LXXXVII.—*Constitutional Influences on the Conversion of Azonaphthols into their Azo-sulphites and their Bearing on the Structure of* α- *and* β-*Naphthol.*

By Albert Theodore King.

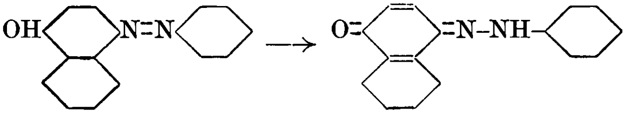
The conversion of azonaphthols into their azo-sulphites is of special significance in the case of dyes derived from them, since this reaction underlies their degree of fastness to sulphur dioxide on alkaline fabric as distinguished from the ordinary stoving test with excess of sulphur dioxide.

The indication previously made (King, J., 1927, 2639), that β-naphthol derivatives are more reactive to sodium bisulphite than α-naphthol derivatives, is supported by observations from the practical dyeing side by Goodall (*J. Soc. Dyers and Col.*, 1928, **44**, 145), who records that whereas all J. R. Geigy & Co.'s azo-dyes with β-naphthol residues proved to be sensitive to sulphur dioxide when tested over the " active range " of alkalinity on wool fabric, not one of the twenty α-naphthol derivatives tested was affected. This difference in activity is further considered in the present paper, more particularly with regard to the positional effect of sulphonic groups.

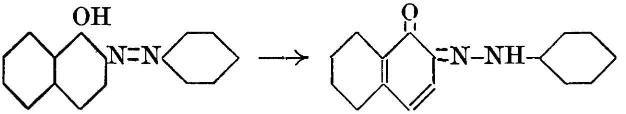
With the naphthol nucleus unsubstituted, the azo-α-naphthol bisulphite compounds form fairly readily, although less so than the corresponding β-naphthol compounds. For example, *p*-sulphobenzeneazo-α-naphthol reacts rather less readily than *p*-sulphobenzeneazo-β-naphthol, and 4-sulpho-α-naphthaleneazo-α-naphthol (Acid Brown R) distinctly less readily than the corresponding β-naphthol compound (Fast Red A). No close comparison of constitutional influences can be drawn here, since the coupling of β-naphthol derivatives occurs at the ortho-position to the hydroxy-group, whereas with the above α-naphthol compounds the coupling is at the para-position to the hydroxy-group.

When the naphthol component is sulphonated, however, so that the coupling is in the ortho-position for both α- and β-naphthol, a wide divergency in reactivity appears. The azo-β-naphtholsulphonic acids show no falling off in reactivity; rather, owing to the increasing solubility accompanying introduction of sulphonic groups, conversion into the azo-sulphite becomes, if anything, more readily effected. The well-characterised sulphites of a number of azo-β-naphtholsulphonic acids are recorded in the experimental part. No example has so far been found where an azo-compound with a β-naphthol residue has failed to form a bisulphite derivative. On the other hand, azo-derivatives of α-naphthol show a striking loss of reactivity with introduction of sulphonic groups, the only case of sulphite formation observed being with a sulphonic group in the 5-position and then only when the azo-derivative is formed from an unsulphonated diazo-compound. For instance, α-naphthaleneazo-α-naphthol-5-sulphonic acid (Double Ponceau) yields the azo-sulphite, but the corresponding 4-sulpho-α-naphthaleneazo-α-naphthol-5-sulphonic acid (Fast Red V.R.) merely undergoes slow fission, without any azo-sulphite formation occurring. The non-reactivity of the following dyes illustrates the general inhibition with a sulphonated α-naphthol component: α-naphthaleneazo-α-naphthol-4 : 8-disulphonic acid (Azo Bordeaux, Bayer), α-naphthaleneazo-α-naphthol-3 : 6-disulphonic acid (Benzyl Bordeaux B, Clayton Aniline Co.), 4-sulpho-α-naphthaleneazo-α-naphthol-4-sulphonic acid (Carmoisine, Sandoz), 4-sulpho-α-naphthaleneazo-α-naphthol-5-sulphonic acid (Fast Red V.R., Bayer), 6-sulpho-β-naphthaleneazo-α-naphthol-4-sulphonic acid (Brilliant Ponceau 4R, Bayer).

