8. *The Decomposition of Arylazo-β-naphthylamines by Sodium Nitrite and Glacial Acetic Acid.*

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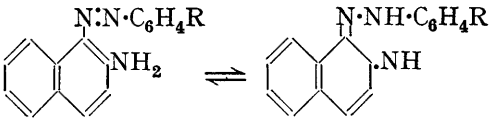
Twenty-nine arylazo-β-naphthylamines have been decomposed by sodium nitrite in the presence of hot glacial acetic acid. The products are usually mixtures of the arylazo-β-naphthyl acetate and the arylazo-β-naphthol, but some of the amines having electron-attracting substituents in the *o*-position of the aryl residue give the arylazo-β-naphthol only. The mechanism of the general reaction is discussed.

Although the substances formed when diazonium compounds react with β-naphthylamine behave like diazoamino-derivatives towards hydrochloric acid (Lawson, *Ber.*, 1885, **18**, 796), it has long been established that they are aminoazo-compounds; the presence of the amino-group, however, has always been difficult to prove. Meldola (J., 1884, **45**, 117), after a study of the action of nitrous acid on

m-nitrobenzeneazo-β-naphthylamine, concluded that a nitroso-derivative was formed and that the amino-group was not present, but Meldola and East (J., 1886, **49**, 463) reported that the nitroso-compounds were in fact acetates, and that the action of sodium nitrite in the presence of acetic acid (glacial) on the foregoing β-naphthylamine derivative and on *p*-nitrobenzeneazo-β-naphthylamine was to displace the amino-group by the acetoxy-group, possibly by the intermediate formation of an unstable diazonium compound.

Zincke and Lawson (*Ber.*, 1887, **20**, 2896), however, describe the actual diazotisation of benzeneazo-β-naphthylamine and some reactions of the diazonium salts, so under the conditions employed the amino-group must have been present; no mention, however, is made of coupling, *e.g.*, with alkaline β-naphthol. In view of the difficulties encountered in diazotising azo-β-naphthylamine compounds,



the current view that there is tautomerism between the aminoazo- and the iminohydrazone structure, with a preponderance of the latter form, is doubtless correct; under special conditions the amino-group can be detected, and its diazotisation performed.

In continuation of this study, Meldola's work has been confirmed for *m*- and *p*-nitrobenzeneazo-β-naphthylamines and extended to 27 other β-naphthylamine derivatives (Table I). Some of the amines, and in particular those with electron-attracting groups, readily yield the acetoxy-compounds

TABLE I.

Arylazo-β-naphthylamines.

The colour produced by concentrated sulphuric acid is given after the analysis, and for a known compound after the reference.

