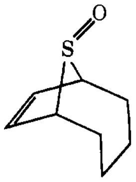
temperatures where starting material is still isomerized. Hence, elimination of SO and readdition are not required in order that isomerization occur.

Although the reported yields of SO–diene adducts and our yields (34–42% after distillation) from the 2,4-hexadienes (1 equiv) are unimpressive, it is possible to trap SO efficiently. From equimolar quantities of isoprene and thiirane oxide in refluxing toluene, 3-methyl-3-thiolene oxide was obtained in 83.4% yield (72% after distillation). The SO–diene reaction in toluene is typically accompanied by formation of an insoluble brown slime, but we have found (subsequent to the above experiments) that some reactions of this type are more efficient and much cleaner in the absence of oxygen. Not surprisingly, use of excess diene can also improve yields.

High stereoselectivity at carbon was observed in our study only at low conversions, but stereoselectivity at sulfur need not be limited by the extent of reaction. Addition of SO to the stereochemically rigid 1,3-cyclooctadiene yields essentially only the sulfoxide **3**. For this reason and because sulfoxides are versatile synthetic intermediates, we believe that the SO–diene reaction will find a useful place in organic synthesis.



3

Acknowledgment. We wish to thank the U. S. Army Cold Regions Research and Engineering Laboratory and the Harvard University Chemistry Department for mass spectra. Financial support from the U. S. Army Research Office (Durham), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. D. M. L. thanks the Alfred P. Sloan Foundation for a research fellowship.

(13) Small scale "instant" SO–diene reactions are conveniently run by coinjecting thiirane oxide and the diene into a gas chromatograph whose injector block is set in the range 300–400° (normal flow rates).

Peter Chao, David M. Lemal*
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

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Sulfur Monoxide Chemistry. The Nature of SO from Thiirane Oxide and the Mechanism of Its Reaction with Dienes

Sir:

Triplet ground state ($^3\Sigma^-$) sulfur monoxide has been identified (microwave spectroscopy) among the thermal decomposition products of thiirane oxide,[1] but the possibility has remained alive that one or both of the low-lying singlet states ($^1\Delta$ and $^1\Sigma^+$, 18.2 and 30.05 kcal/mol above the $^3\Sigma^-$ state, respectively[2]) are generated in this reaction.[3] We wish to present evidence that the ground state is formed exclusively, then to discuss the mechanism of the addition of triplet SO to dienes.

Decomposition of thiirane oxide in 1,2-dibromoethane containing *trans,trans*-2,4-hexadiene (0.048 *M*) yields *trans,trans*- and *cis,trans*-2,5-dimethyl-3-thiolene *S*-oxide[4] in the ratio 88.2:11.8, within experimental error of the 89.5:10.5 ratio obtained when the sulfoxide is heated at the same temperature (115°) in (8.2 *M*) *trans,trans*-2,4-hexadiene containing a bit of toluene as cosolvent.[5] Had the decomposition proceeded with spin conservation, giving initially singlet SO, one might have expected rather different product compositions in these two experiments: the probability of intersystem crossing to the ground state prior to interception by diene is enormously greater with very dilute diene in a heavy-atom solvent than with nearly pure diene.[6,7]

Thermochemical data provide stronger evidence against the formation of singlet SO. The standard heat of reaction for thiirane oxide → ethylene + ($^3\Sigma^-$) SO is calculated to be $\Delta H_r{}^\circ = +21.5$ kcal/mol.[9] Since the activation enthalpy is 35 kcal/mol,[12] the transition state lies only 13.5 kcal/mol above the ground states of the products. Thus formation of $^1\Sigma^+$ SO is definitely excluded, and formation of $^1\Delta$ SO is quite unlikely even when allowance is made for error in the transition state energy. The retro-reaction, $^1\Delta$ SO + ethylene, would probably have to surmount a significant barrier,[13] thereby placing the transition state farther out of reach for the forward reaction.

The lack of stereospecificity in thiirane oxide decompositions argues for a biradical intermediate.[14]

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(1) S. Saito, *Tetrahedron Lett.*, 4961 (1968).

(2) R. Colin, *Can. J. Phys.*, **47**, 979 (1969).

(3) W. H. Breckenridge and T. A. Miller, *J. Chem. Phys.*, **56**, 465 (1972).

