168. *Azo-sulphites of Dis-azo-naphthols and their Fission into the Corresponding Aminoazo-naphthols.*

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THE dis-azo-compounds of the type $X{\cdot}N{:}N{\cdot}Y{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH$, where X and Y represent an aromatic nucleus, *e.g.*, benzene, naphthalene, and diphenyl groups, form an important class of colouring matters, especially in the form of their sulphonic acids.

The significance of azo-sulphite formation as related to fastness to stoving (bleaching with sulphur dioxide) referred to in the case of mono-azo-dyes (J., 1927, 2639) is thus of similar technical importance in the case of these dis-azo-dyes.

The latter in addition show interesting chemical behaviour on treatment with sodium bisulphite, a discussion of which is the object of the present paper.

The stability of the azo-sulphites of certain mono-azo-β-naphthol derivatives towards acidified iodine solution was shown (*loc. cit.*) to allow of the estimation of azo-sulphite and alkali-sulphite mixtures. A number of azo-sulphites which have recently been prepared (J., 1929, 601) show the same stability and this property appears to apply to azo-sulphites generally.

The azo-sulphites have been found to be stable also towards titanous chloride and the proportion of unchanged dye in mixtures of the dye and its azo-sulphite can be approximately estimated by titration (hot) with titanous chloride until no further colour change occurs.

This protective action on the azo-linking is further shown in the case of sodium hydrosulphite, which usually reduces the dye itself rapidly in cold solution but attacks the azo-sulphite comparatively slowly.

Apart from its technical significance in connexion with hydrosulphite stripping and print discharging, this reaction is of synthetic interest, since with dis-azo-compounds where one of the azo-linkages can be protected by azo-sulphite formation the unprotected azo-linkage can be severed by suitable reduction, thus yielding the azo-sulphite of a mono-azo-derivative with an amino-group at the point of fission of the original azo-linkage, along with an amine which can be identified by appropriate means.

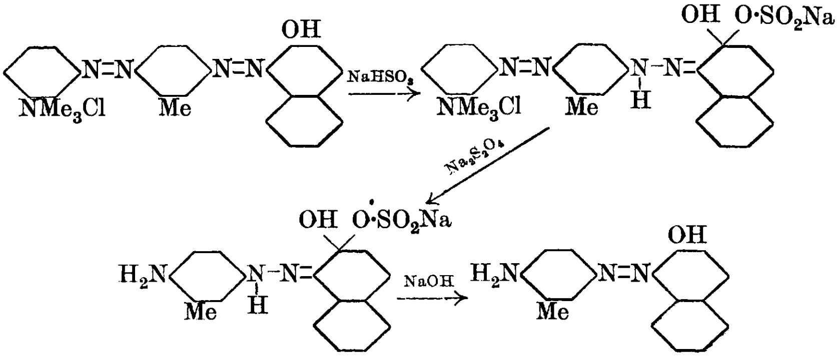
The reaction, as in the case of mono-azo-dyes, is limited by constitutional considerations, and is practically confined to those dis-azo-compounds containing a β-naphthol component.

This provides an additional means of determining the constitution of poly-azo-dyes, and a new method of preparing aminomonoazo-β-naphthols, the only one of which that appears to have been previously described is the parent substance, *p*-aminobenzeneazo-β-naphthol, m. p. 259—260° (Meldola, J., 1905, **87**, 3).

Both benzeneazobenzeneazo-β-naphthol and *p*-sulphobenzeneazobenzeneazo-β-naphthol failed to react to give Meldola's product. Janus Red B (2-hydroxy-1-naphthaleneazo-*m*-tolueneazobenzene-*m*-trimethylammonium chloride), however, reacted smoothly to give the homologous p-*amino*-m-*tolueneazo*-β-*naphthol*, m. p. 251°, closely resembling Meldola's compound.

The isolation of some others of this type is described in the experimental part. That they have the constitution assigned is regarded as reasonably certain from their mode of formation, but it is hoped to characterise them more fully in a subsequent paper.

