Results.—Density values are given in Table 3.

763. *The Action of Sulphur Monochloride on Phenols.*

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

Reaction of phenols with sulphur monochloride gave usually mono- or poly-sulphides and not compounds $(ArO)_2S$ or $(ArO{\cdot}S)_2$. Pentamethylphenol is readily monochlorinated *para* to the hydroxyl group; pentachlorophenol does not react.

Phenols react readily with sulphur monochloride, S_2Cl_2, giving mixtures of mono- and poly-sulphides.[1] Substitution occurs most readily at the *para*-position, but *ortho*-substitution results if the *para*-position is blocked.[2] In attempting to prepare esters of the

---

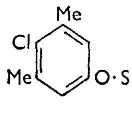
[1] Cook, Albert, Kilbourne, and Smith, *Ind. Eng. Chem.*, 1948, **40**, 1194; Blake, U.S.P. 2,470,545/1949.

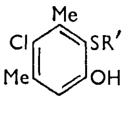
[2] Richter, *Ber.*, 1916, **49**, 1024.

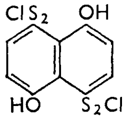
hypothetical acid, HO•S•S•OH, Giacomello[3] treated phenols in benzene with sulphur monochloride at 0°. He isolated a number of compounds to which he gave the probable structures (I; R = 2-naphthyl, *p*-Cl•C_6H_4) or (II; R = Ph, *p*-Cl•C_6H_4, 2-naphthyl). The only other reference to the existence of compounds of these types is to diphenoxy disulphide as a vulcanising agent of rubber;[4] experimental details are not given in that article but they have been supplied to us.[5] Becke-Goehring[6] examined the Raman spectra

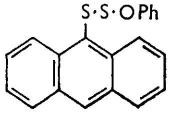
(I) RO·S·OR

(II) RO·S·S·OR


(III)


(IV)


(V)


(VI)

of dimethyl and diethyl "thiosulphite" and assigned them structure (II; R = Me or Et), Earlier workers showed that compounds which have various combinations of carbon sulphur, and oxygen bonds are often unstable. Aromatic sulphenates, RO•SR', are rearranged by hydrogen chloride, *e.g.*, (III) ⟶ (IV).[7]

The action of sulphur monochloride on salts of monobasic acids in inert media gave condensation compounds, $(R{\cdot}CO{\cdot}O)_2S_2$. These quickly decomposed to the anhydride, sulphur dioxide, and sulphur.[8] The similarity in the reactions of the diazonium cation, $Ar{\cdot}N_2^+$, and the polarised sulphur monochloride molecule, $Cl\overset{\delta+}{S_2}-\overset{\delta-}{Cl}$, makes attachment of sulphur to the ring of phenols more likely than attack on the hydroxyl group.

Action of sulphur monochloride on phenols.

Phenol (R in ROH)	Giacomello[3]	Present work
Ph	$(PhOS)_2$	(*p*-OH•C_6H_4•S)$_2$
p-Cl•C_6H_4	(*p*-Cl•C_6H_4•O)$_2$S; (*p*-Cl•C_6H_4•OS)$_2$	(2,5-HO•C_6H_3Cl)$_2$S
2,4,6-$Me_3C_6H_2$	—	(3,2,4,6-HO•C_6HMe_3)$_2S_4$
C_6Me_5	—	4,2,3,5,6-Cl•CH_2•C_6Me_4•OH
2,4,6-$(NO_2)_3C_6H_2$	—	No reaction
C_6Cl_5	—	No reaction
1-$C_{10}H_7$	(1-$C_{10}H_7$•OS)$_2$	(4-OH-$C_{10}H_6$)$_2S_3$
2-$C_{10}H_7$	(2-$C_{10}H_7$•O)$_2$S; (2-$C_{10}H_7$•OS)$_2$	(2-OH-$C_{10}H_6$)$_2$S
1,5-$C_{10}H_6(OH)_2$	—	(V)

The above considerations suggested that the formation of diaryloxy disulphides should be re-investigated and a wider range of phenols examined. The results are summarised in the Table.

The compounds described[3-5] as having structures (I) and (II) are in fact the isomeric hydroxyaryl sulphides. Aryloxy sulphides may be formed and then undergo immediate rearrangement (cf. III ⟶ IV) but of this there is little evidence, beyond perhaps the rapid colour changes during addition of sulphur monochloride to the phenol. Our products had strong infrared hydroxyl bands; such information was presumably not available to Giacomello.[3] The phenolic nature of the products was further shown by their solubility in sodium hydroxide solution and colorations with ferric chloride solution.

The reaction of phenol and sulphur monochloride at 0° gave a good yield of di-(*p*-hydroxyphenyl) disulphide. Phenol and sodium phenoxide at the room temperature

---

[3] Giacomello, *Atti Accad. naz. Lincei*, 1935, [6*A*], **21**, 36.

[4] Sibley, *Rubber Chem. Technol.*, 1951, **24**, 214.

[5] Monsanto Chemical Co., West Virginia, U.S.A., personal communication.

[6] Becke-Goehring, *Ber.*, 1947, **80**, 219.

