Communications

See Editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972)

Sulfine and Sulfene Reactivity[1]

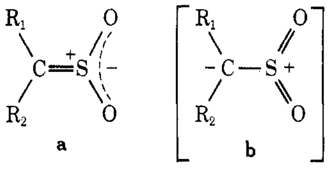
Summary: Semiempirical MO calculations provide a rationale for the reactivity differences observed for the title compounds (thiocarbonyl mon- and dioxides, respectively) and suggest that the dioxides may be stabilized by electron-donating substituents.

Sir: The *S*-oxides of thiocarbonyl derivatives have recently aroused considerable interest. The dioxides (sulfenes) **1** are highly reactive species which must be generated and used *in situ*. Nonetheless they undergo a remarkable variety of exploitable addition and cycloaddition reactions.[2,3] In the absence of an addend, dimer,[4] tetramer,[5] or polymer[6] is obtained. Verification of transient **1** derives from product analysis,[2] rate studies,[7] and most recently from flash vacuum pyrolysis generation of the parent (**1**, $R_1 = R_2 = H$) followed by trapping at −196°.[8] The monoxides (sulfines) **2**, by strong contrast, are often shelf-stable materials[9] which exhibit both a discernible stereochemistry[1,9b,10] and a rich reactivity.[9,11,12]

In the present communication we present the results of MO-SCF-CNDO calculations[13] which provide insight into the reactivity differences between *S*-oxides **1** and **2**. Furthermore tactics for producing stabilized sulfenes, essential to structural and spectroscopic studies of the system, are outlined.

Geometry optimization has been carried out for the parent species **1**[14] and **2**[1] ($R_1 = R_2 = H$). The corresponding charge distributions and frontier orbitals are given in Figure 1.

Both systems are predicted to have a full C–S double bond and partial S–O double bonds. Charge distributions, however, are considerably different. Both C and S of dioxide **1** (*i.e*, **1a**) support exaggerated negative and positive charges, respectively, in comparison to monoxide **2**. Thus any comparable charge controlled[16] reaction for the two would be predicted to occur more rapidly for sulfene. The same conclusion is reached in the event of a comparable frontier controlled process.[16] For example, consider the dimerization of **1** and **2**. In principle it could proceed by a concerted suprafacial–antarafacial route. The available evidence for the dioxide suggests a two-step pathway initiated by attack of carbon on sulfur. A similar event is reasonably invoked for the onset of the majority of sulfene reactions.



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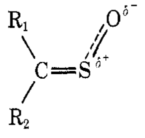

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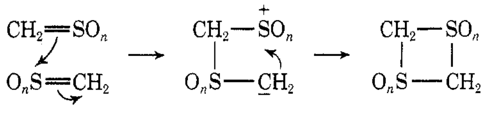

Perturbation MO theory postulates that the π-frontier orbitals are instrumental in directing the early stages of combination.[16] Accordingly the HOMO of one addend will engage the LUMO of the other. Since the HOMO–LUMO energy differences for dioxide and monoxide in the present case are calculated to be nearly the same [ΔE (LUMO–HOMO): **1**, 8.41 eV; **2**, 8.40 eV], the magnitude of orbital coefficients should be a major predictor of reaction course and rate. Figure 1 indicates that the sulfene and sulfine LUMO's share a nearly identical electron distribution. By contrast a comparison of the highest occupied MO's suggests a leakage of charge from oxygen onto carbon and sulfur in the formal transformation from monoxide to dioxide. Specifically carbon and sulfur contributions to the HOMO are 36 and 18% less, respectively, for **2** than for **1**.

The calculations agree nicely with the chemistry of **1** and **2**. Thioketone dioxides are highly reactive car-

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(1) Organo-Sulfur Mechanisms. II. For part I, see J. P. Snyder and D. N. Harpp, *Chem. Commun.*, 1305 (1972).

(2) Several excellent reviews are available: (a) G. Opitz, *Angew. Chem., Int. Ed. Engl.*, **6**, 107 (1967); (b) T. J. Wallace, *Quart. Rev.*, **20**, 67 (1966); H. Ulrich in "Organic Chemistry," Vol. 9, Academic Press, New York, N. Y., 1967, pp 206–240; L. L. Müller and J. Hamer, "1,2-Cycloadditions," Interscience, New York, N. Y., 1967; N. Kharasch, B. S. Thyagarajan, and A. I. Khodair, *Mech. React. Sulfur Compd.*, **1**, 97 (1967); W. E. Truce and L. K. Liu, *ibid*, **4**, 145 (1969); T. Nagai and N. Tokura, *Int. J. Sulfur Chem., B*, **7**, 207 (1972).

