(1)

irradiation of **1** in frozen 2,3-dimethylbutane matrix at −196 °C resulted in a dramatic increase in the relative yield of the primary C–H insertion product (**3**), the ratio of **2:3** being 1.08:1.0. A similar but less dramatic increase in the relative yield of primary C–H insertion product was also observed in *n*-butane. The product distributions in other alkanes were also examined as a function of temperature and are given in Table I on a "per bond" basis. Included for comparison are the results for ether and alcohols. A more extensive temperature study has been performed on 2,3-dimethylbutane (mp −129 °C) and the results are shown in Figure 1. There is a sharp discontinuity (maximum) in the graph as the reaction phase changes from liquid to solid. This clearly indicates that the observed change in the insertion selectivity in the solid is ascribable not to a simple temperature effect at all but totally to a change in environment.

Which multiplicity is responsible for the emerging dominance of the primary C–H insertion product in the solid-phase experiments? It is important to note that, in alcoholic system, the C–H insertion products which were believed to be derived from triplet carbene showed a similar decrease in the insertion selectivity in the solid phase. Equally noteworthy are the results in the ether; the C–O displacement product, i.e., ethyl benzyl ether, formed in the photolysis of **1** in ether solution, apparently via attack of singlet carbene on oxygen atom,[4] was almost

0002-7863/79/1501-0256$01.00/0

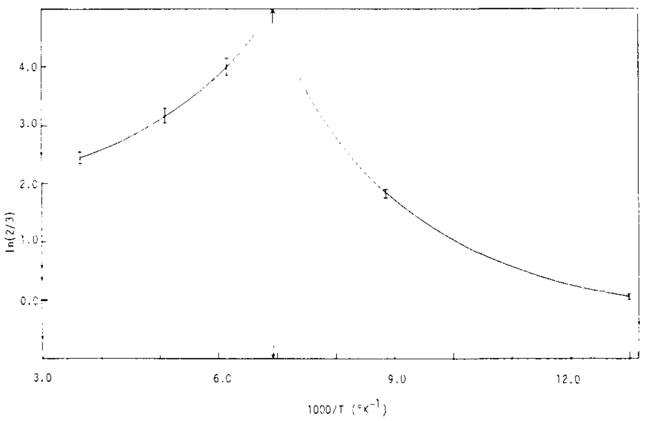


Figure 1. Product ratio as a function of temperature in reaction 1. The point marked ↑ shows melting point of the solvent.

completely suppressed in the solid-phase experiment at −196 °C, and was accompanied by a marked increase in the primary C–H insertion product. This indicates that triplet carbene chemistry is prevailing also in this matrix system and provides another example for the temperature-dependent phenomena of competitive singlet and triplet arylcarbene processes. These results, together with the spectroscopic evidence[5] that triplet arylcarbene can be generated irrespective of the organic matrices in which the low-temperature photolysis of the diazo compound is performed, apparently indicate that the key intermediate leading to the C–H insertion products in each matrix systems would be mostly triplet carbene,[6] while both singlet and triplet would participate in liquid-phase reactions.[4a,b] The decrease in the C–H insertion selectivity observed in rigid matrix is, however, completely unexpected behavior for triplet carbenes since triplet carbenes have been shown to be much more selective intermediates in the C–H insertion reaction than the corresponding singlets in gas- as well as liquid-phase experiments.[4a,b,7] The reason for the marked increase in the primary C–H insertion product in rigid matrix is then an important question.

There is a possibility that the primary C–H insertion product would be formed by combination of a benzyl radical with a primary radical (e.g., i-$C_4H_9\cdot$) produced by photoisomerization of an initially formed tertiary radical (e.g., t-$C_4H_9\cdot$) since such isomerization has been reported[8] to occur by UV (<300 nm) irradiation in low-temperature matrices. However, this seems unlikely since the product distributions at low temperature are essentially independent on the wavelength employed (253~366 nm). A more probable explanation is that the matrix imposes steric demand on the C–H insertion processes. Obviously the molecules which are going to participate in a matrix reaction occupy a space of a certain size and shape which depends on the relative size of guest and host molecules.[9] It is therefore not unreasonable to assume that the size and shape provided by the host molecule and its rigidity impose severe steric hindrance on the guest molecule (i.e., PhCH:) as regards the accessibility of tertiary and/or secondary C–H bonds. A similar argument can be applied to explain the dramatic change in the insertion selectivity toward the secondary C–H bonds of n-pentane with temperature. It is tempting to assume that the carbene is trapped in cages of n-pentane matrix framework in a manner in which the C–H bonds at the 3 position are brought closer to the carbene center than those at other positions. Support is lent to the above argument by examination of the results in Figure 1 which show inversion of tertiary/primary selectivity. Thus, in solution, tertiary abstraction gains over primary abstraction as temperature decreases because tertiary abstraction is favored by a lower activation energy. After the matrix is formed, continued decrease of temperature hardens the matrix and the increasing rigidity then causes primary abstraction to gain relative to tertiary abstraction.[10]

In conclusion, the present results reveal that, in addition to effects on the multiplicity of carbenes and on the mobility of molecules, a matrix imposes severe steric demands on the reactions of carbenes within it. Similar steric effect could be operative in other types of reactions of carbenes and may account for *matrix-fostered* reactions of carbene.

