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BENZYL ALPHA - CHLOROBENZYL SULFOXIDE

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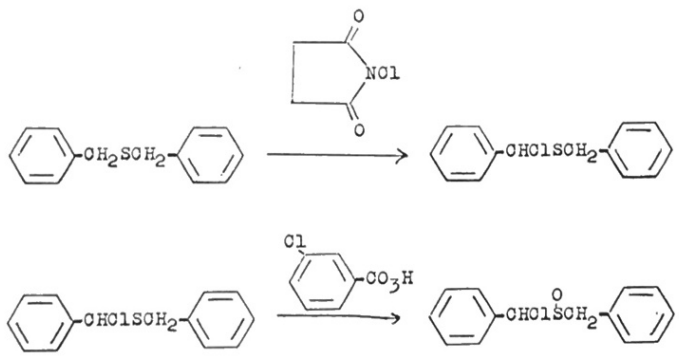
The oxidation of alpha-chloro sulfides with ozone, (1, 2) peroxybenzoic acid (3) and monoperoxyphthalic acid (4) has been employed to prepare chloromethyl aryl sulfoxides, (1, 4) chloromethyl ethyl sulfoxide, (2, 4) bis(chloromethyl) sulfoxide (3) and bis(1-chloroethyl) sulfoxide. (3) We have synthesized benzyl alpha-chlorobenzyl sulfoxide by the oxidation of benzyl alpha-chlorobenzyl sulfide (5) with *m*-chloroperoxybenzoic acid.

A solution of benzyl sulfide in carbon tetrachloride was treated at room temperature with N-chlorosuccinimide to produce benzyl alpha-chlorobenzyl sulfide. Succinimide was removed by filtration and the solvent was removed at reduced pressure. The chloro sulfide was dissolved in ether and oxidized with an equivalent amount of *m*-chloroperoxybenzoic acid, to afford the chloro sulfoxide in 72% yield based on starting sulfide.



The nmr (60 Mc.) spectrum of the chloro sulfoxide (in deuterochloroform) displays, in addition to the aromatic region, a singlet at 5.22 ppm, assigned to the methinyl hydrogen, and a doublet of doublets centered about 4.08 ppm (J=14 cps) assigned to the methylene hydrogens. The methylene protons are rendered nonequivalent by the sites of asymmetry present in the molecule. The major infrared absorption (assigned to the SO moiety) occurs at 1040 cm^{-1}.

As the chloro sulfoxide contains two potentially asymmetric centers (at carbon and sulfur), the possibility of diastereoisomerism exists. Initially, we felt that purification might have separated the isomers. However, the line width of the sharp methinyl singlet in the nmr spectra is the same for the crude chloro sulfoxide and for the purified material. The chloro sulfoxide was treated with acidic dioxane at room temperature, (6) to attempt to convert the chloro sulfoxide to a mixture of the diastereomers. This treatment resulted in the decomposition of the sulfoxide and the formation of benzaldehyde.

We can not, therefore, currently state whether an *erythro-threo* mixture is formed or if the oxidation is a stereospecific process. It seems rather unlikely that the oxidation is totally stereospecific. The possibility that the chemical shifts of the methinyl hydrogens in the two diastereomers are identical also seems improbable. It may well be that the reaction is stereoselective, and that the concentration of the less abundant diastereomer is such that it was not discerned in the nmr spectra.

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EXPERIMENTAL

To a solution of benzyl sulfide (10.0 g., 0.0467 mole) in 50 ml. of spectrograde carbon tetrachloride was added N-chlorosuccinimide (6.23 g., 0.0467 mole). The mixture was stirred magnetically at room temperature; after one hour succinimide was removed by filtration and the solvent was removed by the use of a vacuum pump (use of a water aspirator caused extensive hydrolysis of the chloro sulfide). The residue was dissolved in 50 ml. of anhydrous ether. The ethereal solution was stirred and maintained at 2-4 C while a solution of *m*-chloroperoxybenzoic acid (8.06 g.) in 50 ml. of anhydrous ether was added over a one hour period. The mixture was stirred overnight, washed several times with aqueous sodium bicarbonate solution, washed with water and dried over magnesium sulfate. Removal of the solvent and recrystallization from hexane gave the chloro sulfoxide, m.p. 109-111 C (8.93 g., 72%). Further recrystallization from hexane afforded material of m.p. 112-113 C. (Found: C, 63.33; H, 4.86. $C_{14}H_{13}C10S$ requires C, 63.51; H, 4.95 per cent.)

A solution of the chloro sulfoxide (0.5 g.) in acidic 1,4-dioxane prepared by mixing 16 ml. of dioxane with 8 ml. of concentrated hydrochloric acid was allowed to stand at room temperature for 24 hours. Neutralization was effected with aqueous sodium hydroxide solution; extraction was ether and evaporation of the ethereal layer afforded benzaldehyde as the only immediately recognizable product.

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