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SOME OBSERVATIONS OF THE REACTIONS BETWEEN PHENOL AND SULPHUR

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Abstract—Preliminary investigations of the reactions between phenol and sulphur in the presence of NaOH at 140° and at 180° are reported. With the ratio PhOH:S $\geqslant$ 5:1, the products are mixtures of 2,2'-, 2,4'- and 4,4'-monothiobisphenols and 50% of the incident sulphur is eliminated as hydrogen sulphide. NMR spectra in the presence of hexamethylphosphoramide have demonstrated the intermediate formation of polythobisphenols at 140° and it is suggested that a sequence which involves desulphurations of these polythiobisphenols in a manner similar to that suggested in the previous paper for 4,4'-trithiobisphenol may be involved. With the ratio PhOH:S = 1: $\geqslant$ 1, 50% of the incident sulphur again is eliminated as hydrogen sulphide and in the limit the products appear to be monosulphidically bridged oligonuclear phenols which may be formed by a similar sequence of reactions.

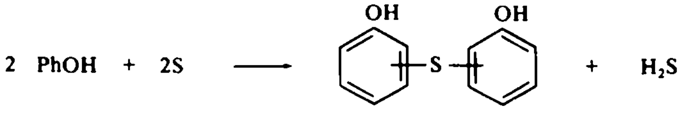
INTRODUCTION

FOLLOWING the investigations of thiobisphenols described in the previous paper[1] we have made some observations of the reactions between phenol and sulphur in the presence of sodium hydroxide which we think are sufficient to indicate the possible courses of these reactions. With the ratio PhOH:S $\geqslant$ 5:1, the products are readily identified as essentially monothiobisphenols and it is possible first to demonstrate the absence of other products and, second, to detect the formation of higher polysulphides which are gradually desulphurated as the reactions proceed. With the ratio, PhOH:S = 1: $\geqslant$ 1, the products are oligomeric phenols which are less easily identified but which appear to be formed by similar routes.

RESULTS AND DISCUSSION

Reactions with PhOH:S $\geqslant$ 5:1

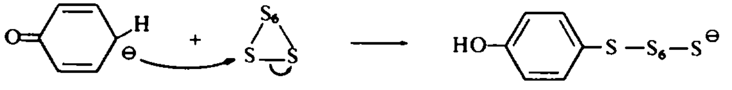
Typical results for these reactions are in Table 1. At 180° the reactions proceed cleanly to produce mixtures of the *ortho-* and *para-*substituted monothiobisphenols and with evolution of 50% of the incident sulphur as H_2S; they may be described by the Eq. (1). As in the cases of the thiobisphenols of the previous paper the present reactions are extremely slow in the absence of sodium hydroxide and no other products have been detected by gas chromatography or by examinations of IR spectra.

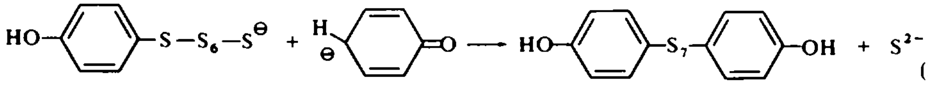


(1)

If higher levels of sodium hydroxide are used reactions at 140° proceed at comparable rates to give similar products and it is for these reactions that the formation of polythiobisphenols has been demonstrated. Previously it has been shown[2] that the NMR signals due to phenolic protons may be distinctly separated by using hexamethylphosphoramide (HMPA) as a H-bonding base to allow analyses of mixtures of phenols. We have shown that a similar method is applicable to the mono-, di- and trithiobisphenols: thus a mixture of phenol, 2,2′-monothiobisphenol, 4,4′-monothiobisphenol, 4,4′- dithiobisphenol, and 4,4′-trithiobisphenol in carbon tetrachloride containing HMPA gives signals at 597, 605, 612, 628 and 636 Hz relative to TMS, which respectively represent the individual phenols. Now when samples are taken from a reaction-mixture initially containing phenol (2 mole), sulphur (0·4 g atom) and sodium hydroxide (0·25 mole) heated at 140° the following distinct signals are observed after the indicated times: 15 min, 601, 625, 650 Hz; 1 hr, 600, 612, 616, 624, 645, 650 Hz; 2 hr, 600, 612, 624, 645, 649 Hz; 24 hr., 600, 611, 624 Hz. The signals at 650 Hz are likely to represent at least tetrathiobisphenols, $HOC_6H_4S_4C_6OH$, and the other observations show how the higher polythiobisphenols are gradually converted to monothiobisphenols. In the present case there appears to be a signal at 624 Hz which would indicate residual dithiobisphenols even after 24 hr; we are not able to offer an explanation for this observation.