The sequence of changes is shown particularly well in the case of Janus Red B above mentioned, which gives easily separated azo-sulphite products at each stage as formulated below:



In general, however, there is a marked tendency for the unprotected azo-linking to split with bisulphite alone, especially on heating. This fission occurs, as already noted (J., 1929, 602), with a number of mono-azo-α-naphthol derivatives which fail to form azo-sulphites, and favours the hydrazone structure in the protected link, rather than the ordinary azo-link, which would be reverted to if the bisulphite addition product lost water.

The product of the bisulphite action thus depends on the relative rates at which the dis-azo-sulphite is formed and the unprotected link reduced.

The Janus Red *azo-sulphite* forms in suspension and, being practically insoluble in bisulphite solution, is relatively resistant to further action.

Where the dis-azo-sulphite first formed is readily soluble in the reaction liquid, subsequent reduction of the unprotected linkage is also prone to occur. Both actions are favoured by rise of temperature, but especially the latter, so that while in general the azo-sulphite of the parent dye can be obtained by reaction in the cold, after being heated at 60° for an hour or so the reaction mixture yields only the mono-azo-derivative.

For example, sodium diphenyldisazo-8-sulpho-β-naphthol-α-naphthylamine-4-sulphonate (Congo Rubine) yields the corresponding *dis-azo-sulphite* by shaking for $\frac{1}{2}$ hour with bisulphite solution and a little pyridine, but with prolonged shaking increasing quantities of the mono-azo-sulphite are formed, and heating at 60° for about an hour yields only the mono-azo-sulphite, *sodium* 4′-*aminodiphenylazo*-8-*sulpho*-β-*naphthyl sulphite.*

Similarly sodium diphenyldisazo-8-sulpho-β-naphthol-α-naphthol-4 : 8-sulphonate (Heliotrope 2B) yields the *dis-azo-sulphite,* but reduction of the latter proceeds slowly even in the cold, and after standing over-night the reaction mixture yields mainly the corresponding mono-azo-sulphite.

This secondary action is naturally influenced not only by the solubility factor, but also by the nature of the group to be split off, and its adjoining group, and so far as is shown by the cases examined, diminishes with increasing complexity of these groups, while diazo-sulphites with a diphenyl middle nucleus appear to be the most stable.

Thus, sodium *p*-sulphobenzeneazobenzeneazo-β-naphthol-8-sulphonate (Croceine Scarlet 3B) yielded a product largely contaminated with the reduced substance, from the reaction in aqueous solution, but by shaking with bisulphite in presence of a third of its volume of pyridine the *dis-azo-sulphite* was obtained from the pyridine layer in fairly pure condition.

The only available dye with a naphthalene middle nucleus was sodium monosulpho-4-amino-α-naphthaleneazo-α-naphthaleneazo-β-naphthol-6-sulphonate (Diazamino Blue BR). This yields the dis-azo-sulphite without difficulty from the cold reaction mixture, but readily suffers reduction on heating.

Of the azo-sulphites of dyes containing a diphenyl middle nucleus which were examined, in addition to those of Congo Rubine and Heliotrope 2B above referred to, that of sodium diphenyldisazo-salicylic acid-β-naphthol-3 : 6-disulphonate (Paramine Fast Bordeaux B) also showed a marked tendency to reduce when the reaction mixture was warmed.

Sodium diphenyldisazophenetole-β-naphthol-6 : 8-disulphonate (Chloramine Red B) gives a less readily reducible *dis-azo-sulphite*, while with sodium diphenyldisazo-3 : 6 : 8-trisulpho-α-naphthol-β-naphthol (Trisulphon Violet B) and especially the corresponding ditolyl derivative (Trisulphon Blue R) the *dis-azo-sulphites* are comparatively stable and only prolonged heating with bisulphite converts them into the mono-azo-derivative. In the latter case the resistance to reduction is probably increased by the steric hindrance of the methyl group in the *o*-position to the azo-group.

The Trisulphon Violet B azosulphite is noteworthy in showing a striking colour change from reddish-purple to steely blue according to whether it is isolated from pyridine solution, or from aqueous solution by salting out.

