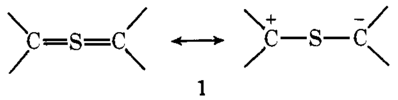
Syntheses and Reactions of Substituent Stabilized Thione Methylides

Sir:

Theoretical consideration of adjacent charge stabilization by sulfur d-orbital conjugation or polarization[1] and the mode of electronic transmission in π-systems containing sulfur has stimulated recent efforts to synthesize various thione ylides (**1**) in order to answer some of these questions.[2] From earlier work unperturbed noncyclic thione ylides appear to be unstable with respect to an electrocyclization to their thiirane valence tautomers[2a] whereas substitution by a combination of π-electron donating and accepting groups ("push-pull") provides sufficient charge stabilization to allow isolation of some representatives of this ylide system.[3] In this communication we wish to report on general synthetic routes to and chemical reactions of some stable thione methylides.



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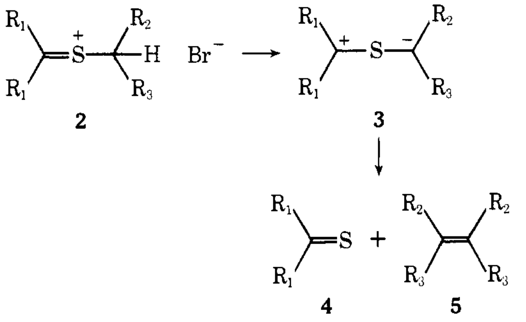
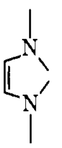
One synthetic approach was derived from consideration of the requirement for stabilizing substituents and led to selection of thiouronium salts as central intermediates whose base catalyzed deprotonation would provide **1**.[4] Tetramethylthiourea and *N,N'*-dimethylimidazolethione[5] were converted to the corresponding *S*-alkylthiouronium salts **2**, by reaction with the appropriate alkyl bromide in CH_2Cl_2 solution at 30°. Treatment of these salts with an equivalent of triethylamine in CH_2Cl_2 or THF solution at temperatures between −78 and 30° led to the immediate formation of the thione methylides, **3**, and triethylamine hydrobromide. Only ylides **3ya–c** and **3za–c** could be isolated at room temperature as crystalline solids which were characterized by their absorption in the ir ($CHCl_3$) at 1650-1700 cm^{-1} (C=O) or 2120-2140 cm^{-1} (C≡N) and consistent mass spectra.[6] Deprotonation of salts



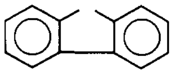
y, $R_1 = NMe_2$

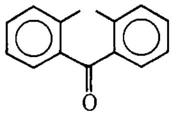
z, R_1 = 

a, $R_2 = R_3 = CN$

b, $R_2 = CN$; $R_3 = CO_2Et$

c, $R_2 = R_3 = CO_2Et$

d, $R_2 = R_3$ = 

e, $R_2 = R_3$ = 

f, $R_2 = Ph$; $R_3 = CO_2Et$

2y,z-d,f with triethylamine in THF at −78° produced solutions of transient ylides which upon warming to ca. −30° led to the formation of **4** and **5**.[7] The decomposition reaction observed for unstable thione methylides is analogous to those reported for many simple 1,2-sulfonium methylides.[8] No products derived from electrocyclic closure to a thiirane were apparent in such ylide decompositions.

As an alternative approach to the general construction of

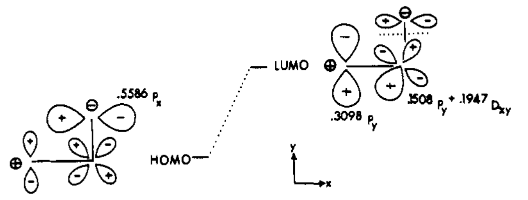
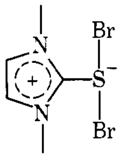


Figure 1. Representation of the HOMO and LUMO of **8** with calculated coefficients. The energy separation is ~11eV.

such "push-pull" substituted ylides we have investigated the possibility of displacement at sulfur by carbon bases on the sulfurane **6**.[9] Our original expectations as to the potential site of substitution were realized when, for example, **6** underwent reaction with 2 equiv of sodio diethylmalonate in THF solution at 0° to provide **3zc**.[7] Such a sulfur ligand exchange reaction parallels those reported for other sulfuranes and probably involves the intermediacy of cation **7** which accepts a nucleophile at sulfur and not carbon.[10]



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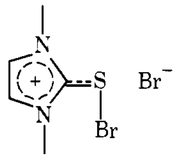

