309. *Benz*-1 : 3-*oxathioles, Benz*-1 : 4-*oxathien, and αω-Bisarylthioalkanes.*

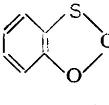
By Douglas Greenwood and Herbert A. Stevenson.

With aliphatic aldehydes or ketones, and with carbonyl chloride, *o*-hydroxybenzenethiol gives respectively 2-alkyl- or 2 : 2-dialkyl-benz-1 : 3-oxathioles (*e.g.*, I), and benz-1 : 3-oxathiol-2-one (III). With alkylene dibromides the thiol forms bis-*o*-hydroxyphenylthioalkanes, though when ethylene dibromide is used, benz-1 : 4-oxathien (VI) is also obtained. *o*-Hydroxyphenylthioacetic acid, from *o*-hydroxybenzenethiol and chloroacetic acid, readily cyclises to 2-ketobenz-1 : 4-oxathien (VII).

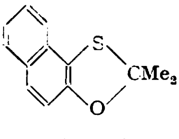
Some of these reactions have been extended to other hydroxyarenethiols, including 2-hydroxynaphthalene-1-thiol.

Although the action of sulphur on sodium phenoxide (Haitinger, *Monatsh.*, 1883, **4**, 166; Palmer, U.S.P. 2,004,728) gives poor yields of a product that is difficult to purify, *o*-hydroxybenzenethiol can be obtained in quantity by a modification of Friedlander and Mauthner's method (*Z. Farben- Textil-chem.*, 1904, **3**, 333; *Chem. Zentr.*, 1904, II, 1176) involving the diazotisation of *o*-aminophenol and reaction with potassium ethyl xanthate. A preliminary study of 5- and 6-membered ring compounds derived from this thiol and from 2-hydroxynaphthalene-1-thiol (Stevenson and Smiles, *J.*, 1930, 1743) has been made.

Under the influence of hydrogen chloride, *o*-hydroxybenzenethiol condenses with aliphatic aldehydes or ketones, to give 2-alkyl- or 2 : 2-dialkyl-benz-1 : 3-oxathioles (*e.g.*, I), together with alkali-soluble by-products, presumably bis-*o*-hydroxyphenylthioalkanes. 2-Hydroxynaphthalene-1-thiol and acetone similarly yielded 2 : 2-dimethylnaphtho-(1′ : 2′-4 : 5)-1 : 3-oxathiole (II). Attempts to extend the reaction to aromatic aldehydes and ketones have so far not given pure 2-arylbenz-1 : 3-oxathioles.



(I)



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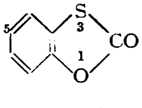


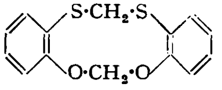
(III)

The reaction is analogous to the preparation of substituted benzo-1 : 3-dithioles from *o*-dimercaptobenzene and aromatic aldehydes and ketones [Guha and Chakladar, *J. Indian Chem. Soc.*, 1925, **2**, 318; Hurtley and Smiles, *J.*, 1926, (*a*) 1821, (*b*) 2263; (*c*) 1927, 534]. Slooff (*Rec. Trav. chim.*, 1935, **54**, 995) prepared the analogous 2 : 2-dialkylbenzo-1 : 3-dioxoles by reaction of catechol with ketones in the presence of phosphoric oxide.

Hurtley and Smiles [*locc. cit.*, (*a*), (*c*)] obtained interesting results on oxidising benzo-1 : 3-dithioles. They found, for example, that 2-phenylbenzo-1 : 3-dithiole and nitric acid yielded a nitrate which on hydrolysis gave 2-phenylbenzo-1 : 3-dithiole 2-oxide. This compound behaved as a pseudo-base, giving sulphonium salts with acids. It is remarkable that these authors observed no normal oxidation products of these cyclic sulphides. We have found that the oxathioles (I) and (II) give sulphoxides on mild oxidation with hydrogen peroxide. Oxidation with neutral permanganate gave sulphones.