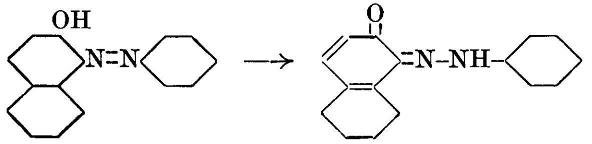
The mechanism of azo-sulphite formation has been well studied by Voroshcov (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 771; 1915, **47**, 1669), who regards the reaction as taking place by addition at the hydroxy-group in its ketonised form, in support of which view he discusses the relative activity of the three typical azo-linkings in their tautomeric forms as shown below:



(I.)



(II.)



(III.)

He observed that compounds (I) and (III) react readily, whereas (II) is non-reactive, and regards this as additional evidence against Spiegel's view (*Ber.*, 1885, **18**, 1479), since if the reaction consisted in addition at the double bond, (II) would offer the least steric hindrance and react most readily, and (III) should react least readily. But "considering the action as jointly concerning the oxy-group, the most restrained oxy-group is in (II), which does not react, and this group in (I) and (III) is placed in equally reactive state."

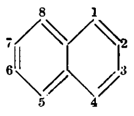
It would not seem, however, that any form of steric hindrance can play more than a minor part, in view of the marked reactivity of heavily substituted azo-β-naphthols, *e.g.*, 4-sulpho-α-naphthalene-azo-β-naphthol-3 : 6 : 8-trisulphonic acid, though the slowness of reaction with *m*-xyleneazo-β-naphthol-3 : 6-disulphonic acid (see experimental part) and also with *o*-carboxybenzeneazo-β-naphthol-3 : 6-disulphonic acid is probably a real steric hindrance effect.

Indeed the view that the naphthol nucleus reacts in a tautomeric keto-form involves the hypothesis that only those azonaphthols which are capable of assuming such tautomeric form can give rise to azo-sulphites, and the difference in behaviour appears to be due rather to some inherent disability of (II) to assume the tautomeric form necessary before any reaction can occur, whereas (I) and (III) can ketonise readily.

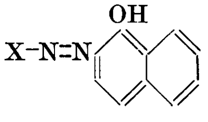
If this is so, Voroshcov's formulation above indicates in fact that (I) should be the least reactive, which point will be reverted to later, but there is no structural indication that tautomerisation should occur in (III) but not in (II) or that it would be prevented by substitution, even in adjacent positions.

On the other hand, the unsymmetrical form of the naphthalene ring would provide for a different behaviour, on the following reasoning, (1—2) in (IV) being regarded as a double-bond position. In the case of compound (II), with the hydroxy-group in position 1 tautomerisation involves no oscillation in the ring, only the swinging of the 1—2 double bond between the hydroxy-group and the 2-nitrogen linkage being required, as in the symmetrical formula. With the hydroxy-group in position 8, however, tautomerisation involves either a complete rearrangement of the double bonds to the symmetrical form, or a cyclic transformation round the whole nucleus into the alternative unsymmetrical formula. This is not absolutely precluded while the naphthol ring remains unsubstituted, but would tend to be blocked by substituents, especially in positions 5 and 6.

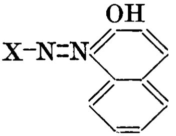
Applying the same reasoning to β-naphthols, if the hydroxy-group is in position 2, only the 1—2 bond oscillates, but if it is in position 7, the same complication obtains as in (8) α-naphthol. The contrast is portrayed by the formulæ for azo-α- (V) and -β-naphthol (VI) derivatives.



(IV.)



(V.) (8) α-.

