162. *The Preparation of Symmetrical Azo-compounds, the Positional Influence of the Nitro-group on the Decomposition of Nitronaphthalenediazonium Sulphates by Cuprous Hydroxide, and an Improved Method for the Production of 2-Nitronaphthalene.*

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The decomposition of diazonium salts in sulphuric acid solution with cuprous hydroxide depends on the positivity of the carbon atom to which the diazo-group is attached. When the positivity is very great, as in 2-nitronaphthalene-1-diazonium sulphate, replacement of the diazo-group by hydrogen occurs and a yield of 85% of 2-nitronaphthalene has been obtained. Gradations of positivity are well exemplified in the decomposition of the diazonium salts from substituted nitronaphthylamines with resulting variations of the predominant product, namely, symmetrical azo-compound (minimum positivity), dinaphthyl (medium positivity), and nitronaphthalene (maximum positivity). The mechanisms of the various reactions are discussed.

THE chief types of reaction to be expected from the decomposition of diazotised amines in sulphuric acid solution by cuprous hydroxide are: (1) Replacement of the diazo-group by hydrogen; (2) production of a diaryl; (3) formation of a symmetrical azo-compound; (4) the competing reaction of anionoid water to form a phenol. The formation of an arylhydrazine seems to be excluded owing to the presence of copper sulphate. All the types may occur simultaneously, as in the decomposition of 4-nitronaphthalene-1-diazonium sulphate.

The prevailing type of decomposition in any one case appears to be related to the degree of positivity of the carbon atom to which the diazo-group is attached (cf. also Hodgson, Birtwell, and Walker, J., 1941, 770). Gradations of positivity are well exemplified in the diazonium salts of substituted naphthylamines (see Table), where replacement of the diazo-group is greatest for maximum positivity as in 2-nitro-1-naphthylamine; formation of symmetrical azo-compound predominates when the positivity is relatively much smaller, as in diazotised 5-nitro-1-naphthylamine and the monochloronaphthylamines; and dinaphthyl formation occurs with intermediate values, as in 8-nitro-1- and 1-nitro-2-naphthylamines. α-Naphthylamine gave small amounts of naphthalene and naphthol together with a tar which could not be further resolved. From 2-nitro-1-naphthylamine, a yield of 85% of 2-nitronaphthalene has been obtained.

The experimental data recorded favour the non-ionic theory of decomposition advanced by Grieve and Hey (J., 1934, 1797) and Waters (J., 1937, 2007; 1938, 843, 1077). In all the reactions now described, the cuprous hydroxide can only function as a reducing agent and not as a catalytic substance, since it dissolves in the aqueous sulphuric acid to become cupric sulphate with electron-release to the diazonium salt. The acceptance of this electron by the diazonium group can involve either (*a*) its scission from the aryl carbon atom as a nitrogen molecule, $:\!N\equiv N\!:$, thereby leaving an aryl radical, $\geqslant C\cdot$, which can combine with another to form a diaryl, or (*b*) its rearrangement with formation of a diazo-radical $\geqslant C-\ddot{N}=\ddot{N}\cdot$, which can then combine with an aryl radical (*a*) previously formed to give a symmetrical azo-compound $\geqslant C-\ddot{N}=\ddot{N}=C\leqslant$. Alternatively the diazonium radical may be formed from the diazo-component of the system,

$$\geqslant C-\overset{\oplus}{N}\equiv N\!: \rightleftharpoons \geqslant \overset{\delta+}{C}-N=\overset{\delta+}{N}-\overset{\delta-}{SO_4}H \text{ (see later).}$$