Kaufmann and Weber (*Arch. Pharm.*, 1929, **267**, 192) obtained 5-methylbenz-1 : 3-oxathiol-2-one from *p*-cresol and thiocyanogen by ring-closure of the 4-methyl-2-thiocyanatophenol to 2-imino-5-methylbenz-1 : 3-oxathiole followed by acid hydrolysis, and Stevenson and Smiles (*loc. cit.*) and Werner (U.S.P. 2,332,418) similarly prepared a number of analogues. However, the parent compound, benz-1 : 3-oxathiol-2-one cannot be prepared in this way because a substituent is required in the phenol nucleus in order to direct the thiocyanato-group into an *ortho*-position. Benz-1 : 3-oxathiol-2-one (III) has now been obtained by two methods. (1) The *o*-thiocyanato-group was introduced by reaction of diazotised *o*-aminophenol with cuprous thiocyanate. Ring-closure and hydrolysis as before gave the compound in small yield. (2) A much better yield was obtained by the direct action of carbonyl chloride on *o*-hydroxybenzenethiol. Similarly, thiocarbonyl chloride gave benz-1 : 3-oxathiole-2-thione, previously isolated by Friedlander and Mauthner (*loc. cit.*) as a by-product of the reaction between diazotised *o*-aminophenol and potassium ethyl xanthate. Hurtley and Smiles [*loc. cit.*, (*a*)] obtained benzo-1 : 3-dithiol-2-one and benzo-1 : 3-dithiole-2-thione by the action of carbonyl chloride and carbon disulphide respectively on *o*-dimercaptobenzene, and found that benzo-1 : 3-dithiol-2-one could be mononitrated but did not afford simple oxidation products owing to disruption of the heterocyclic ring. Benz-1 : 3-oxathiol-2-one (III) behaves analogously, giving a (?5-)nitro-derivative.

Several new bishydroxyarylthioalkanes have been prepared by condensation of *o*- and *p*-hydroxybenzenethiols and 2-hydroxynaphthalene-1-thiol with alkylene dibromides. Those from *o*-hydroxybenzenethiol were acetylated and then oxidised to disulphones by usual methods. Bis-*o*-hydroxyphenylthiomethane, (o-$OH{\cdot}C_6H_4{\cdot}S)_2CH_2$, was condensed with a further equivalent of methylene dibromide, giving 4 : 5-9 : 10-dibenzo-1 : 3-dioxa-6 : 8-dithia*cyclo*deca-4 : 9-diene (IV). Condensation of *p*-tolylthioethyl bromide (from toluene-*p*-thiol and ethylene dibromide) with *o*-hydroxybenzenethiol gave 1-*o*-hydroxyphenylthio-2-*p*-tolylthioethane, isolated as the tetrahydrate (V) of its sodium salt.



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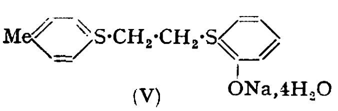

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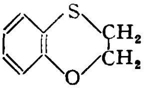
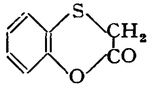


(VI)

o-Hydroxybenzenethiol and ethylene dibromide invariably gave as the main product 1 : 2-bis-*o*-hydroxyphenylthioethane, but under appropriate conditions a small yield of benz-1 : 4-oxathien (VI) was also obtained. An attempt to synthesise benz-1 : 3-oxathiole by a similar reaction between *o*-hydroxybenzenethiol and methylene dibromide failed, as only bis-*o*-hydroxyphenylthiomethane could be isolated.



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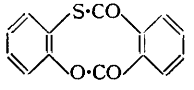

(VIII)

Benz-1 : 4-oxathien (VI) readily gave a sulphoxide on oxidation, and more vigorous neutral oxidation yielded a sulphone.

Condensation of *o*-hydroxybenzenethiol with one equivalent of chloroacetic acid gave an oil, probably *o*-hydroxyphenylthioacetic acid, *o*-$OH\cdot C_6H_4\cdot S\cdot CH_2\cdot CO_2H$ (Friedlander, *Annalen*, 1907, **351**, 414). This compound readily gives 2-ketobenz-1 : 4-oxathien (VII) on attempted distillation (or when heated). *o*-Hydroxybenzenethiol and two equivalents of chloroacetic acid gave *o*-carboxymethylthiophenoxyacetic acid.

Several new *OS*-esters of *o*-hydroxybenzenethiol and of other hydroxyarenethiols are reported, including the cyclic compound (VIII) prepared by means of phthaloyl chloride.