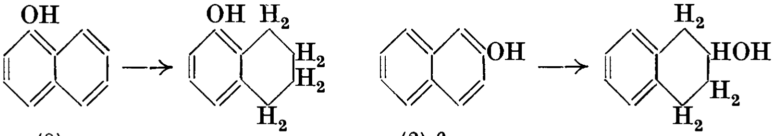


(VI.) (2) β-.

Such a deduction would be very speculative on the single evidence of the contrast in reactivity of α- and β-naphtholazo-derivatives towards bisulphite, but the view that they are differently constituted, in that in the β-naphthol type the ring tends to stabilise with a double bond across the OH-N positions, and in the α-naphthol type with only a single bond, may have a bearing on the conflicting evidence regarding the constitution of azo-α- and -β-naphthols, and the well-known generally greater reactivity of the β-naphthol nucleus.

Further, similar configurations for α- and β-naphthol themselves would accord with certain contrasts in their behaviour, particularly their reduction by sodium and amyl alcohol to the tetrahydro-derivatives, α-naphthol giving almost solely *ar*-tetrahydro-α-naphthol, whereas β-naphthol gives mainly *ac*-tetrahydro-β-naphthol, accompanied by a relatively small quantity of the *ar*-derivative (Bamberger, *Ber.*, 1890, **23**, 197, 215, 888).

The symmetric and the centric formula do not suggest any directive influence in this reaction.



(8) α-. *ar*-. (2) β-. *ac*-.

But with the configurations above, the obvious product from α-naphthol is the *ar*-derivative, since a double bond between the α-position and the adjoining nucleus would be expected to be most resistant to reduction, which can only occur with accompanying rearrangement in the adjoining nucleus, or with the appearance of a double bond between the common carbon atoms.

The β-naphthol formula, on the other hand, clearly favours the formation of the *ac*-derivative, but as in this case the unsubstituted nucleus can oscillate between the unsymmetrical and the symmetrical configuration, the *ar*-derivative also can be produced.

That the initial reduction product from α-naphthol with sodium and ethyl alcohol is the *p*-dihydro-α-naphthol (Rowe and Levin, J., 1921, **119**, 2021), whereas on either the above or the symmetrical formula an *o*-dihydro-derivative would be expected, is presumably accounted for by a bridge operating across the *p*-positions (compare Ingold, J., 1922, **121**, 1133).

On hydrogenation under pressure, however, with a nickel catalyst, the *ac*-tetrahydro-derivative preponderates with α- as well as β-naphthol (Brochet and Cornubert, *Bull. Soc. chim.*, 1922, **31**, 1280), so that these conditions of reduction must over-ride any tendency for the α-naphthol ring to be stabilised as postulated above.

Reverting to formula (I), it will be observed that the 1—4 positions involve the same transposition to the para-quinonoid form whether the symmetrical or the unsymmetrical formula be employed, which is relatively simple, but less so than as formulated in (II) and (III).

The 8—5 positions in the unsymmetrical form entail, not a complete rearrangement as in the 8—7 position already discussed, but a more extensive one than the 1—4 positions require. The assumption of the 8—7 positions for the ortho-coupled α-naphthol would presumably determine the 8—5 positions for the para-coupling, and the observation recorded above, that benzeneazo-α-naphthol and α-naphthaleneazo-α-naphthol do form azo-sulphites but with definitely less readiness than the corresponding β-naphthol compounds, is at any rate in line with the 8—5 unsymmetrical structure.

With regard to the actual composition of the bisulphite compounds, the fission of the azo-linkage which usually occurs under prolonged treatment of azo-dyes of the α-naphthol type with bisulphite is of significance. Voroshcov, in his first paper, regarded the azo-sulphites as formed by loss of water from the intermediate additive product giving an azonaphthol sulphite similar to the naphthyl sulphites described by Bucherer (*J. pr. Chem.*, 1904, **69**, 49). He showed, however, in his second paper that Bucherer's products retain this molecule of water and he inclines to the same hydrated form for the azo-bisulphite compounds, which thus retain the hydrazone linking instead of reverting to the azo-linking, which would necessitate loss of the water molecule.

