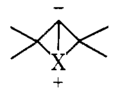
Communications to the Editor

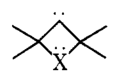
Heterocyclobutanylidenes. A Unique Synthesis of Tetramethylallene Episulfide

Sir:

In order to assess the possibility of generating ylidic bicyclobutanes such as **1a–c**, as well as novel small-ring heterocycles derivable from such ylides (e.g., 1-azabicyclobutanes from **1c** where X = NH), we have initiated a study of the generation of carbene centers at the 3-position of heterocyclobutanes and their interaction with heteroatoms having nonbonded electron pairs at the 1-position as in **2a** and **2b**.[1] We report here some preliminary observations which are of general interest.

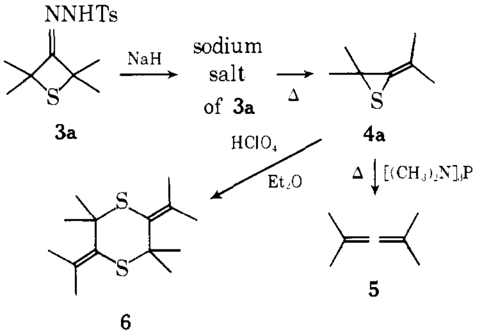


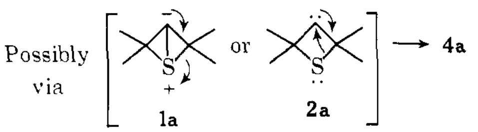
1a, X = S
1b, X = O
1c, X = NR or NH



2a, X = S
2b, X = O

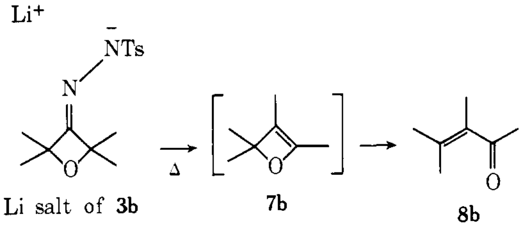
When the dry sodium salt of **3a**, the *p*-toluenesulfonylhydrazone[2] of 2,2,4,4-tetramethylthietanone,[3] was heated slowly to 150 °C in vacuo, tetramethylallene episulfide (**4a**) was the only volatile product formed (40–65% yield). The episulfide **4a** was collected in a cold trap (ca. − 70 °C) as an essentially pure and stable colorless liquid:[2] NMR (CDCl$_3$) δ 1.70 (s, 6 H) and 1.85 (s[br], 6 H); NMR (benzene) δ 1.52 (s, 6 H), 1.65 (s, 3 H) and 1.75 (s, 3 H); ir (CHCl$_3$) 1738 cm^{-1} (w); uv (cyclohexane) 227 nm (ϵ 10 240); MS M$^+$ at *m/e* 128.[4] In further accord with its structure, **4a** underwent desulfurization upon heating with hexamethylphosphoramide in benzene at 65–75 °C for 72 h to yield tetramethylallene (**5**) in 45% yield.[5] Treatment of **4a** with 70% HClO$_4$ in ether afforded the crystalline 1,4-dithiane **6**.[2] Attempts to generate and observe tetramethylthiocyclopropanone by heating **4a**, its valence tautomer, in the presence and absence of suitable traps have been unsuccessful to date.





Similar pyrolyses of the sodium salts of the *p*-toluenesulfonylhydrazones[2] of 2-benzylidine-3-thietanone[6] and dispirocyclohexyl-3-thietanone failed to afford characterizable volatile products.

Pyrolysis (in vacuo) of the dry lithium salt of **3b**, the tosylhydrazone[2] of 2,2,4,4-tetramethyloxetanone,[7] afforded 3,4-dimethyl-3-penten-2-one (**8b**) as the major volatile product in 54% yield.[8,9] No tetramethylallene epoxide (**4b**) or tetramethylcyclopropanone (derivable from **4b**)[10] were observed as volatile products.



A logical intermediate in the formation of **8b** is tetramethyloxetene (**7b**)[11] which may be formed via preferential methyl migration in the initially formed carbene **2b** (as opposed to oxygen migration which would give **4b**).

Comparing the fates of the intermediate carbenes (or related carbenoid species) in the sulfur series (**2a**) vs. the oxygen series (**2b**), our observations strongly suggest (but do not necessarily prove)[12,13] that the sulfur ylide **1a** is an important intermediate in the formation of **4a** whereas the oxygen ylide **1b** is neither necessary nor likely to be involved in the formation of **7b** from the carbene derived from **3b**.[13]

We are continuing in our efforts to directly observe ylidic species such as **1** and extending these studies to the generation of nitrogen and phosphorus analogues of **1**.[14]

Acknowledgments. We thank the Alfred P. Sloan Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

References and Notes

(1) The intramolecular and intermolecular interaction of carbene centers with heteroatoms to yield ylides (or products very likely derived from them) has considerable precedent: S. S. Hixson and S. H. Hixson, *J. Org. Chem.*, **37**, 1279 (1972); K. Kondo and I. Ojima, *Bull. Chem. Soc. Jpn.*, **46**, 1539 (1973); **48**, 1490 (1975), and references cited.

