(Fe2–S3′ = 3.641 (3) Å is the closest ligand atom contact trans to S8).

The structural determination provides unambiguous identification of the copper oxidation states in **2**. For Cu(MNT)$_2^{2-}$, Cu(II)–S(av) = 2.276 (1) Å,[18] a value very close to Cu2–S(av) = 2.261 (1) Å in **2**. For the Cu(MNT)$_2^-$ anion, Cu(III)–S(av) = 2.170 (4) Å,[19] and Cu1–S(av) = 2.180 (1) Å in **2**. As might be expected, the bridging interactions involving sulfur atoms bound to Cu1 are long compared to those originating at Cu2. For both copper complex anions, these bridging interactions result in tetrahedral distortions.

Scheidt and Reed[20] have outlined the structural parameters expected for $S = {}^3/_2$ ferric porphyrins. Fe–N$_p$ bond lengths should be similar to those of low spin derivatives, due to depopulation of the d$_{x^2-y^2}$ orbital. Five-coordinate complexes should exhibit Fe–Ct$_p$ values greater than 0.11 Å (the maximum known for $S = {}^1/_2$ complexes) and less than 0.39 Å (the minimum known for $S = {}^5/_2$ complexes), while six-coordinate $S = {}^3/_2$ complexes must exhibit very long axial bonds.

The five-coordinate Fe2 atom is presumably structurally similar to the iron(III) atoms in **1**. The Fe2–Ct$_p$ distance of 0.22 Å (Fe2–Ct$_N$ = 0.20 Å) observed in **2** falls within the range of 0.11–0.39 Å for five-coordinate $S = {}^3/_2$ ferric porphyrins. The Fe2–Ct$_N$ distance is less than the corresponding distances of 0.26 and 0.28 Å in two mixed-spin ($S = {}^3/_2, {}^5/_2$) five-coordinate ferric porphyrin complexes.[21,22] Since high-spin ferric porphyrins usually exhibit much larger Fe(III)–Ct$_N$ distances (average 0.40 Å),[20] the short Fe2–Ct$_N$ distance in **2** must reflect a higher proportion of $S = {}^3/_2$ character for Fe2 relative to the two admixed spin systems referred to above. As expected for a predominantly intermediate-spin porphyrin, the bonding between Fe2 and the porphyrin nitrogen atoms is strong (Fe2–N$_p$(av) = 1.976 (4), Ct$_N$–N$_p$(av) = 1.966 Å), and the porphyrin core shows significant S_4 ruffling.

The spin state of the six-coordinate Fe1 atom is more difficult to infer from the metric results. Fe1 is clearly not high spin, since this would require a much larger Ct$_N$–N$_p$ value[20] than the average of 1.975 Å observed (Fe1–N$_p$(av) = 1.978 (4) Å). At the same time, the Fe1–Ct$_N$ distance of 0.12 Å is outside the range of 0.00–0.09 Å found for $S = {}^1/_2$ six-coordinate ferric porphyrin complexes.[20] The only structurally characterized $S = {}^3/_2$ ferric porphyrin complex[23] exhibits an iron(III) atom precisely in the plane of the porphyrin core and longer Fe(III)–N$_p$ distances (Fe–N$_p$(av) = 1.995 (3) Å) than those characteristic of Fe1. Nevertheless, Fe1 may also involve a significant degree of intermediate-spin character, on the basis of the short Fe1–N$_p$ distances and the fact that the Fe1–S bond lengths in **2** are much longer than previously known Fe(III)–S bond lengths in ferric porphyrin systems.[20,24,25]

Finally, Powers and Chance[13] reported Fe(III)–S = 2.60, Cu(II)–S = 2.18, and Fe–Cu = 3.75 Å in CcO. The structure of **2** involves similarly long Fe(III)–S linkages and metal–metal distances (Fe2–Cu2 = 3.921 (1), Cu2–Fe1 = 3.857 (1), Fe1–Cu1 = 4.060 Å) that are strikingly close to the Fe–Cu distance reported for the resting enzyme. These similarities, together with the likely intermediate-spin character for iron(III) in **2**, lend support to the suggestion[14] that an intermediate-spin state for Fe(III) in the fully oxidized form of CcO may have much to do with the intriguing magnetic properties of that enzyme.

Acknowledgment. We thank the National Institutes of Health (Grants 2-R01-GM26958 and 7-R01-GM30306) for generous support of this work. The Nicolet R3m/E diffractometer and computing system were purchased with funds provided by the National Science Foundation (Grant CHE8103011).