(3) Nitrogen analogs, the iminosulfenes, are under scrutiny as synthetic intermediates: C. R. Johnson and E. U. Jonsson, *J. Amer. Chem. Soc.*, **92**, 3815 (1970).

(4) G. Opitz and H. R. Mohl, *Angew. Chem., Int. Ed. Engl*,, **8**, 73 (1969).

(5) Professor J. S. Grossert, Dalhousie University, personal communication.

(6) (a) L. A. Paguette, J. P. Freeman, and R. W. Houser, *J. Org. Chem.*, **34**, 2901 (1969); (b) J. F. King, P. de Mayo, and D. L. Verdun, *Can. J. Chem.*, **47**, 4509 (1969)

(7) J. F. King and T. W. S. Lee, *J. Amer. Chem. Soc.*, **91**, 6524 (1969).

(8) J. F. King, R. A. Marty, P. de Mayo, and O. L. Verdun, *ibid.*, **93**, 6304 (1971).

(9) *Cf.* (a) B. Zwanenburg and J. Strating, *Quart. Rep. Sulfur Chem.*, **5**,, 79 (1970); (b) B. Zwanenburg, A. Wagenaar, L. Thijs, and J. Strating, *J. Chem. Soc., Perkin Trans. 1*, 73 (1973).

(10) J. F. King and T. Durst, *Tetrahedron Lett.*, 585 (1963); B. Zwanenburg, L. Thijs, and A. Tangerman, *Tetrahedron*, **27**, 1731 (1971); B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **90**, 614 (1971); A. Tangerman and B. Zwanenburg, *Int. J. Sulfur Chem. A.*, **2**, 204 (1972); B. F. Bonini, L. Lunazzi, G. Maccagnani, and G. Mazzanti, *ibid.*, 211 (1972).

(11) B. Zwanenburg, L. Thijs, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **89**, 687 (1970).

(12) B. Zwanenburg, L. Thijs, J. B. Broens, and J. Strating, *Recl. Trav. Chim. Pays-Bas*, **91**, 443 (1972); L. Thijs, J. Strating, and B. Zwanenburg, *ibid.*, **91**, 1345 (1972).

(13) R. J. Boyd and M. A. Whitehead, *J. Chem. Soc., Dalton Trans.*, 73 (1972); 78 (1972); 82 (1972).

(14) Sulfene **1**: all atoms lie in a common plane; r_{CS} = 1.64 Å, r_{SO} = 1.58 Å, r_{CH} = 1.09 Å, ∠OSO = 129°, ∠HCH = 114°. The predicted geometry in conjunction with representative force constants obtained from the literature permit the ir spectrum of **1** to be computed[15] in reasonable agreement with experiment.[8]

(15) Dr. U. Anthoni, University of Copenhagen, personal communication.

(16) G. Klopman and R. F. Hudson, *Theor. Chim. Acta.*, **8**, 165 (1967); G. Klopman, *J. Amer. Chem. Soc.*, **90**, 223 (1968); R. F. Hudson, *Angew. Chem., Int. Ed. Engl.*, **12**, 36 (1973).

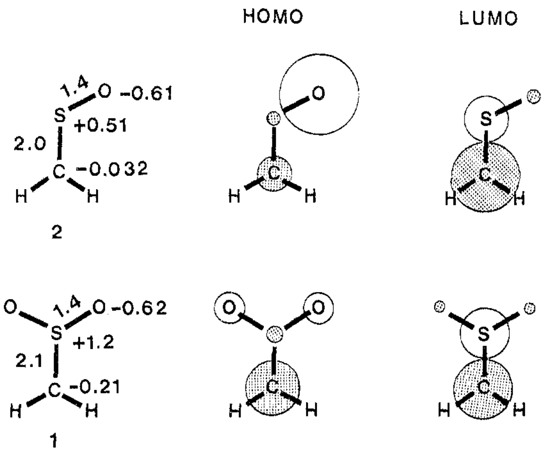


Figure 1.—Computed bond orders [R. J. Boyd, *Can. J. Chem.*, 51, 1151 (1973)], total charge densities, and frontier orbitals for 1 and 2. The MO's are π in character. Circle radii represent relative atomic orbital contributions to the HOMO/LUMO eigen functions.

bon nucleophiles and sulfur electrophiles which self-destruct even at low temperatures.[2,8] Thiocarbonyl monoxides on the other hand are isolable,[9] do not to our knowledge oligomerize, and react in certain cases by nucleophilic attack *at carbon.*[11]

Since the chemistry of the sulfene moiety is characterized primarily by carbon nucleophilicity, resonance structure **1b** has frequently been elected the most important contributor to the system.[17] Furthermore, association of the dipolar nature of **1** with ylide properties (**1b**) has stimulated efforts to prepare unreactive sulfenes by the agency of electron-withdrawing substituents,[6a,18] albeit abortive. We would like to suggest that the ylide analogy is misleading and that sulfenes with *electron-donating* groups should be capable of isolation under normal conditions.

