## **909.** *Action of Sulphur Monochloride on Aromatic Ethers.*

By Z. S. Ariyan and L. A. Wiles.

When the oxygen atom can activate the nucleus, aromatic ethers react with sulphur monochloride, giving sulphides. The reactions show similarities with the bromination of the same ethers.

Many phenols react with sulphur monochloride to give nuclear-substituted sulphides,[1] but there has been little study of the reaction with phenolic ethers. Anisole was found [2] to be readily attacked; although the product was not isolated, it was assumed to be di-(*p*-methoxyphenyl) disulphide since reduction with zinc and dilute sulphuric acid gave *p*-methoxythiophenol. Rây [3] studied the same reaction in the presence of aluminium amalgam. The initial product was again not characterised but distillation gave a mixture of *m*- and *p*-methoxythiophenol. Piperonaldehyde was chlorinated in the nucleus by sulphur monochloride under severe conditions.[4]

The annexed Table lists the ethers which have now been investigated and the products isolated by reaction in ether or benzene, substitution being in each case in the aromatic nucleus. Benzyl methyl ether, 2,6-dibromoanisole, diphenyl ether, 4-methoxybiphenyl, and piperonaldehyde did not react.

| Ether | Product | Ether | Product |
|---|---|---|---|
| PhOMe | Mono-, di-, and tri-sulphide | *p*-$C_6H_4(OMe)_2$ | Monosulphide |
| *o*-$C_6H_4Me{\cdot}OMe$ | Monosulphide | $\underline{C_6H_4{\cdot}O{\cdot}CH_2{\cdot}CH_2}$ | Trisulphide |
| *p*-$C_6H_4Me{\cdot}OMe$ | Disulphide and polymer | *o*-$C_6H_4Br{\cdot}OMe$ | Mixture |
| *o*-$C_6H_4(OMe)_2$ | Trisulphide | *p*-$MeO{\cdot}C_6H_4{\cdot}OPh$ | ,, |
| *m*-$C_6H_4(OMe)_2$ | Polymer | 1,2-$C_6H_4{:}O_2CH_2$ | ,, |

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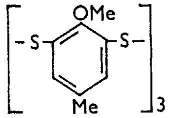
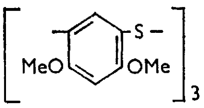
[1] Ariyan and Wiles, *J.*, 1962, 3876, and references quoted therein.
[2] Roberts, Wiles, and Kent, *J.*, 1932, 1792.
[3] Rây, *J.*, 1921, **119**, 1959.
[4] Weisse, *Ber.*, 1910, **43**, 2605.

There is evidence that sulphur monochloride can be polarised, $\overset{\delta+}{S_2Cl}\text{—}\overset{\delta-}{Cl}$, and that the chlorodithio-cation is an active species in formation of aromatic sulphides.[5] The present work confirms the electrophilic nature of the substitution. The mesomeric effect of the methoxyl group can activate the nucleus sufficiently for reaction to occur without a catalyst. It does so preferentially at the *para*-position,[6] and substitution of sulphur usually occurs in that position. Mixtures of sulphides are commonly formed in these reactions. They are sometimes separable; *e.g.*, mono-, di-, and tri-sulphides have now been isolated from anisole; but in some instances, particularly with the more reactive ethers, oils were obtained from which it was not possible to obtain pure compounds. Thus *p*-methylanisole gave two oils; one was a polymeric disulphide (I); the other deposited a solid disulphide after two years. Benzyl methyl ether does not react with sulphur monochloride since the mesomeric effect of the methoxyl group is inoperative and the group then has a small deactivating inductive influence. The dimethoxybenzenes vary greatly in their reactivity. *m*-Dimethoxybenzene is attacked by the undiluted reagent at room temperature with explosive violence; *o*-dimethoxybenzene reacts rapidly but less violently. Both reactions can be moderated by using an inert solvent. Two of the positions available for substitution in *m*-dimethoxybenzene are activated, each by one *p*- and one *o*-methoxyl group, and accordingly the rate of reaction is far greater than with anisole. The product is a polymer (II). The methoxyl groups in *o*-dimethoxybenzene cannot conjugate fully with the nucleus since this would produce an *o*-quinonoid resonance form with similar neighbouring charges. However, the molecule can be attacked in two equivalent positions each *para* to a methoxyl group, and in both of these positions there is a second-order activation from the methoxyl group *meta* to the position attacked. The rate of reaction is therefore rather greater than for anisole. When the two methoxyl groups are *para* to each other, there is again a diminution in their conjugation with the nucleus since negative charges will be formed on neighbouring carbon atoms, and *p*-dimethoxybenzene is attacked only slowly in boiling benzene. The order of reactivity with sulphur monochloride, *i.e.*, $1,4\text{-(MeO)}_2 <$ anisole $< 1,2\text{-(MeO)}_2 \ll 1,3\text{-(MeO)}_2$ is the same as that observed for the electrophilic bromination of these compounds.[7]

