CXLVIII.—*Steric Hindrance in the Naphthalene Series.*

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THE facility with which 1:8-naphthalene derivatives form ring compounds is usually considered to indicate that substituents in the peri-position are relatively situated very similarly to those in the ortho-position in a benzene or naphthalene nucleus. If this be so, the phenomenon of steric hindrance should be exhibited by certain naphthalene compounds having substituents in positions 1, 2, and 8,

and this explanation has been advanced to account for the peculiar behaviour of certain 2:8-derivatives, although exact experimental data are wanting.

Some years ago Witt (*Ber.*, 1888, 21, 3483) found that β -naphthylamine-8-sulphonic acid reacted with diazotised sulphanilic acid to form a diazoamine. Similar results have been obtained with diazonium salts of less molecular weight; it is worthy of mention, however, that in the production of these yellow diazoamines the red colour of the solution is the more pronounced the lower the molecular weight of the diazonium salt used, a result which points to the possibility of a small quantity of the aminoazo-compound being formed, although attempts to isolate such substances from the mother liquors were unsuccessful, as also were experiments undertaken with a view to the conversion of the diazoamino- into the aminoazo-compound. Evidently, with a substituent of large molecular volume in position 8 the intramolecular change is rendered impossible, or is very largely hindered, so that the diazo-complex cannot enter position 1 to form an aminoazo-compound. In accordance with this deduction, it was found that dimethyl- β -naphthylamine-8-sulphonic acid does not react with diazonium salts.

The molecular volume of the nitro-group is much less than that of the sulphonic acid group, and consequently 8-nitro- β -naphthylamine yields aminoazo-compounds in the usual way, although the effect of steric hindrance is manifested by the inability of such compounds to form acetyl derivatives.

The well-known difficulty of obtaining dyes from "G" salt in dilute solution is also due to steric hindrance, the effect of which has been illustrated by comparing the rates at which "G" and "R" salts respectively unite with diazonium compounds under identical conditions.

Hewitt and Mitchell have recently published the results of experiments on the mobility of the halogen atom in 1-bromo- β -naphthol, in which they have shown that the bromine atom is almost instantaneously displaced by diazo-complexes in alkaline solution. Owing to steric hindrance, 1-bromo- β -naphthol-8-sulphonic acid does not react with diazonium salts, whereas the halogen in 1-bromo- β -naphthol-6-sulphonic acid is displaced as readily as from 1-bromo- β -naphthol itself.

EXPERIMENTAL.

Sodium p-Toluenediazo- β -aminonaphthalene-8-sulphonate,
 $C_7H_7N_2 \cdot NH \cdot C_{10}H_6 \cdot SO_3Na.$

To a solution containing 8.16 grams of sodium β -naphthylamine-8-sulphonate and excess of sodium acetate in 500 c.c. of water was

slowly added the solution of the diazonium chloride prepared from 3.6 grams of *p*-toluidine. The mixed solutions immediately became dark red; excess of solid sodium acetate was added, and the orange-red precipitate was collected after fifteen hours, well washed with hot water, dried, and crystallised from alcohol. The diazoamine separates from this solvent in yellowish-brown needles, which darken at 215° and melt and decompose at 219°.

0.7000 gave 0.1306 Na_2SO_4 . $\text{Na} = 6.04$.

0.1002 „ 9.9 c.c. moist nitrogen at 18.5° and 772.5 mm. $\text{N} = 11.7$.

$\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_3\text{SNa}$ requires $\text{Na} = 6.3$ and $\text{N} = 11.6$ per cent.

The substance does not develop a characteristic coloration with concentrated sulphuric acid, and is decomposed by cold concentrated hydrochloric acid, the products of fission yielding a red precipitate with an alkaline solution of β -naphthol.

Sodium Benzenediazo- β -aminonaphthalene-8-sulphonate,

This substance is precipitated when equivalent quantities of sodium β -naphthylamine-8-sulphonate and benzenediazonium chloride react in the presence of excess of sodium acetate. From the dark red solution a reddish-brown precipitate separated, which was collected, washed, dried, and rapidly crystallised from hot water. Light yellow crystals were obtained which were sparingly soluble in alcohol, and insoluble in other organic solvents.

0.1332 gave 14.4 c.c. moist nitrogen at 23° and 781 mm. $\text{N} = 12.2$.

$\text{C}_{16}\text{H}_{12}\text{O}_3\text{N}_3\text{SNa}$ requires $\text{N} = 12.0$ per cent.