To assess reactivity, dimerization will once again serve as reaction model and PMO theory as guide to liability. Three computed reaction indices for a series of substituted *S*-dioxides **1** are detailed in Table I.

TABLE I

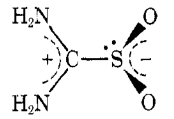
COMPUTED MOLECULAR QUANTITIES FOR SULFENE 1[a]

R_1,R_2	ρ_C[b]	ρ_S[b]	ΔE (LUMO–HOMO), eV	LUMO, ϕ^2	HOMO, ϕ^2
CN, CN	−0.12	+1.3	6.70	0.38	0.22
H, CN	−0.19	+1.3	7.27	0.39	0.26
H, H	−0.21	+1.2	8.41	0.39	0.42
H, NH_2	+0.20	+1.1	8.07	0.29	0.20
NH_2, NH_2	+0.65	+0.91	8.34	0.04	0.07

[a] Standard bond lengths and angles have been employed for substituents and the optimized $R_1 = R_2 = H$ geometry has been maintained around CSO_2. The structure having $R_1 = R_2 = NH_2$ supports a 68° angle between the NCN and OSO planes. All other cases are planar.[14] [b] The variation is due almost entirely to changes in π-electron densities.

As electron-withdrawing substituents are replaced successively with more electron-donating ones, the positive charge on sulfur is diminished while that at carbon undergoes a reversal from negative to positive. Thus for charge-controlled reactions, not only are electron-rich substituents predicted to reduce the electrophilicity of sulfur, but to eliminate altogether the nucleophilicity of carbon. Orbital control for the dimerization requires a concern for both ΔE (LUMO–HOMO) and the magnitude of frontier MO atomic coefficients at the centers being joined. Electron-pulling groups promote oligomerization by increasing addend interaction energy[19] and by maintaining large S-LUMO and C-HOMO π coefficients. The converse is predicted for electron-donating substituents. Thus, strong electron donors should ameliorate sulfene reactivity by introducing electronic properties with sulfine-like character.

There are several pieces of experimental evidence, surprisingly absent from the sulfene literature,[2,20] which lend credence to the calculations. As early as 1910 diaminosulfene **3** (thiourea dioxide) was prepared by the oxidation of thiourea.[21] The substance is an air- and a water-stable material presently used as an industrial reducing agent in dye and photographic processes. Monoalkyl derivatives of **3** have likewise been known for many years.[22] Unfortunately the original report[21] as well as subsequent and current papers[23] have pictured the dioxides as the tautomeric iminosulfinic acids **4**. X-Ray[24,25] and ir[26] studies reveal on the contrary that the parent species in the solid state, although extensively intermolecularly hydrogen bonded, exists as the symmetrical dioxide **3**.[27]



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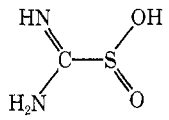

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Very recently a series of mono-, di-, and trisubstituted diaminosulfenes have been isolated as crystalline materials.[28] A curious stability pattern as a function of substitution suggests the importance of *intra*molecular

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[17] G. Hesse, E. Reichold, and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957); W. E. Truce and J. R. Norell, *J. Amer. Chem. Soc.*, **85**, 3231 (1963); A. W. Johnson, "Ylide Chemistry," Academic Press, New York, N. Y., 1966, p 353.

[18] G. Opitz, M. Kleeman, D. Bucher, G. Walz, and K. Rieth, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).

[19] Inversely proportional to ΔE (LUMO–HOMO).

[20] *Cf.*, however, J. F. King and T. Durst, *J. Amer. Chem. Soc.*, **87**, 5684 (1965); P. H. Laur, in "Sulfur in Organic and Inorganic Chemistry," Vol. 3, A. Senning, Ed., Marcel Dekker, New York, N. Y., 1972, pp 167–168.

[21] E. de Barry Barnett, *J. Chem. Soc.*, **97**, 63 (1910); *cf.* L. Vanino and A. Schinner, *Chem. Ber.*, **47**, 699 (1914).