The analyses recorded in the experimental part are all lower than are required by the dehydrated form, but show generally a slightly higher content of SO_2 than is required for the hydrazone form. The difficulty both of purifying and of accurately analysing these compounds makes such evidence untrustworthy as to whether the water molecule is split off or not.

The marked difference in colour, however, between the dye and its bisulphite compound suggests a modified nitrogen linking, and this view is supported by the fact that the nitrogen link in the bisulphite product is stable to further action of bisulphite, whereas the azo-link is reduced.

Consequently, the bisulphite compounds are to be regarded as retaining the additive structure, without reversion to the azo-linking by loss of water.

EXPERIMENTAL.

The azo-sulphites are in general readily obtained by stirring the powdered dye into excess of fairly concentrated sodium bisulphite solution, and warming the liquid at about 60° for an hour or so. The bisulphite solution is conveniently made by adding 10% sodium hydroxide solution to commercial bisulphite solution (20% SO_2) until the latter reacts only faintly acid to litmus paper, an approximately equal volume being required. The ease of isolating the azo-sulphite varies with the azo-compound employed. With the more difficultly soluble dyes it is preferable to use more dilute bisulphite solution, and addition of a little pyridine greatly facilitates the reaction. The hot liquid is filtered, and the filtrate cooled and saturated with sodium chloride. This in many cases causes the azo-sulphite to separate; it can then be purified by crystallisation first from 5% sodium chloride solution and finally from a small quantity of water.

Those azo-sulphites which are not capable of being salted out are most conveniently isolated by shaking the reaction mixture with pyridine ($\frac{1}{3}$ vol.) and adding sufficient sodium sulphate to cause ready separation of the pyridine layer. This contains the azo-sulphite, and is separated and well dried with anhydrous sodium sulphate. The filtered liquid is well stirred with ether (2—3 vols.), and the ether poured off, and this treatment is repeated. A third washing usually suffices for the ether to remain uncoloured, after which dry alcohol is stirred into the oily residue, which is more or less readily converted into a crystalline powder by rubbing. This is washed with dry alcohol and dried in a vacuum desiccator.

The compounds were analysed as previously described (J., 1927, 2644).

Sodium benzeneazo-6-*sulpho*-β-*naphthyl sulphite* (bisulphite compound of Croceine Orange, Bayer) separates readily from the cooled reaction mixture in flocculent form. After recrystallisation from warm water it dries to rather hard lumps which give a canary-yellow powder on rubbing (Found: S as sulphite, 7·2. $C_{16}H_{10}O_6N_2S_2Na_2,H_2O$ requires S, 7·05. $C_{16}H_{10}O_6N_2S_2Na_2$ requires S, 7·3%).

Sodium α-*naphthaleneazo*-6-*sulpho*-β-*naphthyl sulphite* (bisulphite compound of Fast Red B, Bayer). The dye is very slightly soluble in the bisulphite solution. The reaction is facilitated by addition of an equal volume of water and 5% of pyridine. The *azo-sulphite* is slowly salted out and gives a bronze-brown crystalline product on drying (Found: S as sulphite, 6·3. $C_{20}H_{12}O_6N_2S_2Na_2,H_2O$ requires S, 6·35. $C_{20}H_{12}O_6N_2S_2Na_2$ requires S, 6·6%).

Sodium 4-*sulpho*-α-*naphthaleneazo*-6-*sulpho*-β-*naphthyl sulphite* (bisulphite compound of Fast Red EA.S, British Dyestuffs Corpn.) separates readily on addition of sodium chloride and is purified by recrystallisation from dilute sodium chloride solution. The product on drying gives a bright orange crystalline powder (Found: S as sulphite, 5·2. $C_{20}H_{11}O_9N_2S_3Na_3,H_2O$ requires S, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3$ requires S, 5·4%).