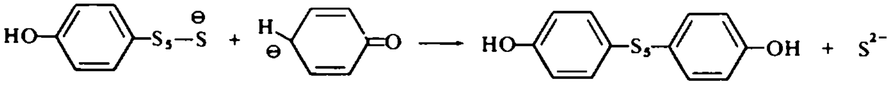
We suggest that these reactions which are extremely slow in the absence of sodium hydroxide; which lead only to *ortho*- and *para*-substituted thiobisphenols and to the evolution of 50% of the incident sulphur as HS; and which involve the intermediate formation of polythiobisphenols, are best interpreted on the basis that initial reactions between phenolate ions and some species of sulphur lead to polythiobisphenols which undergo subsequent desulphurations analogous to those discussed[1] for 4,4′-trithiobisphenol ultimately to give monothiobisphenols. This is illustrated for reactions with S_8 in the Eqns (2) through (6) and in the overall sequence (7); 4 moles of H_2S are obtained from S_8. The actual species of sulphur that are present in dilute


(2)


(3)

$$S^{2-} + 2PhOH \rightarrow 2PhO^{\ominus} + H_2S \quad (4)$$


(5)


(6)

$$S_8 \rightarrow S_7 + H_2S \rightarrow S_5 + H_2S \rightarrow S_3 + H_2S \rightarrow S_1 + H_2S \quad (7)$$

$$S_7 \rightarrow S_6 + H_2S \rightarrow S_4 + H_2S \rightarrow S_2 + H_2S \rightarrow S_1 + \tfrac{1}{2}H_2S \quad (8)$$

solutions in phenol at 180° and at 140° are not known but they may include rings and polymeric biradicals of varying complexity.[3] Odd membered rings may be accommodated by a sequence such as (8) involving the desulphuration of a dithiobisphenol in the final stage (giving 0·5 mole of H_2S per mole of dithiobisphenol and hence, for example, 3·5 moles of H_2S from S_7) but the influence of biradicals, if they participate is more difficult to assess.

TABLE 1. THE FORMATION OF MONOTHIOBISPHENOLS IN REACTIONS BETWEEN PHENOL AND SULPHUR (PhOH:S $\geqslant$ 5:1)

PhOH:S (mole:g atom)	NaOH (mole)	Temp. (°C)	Time (hr)	H_2S (mole)	Yield (%) a	Isomers (%)		
						2,2′-	2,4′-	4,4′-
1:0·05	0·01	180[b]	24	0·025	100	45	45	10
1:0·10	0·0125	180	6	0·050	95	—	—	—
1:0·20	0·0125	180	6	0·10	94	44	42	8
1:0·20	0·125	140	18	0·10	80	53	37	10

[a] The yields of monothiobisphenols after allowing for the loss of incident sulphur as H_2S.

[b] The reactions were done at temps provided by the vapours from boiling phenol (180°) or xylene (140°).

Reactions with PhOH:S = 1: $\geqslant$ 1.

The reactions which use PhOH:S = 1: $\geqslant$ 2 rapidly produce highly viscous products which restrict the evolution of H_2S and which are difficult to isolate. Therefore the present work has been restricted to reactions which use a maximum of 1·5 g atoms of sulphur per mole of phenol. The products were analysed by determinations of OH numbers and by using hydrogenolyses with LAH. The last method allows determinations of polysulphides (Sx; x $\geqslant$ 3) unambiguously but it depends on accurate values of OH numbers for determinations of disulphides.

Typical results for the products are in Table 2 and the observations (i) through (iv) may be made.

(i) If the reactions are allowed to proceed for a sufficient time, 50% of the incident sulphur is eliminated as H_2S.

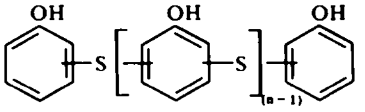
(ii) The products have analyses and IR spectra in agreement with those expected for oligomeric phenols bridged by sulphur at *ortho*- and *para*-positions.

(iii) When the reactions are taken to stages where the evolution of H_2S is close to 50% of the incident sulphur, polysulphides are present in small proportions; owing to difficulties in determinations of OH numbers the absence of disulphides has not been demonstrated but since they are known to be unstable they are probably absent after a sufficient time.

(iv) Phenol is recovered from the reactions.

These observations are all approximately correlated by Eqns such as (9) in which for

2nPhOH + 2nS ——→



+ (n − 1) PhOH + nH_2S (9)

simplicity phenol is regarded as bifunctional, and it is suggested that reactions similar to those discussed previously may be held to account for the products in these cases. Since phenol is trifunctional high polymers and networks are possible[4] when the proportion of sulphur is increased.

TABLE 2. THE FORMATION OF OLIGOMERIC PHENOLS IN REACTIONS BETWEEN PHENOL AND SULPHUR ($PhOH:S = 1: \geqslant 1$).