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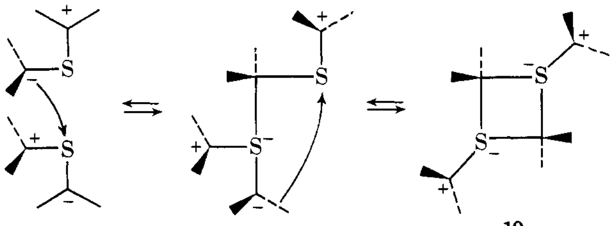
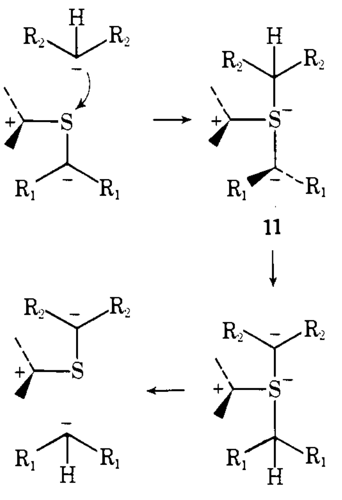
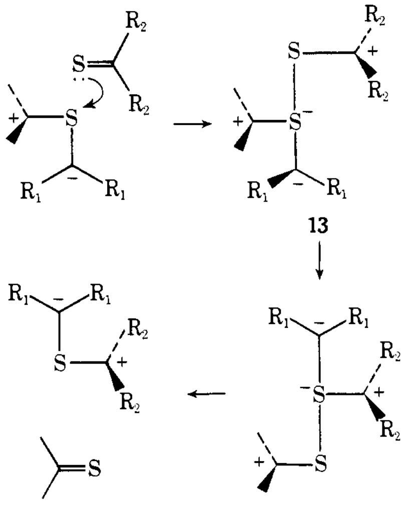
Upon admixture in CH_2Cl_2 solution at 30° a pair of thione methylides which are differentiated by nonidentical sets of π-donor and acceptor substituents undergo rapid ($t_{1/2} < 5$ min) exchange of the latter substituent. For example, **3za** reacts with **3yc** to afford **3ya** and **3zc**, furthermore, the direction of this exchange reaction is enforced by the ready decomposition of **3ya** to **4y** and **5a**.[11] Similar ligand exchange reactions have been reported for sulfonium methylides and a degenerate ligand exchange mechanism has been suggested to account for the facile racemization of chiral sulfur in certain of these ylides.[12] The mechanism of substituent stabilized thione methylide multiple ligand exchange may be rationalized by a sequence (**8** → **10**) whose critical first step requires hypervalent bonding at sulfur rather than attack at the π-donor substituted carbon atom.[13] The intermediate **10** which resembles a bisulfurane stabilized by equatorial π-acceptor substituents but with considerable angle deviation in the apical CSC bonding system can fragment in two possible modes to effect the overall exchange observed. The proposed CS bonding established in **8** is supported by an inspection of the frontier HOMO and LUMO eigenvectors for a model ylide as determined by a SCF-CNDO2 calculation.[14] The HOMO is primarily the carbanion p_x orbital while the LUMO has a greater sulfur p_y contribution than the carbocation p_y (Figure 1)[15] which suggests initial CS union to form sulfurane **9** is the controlling frontier orbital interaction and the same argument also applies to **7**. In a related reaction **3ya** and sodio diethylamalonate in THF solution of 30° gives **3yc** and malononitrile.[7] Again, we visualize this ligand displacement process as proceeding through hypervalent intermediates **11** and **12**.[16] Finally, the thione methylides derived from *N,N'*-dimethylimidazolethione as a precursor undergo a facile reaction with tetramethylthiourea in CH_2Cl_2 solution at 0-30° to afford this





bis(dimethylamino)-substituted ylides.[7] This process, which is equivalent to ligand transfer between ylide and thione, appears to proceed in a direction to provide the ylide with the less effective π-electron donor substituents. Rationalizing this behavior in a manner consistent with the other observed multiple ligand exchange and displacement reactions requires an intermediate **13** in which the equivalent of a 1,2-shift of the π-electron rich group occurs to give **14**; the driving force for the shift is dictated by the formation of the most stable sulfurane as determined by the electron withdrawing ability of the equatorial substituent. In conclusion, the general features of the chemistry of highly perturbed thione methylides closely resemble those of sulfuranes and are certainly unlike those of the unperturbed congeners.



Acknowledgments. We sincerely wish to thank the National Institutes of Health, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation for research grants.

References and Notes

(1) For an excellent discussion, see C. A. Coulson, Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research XVI. Theoretical Chemistry, 1973, pp 61–117.

(2) Especially noteworthy are the studies of (a) R. M. Kellogg, S. Wassenaar, and J. Butler, *J. Org. Chem.*, **37**, 4045 (1972); (b) M. P. Cava and G. E. M. Husbands, *J. Am. Chem. Soc.*, **91**, 3952 (1969). See also E. M. Burgess and H. R. Penton, Jr., *J. Org. Chem.*, **39**, 2885 (1974).

