

CCLXXXVIII.—*Dyes Derived from "Saccharin."* *The Sulphamphthaleins.*

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A NUMBER of sulphonephthaleins have already been prepared by the aid of *o*-sulphobenzoic acid (Remsen, *J. Amer. Chem. Soc.*, 1885, **7**, 180; compare also *ibid.*, 1887, **9**, 372; Blackshear, *ibid.*, 1892, **14**, 455; Remsen and MacKee, *ibid.*, 1896, **18**, 794; Lubs and Clark, *J. Washington Acad. Sci.*, 1915, **5**, 609).

The difficulty of getting pure *o*-sulphobenzoic acid in good yield led the author to investigate the action of "saccharin" on amines and phenols. In this way, condensation products have been obtained which are characterised by their colour and fluorescence and closely resemble the corresponding phthaleins in constitution and behaviour. They differ from the corresponding sulphonephthaleins in having the bivalent imido-group in place of the lactone oxygen atom. Accordingly, they have been named *sulphamphthaleins*.

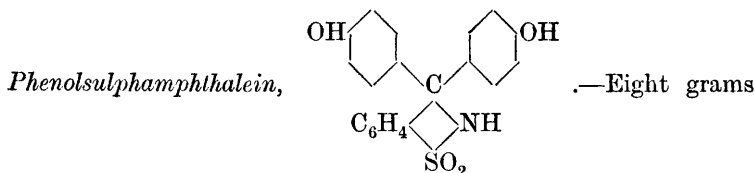
The trimethyl derivative of phenolsulphamphthalein is obtained by the action of methyl sulphate on the trisodium salt, but only the diacetyl and the dibenzoyl derivatives are obtained by similar treatment with acetyl chloride and benzoyl chloride, respectively. The diacetyl derivative is more conveniently obtained by the action of acetic anhydride and pyridine on phenolsulphamphthalein itself.

The following amino- and hydroxy-compounds have been condensed with "saccharin": phenol, resorcinol, orcinol, phloroglucinol, hydroxyquinol, catechol, 1 : 2 : 4 : 5-tetrahydroxybenzene, *m*-phenylenediamine, *m*-aminophenol, *m*-dimethylaminophenol, and 4 : 6-diaminoresorcinol. The colour and dyeing properties of the products closely resemble those of the corresponding phthaleins, but the fluorescence is somewhat stronger. They all decompose on heating.

The "saccharin" employed in the above-mentioned condensations was obtained by extracting the commercial material with sodium hydrogen carbonate, treating the solution with hydro-

chloric acid, and fractionally crystallising the precipitate from ether, the portion melting at 218–220° being utilised.

EXPERIMENTAL.



of "saccharin," 15 grams of phenol, and 5 c.c. of concentrated sulphuric acid were heated together at 100–110° for ten hours. The excess of phenol was distilled off in steam, and the brownish-red residue purified by dissolving it in ammonia and treating the filtered solution with dilute hydrochloric acid. The precipitate crystallised from hot water in yellow prisms, which became red on rubbing. The yield was 15 per cent. of the theoretical. With zinc chloride at 160° as the condensing agent, the yield is only 6 per cent.

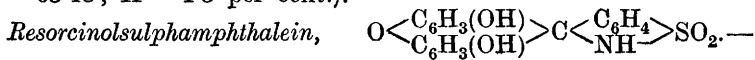
Like phenolphthalein, phenolsulphamphthalein dissolves in alkali with a pink colour. It dissolves in water, acetic acid, or alcohol with a yellow colour, but is insoluble in ether. It has been obtained in two chromoisomeric forms, yellow and red, the former being the more unstable (Found : S = 9.1; N = 4.1. $C_{19}H_{15}O_4NS$ requires S = 9.1; N = 3.9 per cent.).