EXPERIMENTAL

o-*Hydroxybenzenethiol*.—The yield of this compound obtained by Friedlander and Mauthner's method (*loc. cit.*) was improved by addition of further quantities of zinc dust (40 g.) and concentrated hydrochloric acid (120 c.c.) to the residue after steam-distillation. Continuation of the steam-distillation then gave more thiol by reduction of the disulphide present as a by-product. Yields of 30—70% were obtained, varying with the quality and age of the commercial batches of *o*-aminophenol.

If this modification was not applied, di-*o*-hydroxyphenyl disulphide could be isolated as follows. The residue after steam-distillation was extracted with ether, dried, and distilled at 2 mm., the viscous yellow oil of b. p. 160—170° being collected. Trituration with 2N-sodium carbonate gave the monosodium salt, which crystallised from ethanol as prisms of the *pentahydrate*, m. p. 136° (decomp.) [Found: C, 39·55; H, 5·4; H_2O (Karl Fischer), 22·7. $C_{12}H_9O_2S_2Na,5H_2O$ requires C, 39·8; H, 5·25; H_2O, 24·9%]. Haitinger (*loc. cit.*) does not give the m. p. of his hexahydrate of this compound obtained in a similar manner.

The disulphide was also obtained by oxidation of the thiol. Passage of a slow stream of air for 48 hr. through a solution of *o*-hydroxybenzenethiol (6 g.) in ethanol (25 c.c.) containing ammonia (1 c.c., *d* 0·880), and isolation as above, gave a good yield of the monosodium salt. Acetylation gave *di*-o-*acetoxyphenyl disulphide*, needles, m. p. 57° after recrystallisation from light petroleum (b. p. 60—80°) (Found: C, 57·35; H, 3·8. $C_{16}H_{14}O_4S_2$ requires C, 57·5; H, 4·2%).

*Preparation of Benz-*1 : 3-*oxathioles*.—Dry hydrogen chloride was passed into a solution of *o*-hydroxybenzenethiol (18 g.) in acetone (60 c.c., large excess) for 2 hr. without control of temperature, and then for 30 min. at 0°. A red colour developed at the end of the reaction. The mixture was poured into dilute alkali, and the oil extracted with ether, dried, and fractionated. 2 : 2-*Dimethylbenz*-1 : 3-*oxathiole* (9·6 g.) was collected at 60°/1·5 mm., and had a sweet ester-like smell (Found: C, 64·65; H, 5·75%; *M*, 160. $C_9H_{10}OS$ requires C, 65·1; H, 6·0%; *M*, 166). Acidifying the alkaline solution and again extracting with ether gave about 5 c.c. of oil, but on distillation, no fraction of constant b. p. was obtained.

o-Hydroxybenzenethiol (18 g.) and ethyl methyl ketone (60 c.c.) similarly gave 2-*ethyl*-2-*methylbenz*-1 : 3-*oxathiole* (15·4 g.), b. p. 85°/3 mm. (Found: C, 66·7; H, 6·65. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·7%).

2-Hydroxynaphthalene-1-thiol (17 g.) and acetone (150 c.c.) similarly gave 2 : 2-*dimethylnaphtho*(1′ : 2′-4 : 5)-1 : 3-*oxathiole* (8·7 g.), b. p. 135—136°/2·5 mm. (Found: C, 72·1; H, 5·6. $C_{13}H_{12}OS$ requires C, 72·2; H, 5·6%).

o-Hydroxybenzenethiol (24 g.) and acetaldehyde (100 c.c.) reacted similarly. Distillation of the products gave paraldehyde, followed by 2-*methylbenz*-1 : 3-*oxathiole* (9·6 g.), b. p. 70—74°/3 mm. (Found: C, 64·1, 63·0; H, 5·6, 5·85. C_8H_8OS requires C, 63·2; H, 5·3%).