Diazotised amine.	Crystalline form and solvent.	M. p.	% N found.	% N required.	Reference.
m-Fluoroaniline	Orange leaves, dilute alcohol	85°	16·1	15·9	(Violet)
Aniline	Red needles, glacial acetic acid	103	—	—	Lawson, *Ber.*, 1885, **18**, 798, gives m. p. 102 104° (Red-violet)
p-Toluidine	Orange hexagonal prisms, methyl alcohol	114	—	—	Norman, J., 1912, **101**, 1919, gives m. p. 112° (Red-violet)
p-Chloroaniline	Scarlet prisms, glacial acetic acid	116	—	—	Meldola, Forster, J., 1891, **59**, 690, give m. p. 116° (Blue-violet)
p-Fluoroaniline	Orange-red plates, alcohol	120	16·1	15·9	(Red-violet)
o-Toluidine	Deep red parallelepipeds, alcohol	126	—	—	Fischer, *J. pr. Chem.*, 1921, **104**, 113, gives m. p. 125—126° (Red-violet)
p-Anisidine	Deep orange prisms, glacial acetic acid	132—133	—	—	Charrier, Ferreri, *Gazetta*, 1913, **43**, ii, 231, give m. p. 127° (Red-violet)
o-Anisidine	Deep red prisms, alcohol	134	—	—	Sachs, *Ber.*, 1885, **18**, 3130, gives m. p. 133°
p-Bromoaniline	Bright red needles, alcohol	135	—	—	Meldola, Forster, J., 1891, **59**, 697, give m. p. 129° (Violet-red)
o-Chloroaniline	Red needles, glacial acetic acid	142	—	—	Meldola, Forster, J., 1891, **59**, 690, give m. p. 135° (Blue-violet)
β-Naphthylamine	Brown needles, xylene	149	—	—	Norman, J., 1919, **115**, 675, gives m. p. 151° (Blue-violet)
α-Naphthylamine	Dark brown microscopic needles, alcohol	154	—	—	Lawson, *Ber.*, 1885, **18**, 2422, gives m. p. 149° (Blue)
m-Chloroaniline	Red needles, glacial acetic acid	160	15·1	14·9	Elter, *Gazzetta*, 1915, **45**, ii, 315, gives m. p. 154° (Greenish-blue)
2 : 5-Dichloroaniline	Red needles, glacial acetic acid	168	13·5	13·3	(Blue-violet)
p-Iodoaniline	Small red-brown prisms, alcohol	170	11·5	11·3	(Blue)
p-Nitroaniline	Gold needles, alcohol	180	—	—	(Blue)
m-Nitroaniline	Orange needles, alcohol	182	—	—	Meldola, J., 1883, **43**, 431, gives m. p. 180° (Violet-blue)
Anthranilic acid	Carmine-red needles, benzene	183	—	—	Meldola, East, J., 1888, **53**, 463, give m. p. 182° (Violet)
4-Bromo-3-nitroaniline	Dark green masses, toluene	190	15·2	15·1	Fischer, *J. pr. Chem.*, 1923, **107**, 32, gives m. p. 182—183° (Violet-blue)
p-Aminophenol	Orange needles, dilute alcohol	192	—	—	(Blue)
o-Nitroaniline	Bronze scales, glacial acetic acid	198	—	—	Sachs, *Ber.*, 1885, **18**, 3129, gives m. p. 192—193° (Red-violet)
2-Nitro-*p*-toluidine	Brown needles, glacial acetic acid	199	18·5	18·3	Meldola, Hughes, J., 1891, **59**, 373, give m. p. 198° (Blue-violet)
5-Nitro-1-naphthylamine	Dark brown microscopic needles, chlorobenzene	212	16·2	16·4	(Blue-violet)
4-Nitro-1-naphthylamine	Black needles with greenish tinge, chlorobenzene	214	16·6	16·4	(Greenish-blue)
3-Nitro-*p*-toluidine	Dark bronze needles, glacial acetic acid	226	—	—	(Orange-red)
4-Chloro-2-nitroaniline	Dark bronze needles, toluene	255	17·2	17·2	Norman, J., 1919, **115**, 678, gives m. p. 224° (Greenish-blue)
4-Bromo-2-nitroaniline	Dark bronze needles, toluene	259	15·4	15·1	(Blue-violet)
p-Aminobenzoic acid	Minute, red, diamond-shaped crystals, benzene	264	—	—	(Greenish-blue)
Picramic acid	Dark green needles, nitrobenzene	274	20·1	19·9	Fischer, *J. pr. Chem.*, 1923, **107**, 34, gives m. p. 263—264° (Violet-blue)
					(Blue-grey)

under Meldola's conditions, whereas those with electron-repelling groups yield tars. From these tars acetoxy-compounds could not be isolated, owing to experimental difficulties, though they were un-

doubtedly present, and on hydrolysis with alcoholic hydrochloric acid almost the entire product was obtained as arylazo-β-naphthol.

In all cases, the action of sodium nitrite and glacial acetic acid on arylazo-β-naphthylamines appears to be replacement of the amino- by the acetoxy-group, subsequent hydrolysis by the water formed in the reaction converting a portion of the acetate into the arylazo-β-naphthol. From 2 : 5-dichloro-, *o*-nitro-, and *o*-carboxy-benzeneazo-β-naphthylamines the whole product is the arylazo-β-naphthol, but this is readily accounted for by ease of hydrolysis; *e.g.*, 4-bromo-2-nitrobenzeneazo-β-naphthyl acetate, which is formed from 4-bromo-2-nitrobenzeneazo-β-naphthylamine, is hydrolysed at once when attempts are made to crystallise it from acetic acid containing water. Moreover, in those cases where the crystalline acetoxy-compounds separate directly from the reaction mixture, the solution always contains a mixture of acetoxy-compound and the arylazo-β-naphthol, which is completely hydrolysed to the latter compound. Diminished solubility of the acetoxy-compound appears to be favoured by the presence of electron-attracting groups.