The *trisodium* salt, prepared by neutralising an aqueous solution of the sulphamphthalein with N/2-sodium hydroxide (3 equivalents were required) and evaporating the solution to dryness, is a dark red, crystalline substance, which dissolves in water with a brilliant pink colour and is extremely hygroscopic.

The *trimethyl* derivative was prepared by the action of methyl sulphate on the trisodium salt. It crystallises from dilute acetic acid in colourless needles melting at 142° (Found : C = 67.5; H = 5.6. $C_{22}H_{21}O_4NS$ requires C = 67.8; H = 5.3 per cent.).

A *dibenzoyl* derivative was prepared by the action of benzoyl chloride on the sodium salt. It crystallises from hot water in colourless, silky needles melting at 127° (Found : C = 70.5; H = 4.2. $C_{33}H_{24}O_6NS$ requires C = 70.7; H = 4.3 per cent.).

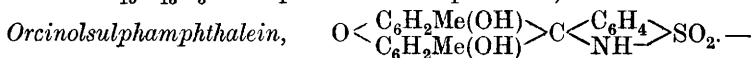
The *diacetyl* derivative, prepared by means of acetic anhydride and pyridine, crystallises from dilute alcohol in colourless needles, m. p. 112° (Found : C = 62.8; H = 4.4. $C_{23}H_{19}O_6NS$ requires C = 63.15; H = 4.3 per cent.).



Eight grams of "saccharin," 11 grams of resorcinol, and 10 grams of

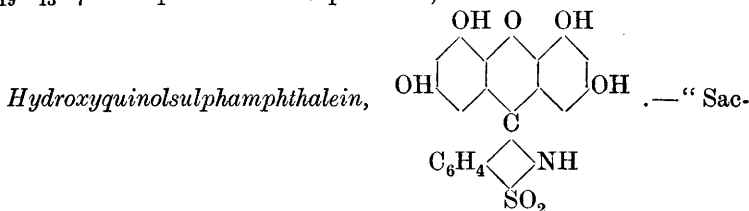
fused zinc chloride were heated at 180—190° for two hours, when the melt became almost solid. The cooled product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, washed with water, and extracted with ether to remove unchanged "saccharin." The product was converted, by the action of lead acetate on the sodium salt, into the lead lake, which was dried, suspended in absolute alcohol, and decomposed by hydrogen sulphide. The alcoholic solution was filtered, concentrated to a small volume, and the dye precipitated with ether, being obtained in microscopic, brownish-yellow needles.

Resorcinolsulphamphthalein is very soluble in alcohol or acetic acid, moderately soluble in water, and insoluble in ether or light petroleum. It dissolves in alkali with an orange colour, and the solution on dilution shows a very intense yellowish-green fluorescence. The sodium salt dyes light yellow shades on wool (Found: $S = 8.4$. $C_{19}H_{13}O_5NS$ requires $S = 8.7$ per cent.).



Eight grams of "saccharin," 13 grams of orcinol, and 11 grams of fused zinc chloride were heated at 180° for about three hours, and the product was isolated as described above. It crystallises from dilute alcohol in brownish-yellow needles and dissolves in alkali with a blood-red colour, the solution, on dilution, showing a brilliant green fluorescence. The sodium salt dyes pink shades on wool (Found: $S = 7.9$. $C_{21}H_{17}O_5NS$ requires $S = 8.1$ per cent.).

Phloroglucinsulphamphthalein.—Prepared from 3.6 grams of "saccharin," 5 grams of phloroglucinol, and 4 grams of fused zinc chloride at 180—190° in about twenty minutes, and isolated in the manner already described, this compound crystallised from hot water in long, brownish-yellow needles. It dissolves in alkali with an orange-red colour, but the solution is not fluorescent. The sodium salt dyes fine orange shades on wool (Found: $S = 8.3$. $C_{19}H_{13}O_7NS$ requires $S = 8.0$ per cent.).



charin" (1.8 grams), hydroxyquinol (2.5 grams), and fused zinc chloride (2 grams) were heated at 160—170° for two hours while a slow stream of dry hydrogen was passed over the molten mass. Purification by means of sodium hydroxide solution having been

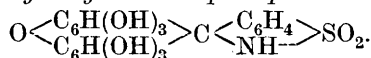
found ineffective, the product was acetylated. The *acetyl* derivative crystallised from dilute alcohol in colourless prisms melting above 300°. The product of its hydrolysis by alkali crystallises from a mixture of alcohol and ether in light reddish-brown, silky needles.