(4) (a) P. Chao and D. M. Lemal, *J. Amer. Chem. Soc.*, **95**, 920 (1973); (b) R. A. Sikstrom, Ph.D. Dissertation, University of Minnesota, 1971.

(5) Because of diene isomerization during the reaction, these ratios are extrapolated to time zero.

(6) For a discussion of radiationless decay of ($^1\Delta$)SO, see ref 3.

(7) The assumption implicit in this argument that different product stereochemistry should result from different electronic states of SO is reasonable in light of the widespread success of the "Skell criterion"[8a] and its extension beyond the borders of carbene chemistry.[8b] The danger in this kind of argument is forcefully illustrated, however, by the stereospecificity of triplet S atom addition to olefins: O. P. Strausz, I. Safarik, W. B. O'Callaghan, and H. E. Gunning, *J. Amer. Chem. Soc.*, **94**, 1838 (1972).

(8) (a) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York, N. Y., 1971, p 267, *et seq.*; (b) see, for example, A. Anastassiou, *J. Amer. Chem. Soc.*, **89**, 3184 (1967).

(9) This value is obtained from the known gas-phase standard heats of formation of thiirane, sulfur monoxide, and ethylene, and the assumption the heat of oxidation of thiirane to its oxide matches that for dimethyl sulfide.[10] The fact that ∠CSC is actually slightly smaller in DMSO than in DMS[11] suggests that the heat of formation of thiirane oxide is not seriously underestimated using this assumption.

(10) J. D. Cox and J. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

(11) R. Thomas, C. B. Shoemaker, and K. Eriks, *Acta Crystallogr.*, **21**, 12 (1966) H. Dreizler and H. D. Rudolph, *Z. Naturforsch. A*, **17**, 712 (1962).

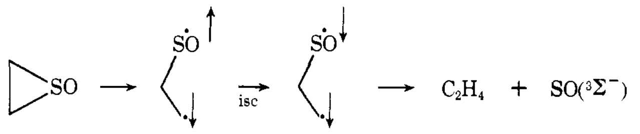
(12) G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, **88**, 2616 (1966).

(13) Preliminary attempts to obtain adducts from simple olefins and SO generated from thiirane oxide have been unpromising.

(14) G. W. Hartzell and J. N. Paige, *J. Org. Chem.*, **32**, 459 (1967); J. E. Baldwin, G. Höfle, and S. C. Choi, *J. Amer. Chem. Soc.*, **93**, 2810 (1971). The former authors suggested a dipolar intermediate, the latter a biradical. We favor a biradical for several reasons, among them the fact that the reaction proceeds at essentially the same rate in acetonitrile as in toluene.[15]

(15) For an excellent discussion of covalent and zwitterionic character in biradicals, see L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

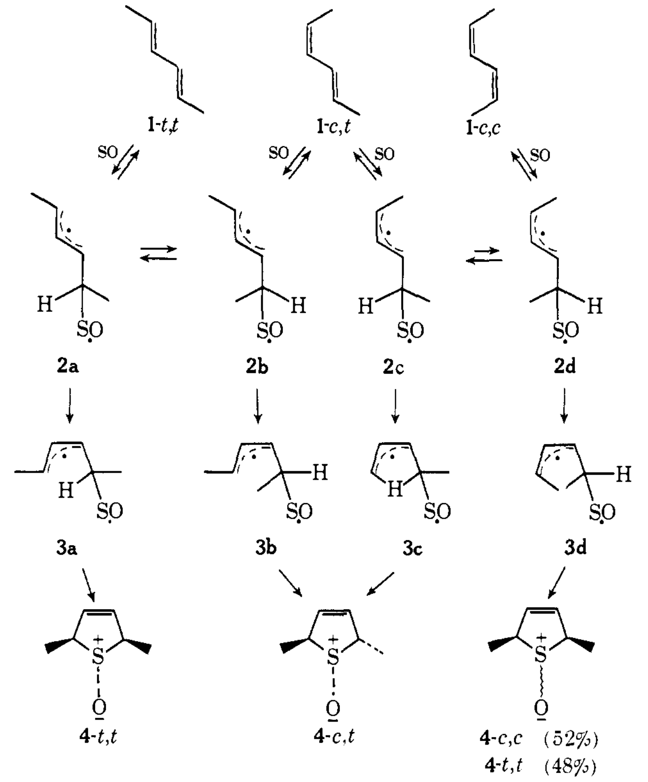
Intersystem crossing probably occurs after its formation, consistent with the observation that the reaction is no faster in the heavy-atom solvent 1,2-dibromoethane than in hydrocarbon media (eq 1).