The mechanism of the reaction under review therefore appears to be initial diazotisation of the amino-group with formation of the diazonium acetate, and its subsequent decomposition by polarised acetic acid or by the acetate anion; the naphthyl acetate formed is partly or wholly hydrolysed by the water formed in the reaction. That the reaction does not proceed *via* initial acetylation of the β-amino-group, followed by formation of a nitrosoacetonaphthalide and subsequent decomposition of its isomeric azo-form, is probably indicated by failure of the arylazo-β-acetonaphthalides to react with sodium nitrite and glacial acetic acid.

Experimental.

(1) *Preparation of Arylazo-β-naphthylamines.*—The general procedure is illustrated by the following example: A solution (or paste) of *p*-chloroaniline (12·75 g.; 0·1 g.-mol.) in hydrochloric acid (25 c.c., *d* 1·16) and water (20 c.c.) was diazotised below 5° with sodium nitrite (7 g.) dissolved in water (35 c.c.), and the filtered solution was stirred gradually into a solution (at 0°) of β-naphthylamine (14·3 g.) in alcohol (220 c.c.), to which fused sodium acetate had been added. After being stirred at 0° for 1 hour longer, the mixture was heated at 50° on the water-bath for 15 minutes and left overnight; the azo-compound had then separated in red crystals, which, recrystallised from glacial acetic acid, were obtained in scarlet prisms, m. p. 116° (Meldola and Forster, J., 1891, **59**, 690, give m. p. 116°).

Twenty-nine arylazo-β-naphthylamines were prepared similarly (see Table I), the only variation being that the toluidines, anisidines, and monohalogenoanilines were diazotised by the direct method (Saunders, "The Aromatic Diazo-Compounds," p. 3), and the halogenonitroamines and other less basic amines by the "inverted method" (Saunders, *op. cit.*, p. 9) or by the method of Hodgson and Walker (J., 1933, 1620). The yields of azo-compounds obtained by the last method were very good except in the case of *m*-fluorobenzeneazo-β-naphthylamine (30% yield), where a considerable amount of tarry matter was produced; this was avoided by adding sufficient alcohol, after coupling had taken place, to dissolve the products (including tar) at 65° and cooling the mixture very slowly.

(2) *Decomposition of Arylazo-β-naphthylamines by Sodium Nitrite and Glacial Acetic Acid.*—A solution of the azo-compound (3 g.) in hot glacial acetic acid (for quantities, see Table II; in some cases solution was not complete and a fine suspension was used) was treated at 70° with the calculated quantity of powdered sodium nitrite, added in portions with stirring, nitrogen being evolved. On completion of the reaction, the clear solution, which had been maintained at 65—70°, was kept for 48 hours at room temperature; the crystalline product was then collected and recrystallised. The filtrate, after dilution with ice to increase its volume fourfold, was kept at room temperature until the ice had melted and the precipitate (if any) was then collected (see below).

(3) *Identification.*—The chief products were (*a*) arylazo-β-naphthols, which were identified by comparison with authentic compounds obtained by coupling the requisite diazonium salts with β-naphthol, and (*b*) arylazo-β-naphthyl acetates, identified by comparison, after hydrolysis, with compounds (*a*) and also by comparison with compounds (*a*) which had been acetylated.

Hydrolysis. The acetyl compound (0·5 g.), dissolved as far as possible in 20—50 c.c. of alcohol containing hydrochloric acid (2 c.c., *d* 1·16), was refluxed for 30 minutes, the mixture cooled, made just alkaline with ammonia, and boiled for 2 minutes, and the arylazo-β-naphthol collected and recrystallised (usually from glacial acetic acid).

Acetylation. The arylazo-β-naphthol was refluxed for 24 hours with anhydrous sodium acetate (1 part) and acetic anhydride (20 parts). The cold solution was kept for 15 minutes, the sodium acetate removed, and the filtrate allowed to crystallise. The product was recrystallised from glacial acetic acid.

Examination of the tars produced in (2). The decomposition of those arylazo-β-naphthylamines named in Table I but omitted from Table II produced tars which could not be crystallised. The tar was collected and dissolved in hot alcohol, a little concentrated hydrochloric acid added, and the mixture refluxed for ½ hour. The cold solution deposited crystals, which were treated with aqueous ammonia. Recrystallisation

TABLE II.

Arylazo-β-naphthyl acetates.

The colour produced by concentrated sulphuric acid is given after the crystalline form.

