probable that the rapid hydrolysis reactions of *N*-acylimidazoles, in contrast to those of usual amides, are due to the partial positive charges on the carbonyl carbon and N-1 and to the stabilized leaving group of the *N*-acylimidazoles. The importance of these features in the hydrolytic reactions is made clear by the observed effects of variation of the leaving group. Thus, these studies of leaving group effects in *N*-acylimidazole hydrolysis have given considerable insight into the various pathways for the hydrolysis of *N*-acylimidazoles.

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Registry No. I, 18773-95-0; I·HCl, 103959-14-4; II, 103959-11-1; II·HCl, 103959-15-5; III, 103959-12-2; III·HCl, 103959-16-6; IV, 103959-13-3; IV·HCl, 104013-72-1; V, 62573-86-8; V·HCl, 103959-17-7; VI, 103959-18-8; VII, 103959-23-5; VIII, 103959-19-9; VIII·HCl, 103959-21-3; IX, 103959-20-2; IX·HCl, 103959-22-4; CH_3COCl, 75-36-5; $(CH_3)_3CCOCl$, 3282-30-2; $(CH_3)_3CCH_2COCl$, 7065-46-5; $Phg(CH_2)_2COCl$, 645-45-4; PhCOCl, 98-88-4; H_2O, 7732-18-5; $H_2PO_4^-$, 14066-20-7; OH^-, 14280-30-9; MES, 4432-31-9; *N*-(3,3-dimethylbutyryl)imidazole, 4122-55-8; 4-methylimidazole, 822-36-6; 4-bromoimidazole, 2302-25-2; formate, 71-47-6; acetate, 71-50-1; benzimidazole, 51-17-2; 4-nitroimidazole, 3034-38-6; *N*-benzoylimidazole, 10364-94-0; chloroacetate, 14526-03-5; pyridine, 110-86-1; cacodylate, 75-60-5; 2,6-lutidine, 108-48-5; imidazole, 288-32-4; *N*-ethylmorpholine, 100-74-3.

Chemistry of Dioxiranes. 6. Electronic Effects in the Oxidation of Sulfides and Sulfoxides by Dimethyldioxirane[1]

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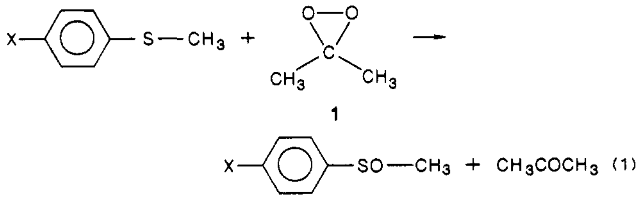
Dimethyldioxirane (1) oxidizes a series of aryl methyl sulfides to the corresponding sulfoxides. In a separate series of reactions the sulfoxides were oxidized by 1 to the corresponding sulfones. The relative rates of oxidation in both series were treated with the Hammett $\rho\sigma$ relationship. The oxidations were found to be electrophilic in character with ρ values for the sulfide and sulfoxide oxidations equal to −0.77 and −0.76, respectively.

Introduction

The availability of pure solutions of dioxiranes[2] has provided an opportunity for a full scale investigation of the chemistry of these interesting peroxides. We have described the reaction of dimethyldioxirane (1) with a number of substrates[2] including, most recently, the remarkable insertion of O atom into carbon–hydrogen bonds of hydrocarbons[3] and nitrogen–hydrogen bonds of amines.[4] The hydrocarbon oxidation work also permitted us to begin a series of investigations directed at understanding the mechanistic details of these interesting oxidations. We have found, for example, that 1 shows a reaction selectivity with one series of hydrocarbon substrates which is quite different from that shown by *tert*-butoxy radical toward the same substrates. Also the primary kinetic isotope effect (k_H/k_D = 4.97) measured[3] for the C–H insertion reaction suggests only a partial breaking of the bond in the transition state. We describe here the results of a study aimed at determining the electronic requirements for oxidation by dimethyldioxirane of a series of sulfides and sulfoxides. The data obtained have been treated with the Hammett linear free energy relationship.

