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THE DEOXYGENATION OF SULFOXIDES WITH ANHYDROUS HCl/KI

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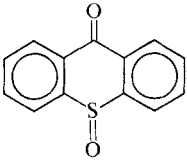
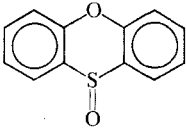
Dialkyl and diaryl sulfoxides can be deoxygenated to their corresponding sulfides in high yields and purity by using anhydrous HCl and KI in chloroform. The reaction is not accompanied by reductive chlorination.

The methods used for the deoxygenation of sulfoxides to sulfides are numerous.¹ We have shown² that the use of anhydrous HCl/phenol/chloroform for the deoxygenation of diaryl sulfoxides affords excellent yields of sulfides. Olah and co-workers³ recently demonstrated that sulfoxides can be reduced by oxalyl chloride/Nal/acetonitrile

very cleanly. The use of Nal prevents the formation of halogenated products and also promotes the reaction.

We have now shown that the use of anhydrous HCl/KI/chloroform can also be used effectively for the reduction of sulfoxides to sulfides. The results are shown in Table I. Even though the reac-

TABLE I
Deoxygenation of sulfoxides with HCl/KI

Sulfoxide	Yield of sulfide	mp or bp/kPa	Lit. ^a mp or bp/kPa
(CH ₃ CH ₂ CH ₂ CH ₂) ₂ SO	93	184-5/101	185-185.5/101
(C ₆ H ₅ CH ₂) ₂ SO	86	39-41	49-50
(C ₆ H ₅) ₂ SO	100	151/1.5	151.5/1.5 ^b
(4-CH ₃ C ₆ H ₄) ₂ SO	98	53-56	57
(4-ClC ₆ H ₄) ₂ SO	98	90-93	93-95
4-CH ₃ OC(=O)C ₆ H ₄ SC(=O)C ₆ H ₅	96	140/0.3	138-140/0.3 ^c
	100	209-12	209
	100	54-55	59-60

^a Handbook of Chemistry and Physics, 55th Ed., Chemical Rubber Co., Cleveland, Ohio, 1974-75.

^b Beilsteins Handbuch Der Organischen Chemie, 6, 299 (1923), Berlin: Springer-Verlag.

^c R. Adams, W. Reefsneider and M. D. Nair, Croat. Chem. Acta, 29, 277 (1957); CA53: 16145 f (1959).

tion is heterogeneous, enough KI dissolves in the chloroform solution to promote deoxygenation. No chlorinated products were observed. The reaction requires about 3 hrs. for completion at 0°C. The work-up is more convenient than that of Olah's.³

Olah and co-workers³ observed that heating at reflux of di-*n*-propyl sulfoxides and sodium iodide in acetonitrile afforded no deoxygenated products, while at 200° in the absence of acetonitrile complete reduction was effected in a few hours. This was also observed with dimethyl sulfoxide. The deoxygenations in the absence of solvent probably occur due to acid catalysis (H⁺, NaI), the acid resulting from the air promoted thermal decomposition of the aliphatic sulfoxides.⁴

EXPERIMENTAL

The sulfoxides used in this work were either commercially available from Aldrich Chemical Co., Inc., or were prepared according to literature methods.^{2,5,6} The products were identified by melting point or boiling point and by comparison of TLC, GC and IR spectral behavior with those of authentic sulfides.

General Procedure for the Deoxygenation of Sulfoxides with HCl/KI

Gaseous HCl is bubbled through a stirred cold (0–5°) solution of sulfoxide (10 mmol) in chloroform (50 ml) containing potassium iodide (20 mmol). Immediately, a red-brown color develops. The progress of the reaction can be followed by TLC or GC. When the reaction is complete, the chloroform solution is washed with sodium thiosulfate (2 × 100 ml), water (100 ml), dried (Na₂SO₄), and evaporated to afford the crude product, which is typically nearly 100% pure.

REFERENCES

1. J. Drabowicz, T. Numata, and S. Oae, *Org. Prep. Proc. Int.*, **9**, 63 (1977).
2. D. W. Chasar, T. M. Pratt, and J. P. Shockcor, *Phosphorus and Sulfur*, accompanying paper.
3. G. A. Olah, R. Malhotra, and S. C. Narang, *Synthesis*, 58 (1979).
4. D. L. Head and D. G. McCarty, *Tetrahedron Lett.*, 1405 (1973); T. M. Santosusso and D. Swern, *J. Org. Chem.*, **41**, 2762 (1976) and references cited therein.
5. T.-L. Ho and C. M. Wong, *Synthesis*, 561 (1972).
6. C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, **87**, 1109 (1965).