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REARRANGEMENTS AND DECOMPOSITIONS OF THIOBISPHENOLS

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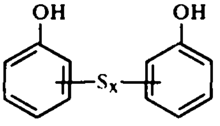
Abstract—2,2′-, 2,4′- and 4,4′-Monothiobisphenol separately rearrange in phenol at 180° in the presence of sodium hydroxide to give similar mixtures containing only 2,2′-, 2,4′- and 4,4′-monothiobisphenol in the approximate ratio, 45:45:10. The rearrangements appear to be intermolecular and they are interpreted in terms of polar processes which lead initially to the formation of *o*- and *p*-monothiobenzoquinones. 2,2′-Dithiobisphenol, 4,4′-dithiobisphenol and 4,4′-trithiobisphenol under similar conditions are desulphurated with the evolution of hydrogen sulphide also to give mixtures containing only 2,2′- 2,4′- and 4,4′-monothiobisphenol whilst 3,3′-dithiobisphenol is stable in alkaline phenol even after long periods at 180°. Similar initial heterolyses to *o*- and *p*-monothiobenzoquinones are suggested as sources of the monothiobisphenols and displacements of sulphide- or hydrosulphide-ions from intermediate benzeneperthiolate ions by carbanions derived from phenol are suggested as sources of the hydrogen sulphide.

INTRODUCTION

It is known that phenol will condense under alkaline conditions with appropriate proportions of formaldehyde and sulphur to give phenol-formaldehyde[1] and phenol-sulphur resins.[2] However, although the details of the condensations with formaldehyde have received some attention[3] it is only recently that attempts[4] have been made to interpret the courses of the condensations with sulphur. On the basis of the more recent work[4] it seemed possible that polythiobisphenols (I) are formed initially and that these undergo subsequent desulphurations to give monothiobisphenols (II; n = 0) when the initial concentration of sulphur is small and monosulphidically bridged polynuclear phenols (II; n > 0) when the initial concentration of sulphur is relatively large.



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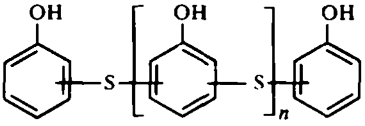


II

Consequently we have examined the behaviour of some mono-, di- and trithiobisphenols in phenol in the presence of sodium hydroxide. These examinations have shown that 2,2′-dithiobisphenol, 4,4′-dithiobisphenol, and 4,4′-trithiobisphenol are desulphurated to give mixtures of 2,2′-, 2,4′-, and 4,4′-monothiobisphenols; that 3,3′-dithiobisphenol is not desulphurated; and that 2,2′-, 2,4′- and 4,4′-monothiobisphenol undergo rearrangements to give mixtures of 2,2′-, 2,4′-, and 4,4′-monothiobisphenol. These reactions are considered in the present paper and the following paper attempts to show how related reactions provide a useful first interpretation of the products obtained in reactions between phenol and sulphur under alkaline conditions.

RESULTS AND DISCUSSION

The rearrangements of monothiobisphenols

The Table 1 shows that the rearrangement of 4,4′-monothiobisphenol to give a mixture of the isomeric monothiobisphenols is rapid (5 hr) and practically quantitative; and that after a sufficient time all the isomers produce high yields of mixtures of similar compositions. The mixtures were analysed by using gas-chromatography and in these analyses and in qualitative examinations of IR spectra, no evidence for *meta*-substituted products was found. The further observations (i) through (iv) have been made.

TABLE 1. THE REARRANGEMENTS OF MONOTHIOBISPHENOLS, $HOC_6H_4SC_6H_4OH$ (0·025 MOLE) IN PHENOL (0·5 MOLE) IN THE PRESENCE OF SODIUM HYDROXIDE (0·01 MOLE) AT 180°C*

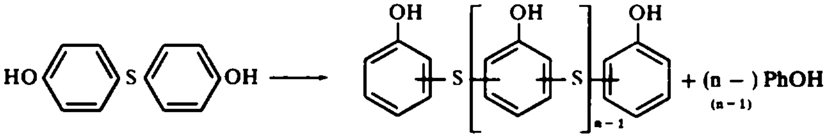
Compound	Time (hr)	Yield (%)	Isomers (%)		
			2,2′-	2,4′-	4,4′-
2,2′-	24	78	55	35	10
2,4′-	24	87	39	49	12
4,4′-	24	95	42	47	10
4,4′-	5	95	21	63	16

* The reaction-mixtures were heated by the vapours from boiling pehnol; an inert atmosphere was maintained by allowing a stream of dry nitrogen (50 ml/min) to pass through the mixtures; indicated temperatures were usually 179°.