Results and Discussion

During our earlier[2] work exploring the range of oxidations accomplished by 1 we had shown that phenyl methyl sulfide is rapidly and efficiently oxidized to the sulfoxide. Indeed this reaction is so rapid and complete that we frequently use phenyl methyl sulfide to quench oxidations by 1 of less reactive substrates. We have now carried out the oxidation of a series of para-substituted phenyl methyl sulfides in order to determine the influence of electron availability on the rate of oxidation. The relative rate studies were carried out by oxidizing the sulfide substrates in pairs, i.e., each pair contained equimolar amounts of phenyl methyl sulfide and one of the para-substituted materials. The oxidations were carried out at room temperature and with the sulfides in excess. Under these conditions the reactions are complete instantaneously. The reaction solutions were analyzed by capillary GC using an internal standard. The GC conditions were established such that all reactant and product peaks were clearly separated and analysis could be carried out with good precision. In all cases the only products observed were the sulfoxides corresponding to the sulfides used (eq 1). The relative rates were calculated by comparing initial and final concentrations of the reacting pair of sulfides. The relative rate data were plotted against Hammett σ values[5] and gave a straight line with ρ = −0.77.



In a similar fashion the influence of para substitution on reaction rate was determined by oxidizing pairs of sulfoxides with 1, i.e., phenyl methyl sulfoxide plus one

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(1) Part 5: Murray, R. W.; Jeyaraman, R.; Mohan, L. *Tetrahedron Lett.* **1986**, *27*, 2335–2336.

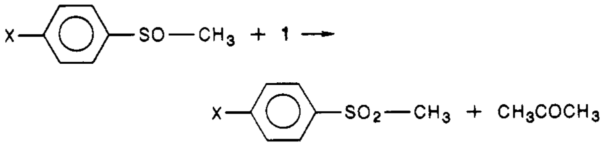
(2) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847–2853. The ^{13}C adsorption at 214 ppm originally assigned to the ring carbon of dimethyldioxirane in this reference has since been found to be an artifact. All other NMR assignments are correct as published. Additional attempts to observe an absorption for the ring carbon using ^{13}C-enriched dioxirane are in progress.

(3) Murray, R. W.; Jeyaraman, R.; Mohan, L. *J. Am. Chem. Soc.* **1986**, *108*, 2470–2472.

(4) Murray, R. W.; Jeyaraman, R.; Mohan, L. *Tetrahedron Lett.* **1986**, *27*, 2335–2336.

(5) The σ values used were taken from Ritchie, C. D.; Sager, W. F. *Progr. Phys. Org. Chem.* **1964**, *2*, 323.

of the para-substituted analogues. The only products observed by capillary GC were the corresponding sulfones (eq 2). As with the sulfides, the oxidation of the sulfoxides appears to be instantaneous at room temperature. The sulfoxide oxidations were carried out to several different conversion levels. While these experiments gave similar results, conversions in the 10–25% range gave the best precision in the relative rate determinations. The relative rate values were calculated by comparing initial and final sulfoxide concentrations. These relative rate data were plotted against Hammett σ values to give a straight line with $\rho = -0.76$.



(2)

The first observation to make about these oxidations is that they proceed at a very rapid rate. In both series, sulfides and sulfoxides, the reactions are apparently instantaneous at room temperature. This is the case even though the substrates are present in low concentration and the instantaneous concentration of 1 is near zero. These observations again point up the remarkable oxidizing power of dioxiranes as seen earlier[2] with a variety of other substrates. In both current cases the ρ values indicate that dimethyldioxirane is an electrophilic oxidizing reagent. The reaction constant ρ is similar to that observed[6] for the oxidation of *p,p'*-dichlorodibenzyl sulfide by para-substituted peroxybenzoic acids ($\rho = +1.06$). In the latter example the substituents are in the oxidant, hence the positive ρ value. In the case of the sulfoxide oxidations by 1, the ρ value is slightly lower than that for the sulfide oxidations. The difference while very small is at least consistent with the expectation[7] that sulfides are more easily oxidized by electrophiles than are sulfoxides.

