

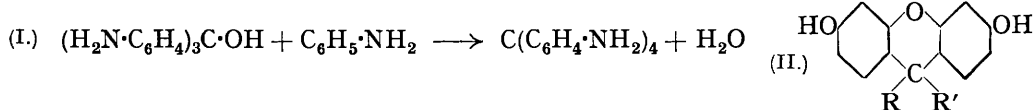
**38.** *The Alleged Colour and Dyeing Properties of Some Derivatives of Tetra-arylmethanes.*

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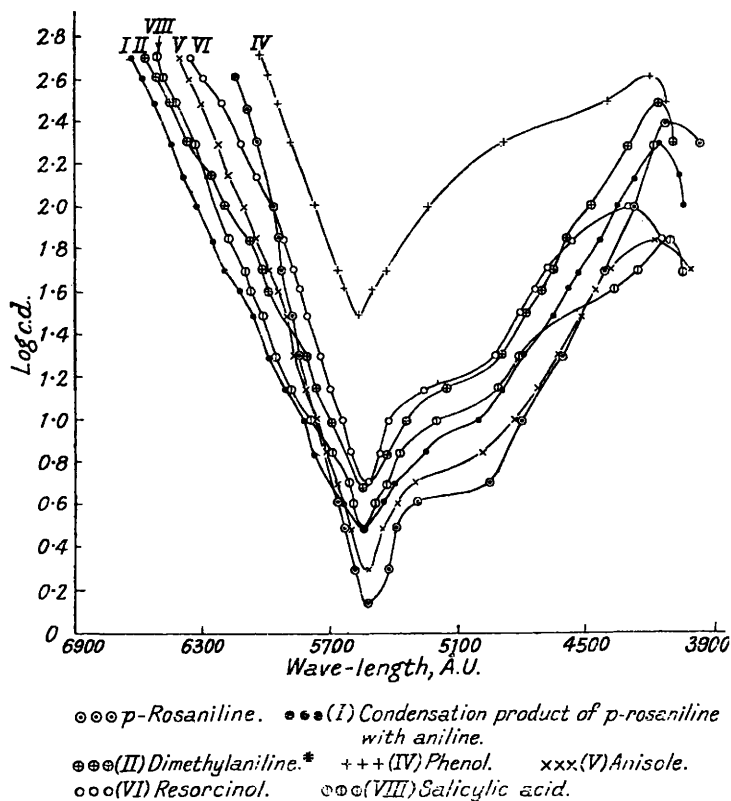
SEN and BANERJEE (*J. Indian Chem. Soc.*, 1931, **8**, 77) have stated that by the condensation of *p*-rosaniline with aniline and some of its derivatives or with certain phenols and phenolic ethers derivatives of tetraphenylmethane are formed in accordance with scheme (I) and that the products are deeply coloured dyes.

Sen, Chattopadhyaya, and Sen-Gupta (*ibid.*, 1930, **7**, 997), by condensing resorcinol with

various ketones, have obtained products to which they allot the structure (II) and which also are described as dyes. These substances cannot be formulated as meroquinoid systems



or as radicals and hence, if the description of their constitution is correct, they would provide a striking exception to the prevailing views on the correlation of colour and constitution. Reinvestigation of both classes of product seemed necessary, since other authors (Steinkopf and Hempel, *Annalen*, 1932, 495, 154; see also Rupe, Collin, and Schmiederer,



*Helv. Chim. Acta*, 1931, 14, 1340) have already drawn theoretical conclusions from their reported properties.

(1) We have repeated the condensations, described by Sen and Banerjee, of *p*-rosaniline with aniline, dimethylaniline, phenol, anisole, resorcinol, and salicylic acid. The absorption spectra of the products, obtained with a Loewe and Schumm evaluating grating spectroscope † (illumination : tungsten arc lamp, slide 0.02 mm.) all show in acid solution (0.05*N*-acetic acid in 94% ethyl alcohol) a strong band at 5525 Å.U. (see fig.) : in alkaline solution the absorption is weak, with no band in the visible region, and occurs at wave-lengths shorter than 4200 Å.U. The light absorption cannot be a property of the actual condensation products themselves, since it is inconceivable that with the variety of substituents the absorption band should remain in the same place. The observed behaviour, however, is the characteristic one of *p*-rosaniline itself, and thus the colour and the dyeing

\* The figures are the same as those in Sen and Banerjee's paper.

† For the apparatus we are indebted to the Notgemeinschaft der deutschen Wissenschaft.

property of the condensation products are to be ascribed to the rosaniline with which they are contaminated: the small differences, as described by Sen and Banerjee, doubtless arise from the different amounts of contamination and traces of other impurities.