[22] (a) R. Kitamura and S. Suzuki, *J. Pharm. Soc. Jap.*, **58**, 818 (1938); (b) E. W. Tillitson, U. S. Patent 2,493,471 (1950) [*Chem. Abstr.*, **45**, 659*b* (1951)]; J. Böeseken, *Recl. Trav. Chim. Pays-Bas*, **67**, 603 (1948).

[23] J. Böeseken, *Recl. Trav. Chim. Pays-Bas*, **55**, 1040 (1936); E. Havas, *Chem. Abstr.*, **33**, 4603 (1939); E. Ballard and T. B. Johnson, *J. Amer. Chem. Soc.*, **64**, 795 (1942); G. L. Wakefield, *Chem. Abstr.*, **53**, P 3959*b* (1959); L. P. Roosens and P. A. Faelens, *ibid.*, **54**, P 17128*d* (1960); Gevaert Photo-Production N.V., *ibid.*, **54**, P 22119*f* (1960); K. V. Rao, *ibid.*, **57**, P 15257*d* (1963); H. R. Kricheldorf, *Justus Liebigs Ann Chem.*, **745**, 81 (1971); O. A. Kunze, O. G. Malan, P. A. Bueger, and W. Fink, *Z. Naturforsch. B*, **26**, 8 (1971); *cf.*, however, ref 22a; E. O. Fischer and W. Hieber, *Z. Anorg. Allgem. Chem.*, **271**, 229 (1953); P. Kerber and J. Starnik, *Chem. Ber.*, **104**, 2035 (1971); K. Nakagawa and K. Minami, *Tetrahedron Lett.*, 343 (1972).

[24] R. A. L. Sullivan and A. Hargreaves, *Acta. Crystallogr.*, **15**, 675 (1962).

[25] The X-ray analysis[24] reveals the SO_2 plane to subtend a 68° angle with the NNC plane. Our calculations are in accord with this result predicting the nonplanar geometry to be lower in energy than the planar form.

[26] Y. Y. Kharitonov and I. V. Prokof'eva, *Dokl. Akad. Nauk SSSR*, **162**, 829 (1965); *Chem. Abstr.*, **63**, 9240*f* (1965).

[27] Rearrangement from the dioxide to the aminoiminosulfinic acid in aqueous solution has been claimed: N. I. Prorokov, Y. Schmukler, P. V. Moryganov, B. N. Melnikov, and A. N. Gruzdeva, *Tekst. Prom. (Moscow)*, **29**, 60 (1969); *Chem. Abstr.*, **72**, 13699w (1970).

[28] (a) W. Walter and G. Randau, *Justus Liebigs Ann. Chem.*, **722**, 80 (1969); (b) W. Walter and K. Ruess, *Chem. Ber.*, **102**, 2640 (1969).

hydrogen bonds. To our knowledge no case of a tetrasubstituted diaminosulfene is known with the exception of an unusual sulfene-like salt.[29] It remains to be seen whether the stability of aminosulfenes and similarly substituted cases is largely a consequence of hydrogen bonding or can be supported by the electronic factors outlined in Table I.

Acknowledgments.—We are grateful to the NATO Research Grants Program for partial funding of the work and to Professor David N. Harpp (McGill University) for hospitality and stimulation. Professor Martin Ettlinger (Copenhagen University) kindly drew our attention to the thiourea dioxide literature.

(29) E. Lindner and H. Weber, *Justus Liebigs Ann. Chem.*, **101**, 2832 (1968).

(30) Camille and Henry Dreyfus Teacher-Scholar Grant Recipient, 1971–1976.

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Photochemistry of Epoxy Olefins. II.[1] The Photosensitized Geometric Isomerization and Rearrangement of the Isomeric 4,5-Epoxy-2-hexenes

Summary: The isomeric monoepoxides of 2,4-hexadiene undergo geometrical isomerization of both the epoxy and olefinic moieties as well as rearrangement to *cis*- and *trans*-4-hexen-2-one when irradiated in acetone solution at 3000 Å.

Sir: In a continuation of our studies of the photochemistry of 3,4-epoxy olefins,[1] we have investigated the acetone-sensitized photolysis of the stereoisomers of 4,5-epoxy-2-hexene. The major results are outlined in Scheme I while representative data are shown in Table I. Photolysis of either **5** or **6** in acetone gives an equilibrium mixture of 55% **5** and 45% **6**. The same equilibrium values are obtained upon prolonged irradiation of **1**, **2**, **3**, or **4**.