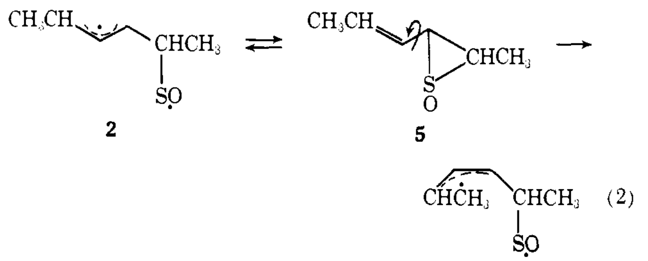


(1)

An important clue to the mechanism of ($^3\Sigma^-$) SO addition to dienes was provided by competition experiments, which established these relative reactivities toward SO (115° in toluene): isoprene (5.6), **1**-*t,t* (2.5), **1**-*c,t* (1.6), **1**-*c,c* (1.0), where the last three are the isomers of 2,4-hexadiene. In this series, attack of SO on s-cisoid diene should slow down dramatically, for that conformation must become strongly twisted and its population must diminish as well. The very modest discrimination among dienes shown by SO thus reveals that even a planar s-cis conformation enjoys no special reactivity.[16] Since the s-trans form predominates heavily even in **1**-*t,t*, one can assume initial formation principally of transoid biradicals **2** from all of the hexadienes.[17,18] This conclusion leads one to expect extensive loss of configuration by C-2–C-3 bond rotation (Chart I,[19] horizontal arrows), for thiolene oxide (**4**) cannot form until rotation occurs about the partially double C-3–C-4 bond to give **3**. *The stereoselectivities observed in these transformations are thus most remarkable.* The sulfoxide from **1**-*t,t* is ~87% **4**-*t,t* and from **1**-*c,t* it is ~95% **4**-*c,t*.[4a] Diene stereochemistry is ~39% retained in the sulfoxide from **1**-*c,c*,[4a] despite considerable steric hindrance to formation of the required precursor **3d**. The fact that intersystem crossing (presumably in **2**) must also occur en route to the thiolene oxides makes these stereoselectivities all the more striking.

Chart I. Pathways to 3-Thiolene *S*-Oxides





(2)

The heretical notion that rotation within an allylic radical [20] occurs faster than about an (apparently) single bond might be avoided by invoking cyclization of biradicals **2** to thiirane oxides **5**. Now rotation about the C-3–C-4 bonds would be facile, and reopening of the rings could yield the required cisoid biradicals **3** (eq 2).[21] Even this scheme seems to require that the C-2–C-3 bonds in **2** possess unexpectedly high rotational barriers, however, for two reasons: (1) the cyclizations **2** → **3** are probably impeded by substantial barriers (*cf.*, for example, trimethylene biradical → cyclopropane, E_a = 8.2 kcal/mol[22]), and, more compellingly, (2) if its C=C linkage is cis, intermediate **5** should, on steric grounds, revert to **2** many times before yielding **3**. The torsional stiffness of the C-2–C-3 bond[23] implies that the p orbital at C-3 interacts strongly with the SO group through the C-2–S bond and/or through space. That interaction may well lower the torsional barrier for the C-3–C-4 bond, but there is at present no clear basis for choice between the direct and indirect pathways from **2** to **3**.

Stereochemistry at sulfur has escaped mention, but it is no less striking than that at carbon. The methyl *cis*-sulfoxide from **1**-*t,t* is well over 99% **4**-*t,t* even though **4**-*c,c* is considerably stabler. This finding argues for a strong preference in **3a** for the transoid (**6**) over the cisoid (**7**) orientation about the C–S bond. Essentially exclusive formation of stereoisomer **8** from *cis,cis*-1,3-cyclooctadiene is further evidence that **6** is preferred over **7**. The almost equal mixture of methyl *cis*-sulfoxides from 1-*c,c* is understandable after ex-

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[16] Bartlett's group has carried out extensive studies of the influence of diene structure and conformation on the mode of cycloaddition to olefins; see particularly P. D. Bartlett, G. E. H. Wallbillich, A. S. Wingrove, J. S. Swenton, L. K. Montgomery, and B. D. Kramer, *J. Amer. Chem. Soc.*, **90**, 2049 (1968); J. S. Swenton and P. D. Bartlett, *ibid.*, **90**, 2056 (1968).

