

2. 2-Thio-orotic acid is desulfurized by the action of chromic acid, or with hydrogen peroxide in alkaline solution to give orotic acid quantitatively. The acid is not desulfurized by the action of chloroacetic acid.

3. 2-Thio-4-hydroxymethyluracil is desulfurized and converted quantitatively into 4-hydroxymethyluracil by digestion with chloroacetic acid in aqueous solution.

4. 2-Thio-orotic acid and 2-thio-4-hydroxymethyluracil interact with alkyl halides in alkaline solution to give alkyl derivatives with substitution on the sulfur atom.

5. The investigation of these compounds is being continued.

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[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

## SUBSTITUTED PHENYLDIHALOARSINES

BY F. F. BLICKE, L. D. POWERS AND G. L. WEBSTER

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A number of substituted phenyldihaloarsines, not described hitherto, have been prepared in the hope that they might be used for the preparation of certain types of arsenicals under investigation in this Laboratory. Since many of them have been found to be unsuitable for our purpose, a brief description of them is published at this time.

Considerable difficulty was experienced in the preparation of many of the dihaloarsines in pure form. The following was found to be a very satisfactory general procedure: preparation of the arylarsonic acid, conversion of the acid into the corresponding aryldichloroarsine, purification of the latter by recrystallization from acetic acid or absolute ether, hydrolysis of the chloride into the arylarsine oxide and treatment of the latter at ordinary temperature with the desired halogen acid.

Arylarsine oxides are sometimes contaminated by small quantities of the arylarsonic acid and as a result of this contamination the preparation of the aryldihaloarsine is often very troublesome. Since the pure oxides usually possess rather indefinite melting points, the detection of the arsonic acid by means of a melting point determination cannot be relied upon. However, since the arylarsonic acid and concentrated hydriodic acid yield the corresponding aryldi-iodoarsine and free iodine, it is merely necessary to add a cubic centimeter of hydriodic acid to a fraction of a gram of the solid oxide in order to determine the presence or absence of the arsonic acid. If the oxide is pure, the mixture assumes the yellow color of the aryldi-iodoarsine; if even a slight amount of arsonic acid is present, the latter is detected by a deep red color due to the free iodine.

## Experimental Part

 TABLE I  
 SUBSTITUTED PHENYLDICHLOROARSINES

	M. p., °C.	Formulas	Chlorine analyses <sup>a</sup>	
			Calcd.	Found
3-Nitro	53-54 <sup>b</sup>	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> NA <sub>2</sub> Cl <sub>2</sub>	26.47	26.36
4-Benzoyl	118-120	C <sub>13</sub> H <sub>9</sub> OAsCl <sub>2</sub>	21.69	21.65
4-(4'-Phenoxy)-benzoyl	83-85	C <sub>19</sub> H <sub>13</sub> O <sub>2</sub> AsCl <sub>2</sub>	16.92	16.61

<sup>a</sup> All halogen analyses were made by the use of the Thompson-Oakdale method, *THIS JOURNAL*, **52**, 1195 (1930). Oxidation was effected with chromic acid.

<sup>b</sup> Michaelis and Loesner [*Ber.*, **27**, 269 (1894)] reported the melting point to be 46-47°.

 TABLE II  
 SUBSTITUTED PHENYLDIBROMOARSINES

	M. p., °C.	Formulas	Bromine analyses	
			Calcd.	Found
2-Nitro	52-54	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> NA <sub>2</sub> Br <sub>2</sub>	44.79	44.91
3-Nitro	63-64	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> NA <sub>2</sub> Br <sub>2</sub>	44.79	44.69
2-Iodo	71-72	C <sub>6</sub> H <sub>4</sub> AsBr <sub>2</sub> I <sup>a</sup>	28.99	28.69
2-Methoxy	84-85	C <sub>7</sub> H <sub>7</sub> OAsBr <sub>2</sub>	46.75	46.54
4-Methoxy	40-41	C <sub>7</sub> H <sub>7</sub> OAsBr <sub>2</sub>	46.75	46.84
4-Carboxy	161-162	C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> AsBr <sub>2</sub>	44.91	44.81
4-Benzoyl	116-118	C <sub>13</sub> H <sub>9</sub> OAsBr <sub>2</sub>	36.91	36.80
4-(4'-Phenoxy)-benzoyl	105-106	C <sub>19</sub> H <sub>13</sub> O <sub>2</sub> AsBr <sub>2</sub>	31.47	31.07

<sup>a</sup> Calcd. for C<sub>6</sub>H<sub>4</sub>AsBr<sub>2</sub>I: As, 17.12. Found: As, 17.16.

