

$\alpha$ -CHLOROSULFOXIDES

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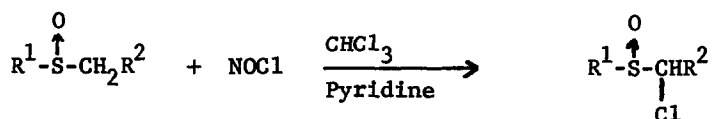
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The inert character of  $\alpha$ -halosulfones and other  $\alpha$ -halosulfonyl compounds toward nucleophilic substitution reactions has been well documented (1) and contrasts dramatically with the behavior of  $\alpha$ -halocarbonyl compounds under similar circumstances. The explanation for this fact attributes a strong negative field to the sulfonyl oxygens which repel the incoming nucleophile (1). It is perhaps surprising that no investigation of the susceptibility of  $\alpha$ -halosulfoxides to nucleophilic substitution reactions has been reported, but a survey of the literature reveals no general method for the preparation of mono- $\alpha$ -halosulfoxides although several members of this group of compounds have been reported (2-5). A priori the two most promising routes to  $\alpha$ -halosulfoxides would appear to be either the halogenation of sulfoxides or the oxidation of  $\alpha$ -halosulfides. The first of these methods suffers from the difficulty that halogenation invariably produces hydrogen halides as by-products which give rise to the rapid Pummerer-Smythe type of cleavage reactions of sulfoxides (6,7). The oxidation of  $\alpha$ -halosulfides with peracids or ozone has only been stopped at the intermediate oxidation stage (sulfoxide) in a few cases and generally produces  $\alpha$ -halosulfones (2,3).

We wish to report a new and general synthesis of  $\alpha$ -chlorosulfoxides which appear to be relatively unreactive toward nucleophiles. Alkylsulfoxides react

smoothly with a nitrosyl chloride-pyridine mixture in chloroform to produce the corresponding  $\alpha$ -chlorosulfoxides in high yields. This reaction is illustrated



I

II

by the following specific case: Treatment of 0.1 mole of dibenzylsulfoxide with 0.3 mole of nitrosyl chloride and 0.3 mole of pyridine in chloroform at 25° gave an 89% yield of  $\alpha$ -chlorodibenzylsulfoxide, mp 118-118.5°. The structural assignment was made on the basis of the elemental analysis\*, its reduction with lithium aluminum hydride to dibenzylsulfide, its oxidation with *m*-chloroperbenzoic acid to  $\alpha$ -chlorodibenzylsulfone, and its spectral data: nmr (CHCl<sub>3</sub>)  $\delta$ 4.1 (AB doublet of doublets, *J* = 13Hz, 2H),  $\delta$ 5.46 (s, 1H),  $\delta$ 7.29 (s, 5H), and 7.39 ppm (s, 5H); ir (CHCl<sub>3</sub>) 1077 cm<sup>-1</sup> (S-O) and bands characteristic of the monosubstituted benzene rings<sup>†</sup>. The magnetic nonequivalence and thus the AB pattern for the two methylene hydrogens is expected here since these are diastereomeric protons (8).

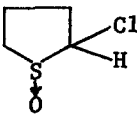
Seven representative  $\alpha$ -chlorosulfoxides have been prepared in analytically pure form and are presented in Table I. The reaction of alkylsulfoxides with nitrosyl chloride in the absence of pyridine leads to extensive cleavage of the Pummerer-Smythe type (9). The best yields of  $\alpha$ -chlorosulfoxides are produced by using a sulfoxide: nitrosyl chloride: pyridine ratio of 1:3:3 and by limiting the reaction time at one to three hours. The reaction of sulfoxides Ia, Ie, If, and IIIa could produce a mixture of diastereomeric  $\alpha$ -chlorosulfoxides but the physical and spectroscopic properties of these products suggests that only one diastereoisomer is being produced in each case. The extent of

\* Anal: Found, C, 63.48; H, 5.11; Cl, 13.22; S, 12.02; Cal'd for C<sub>14</sub>H<sub>13</sub>ClOS, C, 63.40; H, 4.91; Cl, 13.40; S, 12.10

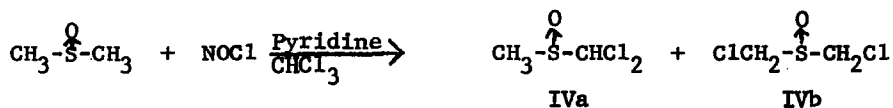
† The physical and spectroscopic properties of IIa agree closely with those recorded by Tuleen and White (3) who have graciously communicated their results to us.

halogenation at the  $\alpha$ -carbon atoms can be increased by employing higher concentrations of nitrosyl chloride and pyridine. A chloroform solution of Id, nitrosyl chloride, and pyridine in a mole ratio of 1:6:6, respectively, produced the

TABLE I

Compound	R <sup>1</sup>	R <sup>2</sup>	mp or bp	% yield
IIa	C <sub>6</sub> H <sub>6</sub> CH <sub>2</sub>	C <sub>6</sub> H <sub>5</sub>	118-118.5 <sup>o</sup>	89
IIb	4ClC <sub>6</sub> H <sub>4</sub>	H	85.5-87 <sup>o</sup>	80
IIc	C <sub>6</sub> H <sub>5</sub>	H	38.5-39.5 <sup>o</sup>	80
IId	CH <sub>3</sub>	H	65 <sup>o</sup> /.05mm	61
IIe	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	122.5-123 <sup>o</sup>	83
IIf	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	106 <sup>o</sup> /.05mm	81
IIIb			95-100 <sup>o</sup> /.05	44

two isomeric dichlorosulfoxides IVa and IVb in a mole ratio of 4:1. The same mixture was produced from IId.



Although work on the mechanism of this transformation is underway, the data at hand permit few conclusions. It has been found, however, that the sulfur-oxygen bond is not broken during the course of the reaction since a O<sup>18</sup> label in Ia is completely retained in the resultant  $\alpha$ -chlorosulfoxide.

Initial data on the susceptibility of IIA and IIC to nucleophilic substitution reactions suggest that their reactivity towards substitution is quite low. Both  $\alpha$ -chlorosulfoxides resist solvolysis in aqueous sulfuric acid, 30% aqueous sodium hydroxide, and acetic acid-sodium acetate and neither compound reacts with aniline under a variety of conditions. Chloromethylphenylsulfoxide (IIC) undergoes extensive alkyl carbon-sulfur bond cleavage in the presence of piperidine but no products of displacement reactions have been detected. All of the  $\alpha$ -chlorosulfoxides are very sensitive to cleavage by halogen acids. IIA reacts with anhydrous hydrogen chloride to give a mixture of products which include benzaldehyde, dibenzyldisulfide, and benzylthiol phenylmethylsulfonate. An extensive study of the chemical and physical properties of  $\alpha$ -halosulfoxides is underway.

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