83. *Some Reactions of the Diazonium Salts of Certain Arylazo-β-naphthylamines.*

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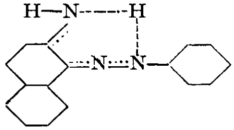
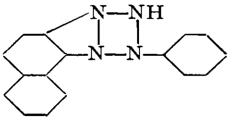
Three methods are described for the preparation of the solid diazonium salts of arylazo-β-naphthylamines. Some of Zincke's work in this field has been confirmed and an alternative explanation of the formation of the diazonium salts is proposed. A revised formula is suggested for the stannous chloride reduction product of 1-benzeneazo-2-naphthalenediazonium chloride. The preparation of arylazo-β-naphthalenediazonium perbromides and their decomposition by glacial acetic acid to 2-bromo-1-arylazonaphthalenes is described.

The condition of the amino-group in arylazo-β-naphthylamines is probably best represented as an example of hydrogen bonding (I), although under certain conditions it may be diazotised (cf. Nietzki and Goll, *Ber.*, 1886, **19**, 1281). Zincke (*Ber.*, 1887, **20**, 2897) found that, though the diazonium chloride of benzeneazo-β-naphthylamine yielded a perbromide, it nevertheless behaved anomalously towards stannous chloride or sulphur dioxide in that it was converted into a white non-basic compound (II), which could be acetylated but was reconverted by acid oxidising agents into the diazonium salt. Some of Zincke's work has now been confirmed and extended,

(I.)





(II.)

whereby an alternative explanation of the formation of the diazonium salts has been derived, and of the action of stannous chloride upon them.

Diazonium salts have been formed from a series of arylazo-β-naphthylamines by three methods : (1) By the addition of solid sodium nitrite to a glacial acetic acid solution of the amine containing hydrochloric acid. It is essential to use only the amount of hydrochloric acid stated in the experimental part, otherwise cleavage of the arylazo-β-naphthylamine may occur during diazotisation, *e.g.*, in the cases of benzeneazo-β-naphthylamine and 1-naphthaleneazo-β-naphthylamine. A test for this cleavage is afforded by bromine in glacial acetic acid, whereby an orange-brown precipitate is obtained which no longer gives a colour reaction with concentrated sulphuric acid and therefore does not contain an azo-group; furthermore, decomposition of the perbromide by hot glacial acetic acid gives a colourless product. The cleavage of the arylazo-β-naphthylamine produces β-naphthylamine, which is subsequently diazotised in the reaction mixture and so gives rise to a second diazonium perbromide. The diazo-solutions obtained by the above method are not very stable, inasmuch as the water present in the acid soon decomposes them with formation of arylazo-β-naphthol. The free diazonium salt isolated by addition of alcohol and ether to the well-cooled solution is obtained in moderate yield and is contaminated with arylazo-β-naphthol.

(2) The solid azo-compound is made into a paste with nitrosylsulphuric acid at 0° and stirred during the gradual addition of glacial acetic acid. A good yield of solid diazonium salt is obtained and the formation of arylazo-β-naphthol is reduced to a minimum, but the method is of limited utility.

(3) As a variant of (2), arylazo-β-naphthylamine, dissolved or suspended in glacial acetic acid, is added to well-stirred nitrosylsulphuric acid at 18°.

Methods (2) and (3) fail with arylazo-β-naphthylamines which, as primary component, have either free amines or those with *op*-directing substituents except chlorine; here cleavage of the azo-compound ensues as in (1).

The above compounds behave like true diazonium salts in the following respects :

(*a*) The diazo-group is replaced by hydroxyl with great ease by a very small amount of water. Previous statements (this vol., p. 30) that arylazo-β-naphthols and their acetates are produced in the decomposition of arylazo-β-naphthylamines by sodium nitrite and glacial acetic acid at 70°, the former by hydrolysis of the latter, must be modified in view of the present work, inasmuch as two simultaneous reactions appear to be taking place, *viz.* (i) the decomposition of the diazonium group by the water produced in the actual diazotisation, and (ii) attack of the diazonium salt by the acetate anion and/or by polarised acetic acid.

(*b*) In fifteen cases arylazo-β-naphthyl acetates are obtained when the diazo-acetate is decomposed in glacial acetic acid solution; this, however, is not a general reaction.

(*c*) They react readily with bromine in glacial acetic acid to form diazo-perbromides, which behave like other perbromides in that on heating with glacial acetic acid the diazo-group is replaced by bromine with evolution of nitrogen.