(2) All new compounds prepared gave satisfactory microanalytical data and, where not discussed, exhibit spectral characteristics in accord with their structures.

(3) G. Claeson, A. Thalén, and L. Schotte, *Ark. Kemi*, **21**, 295 (1963).

(4) The only other known allene episulfide is the perfluorinated derivative of **4a**: W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969).

(5) Desulfurization of thiiranes by tervalent phosphorous compounds to yield olefins has been elegantly applied to a variety of synthetic problems: see M. Roth, P. Dubs, E. Gotschi, and A. Eschenmoser, *Helv. Chim. Acta*, **54**, 710 (1971); D. H. R. Barton, E. H. Smith, and B. J. Willis, *Chem. Commun.*, 1226 (1970); D. H. R. Barton and B. J. Willis, *J. Chem. Soc., Perkin Trans. 1*, 305 (1972).

(6) A. J. Krubsack, T. Higa, and W. E. Slack, *J. Am. Chem. Soc.*, **92**, 5258 (1970).

(7) B. L. Murr, G. B. Hoey, and C. T. Lester, *J. Am. Chem. Soc.*, **77**, 4430 (1955).

(8) The pentenone **8b** was characterized by its ir and NMR spectra (I. Tabushi, K. Fujita, and R. Oda, *Tetrahedron Lett.*, 5455 (1968)) and as its 2,4-DNP derivative, mp 127–128 °C (lit. 129 °C; see R. Heilmann, G. de Gaudemaris, and K. Noack, *Bull. Chim. Soc. Fr.*, 990, 992 (1954); M.-L. Filleux-Blanchard and G. J. Martin, *ibid.*, 2618 (1968)).

(9) The minor volatile product, formed in about 18% yield, appears from ir and NMR data to be the 4-penten-2-one analogue of **8b**.

(10) That **4b** might tautomerize to give tetramethylcyclopropanone is suggested by the following: J. K. Crandall and W. H. Machleder, *J. Am. Chem. Soc.*, **90**, 7347 (1968), and references cited; R. L. Camp and F. D. Greene, *ibid.*, **90**, 7349 (1968); A. Liberles, A. Greenberg, and A. Lesk, *ibid.*, **94**, 8685 (1972). Any tetramethylcyclopropanone formed from **4b**, however, would probably have polymerized before it could be volatilized under the pyrolysis conditons: Cf. N. J. Turro and W. B. Hammond, *Tetrahedron*, **24**, 6017 (1968).

(11) The oxetene **7b** has previously been prepared by irradiation of **8b**, and has

been shown to undergo a thermally induced reversion to **8b** in boiling pentane (35 °C) with a half-life of ~12 h: L. E. Friedrich and G. B. Schuster, *J. Am. Chem. Soc.*, **91**, 7204 (1969); **93**, 4602 (1971).

(12) It should be noted that although the alternative product, tetramethylthiete (**7a**) (which may be formed via methyl migration in **2a**), was not observed as a volatile product, it may have been formed as a minor product and undergone polymerization before volatilization: Cf. D. C. Dittmer, P. L.-F. Chang, F. A. Davis, M. Iwanami, I. K. Stamos, and K. Takahashi, *J. Org. Chem.*, **37**, 1111, 1116 (1972).

(13) In this respect our results appear to follow a pattern similar to that established by Shechter and Robson (*J. Am. Chem. Soc.*, **89**, 7112 (1967)) in which a sulfur atom located *β* to a carbene center migrates in preference to hydrogen, whereas in related compounds having a similarly located oxygen atom, oxygen migration does not show a preference over hydrogen migration. To account for their observations, the authors suggested that more ready formation of a cyclic (thiiranium) ylide (of which **1a** is a bicyclic analogue) in the former case facilitates the observed heteroatom migration.

(14) In the only other published study of the chemistry of a possible 3-heterocyclobutanylidine species, pyrolysis of the sodium salt of the *S*,*S*-dioxide of **3a** was found to yield tetramethylallene in 55% yield: See R. Kalish and W. H. Pirkle, *J. Am. Chem. Soc.*, **89**, 2781 (1967). In an attempt to extend this apparent cycloelimination of SO_2 to an extrusion of atomic sulfur from the 3-diazo analog of **3a** itself, Kalish (Ph.D. Dissertation, University of Illinois—Urbana, 1969) reported that treatment of the corresponding hydrazone with nickel peroxide in ether affords tetramethylallene in 1.7% yield and at least 12 other products (glpc analysis) which include 2,2,4,4-tetramethylthietanone azine (45%) along with the parent thietanone (13%) and thietanol (10%); none of the remaining products, formed in yields ranging from ca. 0.2 to 4.5% each, was identified.