(i) No changes are detectable in the absence of sodium hydroxide.

(ii) When 4,4′-thiobisphenol is heated in boiling alkaline *p*-cresol, phenol is released and 2,2′-thiobis(*p*-cresol) is formed.

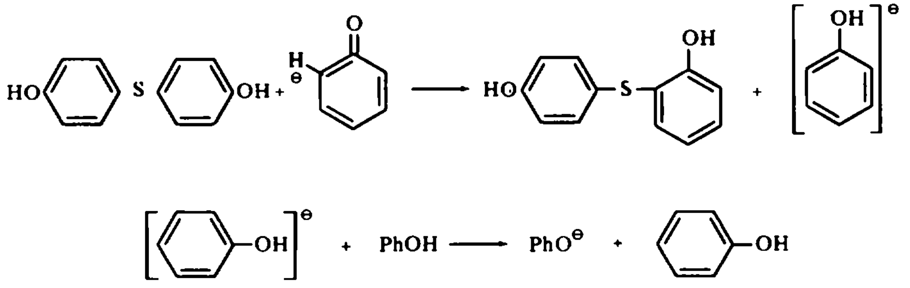
(iii) When 4,4′-thiobisphenol is heated with sodium hydroxide in the absence of other phenols, phenol is eliminated and oligonuclear phenols are formed approximately according to Eq. (1).



(1)

(iv) When 2,2′-thiobis(*p*-cresol) or 4,4′-thiobis(*o*-cresol) are heated with sodium hydroxide, *p*-cresol and *o*-cresol are released to give oligonuclear phenols in a manner similar to that described by Eq. (1).

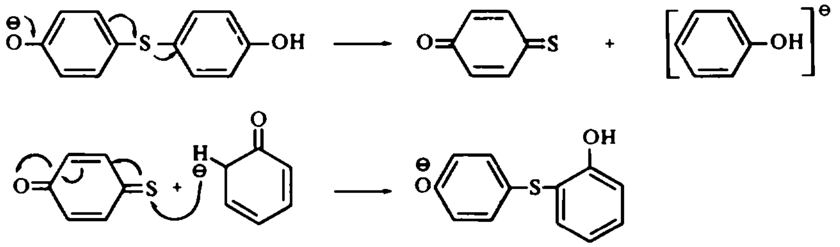
The rearrangements apparently are intermolecular and a possible interpretation is that they involve nucleophilic substitution at sulphur by a strongly nucleophilic[5] carbanion derived from phenol (Eq. 2); only *ortho*- and *para*-substituted products would be obtained. However, neither diphenyl sulphide nor 4-phenylthiophenol ($4\text{-}C_6H_5SC_6H_4OH$) are changed after heating in alkaline phenol under the conditions of the rearrangements and although it might be argued that a process similar to (2) for diphenyl sulphide would involve the benzenide-ion as a leaving group and



(2)

therefore would be less likely (an argument which is less forcible when the easy alkaline decomposition of benzophenone[6] to benzoic acid and benzene is considered), the stability of 4-phenylthiophenol is less easily explained on the basis of (2).

It is considered that the reactions are best interpreted on the basis of a process leading to an incipiently or fully formed monothiobenzoquinone (reaction 3) and that the failure in the case of 4-phenylthiophenol may be owing to the absence of stabilization by H-bonded solvent-molecules in a transition-state such as (4).



