Electrophilic Methylthiolation and Arylthiolation of Aromatic Compounds with Thiosulphonates

By J. K. BOSSCHER, MISS E. W. A. KRAAK, and H. KLOOSTERZIEL*†
(*Laboratory of Organic Chemistry, University of Technology, Eindhoven, The Netherlands*)

Summary Aromatic compounds are methylthiolated by treatment with methyl methanethiosulphonate in the presence of aluminium chloride.

THE substitution of hydrogen in aromatic compounds by a methylthio-group using methanesulphenyl chloride and Friedel–Crafts catalysts has been briefly reported.[1] This reaction has so far not found its place in synthetic organic chemistry.[2] The poor accessibility and stability of alkanesulphenyl chlorides[3] thwart this simple route to aromatic sulphides by electrophilic substitution.

Reaction of $RSSO_2R$ (0·1 *mol*) *with* ArH (A, 100 *ml*; B, 0·1 *mol in* 100 *ml of* $MeNO_2$) *upon gradual addition of* $AlCl_3$ (0·1 *mol*) *at room temperature and stirring for* 8 *h*[a]

Expt.	R	Ar H	Medium	Major product[b]	Yield (%)[c]
1	Methyl	*m*-Xylene	A	Methyl 2,4-xylyl sulphide	71
2	Methyl	Mesitylene	A	Mesityl methyl sulphide	72
3	Methyl	Anisole	A	4-(Methylthio)anisole	85
4	Methyl	*p*-Xylene	A	2,5-Bis(methylthio)-*p*-xylene[d]	51
5	Methyl	Naphthalene	B	1,4-Bis(methylthio)naphthalene	50
6	Methyl	Mesityl methyl sulphide	B	2,4-Bis(methylthio)mesitylene[e]	64
7	*p*-Tolyl	*m*-Xylene	A	*p*-Tolyl 2,4-xylyl sulphide	79
8	*p*-Tolyl	Mesitylene	A	Mesityl *p*-tolyl sulphide	76
9	*p*-Tolyl	*p*-Xylene	B	2,5-Bis-(*p*-tolylthio)-*p*-xylene[f]	59

[a] Work-up: addition of 200 ml of 3N-aqueous HCl; separation of organic layer; addition of 150 ml of $CHCl_3$; washing (H_2O + Na_2CO_3, H_2O); drying ($MgSO_4$); evaporation *in vacuo* of $CHCl_3$, ArH, and/or $MeNO_2$. The residue was distilled (nos. 1, 2, 3, 6, 7) or crystallized from ethanol (nos. 4, 5, 8, 9). [b] Identified by C,H analysis and i.r. and n.m.r. spectroscopy. B.p. or m.p. of known compounds agreed with literature data. [c] Isolated product. [d] M.p. 83—85°. [e] B.p. 110—115°/0·5 mmHg. [f] M.p. 115—117°.

We have now found that the readily accessible and stable methyl methanethiosulphonate[4] serves this purpose.

$$ArH + MeSSO_2Me \xrightarrow{AlCl_3} ArSMe$$

Aryl thiosulphonates can also be used for arylthiolation.

An inherent limitation of the method of introducing an RS group by electrophilic substitution lies in the activation for further substitution by the RS group introduced.[5] This might explain why benzene and toluene, even when used in excess (conditions denoted by A), gave complex mixtures of mono- and poly-substitution products. *o*-Xylene (in excess) yielded a mixture mainly consisting of the 4,5- and 3,6-disubstituted *o*-xylenes.

The Table contains data on experiments with one product prevailing. A ten-fold excess of a benzene derivative with one strongly activating group (no. 3) or with two (nos. 1, 7) or more (nos. 2, 8) moderately activating and mutually reinforcing groups yields the mono-substituted product. When the substituents do not mutually reinforce, disubstitution occurs irrespective of the substrate being used in an equivalent amount (no. 9) or in excess (no. 4). Generally the use of an equivalent amount of the aromatic compound will favour di- over mono-substitution (no. 5), unless *para* (or *ortho*) disubstitution is rendered impossible (no. 6).

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† Present address: Gorlaeus Laboratoria, Postbox 75, The University, Leiden.

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[5] Ref. 2, p. 48, 145, 214.