**Table I.** Effect of Solvent and Quenchers on Indoxazene Photoproducts[a]

| Solvent | Indoxazene, *M* | Quencher (*M*) | Benzoxazole, % | Cyanophenol, % |
|---|---|---|---|---|
| $H_2O$ | $6.2 \times 10^{-4}$ | | 70[b] | 13[b] |
| Diglyme[e] | | | 18 | 17 |
| Cyclohexane | $10^{-4}$ | | nd | 42[d] |
| Cyclohexane | $10^{-4}$ | Cyclohexene (0.1) | nd | 11[d] |
| Cyclohexane | $10^{-4}$ | Cyclohexene (1) | nd | 5[d] |
| Cyclohexane | $10^{-4}$ | Biacetyl (0.1) | nd | 10[d] |
| Cyclohexane | $10^{-3}$ | | 36[c] | 29[d] |
| Cyclohexane | $10^{-3}$ | Cyclohexene (0.1) | 43[c] | 21[d] |
| Cyclohexane | $10^{-4}$ | Piperylene (0.1) | nd | 5[d] |
| Cyclohexane | $10^{-4}$ | Piperylene (0.01) | nd | 22[d] |

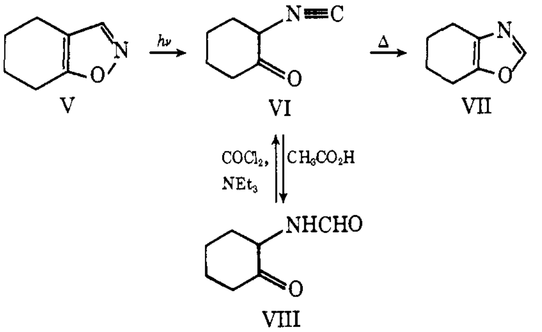
[a] Irradiated with 300-nm light source for 15 min; nd, not determined. [b] Yield determined from uv spectrum. [c] Yield determined by vpc. [d] Yield determined by uv spectra after separation by tlc on silica gel. [e] Details given in ref 7.

both benzene and acetone. These studies, together with our failure to observe the inhibition of benzoxazole formation in the presence of triplet quenchers, suggest singlet sensitization by benzene[3,18] and acetone.[17]

The variation in luminescence and photoproducts with solvent polarity is also consistent with the conclusion derived from the sensitization and quenching experiments. Fluorescence but no phosphorescence is observed in a polar glass (4:1 ethanol–methanol) while phosphorescence is observed along with the fluorescence in a nonpolar glass (5:1 methylcyclohexane–isopentane). Benzoxazole is the predominant product in hydroxylic solvents while cyanophenol is the predominant photoproduct in hydrocarbon solvents. These solvent effects are consistent with benzoxazole formation from a $\pi,\pi^*$ state and cyanophenol formation from a $n,\pi^*$ state.[19]

An isonitrile was also detected in the photochemical conversion of V[20] to VII. A precursor to the isonitrile was detected by an ir band at 1695 $\text{cm}^{-1}$ when V was irradiated for 1–3 hr at −77° with a 254-nm light source.[22] The 1695-$\text{cm}^{-1}$ absorption gradually disappeared and bands at 2160 and 1725 $\text{cm}^{-1}$ gradually appeared when the cryostat was allowed to warm to room temperature. The 2160- and 1725-$\text{cm}^{-1}$ bands are consistent with the ketoisonitrile VI. After 4 hr at room temperature, these maxima disappeared and several of the ir bands characteristic of oxazole VII had formed. The presence of VII together with a lesser amount of 2-cyanocyclohexanone was detected by tlc analysis of the reaction mixture.

A 99% yield of VII was obtained when the photolysis of V was performed at room temperature in ethanol solution. A 50% yield of the formamide VIII[23] was obtained when the photolysis was performed in acetic acid, a result consistent with VI as a reaction intermediate.[11] Furthermore, the ir spectrum of the crude reaction product obtained by the reaction of VIII with phosgene[12] also exhibited an ir band at 2160 $\text{cm}^{-1}$ which decreased in intensity at room temperature; oxazole VII was isolated from this reaction mixture.



**Acknowledgment.** This research was sponsored by the National Institutes of Health in the form of a research grant (GM 15915) and a Research Career Development Award (to J. P. F., GM 6380).

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(18) W. A. Henderson, Jr., R. Lopresti, and A. Zweig, *J. Amer. Chem. Soc.*, **91**, 6049 (1969); J. T. Dubois and F. Wilkinson, *J. Chem. Phys.*, **38**, 2541 (1963).