Oxidation of Benz-1 : 3-*oxathioles*.—2 : 2-Dimethylbenz-1 : 3-oxathiole (1 g.) and hydrogen peroxide (0·8 c.c.; 30%), kept in acetic acid (25 c.c.) at room temperature for 5 days and then diluted with water, gave an oil which solidified after ether-extraction. Recrystallisation from light petroleum (b. p. 60—80°) gave the *sulphoxide*, prisms (0·7 g.), m. p. 38° (Found: C, 59·7; H, 5·45. $C_9H_{10}O_2S$ requires C, 59·3; H, 5·5%). Excess of hydrogen peroxide in acetic acid at 100° appeared to cause decomposition, and no product was isolated.

2 : 2-Dimethylbenz-1 : 3-oxathiole (0·5 g.) was suspended in a little water containing magnesium sulphate (2 g.), and the theoretical amount of potassium permanganate (210 c.c.; 0·1N) added during 1 hr. at 80—85°. After treatment with sulphur dioxide, chloroform-extraction gave an oil which crystallised. Recrystallisation from light petroleum (b. p. 60—80°) gave the *sulphone*, needles (0·1 g.), m. p. 75° (Found: C, 54·35; H, 4·65. $C_9H_{10}O_3S$ requires C, 54·5; H, 5·05%).

2 : 2-Dimethylnaphtho(1′ : 2′-4 : 5)-1 : 3-oxathiole was converted similarly into its *sulphoxide*, needles, m. p. 134° [from light petroleum (b. p. 60—80°)] (Found: C, 67·4; H, 5·15. $C_{13}H_{12}O_2S$

requires C, 67·2; H, 5·2%), and *sulphone*, needles (from ethanol), m. p. 155° (Found : C, 63·2; H, 4·55. $C_{13}H_{12}O_3S$ requires C, 62·9; H, 4·8%).

Benz-1 : 3-*oxathiol*-2-*one*.—*Method* 1. *o*-Aminophenol (100 g.) was diazotised, and treated with cuprous thiocyanate (223 g.) and sodium thiocyanate (180 g.). The mixture was warmed slowly until evolution of nitrogen was complete, refluxed for 1 hr. to hydrolyse the 2-imine, and then steam-distilled. The distillate was extracted with ether, and the ether dried and evaporated. The residue on distillation at 2·5 mm. yielded phenol (5 g.), followed by the *product* (20·5 g.) at 93—96°. This had m. p. 26° (Found : C, 55·1; H, 2·5. $C_7H_4O_2S$ requires C, 55·3; H, 2·6%).

Method 2. Carbonyl chloride was passed into a solution of *o*-hydroxybenzenethiol (6·5 g.) in 0·5N-sodium hydroxide (520 c.c.). Benz-1 : 3-oxathiol-2-one, precipitated as an oil, was extracted with ether, dried, and distilled (b. p. 94°/2 mm., m. p. 26°; 4·9 g.).

Benz-1 : 3-oxathiol-2-one (1 g.) and nitric acid (10 c.c.; *d* 1·4) were refluxed for 2½ hr., then cooled and diluted with water. One recrystallisation from dilute acetic acid and two from ethanol then gave long colourless needles of (?5-)*nitrobenz*-1 : 3-*oxathiol*-2-*one*, m. p. 182—183° (Found : N, 7·1. $C_7H_3O_4NS$ requires N, 7·1%).

Benz-1 : 3-*oxathiole*-2-*thione*.—A solution of *o*-hydroxybenzenethiol (20 g.) and sodium hydroxide (16 g.) in water (250 c.c.) was shaken with a slight excess of thiocarbonyl chloride (15 c.c.) for 3 hr. The oily product was separated and recrystallised four times from ethanol, giving yellow needles (5·8 g.), m. p. 97—98°. Friedlander and Mauthner (*loc. cit.*) give m. p. 99·5°.

