CCCXXVII.—*Resorcinolphenylsuccinein.*

By ARTHUR LAPWORTH and JOHN ALEXANDER MCRAE.

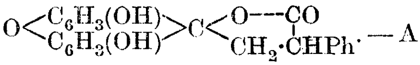
THE improvements in the modes of preparing succinic acids containing aromatic substituents, described by the authors in another communication (this vol., p. 1699), make it possible to obtain many of these compounds cheaply and if necessary in large quantity. It therefore seemed worth while to examine their application for the preparation of colouring matters, where there is a very wide field to be explored. The time which it was necessary to devote to the study of other aspects of the syntheses of the succinic acids deflected attention from what was the original line of work; the preparation and characterisation of resorcinolphenylsuccinein and its tetrabromo-derivative were completed, however, and as the authors are no longer able to work in collaboration, the results are here recorded.

The methods described in the literature for the preparation of resorcinolsuccinein by the condensation of succinic anhydride and resorcinol (Nencki and Sieber, *J. pr. Chem.*, 1881, [ii], **23**, 152), and of fluorescein, do not seem at first sight to offer any great difficulty; but a closer examination shows that these substances are formed along with by-products from which sometimes it is not easy to obtain the pure compound. Considerable doubt seems to be associated with the characterisation of fluorescein, for H. v. Liebig (*J. pr. Chem.*, 1912, [ii], **85**, 97, 241) claims to have isolated five different modifications of this substance.

It was found a relatively simple matter to effect the condensation of phenylsuccinic acid with resorcinol, but it was with considerable difficulty that a pure crystalline specimen of the product was isolated. Phenylsuccinein appears to give two bromo-derivatives, one colourless and crystalline, the other red and amorphous.

The colourless form dissolves in dilute alkali to give an intensely red solution which yields on acidification an amorphous, red substance. The relation of these substances was not investigated in detail, but it may be noted that Pratt, Hutchinson, and Harvey (*J. Amer. Chem. Soc.*, 1919, **41**, 1293) obtained tetrabromoeosin by the bromination of tetrabromofluorescein as a faintly pink substance giving intensely coloured solutions in alkali from which acids precipitated a voluminous hydrate.

Resorcinolphenylsuccinein,



$\mathrm{O}<\begin{matrix}\mathrm{C_6H_3(OH)}\\ \mathrm{C_6H_3(OH)}\end{matrix}>\mathrm{C}<\begin{matrix}\mathrm{O}\text{---}\mathrm{CO}\\ \mathrm{CH_2\cdot CHPh}\end{matrix}$ —A mixture of phenylsuccinic acid (146 grams) and resorcinol (170 grams) was heated in an oil-bath at 135° and 19·5 grams of freshly fused and finely powdered zinc chloride, prepared according to

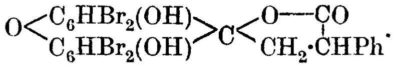
Copisarow (T., 1920, **117**, 209), were stirred in. The mixture was heated for seven hours at 135—145°, by which time the contents of the flask had become solid. The melt was dissolved in very dilute caustic soda (about 3 per cent.) and then acidified slowly with dilute hydrochloric acid, avoiding any temporary local excess of acid, which caused the precipitate to " ball " together. The brown, amorphous precipitate after drying was boiled with alcohol, leaving a residue of 9 grams, which was dissolved in hot phenol and filtered while hot from a small amount of insoluble material; on the addition of alcohol to the filtrate a yellow, semi-crystalline substance was precipitated. This was collected, washed well with alcohol, and heated under reduced pressure at 100° until the odour of phenol disappeared. It melted and decomposed at 249° (Found: C = 74·0; H = 4·4. $C_{22}H_{16}O_5$ requires C = 73·33; H = 4·44 per cent.).

Resorcinolphenylsuccinein is an orange, semi-crystalline substance very slightly soluble in water and sparingly soluble in alcohol, giving a yellow solution with green fluorescence. The dried substance dissolves slowly in ether, although the freshly precipitated material dissolves readily. It is readily soluble in acetone or acetic acid, very slightly soluble in benzene, and moderately soluble in hot phenol. On boiling with benzene, it becomes dark red.

It dissolves in concentrated sulphuric acid forming a deep yellow solution with a bluish-green fluorescence; with dilute caustic soda it gives a red solution which on dilution has an intense green fluorescence, and a direct comparison showed that the intensity was of the same order as with fluorescein in similar circumstances.

A number of other condensing agents were tried for the preparation of this succinein, including concentrated sulphuric acid and phosphoryl chloride. Some experiments with stannic chloride, made almost at the end of the work on the phenylsuccinein, seemed to show that it could replace zinc chloride with advantage. In another experiment, the method used by Friedl, Weizmann, and Wyler (T., 1907, **81**, 1585) in the making of the fluorescein of 4-hydroxyphthalic acid was tried, with favourable results; the method as applied to the present case consisted in heating phenylsuccinic acid and resorcinol with a large excess of a concentrated solution of zinc chloride.

Bromination of Resorcinolphenylsuccinein. Phenylsuccinyleosin,



$$O{<}\begin{matrix}C_6HBr_2(OH)\\C_6HBr_2(OH)\end{matrix}{>}C{<}\begin{matrix}O\text{——}CO\\CH_2\cdot CHPh\end{matrix}.$$

—Three grams of resorcinolphenylsuccinein were suspended in 20 c.c. of alcohol and 6 grams of bromine (slightly more than 4 mols.) were dropped in, the succinein going into solution as the reaction took place. The solvent was allowed to evaporate and the residue rubbed up with benzene, which dissolved the greater part but left a faintly coloured residue; this, when recrystallised three times from alcohol, gave an almost colourless substance softening at 283° and melting at 295°. It became slightly pink on standing in the vacuum desiccator (Found: by Robertson's method, Br = 46·46. $C_{22}H_{12}O_5Br_4$ requires Br = 47·33 per cent.).

The substance dissolves in alkali to give an intensely purple-red solution, which on standing deposits an amorphous, brown precipitate which no longer dissolves in alkali. If the alkaline solution is acidified quickly, a red, amorphous precipitate is obtained which can again be dissolved in alkali to give a red solution but not of the original intensity.

A crystalline compound was not isolated from the benzene extract of the bromination product. Only a red, amorphous substance could be obtained.

The authors' thanks are due to the Canadian Honorary Advisory Council for Scientific and Industrial Research for the grant of a fellowship to one of us (J. A. M.) which enabled him to take part in this work.

Organic Chemical Laboratories,
The University, Manchester.

[*Received, November 3rd*, 1922.]