SHORT COMMUNICATIONS

REACTION OF SODIUM DIMETHYL SULPHOXIDE WITH 2-BROMOANISOLE

By A. J. Birch,* K. B. Chamberlain,* and S. S. Oloyede*

[Manuscript received March 25, 1971]

In dimethyl sulphoxide solution reactions of potassium t-butoxide with 1- or 2-bromonaphthalene or bromobenzene proceed through dehydroaromatic intermediates and result in aryl t-butyl ethers, phenols, and other products, including small yields (5–10%) of o-methylthiophenols.1–3 The halonaphtalenes give a mixture of 1,2-isomers of the last type, in which the 1-methylthio-2-naphthol predominates.2 Reactions of potassium t-butoxide on 2-bromoanisole, without solvent, give mainly the m-t-butoxyanisole through the 3-methoxybenzyne,4 reaction of which with anions, such as amide,5 is known to occur meta to the methoxyl.

The sulphinyl(dimethyl) carbanion in dimethyl sulphoxide might be expected to give a higher yield of the methylthiophenol, e.g. (2), on the basis of the mechanism shown, in the absence of competing butoxide anions. However, with bromobenzene the reaction was reported to give mainly benzyl methyl sulphonoxide,6 and by other workers7 to give an even lower yield (2%) of the thiophenol derivative.

The phenol (2) was required as a model in connection with investigations of pharmacologically active substances and the reaction of 2-bromoanisole with sodium dimethyl sulphoxide in dimethyl sulphoxide was examined. The alkali-soluble product, obtained in about 30% yield, has the structure (2). The structure of (2) is based partly on its desulphurization by Raney nickel to 3-methoxyphenol, and

* Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600.


partly on the n.m.r. spectrum of its crystalline methyl ether: \( \delta 2.36 \) (s, 3H, SCH\(_3\)), \( 3.88 \) (s, 6H, 20cH\(_3\)), \( 7.54 \) (d, 2H, meta protons to SCH\(_3\)), \( 8.18 \) (t, 1H, para proton to SCH\(_3\)), which resembles in the aromatic region the spectrum of 1,2,3-trimethoxybenzene.

The orientation of the hydroxyl and methylthio groups in (2) tends to support the mechanism shown, the polarization of the methoxybenzyne (1) in the direction shown probably depending on the inductive effect of the methoxyl. 4-Bromoanisole underwent a similar reaction to give the two possible 3,4-isomers.

**Experimental**

All g.l.c. examinations were carried out on an SE30 column (3%); n.m.r. spectra were recorded in deuterochloroform.

To stirred pure dimethyl sulphoxide (100 ml) was added sodium hydride (5.02 g) over 15 min under nitrogen. 2-Bromoanisole (10 g) was slowly added and the temperature kept at 60–65° for 1.5 hr. Water was then cautiously added and the solution extracted with ether to remove neutral products, which contained some starting material (g.l.c.). The aqueous solution was acidified and the product (2.5 g) extracted with ether. The product, \( R_t 6 \) min at 155°, appeared from the spectral data: \( \nu_{\text{max}} 3370 \text{ cm}^{-1}; \ \delta 1.25 \) (s, 3H, SCH\(_3\)), \( 3.88 \) (s, 3H, OCH\(_3\)), \( 6.54 \) (m, 2H, m to SCH\(_3\)), \( 7.18 \) (t, 1H, p to SCH\(_3\)), \( 7.02 \) (s, 1H, OH), to be essentially pure 3-methoxy-2-methylthiophenol. It could be distilled, b.p. 84°/1 mm, to yield a lighter-coloured product, but this operation was accompanied by some decomposition. Desulphurization by Raney nickel in ethanol gave 3-methoxyphenol, inseparable on g.l.c. from an authentic specimen, \( R_t 3 \) min at 160°. Methylation with dimethyl sulphate and aqueous sodium hydroxide gave 1,3-dimethoxy-2-methylthiobenzene, m.p. 80°.

The 3,5-dinitrobenzoate of 3-methoxy-2-methylthiophenol had \( m/e 364; \ \delta 2.26 \) (s, 3H, SCH\(_3\)), \( 3.88 \) (s, 3H, OCH\(_3\)), \( 6.9 \) (m, 2H, m to SCH\(_3\)), \( 7.3 \) (t, 1H, p to SCH\(_3\)), \( 9.37 \) (m, 3H, protons of dinitrobenzoate); m.p. 148–148°.

4-Bromoanisole, allowed to react similarly, gave 30% yield of product, b.p. 87–90°/1 mm. The n.m.r. spectrum showed two SMe resonances at \( \delta 2.2 \) and 2.3 and two OMe groups at 3.73 and 3.75 of about equal intensities, and a mixture of about equal proportions of the isomeric 3-SMe,4-OH and 4-SMe,3-OH compounds must be present.