[17] Product stereochemistry is the same for 1-*t,t* in acetonitrile as in toluene. Were dipolar intermediates involved,[15] coulombic considerations would favor attack on s-cis over s-trans diene, an effect which should be attenuated by increasing solvent polarity.

[18] A referee has argued that the reaction may be diffusion controlled, or nearly so, but that during the encounter lifetime in solution diene acquires the s-cisoid conformation and is then attacked by the SO. We are very skeptical about this interesting idea for several reasons, but cannot rigorously exclude it.

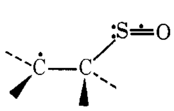
[19] Though not shown on the chart, six-ring sulfenates may be formed reversibly in SO–diene reactions: see, for example, P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, **90**, 4869 (1968).

[20] The rotational barrier in allyl radical itself has been estimated at about 12 kcal/mol: S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968, p 42.

[21] Oxidation of 2-vinylthiirane with hydrogen peroxide at room temperature gives 3-thiolene *S*-oxide, so the **5** → **4** transformation is probably very facile: F. Lautenschlaeger, *J. Org. Chem.*, **34**, 3998 (1969).

[22] S. W. Benson, *J. Chem. Phys.*, **34**, 521 (1961); see also S. W. Benson and P. S. Nangia, *ibid.*, **38**, 18 (1963).

[23] We estimate 6–10 kcal/mol barriers.



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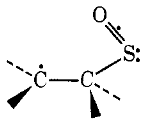

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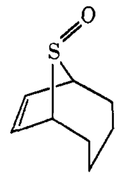

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amination of models, for the C–S transoid conformation in **3d** (but not the cisoid) leads to serious interference between a methyl and the oxygen in the transition state for cyclization.

The retrograde SO–diene reaction is only slightly stereoselective, and interconversion of the thiolene oxides competes effectively against SO extrusion. Together with the fact that diene isomerization accompanies the forward reaction (SO + diene), these observations reveal that the barriers for cleavage of the C–S bonds in the biradical intermediates are similar in magnitude to the rotational barriers discussed above.

If any moral is to be drawn from our study, it is this: the assumption that internal barriers in biradicals are similar to those in stable, closed-shell molecules can be a dangerous oversimplification.[24] The challenging problem of establishing that a particular reaction occurs concertedly is compounded by the possibility that even a rather long-lived intermediate can possess sufficient stereochemical integrity to go undetected.

Our exploration of sulfur monoxide chemistry continues, with the goal, among others, of developing mild methods for generating singlet as well as triplet SO in solution.

Acknowledgment. We are grateful to the U. S. Army Research Office (Durham), the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society, for finanical support of this work. D. M. L. wishes to thank the Alfred P. Sloan Foundation for a Research Fellowship.

(24) Theoretical predictions of rotational barriers in simple biradicals have been made recently by Hoffmann's and Salem's groups: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970); J. Jean, L. Salem, J. S. Wright, J. A. Horsley, C. Moser, and R. M. Stevens, *Pure Appl. Chem. Suppl.* (23rd Congress), **1**, 197 (1971); J. A. Horsley, Y. Jean, C. Moser, L. Salem, R. M. Stevens, and J. S. Wright, *J. Amer. Chem. Soc.*, **94**, 279 (1972); see also ref 15.

David M. Lemal,* Peter Chao
Department of Chemistry, Dartmouth College
Hanover, New Hampshire 03755

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Bis(π-cyclopentadienyl)germanium(II)

Sir:

We wish to report the synthesis of the first monomeric germanium(II) compound containing direct carbon–germanium bonds, bis(π-cyclopentadienyl)germanium(II) (germanocene).

Only a few well-characterized compounds of divalent germanium are known.[1] In this respect, germanium lies between carbon and lead. In the former case, all divalent carbon species are highly reactive intermediates (carbenes) whereas the +2 oxidation state of lead is more stable than the +4 state.