Hydroxyquinolsulphamphthalein is very soluble in alcohol or acetic acid, moderately soluble in hot water, and sparingly soluble in ether or cold water. It dissolves in alkali with a pink colour, the solution showing a feeble yellow fluorescence. The sodium salt dyes fine pink shades on wool (Found : S = 7·8. $C_{19}H_{13}O_7NS$ requires S = 8·0 per cent.).

Catecholsulphamphthalein.—Eight grams of "saccharin," 11 grams of catechol, and 10 grams of fused zinc chloride were heated at 180–190° for three hours. The cold product was powdered, washed with concentrated hydrochloric acid, and crystallised from ether, minute brown needles being obtained.

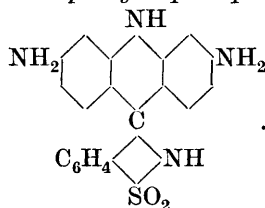
Catecholsulphamphthalein is very soluble in water, alcohol, or acetic acid, and sparingly soluble in ether. It dissolves in alkalis with a green colour (Found : S = 8·6. $C_{19}H_{13}O_5NS$ requires S = 8·7 per cent.).

1 : 2 : 4 : 5-Tetrahydroxybenzenesulphamphthalein,



—"Saccharin" (0·8 gram) and 1 : 2 : 4 : 5-tetrahydroxybenzene (1·4 grams) were heated at 160° with 0·5 gram of fused zinc chloride for about two hours. The product was finely powdered, digested with concentrated hydrochloric acid for half an hour, filtered, dried, and acetylated by the usual method. The *hexa-acetyl* derivative crystallised from dilute acetic acid in white, silky needles which did not melt at 290° (Found : C = 54·1; H = 3·6. $C_{31}H_{25}O_{15}NS$ requires C = 54·5; H = 3·7 per cent.). On hydrolysis with alkali, the pure dyestuff was obtained, which crystallised from hot water in dark brown needles with a green, metallic lustre. It dissolves in alkali with a pink colour but without fluorescence (Found : S = 7·0. $C_{19}H_{13}O_9NS$ requires S = 7·4 per cent.).

4 : 4'-Diamino-2 : 2'-iminophenylsulphamphthalein,

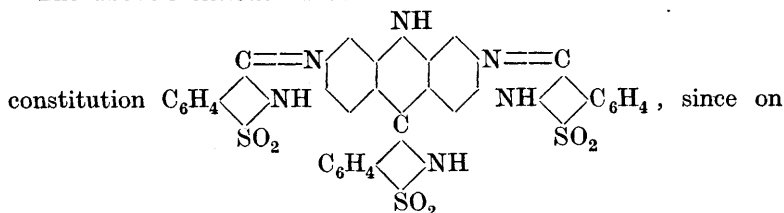


—"Saccharin" (1·8 grams) and *m*-phenylenediamine hydrochloride

(3.6 grams) were heated at 230° for about fifteen minutes. The melt was extracted with ether to remove unchanged "saccharin" and dissolved in hot alcohol. The alcoholic solution, on cooling, deposited a quantity of brown needles, which were removed. The mother-liquor was concentrated to small bulk and cautiously diluted with water, when the sulphamphthalein was deposited in bright yellow, prismatic needles (Found: S = 8.7; N = 15.1. $C_{19}H_{16}O_2N_4S$ requires S = 8.7; N = 15.4 per cent.).