[7] Learmonth and Smiles, *J.*, 1936, 327.

[8] Denham, *J.*, 1909, **95**, 1235.

both gave yellow oils. These contained the same disulphide, probably mixed with other di(hydroxyphenyl) sulphides. 2,4,6-Trimethylphenol reacted slowly with sulphur monochloride at the room temperature, giving a tetrasulphide; substitution occurred *meta* to the hydroxyl group. This phenol is similarly brominated in the *meta*-position under mild conditions.[9]

Picric acid and pentachlorophenol did not react with sulphur monochloride, but pentamethylphenol did so vigorously in boiling benzene, to give 4-chloromethyl-2,3,5,6-tetramethylphenol in good yield. The structure of this compound was proved by its formation on chloromethylation of 2,3,5,6-tetramethylphenol. We know of no other chlorination of an alkyl group by sulphur monochloride at such a low temperature.

Naphthalene-1,5-diol reacts vigorously with sulphur monochloride. The dark blue solid product fumed in moist air. Its reactivity suggested that it was a chlorodithio-compound,[10] and approximate analytical results for compound (V) were obtained after several attempts. Chlorodithio-compounds which have a *peri*-hydrogen atom can form cyclic disulphides by elimination of hydrogen chloride,[10] but a similar cyclisation was not successful with this product. Molecular models show that there would be overcrowding in the bridge of two sulphur atoms and one oxygen atom.

The instability of aromatic compounds which have sulphur–oxygen bonds was further shown by condensation of 9-chlorodithioanthracene with sodium phenoxide, which gave a highly reactive compound. This we consider to be 9-phenoxydithioanthracene (VI), a type of structure not hitherto reported.

EXPERIMENTAL

Sulphur monochloride was purified as previously described.[11] The infrared spectra were measured for mulls in hexachlorobutadiene in a Perkin–Elmer " Infracord " spectrophotometer.

Reaction of Sulphur Monochloride with Phenol.—Sulphur monochloride (13·5 g., 0·1 mole) in benzene (100 ml.) was slowly added to phenol (9·4 g., 0·2 mole) in benzene (150 ml.) at 0° with stirring and in a stream of nitrogen. The initial reddish-brown colour of the mixture quickly vanished and a white precipitate appeared. Recrystallised from benzene this had m. p. 151° (78%) [in agreement with Leuckart's value [13] for di-(*p*-hydroxyphenyl) disulphide] and $\nu_{max.}$ 3570 cm.$^{-1}$ (bonded OH) (Found: C, 57·4; H, 4·2; S, 25·1. Calc. for $C_{12}H_{10}O_2S_2$: C, 57·6; H, 4·0; S, 25·5%). Benzoylation and recrystallisation from 1 : 1 benzene–alcohol gave a dibenzoate, m. p. 167° (lit.,[12] 165—166°) (Found: C, 68·1; H, 4·0; S, 14·0. Calc. for $C_{26}H_{18}O_4S_2$: C, 68·5; H, 4·0; S, 13·5%).

Reaction of Sulphur Monochloride with Sodium Phenoxide.—Sodium phenoxide was prepared by adding sodium (2·3 g.) to freshly distilled phenol (9·4 g.) in toluene (150 ml.) and refluxing the mixture (6 hr.). The toluene was removed and the sodium phenoxide, dried at 200°/3 mm., was used immediately. Sulphur monochloride (6·7 g., 0·05 mole) in light petroleum (b. p. 40—60°; 30 ml.) was added dropwise to sodium phenoxide (11·6 g., 0·1 mole) in light petroleum (120 ml.) with stirring. Filtration and removal of the ether gave a yellow oil with a phenolic odour. Its infrared spectrum was identical with that of di-(*p*-hydroxyphenyl) disulphide. Acetylation gave the diacetate as leaflets (from alcohol), m. p. 89° in agreement with Leuckart's value [13] (Found: C, 57·2; H, 4·6; S, 19·2. Calc. for $C_{16}H_{14}O_4S_2$: C, 57·5; H, 4·2; S, 19·2%).

Di-(5-chloro-2-hydroxyphenyl) Sulphide.—Sulphur monochloride (13·5 g., 0·1 mole) in benzene (60 ml.) was added to *p*-chlorophenol (25·8 g., 0·2 mole) in benzene (150 ml.) at 0° in a stream of nitrogen, and the mixture was left for 4 days at room temperature. The sulphide separated and, recrystallised from benzene, had m. p. 177° (79%) (Richter [2] reports m. p. 174°) and $\nu_{max.}$ 3450 cm.$^{-1}$ (free OH) [Found: C, 50·4; H, 2·9; S, 11·1%; *M* (Rast), 272. Calc. for $C_{12}H_8Cl_2O_2S$: C, 50·7; H, 2·8; S, 11·2%; *M*, 287].

Di-(3-hydroxy-2,4,6-trimethylphenyl) Tetrasulphide.—Sulphur monochloride (2·8 g., 0·02

---

[9] Jacobsen, *Annalen*, 1879, **195**, 270.

[10] Ariyan and Wiles, *J.*, 1962, 1725.