(3) Thione methylides have been isolated from the reaction of trithiones with electrophilic diazo compounds (S. Tamagaki and S. Oae, *Tetrahedron Lett.*, 1159 (1972)) and from thioureas and 2,2-dicyano-3,3-bis(trifluoromethyl)-oxirane (W. J. Middleton, *J. Org. Chem.*, **31**, 3731 (1966)).

(4) This approach was reported to be unsuccessful by earlier workers. M. Takaku, S. Mitamura, and H. Nozaki, *Tetrahedron Lett.*, 3651 (1969).

(5) R. Grigg, T. J. King, and G. Shelton, *Chem. Commun.*, 56 (1970).

(6) Satisfactory (±0.3%) elemental analysis (C, H, N, S) have been obtained for all new isolated compounds.

(7) Identified by mixture melting point and/or ir spectral comparison with authentic samples.

(8) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 3782 (1962); **87**, 1353 (1965); A. W. Johnson, V. J. Hruby, and J. L. Williams, *ibid.*, **86**, 918 (1964); V. Franzen and H. E. Driessen, *Chem. Ber.*, **96**, 1881 (1963); C. G. Swain and E. R. Thornton, *J. Am. Chem. Soc.*, **83**, 4033 (1961).

(9) A. J. Arduengo and E. M. Burgess, unpublished results.

(10) J. C. Martin and L. J. Kaplan, *J. Am. Chem. Soc.*, **95**, 793 (1973); J. C. Martin and R. J. Arhart, *ibid.*, **93**, 2339 (1971).

(11) We exclude an ylide to carbene dissociative mechanism by our failure to obtain trapped carbene products with added thioethers or alkenes.

(12) H. Nozaki et al., *Tetrahedron*, **23**, 4279 (1967).

(13) This proposal has certain features in common with the proposed mechanisms for chiral sulfoxide and sulfimide interconversions. D. J. Cram, F. G. Yamagishi, D. R. Rayner, and E. T. Zwicker, *J. Am. Chem. Soc.*, **95**, 1916 (1973); D. J. Cram, D. C. Garwood, and M. R. Jones, *ibid.*, **95**, 1925 (1973).

(14) The geometrical parameters used were those of **2zc** as determined by x-ray crystallography. A. J. Arduengo and E. M. Burgess, *J. Am. Chem. Soc.*, following paper in this issue.

(15) The calculated composition of π-LUMO at sulfur is $0.1508p_y - 0.1947d_{xy} - 0.0567p_x$ and the resultant hybrid is shown in Figure 1.

(16) An analogous mechanism has been proposed for ligand displacements at selenium in ylides. S. Tamagaki and K. Sakaki, *Tetrahedron Lett.*, 1059 (1974).

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The Structure of a Substituent Stabilized Thione Methylide

Sir:

The pericyclic chemistry observed for 1,3-dipolar ylides ($R_2C{=}X^+{-}C^-R_2$) containing certain first-row central atoms ($X = N, O$) has been correlated using the occupied π-molecular orbitals associated with an "allyl anion" bonding model requiring a planar geometry for the substituted ylide.[1] Extension of this model to define the stereochemistry of second-row ($X = S$) symmetrically substituted thione methylide electrocyclic closures to thiiranes has been successful.[2] The potential surface for conrotation of a thione methylide (**1**) to thiirane (**2**) is to the first approximation dependent upon the energetic behavior of key high-lying molecular orbitals as determined by symmetry conservation (Woodward-Hoffman).[3] The alteration of this surface by a large deviation from symmetry could possibly provide intermediates of lower energy than either end-point reactant as well as change the preference for a particular ring closure mode as indicated by a recent theoretical investigation.[4] Snyder has calculated the shape of the one-dimensional surface (Figure 1) for the conversion of an unperturbed symmetric planar thione methylide, **1a**, to the corresponding thiirane **2a**, using a conrotatory motion (the forbidden disrotatory transition state lies > 7 kcal/mol above the allowed one) in agreement with the observed stereochemistry.[3] We have examined this analogous surface for the closure of an asymmetric thione methylide **1b** perturbed with π-donor

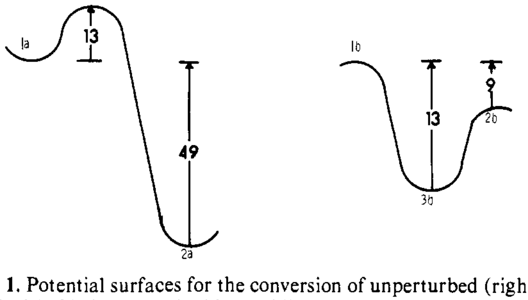

Figure 1. Potential surfaces for the conversion of unperturbed (right) and perturbed (left) thione methylides to thiiranes. The energy differences are shown in kilocalories per mole.