EXPERIMENTAL.

The *sulphite* of 2-hydroxy-1-naphthaleneazo-*m*-tolueneazobenzene-*m*-trimethylammonium chloride was obtained from the dye suspension in 5% sodium bisulphite solution, maintained at about 60°; the colour gradually changed to orange-red. The product, after being washed with water and with alcohol to remove unchanged dye and dried in a desiccator, was an orange-red powder, sparingly soluble in water and alcohol (Found: S as sulphite, 5·9. $C_{26}H_{27}O_4N_5ClSNa$ requires S, 5·7%).

Sodium p-*amino*-m-*tolueneazo*-β-*naphthyl sulphite* was obtained by stirring a suspension of the preceding sulphite in water and gradually adding concentrated sodium hydrosulphite solution until the colour changed to dull brown. The product, washed, crystallised from aqueous alcohol, and dried, formed a yellowish-brown powder (Found: S as sulphite, 8·45. $C_{17}H_{16}O_4N_3SNa$ requires S, 8·4%).

p-*Amino*-m-*tolueneazo*-β-*naphthol* was obtained from the foregoing, on treatment with dilute sodium hydroxide solution, as a dark brownish powder. Evaluation with titanous chloride gave 98%

(Found: N, 14·9. $C_{17}H_{15}ON_3$ requires N, 15·2%). The *acetyl derivative*, m. p. 251°, formed bright brick-red crystals resembling acet-*p*-amidobenzeneazo-β-naphthol, m. p. 259—260° (compare Meldola, *loc. cit.*).

Sodium diphenyldisazo-4-sulpho-α-naphthylamine-8-sulpho-β-naphthyl sulphite, obtained by ½ hour's shaking in the cold with bisulphite solution and ⅓ vol. of pyridine, and isolated from the pyridine layer as previously described, was a dark purplish, rather deliquescent, crystalline powder (Found: S as sulphite, 4·2. $C_{32}H_{22}O_{10}N_5S_3Na$ requires S, 4·2%).

Sodium 4′-aminodiphenylazo-8-sulpho-β-naphthyl sulphite, obtained either from Congo Rubine or its azo-sulphite above, by heating with sodium bisulphite solution for an hour at 60°, was isolated by the pyridine method as a dull brown, crystalline powder (Found: S as sulphite, 5·95. $C_{22}H_{17}O_7N_3S_2Na_2$ requires S, 5·9%).

4′-Aminodiphenylazo-β-naphthol-8-sulphonic acid, obtained by treating the foregoing with dilute sodium hydroxide solution and then boiling it with hydrochloric acid, separated on cooling as a dark violet, crystalline precipitate.

Sodium diphenyldisazo-4:8-disulpho-α-naphthol-8-sulpho-β-naphthyl sulphite was obtained, in similar manner to the Congo Rubine derivative above, as a deep reddish-purple, deliquescent, crystalline powder (Found: S as sulphite, 3·5. $C_{32}H_{20}O_{14}N_4S_4Na_4$ requires S, 3·55%). It yielded, when heated at 60° with bisulphite solution, a product identical with the fission product from Congo Rubine described above (Found: S as sulphite, 5·9%).

Sodium diphenyldisazosalicylic acid-3:6-disulpho-β-naphthyl sulphite was obtained by reaction at the ordinary temperature and isolated by the pyridine method as a deep purplish-brown product (Found: S as sulphite, 4·3. $C_{29}H_{18}O_{13}N_4S_3Na_4$ requires S, 3·91%), considerably contaminated with the fission product, *sodium 4′-aminodiphenylazo-3:6-disulpho-β-naphthyl sulphite*, which is obtained in pure condition, by reaction at 60° and extraction by the pyridine method, as a rather deliquescent, dark reddish-brown, crystalline powder (Found: S as sulphite, 5·1. $C_{22}H_{16}O_{10}N_3S_3Na_3$ requires S, 5·0%).

