CHEMISTRY LETTERS, pp. 119-122, 1972. Published by the Chemical Society of Japan

INTRAMOLECULAR FORMATION OF YLIDES FROM CARBENES BEARING SULFUR ATOM ON γ-POSITION

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The thermal decomposition of a sodium salt of 4-phenylthio-4-methyl-2-pentanone tosylhydrazone in diglyme at 150-160°C afforded a mixture of 1,2,2-trimethylcyclopropyl phenyl sulfide (17 %), 2,2,3a-trimethyl-1,2,3,3a-tetrahydro-1-thiaazulene (9 %), and isomeric 4-phenylthio-4-methylpentenes (74 %). Analogous mixtures in varying amounts were obtained from tosylhydrazones derived from 4-phenylthio-2-butanone, 3-phenylthiobutyrophenone, and 3-phenylthio-3-methylbutyrophenone.

Many reports on the formation of ylides by the intermolecular electrophilic addition of carbenes to the lone pair of hetero atoms can be found in literature$^{1)}$. Relatively little is known, however, on the intramolecular counterpart of this addition, especially, in view of the ylide formation$^{2)}$. Present communication is concerned with the intramolecular formation of ylides from carbenes bearing sulfide linkage on γ-position and a novel type rearrangement of these ylides.

For the *in situ* generation of the aforementioned carbene, we decomposed a sodium salt of 4-phenylthio-2-butanone tosylhydrazone (**1a**) in diglyme at 150-160°C. Products were separated and purified by column chromatography on silica and/or by preparative vpc. The structural assignments were based on spectra and analyses$^{3)}$. Following compounds were identified in the product from **1a**; 1-methylcyclopropyl phenyl sulfide (**2a**), 2-butenyl phenyl sulfide (**3a**), 3-butenyl phenyl sulfide (**4a**), and 3a-methyl-1,2,3,3a-tetrahydro-1-thiaazulene (**5a**). The nmr data for **2a** and **5a** are as follows (CCl_4, TMS); 2a:τ9.14 (ABq, *J*=7.0 Hz, 4H), 8.56 (s, 3H), and 3.00-2.70 (m, 5H); **5a**: 9.15 (s, 3H), 7.65 (oct., 2H), 7.20 (oct., 2H), 5.01 (d, *J*=10 Hz, 1H), and 4.20-3.80 (m, 4H). Similar decomposition of tosylhydrazone **1b** afforded a mixture of cyclopropyl sulfide **2b**, olefins **3b** and **4b**, and tetrahydrothiaazulene **5b**. Total yields and ratios of the products are collected in Table 1. When the substituent on carbene carbon was changed from methyl to phenyl, the yield of cyclopropyl sulfides (**2c** and **2d**) increased remarkably and tetrahydrothiaazulene corresponding to formula **5** could not be obtained. The formation of these products can be rationalized by the following scheme.

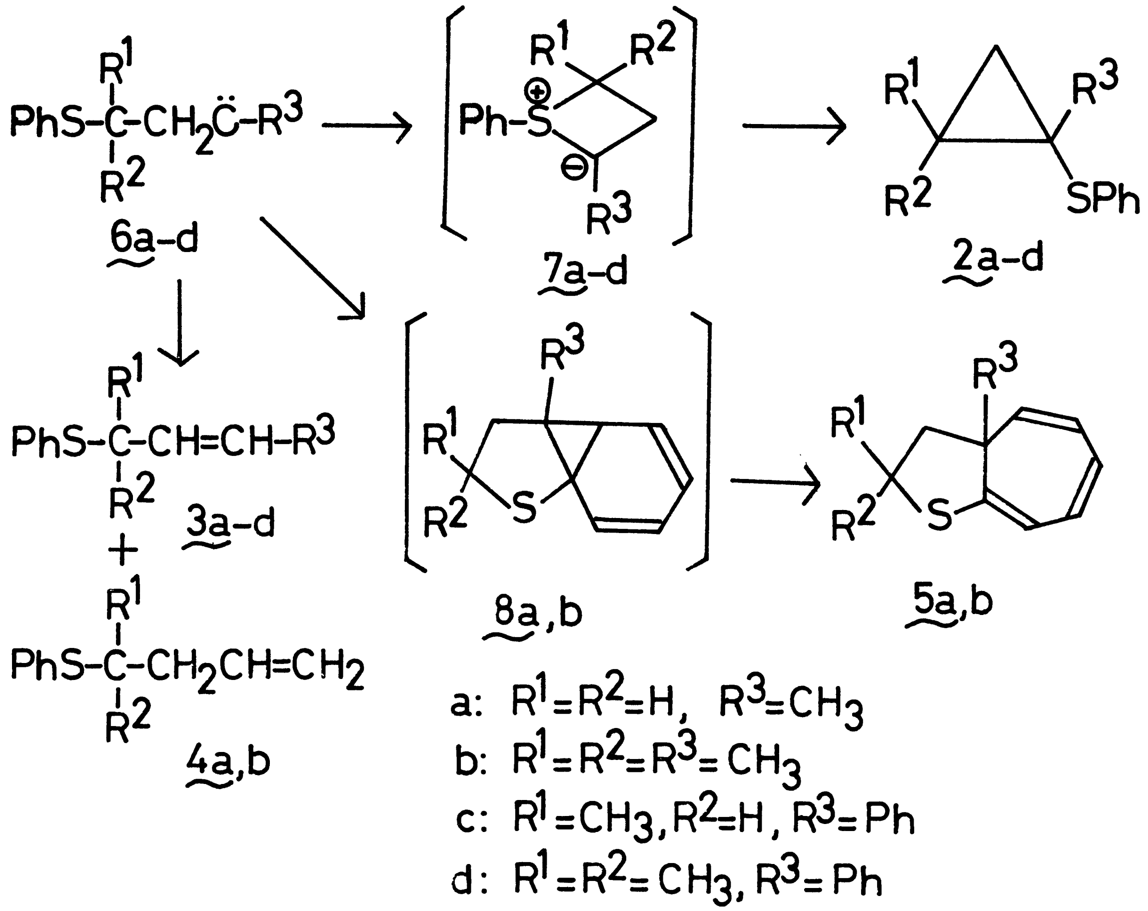

Table 1. Substituent Effect on the Product Yields observed in the Intramolecular Reaction of γ-Thioalkylcarbenes in Diglyme