We had earlier reported[8] that a series of para,para'-disubstituted benzophenone carbonyl oxides oxidize diphenyl sulfide in an electrophilic reaction ($\rho = +0.90$). This same series of carbonyl oxides also transfers O atom to naphthalene in an electrophilic process.[9] It is instructive to make comparisons between the chemistry of dioxiranes and carbonyl oxides. One of the our continuing goals is to provide methods which will allow one to distinguish between dioxiranes and carbonyl oxides when these species are likely candidates for intermediates in chemical reactions.

The examples of electrophilic O atom transfer by carbonyl oxides cited above may be special cases inasmuch as the aromatic substituents provide access to resonance stabilization that could favor an electron distribution giving a positive terminal oxygen. Ando and co-workers have also observed[10] electrophilic O atom oxidation of a sulfide by benzoyl phenyl carbonyl oxide. In this case also the carbonyl oxide used has available a resonance stabilized form with a positive terminal oxygen. On the other hand Ogata et al. have found[7] that the oxidation of para-substituted diphenyl sulfoxides to the corresponding sulfones by fluorenone carbonyl oxide is a nucleophilic process. One might have expected that favorable electron stabilization in this carboxyl oxide would also lead to electrophilic O atom transfer. These latter results stand in sharp contrast to our observation that dimethyldioxirane oxidizes sulfoxides to sulfones in an electrophilic fashion.

Ogata et al. also found[7] that sulfoxides are very much more reactive than sulfides toward fluorenone oxide. Based on the absence of any sulfone products in our sulfide oxidations with 1, we conclude that dioxiranes are more reactive with sulfides than with sulfoxides. Thus the work reported here provides two additional[2] examples of differences between carbonyl oxides and dioxirane chemistry, namely, the electronic character of the oxidation of sulfoxides, electrophilic for dioxiranes and nucleophilic for carbonyl oxides, and the relative rate of oxidation of sulfides and sulfoxides, sulfides apparently faster for dioxiranes and sulfoxides faster for carbonyl oxides. We plan to carry out absolute rate determinations using 1 with sulfides and sulfoxides in order to further elaborate the apparent rate difference.

Experimental Section

Instrumentation. Gas chromatography was performed on a Perkin-Elmer Sigma 2000 gas chromatograph interfaced with a Model 3390-A Hewlett Packard integrator. ^1H NMR spectra were recorded with a Varian T-60 NMR spectrometer using $CDCl_3$ with 1% Me_4Si as solvent. Mass spectra were obtained on an Associated Electronic Industries Model MS-1201 B mass spectrometer at a 70-eV ionizing voltage. Melting points were determined on a Thomas-Hoover capillary melting point apparatus.

Chromatography. Gas chromatography was performed with a Supelco column, SPB-5 fused silica capillary column, 15 m, 0.25 μm liquid thickness, 0.25 mm i.d., or a J and W Durabond fused silica capillary column, DB-1701, 30 m × 0.329 mm, 0.15 μm liquid thickness using split injection (1:50).

