other ROX type intermediates with ethyl iodide could give ether. To shed light on the mechanism of ether formation, reactions of alkyl iodides with hypochlorites were studied.

$$RI + ROX \longrightarrow RI\begin{matrix}X\\ \diagup\\ \diagdown\\ OR\end{matrix} \longrightarrow ROR + IX$$

Chlorine oxide, Cl_2O, and I_2O_5 could be formed from $IClO_3$ by a self-oxidation reaction, with transfer of oxygens from chlorine to iodine. The reaction of chlorine oxide with 2 mol of ethyl iodide in carbon tetrachloride at 0° was found to give ethyl chloride (40% yield), diethyl ether (20%), and ethyl acetate (8%). Since chloride was not detected in the dichlorine heptoxide reaction, chlorine oxide cannot be the reactive intermediate.

Ethyl hypochlorite was also treated with alkyl iodides at 0° in carbon tetrachloride. Equimolar amounts of ethyl hypochlorite and methyl iodide gave a quantitative yield of ethyl hypoiodite and methyl chloride. The latter was easily removed under vacuum to provide a convenient source of hypoiodite solution. Similarly, ethyl hypochlorite and ethyl iodide gave ethyl hypoiodite and ethyl chloride. The structure of ethyl hypoiodite was established by independent synthesis. Ethyl hypochlorite and iodine gave the same material contaminated with iodine chloride. This method has been reported for the synthesis of *tert*-butyl hypoiodite from *tert*-butyl hypochlorite.[14,15] Ethyl hypoiodite was

$$C_2H_5OCl + C_2H_5I \longrightarrow C_2H_5OI + C_2H_5Cl$$

$$C_2H_5OCl + CH_3I \longrightarrow C_2H_5OI + CH_3Cl$$

$$C_2H_5OCl + I_2 \longrightarrow C_2H_5OI + ICl$$

found to react with ethyl iodide to give diethyl ether and ethyl acetate. This result is significant with respect to the dichlorine heptoxide reaction since a hypoiodite is a possible intermediate. Other types of R–OX intermediates cannot be ruled out, however.

Experimental Section

NMR spectra were recorded with a Varian T-60 spectrometer and ir spectra were recorded with a Perkin-Elmer 700 spectrometer. A Varian 920 chromatograph with a 5 ft × 0.25 in. column of 12% QF-1 on Chromosorb W was used for GLC determinations.

Dichlorine heptoxide was utilized as a 0.3 *M* reagent in carbon tetrachloride, prepared by the previously described method.[16] Alkyl perchlorates are sensitive explosives if not diluted with solvent, and previously noted precautions should be observed.[16]

Reaction of Ethyl Iodide with Dichlorine Heptoxide. Ethyl iodide (0.0936 g, 0.6 mmol) was added dropwise with stirring to 2 ml of 0.3 *M* dichlorine heptoxide in carbon tetrachloride at 0°. A granular solid, identified by elemental analysis as iodine pentoxide, and a purple solution were formed immediately. The solution was filtered. Analysis by NMR integration, using added chlorobenzene as a quantitative internal standard, showed 0.378 mmol of ethyl perchlorate (63%) and 0.066 mmol (22%) of ethyl acetate. A similar experiment using 0.187 g (1.2 mmol) of ethyl iodide and 2 ml of 0.3 *M* dichlorine heptoxide solution gave 0.40 mmol (33% based on ethyl iodide) of ethyl perchlorate, 0.078 mmol (13%) of ethyl acetate, and 0.126 mmol (21%) of diethyl ether. The identity of the components was confirmed by ir and GLC comparison with authentic samples.

Reaction of Methyl Iodide with Dichlorine Heptoxide. The reaction of 0.3 mmol of methyl iodide with 1 ml of 0.3 *M* dichlorine heptoxide reagent by the above procedure gave methyl perchlorate (45%) and dimethyl ether (12%). Similarly, 0.6 mmol of methyl iodide gave methyl perchlorate (24%) and dimethyl ether (26%).