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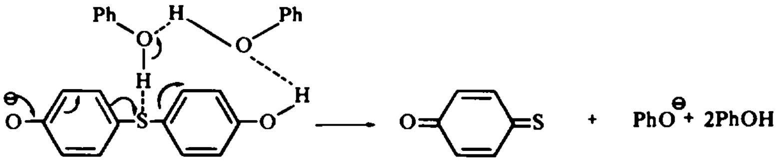
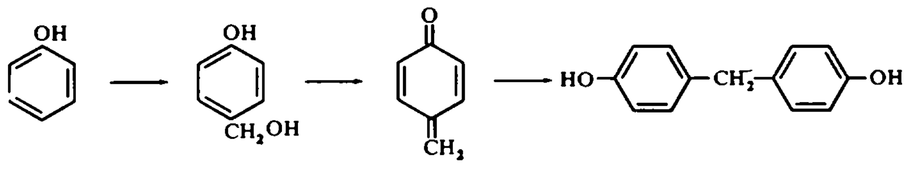


(4)

Rearrangements that are analogous to those described here for the thiobisphenols have not been reported previously but similar processes have been suggested, first, for the formation[7] of methylenebisphenols from phenols and formaldehyde in basic

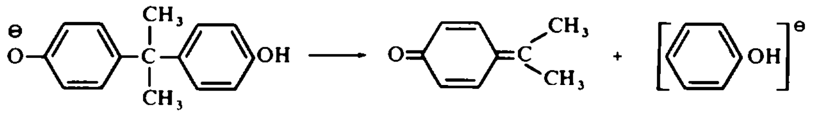


(5)

media (5) and, second, for the alkaline decomposition[8] of 4,4′-isopropylidenebisphenol (6). In the second case it was shown that 4-cumylphenol ($4\text{-}C_6H_4C(CH_3)_2C_6H_5OH$) failed to decompose.

The decompositions of dithiobisphenols and of 4,4′-trithiobisphenol

The decompositions (Table 2) proceed approximately according to Eqs (7) and


(6)

(8) to give mixtures of the monothiobisphenols which after a sufficient time have compositions closely similar to those obtained from the rearrangements. They are complicated by the fact that the initial relatively rapid reactions according to (7) and (8) appear to be followed by slow reactions which ultimately give hydrogen sulphide which is slightly in excess of that given by (7) and (8) and yields of monothiobisphenols which are slightly lower than those given by (7) and (8). No explanation has been found for these deviations but they may mean that the main reactions are accompanied by minor reactions of a different type. One suggestion is that at 180° disulphides and trisulphides are capable of undergoing S–S homolysis. However

TABLE 2. THE DECOMPOSITIONS OF 2,2′-DITHIOBISPHENOL, 4,4′-DITHIOBISPHENOL and 4,4′-TRITHIOBISPHENOL (ALL 0·025 MOLE) IN PHENOL (0·5 MOLE) IN THE PRESENCE OF SODIUM HYDROXIDE (0·01 MOLE) AT 180°

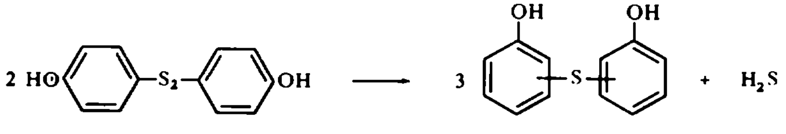
Compound	Time (hr)[a]	H_2S[a]	Yield (%)[b]	Isomers (%)		
				2,2′-	2,4′-	4,4′-
2,2′-S_2-	24	0·62	90	46	44	10
3,3′-S_2-	24	—	—	—	—	—
4,4′-S_2						
(i)[c]	21	0·58	95	40	52	8
(ii)[c]	21	0·58	93	37	52	11
(iii)[d]	30	0·54	90	36	52	12
4,4′-S_3-						
(i)	6	1·0	100	20	62	18
(ii)	23	1·2	100	40	49	11

[a] The H_2S evolved is recorded as moles per mole of the incident bisphenol. The reactions were allowed to continue for 20–30 hr since a relatively slow evolution of H_2S usually took place in the period 5–30 hr. Thus for 4,4′-dithiobisphenol and for 4,4′-trithiobisphenol the initial relatively rapid reaction during 5 hr invariably gave 0·50 mole and 1·0 mole of H_2S respectively.

[b] The yield of monothiobisphenols after allowing for the loss of incident sulphur as H_2S.

[c] The recorded results are the mean values from six experiments (i) and from three experiments (ii) done at different times.