Materials. Phenyl methyl sulfide (Matheson, Coleman and Bell) and *p*-tolyl methyl sulfide (Eastman) were redistilled: bp 192–194 °C/755 mm and 65–68 °C/0.8 mm, respectively. All other sulfides were prepared from the corresponding thiophenols by being treated with excess dimethyl sulfate in the presence of 1 N NaOH, followed by column chromatography on silica gel and distillation or recrystallization. The following sulfides were prepared in this manner; *p*-chlorophenyl methyl sulfide (bp 70–72 °C/0.5 mm); *p*-nitrophenyl methyl sulfide (mp 71–72 °C); and *p*-methoxyphenyl methyl sulfide (bp 185–186 °C/0.5 mm). The purity of the sulfides was verified by ^1H NMR data and capillary GC analysis. All were found to be >99.5% pure. Acetone (99.5%, ACS certified) was used as such for preparing dimethyldioxirane. Fractionally distilled (over K_2CO_3) acetone was used for making up solutions of the sulfides. Authentic samples of the sulfoxide products were synthesized from the corresponding sulfides by using either *m*-chloroperbenzoic acid or H_2O_2/CH_3COOH. The sulfoxides were purified by column chromatography (silica gel, 100–200 mesh, hexane eluent) and then distilled in vacuo or recrystallized from hexane/CH_2Cl_2: phenyl methyl sulfoxide (bp 85–86 °C/0.5 mm); *p*-tolyl methyl sulfoxide (mp 41–42 °C); *p*-chlorophenyl methyl sulfoxide (mp 47–78 °C); *p*-nitrophenyl methyl sulfoxide (mp 147–148 °C); *p*-bromophenyl methyl sulfoxide (mp 82.5–84 °C); and *p*-methoxyphenyl methyl sulfoxide (collected by prep GC, 3% OV-17, Gaschrom a, 100 °C). All were >99% pure. Authentic samples of the sulfones were prepared from the corresponding sulfoxides by using *m*-chloroperbenzoic acid or H_2O_2/CH_3COOH. The sulfones were purified by column chromatography and then recrystallization. Hexadecane and decane (>99% pure) were obtained from Aldrich Chemical Co. and, after confirming the purity, were used as such.

Determination of Relative Oxidation Rates. a. Sulfides. Standard acetone solutions of phenyl methyl sulfide (0.10 M, 10 mL) and the substituted aryl methyl sulfides (0.10 M, 10 mL) were prepared. A solution of the internal GC standard (decane, 0.10 M, 10 mL) in acetone was also prepared. The GC response factors relative to decane were determined for each of the sulfides

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(6) Overberger, C. C.; Cummins, R. W. *J. Am. Chem. Soc.* **1953**, *75*, 4250–4254.

(7) Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832–3837. Adam, W.; Haas, W.; Sieker, G. *J. Am. Chem. Soc.* **1984**, *106*, 5020.

(8) Agarwal, S. K.; Murray, R. W. *Isr. J. Chem.* **1983**, *23*, 405–408.

(9) Agarwal, S. K.; Murray, R. W. *Photochem. Photobiol.* **1982**, *35*, 31–35.

(10) Ando, W.; Miyazaki, H.; Kohmoto, S. *Tetrahedron Lett.* **1979**, 1317–1320.

Table I

substit (X)	k_X/k_H	log (k_X/k_H)	σ^a
OCH_3	1.548	0.1899	−0.27
CH_3	1.237	0.1269	−0.17
Cl	0.6598	−0.1806	0.23
Br	0.6356	−0.1968	0.23
NO_2	0.2093	−0.6140	0.78

[a] Taken from ref 5.

Table II

substit (X)	k_X/k_H	log (k_X/k_H)	σ^a
OCH_3	1.857	0.269	−0.27
CH_3	1.337	0.1261	−0.17
Cl	0.7185	−0.1435	0.23
NO_2	0.2762	−0.5587	0.78

[a] Taken from ref 5.

by mixing known volumes (0.50–0.30 μL) of the sulfide and decane solutions and measuring the GC areas.

For the oxidation experiments, 1.0-mL portions of the decane, phenyl methyl sulfide, and para-substituted phenyl methyl sulfide solutions were mixed at room temperature. To this mixture was added 0.50 mL of a freshly prepared[2] solution of dimethyldioxirane in acetone (0.06–0.08 M) dropwise, with shaking, in a 1-min period. The reaction mixtures were immediately analyzed by capillary GC. Each reaction mixture was analyzed at least three times. The relative rates of oxidation of the sulfides were calculated by using eq 3, where $[X_0]$ and $[H_0]$ are initial concentrations of

$$\frac{k_X}{k_H} = \frac{[X_0] - [X_1]}{[H_0] - [H_1]} \qquad (3)$$

substituted and unsubstituted phenyl sulfides, respectively, and $[X_1]$ and $[H_1]$ are final concentrations of the same sulfides.

A summary of the relative rate so obtained is given in Table I.

These relative rate data were treated with the Hammett linear free energy relationship and gave a straight line plot with $\rho = -0.77 \pm 0.05$ (correlation coefficient = 0.984).

