The *α*-Chlorination of Sulfoxides with *N*-Chlorosuccinimide

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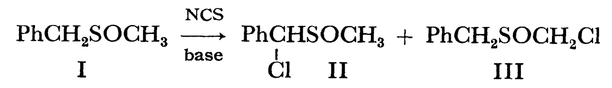
Dimethyl sulfoxide, the only sulfoxide that is industrially produced, has been frequently used as a solvent and a reagent.[1] It is very significant that this sulfoxide is further utilized by its transformation into other useful sulfoxides; chloromethyl methyl sulfoxide seems to be an important intermediate for this purpose.[2] Although many efforts have been exerted on the α-chlorination of sulfoxides,[3] it has been difficult to isolate the monochloro derivative in a high yield by the chlorination of dimethyl sulfoxide because of the formation of such by-products as bis(chloromethyl) sulfoxide, and dichloromethyl methyl sulfoxide.[4] In this communication, we wish to report on the chlorination of sulfoxides with *N*-chlorosuccinimide (NCS), with which dimethyl sulfoxide reacts to give only chloromethyl methyl sulfoxide in an excellent yield.

$$CH_3SOCH_3 \xrightarrow[\text{base}]{\text{NCS}} \underset{87\text{—}90\%}{CH_3SOCH_2Cl}$$

To a stirred solution of dimethyl sulfoxide (3.91 g) in dichloromethane (30 m*l*), we added NCS (7.00 g) and potassium carbonate (2.0 g) at room temperature. Stirring was then continued for 15 min. After the subsequent addition of dichloromethane (50 m*l*), the solution was filtered and the filtrate was fractionally distilled. A colorless oil (5.01 g, 90% yield) was thus obtained; it was confirmed to be pure chloromethyl methyl sulfoxide by spectroscopic and tlc analyses: bp 90°C/4 mmHg; $n^{24°}$ 1.5051; the NMR spectrum (in $CDCl_3$): δ 2.69 s (3H) and 4.38 s (2H); the IR spectrum (film): ν_{SO} 1058 cm^{-1}. Found: C, 21.51; H, 4.66; S, 28.47%. Calcd for C_2H_5ClOS: C, 21.34; H, 4.48; S, 28.48%.

A similar treatment of dimethyl sulfoxide with NCS in the presence of pyridine afforded chloromethyl methyl sulfoxide in a 87% yield, but this reaction required a longer period of time than that in the presence of potassium carbonate.

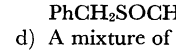
Similarly the reactions of methyl phenyl sulfoxide, dibenzyl sulfoxide, and thiolane 1-oxide with NCS in the presence of pyridine gave the corresponding α-chlorosulfoxides in 89, 91, and 60% yields respectively. Benzyl methyl sulfoxide (I) also reacted with NCS in the presence of pyridine to afford α-chlorobenzyl methyl sulfoxide (II) and benzyl chloromethyl sulfoxide (III) in 51 and 34% yields respectively. When potassium acetate was used as the base, II was obtained in a 77% yield, while III was not detected in the reaction mixture. This result may suggest that two mechanisms are operative in the α-chlorination of sulfoxides with NCS; *i.e.*, the reaction is



$$\underset{\text{I}}{PhCH_2SOCH_3} \xrightarrow[\text{base}]{\text{NCS}} \underset{\text{II}}{Ph\underset{Cl}{C}HSOCH_3} + \underset{\text{III}}{PhCH_2SOCH_2Cl}$$

(a) mainly ionic in the presence of pyridine and (b) radicalic in the presence of such insoluble bases as potassium carbonate and potassium acetate. This consideration is supported by the following observations: (1) an induction period clearly exists in the reaction of dimethyl sulfoxide with potassium carbonate; (2) the addition of hydroquinone changes the amount of II produced by the chlorination of I with NCS in the presence of pyridine, but the yield of III remains unchanged (Table 1).

TABLE 1. CHLORINATION OF I WITH NCS[a)]

	Distribution[b)]			II/III
	I	II	III	
0	9.1	52.4	38.9	1.36
0.3 eq.	37.7	29.3	33.0	0.88
1.0 eq.	36.5	28.3	35.3	0.80
0[c)]	27.1	20.2	52.6	0.38
0[d)]	7.9	72.1	20.1	3.59

a) I, 150 mg; pyridine, 0.5 m*l*; CCl_4, 10 m*l*.
b) Determined by a NMR analysis.
c) A mixture of $PhCD_2SOCH_3$, $PhCDHSOCH_3$, and $PhCH_2SOCH_3$ (90.6:8.9:0.5).
d) A mixture of $PhCH_2SOCD_3$, $PhCDHSOCD_3$, and $PhCH_2SOCD_2H$ (84.0:5.6:10.5).

Kinetic isotope effects were examined by using two deuterio derivatives of I, *i.e.*, $PhCD_2SOCH_3$ and $PhCH_2SOCD_3$. The results are shown in Table 1. The deuterium isotope effects (k_H/k_D) for both benzyl and methyl positions were calculated to be within the range of 3.0—3.5. This magnitude of isotope effects implies that proton transfer is the rate-determining step for the ionic path of the reaction.

Studies of the detailed mechanism of this reaction are now being undertaken.

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[1] For a recent review; see T. Durst, "Advances in Organic Chemistry," Vol. 6, ed. by E. C. Taylor and H. Wynberg, Interscience Publishers, New York, N. Y. (1969), p. 285.

[2] We have already reported on the nucleophilic substitution of chloromethyl methyl sulfoxide: K. Ogura and G. Tsuchihashi, *Chem. Commun.*, **1970**, 1689.

[3] G. Tsuchihashi, K. Ogura, S. Iriuchijima, and S. Tomisawa, *Synthesis*, No. 2, 89 (1971), and the references cited therein.

[4] D. Martin, A. Berger, and R. Peschel, *J. Prakt. Chem.*, **312**, 684 (1970).