[d] This experiment was done in duplicate at 140° with 4,4′-dithiobisphenol (0·025 mole), phenol (0·5 mole) and sodium hydroxide (0·05 mole).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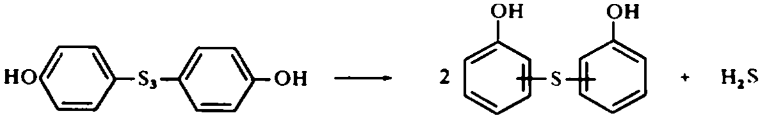
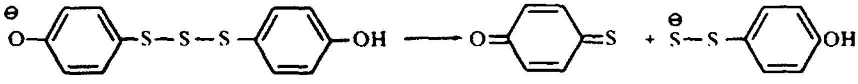

(8)

the participation of radicals is considered unlikely for the following reasons: (i) the reactions have not been observed in the absence of sodium hydroxide; (ii) the possible consequences of such participation, namely the formation of meta-substituted products and of biphenyldiols or phenoxyphenols, are not observed; (iii) 4,4′-dithiobisphenol gives the same products at 140° and at 180° (homolytic processes have been considered[9] to be less likely at 140°); (iv) it would be difficult to account for the products from disulphides on the basis of a major reaction involving initial S–S homolysis; (v) 3,3′-dithiobisphenol does not decompose under alkaline conditions in phenol even after long periods at 180°.

Therefore we suggest that these desulphurations of di- and trithiobisphenols may be accommodated best by using a scheme which, like the rearrangements of monothiobisphenols, involves the initial formation of monothiobenzoquinones and that, for example, 4,4′-trithiobisphenol decomposes in alkaline phenol largely according



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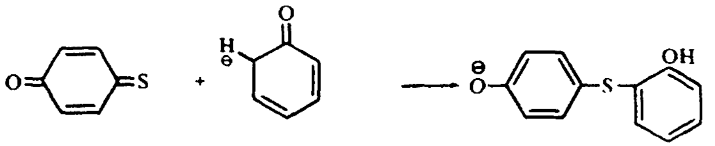

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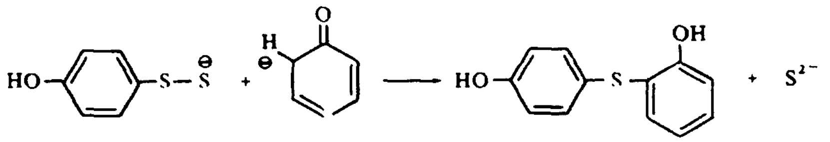
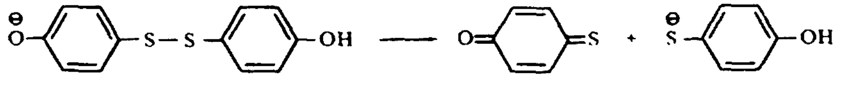


(11)

$$S^{2-} + 2PhOH \rightarrow 2PhO^{\ominus} + H_2S \qquad (12)$$

to the equations (9) through (12). The initial heterolysis (9) generates 4-hydroxybenzeneperthiolate ion which is decomposed either as such (11) or as the corresponding hydrosulphide and the displaced sulphide- or hydrosulphide-ion is rapidly converted to hydrogen sulphide in the acid-base reaction (12; it can be shown that sodium sulphide and sodium hydrosulphide are rapidly and completely converted to hydrogen sulphide in boiling phenol).



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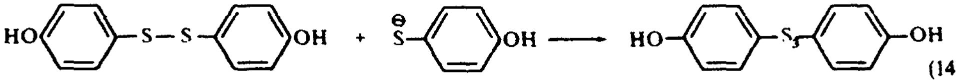

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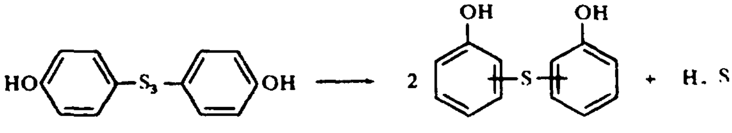

(15)

A corresponding scheme for *ortho*- and *para*-dithiobisphenols generates a hydroxybenzenethiolate ion (13) which must then be a source of hydrogen sulphide. We suggest that the generation of the trisulphide (14) may be involved (15) although we have not been successful in attempts to detect significant quantities in partly complete (25% and 50%) reactions.