(19) E. Lim and J. Yu, *ibid.*, **45**, 4742 (1966).

(20) Previous syntheses yielded a mixture of V and another isomer.[21] A new synthesis was devised which yields only V. The details of this synthesis will be reported later.

(21) K. v. Auwers, Th. Bahr, and E. Frese, *Justus Liebigs Ann. Chem.*, 441, 54 (1925).

(22) The structure of this intermediate is currently under investigation.

(23) Satisfactory analytical and spectral data have been obtained on this new compound.

## Sulfur Monoxide Chemistry. Stereochemistry of the Thiirane Oxide–Diene Reaction

*Sir:*

Dodson and his coworkers[1] discovered that SO generated by thermolysis of thiirane oxide[2] could be trapped by dienes and trienes in the form of 2,5-dihydrothiophene (3-thiolene) and 2,7-dihydrothiepin *S*-oxides. Following up an earlier study of the $SO_2$–diene reaction in this laboratory,[3] we have now examined the stereochemistry of the theoretically interesting[4] SO–diene cycloaddition.

The three 2,4-hexadienes **1** were chosen for this purpose, and all three of the related 3-thiolene *S*-oxides **2** were obtained (eq 1, Table I).[5] Mixtures of the isomers were separated by column chromatography on silica gel. All three compounds displayed strong sulfoxide S–O stretching absorption; all suffered SO and (SO + methyl) loss as major fragmentation path-

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(1) R. M. Dodson and R. F. Sauers, *Chem. Commun.*, 1189 (1967); R. M. Dodson and J. P. Nelson, *ibid.*, 1159 (1969). The reaction with dienes has also been used to trap SO from another source: Y. L. Chow, J. N. S. Taru, J. E. Blier, and H. H. Szmant, *ibid.*, 1604 (1970).

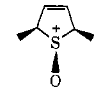
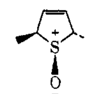
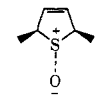
(2) G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, **88**, 2616 (1966).

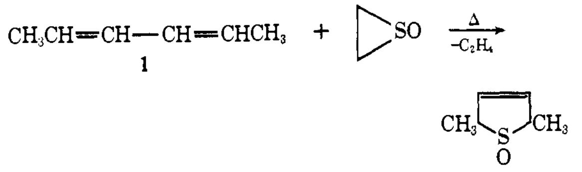
(3) S. D. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966); see also W. L. Mock, *ibid.*, **88**, 2857 (1966).

(4) D. M. Lemal and P. Chao, *ibid.*, **95**, 922 (1973).

(5) Dodson and Sikstrom have studied the same reactions: R. A. Sikstrom, Ph.D. Dissertation, University of Minnesota, 1971.

Table I. Properties of the 2,5-Dimethyl-3-thiolene *S*-Oxides

| Compd | Bp (mp), °C | Ir $\lambda_{max}$, cm$^{-1}$ | Nmr $\delta$, $CDCl_3$: Vinyl | Nmr $\delta$, $CDCl_3$: Methine | Nmr $\delta$, $CDCl_3$: Methyl |
|---|---|---|---|---|---|
|  | (74.5–75.5) | 1040<br>1048<br>(KBr) | 5.70<br>(d, $J$ = 0.5 Hz) | 3.80<br>(d of q,<br>$J$ = 0.5, 7 Hz) | 1.47<br>(d, $J$ = 7 Hz) |
|  | 57–58<br>(0.5 mm) | 1039<br>(neat) | 5.79 (m) | 3.83 (m) | 1.41<br>(d, $J$ = 7 Hz)<br>1.37<br>(d, $J$ = 7 Hz) |
|  | 57–58<br>(0.5 mm) | 1041<br>1060<br>1072<br>(neat) | 5.79<br>(d, $J$ = 0.5 Hz) | 3.76<br>(d of q,<br>$J$ = 0.5, 7 Hz) | 1.41<br>(d, $J$ = 7 Hz) |

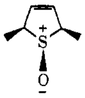
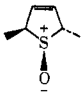
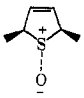
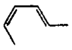


1

2

(1)

Table II. Reactions of Thiirane Oxide with 2,4-Hexadienes[a]

| Diene | Relative % yields[b] | | | % diene isomerization after 2 hr[c] |
|---|---|---|---|---|
| |  |  |  | |
|  | 0 | 13 | 87 | 5 |
|  | Trace | 95 | 5 | 8 |
|  | 20 | 61 | 19 | 22 |