The formation of such a diazo-radical (*b*) and its subsequent combination with an aryl radical (*a*) will depend upon the electron restraint exercised by the substituent group or groups, *i.e.*, upon the degree of positivity of the carbon atom. Where this is great, as in diazotised 2-nitro- and 2 : 4-dinitro-naphthylamine, it is doubtful whether diazo-radical (*b*) is formed at all, since azo-formation has never been observed. Similarly for a somewhat lower though still high degree of positivity as in 8-nitro- and 2-nitro-1-naphthylamine the formation of (*b*) is also doubtful, and in both cases the diazo-group is probably kept in the diazonium structure by the powerful inductive ($-I$) effects of the substituents. In these compounds also, the aryl radicals formed after evolution of the nitrogen have their odd electron so restrained that in the former case only nascent hydrogen will form a pair with it, whereas with slightly less restraint the radicals (*a*) can combine. On the other hand, when the electron restraint is small or even reversed, the diazo-radical (*b*) can exist for a sufficient period to unite with radical (*a*). The positivity in 2-nitronaphthalene-1-diazonium sulphate is found experimentally to be greater than that in 1-nitronaphthalene-2-diazonium sulphate; this must be due to the unrestricted negative ($-I$) inductive effect of the second nucleus in the 2-nitro-compound (cf. Hodgson and Elliott, J., 1935, 1850; *J. Soc. Dyers and Col.*, 1938, **54**, 264).

Saunders ("The Aromatic Diazo-Compounds," 1936, p. 149) suggests that azo-compounds are probably formed during the decomposition of diazo-compounds "by a process exactly analogous to the coupling reaction, the loss of a diazo-group in one nucleus leaving a charged pole equivalent to that para to the hydroxyl group in a phenol, and to this an undecomposed diazo-molecule attaches itself." Such an ionic point of view is invalidated by the fact of diaryl or dinaphthyl formation in certain circumstances, particularly when a nitro-group is present. Such a group should promote the formation of the negative ion (see above), and thereby prevent diaryl (or dinaphthyl) formation, which requires the combination of free radicals. Further, the negative-ion theory demands the replacement of the diazo-group by the hydrogen ion and by positive chlorine in the Sandmeyer reaction, whereas actually the reducing agent supplies atomic (nascent) hydrogen and the cuprous chloride complex supplies either neutral or negative chlorine, none of which would combine with negative carbon.

In the benzene series, azo-formation is predominant throughout, and with diazotised *o*- and *p*-nitroaniline, where no diaryl formation has been observed, the results are in striking contrast to those of Niementowski (*Ber.*, 1901, **34**, 3325) and Ullmann and Forgan (*ibid.*, p. 3802), who, by using copper bronze or even copper chloride in hydrochloric acid solution, obtained considerable yields of 2 : 2′-dinitrodiphenyl from diazotised *o*-nitroaniline. When water is present in minimum amount, diaryl formation is completely suppressed (Hodgson and Walker, J., 1933, 1620). In the benzene series, notwithstanding the presence of the nitro-group, the significant carbon atom is much less positive than that in the naphthalene series owing to the greater electronic mobility in the benzene nucleus for relief of electronic strain. From diazotised *m*-nitroaniline, both diaryl and azo-compounds were obtained, and this would indicate a more even distribution of diazonium and diazo-forms in the equilibrium mixture. The nature and the concentration of the acid are thus important factors in the type of reaction favoured.

The yields of the various products are almost independent of the mode of treatment by the cuprous hydroxide, *i.e.*, whether the diazo-solution is added to it or vice versa.

In the course of this work, the experiments of Scholl, Seer, Weitzenböck, and Ertl (*Monatsh.*, 1921, **42**, 405) were confirmed, *viz.*, the formation of 5 : 5′-dinitro-1 : 1′-dinaphthyl by the action of copper on 1-iodo-5-nitronaphthalene. This observation is definitely opposed to the generalisation of Chudŏzilov (*Chem. Listy*, 1925, **19**, 187; cf. also Cumming and Howie, J., 1931, 3176) with respect to the unique homonuclear activity of the iodonitronaphthalenes, as also is the preparation of 8 : 8′-dinitro-1 : 1′-dinaphthyl by the action of copper on 1-iodo-8-nitronaphthalene (Hodgson and Crook, J., 1937, 571).

1 : 2-, 2 : 1-, and 1 : 4-Chloronaphthylamines give colour reactions with ferric chloride by which they may be distinguished. 2-Chloro-1-naphthylamine is much more steam-volatile than 1-chloro-2-naphthylamine.

EXPERIMENTAL.

Preparation of the Chloronaphthylamines.—Reduction of the chloronitronaphthalenes by stannous chloride in concentrated hydrochloric acid, by iron and acetic acid, or by West's method (J., 1925, **127**, 494) gave very similar yields (80—90%).