Sodium benzeneazo-3 : 6-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Acid Orange R, British Dyestuffs Corpn.) is readily salted out from the cooled bisulphite solution. Recrystallised from warm water, it yields a dull yellow crystalline powder (Found : S as sulphite, 5·8. $C_{16}H_9O_9N_2S_3Na_3,H_2O$ requires S, 5·75. $C_{16}H_9O_9N_2S_3Na_3$ requires S, 5·95%).

Sodium m-*xyleneazo*-3 : 6-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Ponceau 2RE, Geigy), in contrast with the other products described, forms only with difficulty, as already stated. Heating with dilute bisulphite solution and a little pyridine to 60° gradually brings the dye into solution, the latter eventually turning deep orange. The product, isolated by the pyridine method, is obtained as a buff yellow crystalline powder (Found : S as sulphite, 5·5. $C_{18}H_{13}O_9N_2S_3Na_3,H_2O$ requires S, 5·5. $C_{18}H_{13}O_9N_2S_3Na_3$ requires S, 5·65%).

Sodium o-*carboxybenzeneazo*-3 : 6-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Solochrome Red B, British Dyestuffs Corpn.) is obtained more readily in presence of pyridine. Isolation by means of the pyridine method gives a dull orange crystalline powder (Found: S as sulphite, 5·0. $C_{17}H_8O_{11}N_2S_3Na_4,H_2O$ requires S, 5·1. $C_{17}H_8O_{11}N_2S_3Na_4$ requires S, 5·3%).

Sodium α-*naphthaleneazo*-3: 6-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Bordeaux B, Sandoz) also is obtained more readily in presence of pyridine. It is not salted out and is obtained from the pyridine extract as a brick-red crystalline powder (Found : S as sulphite, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3,H_2O$ requires S, 5·3. $C_{20}H_{11}O_9N_2S_3Na_3$ requires S, 5·4%).

Sodium 4-*sulpho*-α-*naphthaleneazo*-3: 6-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Azo Rubine S, Sandoz) is isolated from the pyridine extract as an orange-brown crystalline powder (Found : S as sulphite, 4·6. $C_{20}H_{10}O_{12}N_2S_4Na_4,H_2O$ requires S, 4·5. $C_{20}H_{10}O_{12}N_2S_4Na_4$ requires S, 4·6%).

Sodium 4-*sulpho*-α-*naphthaleneazo*-6 : 8-*disulpho*-β-*naphthyl sulphite* (bisulphite compound of Scarlet 5/O, British Dyestuffs Corpn.) is isolated from pyridine as a dull yellow crystalline powder (Found : S as sulphite, 4·6. $C_{20}H_{10}O_{12}N_2S_4Na_4,H_2O$ requires S, 4·5. $C_{20}H_{10}O_{12}N_2S_4Na_4$ requires S, 4·6%).

Sodium 4-*sulpho*-α-*naphthaleneazo*-3 : 6 : 8-*trisulpho*-β-*naphthyl sulphite* (bisulphite compound of Ponceau 6R, Bayer) is isolated from pyridine as a deep orange crystalline powder, deliquescing rapidly in air (Found : S as sulphite, 4·0. $C_{20}H_9O_{15}N_2S_5Na_5,H_2O$ requires S, 3·95. $C_{20}H_9O_{15}N_2S_5Na_5$ requires S, 4·0%).

Sodium α-*naphthaleneazo*-5-*sulpho*-α-*naphthyl sulphite* (bisulphite compound of Double Ponceau 2R, Bayer) is readily salted out from the reaction mixture and is obtained on recrystallisation from water as an orange crystalline powder (Found : S as sulphite, 6·4.

$C_{20}H_{12}O_6N_2S_2Na_2,H_2O$ requires S, 6·35. $C_{20}H_{12}O_6N_2S_2Na_2$ requires S, 6·6%).

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