not afford the expected dimer[14] of tri-*tert*-butylcyclobutadiene. Rather, the exclusive product in essentially quantitative yield was cyclopropenyl ketone **6**.

The fact that **6** was also formed from the solvolysis of **1** suggests that cationic intermediates[15] may be involved in the oxidation of **2** as well. Details of the mechanism of this latter transformation remain obscure at the present time. Efforts to provide information in this area are in progress.

Acknowledgments. Acknowledgment is made to the Research Corporation for financial support of this work. We thank Mr. J. G. Henkel for the use of his computer program and Mr. S. Cichanowski for the dipole moment determination.

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[14] We have obtained a compound which possesses the expected analytical and spectroscopic data for a dimer of tri-*tert*-butylcyclobutadiene, namely 1,3,4,5,7,8-hexa-*tert*-butyltricyclo[4.2.0.0^{2,5}]octa-3,7-diene (**10**) by reaction of **1** with lithium amalgam in ether. This dimer may be formed by a stepwise double Wurtz reaction. *Cf.* discussion in ref 6.

[15] J. D. Fitzpatrick, Ph.D. Thesis, University of Texas, 1966.

[16] National Science Foundation Trainee, 1970–1971.

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Meisenheimer Rearrangement of Methoxymethyl Phenyl Sulfoxide. The Formation and Disproportionation of Methoxymethyl Benzenesulfenate[1]

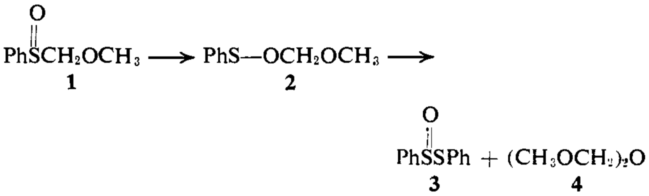
Sir:

The Meisenheimer rearrangement of amine *N*-oxides to substituted hydroxylamines invariably favors the N → O 1,2 shift.[2] In sharp contrast with this are the generally preferred thermal O → S 1,2 shifts of the sulfoxylate → sulfinate,[3] sulfinate → sulfone,[4] and sulfenate → sulfoxide[5] rearrangements, as well as the thermal O → P 1,2 shift in the phosphinite → phosphine oxide rearrangement.[6]

In a few cases the Meisenheimer rearrangement of a sulfoxide to sulfenate has been reported, but either an equilibrium mixture of the two was established in which the sulfoxide predominated greatly,[5] or the sulfenate was removed from the equilibrium by an irreversible decomposition reaction.[5,7]

We now wish to report the facile Meisenheimer rearrangement of a sulfoxide to sulfenate where the sulfenate is isolated exclusively. This was facilitated by the synthesis of a new α-alkoxy sulfoxide,[8] methoxymethyl phenyl sulfoxide (**1**, 90% yield), by oxidation of methoxymethyl phenyl sulfide[9] with *m*-chloroperbenzoic acid.

Methoxymethyl phenyl sulfoxide (**1**) rearranged completely to methoxymethyl benzenesulfenate (**2**) in 2 days at 36°. The sulfenate **2** is likewise unstable and reacts further in a manner that is unprecedented for sulfenate esters. After 4–5 days at 36°, **2** disproportionates to phenyl benzenethiolsulfinate (**3**, 81%), bismethoxymethyl ether (**4**, 41%), and among other products some phenyl disulfide and phenyl benzenethiolsulfonate. Both **1** and **2** are unstable at room temperature and must be stored at or below −5°. Even at −5° the sulfenate **2** decomposed about 10% in 1 month.



$$\mathrm{Ph\overset{\displaystyle O}{\overset{\|}{S}}CH_2OCH_3}\ (\mathbf{1}) \longrightarrow \mathrm{PhS{-}OCH_2OCH_3}\ (\mathbf{2}) \longrightarrow \mathrm{Ph\overset{\displaystyle O}{\overset{\|}{S}}SPh}\ (\mathbf{3}) + \mathrm{(CH_3OCH_2)_2O}\ (\mathbf{4})$$