EXPERIMENTAL

The rearrangements and decompositions were done in glass vessels which could be heated by the vapours from boiling phenol (180°) or xylene (140°). A vigorously stirred mixture of the appropriate thiobisphenol and phenol was heated in an atmosphere which was maintained inert by a stream of dry N_2 (usually 50 ml/min) and the catalyst was added at the reaction-temp. The exit-gases were led through a sintered glass gas distributor into NaOHaq and H_2S was determined[10] by addition to acidified I_2 and subsequent titration with $Na_2S_2O_3$. The products were taken into benzene, washed with dil HCl and with water, dried and either analysed as such or after removal of the benzene. The gas chromatographic analyses were done by using *o*-terphenyl as an internal standard and by using (a) 4 ft of 3% MS-710 on acid-washed, DCMS-treated Chromosorb G or on Gas Chrom Q at 220–260° and a flame ionization detector, or (b) 4 ft of 4% OV-17 on Gas Chrom Q at 215° and a flame ionization detector; when phenol was determined the temp was programmed from 150–210° at 6°C/min. These results and the IR spectra were supplied by Mr. R. A. Lidgett of these laboratories.

2,2′-*Thiobisphenol*. This was obtained[11] as a white crystalline solid (m.p. 139–141°) from the debromination of 2,2′-thiobis(4-bromophenol).

2,4′-*Thiobisphenol*. The following methods failed to yield significant quantities of 2,4′-thiobisphenol: (i) potassium *p*-hydroxybenzenethiolate and *o*-bromophenol in N,N-dimethylacetamide in a manner similar to that described by Campbell;[12] (ii) demethylation of 2,4′-thiobisanisole by $AlCl_3$ in boiling xylene or by 40% HBr in Ac_2O at 95°; (iii) diazotization of 2,4′-thiobisaniline[13] followed by hydrolysis with boiling H_2SO_4aq or boiling $CuSO_4$aq. Therefore it was isolated from the products of the rearrangement of 4,4′-thiobisphenol and characterized by conversion to 2,4′-dimethoxydiphenylsulphone.

A stirred mixture of 4,4′-thiobisphenol (164 g, 0·75 mole), phenol (470 g, 5·0 mole) and NaOH (12 g, 0·3 mole) was heated under reflux in a N_2-atm for 4·5 hr. The cooled product was washed with 2N HCl and then with water and the excess of phenol was removed by distillation at 15 mm. The residue gave an oil, b.p. 162–168°/1 mm (102 g) which solidified and fractional crystallization from benzene gave 2,4′-*thiobisphenol*, m.p. 100–101·5 (18 g, 11%). (Found: C, 65·9; H, 4·57; S, 14·4. $C_{12}H_{10}O_2S$ requires: C, 66·0; H, 4·62; S, 14·7%). Gas chromatography showed that this was a pure compound. It was heated with Me_2SO_4 in 2N NaOH and the product taken into ether, washed, dried and the ether removed to leave a solid which was dissolved in glacial AcOH and oxidized by boiling with H_2O_2. The resulting soln was poured into water and the ppt crystallized from EtOH; it had m.p. 125–127° and it was identical (mixed m.p.; IR spectrum) with 2,4′-dimethoxydiphenyl sulphone.

2,4′-*Dimethoxydiphenyl sulphone*. 2,4′-Thiobisanisole was made by a method similar to those used by Adams.[14] A stirred mixture of cuprous 4-methoxybenzenethiolate containing some cuprous oxide (38 g), *o*-bromoanisole (31·8 g, 0·17 mole), quinoline (160 ml) and pyridine (7 ml) was heated under reflux for 3 hr after a homogeneous soln had been obtained. The resultant mixture was poured on to ice-HCl and extracted into ether which was washed with 2N HCl, with water, dried and distilled to give 2,4′-*thiobisanisole*, b.p. 140–142°/0·03 mm, m.p. 40–43° (31 g, 74%). This anisole (2 g) in glacial AcOH (20 ml) was heated under reflux with H_2O_2 (30%; 5 ml) for 1 hr and the resultant soln was poured into water to give solid which crystallized from EtOH as 2,4′-*dimethoxydiphenyl sulphone*, m.p 125–127°. (Found: C, 60·1; H, 5·12; S, 11·7. $C_{14}H_{14}O_4S$ requires: C, 60·4; H, 5·03; S, 11·5%).

4,4′-*Thiobisphenol*. Sulphur dichloride (206 g, 2 mole) in CCl_4 (1 l.) was added to a stirred soln of phenol (376 g, 4 mole) in CCl_4 (1 l.) during 2·5 hr so that the temp did not exceed 25°. After a further 3 days at room temp the ppt was washed with CCl_4 and crystallized from xylene to give grey needles, m.p. 149–151° (243 g, 55%). Tassinari[15] gives m.p. 151°.