Potassium Dimethyl- β -naphthylamine-8-sulphonate,

Twenty grams of sodium β -naphthylamine-8-sulphonate and 12 grams of sodium hydroxide were dissolved in 125 c.c. of water and the solution warmed to 50—60° on the water-bath. An excess of dimethyl sulphate (38 grams) was very slowly added; the oily drops rapidly disappeared on shaking and the liquid became appreciably hotter. After cooling, the mixture was extracted once with ether to remove unchanged dimethyl sulphate, then slightly acidified with sulphuric acid and evaporated to a small bulk. After removing the separated sodium sulphate and sodium methyl sulphate, the filtrate was evaporated with absolute alcohol and the residual syrup cooled in a desiccator. A white, crystalline substance was thus obtained which is exceedingly deliquescent, very soluble in water, and quite insoluble in

organic solvents. From these properties the substance is probably very similar to the trimethyl anhydro-salt, $C_6H_4 \langle \begin{smallmatrix} SO_2 \\ NMe_3 \end{smallmatrix} \rangle O$, formed from sulphanilic acid (Griess, *Ber.*, 1879, 12, 2116), which has corresponding physical properties, but it has not yet been obtained in the pure state, a slight residue being left after ignition. When the substance was heated for five hours with concentrated aqueous potassium hydroxide, methyl alcohol was formed, which was removed by distillation and recognised by converting it into methyl salicylate. From the cold alkaline solution, crystals of potassium dimethyl- β -naphthylamine-8-sulphonate were obtained and were purified by repeated crystallisation from water. The salt forms white, anhydrous, lustrous crystals, and is easily soluble in water or alcohol.

0.2775 gave 0.0844 K_2SO_4 . $K = 13.76$.

$C_{12}H_{12}O_3NSK$ requires $K = 13.5$ per cent.

Dimethyl- β -naphthylamine-8-sulphonic acid was obtained by adding concentrated hydrochloric acid to a saturated solution of the potassium salt. The precipitate was recrystallised from hot dilute hydrochloric acid and then twice from water. The acid forms anhydrous white needles and melts at 244° . It is sparingly soluble in cold water, but dissolves readily in hot water or alcohol; the solutions exhibit a beautiful blue fluorescence. The acid does not form a nitroso-compound.

0.1988 gave 10.1 c.c. moist nitrogen at 18° and 764.4 mm. $N = 5.8$.

0.4804 required 19.25 c.c. N/10 KOH. M.W. = 249.5.

$C_{12}H_{12}O_3NS$ requires M.W. = 251 and $N = 5.6$ per cent.

Behaviour with Diazonium Salts.—A solution containing 0.21 gram of *p*-toluidine was diazotised and added to the solution of the equivalent quantity of dimethyl- β -naphthylamine-8-sulphonic acid. By the addition of excess of sodium acetate, a red colour was developed which did not become intensified after five hours. The solution was therefore slowly poured into a cold alkaline solution of β -naphthol, and the red precipitate of *p*-tolueneazo- β -naphthol was collected at the pump on a Gooch crucible, well washed with hot water, and dried at 116° . From the weight of the azo-compound, 0.48 gram, it was calculated that more than 91 per cent. of the diazonium salt had remained uncombined after an interval of five hours.

In a similar experiment with benzenediazonium chloride, 87 per cent. remained unchanged after the same interval of time.

p-Tolueneazo-β-amino-8-nitronaphthalene,
 $C_7H_7N_2 \cdot C_{10}H_5(NH_2)NO_2$.

A solution containing 1·6 grams of *p*-toluidine was diazotised and added to 2·8 grams of 8-nitro-β-naphthylamine dissolved in 700 c.c. of water containing a small quantity of acetic acid. The mixed solutions became faintly turbid, and after the addition of excess of sodium acetate a bright red solution was produced, from which a bulky, flocculent precipitate slowly separated; this was collected, washed, and dried. The substance is very sparingly soluble in organic solvents of low boiling point, and is therefore best purified by crystallisation from ethyl benzoate, from which it separates in reddish-brown needles with a green reflex. The crystals were washed with alcohol to remove the last traces of the solvent, and dried at 100°.

0·1301 gave 22·2 c.c. moist nitrogen at 23° and 740 mm. $N = 18·2$.

$C_{17}H_{14}O_2N_4$ requires $N = 18·3$ per cent.

The substance melts at 253°, develops an intense reddish-violet coloration with concentrated sulphuric acid, is not decomposed by cold concentrated hydrochloric acid, and does not form an acetyl derivative when heated with acetic anhydride in glacial acetic acid solution.

In the hope of obtaining a diazoamine by the use of a diazo-complex of large molecular volume, 8-nitro-β-naphthylamine (2 mols.) was treated with nitrous acid (1 mol.), but after the addition of sodium acetate a dark red precipitate was obtained which gave an intense blue coloration with sulphuric acid, and was not decomposed by cold hydrochloric acid; this was evidently therefore an aminoazo-compound, but was not further examined.

Rate of Reaction of "G" and "R" Salts with Diazonium Salts.

The different behaviour of these isomeric β-naphthol disulphonic acids,

towards diazonium compounds has long been known, but hitherto a strict comparison between the action of the salts under identical conditions has not been instituted. For this purpose a dilute alkaline solution of "G" or of "R" salt was brought into contact with the solution of the diazonium salt, and after definite intervals of time the

amount of uncombined *p*-toluenediazonium chloride was estimated in the form of *p*-tolueneazo- β -naphthol, as previously described.