Reaction of Ethyl Iodide with Chlorine Oxide. Ethyl iodide (0.0936 g, 0.6 mmol) was added to 1 ml of a 0.3 *M* solution of Cl_2O in carbon tetrachloride[17] with stirring at 0°. NMR analysis of the solution showed 0.24 mmol (40%) of ethyl chloride, 0.06 mmol (20%) of diethyl ether, and 0.024 mmol (8%) of ethyl acetate.

Reaction of Ethyl Hypochlorite with Alkyl Iodides. Methyl iodide (0.0852 g, 0.6 mmol) was added with stirring at 0° to a solution of 0.6 mmol of ethyl hypochlorite[18] in 2 ml of carbon tetrachloride. The NMR spectrum of the resulting colorless solution showed a quantitative yield of methyl chloride and of ethyl hypoiodite. The methyl chloride was removed under vacuum to give a solution of ethyl hypoiodite for spectral characterization: NMR (CCl_4) δ 4.37 (q, 2 H, J = 6.5 Hz, CH_2) and 1.32 ppm (t, 3 H, J = 6.5 Hz, CH_3); ir (CCl_4) 2970 (m), 1480 (m), 1450 (w), 1270 (m), 1240 (m), 1010 (s), and 870 cm^{-1}. The identical compound, contaminated by iodine chloride, was obtained by adding an equimolar amount of iodine to the ethyl hypochlorite solution, a procedure reported for the preparation of *tert*-butyl hypoiodite from *tert*-butyl hypochlorite.[14]

By the above procedure, the reaction of ethyl iodide with an equimolar amount of ethyl hypochlorite gave a quantitative yield of ethyl chloride and ethyl hypoiodite.

Reaction of Ethyl Hypoiodite with Ethyl Iodide. An equimolar amount of ethyl iodide was added at 0° to a solution of ethyl hypoiodite prepared as above. Reaction took place over a period of 1 hr, giving a purple solution. NMR analysis showed ethyl acetate (12%) and diethyl ether (41%).

Registry No.—Ethyl iodide, 75-03-6; dichlorine heptoxide, 10294-48-1; methyl iodide, 74-88-4; chlorine oxide, 7791-21-1; ethyl hypochlorite, 624-85-1; ethyl hypoiodite, 55661-06-8.

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Restricted Rotation in Hindered Aryl Methyl Sulfoxides as Detected by Low-Temperature Proton Magnetic Resonance

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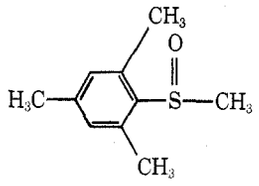
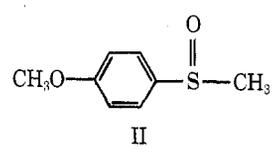
The degree of conjugation between an aromatic ring and the methylsulfinyl group has been the object of considerable attention in the recent literature. Katritsky et al.[1] on the basis of infrared spectral intensities have suggested that the MeSO group is a net resonance donor except when para to a strong electron-donating function. Results of a recent ^{13}C NMR examination,[2] however, do not support this concept. Also, rather little is known regarding the preferred conformations of methyl phenyl sulfoxides, although X-ray[3] and dipole moment[4] studies on the corresponding sulfones indicate a preference for the conformation in which the methyl group is orthogonal to the plane of the benzene ring.

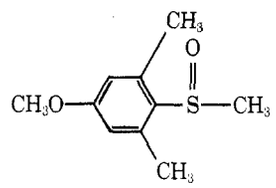
In order to gain more insight into the above matters we have examined the ^1H NMR spectra of sulfoxides I, II, and III at various temperatures.



I



II

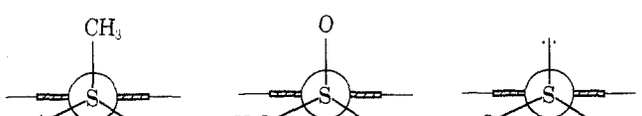


III

At room temperature in 1:1 CS_2–$CDCl_3$ solution, the ortho methyl protons of I appear as a singlet at δ 2.58. Below −87° this resonance separates into signals of 1:1 intensity separated by 29.8 Hz. Application of the Eyring equation yields a barrier ($\Delta G^\ddagger$) at −87° of 9.2 ± 0.3 kcal/mol. (The limiting chemical shifts for the anisochronous methyl groups at low temperature are δ 2.73 and 2.43, respectively.) It has been determined that the enthalpy of activation for atomic inversion at sulfur is 34 kcal/mol[5] for compound I. We therefore attribute the present observation to slow aryl–S rotation on the NMR time scale at low temperature.