2,2′-*Dithiobisphenol*. 2-Hydroxybenzenethiol was made from *o*-aminophenol[16] and it had b.p. 88–91°/12 mm. 2-Hydroxybenzenethiol (12·6 g, 0·1 mole) was added to NaOH (4·0 g, 0·1 mole) in aqueous EtOH (95%) and the resultant soln was cooled in a water-bath whilst I_2 (12·7 g, 0·1 g atom) was added. The reaction-mixture was poured into water, extracted into ether, washed with $Na_2S_2O_3$aq, dried (Na_2SO_4) and the ether removed to give a pale yellow oil. (Found: C, 57·3, 57·5; H, 4·33, 3·97; S, 25·2, 26·0. Calc.

for $C_{12}H_{12}O_2S_2$: C, 57·6; H, 4·03; S, 25·6%). This oil could not be distilled without decomposition (compare Ref. 17).

3,3′-*Dithiobisphenol*. *m*-Aminophenol was converted to 3-hydroxybenzenethiol, b.p. 116–118°/10 mm. (Found: C, 57·1; H, 4·70. Calc. for C_6H_6OS: C, 57·1; H, 4·76%) and this thiol was oxidized in a manner closely similar to that described for 2-hydroxybenzenethiol to give 3,3′-dithiobisphenol, which crystallized from benzene–petrol with m.p. 93–94°. (Found: C, 57·8; H, 4·06; S, 25·4. Calc. for $C_{12}H_{10}O_2S_2$: C, 57·6; H, 4·03; S, 25·6%).

4,4′-*Dithiobisphenol*. Thionyl chloride (314 ml) was added during 2·5 hr to a stirred, cooled (water-bath) suspension of sodium *p*-acetoxybenzenesulphonate (490 g, obtained from the acetylation of sodium *p*-hydroxybenzenesulphonate by Ac_2O) in N,N-dimethylformamide (2·5 l.). Then the resultant suspension was poured into ice-water and the white ppt was washed thoroughly with water, dried in a vacuum-desiccator and taken as *p*-acetoxybenzenesulphonyl chloride (473 g). This sulphonyl chloride (300 g) was added to a stirred mixture of conc H_2SO_4 (530 ml) and ice and then Zn dust (485 g) was added gradually so that the temp did not exceed 0°. Gradual heating to 65° initiated an exothermic reaction which caused the mixture to reflux. After 1·5 hr under reflux the mixture was extracted into ether (2 l.), washed with water, dried (Na_2SO_4) and distilled through a Vigreux column (18 in) to give 4-hydroxybenzenethiol,[18] b.p. 130–133°/12 mm, as a colourless liquid (120 g) which solidified (m.p. 35–42°). This thiol was oxidized as for 2- and 3-hydroxybenzenethiol to give 4,4′-dithiobisphenol which crystallized from toluene as pale yellow crystals, m.p. 148–151°. (Found: C, 57·9, 57·6; H, 3·91, 4·11; S, 25·5, 25·7. Calc. for $C_{12}H_{10}O_2S_2$: C, 57·6; H, 4·03; S, 25·6%).

4,4′-*Trithiobisphenol*. Na (11·5 g, 0·5 g atom) was dissolved in MeOH (150 ml) and the soln added gradually (80 min) to a vigorously stirred soln of 4-hydroxybenzenethiol (63 g, 0·5 mole) in xylene (500 ml) under a N_2-atm whilst MeOH was distilled from the mixture through a Vigreux column (18 in). The resultant suspension of sodium 4-hydroxybenzenethiolate was cooled to −10° and sulphur dichloride was added during 1 hr. After a further 1 hr at −10° the mixture was allowed to come to room temp during 2 hr and the solid was filtered off, washed with water, roughly dried and crystallized from toluene as small yellow crystals of 4,4′-*trithiobisphenol*, m.p. 150–152° (20 g, 22%). (Found: C, 50·5, 51·0; H, 3·51, 3·56; S, 33·4, 33·9; M, 283, 285. $C_{12}H_{10}O_2S_3$ requires: C, 51·0; H, 3·57; S, 34·0%; M, 282).

