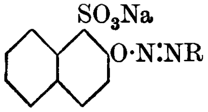
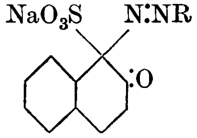
CXXXVI.—*A New Reaction of Certain Diazosulphonates derived from β-Naphthol-1-sulphonic Acid. Part IV. The Constitution of the Condensation Products of Diazo-compounds with β-Naphthol Derivatives substituted in the 1-Position.*

By Frederick Maurice Rowe and Arnold Thornton Peters.

In Part I (J., 1926, 690) the condensation products of diazo-compounds with derivatives of β-naphthol, in which a sulpho- or a methyl group, or bromine or chlorine, is substituted for hydrogen in position 1, were discussed. All diazo-compounds condense with β-naphthol-1-sulphonic acid in acid solution to form comparatively stable aryl-2-naphthol-1-diazosulphonates quantitatively. These, on treatment with a limited quantity of alkali, all give very reactive substances, some of which are converted by sodium hydroxide into complex phthalazine derivatives (*loc. cit.*, p. 692; J., 1928, 2556; and following papers), and all are converted quantitatively into the corresponding azo-derivatives of β-naphthol, with elimination of the sulpho-group, when a freshly prepared cold aqueous solution is acidified. Bucherer (*Ber.*, 1909, **42**, 47) and Wahl and Lantz (*Bull. Soc. chim.*, 1923, **33**, 97) regarded these reactive substances as diazo-oxides (I). The above results, however, indicated that they are actually sodium 1-arylazo-β-naphthaquinone-1-sulphonates (II).

(I.)





(II.)

Such a hemi-quinonoid formula (II) was limited to the derivatives of β-naphthol-1-sulphonic acid, and it was not suggested that the condensation products of other 1-substituted derivatives of β-naphthol with diazo-compounds were of a similar type. In fact, the products from 1-methyl-β-naphthol and diazo-compounds were stated to be probably diazo-oxides, and the further statement that Para-red is produced under all conditions from diazotised *p*-nitroaniline and 1-bromo-β-naphthol referred only to the decomposition of the condensation product when treated subsequently with alkali, or when attempts were made to purify it by crystallisation (*loc. cit.*, p. 693). Since the last publication in the present series, two papers bearing on this subject have appeared and have necessitated the re-investigation of some of these compounds.

Pollak and Gebauer-Fülnegg have examined the condensation products of diazotised *p*-nitroaniline with 1-bromo (or chloro)-, 1 : 6-dibromo-, and 1-methyl-β-naphthol, etc. (*Monatsh.*, 1928, **50**, 310). As a result they have suggested the possibility of the simultaneous existence of the diazo-oxide (*O*-azo) and the hemi-quinonoid type, one or other form predominating in a particular case (*loc. cit.*, p. 314; and private communication). There appear to be no grounds for such an assumption, however, as all their observations agree with the constitution of diazo-oxides of varying degrees of stability. That Pollak and Gebauer-Fülnegg's compounds are all diazo-oxides is clearly indicated by their entirely different behaviour with sodium hydroxide from that of the condensation product of diazotised *p*-nitroaniline and β-naphthol-1-sulphonic acid. For instance, the latter under suitable conditions is converted into disodium 3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetate-1-sulphonate, whereas the former are merely decomposed, or converted into Para-red, with elimination of the 1-halogen atom, in the case of halogen derivatives. On the other hand, although only certain sodium 1-arylazo-β-naphthaquinone-1-sulphonates are sufficiently stable to react with sodium hydroxide to form phthalazine derivatives, no evidence has been found to support the view that those which do not behave in this way are even variable mixtures with the diazo-oxide form.

Bucherer and Tama have studied the conditions of the formation of the condensation product of diazotised *p*-nitroaniline and β-naphthol-1-sulphonic acid, and the decomposition of its solutions under various conditions of acidity and alkalinity (*J. pr. Chem.*, 1930, **127**, 39). The results, and the fact that a neutral solution of equimolecular proportions of sodium *p*-nitrophenylnitrosoamine and sodium β-naphthol-1-sulphonate becomes alkaline with sodium hydroxide on keeping, were considered to support the diazo-oxide (diazo-ether) formula. Their observations, however, give no reason to doubt that the correct constitution is sodium 1-(4′-nitrobenzeneazo)-β-naphthaquinone-1-sulphonate. They described this compound as a pale orange-brown substance obtained in a flocculent condition by salting-out (*loc. cit.*, p. 60), but actually there is no difficulty in obtaining it in almost colourless leaflets, although the dry compound cannot be analysed because it is readily converted into Para-red.

Bucherer and Tama (*loc. cit.*, p. 55) also state that " Various other diazo-compounds can be converted through their 2-naphthol-1-diazosulphonates into the corresponding hydroxyazo-compounds . . . the choice of the diazo-component is limited, however, as only those of great coupling power react readily in this direction.

Thus, attempts to obtain diazo-oxides with, *e.g.*, diazobenzene chloride, in general gave negative results." This limitation is quite incorrect, because all diazo-compounds readily form 2-naphthol-1-diazosulphonates, and all of the latter yet examined, including that from diazobenzene chloride, are converted by sodium carbonate into sodium 1-arylazo-β-naphthaquinone-1-sulphonates, which give the corresponding azo-β-naphthols merely by acidification.

Finally, Bucherer and Tama (*loc. cit.*, p. 72), by the action of aqueous sodium hydroxide on 4′-nitrobenzene-2-naphthol-1-diazosulphonate, obtained in low yield a "readily soluble yellow compound," to which they gave the formula $C_{16}H_{10}O_6N_3SNa,H_2O$ on the basis of one nitrogen determination.[1] By boiling an aqueous solution of this with hydrochloric acid, sulphur dioxide being eliminated, they obtained a "sparingly soluble yellow compound," m. p. 310—315°, to which they gave the formula $C_{16}H_{11}O_3N_3,2H_2O$ on the basis of one nitrogen determination. (Professor Bucherer in a private communication states that m. p. 310—315° is an error for 239°.) Preparation of these substances according to Bucherer and Tama's methods has now shown that they are sodium hydrogen 3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-1-sulphonate-4-acetic acid and 1-hydroxy-3-(4′-nitrophenyl)-1 : 3-dihydrophthalazine-4-acetic acid, m. p. 241°, respectively (compare J., 1926, 699).

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