References and Notes

(1) (a) H. Tomioka and Y. Izawa, *J. Am. Chem. Soc.*, **99,** 6128 (1977). (b) H. Tomioka, T. Inagaki, and Y. Izawa, *J. Chem. Soc., Chem. Commun.*, 1023 (1976); *J. Chem. Soc., Perkin Trans. 1*, in press.

(2) (a) R. A. Moss and U.-H. Dolling, *J. Am. Chem. Soc.*, **93,** 954 (1971); (b) R. A. Moss and M. A. Joyce, *ibid.*, **99,** 1262 (1977); (c) R. A. Moss and J. K. Huselton, *ibid.*, **100,** 1315 (1978); (d) R. A. Moss and M. A. Joyce, *ibid.*, **100,** 4475 (1978).

(3) (a) Main product of triplet Ph_2C in liquid alcohol has been shown to be Ph_2CH_2; see, for example, D. Bethell, G. Stevens, and P. Tickle, *Chem. Commun.*, 792 (1970). (b) Moritani et al. showed that triplet $PhCCH_3$ generated in 2-butene solutions by photosensitized decomposition of the diazo compound resulted in nonstereospecific addition and no detection of C–H insertion product: Y. Yamamoto, S.-I. Murahashi, and I. Moritani, *Tetrahedron*, **31,** 2663 (1975). (c) Reference 2c shows, however, continuous behavior of the Ph_2C triplet–isobutene abstraction reaction from 0 to −196 °C.

(4) (a) W. Kirmse, "Carbene Chemistry", 2nd ed., Academic Press, New York, N.Y., 1971, p 430; (b) R. A. Moss and M. Jones, Jr., Ed., "Carbenes", Vol. I, Wiley, New York, N.Y., 1974, p 114; (c) H. Iwamura, Y. Imahashi, K. Kushida, K. Aoki, and S. Satoh, *Bull. Chem. Soc. Jpn.*, **49,** 1690 (1976); (d) G. K. Agopian, D. W. Brown, and M. Jones, Jr., *Tetrahedron Lett.*, 2931 (1976).

(5) A. M. Trozzolo, *Acc. Chem. Res.*, **1,** 329 (1968), and references cited therein.

(6) (a) Abstraction of hydrogen from C–H bonds by triplet carbene, followed by recombination, leads to apparent "insertion" products. (b) We do not completely exclude the intervention of singlet carbene in rigid matrix experiment since rapid and reversible singlet–triplet equilibrium has been assumed[4a,b] to be involved in phenylcarbene reactions. However one-step insertion of singlet carbene would become less favorable at lower temperature since the process should have a higher activation energy compared with other radical processes if one assumes triangle transition state: C. D. Gutsche, G. L. Bachman, W. Udell, and S. Bäuerlein, *J. Am. Chem. Soc.*, **93,** 5172 (1971).

(7) Part of the apparent selectivity has been due to the selectivity of the abstraction reaction: R. W. Carr, Jr., *J. Phys. Chem.*, **70,** 1971 (1966); B. M. Herzog and R. W. Carr, Jr., *ibid.*, **71,** 2688 (1967); M. L. Halberstadt and J. Crump, *J. Photochem.*, **1,** 295 (1972/72); M. Jones, Jr., W. Ando, M. E. Hendrick, A. Kulczycki, Jr., P. M. Howley, K. F. Hummel, and D. S. Malament, *J. Am. Chem. Soc.*, **94,** 7469 (1972).

(8) M. Iwasaki and K. Toriyama, *J. Chem. Phys.*, **46,** 2852 (1967).

(9) (a) B. Meyer, "Low Temperature Spectroscopy", Elsevier, New York, N.Y., 1971; (b) A. M. Bass and H. P. Broida, Ed., "Formation and Trapping of Free Radicals", Academic Press, New York, N.Y., 1960.

(10) We thank a referee for drawing our attention to this point.

Hideo Tomioka
Department of Industrial Chemistry
Faculty of Engineering, Mie University
Tsu, Mie, 514 Japan

Received May 29, 1978

Thionium Ions as Reactive Carbonyl Equivalents in Cyclization Reactions

Sir:

The high polarity and low π-bond order of the thionium group suggests that it should be more reactive toward weak nucleophiles such as aromatic rings than a simple carbonyl group. The lower activity of the latter has restricted cyclizations involving such a functional group to non-acid-labile systems. We report that thionium ions allow formation of six-membered rings with electron-rich aromatic systems.[1] Furthermore, the mildness of the conditions and the potential utility in the ergot alkaloid field is illustrated by the application to the acid-sensitive and difficultly accessible 4-substituted, 2,3-unsubstituted indole system.

Thionium ions for cyclization (eq 1) were generated in one of three ways, ionization of a thioketal, ionization of a monosulfoxide of a thioketal, or protonation of a vinyl sulfide. Since

0002-7863/79/1501-0257$01.00/0