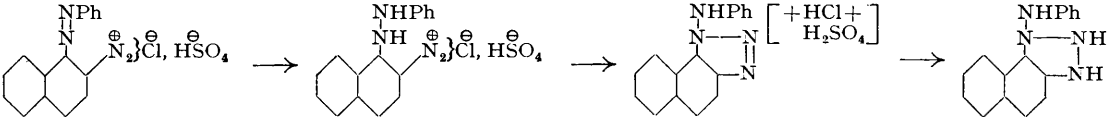
(*d*) Stable double salts are formed by the diazonium chlorides with zinc chloride and platinum chloride.

The points of difference between these salts and ordinary diazonium compounds are :

(*e*) They do not couple with phenol or β-naphthol (four different methods have been tried).

(*f*) They do not form hydrazines on reduction with stannous chloride.

These differences can be accounted for, (*e*) by the ease with which the diazo-group is replaced by hydroxyl, since diazo-compounds already containing an azo-group couple slowly and in many cases decompose before coupling (cf. Saunders, " The Aromatic Diazo-compounds and their Technical Applications," E. Arnold and Co., London, 1936, p. 115), and (*f*) by reduction of the arylazo-β-naphthalenediazonium salt according to the reactions depicted in (III). The diazonium salt (III*a*) is reduced to an arylhydrazo-β-naphthalenediazonium salt (III*b*), internal coupling follows similar to that which occurs when *o*-diamines are treated with nitrous acid (III*c*), and finally reduction to an internal colourless compound (III*d*) takes place.



(III*a*.) (III*b*.) (III*c*.) (III*d*.)

The structure (III*d*), containing a 5-membered ring, for the reduction product of benzeneazo-β-naphthalenediazonium chloride is more probable than that assigned by Zincke (II) containing a 4-membered nitrogen ring. The structure (III*d*) also readily accounts for the regeneration of the original benzeneazo-β-naphthalenediazonium salt by acid oxidising agents and the formation of a diazonium perbromide by bromine in acetic acid.

EXPERIMENTAL.

Preparation of Arylazo-β-naphthalenediazonium Salts.—(1) The arylazo-β-naphthylamine (3 g.) was heated to boiling with glacial acetic acid (20 c.c.), and the mixture stirred until room temperature was attained; hydrochloric acid (3 c.c., *d* 1·16) was then added, and the resulting paste agitated vigorously during the gradual addition of the calculated quantity of powdered sodium nitrite and for 15 minutes afterwards. The solution so obtained was rapidly filtered and diluted with alcohol–ether (1 : 1); on strong cooling, the diazonium chloride, contaminated with some arylazo-β-naphthol, was precipitated in moderate yield.

(2) The suspension obtained by cooling 2 : 5-dichlorobenzeneazo-β-naphthylamine (3 g.) in hot glacial acetic acid

(50 c.c.) was added portionwise to a well-stirred solution of sodium nitrite (0·8 g.) in concentrated sulphuric acid (10 c.c.) at 18—20°. After 30 minutes the dark red paste of diazonium sulphate was diluted with ether (100 c.c.), cooled to $-5°$, stirred for 15 minutes, collected, washed with ether, and dried over sulphuric acid in a vacuum desiccator. The yield was good, but the diazonium salt was contaminated with inorganic material. It gave a red-brown colour with concentrated sulphuric acid, which turned orange-red on dilution.

(3) Finely powdered 4-nitrobenzeneazo-β-naphthylamine (3 g.) was added gradually to a well-agitated solution of sodium nitrite (0·75 g.) in concentrated sulphuric acid (10 c.c.) at 0°; to the paste obtained, glacial acetic acid (30 c.c.) was added below 20° during 15 minutes. The diazonium sulphate was isolated as in (2).

The diazonium sulphates from the following arylazo-β-naphthylamines have been isolated by methods (2) and (3): *o*-chlorobenzeneazo-, *p*-chlorobenzeneazo-, 3-nitro-4-methyl-benzeneazo-, and 2-nitro-4-methylbenzeneazo-β-naphthylamine. They are deep red or red-brown powders which are stable when dry.

Decomposition of Arylazo-β-naphthalenediazonium Sulphates.—(a) *By water.* 4-Nitrobenzeneazo-β-naphthalenediazonium sulphate (1 g.) was suspended in glacial acetic acid (15 c.c.) and water (2 c.c.); an immediate slow evolution of nitrogen occurred, which was accelerated by heating, and a red substance separated. After the evolution ceased, sufficient glacial acetic acid was added to dissolve the product when the mixture was boiled; on cooling, red-brown needles of 4-nitrobenzeneazo-β-naphthol separated, m. p. and mixed m. p. 250° (Rowe and Levin, *J. Soc. Dyers and Col.*, 1924, **40**, 220, give m. p. 250°). The yield was quantitative (Found : N, 14·1. Calc. for $C_{16}H_{11}O_3N_3$: N, 14·3%).