(I)





(II)

The cyclic ether, coumaran, has the alkoxyl group held in the best position for conjugation with the nuclei,[8] and a trisulphide is readily obtained. With 2,6-dibromoanisole the steric inhibition of resonance of the methoxyl group by the two bulky *ortho*-groups prevents reaction, but *o*-bromoanisole is attacked. Diphenyl ether is unreactive but *p*-methoxydiphenyl ether is sufficiently activated to give a slow reaction. Brewster and Slocombe [9] found that *p*-methoxydiphenyl ether was brominated in the unsubstituted phenyl group faster than was diphenyl ether. There is insufficient conjugation between the nuclei for reaction with *p*-methoxybiphenyl. Piperonaldehyde, although chlorinated under severe conditions,[4] does not react in boiling benzene, but methylenedioxybenzene undergoes a complex reaction in which sulphur dioxide and hydrogen chloride are evolved and a polysulphide is formed. Methylenedioxybenzene is known to yield condensation products of high molecular weight with strong acids.[10]

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[5] Ariyan and Wiles, *J.*, (*a*) 1961, 4510; (*b*) 1962, 1725.

[6] de la Mare, *J.*, 1949, 2871.

[7] de la Mare and Vernon, *J.*, 1951, 1764.

[8] Baddeley, Holt, Smith, and Whittaker, *Nature*, 1951, **168**, 386; Baddeley, Smith, and Vickars, *J.*, 1956, 2455.

[9] Brewster and Slocombe, *J. Amer. Chem. Soc.*, 1945, **67**, 562.

[10] Späth and Quietensky, *Ber.*, 1927, **60**, 1882.

## EXPERIMENTAL

*General Procedure.*—Sulphur monochloride was purified as described previously.[5a] The products from the reactions of the ethers and sulphur monochloride were purified by steam-distillation to remove excess of the ether, chromatographed through an alumina column, and recrystallised.

*Reaction with Anisole.*—Anisole (21·6 g., 0·2 mole) and sulphur monochloride (13·5 g., 0·1 mole) in dry ether (200 ml.) were stirred for 3 days at room temperature. After purification, the yellow, viscous oil (25 g.) was kept at 0° for several days; it deposited yellow crystals (3·8 g.). Repeated recrystallisation from ethanol gave a pale yellow *di-(*p*-methoxyphenyl) trisulphide*, m. p. 73° (Found: C, 54·2; H, 4·8; S, 30·8. $C_{14}H_{14}O_2S_3$ requires C, 54·2; H, 4·6; S, 31·0%). Reduction of this with zinc and dilute hydrochloric acid gave *p*-methoxythiophenol (b. p. 227°) and hydrogen sulphide. The remaining oil, when distilled at 1·5 mm., gave a fraction (b. p. 184—200°) which solidified and after recrystallisation from ethanol afforded di-(*p*-methoxyphenyl) sulphide as colourless plates, m. p. 45° (lit.,[11] 46°) (5·3 g.) (Found: C, 67·9; H, 5·7; S, 13·0. Calc. for $C_{14}H_{14}O_2S$: C, 68·3; H, 5·7; S, 12·9%). Oxidation with hydrogen peroxide in glacial acetic acid gave a sulphone, m. p. 129° (lit.,[12] 129°). The oil remaining in the distillation flask was dissolved in ethanol. It deposited pale yellow crystals of di-(*p*-methoxyphenyl) disulphide, m. p. 45° (lit.,[13] 44—45°) (2·5 g.) (Found: C, 59·7; H, 5·35; S, 23·45. Calc. for $C_{14}H_{14}O_2S_2$: C, 60·4; H, 5·1; S, 23·0%). This disulphide gave no m. p. depression when mixed with the compound obtained by oxidising *p*-methoxythiophenol with ferric chloride solution. A mixture of the mono- and the di-sulphide gave an oil whose infrared spectrum was identical with that of the oil from the anisole–sulphur monochloride reaction after removal of the trisulphide.

