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The Synthesis of Sulfoxides by the Oxidation of Sulfide with the Bromine Complex of 1, 4-Diazabicyclo(2, 2, 2)octane^{1, 2)}

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1, 4-Diazabicyclo(2, 2, 2)octane readily forms an addition complex with two moles of bromine. This complex has been found to be an excellent oxidizing agent for the selective oxidation of various sulfides to the corresponding sulfoxides when the reaction is performed in an aqueous medium. The bromine-addition complexes of pyridine and quinoline have also been found to be useful for the same purpose. The reaction has been shown to be a superb way of incorporating ¹⁸O into sulfoxides.

A number of methods for the oxidation of sulfides to sulfoxides are known.³⁾ Among these, the oxidation by halogenating agents, such as molecular halogens or hypohalites, is one of the least-studied procedures. Molecular halogens have been known to add to sulfides to form addition compounds which are then readily hydrolyzed to give sulfoxides; on the other hand, hypohalites have been shown to oxidize higher dialkyl sulfides to the corresponding sulfoxides,³⁾ while lower sulfides are likely to be oxidized by the reagents directly to their sulfones.³⁾ However, the use of such halogenating agents for the oxidation of sulfides has been limited to only

a certain type of sulfides, since many sulfides are known to undergo different reactions to give undesirable side products.

Recently we have found that some sulfides are successfully oxidized to the corresponding sulfoxides in high yields when the sulfides are treated with *N*-bromosuccinimide (NBS) in aqueous media.⁴⁾ Meanwhile, *p*-substituted phenyl methyl sulfides have been found to form, with bromine, the corresponding bromine addition complexes which, upon hydrolyses, are found to afford the corresponding sulfoxides.⁵⁾ The same sulfides, however, gave only the C-S bond cleavage products when treated with NBS. These observations seem to

1) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society.

2) Paper X on Sulfoxides.

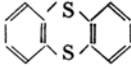
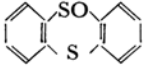
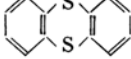
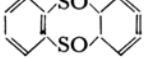
3) H. H. Szmant, Chapter 16, in "Organic Sulfur Compounds," Pergamon Press, London (1961).

4) W. Tagaki, K. Kikukawa, K. Ando and S. Oae, *Chem. & Ind.*, **1964**, 1924.

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b) S. Oae, W. Tagaki and K. Kikukawa, unpublished work.

TABLE I. THE OXIDATION OF SULFIDES WITH THE BROMINE COMPLEXES OF TERTIARY AMINES IN 70% AQUEOUS ACETIC ACID

Sulfide	Product	Yield, %			
		NBS ^{a)}	C ₆ H ₁₂ N ₂ nBr ₂ ^{b)}	C ₅ H ₅ NBr ₂ ^{c)}	C ₉ H ₇ NBr ₂ ^{d)}
(<i>n</i> -C ₄ H ₉) ₂ S	(<i>n</i> -C ₄ H ₉) ₂ SO	C-S cleavage	85	—	—
<i>p</i> -CH ₃ C ₆ H ₄ SCCH ₃	<i>p</i> -CH ₃ C ₆ H ₄ SOCH ₃	C-S cleavage	85	—	—
C ₆ H ₅ CH ₂ SC ₂ H ₅	C ₆ H ₅ CH ₂ SOC ₂ H ₅	C-S cleavage	70	—	—
C ₆ H ₅ CH ₂ SC ₆ H ₅	C ₆ H ₅ CH ₂ SOC ₂ H ₅	85	95	65	90
C ₆ H ₅ SC ₆ H ₅	C ₆ H ₅ SOC ₆ H ₅	75	95	—	—
		60	95	—	—
		30	95	—	—

a) Previous results, Ref. 4. b) The bromine complex of 1,4-diazabicyclo(2,2,2)octane. c) The bromine complex of pyridine. d) The bromine complex of quinoline.

suggest that the mode of oxidation varies with the type of halogenating agent.

In the present investigation, we have examined the possibility of the oxidation of sulfides by the bromine complexes of a few stable tertiary amines; we have found that the bromine complex of 1,4-diazabicyclo(2,2,2)octane can oxidize a variety of sulfides to sulfoxides without the formation of sulfones. Some of the sulfides which could not be oxidized to the corresponding sulfoxides either by NBS or molecular bromine were readily oxidized to the sulfoxides by this reagent.

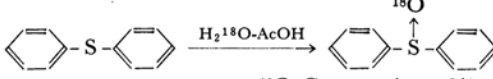
Tertiary amines, such as pyridine and quinoline, are known to form bromine-addition complexes when treated with bromine in an inert solvent,⁶⁻¹² and these complexes can be used in situ as brominating agents.^{8,9} These complexes are usually very sensitive to light, heat and moisture, and hence have to be used immediately after they are prepared. Unlike the bromine complexes of other amines, however, that of 1,4-diazabicyclo(2,2,2)octane is very stable,¹³ although its structure and the reason for its stability are not well understood yet.

The six different sulfides subjected to this oxidation were dialkyl, aryl-alkyl, benzyl-alkyl, benzyl-aryl, diaryl sulfides and thianthrene. The first three sulfides undergo C-S bond cleavage by NBS, but they were found to be readily oxidized selectively by the new method to the corresponding sulfoxides. All these sulfides were oxidized with the above three complexes in 70% aqueous acetic acid. The reactions were very rapid, like the similar oxidation by NBS. When the reaction

proceeded nicely, the initial heterogeneous reaction mixture usually turned to a homogeneous solution within a few minutes, with or without heating. Therefore, one could use the rapid change of the state of solution for the diagnosis of the successful oxidation. The results are shown in Table I, where they may be compared with the results obtained by the oxidation with NBS.