Supplementary Material Available: Table I, containing a listing of the atomic coordinates and equivalent isotopic thermal parameters for **2** (3 pages). Ordering information is given on any current masthead page.

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(18) Plumlee, K. W.; Hoffman, B. M.; Ibers, J. A. *J. Chem. Phys.* **1975**, *63*, 1926–1942.

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Conversion of Thiourea Dioxides to Dioxygen

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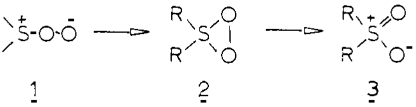
Received July 25, 1983

The oxygen atom transfer[1] reaction of 1,2- and 1,3-dipoles[2] containing one or more oxygen atoms has received considerable recent attention. Prominent among these reactive intermediates are persulfoxides, **1**, which result from the action of singlet oxygen on sulfides[3] or hydrogen peroxide on fluoro derivatives of trialkoxysulfuranes.[4] It has been shown that **1** (R = alkyl) can transfer an oxygen atom to sulfides to give sulfoxides and more rapidly converts sulfoxides to sulfones. If **1** is derived from a trialkoxysulfurane it is electrophilic enough to epoxidize alkenes.[4] In the absence of oxidizable reagents, **1** is ultimately converted into the sulfone, **3**, possibly via the electrocyclization product, the hypervalent thiadioxirane **2**. From studies of the solvent effects on efficiency of oxygen atom transfer the primary species present seems to be **1**.[3,5] However, when **1** (R = Ph) is generated via the sulfurane route in the presence of a triplet energy acceptor such as 9,10-dibromoanthracene, chemiluminescence of the latter is observed.[6] This suggests that **3** is derived from **2** in a triplet state. Clearly, the reaction surface connecting **1** and **3** is most unique.



1 2 3

We thought that the reaction above could be reversed, **3** → **2** → O$_2$. If **3**, by proper substitution, were made less stable than **2**, since an electron acceptor substituent with an energetically low-lying unoccupied molecular orbital (LUMO) of the π-type attached to sulfur stabilizes a tricoordinate hypervalent sulfurane bonding array >, a possible reaction might be the sequence **4** → **5** → **6**. In this communication we describe our observations on this strategy using an imidazolium or a dimethylamino group to adjust the carbonium ion substituent LUMO energy.

It has been reported that diaminocyclopropenium[8] and dihydrodiazepinium[9] salts may be lithiated by alkyllithium reagents[8] to give substituent stabilized lithiocarbenium ions which readily undergo SE reactions with weak electrophiles. Following these

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(1) Hamilton, G. A. In "Molecular Mechanism of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405.

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(7) Burgess, E. M.; Arduengo, A. J. *J. Am. Chem. Soc.* **1977**, *99*, 2376.

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(9) Lloyd, C. D.; McNab, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 459.

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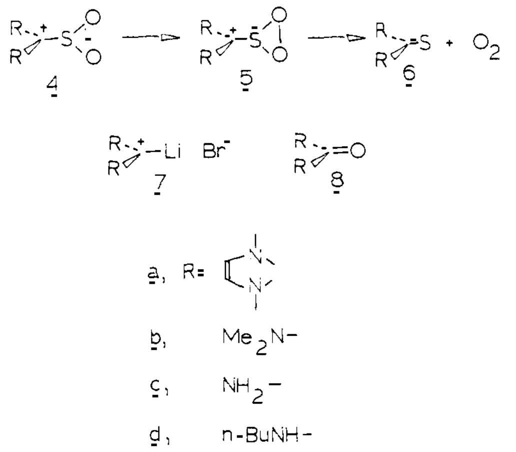

observations, we treated an anhydrous diethyl ether suspension of *N,N'*-dimethyllimidazolium bromide under an argon atmosphere with an excess of *n*-butyllithium (1.6 M in hexane) to give **7a**. After 6 h at 30 °C sulfur dioxide was introduced, and upon standing for 20 h unreacted starting material, lithium bromide, and **6a** were isolated (quantitative yield based on a 36.8% conversion conversion).[10] No trace of urea **8a** could be detected, and if **4a** was an intermediate it was converted only to **6a**.