Bisarylthioalkanes.—*o*-Hydroxybenzenethiol (40 g.), methylene dibromide (27·6 g.), and sodium ethoxide (24 g.) were refluxed in ethanol (600 c.c.) for 3 hr. Cooling and addition of dilute hydrochloric acid gave an oil which crystallised. Two recrystallisations from light petroleum (b. p. 60—80°) gave needles (24 g.) of *bis*-o-*hydroxyphenylthiomethane*, m. p. 67—68° (Found : C, 59·5, 59·05; H, 4·4, 4·2. $C_{13}H_{12}O_2S_2$ requires C, 59·1; H, 4·5%). Acetylation gave *bis*-o-*acetoxyphenylthiomethane*, prisms, m. p. 52° [from light petroleum (b. p. 60—80°)] (Found : C, 58·65; H, 4·6. $C_{17}H_{16}O_4S_2$ requires C, 58·6; H, 4·6%). Condensation of bis-*o*-hydroxyphenylthiomethane with a further equivalent of methylene dibromide gave 10% of a pale yellow powder insoluble in alkali. After one recrystallisation from dilute acetic acid and four from dilute ethanol, the product, probably 4 : 5-9 : 10-*dibenzo*-1 : 3-*dioxa*-6 : 8-*dithia*cyclo*deca*-4 : 9-*diene*, had m. p. 151° (Found: C, 60·4; H, 4·4. $C_{14}H_{12}O_2S_2$ requires C, 60·9; H, 4·35%).

Similarly, *o*-hydroxybenzenethiol (20 g.) and ethylene dibromide (16·6 g.) gave 1 : 2-*bis*-o-*hydroxyphenylthioethane*, needles (16·6 g.), m. p. 108° [from light petroleum (b. p. 60—80°)] (Found : C, 60·7; H, 5·1%; *M*, 272·5. $C_{14}H_{14}O_2S_2$ requires C, 60·4; H, 5·0%; *M*, 278). Acetylation gave 1 : 2-*bis*-o-*acetoxyphenylthioethane* (94%), plates, m. p. 79° [from light petroleum (b. p. 60—80°)] (Found : C, 60·15; H, 4·75. $C_{18}H_{18}O_4S_2$ requires C, 59·7; H, 5·0%). Oxidation of this compound (34 g.) with hydrogen peroxide (65 c.c., 30%) in acetic acid (350 c.c.) at 100° for 4 hr. gave 1 : 2-*bis*-o-*acetoxyphenylsulphonylethane* (11·2 g.), plates, m. p. 204—205° (from 50% acetic acid) (Found : C, 50·3, 50·8; H, 4·3, 4·2. $C_{18}H_{18}O_8S_2$ requires C, 50·7; H, 4·2%).

o-Hydroxybenzenethiol (11·2 g.) and 1 : 10-dibromodecane (13·5 g.) gave 1 : 10-*bis*-o-*hydroxyphenylthiodecane* as an oil characterised as its *diacetate* (19 g.), plates, m. p. 65—66° after three recrystallisations from light petroleum (b. p. 60—80°) (Found : C, 65·4, 66·1; H, 6·9, 7·25. $C_{26}H_{34}O_4S_2$ requires C, 65·8; H, 7·2%).

p-Hydroxybenzenethiol (12 g.) and ethylene dibromide (9·6 g.) gave 1 : 2-*bis*-p-*hydroxyphenylthioethane* (7·2 g.), an amorphous powder, m. p. 168° (from chloroform) (Found : C, 60·05; H, 5·1. $C_{14}H_{14}O_2S_2$ requires C, 60·4; H, 5·0%).

2-Hydroxynaphthalene-1-thiol (15·2 g.) and ethylene dibromide (8·2 g.) gave 1 : 2-*bis*-(2-*hydroxy*-1-*naphthylthio*)*ethane* (12 g.), needles, m. p. 155° (from ethanol) (Found : C, 70·05; H, 5·2. $C_{22}H_{18}O_2S_2$ requires C, 69·8; H, 4·8%).

When toluene-*p*-thiol (35 g.), sodium ethoxide (20 g.), and ethylene dibromide (30·5 g.) were refluxed in acetone (500 c.c.) for 2 hr., only a 25% yield of 1 : 2-bis-*p*-tolylthioethane was obtained. The main product, isolated by further addition of water to the reaction mixture, was an oil, b. p. 132°/4 mm., 118°/2 mm., probably 2-p-*tolylthioethyl bromide* (Found : C, 48·8; H, 4·8. $C_9H_{11}BrS$ requires C, 46·8; H, 4·8%). The high carbon content was probably due to presence of 2-*p*-tolylthioethanol (Calc. for $C_9H_{12}OS$: C, 64·3; H, 7·1%). The identity of the compound was verified by condensation with a second equivalent of toluene-*p*-thiol, a 98% yield of 1 : 2-bis-*p*-tolylthioethane being obtained (m. p. and mixed m. p. 80°). Condensation of 2-*p*-tolylthioethyl bromide (8·4 g.) with *o*-hydroxybenzenethiol (4·2 g.) gave a solid melting at *ca.* 20°. Trituration with 2N-sodium hydroxide gave the sodium salt of 1-*o*-hydroxyphenylthio-2-*p*-tolylthioethane as a *tetrahydrate*, which formed plates (7·0 g.), m. p. 79—80°, from benzene [Found: C, 48·75; H, 6·4; H_2O (Karl Fischer), 15·15. $C_{15}H_{15}OS_2Na,4H_2O$ requires C, 48·65; H, 6·2; H_2O, 19·5%].