*Reaction with* o*-Methylanisole.*—*o*-Methylanisole (24·4 g., 0·2 mole) and sulphur monochloride (13·5 g., 0·1 mole) were left in dry ether (400 ml.) for a week at room temperature. After purification and storage for several weeks the oil (19 g.) deposited pale yellow crystals of di-(4-methoxy-3-methylphenyl) sulphide, m. p. 37° (lit.,[14] 38°) (1·1 g.) (Found: C, 70·3; H, 6·4; S, 11·3. Calc. for $C_{16}H_{18}O_2S$: C, 70·0; H, 6·6; S, 11·7%). Oxidation of this by hydrogen peroxide in glacial acetic acid and recrystallisation from ethanol gave a sulphone, m. p. 140° (lit.,[14] 138°) (Found: C, 62·6; H, 6·1; S, 10·8. Calc. for $C_{16}H_{18}O_4S$: C, 62·7; H, 5·9; S, 10·5%). The oil remaining after removal of the monosulphide did not solidify.

*Reaction with* p*-Methylanisole.*—The same procedure as for *o*-methylanisole gave two fractions on chromatography in benzene. The first yielded a yellow, plastic solid (21 g.) which was largely a *trimer* (I) [Found: C, 52·5; H, 4·75; S, 32·6%; *M* (Rast), 537. $C_{24}H_{24}O_3S_6$ requires C, 51·9; H, 6·2; S, 34·6%; *M*, 552]. The second fraction gave a yellow oil which crystallised during 2 years. Recrystallised from light petroleum (b. p. 40—60°)–benzene this gave di-(2-methoxy-5-methylphenyl) disulphide, m. p. 64·5° (lit.,[13] 64·5°,[15] 67°) (3 g.) (Found: C, 62·8; H, 6·0; S, 20·5. Calc. for $C_{16}H_{18}O_2S_2$: C, 62·7; H, 5·9; S, 20·9%).

*Reaction with* o*-Dimethoxybenzene.*—*o*-Dimethoxybenzene (27·6 g., 0·2 mole) and sulphur monochloride (13·5 g., 0·1 mole) in dry benzene (250 ml.) were kept at 0° for 2 days. Purification and recrystallisation from ethanol gave yellow needles of *bis-(3,4-dimethoxyphenyl) trisulphide*, m. p. 114·5° (53%) (Found: C, 51·7; H, 5·1; S, 25·6. $C_{16}H_{18}O_4S_3$ requires C, 51·9; H, 4·9; S, 26·0%).

*Reaction with* m*-Dimethoxybenzene.*—The same procedure as for *o*-dimethoxybenzene gave a yellow product (13 g.), probably largely the trimer (II) [Found: C, 54·9; H, 4·7; S, 22·4%; *M* (cryoscopic in benzene), 526. $(C_8H_8O_2S)_3$ requires C, 57·1; H, 4·8; S, 19·0%; *M*, 504].

*Reaction with* p*-Dimethoxybenzene.*—The same quantities of materials as for *o*-dimethoxybenzene were refluxed for 6 days. A yellow oil gave, from ethanol, bis-(2,5-dimethoxyphenyl) sulphide, m. p. 97—98° (lit.,[12] 97—100°) (7%) (Found: C, 62·2; H, 5·6; S, 9·9. Calc. for $C_{16}H_{18}O_4S$: C, 62·7; H, 5·9; S, 10·4%).

*Reaction with Coumaran.*—Coumaran (3·6 g., 0·03 mole) and sulphur monochloride (2·8 g., 0·02 mole) in dry benzene (50 ml.) were refluxed for 1 day. Purification and recrystallisation

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[11] Loth and Michaelis, *Ber.*, 1894, **27**, 2540.

[12] Smiles and Le Rossignol, *J.*, 1908, **93**, 756.

[13] Gattermann, *Ber.*, 1899, **32**, 1148.

[14] Kolhatkar and Bokil, *J. Indian Chem. Soc.*, 1930, **7**, 843.

[15] Stewart, *J.*, 1922, **121**, 2558.

from ethanol gave pale yellow *dicourmaran-5-yl trisulphide*, m. p. 116° (57%) [Found: C, 58·6; H, 4·4; S, 29·4%; *M* (cryoscopic in benzene), 330. $C_{16}H_{14}O_2S_3$ requires C, 57·5; H, 4·2; S, 28·8%; *M*, 334].

*Reaction with* o-*Bromoanisole,* p-*Methoxydiphenyl Ether, and Methylenedioxybenzene.*—These compounds reacted with sulphur monochloride giving yellow oils from which pure compounds could not be isolated. Analytical data indicated that they were mixtures of sulphides.

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