Mono-, di-, and trialkylthiourea *S,S*-dioxides have recently been prepared,[11] and the unsubstituted thiourea *S,S*-dioxide (**4c**) is a well-known industrial reducing agent. No reports have appeared to the thermal decomposition of these dioxides in aprotic solvents, only that solid *N,N'*-di-*sec*-butylthiourea *S,S*-dioxide decomposes to sulfur dioxide and the corresponding formamidine at 100 °C or that **4c** gives the analogous products in refluxing acetic acid.[14]

We find that **4c** *decomposes to thiourea, urea* (*2:3*) *ratio*), *and dioxygen in refluxing anhydrous acetonitrile with a 98% conversion after 0.7 h.* For analysis, **6d** (mp 85–86 °C dec)[13] was prepared by the hydrogen peroxide oxidation of *N,N'*-di-*n*-butylthiourea.[11] This derivative in acetonitrile provided the thiourea and formamidine (1:2.8 ratio) in a first-order reaction with a composite $k_1 = 1.0 \times 10^{-4}$ ($r = 0.9972$) at 45 °C.

SCF-MO calculations reveal that the lowest energy mode of decomposition of **4c** is dissociation into the singlet carbene and sulfur dioxide complex (C–S bond length of 2.05 Å) lying only 2–3 kcal above the bound dioxide. This result accounts for the equilibrium of **7a** and sulfur dioxide with **4a** leading to isolation of starting imidazolium salt after 20 h. The formamidine isolated in the decomposition of **4d** also may result from tautomerization and loss of sulfur dioxide from this complex. This reaction is also theoretically characterized at the molecular orbital level[15] at a higher activation energy by the linear departure (mirror symmetry about an *xy* plane) of a singlet dioxygen fragment from singlet **5**. Along this fragmentation reaction coordinate an occupied–unoccupied orbital crossing occurs if a rotation about the *z* axis of the oxygen p_y and P_x orbitals is assumed. This provides the oribtal reactant to product correspondence (the stationary thione fragment acting as an orbital symmetry reference) shown in Figure 1.[16] At this crossing point the oribtal rotation creates orbital angular momentum along the *z* axis, which is favorable for a large spin–orbit coupling matrix element between the triplet and singlet state. Intersystem crossing to the triplet reacting complex can occur to give exothermically the lower energy triplet dioxygen.

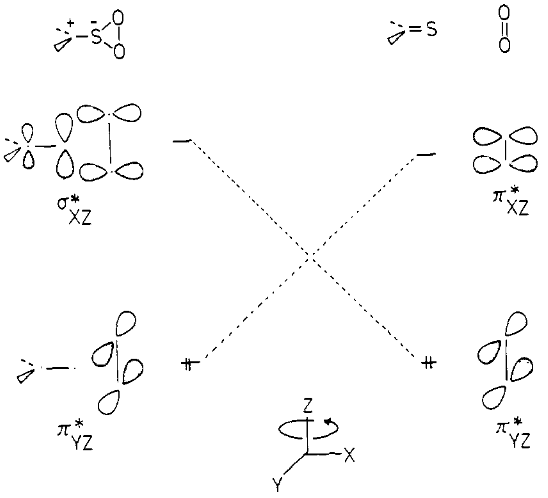

Figure 1. Orbital correspondence for the fragmentation of a hypervalent substituted thiadioxirane to dioxygen. Rotation of the O–O fragment occurs about the *z* axis.

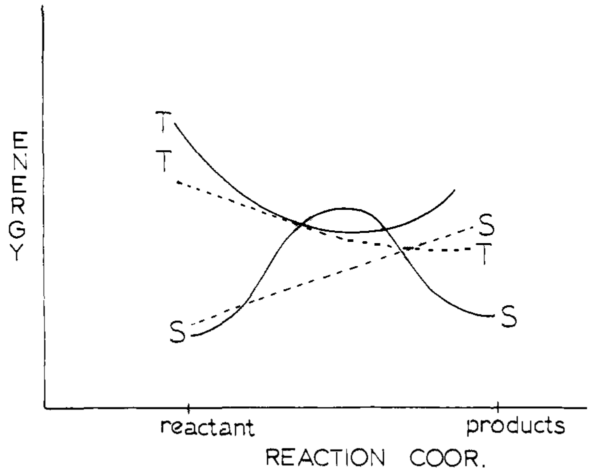

Figure 2. Surfaces for pericyclic reactions. S is the lowest singlet state (ground state) and T the lowest triplet state. The solid line represents the path with two crossing points associated with most forbidden pericyclic reactions. The dotted line is characteristic of reactions producing a stable ground-state triplet product such as dioxygen. If both states have the same symmetry, intersystem crossing may occur in the shaded regions.

This is a unique example, unlike most forbidden pericyclic reactions, in which the triplet surface remains energetically below the singlet beyond the crossing point (Figure 2).

If intersystem crossing occurs before the rate-determining step transition state the production of the triplet product might be enhanced by an external heavy atom effect. Unfortunately, we could find no change in product ratios for decomposition of **6d** in the presence of 5 equiv of mono- or diiodobenzene. This suggests that the crossing point does not meet the above criteron or that the internal orbital motion produces a torque that is much greater than any external heavy atom can provide.