Bis-*p*-tolylthiomethane (18 g.) was obtained from toluene-*p*-thiol (20 g.) and methylene dibromide (15 g.) as needles, m. p. 32° (from ethanol) (Found: C, 69·1; H, 5·9. Calc. for $C_{15}H_{16}S_2$: C, 69·2; H, 6·15%). Fromm, Forster, and von Scherschewitzki (*Annalen*, 1912, **394**, 348) described this compound as an oil.

Benz-1 : 4-*oxathien.*—An attempt was made to prepare this compound by way of 2-*o*-hydroxyphenylthioethyl bromide. However, condensation of *o*-hydroxybenzenethiol with excess of ethylene dibromide gave none of the required intermediate, only 1 : 2-bis-*o*-hydroxyphenylthioethane being isolated. The reaction was therefore carried out in one stage using equivalent quantities of the reactants.

o-Hydroxybenzenethiol (100 g., 1 mol.), ethylene dibromide (149 g., 1 mol.), and sodium ethoxide (120 g., slightly >2 mol.) were refluxed in ethanol (2·5 l.) for 24 hr. Most of the solvent was removed by distillation, and the residue added to water, made alkaline, and extracted with ether. The extract, dried and fractionated, yielded a little ethylene dibromide followed by *benz*-1 : 4-*oxathien* (24·2 g.), b. p. 90°/2 mm. (Found: C, 62·75, 62·7; H, 5·5, 5·2. C_8H_8OS requires C, 63·2; H, 5·3%). Acidifying the alkaline solution gave 1 : 2-bis-*o*-hydroxyphenylthioethane (25·5 g.).

Benz-1 : 4-oxathien (1 g.) and hydrogen peroxide (0·75 c.c.; 30%) were kept in acetic acid (25 c.c.) at room temperature for 5 days, then poured into excess of dilute aqueous alkali. The oily product crystallised after ether-extraction, and recrystallisation from light petroleum (b. p. 60—80°) gave *benz*-1 : 4-*oxathien* 4-*oxide* (0·75 g.) as plates, m. p. 85° (Found: C, 57·2; H, 4·5. $C_8H_8O_2S$ requires C, 57·15; H, 4·8%)

Benz-1 : 4-oxathien (1 g.) was suspended in a little water containing magnesium sulphate (2 g.), and 0·1N-potassium permanganate (450 c.c.) was slowly added at 70°. Decolorisation with sulphur dioxide and chloroform-extraction gave *benz*-1 : 4-*oxathien* 4-*dioxide* as needles (0·6 g.), m. p. 82° [from light petroleum (b. p. 60—80°)] (Found: C, 52·1; H, 4·5. $C_8H_8O_3S$ requires C, 52·2; H, 4·35%).

o-*Hydroxybenzenethiol and Chloroacetic Acid.*—To a solution of potassium hydroxide (30 g.) in water (300 c.c.) was added *o*-hydroxybenzenethiol (24 g.), followed by chloroacetic acid (24 g.). The solution was refluxed for 30 min., acidified, and evaporated to dryness. The product was extracted with ether, and the extract dried and evaporated. *o*-Hydroxyphenylthioacetic acid was obtained as an oil (35 g.) [Found: equiv. (by titration), 182, 178, 177, 176. Calc. for $C_8H_8O_3S$: equiv., 184]. On attempting to distil this compound at 3 mm., water was evolved and the resulting distillate (b. p. 128°) was insoluble in water or dilute alkali. Ring-closure had evidently occurred. The best yield was obtained by the following method:

Crude *o*-hydroxyphenylthioacetic acid (12 g.), obtained as above, was heated at 100°/3 mm. for 4 hr. Water and a solid distilled. The solid was identified by a mixed m. p. determination as chloroacetic acid (0·7 g.), doubtless present as an impurity in the starting material. 2-*Keto-benz*-1 : 4-*oxathien* (8·85 g.) was later collected at 128°/3 mm. (Found: C, 57·9; H, 3·7%; *M*, 162, 165. $C_8H_6O_2S$ requires C, 57·8; H, 3·6%; *M*, 166).