The gas chromatography conditions used in analyzing the oxidation mixture are available. See paragraph at end of paper about supplementary material.

b. Sulfoxides. Solutions of phenyl methyl sulfoxide (0.20 M) and the para-substituted phenyl methyl sulfoxide (0.20 M) in acetone were prepared separately in 10-mL volumetric flasks. An acetone solution of the internal standard, hexadecane, was also prepared (0.10 M). The relative GC responses of the individual sulfoxides with respect to hexadecane were determined by mixing 500-μL portions of phenyl methyl sulfoxide, a para-substituted phenyl methyl sulfoxide, and hexadecane solutions and then injecting 0.5-μL portions into the capillary GC (DB-1701).

The oxidation experiments were carried out by adding, dropwise, 200–500 μL of a freshly prepared solution of dimethyldioxirane (0.06–0.08 M) to a mixed solution of phenyl methyl sulfoxide and one of the para-substituted phenyl methyl sulfoxides. The oxidation reaction occurred instantaneously. Using a precision syringe, 0.5- or 1.0-μL portions of the oxidation mixtures were analyzed by using capillary GC. By studying the rates of oxidation at several different conversion levels, it was determined that conversions in the 10–25% range gave the best precision in determining relative rate constants. The relative rates were determined at least three times for each reaction pair. The relative rates were calculated in the same manner used in the sulfide oxidations. The reaction solutions were evaporated and the sulfone products were recrystallized from CH_2Cl_2–hexane to give nice crystals in each case. The individual sulfones were identified by comparing melting point, mass spectra, and ^1H NMR data with those of the authentic compounds. A summary of the relative rate data obtained is given in the Table II.

These data were treated with the Hammett linear free energy relationship and gave a straight line plot with $\rho = -0.76 \pm 0.025$ (correlation coefficient = 0.989).

The gas chromatography conditions used in analyzing the oxidation mixtures are available. See paragraph at the end of paper about supplementary material.

Acknowledgment. We are grateful to the National Institute of Environmental Health Sciences and the Office of Naval Research for financial support of this work. The Varian XL-300 NMR spectrometer was purchased with support from the National Science Foundation. We also acknowledge helpful discussions with Dr. David W. Larsen and Mr. John Boylan concerning the NMR experiments.

Supplementary Material Available: Full gas chromatography conditions and retention times for the oxidation mixtures (2 pages). Ordering information is given on any current masthead page.

Note Added in Proof: The labeling experiment described in ref 2 has been completed. The ^{13}C absorptions of 1 occur at 102.25 and 22.68 ppm, which are assigned to the ring and methyl carbons, respectively. These absorptions disappear upon addition of 1 drop of dimethyl sulfide to the NMR tube. Guided by our knowledge of the location of the 102 ppm peak, we have identified NMR spectrometer settings (5081 scans and a 10-s delay between pulses) which permit observation of the ring carbon absorption in 1 without ^{13}C enrichment as well as in other dioxiranes.

Palladium-Catalyzed Coupling of Aryl Halides with (Trimethylstannyl)diphenylphosphine and (Trimethylsilyl)diphenylphosphine

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The palladium-catalyzed reaction of aryl halides with either (trimethylsilyl)diphenylphosphine or (trimethylstannyl)diphenylphosphine gives aryldiphenylphosphines in good yields, under relatively mild conditions (50–70 °C, benzene). The reaction tolerates a number of functional groups including methyl ethers, esters, ketones, nitriles, anilides, and certain halogens. The nitro and aldehyde groups as well as compounds containing groups such as amino and hydroxyl are not tolerated.

Introduction

Triarylphosphines are an important class of compounds, both as ligands for various transition metals and as intermediates in organic synthesis. The numerous synthetic methods for preparation of triarylphosphines[1,2] can be divided into three major categories: the preparation from halophosphines and organometallic reagents, from meta-

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(1) *Organic Phosphorus Compounds*, 2nd ed.; Kosolapoff, G. M., Maier, L., Eds.; Wiley-Interscience: New York, 1972; Vol. 1.

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