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The Temperature Dependence of an Electron Impact Induced Stereoselective Rearrangement Reaction

Sir:

In spite of the enormous energies utilized in the ionization process, rearrangement reactions occurring from organic molecular ions in mass spectrometers exhibit remarkable stereosensitivity to energetically small conformational differences.[1] Moreover, intramolecular transfer of diastereotopic hydrogens in parallel rearrangement reactions of chiral substrates in mass spectrometers and in solution actually show *quantitatively* similar stereoselectivities.[2] The question immediately arises as to the source of this similarity. The reacting molecules in solution are subject to a Maxwell-Boltzmann energy distribution defined by their temperature. On the contrary, in the mass spectrometer the molecular ions are not only of uncertain energy distribution because of their mode of formation by electron impact, but as well the temperature cannot be experimentally defined because of the absence of intermolecular or wall collisions for the detected ions.[3]

The source of this kinetic similarity[2] may be understood by a few simple considerations centered around the quasi-equilibrium theory of mass spectrometry.[4] The theory predicts, and experiments bear out, that rearrangement reactions in mass spectrometers occur from molecular ions of the lowest internal energies.[5] Photoelectron spectroscopy demonstrates that in molecules with nonbonding electrons these lowest internal energy ions, in focus here, are produced by removal of an electron from these nonbonding orbitals and furthermore that such ionization gives rise to discrete and relatively narrow bands often separated by an energy space from the broader bands involving higher energy ionization of bonding electrons.[6] As has been pointed out by Turner[7] such promotion of nonbonding electrons will produce an ionized state which within reasonable approximation will have the same bonding parameters as the neutral precursor. This is a key point with regard to our inquiry because it follows from the Franck–Condon principle that such a circumstance of equivalent potential surfaces for the ion and its neutral precursor will lead to producing the ionized molecule with the same vibrational and rotational energy as the neutral.[7,8] In other words, the temperature of the ion produced by removal of a nonbonding electron, within the limits of the above approximations, will be the same as the temperature of the neutral from which it is formed.[9] It thereby becomes clear why quantitatively similar rearrangement stereoselectivities[2] are observed in solution and in mass spectrometers. We can, though, go a step further.

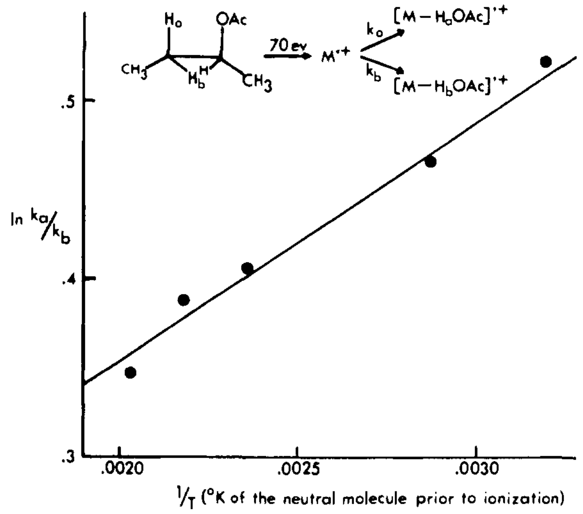

Figure 1. Measured on an MS-902 mass spectrometer at 70 eV beam energy. The construction of this instrument allows varying in consort the temperature of the inlet, ion chamber, and source walls. The temperature is accurate to ±2 °C. The experiments were conducted four times over a period of 6 months and gave the same line within experimental error. Each experiment consisted of at least five measurements at each temperature of 2-butylacetate and the two deuterated diastereomers necessary to calculate k_a/k_b.[2] The data were handled by a computer program written here which yielded the stereoselectivities and the accuracy. Each point was calculated to 95% confidence (2σ) and then used to generate the linear least-squares line shown. The line has a correlation coefficient of 0.991. Another experiment varying only the ion chamber temperature and leaving the inlet system at ambient temperature gave the same line as above with the lowered correlation coefficient of 0.968. The elimination of acetic acid is known not to be pyrolytic under these conditions.[12] The experimental data here show no time dependency at the temperatures reported and as well we have subjected 2-butylacetate to gas chromotography on steel columns and throughout this temperature range there is no evidence for pyrolysis.

If the temperature of the neutral is an accurate measure of the immeasurable temperature of the ions produced it would follow that the rearrangement rate constant for the electron impact induced reaction should depend on the temperature of the neutral precursor in the form of the Arrhenius expression. The precision of the Arrhenius dependency would moreover constitute a measure of the assumptions leading to the prediction of temperature equivalence in the ionization process producing the rearranging ions. Because a stereoselectivity involves a rate ratio which cancels out temperature dependent instrumental parameters[10] and also obviates the otherwise extreme difficulty of measuring an absolute rate constant in a mass spectrometer, we were placed in a position to test for Arrhenius temperature dependency.[11] The reaction chosen for this purpose was the stereoselective rearrangement elimination of acetic acid from electron impact produced 2-butylacetate cation radical.[2] Figure 1 shows this process as well as a plot of the stereoselectivity (k_a/k_b) as a function of the temperature of the precursor neutral.

The Arrhenius equation may be derived from Boltzmann's law[13] and thus the clear Arrhenius dependency exhibited in Figure 1 is strong evidence that the rearranging molecular