Sodium p-*sulphobenzeneazobenzeneazo-8-sulpho-β-naphthyl sulphite*, obtained by shaking the dye with bisulphite solution and pyridine for ½ hour, was isolated from the pyridine layer as an orange crystalline powder (Found: S as sulphite, 5·0.

$$C_{22}H_{15}O_{10}N_4S_3Na_3$$

requires S, 4·8%).

Sodium p-*aminobenzeneazo-8-sulpho-β-naphthyl sulphite* was obtained from the foregoing reaction at 60°; the pyridine layer yielded a deep orange-brown, crystalline powder, rapidly deliquescing in the air (Found : S as sulphite, 6·7. $C_{16}H_{13}O_7N_3S_2Na_2$ requires S, 6·8%).

Sodium monosulpho-4-amino-α-naphthaleneazo-α-naphthaleneazo-6-sulpho-β-naphthyl sulphite was obtained as a purplish-brown crystalline powder from reaction in the cold, but satisfactory analyses could not be made by iodine titration owing to the deep blue colour of the original dye regenerated on decomposition with dilute alkali.

Sodium diphenyldisazophenetole-6 : 8-*disulpho*-β-*naphthyl sulphite* is fairly stable to warm bisulphite solution and after an hour's heating at 60° a portion of the dis-azo-sulphite, which is relatively insoluble in bisulphite solution, remains unreduced and can be recovered by salting out. From the reaction in bisulphite and pyridine in the normal manner, it was isolated as a deep orange, crystalline powder (Found : S as sulphite, 4·1. $C_{30}H_{23}O_{11}N_4S_3Na_3$ requires S, 4·1%).

Sodium 4′-*aminodiphenylazo*-6 : 8-*disulpho*-β-*naphthyl sulphite* is formed from the orange product above by heating at 60° with bisulphite until it gives a dark brown solution. Extraction with pyridine yields a brown crystalline powder (Found : S as sulphite, 4·8. $C_{22}H_{16}O_{10}N_3S_3Na_3$ requires S, 5·0%). *p*-Phenetidine is readily isolated from the dark brown aqueous reaction mixture, made alkaline, by steam distillation.

Sodium diphenyldisazo-3 : 6 : 8-*trisulpho*-α-*naphthol*-β-*naphthyl sulphite* is formed by warming the dye with bisulphite solution; the colour soon changes to a rich violet-red and extraction with pyridine yields a dark purple, crystalline powder. The product is also readily salted out, with striking colour change of the solution to deep blue, and deposition of a steely blue, crystalline powder, which on solution and recovery from pyridine reverts to the purple form (Found : S as sulphite, 3·7. $C_{32}H_{20}O_{14}N_4S_4Na_4$ requires S, 3·5%).

Sodium 4′-*aminodiphenylazo*-β-*naphthyl sulphite* is formed from the above on more prolonged heating, the solution eventually changing to a deep orange-brown. Extraction with pyridine yields a bright brown, crystalline powder (Found : S as sulphite, 7·1. $C_{22}H_{18}O_4N_3SNa$ requires S, 7·2%).

4′-Aminodiphenylazo-β-naphthol is formed on decomposing the foregoing with alkali, and gives almost black, purplish crystals from hot alcohol. It readily forms an acetyl derivative in dull red crystals, m. p. 275°.

Sodium ditolyldisazo-3 : 6 : 8-*trisulpho*-α-*naphthol*-β-*naphthyl sulphite* is a crystalline powder, darker and bluer in shade than the

Trisulphon Violet derivative, with similar but less marked colour change on salting out (Found : S as sulphite, 3·4. $C_{34}H_{24}O_{14}N_4S_4Na_4$ requires S, 3·43%).

Sodium p-*aminoditolylazo*-β-*naphthyl sulphite* is preferably obtained from the foregoing by gradual addition of hydrosulphite solution in the cold until the colour change to yellowish-brown is complete, and salting out; when dried, it forms a dull brown powder (Found : S as sulphite, 6·65. $C_{24}H_{22}O_4N_3SNa$ requires S, 6·8%). With alkali it yields the corresponding *p*-aminoditolylazo-β-naphthol, whose acetyl derivative forms brownish-red crystals, m. p. about 233°.

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