Steam-volatility of the Chloronaphthylamines and their Colours with Aqueous Ferric Chloride.—2-Chloro-1-naphthylamine : 3·9 g. per l. of distillate; orange-brown. 1-Chloro-2-naphthylamine : 1·7 g. per l.; greyish-violet (β-naphthylamine gave a brown colour). 4-Chloro-1-naphthylamine : 1·6 g. per l.; blue (α-naphthylamine gave a deep blue).

Decomposition of Diazonium Sulphates by Cuprous Hydroxide.—Preparation of the cuprous hydroxide. A well-stirred solution of cuprous chloride (20 g.) in hydrochloric acid (75 c.c., *d.* 1·16), was treated gradually at 0° with 20% aqueous sodium hydroxide until it was just alkaline to litmus. After 30 minutes' stirring, the cuprous hydroxide was washed by decantation until free from chloride and alkali and suspended in about 100 c.c. of water (the minimum for efficient stirring during decomposition).

Preparation of the diazo-solutions. These were made either directly, *e.g.*, the suspension of fine crystals obtained from 5-nitro-1-naphthylamine (2 g.), sulphuric acid (10 c.c., *d* 1·84), and water (40 c.c.) was diazotised with sodium nitrite at 5—10°, or by Hodgson and Walker's method (J., 1933, 1620).

Decomposition. The diazo-solution was stirred at room temperature into the cuprous hydroxide suspension; the temperature rose to 28—30° and nitrogen was evolved. The mixtures were kept until coupling with alkaline β-naphthol no longer occurred. In the cases where the phenols or naphthols were not steam-volatile, the precipitates were filtered off and extracted with aqueous ammonia, and the residues steam-distilled; in others, the reaction mixtures were steam-distilled without previous treatment.

2 : 2'-*Dichloro*-1 : 1'-*azonaphthalene*, was prepared for comparison by direct diazotisation of 2-chloro-1-naphthylamine (5 g.) in hydrochloric acid (50 c.c., *d* 1·16) and water (20 c.c.), destruction of the mineral acid by sodium acetate crystals, and immediate addition of crystallised sodium sulphite (10 g.) in water (50 c.c.). The mixture was kept at room temperature for 30 minutes, heated to 60°, and cooled. The azonaphthalene crystallised from alcohol in red plates, m. p. 173—174° (Found: N, 8·0; Cl, 20·1. $C_{20}H_{12}N_2Cl_2$ requires N, 8·0; Cl, 20·2%), which gave a blue colour with concentrated sulphuric acid.

1 : 1'-*Dichloro*-2 : 2'-*azonaphthalene*, similarly prepared from 1-chloro-2-naphthylamine, crystallised from alcohol in orange-yellow plates, m. p. 170—171° (Found : N, 8·1; Cl, 20·0%), which gave a red colour with concentrated sulphuric acid.

4 : 4'-Dichloro-1 : 1'-azonaphthalene, prepared from 4-chloro-1-naphthylamine, crystallised from benzene or glacial acetic acid in small reddish-brown needles, m. p. 262—263° (Found : N, 8·2; Cl, 20·2%), which gave an ultramarine-blue colour with concentrated sulphuric acid.

Reactions of 5-*Nitro*-1-*naphthalenediazonium Sulphate.*—(a) *With copper paste.* The fine suspension obtained by chilling a solution of 5-nitro-1-naphthylamine (3·2 g.) in boiling sulphuric acid (20 c.c., *d* 1·84) and water (200 c.c.) was diazotised with sodium nitrite (2 g. in 10 c.c. of water). After 1 hour the liquid was filtered, nitrous acid destroyed by urea, and copper paste [freshly prepared from hot crystallised copper sulphate (30 g.) in water (200 c.c.) and zinc dust (10 g.) and washed by decantation] added. Nitrogen was evolved immediately, and the decomposition was completed on the water-bath. Steam-distillation removed 1-nitronaphthalene (0·2 g.); the residue consisted of a very small amount of 5-nitro-1-naphthol (extracted by alkali) and 5 : 5'-dinitro-1 : 1'-azonaphthalene (0·9 g.), which was extracted by boiling benzene.