SCHEME I
PHOTOCHEMICAL INTERCONVERSIONS

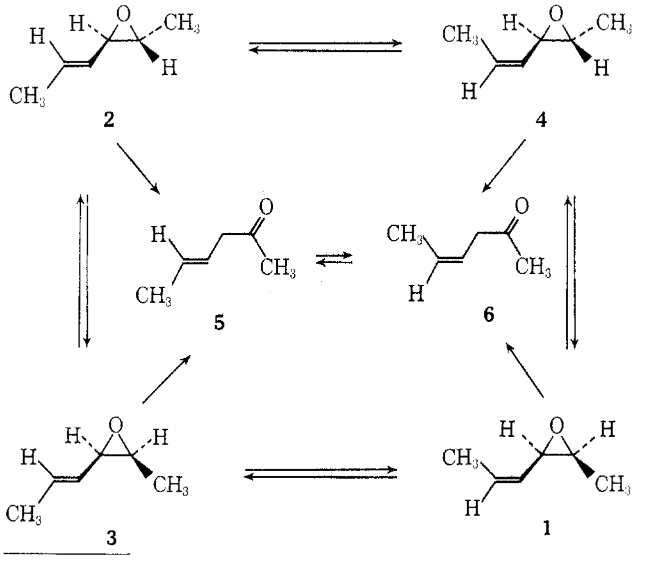

TABLE I

Substrate	Photolysis products,[a] % 1	2	3	4	5	6
1	12	13	6	17	25	27
2	3	12	2	12	37	34

[a] Photolyses were carried out in acetone solutions using a 450-W Hanovia medium-pressure mercury lamp equipped with a Pyrex filter. Values given are per cent of volatile product after irradiation of 0.6 g in 125 ml of acetone for 2.5 hr. The analyses were carried out by gas chromatography on a Carbowax 20M column. The products were identified by direct comparison with authentic samples.

The most striking feature of this work is the very facile geometric isomerization of the epoxide moieties. In their photochemical studies of phenyl-substituted oxiranes, Griffin and Trozzolo[2] did not observe any isomerization of epoxide isomers. Geometric isomerization of epoxides has been observed photochemically only in the case of the α,β-epoxy ketone system.[3]

In Scheme II are shown two possible modes of epoxide geometrical isomerization with the asterisk indicating either ionic or radical centers. Thermal and Lewis acid catalysis of the epoxides was investigated to determine if ground electronic state ionic or radical intermediates would also produce geometrical isomerization of the epoxides. Both thermolysis and Lewis acid catalysis (Table II) gave the same ketones which are ob-

SCHEME II

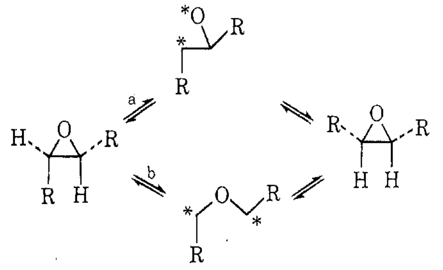

TABLE II
LEWIS ACID AND THERMAL CATALYZED REARRANGEMENTS

Substrate	Temp, °C	Products (%)		
1[a]	25	1 (0)	5 (98)	6 (2)
2[a]	25	2 (0)	5 (40)	6 (60)
1[b]	200	1 (89)	5 (trace)	6 (5)
1[b]	250	1 (68)	5 (2)	6 (26)
1[b]	300[c]	1 (9)	5 (20)	6 (64)
2[b]	200	2 (88)	5 (9)	6 (0)
2[b]	250	2 (64)	5 (32)	6 (0)
2[b]	300[c]	2 (4)	5 (47)	6 (21)

[a] Rearrangement induced by treating substrate with MgI_2 in ether as described by N. Heap, G. E. Green, and G. H. Whitham, *J. Chem. Soc. C*, 1525 (1969). [b] The pyrolyses were carried out (15 min) in sealed Pyrex ampoules using 20 mg of substrate. Less than 1% of the epoxide isomers could have been detected if present. [c] At 300° and above several unidentified products were obtained.

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(1) For the previous paper in this series, see D. R. Paulson, G. Korngold, and G. Jones, *Tetrahedron Lett.*, 1723 (1972).

(2) T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, *J. Amer. Chem. Soc.*, **92**, 1402 (1970), and references contained therein.

(3) C. K. Johnson, B. Dominy, and W. Reusch, *J. Amer. Chem. Soc.*, **85**, 3894 (1963).