Sulfide Oxidation with N-Halosuccinimides

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Numerous methods have been developed for the oxidation of sulfides[1,2] to sulfoxides in reactions usually giving the sulfoxide contaminated with sulfide and/or sulfone. More recently the use of *t*-butyl hypochlorite as a reagent for the oxidation of sulfides to sulfoxides has been reported.[3,4] These reports prompted us to disclose our results on the use of N-halosuccinimides in methanol as the oxidizing agents. It has been previously shown[5] that aromatic sulfides are oxidized cleanly to sulfoxides in aqueous media when treated with N-bromosuccinimide, but that aliphatic sulfides undergo C–S bond cleavage under identical conditions. In our study, the oxidation of sulfides was carried out in anhydrous methanol employing N-bromo- (NBS) and N-chlorosuccinimide (NCS). Sulfoxides were isolated in all instances independent of the type of sulfide, and particular emphasis was placed on the oxidation of dialkyl sulfides, their ease of isolation, and state of purity. The use of excess N-halosuccinimide gave the sulfone with aromatic sulfides and the usual cleavage-type reactions with aliphatic sulfides.

Typical conditions involved the use of a 1:1 molar ratio of sulfide to N-halosuccinimide in a large volume of methanol. In all instances incremental addition of the N-halosuccinimide to the sulfide in methanol was preferred to ensure maximum yields of the sulfoxides. A rapid and exothermic reaction occurred with the appearance of coloration which faded on completion of the reaction. The sulfoxides were isolated by distillation or recrystallization and characterized by their infrared spectra, elemental analysis, boiling or melting point, and where applicable by comparison of their glpc retention times with authentic samples (Table I). Product yields, while not optimized, ranged from 60 to 90%. No significant differences were experienced between N-bromo- or N-chlorosuccinimide.

Attempts to carry the oxidation to the sulfone stage were successful with diphenyl sulfide. Dialkyl sulfides gave cleavage products which were not characterized to any great extent. Benzyl sulfide gave significant quantities of benzyl chloride along with two other identical products. Molar ratios of sulfide to N-halosuccinimide were 1:2 with other conditions being similar to those described above.

The probable mechanism for the formation of sulfoxides in this system is considered to parallel that suggested by Oae and coworkers[5] involving the initial formation of an intermediate halosulfonium compound which reacts with the excess methanol to yield an alkoxysulfonium salt as has been described previously.[6]

Table I

Characterization Data for Sulfoxides

	Yield, %			$\nu_{\max}$(S═O),	
Sulfoxide	NCS	NBS	Bp (mp), °C	cm^{-1}	$n^{20}{}_D$
Dimethyl	62	73	51–52 (1 mm) [lit.[a] 80 (18 mm)]	1051	1.4763
Diethyl	66	65	58–59 (1 mm) [lit.[a] 95 (18 mm)]	1049	1.4718
Di-*n*-propyl	73	76	63 (0.3 mm) [lit.[a] 80 (3 mm)]	1048	1.4675
Dibenzyl[b]	86	81	(134–136) [lit.[c] 135–136]	1027	
Benzyl phenyl[b]	80	82	(123–124) [lit.[d] 123]	1028	
Diphenyl[e]	93	87	(70–71) [lit.[a] 70[f]]	1031	

[a] C. C. Addison and J. C. Sheldon, *J. Chem. Soc.*, 2705 (1956). [b] Recrystallized from chloroform. [c] Reference 2. [d] R. L. Shriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, **52**, 2060 (1930). [e] Recrystallized from 60:40 petroleum ether (bp 65–110°)-benzene. [f] Reference 3.

These alkoxysulfonium salts have been postulated as intermediates in the *t*-butyl hypochlorite oxidation of sulfides to sulfoxides.[3,7] They are generally unstable and decompose with the formation of a sulfoxide. A reaction sequence as described is preferred over the alternate mechanism involving the direct action of methyl hypohalite on the sulfide due to the slow reaction of N-halosuccinimides with methanol at temperatures of 0–25° which contrast sharply with the observed rapid reactions in this investigation. A similar mechanism was proposed in the *t*-butyl hypochlorite oxidations.[4]

This limited study demonstrates a convenient laboratory method for the oxidation of sulfides to sulfoxides and should be of considerable interest since it is applicable to dialkyl sulfides. In addition, the reaction with diaryl sulfides can be controlled to give either the sulfoxide or sulfone in good yields and purity. The convenience of the method and the ease of isolation of products are considered important advantages of this oxidation reaction for the laboratory synthesis of sulfoxides.