2,2′-*Thiobis*(*p-cresol*). Sulphur dichloride (10·3 g, 6·4 ml, 0·1 mole) was added during 30 min to a cooled (ice-bath), stirred soln of *p*-cresol (54 g, 0·5 mole) in CCl_4 (100 ml). After a further 1 hr, the solvent was removed at atm press and the excess of *p*-cresol up to 100°/19 mm. The residue gave a yellow oil (b.p. 156–162°/0·1 mm) which formed a waxy solid and crystallized from petrol (b.p. 60–80°) benzene (4:1) with m.p. 116–117° (Ref. 11: m.p. 114–115). (Found: C, 68·2; H, 5·65; S, 13·8. Calc. for $C_{14}H_{14}O_2S$: C, 68·3; H, 5·69; S, 13·1%).

4,4′-*Thiobis*(*o-cresol*). Sulphur dichloride (59·8 g, 0·58 mole) was added during 1·5 hr to a cooled (ice-bath), stirred soln of *o*-cresol (102 g, 0·95 mole) in trichloroethylene (350 ml). After a further 1 hr at room temp the mixture was kept at 30° for 3 hr and the green ppt was crystallized from benzene to give grey crystals, m.p. 124–127° (32·5 g, 27%). (Found: C, 68·2; H, 5·95; S, 13·2. Calc. for $C_{14}H_{14}O_2S$: C, 68·3; H, 5·69; S, 13·1%).

4-*Phenylthiophenol*. 4-Nitrodiphenylsulphide, m.p. 53–57°, was obtained from sodium benzenethiolate and 4-chloronitrobenzene in aqueous N,N-dimethylformamide and it was reduced to 4-phenylthioaniline, m.p. 95–97°, by Zn dust—HCl. 4-Phenylthioaniline (74·7 g, 0·37 mole) in a mixture of glacial AcOH (1 l.) and conc HCl (83 ml) was diazotized at 0–10° by $NaNO_2$ (34 g) in water (70 ml) and the diazonium soln was decomposed in boiling water (1·5 l.). The phenol was extracted from ether into 2N NaOH and the alkaline soln was acidified, extracted with ether and the ethereal soln washed with water, dried (Na_2SO_4) and distilled to give 4-phenylthiophenol, b.p. 151–157°/0·7 mm, m.p. 48–50° (30 g, 40%). Hilbert[19] gives m.p. 50–51°. It formed 4-methoxydiphenyl sulphone, m.p. 85–87, (Found: C, 63·1; H, 5·01; S, 12·5. Calc. for $C_{13}H_{12}O_3S$: C, 62·9; H, 4·87; S, 12·9%).

The decomposition of 4,4′-*thiobisphenol in the absence of added phenol*. A mixture of 4,4′-thiobisphenol (43·6 g, 0·20 mole) and NaOH (0·4 g, 0·01 mole) was heated to a bath temp of 180° under N_2 at an indicated press of 18 mm. Phenol (15·2 g, 0·16 mole; 94% according to Eq. (1) with $n = 7$) rapidly distilled from the mixture. The distillation-residue was dissolved in EtOH and HCl passed through the soln. The NaCl ppt was filtered off and the filtrate added gradually to water (2 l.) to give a white solid which was dried at 56°/15 mm (24·7 g, 90%). (Found: C, 59·8; H, 3·35; S, 23·1; M, 980. $C_{48}H_{34}O_8S_7$ requires: C, 59·9; H, 3·53; S, 23·3%; M, 962). These observations are in good agreement with Eq. (1) with $n = 7$. The IR spectrum of the product (strong absorption at 820 cm^{-1} with relatively weak absorption at 750 and 720 cm^{-1}) suggests that *p*-substitution is dominant.