In general acetic acid was found to be the most satisfactory solvent from which to recrystallize the dihaloarsines; absolute ether was used in a few instances.

 TABLE III  
 SUBSTITUTED PHENYLDI-iodoARSINES

	M. p., °C.	Formulas	Iodine analyses	
			Calcd.	Found
2-Nitro	83-84	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> NA <sub>2</sub> I <sub>2</sub>	56.30	56.08
3-Nitro	64-65	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> NA <sub>2</sub> I <sub>2</sub>	56.30	56.49
2-Iodo	97-98	C <sub>6</sub> H <sub>4</sub> AsI <sub>3</sub>	71.47	71.63
2-Methoxy	74-76	C <sub>7</sub> H <sub>7</sub> OAsI <sub>2</sub>	58.24	58.43
4-Methoxy	38-40	C <sub>7</sub> H <sub>7</sub> OAsI <sub>2</sub>	58.24	58.31
2-Benzoyl	115-117	C <sub>13</sub> H <sub>9</sub> OAsI <sub>2</sub>	49.78	49.59
4-Benzoyl	92-93	C <sub>13</sub> H <sub>9</sub> OAsI <sub>2</sub>	49.78	49.81
4-(4'-Phenoxy)-benzoyl	127-128	C <sub>19</sub> H <sub>13</sub> O <sub>2</sub> AsI <sub>2</sub>	42.17	41.94

The melting point of 4-carboxyphenyldi-iodoarsine was reported to be 153° by La Coste [*Ann.*, **208**, 13 (1881)] and 172° by Berthelm [*Ber.*, **41**, 1857 (1908)]; we found the melting point to be 168-169°.

Lewis and Cheetham [*THIS JOURNAL*, **45**, 514 (1923)] stated that 4-(4'-methoxy)-benzoylphenyldi-iodoarsine melts at 105°, while we observed the melting point to be 110-111°.

### Summary

The preparation of a number of new substituted phenyldihaloarsines has been described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WASHINGTON]

## SALTS OF PHENOLPHTHALEIN

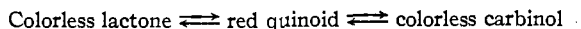
BY WILLIAM M. DEHN

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The problem of constitution of the salts<sup>1</sup> of phenolphthalein has engaged the interest of many chemists since 1871, the date of discovery by Baeyer<sup>2</sup> of free phenolphthalein, which later he showed<sup>3</sup> possesses the lactone structure. The exact constitution of its salts, the reddening and fading effects produced by a variety of influences, and the correlations of chemical and color changes in solutions have been the chief problems giving rise to different opinions.

It is usually suggested that the color changes of phenolphthalein are in accordance with equilibrium of the following forms<sup>4</sup>



However, since the solid colorless mono-, di- and tri-basic salts all yield by dehydration corresponding red salts, it seems probable that more than one colored quinoid form and colorless carbinol forms are involved in equilibria both of the solid salts and in their solutions. Furthermore, no structures depict water of crystallization, which is always present in the colorless salts and in some of the red salts, and it seems certain that equilibria of such water molecules are involved in solutions, at least in saturated solutions, as well as in the dry salts. Then, too, it must be remembered, whereas isomerization, neutralization, hydrolysis, hydration and de-

<sup>1</sup> Only a few salts have hitherto been prepared, namely, salts of sodium, potassium, calcium and silver, and these possess different colors. The dry hydrated salts of sodium and potassium are colorless and their anhydrous salts are red. The silver salt is red. Red and green salts of calcium were described by Meyer and Posner, *Ber.* **44**, 1954 (1911). See experimental part of this paper.

<sup>2</sup> Baeyer, *Ber.*, **4**, 659 (1871).

<sup>3</sup> Baeyer, *Ann.*, **202**, 36 (1880).

<sup>4</sup> Apparently Berntsen was the first to use the quinoid formula in connection with phenolphthalein, *Chem.-Ztg.*, **16**, 1956 (1892). Also see Dehnst, *ibid.*, **17**, 654 (1893); Friedländer, *Ber.*, **26**, 172 (1893); Armstrong, *Proc. Roy. Soc. (London)*, **55** (1893). For opinions of the non-existence of the quinoid form for phenolphthalein, see Hjelt, *Chem.-Ztg.*, **18**, 3 (1894); Herzig and Meyer, *Ber.*, **29**, 138 (1896); Bistrzynski and Nencki, *ibid.*, **29**, 131 (1896); Schestakov and Nocken, *ibid.*, **47**, 331 (1914); Oddo, *ibid.*, **47**, 967 (1914); Consonno and Apostolo, *Gazz. chim. ital.*, **51**, [1] 50 (1921).