(b) *With copper bronze* (5 g.). The products were 1-nitronaphthalene (0·2 g.), 5 : 5'-dinitro-1 : 1'-azonaphthalene (1·4 g.), and 5-nitro-1-naphthol (small amount, not estimated).

(c) *With copper bronze* (5 g.) *and ethyl alcohol* (50 c.c.). The diazo-solution (a) yielded α-nitronaphthalene (1·05 g.); the other products were not identified.

(d) *With cuprous hydroxide.* See Table.

Table of Individual Decompositions.

Amine diazotised (g.).	Azo-compound, g.	Azo-compound, %.	Phenol or naphthol, g.	Phenol or naphthol, %.	Deaminated product, g.	Deaminated product, %.	Remarks.
Aniline (3·4)	1·1	33·0	0·9	26·5	0·8	27·5	
o-Chloroaniline (2·2)	1·75	80·0	Trace	—	Trace	—	
m-Chloroaniline (3·2)	None	—	0·9	28·0	,,	—	1 G. of *mm'*-dichlorodiphenyl (35%)
p-Chloroaniline (2·2)	1·5	70·0	0·4	31·0	,,	—	
o-Nitroaniline (3·4)	1·2	35·0	Trace	—	1·2	39·5	
m-Nitroaniline (3·4)	See remarks		,,	—	0·5	13·0	→ Fractional crystallisation from a mixture of equal parts of methy alcohol and glacial acetic acid indicated the bulk of the product to be *mm'*-dinitroazobenzene and *mm'*-dinitrodiphenyl
p-Nitroaniline (3·4)	1·2	35·0	0·45	13·0	0·25	8·0	
β-Naphthylamine (3·6)	1·9	54·0	Trace	—	1·1	34·0	
2-Chloro-1-naphthylamine (2·2) ...	1·4	65·0	,,	—	0·5	25·0	
1-Chloro-2-naphthylamine (2·2) ...	1·9	87·5	,,	—	Trace	—	
4-Chloro-1-naphthylamine (2·2) ...	1·7	78·3	,,	—	,,	—	
2-Nitro-1-naphthylamine (2·3) ...	None	—	,,	—	1·8	85·0	
1-Nitro-2-naphthylamine (2·3) ...	,,	—	,,	—	0·2	10·0	1·35 G. of 1 : 1'-dinitro-2 : 2'-dinaphthyl
4-Nitro-1-naphthylamine (2·3) ...	Trace	—	0·75	32·5	0·65	31·0	
5-Nitro-1-naphthylamine (2·3) ...	0·8	40·5	0·3	15·0	0·8	42·0	

5 : 5'-*Dinitro*-1 : 1'-*azonaphthalene*, which was also prepared by the sulphite method described above, crystallised from boiling nitrobenzene in yellowish-brown needles, m. p. 322—323° (Found : N, 15·2. $C_{20}H_{12}O_4N_4$ requires N, 15·1%), which were obtained in orange-yellow needles, m. p. 322—323°, by sublimation. It was sparingly soluble in boiling alcohol, glacial acetic acid, and benzene; the colour with concentrated sulphuric acid was reddish-violet, which changed to yellow on heating.

5 : 5'-*Dinitro*-1 : 1'-*dinaphthyl*.—5-Iodo-1-nitronaphthalene (3 g.) [purified by vacuum sublimation and by crystallisation from alcohol; small yellow needles, m. p. 165° (Scholl, Seer, Weirzenböck, and Ertl, *loc. cit.*, give m. p. 164°)] was heated with copper bronze at 220—230° for 90 minutes. The material extracted by boiling benzene was recovered and extracted repeatedly with ether to remove unchanged 5-iodo-1-nitronaphthalene. The residual 5 : 5'-dinitro-1 : 1'-dinaphthyl (0·95 g.) crystallised from glacial acetic acid (charcoal) in light brown plates, m. p. 228—229° (Scholl, Seer, Weitzenböck, and Ertl give m. p. 228—228·5°) (Found : N, 8·2. Calc. : N, 8·1%).

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