The structure of **1** is supported by the following data: ir (CCl_4) 1047 cm^{-1} (S═O); nmr (CCl_4, 60 MHz) δ 3.67 (s, 3, OCH_3), 4.23, 4.35 (AB q, 2, J = 10 Hz, diastereotopic CH_2), 7.2–7.7 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity) 170 (52, molecular ion), 154 (20), 140 (31), 125 (62), 109 (78), 97 (50), 83 (90), 82 (64), 45 (100). Oxidation of **1** with *m*-chloroperbenzoic acid gave a product which was identical (melting point, ir, nmr) with methoxymethyl phenyl sulfone.[10] The structure of **2** is supported as follows: ir (CCl_4) 937 cm^{-1} (strong, -S-O-); nmr (CCl_4) δ 3.34 (s, 3, OCH_3), 4.81 (s, 2, CH_2), 7.0–7.7 (m, 5, C_6H_5); mass spectrum (70 eV) *m/e* (rel intensity): 170 (53, molecular ion), 157 (14), 155 (13), 140 (36), 138 (39), 125 (42), 109 (68), 83 (29), 82 (83), 75 (56), 45 (100). Phenyl benzenethiolsulfinate (**3**),[11] phenyl benzenethiolsulfonate,[12] and phenyl disulfide were identical (melting point and ir) with independently prepared samples. Bismethoxymethyl ether (**4**)[13] was identified from the following spectral data: ir (CCl_4) 1132, 1104, 995, and 934 cm^{-1}; nmr (CCl_4) δ 4.63 (s, 4) and 3.36 (s, 6); mass spectrum (70 eV) *m/e* (rel intensity) 105 (33, M − 1), 76 (49), 75 (88), 74 (75), 46 (34), 45 (100), 44 (46).

The reactions were easily followed by monitoring ir and nmr spectra. The sulfoxide band of **1** was observed to disappear simultaneously with the appearance of the strong sulfenate band of **2**. Likewise, the methylene and methyl nmr absorptions of **1** decreased as the corresponding peaks of **2** increased. Subsequent decomposition of **2** was followed in the same way.[14]

The rearrangement of **1** to **2** was inhibited by weak acids and hydroxylic compounds such as carboxylic acids and phenols. Thus, it was necessary to extract **1** with sodium carbonate and dry carefully before it would

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[1] Presented in part at the 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March, 1971, paper ORGN-13.

[2] (a) J. Meisenheimer, *Ber.*, 52, 1667 (1919); (b) A. H. Wragg, T. S. Stevens, and D. M. Ostle, *J. Chem. Soc.*, 4057 (1958); (c) G. P. Shulman, P. Ellgen, and M. Conner, *Can. J. Chem.*, 43, 3459 (1965); (d) U. Schöllkopf, M. Patsch, and H. Schafer, *Tetrahedron Lett.*, 2515 (1964).

[3] Q. E. Thompson, *J. Org. Chem.*, 30, 2703 (1965).

[4] D. Darwish and E. A. Preston, *Tetrahedron Lett.*, 113 (1964).

[5] (a) E. G. Miller, D. R. Rayner, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3139 (1966); (b) E. G. Miller, D. R. Rayner, H. T. Thomas, and K. Mislow, *ibid.*, **90**, 4861 (1968).

[6] A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948); R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. C*, 722 (1966).

[7] W. Carruthers, I. D. Entwistle, R. A. W. Johnstone, and B. J. Millard, *Chem. Ind. (London)*, 342 (1966).

[8] Another synthetic method has been reported by K. Ogura and G. Tsuchihashi, *Chem. Commun.*, 1689 (1970).

[9] J. deLattre, *Bull. Soc. Chim. Belg.*, **26**, 323 (1912); *Chem. Abstr.*, 7, 1361 (1913).