Owing to peak overlap with the $SOCH_3$ and the para CH_3 resonance at low temperatures, detailed line shape analysis of this spectrum did not yield meaningful parameters.

If eclipsed forms are excluded, three possibilities exist for the conformation of a given enantiomer of I (shown below).

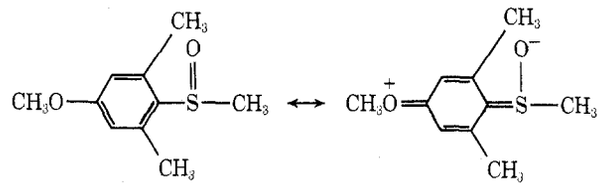


Ia Ib Ic

Since severe van der Waals repulsion is expected between methyl groups in Ib and Ic, Ia is likely to be favored. On the basis of the anisotropic effect of the S=O group[6] one can assign the ortho methyl resonance at lower field to the CH_3 which is cis to the S=O function.

The need for steric bulk at the ortho positions in order to render the aryl–S rotational process observable by ^1H NMR (at 100 MHz) is shown by the lack of change in the ^1H spectrum of II to −130°. This can be contrasted with the behavior of *p*-methoxybenzaldehyde,[7] in which the ortho ring protons show a shift difference of 1.46 ppm in the low-temperature limit, indicative of a barrier ($\Delta G^\ddagger$) of 9.4 kcal/mol at the coalescence temperature of −75°. Presumably the findings for II are a consequence of a lower degree of conjugation between the phenyl ring and the S atom, and the longer aryl–S bond.

Sulfoxide III was examined to ascertain the possible electronic influence of substitution on the rotational process. Katritsky's findings[1] suggest that resonance form IIIB may be a substantial contributor. If so, the rotational barrier in III should be higher than in I owing to the increased aryl–S double bond character.



IIIA IIIB

At room temperature in CD_2Cl_2 solution, III exhibits resonances at δ 6.61 (2 H, s), 3.82 (3 H, s), 2.90 (3 H, s), and 2.60 (6 H, s). On cooling, the resonance at δ 2.60 gradually broadens and coalescence is observed at −92°. The limiting chemical shifts at low temperature for the anisochronous CH_3 groups are 2.73 and 2.47 ppm. From the Eyring equation $\Delta G^\ddagger$ for aryl–S rotation is 8.9 ± 0.3 kcal/mol at −92°.

The similarity in the results for I and III is taken as evidence for minimal conjugative electron release by the para methoxy function into the aryl–S bond, in contrast to the earlier suggestion.[1] Further experiments using Fourier transform ^{13}C NMR are in progress with the aim of determining $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values.

Experimental Section

NMR spectra were recorded at 100 MHz on a Varian XL-100-12 spectrometer. Temperatures were calibrated with a copper–constantan thermocouple and are judged accurate to ±2°. Samples were contained in 5-mm tubes and were degassed via a freeze–pump–thaw cycle.

Compounds I and II were synthesized according to published procedures.[8] Elemental analyses were done by Spang Microanalytical Laboratory, Ann Arbor, Mich.

4-Methoxy-2,6-dimethylbenzenesulfonyl Chloride. Freshly distilled chlorosulfonic acid (10 g, 0.086 mol) was added at 0° to a stirred solution of 2.0 g (0.0147 mol) of 3,5-dimethylanisole (K and K laboratories) in 30 ml of dry chloroform. After a total addition time of 9 min, the reaction[9] mixture was poured into 50 g of crushed ice and extracted with ten 20-ml portions of chloroform. The chloroform extracts were then washed with water and dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure gave 2.9 g (54%) yield of the sulfonyl chloride as a viscous yellow liquid. The ^1H NMR spectrum in $CDCl_3$ exhibited resonances at δ 6.67 (2 H, s), 3.85 (3 H, s), and 2.70 (6 H, s).

