

DEMETHYLATION OF ARYL METHYL SULFIDES · PREPARATION OF THIOPHENOLS

J. M. Lavanish

PPG Industries

Barberton, Ohio 44203

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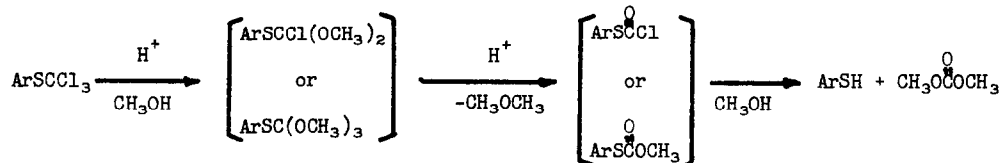
We wish to describe a two-step method for the demethylation of aryl methyl sulfides which provides a high yield synthetic route to thiophenols.

Chlorination of aryl methyl sulfides has long been known to produce aryl trichloromethyl sulfides (1). When this reaction was carried out in the temperature range of 20-30°C, we found that the methyl group was chlorinated selectively. Acid catalyzed methanolysis of the trichloromethyl sulfides thus prepared led to conversion to the corresponding thiophenols.

The method is best illustrated by a sample preparation. Chlorine was bubbled into a solution of 5.0 g (0.040 mole) of phenyl methyl sulfide in 50 ml of carbon tetrachloride at room temperature. The reaction was followed by glpc (5' x 1/4" column, 20% SE 30 on Chromosorb W, 200°C). There appeared sequentially peaks corresponding to the mono-, di-, and trichloro-sulfide. Addition of chlorine was continued until only the trichloro-sulfide remained. Removal of the solvent at room temperature and ca. 40 mm Hg gave 9.2 g (0.040 mole, 100%) of product. To this trichloromethyl phenyl sulfide was added 50 ml of methanol and 0.3 g of Amberlyst 15 resin (2). Solvent was removed via distillation through a 6" Vigreux column until the head temperature reached 64°C. Inspection of the remaining liquid by glpc showed only volatile materials and thiophenol. Filtration to remove the catalyst and removal of the remaining volatiles under vacuum produced essentially pure thiophenol (4.4 g, 0.40 mole, 100%). The entire sequence consumes about two hours.

Similar treatment of 4-(methylthio)phenyl acetate served to produce 4-mercaptophenol in 86% yield (the acetate was used because the free phenol undergoes side reactions in the presence of chlorine). In this case the distillate from the methanolysis was investigated by glpc. In addition to methylacetate, from the transesterification of the acetate, there

was also detected an approximately equal amount of dimethyl carbonate. This suggests that the trichloromethyl sulfide is degraded via a path similar to those depicted below. No attempt was made to detect the dimethyl ether, which presumably was lost during distillation.



The method finds its utility in the preparation of thiophenols for the reason that there exist several high yield reactions (3) for the direct introduction of the methylthio moiety on an aromatic ring whereas there is no simple direct method for the introduction of -SH.

References

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