Experimental Section

The sulfides and N-halosuccinimides were purchased from commercial sources and used as received. An Infracord spectrophotometer was used to obtain the ir spectra. All glpc data were obtained on an Aerograph instrument, Model A-100-C, using a 5-ft dinonyl phthalate on Chromosorb column. Typical oxidation reactions are represented by the use of dimethyl and diphenyl sulfides.

General Technique.—To a mixture of the sulfide (0.2 mol) in 60 ml of anhydrous methanol contained in a three-necked flask fitted with thermometer, magnetic stirrer, and condenser covered with a Drierite drying tube and precooled externally in an ice-water bath to 0–5° was added in increments (~5 g) a total of 0.2 mol of NCS. The addition rate was controlled such that the exothermic reaction did not exceed 10°. The reaction was very rapid with the NCS dissolving immediately upon addition, and a slight yellow color formed which disappeared within minutes. After 1 hr at below 10°, the mixture was warmed to room temperature. Methanol was removed on a rotatory evaporator under reduced pressure to give a liquid–solid residue which was extracted with ether to effect the separation of the sulfoxide from succinimide to a major extent. Evaporation of the ether left a liquid residue which was distilled at reduced pressure. Products

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(1) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. II, Chemical Publishing Co., Inc., New York, N. Y., 1960, pp 64–66.

(2) N. J. Leonard and C. R. Johnson, *J. Org. Chem.*, **27**, 282 (1962).

(3) C. Walling and M. J. Mintz, *ibid.*, **32**, 1286 (1967).

(4) L. Skattebol, B. Boulette, and S. Solomon, *ibid.*, **32**, 3111 (1967).

(5) W. Tagaki, K. Kikukawa, K. Ando, and S. Oae, *Chem. Ind.* (London), 1624 (1964).

(6) H. Meerwein, K. Zenner, and R. Gipp, *Ann.*, **688**, 67 (1965).

(7) P. S. Skell and M. F. Epstein, Abstracts, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, p 26N.

were characterized by their ir spectra, refractive indices, and elemental analyses.

The solid sulfoxides were isolated by dissolving the mixture in 200 ml of methylene chloride and washing thoroughly with water. After the solution was dried and the solvent was evaporated, the solids were recrystallized.

Registry No.—NCS, 128-09-6; NBS, 128-08-5.

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Electron-Impact Fragmentation of Triptycene. The Question of Bridgehead Carbonium Ions[1]

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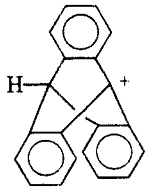
The mass spectrum of triptycene was recently reported by Bruce.[2] The presence of relatively abundant ions at $(M - 1)^+$ and $(M - 2)^{2+}$ was explained by postulating structures **1** and **2**, respectively, for these ions. By analogy with the stabilized triphenylmethyl cation, which is obtained by loss of hydrogen from triphenylmethane upon electron impact, it was suggested that **1** and **2** should also be stabilized.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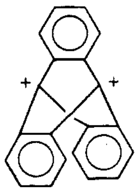
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We desired to obtain further evidence concerning the structures of these ions. Stability considerations argue against formulations **1** and **2**. Because of the rigid carbon framework involved, ions **1** and **2** should not be stabilized by orbital overlap as is the triphenylmethyl cation. As a possible test of structures **1** and **2**, we decided to investigate the electron-impact fragmentation of triptycene and 9,10-dideuteriotriptycene under the same conditions. If **1** and **2** are correct, the $(M - 1)^+$ and $(M - 2)^{2+}$ ions of triptycene should be shifted in the mass spectrum of 9,10-dideuteriotriptycene to $(M - 2)^+$ and $(M - 4)^{2+}$, respectively. Table I lists the relative intensities of the singly charged ions of triptycene and 9,10-dideuteriotriptycene in the neighborhood of the molecular ions as obtained on Hitachi Perkin-Elmer RMU-6D and Jeolco JMS-01SG mass spectrometers. Because the 9,10-dideuteriotriptycene contains 85% d_2, 14% d_1, and 1% d_0 (see Experimental Section), exact quantitative comparisons cannot be made. Also included in Table I are the calculated spectra of this mixture. (The reasonable assumptions are made here that the ionization efficiencies[3] and volatilities of the three species are the same, *no bridgehead C–H or C–D bonds are broken*, and secondary isotope effects are negligible.)