4-Methoxy-2,6-dimethylthiophenol. In a 250-ml three-necked flask fitted with a pressure-equalized funnel, a reflux condenser, and a thermometer was placed 0.5 g (0.013 mol) of $LiAlH_4$ in 55 ml of dry ether. To this stirred slurry was added over 35 min a solution of the sulfonyl chloride (0.9 g, 0.0038 mol) in 100 ml of ether. After the initial reaction subsided, the mixture was stirred and gently refluxed for 4 hr. Excess hydride was decomposed by careful addition of water, followed by 10 ml of 10% H_2SO_4. After the evolution of H_2, a 10% excess of H_2SO_4 was added to dissolve the precipitate.

Acidification to pH 5–6 with 1 *N* HCl was followed by ether extraction. Drying over anhydrous magnesium sulfate, filtration, and evaporation of the solvent *in vacuo* gave 0.50 g (80%) of the thiophenol as a yellow, viscous liquid. Recrystallization from 30–60° petroleum ether yielded white needles, mp 101–102°. The ^1H NMR spectrum in $CDCl_3$ showed resonances at δ 6.65 (2 H, s), 3.75 (3 H, s), 2.94 (1 H, s), and 2.28 (6 H, s). Addition of D_2O diminished the peak at δ 2.94. Anal. Calcd for $C_9H_{12}OS$: C, 64.25; H, 7.19; O, 9.51; S, 19.05. Found: C, 64.20; H, 7.11; O, 9.62; S, 19.07.

4-Methoxy-2,6-dimethylphenyl Methyl Sulfide. A solution of 4-methoxy-2,6-dimethylthiophenol (0.5 g, 0.003 mol) in 3 ml of 2 *N* NaOH was stirred with dimethyl sulfate (0.76 g, 0.006 mol) for 3 hr at room temperature. Water (2 ml) was added to the reaction mixture and the organic component was extracted with four 10-ml portions of ether. The ether extracts were dried over anhydrous $CaCl_2$ and the solvent was evaporated to yield 0.42 g (73%) of the sulfide, bp 114–116° (9 mm). ^1H NMR in $CDCl_3$ has resonances at δ 6.80 (2 H, s), 3.86 (3 H, s), 2.62 (6 H, s), and 2.20 (3 H, s).

4-Methoxy-2,6-dimethylphenyl Methyl Sulfoxide. The sulfide (0.5 g, 0.0028 mol) in 4 ml of MeOH was added dropwise to a solution of sodium metaperiodate (0.6 g, 0.0028 mol) in 5 ml of water. After room temperature stirring overnight the sodium io-

date precipitate was removed by filtration and the filter cake was washed with 15 ml of $CHCl_3$. Extraction with $CHCl_3$, drying over anhydrous sodium sulfate, and removal of the solvent at reduced pressure yielded the sulfoxide as a brown oil. Recrystallization from benzene–petroleum ether gave 0.41 g (74%) of the sulfoxide: mp 71–72°; ^1H NMR ($CDCl_3$) δ 6.60 (2 H, s), 3.84 (3 H, s), 2.91 (3 H, s), and 2.60 (6 H, s).

Anal. Calcd for $C_{10}H_{14}O_2S$: C, 60.58; H, 7.12; S, 16.17; O, 16.13. Found: C, 60.46; H, 7.08; S, 16.18; O, 16.28.

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Registry No.—I, 7321-59-7; II, 3517-99-5; III, 55661-07-9; 4-methoxy-2,6-dimethylbenzenesulfonyl chloride, 55661-08-0; chlorosulfonic acid, 7790-94-5; 3,5-dimethylanisole, 874-63-5; 4-methoxy-2,6-dimethylthiophenol, 701-69-9; 4-methoxy-2,6-dimethylphenyl methyl sulfide, 55661-09-1; dimethyl sulfate, 77-78-1.

