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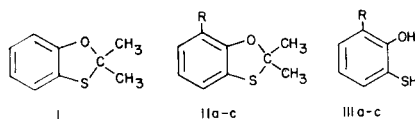
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A convenient synthesis of 3-substituted-2-hydroxybenzenethiols utilizing 7-substituted-1,3-benzoxathioles is described. The structures of the prepared compounds were determined by spectroscopic methods.

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It is well known that 3-substituted-2-hydroxybenzenethiols can be synthesized by the Leuckart reaction of the diazonium salts of 2-hydroxyanilines, obtained by reduction of the respective nitroderivatives (1). Although the latter compounds are easily prepared by nitration of 2-substituted phenols, they are never obtained with satisfactory yields since both *ortho* and *para* nitro derivatives result from this reaction, the latter isomer being the major product.

On the basis of our recent studies on metallation reactions (2), we have devised a simple method for preparing 3-substituted-2-hydroxybenzenethiols starting from 1,3-benzoxathiole derivatives. The lithiation of 2,2-dimethyl-1,3-benzoxathiole (I), followed by treatment of the reaction mixture with solid carbon dioxide, yields the acid IIa. On the other hand, the treatment of the lithium derivatives of I with 3-pentanone or benzaldehyde affords the alcohols IIb and IIc, respectively. The 3-substituted-2-hydroxybenzenethiols (IIIa-c) are then easily obtained in very good yields by refluxing 1,3-benzoxathioles (IIa-c) with sodium and pyridine.



- a, R = -CO<sub>2</sub>H  
b, R = Et<sub>2</sub>CHOH  
c, R = C<sub>6</sub>H<sub>5</sub>-CHOH

## EXPERIMENTAL

The literature procedure was followed in the preparation of 2,2-dimethyl-1,3-benzoxathiole (I) (3). Melting points were determined on a Tottoli apparatus and are uncorrected. The ir spectra were obtained on a Perkin-Elmer model 157C spectrophotometer using either potassium bromide mulls or neat liquids between sodium chloride plates. The nmr spectra were recorded in deuteriochloroform on a Varian FT 80A spectrometer using tetramethylsilane as internal standard. Microanalyses for CH were carried out on a Perkin-Elmer model 240 Elemental Analyzer; analyses for S were performed by the literature procedure (4).

General Method for the Preparation of 7-Substituted-1,3-benzoxathioles (IIa-c).

A solution of I (36 mmoles) in dry diethyl ether (60 ml.) was treated with *n*-butyllithium in hexane (25 ml., 39 mmoles). When the addition was complete, the mixture was stirred under reflux for 1 hour. The synthesis of IIa was carried out as previously described (2).

In the synthesis of IIb and IIc, the metallation mixture was treated dropwise with a solution of the appropriate reactant (3-pentanone, or benzaldehyde) (36 mmoles) in dry diethyl ether (50 ml.) and the resulting mixture was stirred under reflux for 2 hours. The mixture was then poured into water, acidified with 10% aqueous hydrochloric acid and extracted with diethyl ether. The organic layers were combined, washed with water and dried over anhydrous sodium sulphate. After solvent evaporation, the residue was distilled under reduced pressure.

Melting or boiling points, yields, analytical data and physical properties of the products are summarized in Tables I and II.

General Procedure for the Preparation of 3-Substituted-2-hydroxybenzenethiols (IIIa-c).

A mixture of IIa-c (8 mmoles), dry pyridine (25 ml.) and sodium (100 mmoles) was refluxed with stirring for 2 hours. The mixture was then poured into water, washed with diethyl ether, acidified with 10% aqueous hydrochloric acid and extracted with diethyl ether. The extracts were washed with water and dried over anhydrous sodium sulphate. After

Table I

Compound No.	M.p. (°C) or B.p. (°C/mm)	Yield (%)	Analytical Data of Compounds IIa-c and IIIa-c			Found			
			Empirical Formula	C	H	S	C	H	S
IIa	138-140 (a)	61	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub> S						
IIb	147-148/5 (b)	70	C <sub>14</sub> H <sub>20</sub> O <sub>2</sub> S	66.63	7.99	12.70	66.51	7.93	12.58
IIc	175-177/2 (c)	55	C <sub>16</sub> H <sub>16</sub> O <sub>2</sub> S	70.56	5.92	11.77	70.48	5.85	11.61
IIIa	165-166	85	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> S	54.53	3.92	20.79	54.39	3.95	20.66
IIIb	Syrup (d)	88	C <sub>11</sub> H <sub>16</sub> O <sub>2</sub> S	62.23	7.60	15.10	62.11	7.52	14.97
IIIc	Syrup (e)	77	C <sub>13</sub> H <sub>12</sub> O <sub>2</sub> S	67.21	5.21	13.80	67.15	5.17	13.68

(a) Lit. (2) m.p. 138-140°. (b)  $n_D^{18}$  1.5539. (c)  $n_D^{18}$  1.5975. (d)  $n_D^{18}$  1.5580. (e)  $n_D^{18}$  1.6140.

Table II  
Spectrophotometric Data of Compounds IIa-c and IIIa-c

Compound No.	cm <sup>-1</sup>	Ir $\nu$	$\delta$	Nmr Assignment
IIa (a)				
IIb	3450	OH	0.77 1.81 1.83 2.67 7.00	(t, 6, -CH <sub>2</sub> -CH <sub>3</sub> ) (q, 4, -CH <sub>2</sub> -CH <sub>3</sub> ) (s, 6, >C(CH <sub>3</sub> ) <sub>2</sub> ) (s, 1, -OH) (m, 3, Ar-H)
IIc	3350	OH	1.68 2.59 5.85 7.02	(s, 6, >C(CH <sub>3</sub> ) <sub>2</sub> ) (d, 1, -OH) (d, 1, >CHOH) (m, 8, Ar-H)
IIIa	3100 2520 1650	OH SH C=O	3.90 7.10 7.20 10.80	(s, 1, -SH) (s, 1, Ar-OH) (m, 3, Ar-H) (s, 1, -CO <sub>2</sub> H)
IIIb	3300 2560	OH SH	0.86 1.83 2.28 3.80 6.89 9.85	(t, 6, -CH <sub>2</sub> -CH <sub>3</sub> ) (q, 4, -CH <sub>2</sub> -CH <sub>3</sub> ) (s, 1, >C-OH) (s, 1, -SH) (m, 3, Ar-H) (s, 1, Ar-OH)
IIIc	3350 2530	OH SH	1.81 3.97 6.30 7.23 7.25	(d, 1, >CH-OH) (s, 1, -SH) (d, 1, >CH-OH) (s, 1, Ar-OH) (m, 8, Ar-H)

(a) Reference 2.

solvent evaporation *in vacuo*, the crude product was chromatographed on a silica gel column, using diethyl ether-petroleum ether (3:1) as eluent.

Melting or boiling points, yields, analytical data and physical properties of the products are listed in Tables I and II.

#### Acknowledgment.

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