TABLE I

MASS SPECTRA OF TRIPTYCENE AND 9,10-DIDEUTERIOTRIPTYCENE. SINGLY CHARGED IONS

	Triptycene		9,10-Dideuteriotriptycene[a]			
	m/e	Rel intensity	m/e	Rel intensity	Calcd rel intensity[b]	Difference[c]
Hitachi Perkin-Elmer RMU-6D Mass Spectrometer[d]						
$(M + 2)^+$	256	2.4	258	2.1	2.2	0
$(M + 1)^+$	255	20	257	19	19	0
$(M)^+$	254	91	256	89	85	+4
$(M - 1)^+$	253	100[e]	255	100[e]	104	−4
$(M - 2)^+$	252	54	254	58	64	−6
$(M - 3)^+$	251	9.0	253	25	17	+8
$(M - 4)^+$	250	16	252	12	16	−4
$(M - 5)^+$	249	2.6	251	10	4.8	+5
Jeolco JMS-01SG Mass Spectrometer[f]						
$(M + 2)^+$	256	2.7	258	2.3	2.5	0
$(M + 1)^+$	255	22	257	21	21	0
$(M)^+$	254	100[e]	256	100[e]	97	+3
$(M - 1)^+$	253	94	255	100[e]	103	−3
$(M - 2)^+$	252	50	254	58	62	−4
$(M - 3)^+$	251	6.6	253	22	15	+7
$(M - 4)^+$	250	17	252	11	18	−7
$(M - 5)^+$	249	1.5	251	8.5	4.1	+4

[a] Contains 85% d_2, 14% d_1, and 1% d_0 (see Experimental Section). [b] Calculated by assuming that each of the three species present exhibits a mass spectrum in the neighborhood of the molecular ion identical with that of triptycene, but displaced by one mass unit. These results are then adjusted for the small difference in total ionization (in the neighborhood of the molecular ion) compared to 9,10-dideuteriotriptycene, in order to make the calculated spectrum directly comparable with that of 9,10-dideuteriotriptycene. [c] Relative intensity minus calculated relative intensity, to the nearest whole number. [d] Morgan-Schaffer Corp., Montreal, Canada, 70 eV. [e] Base peak. [f] Jeolco, Inc., Medford, Mass., 75 eV.

A close parallel is observed between the calculated and experimental mass spectra of 9,10-dideuteriotriptycene from both instruments. We conclude that **1** is not the correct structure for the $(M - 1)^+$ ion of triptycene. Because the loss of a hydrogen atom is approximately equally probable from both compounds under study, the $(M - 1)^+$ ion must arise by loss of hydrogen originally bonded to one of the aromatic rings. Compared to the calculated spectra, the experimental spectra of 9,10-dideuteriotriptycene each show the same slight decrease in intensity of the $(M - 2)^+$ and $(M - 4)^+$ ions and a corresponding increase in intensity of the $(M - 3)^+$ and $(M - 5)^+$ ions. This suggests that, possibly in small part, the $(M - 2)^+$ and $(M - 4)^+$ ions of triptycene involve loss of a bridgehead hydrogen atom. Such cleavage with 9,10-dideuteriotriptycene would result in a shift to $(M - 3)^+$ and $(M - 5)^+$, and therefore to an increase in the intensity of these ions.[4]

Table II lists the relative intensities of the doubly charged ions of species in the neighborhood of the

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(2) M. I. Bruce, *Chem. Commun.*, 593 (1967).

(3) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 212.

(4) In order to definitely establish this point a mass spectrometer with resolution (M/ΔM) of approximately 160,000 would be required. The author does not have access to such an instrument.