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Oxidation of Hydrocarbons. VI. Oxidation of Cycloalkanes by Ruthenium Tetroxide[1]

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The selective oxidation of saturated hydrocarbons by inorganic oxidants is an important and often difficult procedure because the required vigorous conditions also promote second-stage oxidation accompanied by C–C bond cleavage and subsequent degradation to carbon dioxide. The limited use of various transition metal oxides for such conversions has been recently reviewed.[2] In addition to other known methods we have found ruthenium tetroxide to be a convenient oxidant for cycloalkanes. Its value as a reagent for these reactions is enhanced because of its high solubility in nonpolar hydrocarbon solutions[3] and because it can be used in conjunction with inexpensive cooxidants such as aqueous sodium hypochlorite (household bleach).[4] Furthermore, the products are easily retrievable from the reaction mixture.

Experimental Section

All reactions were carried out as previously described[5] using either sodium metaperiodate or sodium hypochlorite as cooxidants. Since little difference in yields or products could be detected with either of these cooxidants, it would appear that most of the oxidative conversion is by ruthenium tetroxide, although the possibility of some direct oxidation of the intermediates by the cooxidants cannot be eliminated.[6]

Each reaction was initiated by combining 100 ml of cooxidant solution (1.46 *M* NaOCl or 0.46 *M* $NaIO_4$), 0.01 g of $RuO_2 \cdot 2H_2O$, and 5.0 ml of hydrocarbon in a flask. The flask was closed and the heterogenous mixture was agitated on a wrist shaker until all of the cooxidant had been consumed. The hydrocarbon layer was then separated and the remaining aqueous solution was made basic (pH $\geq$ 10) by the addition of 6 *M* NaOH and extracted with 3 × 50 ml of ether to recover nonacidic products and starting material. The remaining solution was acidified (pH $\leq$ 3) by the addition of concentrated H_2SO_4, saturated with NaCl, and extracted with 3 × 50 ml of ether to recover acidic products. Each set of ether extracts was combined, dried over anhydrous $MgSO_4$, and analyzed by GLC. They were then concentrated to 10 ml or less and the nonacidic products were separated and collected by preparative GLC. The isolated products were identified by GLC, TLC, NMR, ir, and melting points. The results are summarized in Table I. Each reaction was carried out three times and the average yield reported.

In a second series of experiments, the relative rates of reaction of cyclopentane, cyclohexane, cycloheptane, and cyclooctane were compared by subjecting all four compounds to oxidation under identical conditions. To 500 ml of 1.64 *M* NaOCl was added 20 mg of $RuO_2 \cdot 2H_2O$ and the solution was stirred until all of the ruthenium dioxide had been converted into ruthenium tetroxide. Ten milliliters of each substrate was then shaken with 50 ml of this solution and 1.00-ml aliquots were withdrawn and titrated periodically. The results of these experiments are found in Table II.

Results and Discussion

When a two-phase system is used, oxidation of the organic substrates by ruthenium tetroxide takes place in the nonaqueous phase. The ruthenium dioxide precipitate formed in this process then migrates to the interface (as in Scheme I), where it is converted back into ruthenium te-

Table I
Products from the Ruthenium Tetroxide Oxidation of Cycloalkanes

Alkane	Registry no.	Reaction time, days	Products	% yield[a]	Registry no.
Cyclopentane	287-92-3	7	Cyclopentanone	18	120-92-3
			Glutaric acid	63	110-94-1
Cyclohexane	110-82-7	8	Cyclohexanone	26 (23)	108-94-1
			Adipic acid	58 (45)	124-04-9
Cycloheptane	291-64-5	2	Cycloheptanone	68	502-42-1
			Pimelic acid	20	111-16-0
Cyclooctane	292-64-8	1	Cyclooctanone	55 (55)	502-49-8
			Suberic acid	23 (33)	505-48-6
trans-Decahydronaphthalene	493-02-7	1	*trans*-9-Decahydronaphthol	55	1654-87-1
			Decalones	7	21370-71-8
					16021-08-2

[a] The yields in parentheses were obtained using sodium periodate as the cooxidant; all other results were obtained using sodium hypochlorite as the cooxidant. In each case the yield calculation was based on the amount of cooxidant used.