[10] R. J. Mulder, A. M. van Leusen, and J. Strating, *Tetrahedron Lett.*, 3057, 3061 (1967).

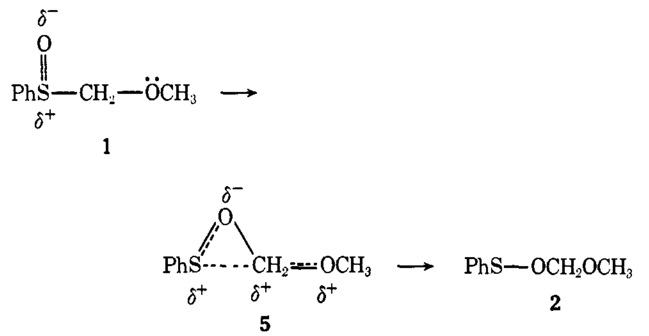
[11] P. Koch, E. Ciuffarin, and A. Fava, *J. Amer. Chem. Soc.*, **92**, 5971 (1970).

[12] H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, 73, 129 (1954).

[13] G. Allen, R. Warren, and K. J. Taylor reported (*Chem. Ind. (London)*, 623 (1964)) nmr (in *p*-chlorophenol) δ 4.72 (s) and 3.36 (s).

[14] The reactions were monitored for solutions of **1** and **2** in undegassed carbon tetrachloride.

rearrange. These results suggest that **1** rearranges through a polarized activated complex (**5**), because

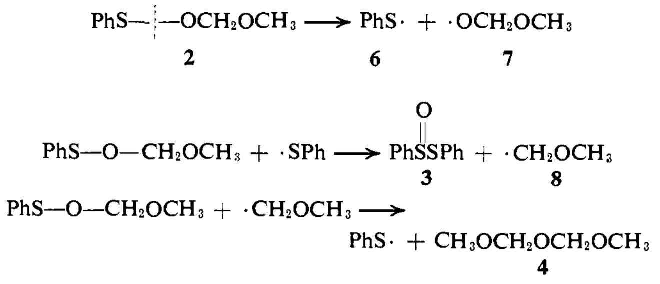


protonation of or hydrogen bonding with the sulfoxide oxygen should reduce its nucleophilicity. Further supporting evidence is the facilitation of rearrangement by the electron-releasing methoxyl group compared with the reluctance of the benzoyloxy-substituted sulfoxide to react below 110°.

Acids had just the opposite effect on the decomposition of **2** by acting as a catalyst, increasing the rate with stronger acids, and affording different products. Hydroquinone, however, was too weak an acid to catalyze the decomposition of **2**, but instead had a dramatic inhibitory effect on **2** (about 20% decomposition in 1 month at 36°). Hydroquinone also retarded the rearrangement of **1**. Whether hydroquinone inhibits the reactions of **1** by hydrogen bonding or of **1** and **2** by free-radical quenching can be considered.[15]

We found no significant change in the hydroquinone concentration (5 mol %) during the retarded rearrangement of **1** to **2** until an appreciable amount of **2** was formed (50%, 1 week). The slow decomposition of **2** was paralleled by a decrease in the hydroquinone nmr absorption with a concomitant appearance of the absorption peak of benzoquinone. Hydroquinone did not significantly change the product composition because of its low concentration.