Finally, another substituent with an energetically low-lying unoccupied orbital of the π*-type which would stabilize a tricoordinate sulfurane bonding system, is the phosphonium group. We explored the possibility of **9** → **10** → **11** → **12**.

The treatment of **9**[17] (neat) with an excess of sulfur dioxide at −78 °C gave a 72% yield of the phosphine oxide (**13**) and sulfide (**12**) in a ratio of 3:4.[18] A 1:1 mixture of **12** and **13** could be accounted for by the reaction below[19] without the intervention

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(10) At no time did the reaction mixture become homogeneous. Neither *N,N'*-dimethylimidazolium perchlorate in methylene chloride solution or the triflate salt in THF solution give any detectable amounts of **6a** in this reaction. Traces of **6a** were found in the reaction of the triflate as a suspension in diethyl ether. The origin of this solvent effect is unknown.

(11) Walter, W.; Randau, G. *Liebigs Ann. Chem.* **1969**, *722*, 80.

(12) Identified by mass spectroscopy.

(13) A satisfactory elemental analysis was obtained.

(14) Havel, J. J.; Kluttz, R. Q. *Synth. Commun.* **1974**, 389.

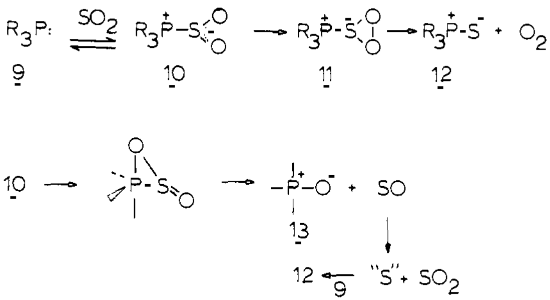
(15) MINDO/3 with geometry–energy optimization.

(16) An excellent discussion of favorable orbital orientation for intersystem crossing may be found in: Salem, L.; Rowland, C. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 92.

(17) Kindly provided by Dr. Kent Barefield.

(18) The balance of the reaction mixture was single unidentified SO_2-containing product.

(19) A similar mechanism accounts for the formation of urea in the decomposition of **4c**.



of **11** and its subsequent fragmentation. However, when this reaction was carried out under the same conditions in the presence of an equimolar amount of *o*-dibromobenzene the yield was unchanged but the ratio of **13** to **12** was 3:7. It is amusing to speculate that in this case an external heavy atom catalyst was responsible for an increased intersystem crossing efficiency in the fragmentation of an intermediate such as **11**.

Acknowledgment. We wish to thank the NSF and NIH for generous financial support and Drs. Charles Liotta and Kent Barefield for their interest and suggestions.

Two-Flask Preparation of α-Lithio Cyclic Ethers from γ- and δ-Lactones. Reductive Lithiation as a Route, via Radical Intermediates, to Axial 2-Lithiotetrahydropyrans and Their Equilibration to the Equatorial Isomers

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Received August 5, 1983

In this paper, we report a two-flask procedure for preparing α-lithio derivatives of tetrahydrofurans and tetrahydropyrans by a two-stage reduction of widely available γ- and δ-lactones, we demonstrate the utility of this method by describing a very efficient stereospecific total synthesis, the first recorded,[1] of (±)-*trans*-rosoxide (**6**), which also includes a new procedure for the vinylation of carbanions, and we reveal that axial 2-lithiotetrahydropyrans are the proximate products of reductive lithiation of 2-(phenylthio)tetrahydropyrans but that they can be equilibrated to the more stable equatorial organolithiums.

A recent report from this laboratory revealed that reductive lithiation of α-phenylthio ethers, preferably by readily preparable lithium 1-(dimethylamino)naphthalenide (LDMAN), constitutes the first general method for preparing α-lithio ethers.[2] The general method reported here for producing α-phenylthio cyclic ethers in both the five- and six-member ring series and the demonstration that α-lithio ethers can be produced from them and trapped by aldehydes and ketones should have considerable value in synthesis since five- and six-member oxygen heterocycles are distributed widely in nature.