Crude *o*-hydroxyphenylthioacetic acid (10 g.), potassium hydroxide (11 g.), and chloroacetic acid (6 g.), refluxed in water (100 c.c.) for 3 hr. and then cooled and acidified, gave a pale brown solid (4·55 g.; m. p. 176—179°). Evaporation of the mother-liquor to dryness, ether-extraction, removal of the ether, and trituration of the residue with benzene gave only a trace of less pure product. Two recrystallisations from nitrobenzene gave o-*carboxymethylthiophenoxyacetic acid* (4·2 g.), m. p. 183° [Found: C, 49·3; H, 4·3%; equiv. (by titration), 124, 124. $C_{10}H_{10}O_5S$ requires C, 49·6; H, 4·1%; equiv., 121]. The compound was also obtained directly from *o*-hydroxybenzenethiol and 2 mols. of chloroacetic acid.

Esters of Hydroxyarenethiols.—Acetylation of *o*-hydroxybenzenethiol (6 g.) gave o-*acetylthiophenyl acetate* (7·85 g.), b. p. 130°/2 mm., 145°/5 mm., 154°/7 mm. (Found: C, 57·1; H, 4·9. $C_{10}H_{10}O_3S$ requires C, 57·15; H, 4·8%).

Similarly, 2-hydroxynaphthalene-1-thiol (10 g.) gave 1-*acetylthio*-2-*naphthyl acetate*, b. p. 196—198°/2 mm. The viscous oil solidified very slowly at 0°, and then recrystallised from light petroleum (b. p. 60—80°) as prisms (4·8 g.), m. p. 57° (Found: C, 64·5; H, 4·6. $C_{14}H_{12}O_3S$ requires C, 64·6; H, 4·6%).

Schotten–Baumann reactions gave o-*benzoylthiophenyl benzoate* (82%), needles, m. p. 68° (from ethanol) (Found: C, 71·6; H, 4·2. $C_{20}H_{14}O_3S$ requires C, 71·9; H, 4·2%), and o-(2 : 4-

dichlorobenzoylthio)phenyl 2 : 4-*dichlorobenzoate*, prisms, m. p. 101—104° (from ethanol) (Found : C, 50·3, 51·3; H, 2·05, 2·0. $C_{20}H_{10}O_3SCl_4$ requires C, 50·85; H, 2·1%).

Refluxing *o*-hydroxybenzenethiol (1 mol.) and benzoyl chloride (1 mol.) in benzene until evolution of hydrogen chloride had almost ceased (40 hr.) gave a small yield of o-(*benzoylthio*)-*phenol*. After the benzene solution had been washed with N-sodium carbonate, the product was isolated by extraction with 2N-sodium hydroxide. Acidification gave a solid which recrystallised from light petroleum (b. p. 60—80°) as needles, m. p. 122°. The compound gave a greenish-brown colour with ferric chloride, but gave no colour change with alkaline nitroprusside solution, showing that it still contained the hydroxy-group, but no longer contained the thiol group (Found : C, 67·4; H, 4·7. $C_{13}H_{10}O_2S$ requires C, 67·8; H, 4·35%).

o-Hydroxybenzenethiol (2·5 g.) and phthaloyl chloride (4·9 g.) gave 5 : 8-*diketo*-2 : 3-6 : 7-*dibenz*-1-*oxa*-4-*thia*cyclo*octa*-2 : 6-*diene* (VIII) (2·6 g.), a colourless powder of m. p. *ca.* 72° (decomp.) [from benzene–light petroleum (b. p. 60—80°)] (Found: C, 65·65; H, 3·45. $C_{14}H_8O_3S$ requires C, 65·6; H, 3·1%).

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