[11] Ariyan and Wiles, *J.*, 1961, 4510.

[12] Magnusson, Christian, and Jenkins, *J. Amer. Pharmaceut. Assoc.* (*Sci. Edn.*), 1947, **36**, 257.

[13] Leuckart, *J. prakt., Chem.* 1890, **41**, 196.

mole) in benzene (20 ml.) was added to 2,4,6-trimethylphenol (5·6 g., 0·04 mole) and the whole was stirred for 3 days at room temperature, then neutralised with sodium hydroxide solution, washed with water until the red colour disappeared, and chromatographed on alumina. Recrystallisation from benzene–light petroleum (b. p. 40—60°) gave bright yellow prisms of the *tetrasulphide*, m. p. 159—160° (52%), $\nu_{max.}$ 3510 cm.$^{-1}$ (Found: C, 54·05; H, 5·6; S, 31·8. $C_{18}H_{22}O_2S_4$ requires C, 54·2; H, 5·6; S, 32·1%).

4-*Chloromethyl*-2,3,5,6-*tetramethylphenol*.—(*a*) Sulphur monochloride (3·5 g., 0·05 mole) and pentamethylphenol (4·1 g., 0·05 mole) in benzene (50 ml.) were refluxed until evolution of hydrogen chloride ceased (3 hr.). A white *product* separated which, recrystallised from benzene–light petroleum (b. p. 40—60°), had m. p. 152° (59%), $\nu_{max.}$ 3450 cm.$^{-1}$ (free OH) [Found: C, 66·6; H, 7·6; Cl, 18·5%; *M* (Rast), 179. $C_{11}H_{15}ClO$ requires C, 66·5; H, 7·6; Cl, 17·8%; *M*, 199].

(*b*) A mixture of 2,3,5,6-tetramethylphenol (5 g., 0·03 mole), concentrated hydrochloric acid (100 ml.), and 40% aqueous formaldehyde (3 g.) was stirred and heated at 60—65° for 6 hr., a further quantity (3 g.) of formaldehyde being added after 3 hr. The mixture was left for 1 day at room temperature. A white precipitate, recrystallised from benzene–light petroleum (b. p. 60—80°), had m. p. 151—152° (85%) alone or mixed with the previous product; the infrared spectra were identical.

Di-(4-*hydroxy*-1-*naphthyl*) *Trisulphide*.—Sulphur monochloride (13·5 g., 0·1 mole) in benzene (50 ml.) was added to 1-naphthol (30 g., 0·2 mole) at 0° in a stream of nitrogen. The white solid product, recrystallised from acetic acid, had m. p. 195° (decomp.) (63%) [Onufrowicz [14] reports 190° (decomp.)], $\nu_{max.}$ 3280 cm.$^{-1}$ (bonded OH) (Found: C, 63·1; H, 4·0; S, 24·9. Calc. for $C_{20}H_{14}O_2S_3$: C, 62·9; H, 3·7; S, 25·2%).

The trisulphide (7·6 g., 0·02 mole) in acetic acid (25 ml.) was refluxed for 1 hr. with zinc and concentrated hydrochloric acid. Steam-distillation and recrystallisation from light petroleum (b. p. 60—80°) gave 4-mercapto-1-naphthol, m. p. 113—114° (cf. Zincke and Ruppersberg [15]), soluble in sodium hydroxide solution and reprecipitated therefrom by acid.

Di-(2-*hydroxy*-1-*naphthyl*) *Sulphide*.—Sulphur monochloride (13·5 g., 0·1 mole) in benzene (100 ml.) was added to 2-naphthol (30 g., 0·2 mole) in benzene (500 ml.) at 0° in a stream of nitrogen. The precipitated white sulphide, recrystallised from alcohol, had m. p. 215° (57%) (cf. Henriques [16]), $\nu_{max.}$ 3335 cm.$^{-1}$ (free OH).

9-*Phenoxydithioanthracene* (VI).—Sodium phenoxide (1·2 g., 0·01 mole) was added to 9-chlorodithioanthracene [10] (2·7 g., 0·01 mole) in chloroform (50 ml.), and the mixture shaken for a day at room temperature. The red filtrate was washed with water, then dried, concentrated, and chromatographed on alumina, and the products were eluted with benzene. The first (red) fraction (25%) gave on evaporation a red oily *product*, decomposed on distillation (Found: C, 71·2; H, 4·8; S, 19·7. $C_{20}H_{14}OS_2$ requires C, 71·7; H, 4·2; S, 19·2%). The infrared spectrum showed no hydroxyl band.

We acknowledge a gift of 2,3,5,6-tetramethylphenol from R. Graesser Ltd.

DEPARTMENT OF CHEMISTRY AND METALLURGY, ROYAL MILITARY COLLEGE OF SCIENCE,
SHRIVENHAM, SWINDON, WILTS.

[*Received, March* 31*st*, 1962.]

---

[14] Onufrowicz, *Ber.*, 1890, **23**, 3355.
[15] Zincke and Ruppersberg, *Ber.*, 1915, **48**, 127.
[16] Henriques, *Ber.*, 1894, **27**, 2993.