The procedure is demonstrated by a three-flask preparation of (±)-*trans*-rosoxide (Scheme I),[3] a substance that is found in roses and geraniums[4] and is used in the perfume industry. Commercially available lactone **1** is reduced with diisobutylaluminum hydride, and the resulting aluminum salt of the lactol is treated directly with 1.2 M equiv of thiophenol containing 2–3 M equiv of $BF_3{\cdot}OEt_2$ to yield the mixture of stereoisomers **2**. Reductive lithiation of the mixture with LDMAN yields only the *trans*-2-lithio-4-methyltetrahydropyran (**3**) which adds in a 1,2 fashion to methacrolein; the resulting alkoxide salt **4** reacts with CS_2, and the methyl xanthate, produced by S-methylation of the product, undergoes a [3,3]-sigmatropic rearrangement[5] to yield a single isomer, assumed to have an *E* double bond (**5**), in very satisfactory yield. Reductive desulfurization[6] produces racemic *trans*-rosoxide (**6**).[1] This novel method of vinylation of carbanions is quite promising;[7] a preliminary experiment has shown that methyl vinyl ketone can be substituted for methacrolein.

Scheme I

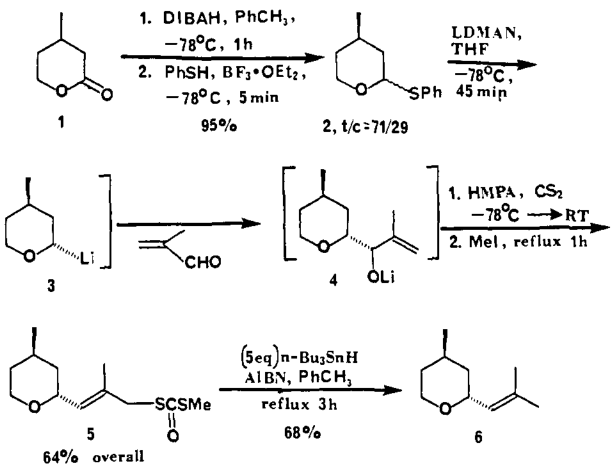
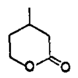
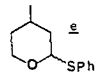
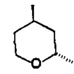
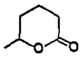
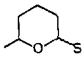
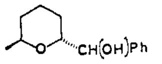
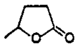
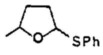
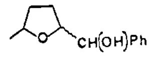
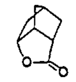
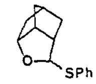
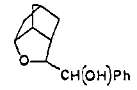
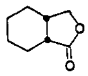
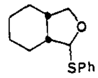
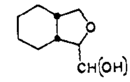


Table I. Conversion of Lactones to α-Lithio Ethers

lactone[a]	α-phenylthio ether[b]	yield, %	product of RLi + electrophile[b-d]	yield, %
	 [e]	95	 Y = PhCH(OH) Y = $Ph_2C(OH)$[f] Y = $Me_2C(OH)$[g]	63 65 68
 [h]	 [i]	74		56
		97		51
 [j]		94		46
 [k]		76		56

[a] The lactones are commercially available except where noted. [b] Wavy lines indicate mixture of stereoisomers. [c] Except in the cases noted, the electrophile was benzaldehyde. [d] The products of trapping with aldehydes were pairs of threo and erythro isomers. [e] Cis:trans = 29:71. [f] The electrophile was benzophenone. [g] The electrophile was acetone. [h] Reference 23. [i] Cis:trans = 9:91. [j] Reference 24. [k] Reference 25.

As indicated by the representative examples in Table I, other δ-lactones as well as γ-lactones behave in a similar fashion,[3] but we have been unable to convert ε-caprolactone to the seven-membered ring α-phenylthio ether by this method.

The apparently stereospecific production of trans products in the reductive lithiation of the 4- and 6-methyl-2-(phenylthio)-

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[1] In all syntheses, the trans isomer is produced as a mixture with the cis isomer in which the latter is usually the major component. For example, see: Eschinasi, E. H. *J. Org. Chem.* **1970**, *35*, 1097.

[2] Cohen, T.; Matz, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900.

[3] New compounds have been characterized by ^1H NMR, IR, and mass spectroscopy and either by their exact masses or by combustion analyses.

[4] Naves, Y.-R.; Lamparsky, D.; Ochsner, P. *Bull. Soc. Chim. Fr.* **1961**, 645. Seidel, C. F.; Felix, D.; Eschenmoser, A.; Biemann, K.; Palluy, E.; Stoll, M. *Helv. Chim. Acta* **1961**, *44*, 598.

[5] Harano, K.; Taguchi, T. *Chem. Pharm. Bull. (Tokyo)* **1972**, *20*, 2348, 2357.

[6] Barton, D. H. R.; Motherwell, W. B. *Pure Appl. Chem.* **1981**, *53*, 1081. Ueno, Y.; Sano, H.; Okawara, M. *Tetrahedron Lett.* **1980**, 1767.

[7] For a discussion of some other methods, see: Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251.

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