[a] In toluene at 108°. [b] These are approximate values because they were extrapolated to time zero and because resolution was incomplete in the glc analysis. [c] Decomposition of thiirane oxide was roughly one-third complete at this time. Due to catalysis by decomposition products, this reaction does not follow first-order kinetics to high conversions.

ways on electron impact. Sulfoxide **2**-*c*,*t*[6] was easily recognized by the nonequivalence of its methyls in the nmr spectrum, and the assignment was confirmed by oxidation with *m*-chloroperbenzoic acid to the known *trans*-2,5-dimethyl-3-sulfolene.[3] Both **2**-*t*,*t* and **2**-*c*,*c* gave *cis*-2,5-dimethyl-3-sulfolene when similarly oxidized.[3] The finding that one of these had the longest and the other the shortest glc retention time of the three isomers hinted strongly that they were **2**-*t*,*t* and **2**-*c*,*c*, respectively, since retention times of sulfoxides tend to increase with exposure of the oxygen atom.[7] These assignments were corroborated through the use of the nmr shift reagent $Eu(DPM)_3$.[8] In **2**-*t*,*t* the methine protons were found to suffer downfield shifts roughly three times as large as those of the methyl protons, whereas in **2**-*c*,*c* the methyl shifts were more than three times the methine.

Thermal interconversion experiments revealed this order of thermodynamic stabilities: **2**-*c*,*c* > **2**-*c*,*t* > **2**-*t*,*t*. In confirmation, treatment with hydrogen chloride in dioxane (which equilibrates sulfoxides at sulfur)[9] transformed **2**-*t*,*t* almost entirely into **2**-*c*,*c*. Though casual inspection tempts one to predict the opposite stability order on steric grounds, scale models show that the closest approach of methyl hydrogens to the sulfoxide oxygen in **2**-*c*,*c* is very close to the sum of the van der Waals radii,[10] Moreover, *cis*-2-methylthiolane oxide is known to be stabler than the trans isomer.[7]

In Table II are summarized the results of experiments in which a toluene solution 0.8 *M* each in thiirane oxide and a 2,4-hexadiene was heated under reflux (108°). Since diene isomerization accompanied the SO-transfer reaction, the reported product compositions have been extrapolated to zero reaction time. Additions of SO to **1**-*t*,*t* and **1**-*c*,*t* are highly stereoselective at carbon. Stereochemical control at sulfur is detectable only in methyl *cis*-sulfoxides, of course, but it is noteworthy that the methyl *cis*-sulfoxide from **1**-*t*,*t* is *exclusively the less stable isomer* **2**-*t*,*t*. In the accompanying paper,[4] evidence is presented that these additions proceed *via* attack of triplet SO on (mainly) s-trans diene;[11] within the framework of this mechanistic hypothesis, the high degree of stereoelectronic control is most surprising.

The SO–diene cycloaddition can be reversed thermally. Whether run in xylene at temperatures as low as 135° or in the injection port of a gas chromatograph in the 250–400° range, the retro reaction shows little stereoselectivity, and extensive starting material stereoisomerization is observed. If excess isoprene is coinjected with a 2,5-dimethyl-3-thiolene oxide at a high temperature, one obtains some of the SO–isoprene adduct, 3-methyl-3-thiolene oxide,[12,13] but not at lower

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(6) The symbols *c* and *t* refer to cis and trans, but note that these designate stereochemical features in the sulfoxides different from those in the dienes.

(7) J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, **35**, 3655 (1970).

(8) Others have used this reagent for assignment of configuration to sulfoxides. R. R. Fraser and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970); J. L. Green, Jr., and P. B. Shevlin, *ibid.*, 1092 (1971); M. Kishi, K. Tori, T. Komeno, and T. Shingu, *Tetrahedron Lett.*, 3525 (1971).

(9) H. Kwart and H. Omura, *J. Amer. Chem. Soc.*, **93**, 7250 (1971).

(10) The methyl groups in this molecule are probably quasi-equatorial, but the minimum O–H distance varies little with conformation. See ref 7 and references therein regarding conformational energies of sulfoxides.

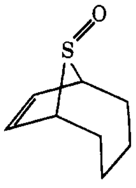
(11) The rate of decomposition of thiirane oxide is not increased by raising the diene concentration, so direct attack of thiirane oxide on diene is ruled out.

(12) This compound has been synthesized *via* another route by D. W. Kreh and R. C. Krug, *J. Org. Chem.*, **32**, 4057 (1967).

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).

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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).