In the first set of experiments, the following solutions were prepared:

(a) 3.48 grams of "G" salt and 3.5 grams of sodium carbonate in 200 c.c. of water.

(b) A solution of "R" salt of the same composition.

(c) 1.07 grams of *p*-toluidine and 6.5 c.c. of concentrated hydrochloric acid were diazotised with 0.69 gram of sodium nitrite, and the resulting solution made up to 250 c.c.

(d) Five grams each of β -naphthol and potassium hydroxide dissolved in 200 c.c. of water.

The experiments were carried out at 0° in the following way. Fifty c.c. of (a) or of (b) and 50 c.c. of (c) were thoroughly mixed, and after definite intervals of time 10 c.c. of the mixture were run into 50 c.c. of (d); the precipitate of *p*-tolueneazo- β -naphthol was collected, washed, and weighed. The results are expressed in the table, in which the second and third columns give the weight of *p*-tolueneazo- β -naphthol and the percentage of uncombined diazonium salt respectively for the solution containing the "G" salt, and the fourth and fifth columns the corresponding data for the "R" salt.

Time in minutes.	II.	III.	IV.	V.
0	0.0486	100.0	0.0486	100.0
2	0.0480	98.8	0.0032	6.6
5	0.0466	95.8	nil	
10	0.0415	84.4	"	
20	0.0402	82.8	"	
120	0.0354	72.8	"	
14 hours	0.0190	39.0	"	

In this series of experiments a viscous precipitate separated directly the solutions of the "R" salt and of the diazonium chloride were mixed, a proceeding which may have tended to vitiate the comparison. A second series was therefore performed with the following solutions:

(a) 3.48 grams of "G" salt in 500 c.c. of water.

(b) 3.48 grams of "R" salt in 500 c.c. of water.

(c) A solution made by diazotising 1 gram of *p*-toluidine and diluting to 500 c.c.

(d) A solution containing 0.0144 gram each of β -naphthol and potassium hydroxide per c.c.

Two hundred c.c. of (a) or of (b) were mixed with 30 c.c. of *N*-sodium carbonate solution and 200 c.c. of (c). A precipitate did not separate. After definite intervals 50 c.c. of the mixed solutions were added to 20 c.c. of (d) and the precipitated azo-compound treated as before.

Time in minutes.	II.	III.	IV.	V.
0	0.1131	100.0	0.1134	100.0
5	0.1062	94.0	0.0143	12.6
15	0.0956	84.5	nil	
180	0.0873	77.2	„	
24 hours	0.0351	31.0	„	

These figures indicate very clearly the steric hindrance produced by the presence of the SO_3H group in position 8.

Sodium 1-Bromo- β -naphthol-8-sulphonate.

A cold saturated aqueous solution containing 25 grams of sodium β -naphthol-8-sulphonate (1 mol.) was slowly treated with 16 grams (1 mol.) of bromine. The halogen quickly disappeared, and the solution became warm and acquired a dark green colour which changed to reddish-brown. After several hours the brown precipitate, which showed an acid reaction, was collected, washed once with a strong solution of sodium hydroxide, and thrice recrystallised from water, whereby the substance was obtained in colourless, glistening leaflets which turn brown in the air.

1.2106 lost 0.1667 at 110° . $\text{H}_2\text{O} = 13.8$.

$\text{C}_{10}\text{H}_6\text{O}_4\text{BrSNa} \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 14.2$ per cent.

0.3689, dried at 110° , gave 0.2104 AgBr. Br = 24.3.

$\text{C}_{10}\text{H}_6\text{O}_4\text{BrSNa}$ requires Br = 24.6 per cent.

Behaviour with p-Toluenediazonium Chloride.—A solution containing 0.9 gram of the anhydrous salt was treated with the diazonium chloride obtained from 0.3 gram of *p*-toluidine. After the addition of sodium acetate the mixture was thoroughly stirred. The colour of the solution did not change for several hours, when it became red. After five minutes, three hours, and nine hours respectively, 25 c.c. of the solution were added to an alkaline solution of β -naphthol, and the weights of the washed and dried *p*-tolueneazo- β -naphthol were:

0.1230	gram after 5 minutes
0.1232	„ 3 hours
0.1226	„ 9 „

Evidently the group in position 8 had completely hindered the elimination of the halogen by the diazonium salt. For comparison, sodium 1-bromo- β -naphthol-6-sulphonate was treated with *p*-toluene diazonium chloride, when, after the addition of sodium acetate, a dark red solution was immediately obtained, from which excess of sodium acetate precipitated the sodium salt of an azo-compound which was free from halogen. The free acid was dark red in colour, whereas

p-tolueneazo- β -naphthol-6-sulphonic acid prepared directly from its constituents forms bright red crystals with a green reflex. This difference, together with the fact that benzeneazo- β -naphthol, obtained from 1-bromo- β -naphthol and benzenediazonium chloride, is very difficult to crystallise, makes it advisable to examine more thoroughly the elimination of the halogen from brominated naphthols by diazonium salts.

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