2 : 5-Dichloro-, *p*-chloro-, *o*-chloro-, 2-nitro-4-methyl-, and 3-nitro-4-methyl-benzeneazo-β-naphthalenediazonium sulphates similarly afforded theoretical yields of the corresponding azo-β-naphthols. The compositions of the products were confirmed by comparison with authentic specimens in conjunction with micro-analyses for nitrogen. It was not necessary to isolate the diazonium salt in any of the three methods given; addition of water to the diazo-solution was sufficient to cause decomposition with formation of the arylazo-β-naphthol.

(b) *By ethyl alcohol.* 2 : 5-Dichlorobenzeneazo-β-naphthalenediazonium sulphate (0·5 g.) was refluxed with sufficient alcohol (40 c.c., not rendered anhydrous) to effect solution of the 2 : 5-dichlorobenzeneazo-β-naphthol formed; this crystallised, on cooling, in red, disc-like clusters, m. p. and mixed m. p. 184° (Found: N, 9·0. Calc. for $C_{16}H_{10}ON_2Cl_2$: N, 8·8%).

(c) *By stannous chloride.* *o*-Chlorobenzeneazo-β-naphthylamine (3 g.) was diazotised by method (2) or (3); when the resulting paste of diazonium sulphate was treated at 0° with a solution of crystallised stannous chloride (7 g.) in hydrochloric acid (30 c.c., *d* 1·16), a dark red precipitate formed. This dissolved when a further addition of stannous chloride (7 g.) in hydrochloric acid (30 c.c., *d* 1·16) was made and the well-stirred mixture heated on the water-bath. The yellowish-green liquid was filtered and diluted with ice-water. The precipitate thus obtained separated from toluene in colourless needles, m. p. 196° (decomp. at 197°) (Found : N, 19·2. $C_{16}H_{13}N_4Cl$ requires N, 18·9%).

Benzeneazo-β-naphthylamine, when diazotised and treated in the same way, yielded Zincke's white compound (*loc. cit.*), which, after purification with alcohol, crystallised from toluene in colourless needles, m. p. 204° (Zincke gives m. p. 204—205°).

(d) *By sodium sulphite.* When the diazo-solution prepared from *o*-chlorobenzeneazo-β-naphthylamine was treated with excess of sodium sulphite solution and heated, nitrogen was evolved. The *o*-chlorobenzeneazo-β-naphthol obtained crystallised from toluene in orange leaflets, m. p. and mixed m. p. 167°.

Preparation of Arylazo-β-naphthalenediazonium Perbromides.—A typical procedure is as follows: 2 : 5-Dichlorobenzeneazo-β-naphthylamine (3 g.), dissolved in glacial acetic acid (80 c.c.), is treated with hydrochloric acid (10 c.c., *d* 1·16) below 20°, followed by finely powdered sodium nitrite (0·8 g.) added portionwise with vigorous stirring. After 15 minutes the filtered solution is treated with bromine (2 c.c.) in glacial acetic acid (20 c.c.), the well-agitated solution kept for a further 15 minutes, and the precipitated perbromide then removed.

The following compounds were thus converted into perbromides : benzeneazo-, *p*-bromobenzeneazo-, *m*-chlorobenzeneazo-, *p*-chlorobenzeneazo-, and 2-nitro-4-methylbenzeneazo-β-naphthylamines. The yields in all cases were good.

Decomposition of Arylazo-β-naphthalenediazonium Perbromides by Glacial Acetic Acid.—2 : 5-Dichlorobenzeneazo-β-naphthalenediazonium perbromide (2 g.) was added portionwise to hot glacial acetic acid (25 c.c.), and the mixture boiled until evolution of nitrogen ceased. The hot filtered solution, on cooling, deposited red needles of 2-*bromo*-1-2′ : 5′-*dichlorobenzeneazonaphthalene*, m.p. 138°. Yield, 1·27 g. (95%) (Found : N, 7·55. $C_{16}H_9N_2Cl_2Br$ requires N, 7·4%).

2-*Bromo*-1-3′-*chlorobenzeneazonaphthalene*, prepared by the above method, crystallised from glacial acetic acid in red needles, m. p. 123° (Found : N, 8·4. $C_{16}H_{10}N_2ClBr$ requires N, 8·1%).

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