Our analyses of the products give nitrogen contents which differ markedly from those of Sen and Banerjee, although our preparations correspond to theirs in appearance and in ability to dye wool and silk. We find, however, that the nitrogen content of the product from rosaniline and phenol varies with the agent used to precipitate it; if ammonia is used, the nitrogen content is 12.4%, whereas with sodium acetate it is 9.0%. It would thus seem that the analytical data are of little value. We have been unable to cause the products to crystallise from alcohol—the final step of the purification as reported by Sen and Banerjee—with the exception of the product from rosaniline and resorcinol, and have purified them finally by partial extraction with alcohol and recovery from the solution by evaporation. But the residues, about 10% of the extracted material, were also deeply coloured and showed, on spectroscopic analysis, similar proportions of *p*-rosaniline to those in the products obtained from the solutions. The product obtained from resorcinol we recrystallised in the proper sense: the crystals showed an even higher percentage of *p*-rosaniline than the product got by evaporation of the mother-liquor.

The condensation products from rosaniline, therefore, are complex, but probably do contain derivatives of tetraphenylmethane. The absorption data showed that the product from phenol is the least contaminated with rosaniline, and from this we have been able to isolate a colourless substance, m. p. 257° (decomp.; corr.), whose molecular weight and analysis indicate that it is pp'p''-triamino-p'''-hydroxytetraphenylmethane: it is colourless and shows no dyeing properties, even after treatment with lead dioxide, and hence cannot be *N*-phenyltriaminotriphenylcarbinol or *N*-hydroxyphenyltriaminotriphenylmethane. Dissolved in sodium hydroxide solution or aqueous ammonia, it does not show any fluorescence at all, whereas Sen and Banerjee state that the hydroxy-derivatives fluoresce. Although the crude triaminohydroxytetraphenylmethane contained only 4% of *p*-rosaniline according to the spectroscopic analysis, the yield of the colourless product was small (16.3%) and did not encourage similar purifications with the remaining products.

(2) With regard to the products (II) obtained by condensing resorcinol with ketones, we are of the opinion that the colour and dyeing properties are due to substances formed from the resorcinol alone by the action of the dehydrating agents used for the condensation or at high temperatures, and mentioned by various authors (*e.g.*, Grimaux, *Compt. rend.*, 1895, 121, 88; Meyer and Marx, *Ber.*, 1907, 40, 1450). An attempt to isolate the orange-coloured matter which shows bright green fluorescence is being made. That substances of the formula (II) should be dyes and of dark colour seems impossible, not only on general grounds but also because 3:6-dihydroxyxanthone is described as yellow (Meyer and Conzetti, *Ber.*, 1897, 30, 969; Kehrmann, *Annalen*, 1910, 372, 304): it is difficult to understand how dyes having the properties reported by Sen and his co-workers can result by replacement of the ketonic oxygen atom by hydrocarbon radicals. The products obtained from resorcinol and zinc chloride both with and without the addition of benzophenone are similar, dark brown powders, which show a strong green fluorescence when dissolved in alkali. Their absorption spectra are nearly the same and their behaviour shows that they are not homogeneous.

It appears, therefore, that both series of compounds described by Sen and his collaborators are not pure substances and owe to impurities the properties which make them so remarkable.

*Purification of pp'p''-Triamino-p'''-hydroxytetraphenylmethane.*—A solution of 5 g. of the condensation product of *p*-rosaniline and phenol, prepared according to Sen and Banerjee, in 160 c.c. of 96% ethyl alcohol was slowly mixed with 460 c.c. of water and kept for 15 hours at 0°; the precipitate was then drained and dried over calcium chloride at 100°/14 mm., 3.3 g. of a substance a little lighter in colour than the initial material being obtained. 2.5 G. of this product, finely powdered, were boiled during 15 minutes with 50 c.c. of water, the solution was filtered hot, and the residue dissolved in 40 c.c. of 3.5*N*-hydrochloric acid. This deeply coloured

opaque solution was boiled under reflux for 10 minutes with 0.02 g. of charcoal (*carbo medicinalis*, Merck, which had been boiled for several days with hydrochloric acid till this after filtration evaporated without residue), the operation being repeated 8 times. The solution, now almost colourless, was neutralised, and the substance was precipitated with saturated sodium acetate solution, collected after 24 hours, washed with water, and dried as mentioned above; yield, 1.16 g. The initially pure white precipitate became greyish on filtering and drying. It was therefore dissolved in 30 c.c. of absolute ethyl alcohol, filtered from traces of inorganic substance, mixed with aqueous ammonia dropwise till neutral to litmus, and precipitated with water in two fractions: 40 c.c. of water precipitated 0.4 g. of a greyish substance, m. p. 247° (decomp.; uncorr.) after sintering at 230°. The solution was twice boiled with 0.1 g. of carboraffin (Lurgi) and treated with 100 c.c. of water, which precipitated 0.62 g. of a colourless product, m. p. 250° (decomp.; uncorr.) (257° corr.) after sintering at 232° (Found: C, 78.6; H, 6.2; N, 11.1; *M*, in dioxan, 370.  $C_{25}H_{23}ON_3$  requires C, 78.7; H, 6.1; N, 11.0%; *M*, 381.2).

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