In all cases, the bromine complex of 1,4-diazabicyclo(2,2,2)octane gave the corresponding sulfoxides in satisfactory yields. Neither the cleavage of the aliphatic C-S bond, which was observed in the oxidation of aliphatic sulfides by NBS, nor the bromination of the aromatic ring, which takes place in the oxidation by molecular bromine, was observed. Here again the sulfoxides thus obtained were found to be completely free from the sulfones. When ¹⁸O-enriched water was used in the reaction of diphenyl sulfide, a ¹⁸O-labeled sulfoxide was obtained in which the sulfoxide oxygen was found to be incorporated with almost the same ¹⁸O-enrichment as that of the original water, as is shown in Table II. This implies that the ¹⁸O scrambling between acetic acid and water is not important in this rapid reaction. The present oxidation is therefore, a more convenient and a better method for labeling sulfoxide oxygen with ¹⁸O than our previous methods, that by the oxygen-exchange reaction of sulfoxide in concentrated sulfuric acid^{14,15} or

TABLE II. ¹⁸O-LABELING WITH THE BROMINE COMPLEX OF 1,4-DIAZABICYCLO(2,2,2)OCTANE

	
H ₂ ¹⁸ O used	1.65
Sulfoxide	1.45

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that by the oxidation of sulfide with NBS in ^{18}O -enriched water.⁴⁾

Experimental

Oxidation with Bromine Complexes of Pyridine and Quinoline.—The quinoline-bromine complex was prepared by slowly mixing equimolecular amounts of quinoline and bromine in carbon tetrachloride.¹¹⁾ The pyridine-bromine complex was prepared similarly.

To a solution of benzyl phenyl sulfide (0.68 g., 0.0034 mol.) in 70% aqueous acetic acid, the freshly-prepared quinoline-bromine complex (0.99 g., 0.0034 mol.) was added; the whole mixture was then stirred at room temperature until it became homogeneous (within a few minutes). The resulting solution was poured into an excess of water, and the benzyl phenyl sulfoxides which separated were collected and recrystallized; yield, 0.65 g. (89%). If necessary, the quenched reaction mixture was made alkaline with potassium carbonate, and the sulfoxide was extracted with ether. The oxidation by the pyridine-bromine complex was carried out similarly. The results are shown in Table I.

The Bromine Complex of 1,4-diazabicyclo(2,2,2)octane.—The diamine was supplied by the Houdry Corp. and was recrystallized from *n*-hexane before use. Into the diamine solution of an inert solvent, such as carbon tetrachloride or benzene, equimolar amounts of bromine in the same solvent were slowly stirred at room temperature in the case of benzene and warmed up to 50°C in the case of carbon tetrachloride. The pale yellow precipitates which formed immediately were collected, washed with a fresh solvent, and dried (m. p. 150–160°C with decomposition). The same precipitates (m. p. 150–160°C with decomposition) were also obtained by adding two moles of bromine. The complexes can be used for the reaction in a similar manner.

Calcd. for $\text{C}_6\text{H}_{12}\text{N}_2\text{Br}_2$: Br, 74.07; found Br, 70.80

(obtained from the treatment of 1-to-1 mol. of bromine) and 73.30% (obtained from the treatment of 2 mol. of bromine).

Oxidation with the Bromine Complex of 1,4-diazabicyclo(2,2,2)octane.—Half-molar amounts of the complex which had been prepared by treatment with 2 mol. of bromine were used, and a small excess was employed for the complex which had been prepared by treatment with 1 mol. of bromine. Diamine could be recovered from the reaction mixture as a hydrobromide salt. The procedure for the oxidation of various sulfides with the diamine-bromine complex was similarly applied to those of pyridine- or quinoline-dibromide.

The Identification of the Sulfoxides.—*Di-n-butyl Sulfoxide*, $(n\text{-C}_4\text{H}_9)_2\text{SO}$.—B. p. 105°C/3 mmHg; very hygroscopic.

p-Tolyl Methyl Sulfoxide, $p\text{-CH}_3\text{C}_6\text{H}_4\text{SOCH}_3$.—B. p. 107°C/3 mmHg; m. p. 38.5°C (from benzene-hexane).

Found: C, 62.69, H, 6.75. Calcd. for $\text{C}_8\text{H}_{10}\text{SO}$: C, 62.33, H, 6.49%.

Benzyl Ethyl Sulfoxide, $\text{C}_6\text{H}_5\text{CH}_2\text{SOC}_2\text{H}_5$.—B. p. 141°C/3 mmHg; m. p. 51–52°C (from benzene-hexane).

Found: C, 64.52, H, 7.22. Calcd. for $\text{C}_9\text{H}_{12}\text{SO}$: C, 64.28, H, 7.14%.

Benzyl Phenyl Sulfoxide, $\text{C}_6\text{H}_5\text{CH}_2\text{SOC}_6\text{H}_5$.—M. p. and mixed m. p. 122–123°C (with an authentic sample).

Thianthrene Monoxide, $\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$.—M. p. and mixed m. p. 143°C (with an authentic sample).

Thianthrene dioxide, $\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$.—M. p. and mixed m. p. >200°C (sublimation).

Diphenyl sulfoxide, $\text{C}_6\text{H}_5\text{SOC}_6\text{H}_5$.—M. p. and mixed m. p. 69–71°C (with an authentic sample).

All these sulfoxides showed the infrared bands at 1040–1050 cm^{-1} characteristic of sulfoxides.