Carbene	Total Yields(%)[a]	Product Yields(%)[a] 2	3	4	5	Yr[b]
6a	81.2	5.4	77.3[c]	10.6	6.8	7.0
6b	90.0	17.4	66.0[d]	7.2	9.4	26.4
6c	93.5	31.8	68.2[e]			46.6
6d	94.0	45.5	54.5[d]			83.5

[a] Yields were calculated by comparing the vpc peak area of crude products with that of pure samples using a column (1 m) packed with 20% SE-30 or 10% QF-1 on chromosorb W at 140-220°C. [b] Defined as 2/3 x 100. [c] cis/trans = 17/83. [d] cis/trans = 0/100. [e] The olefin 3 (cis/trans = 4/96) contained 38% 3-phenyl-1-methyl-1-propenyl phenyl sulfide, which was proved to be an isomerization product of 3c by controlled experiment under the reaction condition.

The well-known 1,2-hydride shift in alkyl carbene **6** will afford olefins **3** and/or **4**. The intramolecular cycloaddition of reactive carbenes **1a** and **1b** to the aromatic nuclei and the valence isomerization of resulting norcaradiene **8** are a reasonable route to tetrahydrothiaazulene **5**. The intramolecular nucleophilic addition of sulfide sulfur to the electron deficient center may produce hypothetical thietanium ylide **7**. The Stevens type rearrangement4) of this labile ylide will result in the formation of cyclopropyl sulfide **2**5). Accordingly, **3**,**4**, and **5** are supposed to be the products from carbene process, while **2** from ylide process. These two competitive processes are affected both by substituents on carbene carbon and β-carbon.

The relative ratio of **2** to **3** (Yr in Table 1) might be a qualitative measure for the ylide process, as we could assume that the rates of 1,2-hydride shift from the adjacent methylenes to carbene carbons would be similar for these carbene processes. The Yr-value indicates that the ylide process is substantially favored by changing the substituent on carbene from methyl to phenyl and by increasing the number of substituents on β-carbon. These facts seem to reflect the relative stability of intermediate thietanium ylide **7**. Thus, the phenyl on ylide carbon may stabilize the ylide by inductive effect and methyls on β-carbon may favor the formation of four-membered ring by their steric repulsion.

In conclusion, it may be stated that the intramolecular formation of ylide from carbenes having sulfur atom on γ-position is a general phenomenon, though the resulting four-membered ring seems to be a highly unfavorable system due to strain.

Acknowledgment: This work was supported in part by Kawakami Memorial Foundation.

1) G. Wittig and M. Schlosser, *Tetrahedron*, **18**, 1023 (1962); W. E. Parham and R. Koncos, *J. Amer. Chem. Soc.*, **83**, 4034 (1961); W. E. Parham and S. H. Groen, *J. Org. Chem.*, **29**, 2214 (1964); W. Ando, T. Yagihara, S. Tozune, and T. Migita, *J. Amer. Chem. Soc.*, **91**, 2786 (1969); V. Franzen and L. Finketsher, *Ann. Chem.*, **617**, 1 (1958); J. Dieckmann, *J. Org. Chem.*, **28**, 2933 (1963); M. Saunders and R. W. Murray, *Tetrahedron*, **6**, 88 (1959); H, Nozaki, R. Noyori, and K. Sisido, *ibid.*, **20**, 1125 (1964).

2) As for β-alkoxyalkylcarbenes, see W. Kirmse and M. Buschhoff, *Chem. Ber.*, **100**, 1491 (1967) and β-arylthioalkylcarbenes, see J. H. Robson and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 7112 (1967). In the latter communication, they observed an exclusive 1,2-shift of β-arylthio group to the electron deficient center and interpreted the reaction as a concerted process through an ylide-like transition

state.

3) All new compounds gave correct microanalyses and showed molecular ion peaks and reasonable fragmentations in their mass spectra.

4) H. E. Zimmerman in " Molecular Rearrangements" Part I, P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p. 345; U. Schöllkopf, G. Ostermann and J. Schossig, *Tetrahedron Lett.*, 2619 (1969); J. E. Baldwin and R. E. Hackler, *J. Amer. Chem. Soc.*, **91**, 3646 (1969); J. E. Baldwin and J. E. Brown, *ibid.*, **91**, 3647 (1969).

5) The configuration of cyclopropyl sulfide **2c** was assigned as *cis* with respect to methyl and phenyl by the following nmr data (CCl_4, TMS); τ 9.17 (d, *J*=6.0 Hz, 3H), 9.00-8.20 (m, 3H), and 3.10-2.75 (m, 10H): cf., G. L. Closs and R. A. Moss, *J. Amer. Chem. Soc.*, **86**, 4042 (1964). Inspection of the Dreiding model indicated that the most stable conformation of the ylide **7c** should be as follows.

7c **2c**

Thus, in order to accomodate the observed stereospecificity, an inversion of the configuration at C_1 or C_2 must occur during the migration.

(Received November 26, 1971)