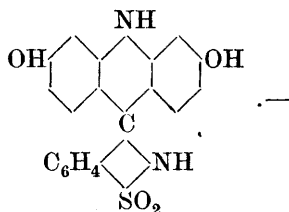
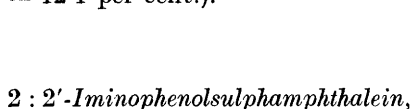
The substance is very soluble in alcohol or acetic acid, sparingly soluble in water, and insoluble in ether. Its solution shows an intense yellow-green fluorescence, which is very similar to that of fluorescein.

The above-mentioned brown substance was found to have the



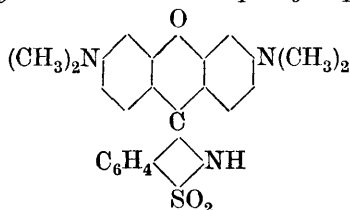
boiling with alkali it decomposed yielding "saccharin" and the diaminoiminophenylsulphamphthalein. It was also formed when these two substances were heated with zinc chloride at 160° .

It is slightly soluble in alcohol or acetic acid, and insoluble in water or ether. The solution shows a brilliant green fluorescence (Found: S = 13.4; N = 12.3. $C_{33}H_{22}O_6N_6S_3$ requires S = 13.8; N = 12.1 per cent.).



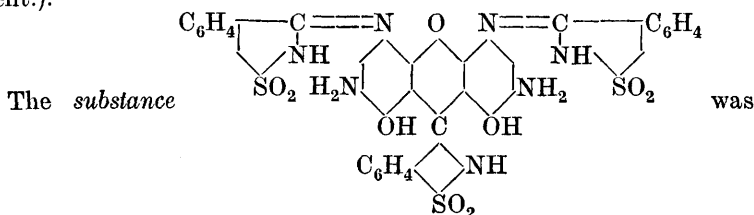
"Saccharin" (3.6 grams), *m*-aminophenol (4.5 grams), and fused zinc chloride (4 grams) were heated at 180 — 190° for two hours. The melt was dissolved in dilute caustic soda and the filtered solution precipitated with hydrochloric acid. The compound, which could not be crystallised, was purified by means of the lead lake, as described in the case of the resorcinol compound. It is a dark brown substance which dissolves in alkali with a brown colour, but without fluorescence. Its solutions in alcohol and acetic acid show a fine moss-green fluorescence (Found: N = 7.2. $C_{19}H_{14}O_4N_2S$ requires N = 7.6 per cent.).

4 : 4'-Tetramethyldiamino-2 : 2'-oxidophenylsulphamphthalein,



—"Saccharin" (1·8 grams), *m*-dimethylaminophenol (2·8 grams), and fused zinc chloride (1·5 grams) were heated at 180—190° for about one hour, when the melt assumed a deep pink colour and solidified completely. The product was powdered and boiled with alcohol and a little bone black; the filtered solution slowly deposited the condensation product in small, pink needles with a golden lustre.

The substance is very soluble in alcohol, acetic acid, or ether, slightly in water, and dissolves in dilute mineral acids with a pink colour and a strong yellow fluorescence. It dyes fine pink shades on wool (Found : S = 7·5. $C_{23}H_{23}O_3N_3S$ requires S = 7·6 per cent.).



prepared by heating 1·8 grams of "saccharin," 4·5 grams of 4 : 6-diaminoresorcinol hydrochloride, and 3 grams of fused zinc chloride at 160° for three hours while a slow stream of dry hydrogen was passed over the molten mass. The cold product was finely powdered, digested with concentrated hydrochloric acid for half an hour, and purified by means of the lead lake. It could not be crystallised. It is a dark brown substance which dissolves in alkali with a splendid blue colour, but without fluorescence (Found : S = 12·8. $C_{33}H_{23}O_9N_7S_3$ requires S = 12·7 per cent.).

Further work in this direction is in progress.

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