The decomposition of 4,4′-*thiobisphenol in* p-*cresol.* A stirred mixture of 4,4′-thiobisphenol (21·8 g, 0·1 mole), *p*-cresol (216 g, 2·0 mole) and NaOH (1·6 g, 0·04 mole) was heated under reflux in N_2-atm for 5 hr, cooled, dissolved in benzene, washed with 2N HCl and with water, combined with benzene-extracts of the aqueous layers and dried (Na_2SO_4). The benzene was removed at 50°/40 mm and then distillation gave a series of colourless liquids (204 g, b.p. 80–83°/9 mm) which were analysed by gas-chromatography (4 ft of 10% polyethylene glycol on Embacel at 200°; flame ionization detector; 3,5-xylenol as an internal standard). They contained phenol (18·2 g, 97%) and *p*-cresol. The distillation residue (24 g) was crystallized several times from benzene to give colourless crystals, m.p. 116–118° (3·6 g, 14%) which were identical with an authentic specimen (qv) of 2,2′-thiobis(*p*-cresol). The combined mother-liquors were evaporated to give an oil which had an IR spectrum closely similar to that of the oligomers obtained by heating 2,2′-thiobis-(*p*-cresol) either in the presence of NaOH (qv) or in alkaline *p*-cresol. When a similar mixture of 4,4′-thiobisphenol, *p*-cresol, and NaOH was heated for 5 hr in a N_2 atm by the vapour from boiling phenol, the initial distillate contained phenol (11·5 g, 61%) and the residue was very similar (IR spectrum) to the mixture of oligomers obtained above.

The decomposition of 2,2′-*thiobis*(p-*cresol*). The method was similar to that described for 4,4′-thiobisphenol with 2,2′-thiobis(*p*-cresol) (49·2 g, 0·2 mole) and NaOH (0·4 g, 0·01 mole). *p*-Cresol (8·9 g, 0·083 mole; 83% according to an equation analogous to (1) with n = 2) rapidly distilled and the residue provided a viscous oil (35·8 g, 93%). (Found: C, 65·9; H, 5·21; S, 16·3; M, 380. $C_{21}H_{20}S_2O_3$ requires: C, 65·6; H, 5·21; S, 16·7%; M, 385).

The decomposition of 4,4′-*thiobis*(o-*cresol*). As in the previous section with 4,4′-thiobis(*o*-cresol) (49·2 g, 0·2 mole) and NaOH (0·4 g, 0·01 mole). *o*-Cresol (18·3 g, 106% by an equation analogous to (1) with n = 5) rapidly distilled and the residue provided a buff solid (30 g, 94%). (Found: C, 63·6; H, 4·82; S, 20·0; M, 774. $C_{42}H_{38}O_6S_5$ requires: C, 63·2; H, 4·76; S, 20·1%; M, 798).

Attempted reactions of diphenyl sulphide and 4-phenylthiophenol in alkaline phenol. Diphenyl sulphide or 4-phenylthiophenol (0·025 mole), phenol (0·5 mole) and NaOH (0·01 mole) were heated at 180° for 5 hr and the products were isolated as for the thiobisphenols. Gas-chromatography failed to detect changes.

Decomposition of sodium sulphide and of sodium hydrosulphide in phenol. Water was removed from $Na_2S . 9H_2O$ by boiling with benzene and the recovered solid contained 74% Na_2S (iodometric analysis). This solid (1·05 g, 0·01 mole Na_2S) was added to stirred boiling phenol (188 g, 2 mole) and the gases swept by N_2 into NaOHaq. Nearly complete decomposition (0·0097 mole of H_2S) had occurred after 10 min.

Similarly anhyd NaSH[20] (99% NaSH; 0·56 g, 0·01 mole) was added to phenol (2 mole) heated by the vapours from boiling phenol. Nearly complete decomposition (0·0093 mole of H_2S) had occurred after 5 min and decomposition was complete (0·0101 mole of H_2S) after 10 min.

Determinations of trithiobisphenol during desulphurations of 4,4′-*dithiobisphenol.* (a) A mixture of 4,4′-dithiobisphenol (6·25 g, 0·025 mole) and phenol (47 g, 0·5 mole) was heated under reflux in a N_2 atm and then NaOH (0·4 g, 0·01 mole) was added. After 1 hr, H_2S (0·0075 mole) had been evolved and the mixture was cooled rapidly, dissolved in benzene, washed with 2N HCl and with water and the solvent evaporated. The excess of phenol was distilled ($\ngtr$ 140°/12 mm) to give a residue (7·6 g) which was analysed for trisulphide, (Found: 0·0012 mole per mole of incident dithiobisphenol) as is described in the following paper.

(b) A similar mixture was heated by the vapour from boiling mesitylene (indicated temp, 163°). After 2 hr, H_2S (0·0036 mole) had been evolved and the residue had 0·016 mole of trisulphide per mole of dithiobisphenol.

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