PhOH:S (mole:g atom)	NaOH (mole)	Temp (°C)	Time (hr)	H_2S (mole)	$(PhOH)_r$[a] (mole)	M.Wt.[b]	Hydroxyl Number	Sx ($x \geqslant 3$) (mole)[c]
1:1	0·125	140	10	0·48	0·20	390	3·0	0·01
1:1	0·125	180	24	0·50	0·25	318	2·5	0·00
1:1·1	0·125	140	9	0·56	0·14	350	3·3	0·00
1:1·2	0·125	140	13	0·58	0·01	435	3·0	0·08
1:1·5	0·125	140	13	0·70	0·01	435	3·7	0·23

[a] $(PhOH)_r$: recovered phenol; the values are approximate since phenol was lost owing to the formation of emulsions during isolations.

[b] Molecular weights were determined by using a Mechrolab osmometer.

[c] Polysulphides are recorded as moles per mole of product.

EXPERIMENTAL

The reactions were done similarly to the rearrangements and decompositions of the previous paper: phenol and sulphur were heated to the reaction temp by vapours from boiling phenol or xylene and then NaOH was added. In the cases ($PhOH:S \geqslant 5:1$) the products were analysed by gas chromatography as described previously whilst in the cases ($PhOH:S = 1: \geqslant 1$) phenol was removed by distillation before analyses by methods to be described. In the early experiments sublimed sulphur (BDH) was used but later this was replaced by crystalline sulphur (BDH); this change did not alter rates (evolution of H_2S) or products.

OH numbers were estimated by the standard acetylation procedure.[5] The method is not accurate for thiobisphenols (Table).

Compound	Hydroxyl Number (found)	H_2 from LAH Calc. (mole)	H_2 from LAH Calc. (cc/gm)	H_2 from LAH Found (cc/gm)	S_x ($x \geqslant 3$) Calc.	S_x ($x \geqslant 3$) Found
p-$HOC_6H_4SC_6H_4OH$	1·6	2	205	203	0	0
p-$HOC_6H_4S_2C_6H_4OH$	1·5	3	269	266	0	0·05
p-$HOC_6H_4S_3C_6H_4OH$	1·7	4	318	331	1·0	1·15
C_6H_5OH	1·00	—	—	—	—	—

Difficulties with the method have been discussed[6] and it has been shown to be inapplicable to phenol-formaldehyde resins.[7] In the present cases it has been retained despite its inaccuracies because available alternatives using benzenesulphonyl chloride[7] and phenyl isocyanate[8] were less successful.

The use of LAH for the analyses of mixtures of alk(en)yl polysulphides has been described.[9] The reduction and subsequent hydrolysis of the polysulphide, RS_xR_1, provides thiols and H_2S according to the Eqn (10). More

$$RS_xR_1 \rightarrow RSH + R_1SH + (x-2)\,H_2S \tag{10}$$

$$RS_xR_1 + 2(x-1)\,H^{\ominus} \rightarrow RS^{\ominus} + R_1S^{\ominus} + (x-1)\,H_2 + (x-2)\,S^{2-} \tag{11}$$

generally the hydrogenolyses are represented by the Eqn (11) and, formally, average values of x may be obtained from measurements of H_2 before acidification and H_2S after acidification. This method is applicable to polythiobisphenols as is indicated in the Table if allowance is made for the evolution of H_2 from OH groups. In the case of the phenol-sulphur products it is clear that estimations of disulphides based on the evolution of H_2 depend on accurate OH numbers and on the complete removal of water and phenol. The method overestimates the H_2S from 4,4'-trithiobisphenol and this may be owing to the volatilization of 4-hydroxybenzenethiol under the conditions used here. However when H_2S is not evolved from experimental materials the absence of polysulphides S_x ($x \geqslant 3$) evidently is demonstrated.

The sample (0·3 g) in dry THF (25 ml) was added slowly to LAH (0·5 g) in the same solvent (50 ml) so that a gentle reflux was maintained. After the addition, conc HCl (20 ml) was added at such a rate that the reflux was maintained and the gases evolved were led through 2N NaOH (50 ml). Sulphide was determined iodometrically.

The IR spectra were obtained by using KBr discs or films deposited from solns in $CHCl_3$. In the cases PhOH : S $\geqslant$ 5 : 1 the spectra were closely similar to those of mixtures of the monothiobisphenols and to those of the products from the decompositions of mono-, di and trithiobisphenols in alkaline phenol. In the cases PhOH : S = 1 : $\geqslant$ 1 the spectra were similar to that of the product obtained from the alkaline decomposition if 4,4'-thiobisphenol in the absence of other phenols except that equally strong absorption bands at 755 cm^{-1} and 830 cm^{-1} from the phenol-sulphur products are indicative of ortho- and para-substitution being equally important.

The ^1H NMR spectra were obtained by using a Perkin–Elmer R10 spectrometer at 60 MHz and TMS as an internal reference on solutions (10% w/w) of the phenol or of the phenol-sulphur product in CCl_4 containing 2–4 moles of HMPA per mole of phenol. The spectra were supplied by Mrs. J. Ellis of these laboratories.

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