Among the organic derivatives of divalent group IVa metals, only dicyclopentadienyltin[2] and dicyclopentadienyllead[3] have been characterized. Attempts to prepare simple alkyl or aryl derivatives of germanium(II) containing direct bonds to carbon led to cyclic oligomers and linear polymers.[4–7] However, divalent germanium species are postulated as fleeting intermediates in several reactions of group IVa compounds,[8] and the dihalides are useful intermediates in syntheses.[9,10]

The reaction of sodium cyclopentadienide (−78°, ethyl ether solvent, 2 hr) or thallium(I) cyclopentadienide (20°, THF, 30 min) with freshly prepared germanium dibromide[9] gave good yields (up to 60%) of germanocene. The use of a solvent in which the cyclopentadienide salt is sparingly soluble is essential to the success of the preparation. No monomeric product can be isolated if THF is used as the solvent for sodium cyclopentadienide. Apparently, a slow, solubility-controlled reaction rate is necessary to minimize polymer formation. The solvents must also be dry and deaerated.

The product was isolated and purified by filtering the cold reaction mixture, removing the solvent under vacuum, and subliming the residue at 20° onto a liquid nitrogen cooled probe. A melting point could not be obtained since germanocene polymerizes rapidly when heated (see below). The resulting polymer does not melt up to 300°. The formula Cp_2Ge was indicated by analysis for both the old (polymerized) and freshly prepared product. *Anal.* Calcd for $C_{10}H_{10}Ge$: C, 59.45; H, 4.79; Ge, 35.76. Found: C, 59.51; H, 5.02; Ge, 35.44. The molecular weight, determined cryoscopically in benzene, was found to be 208 ± 16 ($C_{10}H_{10}Ge$ requires 202.4), thus confirming the monomeric structure. While stannocene is 90% polymerized in 5 days at room temperature,[11] polymerization of solid germanocene to a pale yellow solid, insoluble in common organic solvents, is complete in about 3 hr. Characterization of the polymer was severely hampered by the apparent ease of cleavage of the C_5H_5 groups with halogens and the low solubility, but the yellow color suggests the presence of Ge–Ge bonds in the solid (similar catenates of silicon are yellow[12]). In the presence of air, germanocene is rapidly oxidized through a yellow intermediate to a white, insoluble solid.

The structure of germanocene is presumably similar to those of stannocene and plumbocene which have been found to be angular in the gas phase.[13] The pmr spec-

(1) O. H. Johnson, *Chem. Rev.*, **51**, 431 (1952); F. Glockling, "The Chemistry of Germanium," Academic Press, New York, N. Y., 1969.

(2) E. O. Fischer and H. Grubert, *Z. Naturforsch. B*, **11**, 423 (1956).

(3) E. O. Fischer and H. Grubert, *Z. Anorg. Chem.*, **286**, 237 (1956).

(4) H. Gilman and G. L. Schwebke, *Advan. Organometal. Chem.*, **1**, 90 (1964).

(5) O. M. Nefedov and S. P. Kolesnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 201 (1966).

(6) W. P. Neumann and E. K. Konig, *Justus Liebigs Ann. Chem.*, **677**, 1 (1964).

(7) L. C. Willemsens and G. J. M. van der Kerk, *J. Organometal. Chem.*, **2**, 271 (1964).

(8) O. M. Nevedov and M. N. Manakov, *Angew. Chem., Int. Ed. Engl.*, **5**, 1021 (1966); further literature cited there.

(9) M. D. Curtis and P. Wolber, *Inorg. Chem.*, **11**, 431 (1972).

(10) J. V. Scibelli and M. D. Curtis, *J. Organometal. Chem.*, **40**, 317 (1972).

(11) P. G. Harrison and J. J. Zuckerman, *J. Amer. Chem. Soc.*, **91**, 6885 (1969).

(12) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *ibid.*, **92**, 519 (1970), and references therein.

(13) (a) A. Almenningen, A. Haaland, and T. Motzfeldt, *J. Organometal. Chem.*, **7**, 97 (1967); (b) Cp_2Pb contains bridging Cp groups in the solid: C. Panattoni, G. Bombieri, and U. Croatto, *Acta Crystallogr.*, **21**, 823 (1966).