The product composition and inhibitory effect of hydroquinone suggest that **2** decomposes by a free-radical chain mechanism. It is plausible that initiation occurs by homolytic cleavage of the S–O bond of **2** to give the thiophenoxyl (**6**) and methoxymethoxyl (**7**) radicals. Each of these conceivably could initiate a chain process by reacting with **2**. The following sequence is one in which **6** and methoxymethyl (**8**) radicals are chain carriers. The alternative involvement of **7** is unlikely, as it would require an unprecedented free-radical displacement reaction at carbon.



$$\underset{\mathbf{2}}{\mathrm{PhS{-}\!\!\vdots\!\!{-}OCH_2OCH_3}} \longrightarrow \underset{\mathbf{6}}{\mathrm{PhS\cdot}} + \underset{\mathbf{7}}{\mathrm{\cdot OCH_2OCH_3}}$$

$$\mathrm{PhS{-}O{-}CH_2OCH_3} + \mathrm{\cdot SPh} \longrightarrow \underset{\mathbf{3}}{\mathrm{Ph\overset{O}{\overset{\|}{S}}SPh}} + \underset{\mathbf{8}}{\mathrm{\cdot CH_2OCH_3}}$$

$$\mathrm{PhS{-}O{-}CH_2OCH_3} + \mathrm{\cdot CH_2OCH_3} \longrightarrow \mathrm{PhS\cdot} + \underset{\mathbf{4}}{\mathrm{CH_3OCH_2OCH_2OCH_3}}$$

The sensitivity of **2** to acids is not surprising, as it is an acetal of formaldehyde. What is at first surprising is again the formation of **3** as the major product. The formation of **3** in the acid-catalyzed reaction could be explained by the intermediacy of benzenesulfenic acid through a general scheme proposed by Kice and Cleveland.[16] The fate of the methoxymethyl group is complex.

Acknowledgments. This investigation was supported in part by a Frederick Gardner Cottrell grant from Research Corporation and a National Science Foundation Institutional Undergraduate Research grant.

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(15) A radical pair has been implicated in benzyl migration in the Meisenheimer rearrangement of amine oxides.[2c,d]

(16) J. L. Kice and J. P. Cleveland, *J. Amer. Chem. Soc.*, **92**, 4757 (1970).

(17) National Science Foundation Undergraduate Research Participant, 1970.

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Received March 15, 1972

X-Ray Photoelectron Spectroscopy of Some Nickel Dithiolate Complexes

Sir:

The remarkable oxidation–reduction behavior of metal dithiolate compounds $[M(S_2C_2R_2)_n]^z$, where M is a large variety of transition metals, n is generally 2 or 3, R is CF_3, CN, C_6H_5, H, CH_3, etc., and z is 0, −1, or −2 (and sometimes −3 when n is 3), has generated an intense interest in the synthetic and theoretical aspects of these compounds.[1] In particular, the theoretical descriptions[2–4] of the nickel compounds have variously described the oxidation state of nickel in $[Ni(S_2C_2R_2)_2]$ as 0, +2, and +4. Because of the square stereochemistry about nickel, the zero oxidation state was considered unreasonable. The paramagnetic species $[Ni(S_2C_2R_2)_2]^-$ has been described as Ni(I) and Ni(III) and as indeterminate in the usual oxidation state formalism. There has been agreement that $[Ni(S_2C_2R_2)_2]^{2-}$ is best described as Ni(II) with two dianionic ligands.

X-Ray photoelectron spectroscopy[5] affords a unique opportunity for a fresh insight into this fairly complex bonding system, since both the metal and sulfur binding energies can easily be measured and the "formal" oxidation states determined.

We have obtained the nickel 2p $^3/_2$ and sulfur 2p binding energies for a series of nickel dithiolate compounds, $\{Ni[S_2C_2(C_6H_5)_2]_2\}^{0,-1,-2}$ and $\{Ni[S_2C_2(CN)_2]_2\}^{-1,-2}$, and some other pertinent materials by measurement with a Varian IEE-15 electron spectrometer. The samples were run as powders dusted onto cellophane tape. Air-sensitive samples were loaded in a glove bag under nitrogen. In the case of elemental nickel, it was necessary to sputter clean the powder with Ar^+ to remove the surface oxides. To compensate for sample charging, the spectra were referenced to the Au (4f $^7/_2$) electrons (E_b = 83.0 eV) from gold which was vacuum deposited onto each sample. The results re-

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