Diazotised amine.	Acetic acid, c.c.	Sodium nitrite, g.	Product.	%Yield.	Crystalline form and solvent.	M. p.	% N found.	% N required.
m-Chloroaniline	30	0·75	m-*Chlorobenzeneazo-β-naphthyl acetate*	46·5	Small red needles, alcohol and glacial acetic acid (Violet-red)	81°	8·9	8·6
Aniline	100	0·9	*Benzeneazo-β-naphthyl acetate*	42·6	Red microscopic needles, glacial acetic acid (Violet-red)	117	9·8	9·6
p-Fluoroaniline	25	0·8	p-*Fluorobenzeneazo-β-naphthyl acetate*	43·0	Deep red needles, glacial acetic acid (Violet-red)	130	9·3	9·1
3-Nitro-*p*-toluidine	230	0·7	2-*Nitro-4-methylbenzeneazo-β-naphthyl acetate*	58·4	Red needles, alcohol (Violet-red)	133	12·0	12·0
p-Chloroaniline	40	0·75	p-*Chlorobenzeneazo-β-naphthyl acetate*	49·0	Deep red needles, alcohol (Violet-red)	134	8·7	8·6
p-Bromoaniline	34	0·65	p-*Bromobenzeneazo-β-naphthyl acetate*	44·0	Orange-red needles, alcohol (Violet-red)	136	7·8	7·6
4-Nitro-1-naphthylamine	250	0·62	4-*Nitronaphthaleneazo-β-naphthyl acetate*	56·3	Dark red-brown needles, glacial acetic acid (Dark violet-red)	155	10·9	10·9
2-Nitro-*p*-toluidine	230	0·7	3-*Nitro-4-methylbenzeneazo-β-naphthyl acetate*	73·7	Brown needles, glacial acetic acid (Violet-red)	157	12·2	12·0
4-Bromo-2-nitroaniline	300	0·57	4-*Bromo-2-nitrobenzeneazo-β-naphthyl acetate*	60·0	Fine carmine-red needles, alcohol (Red-violet)	160	10·3	10·2
m-Nitroaniline	210	0·72	m-*Nitrobenzeneazo-β-naphthyl acetate*	61·0	Red needles, glacial acetic acid (Violet-red)	162	12·9	12·6
4-Chloro-2-nitroaniline	300	0·65	4-*Chloro-2-nitrobenzeneazo-β-naphthyl acetate*	59·0	Fine carmine-red needles, glacial acetic acid (Red-violet)	163—164	11·5	11·4
4-Bromo-3-nitroaniline	200	0·57	4-*Bromo-3-nitrobenzeneazo-β-naphthyl acetate*	50·8	Orange needles, glacial acetic acid (Violet-red)	167	10·3	10·2
5-Nitro-1-naphthylamine	250	0·62	5-*Nitronaphthaleneazo-β-naphthyl acetate*	53·3	Carmine-red needles, glacial acetic acid (Red-violet)	180	10·9	10·9
Picramic acid	240	0·6	3 : 5-*Dinitro-2-hydroxybenzeneazo-β-naphthyl acetate*	77·5	Minute brownish-black needles, chlorobenzene (Red-violet)	184	14·5	14·2
p-Nitroaniline	300	0·72	*p*-Nitrobenzeneazo-β-naphthyl acetate	61·0	Red flattened needles, glacial acetic acid (Violet-red)	193 *	—	—
p-Aminobenzoic acid	220	0·74	p-*Carboxybenzeneazo-β-naphthyl acetate*	61·0	Red crystalline powder, glacial acetic acid (Red-violet)	206	8·6	8·4
o-Nitroaniline	175	0·72	*o*-Nitrobenzeneazo-β-naphthol	100	Orange-red needles, glacial acetic acid (Red-violet)	210 †	—	—
Anthranilic acid	120	0·74	*o*-Carboxybenzeneazo-β-naphthol	100	Red crystalline powder, glacial acetic acid (Violet-red)	276 ‡	—	—

* Meldola, East, J., 1888, **53**, 466, give m. p. 192—193°.
† Rowe, Levin, *J. Soc. Dyers and Col.*, 1924, **40**, 222, give m. p. 212°.
‡ *Idem, ibid.*, p. 222, give m. p. 276°.

of the product from glacial acetic acid or alcohol gave the arylazo-β-naphthol, identified by m. p. and mixed m. p., in almost quantitative yield.

Examination of the precipitates obtained by the addition of ice to the filtrates in (2). The addition of ice produced either a tar or a precipitate of indefinite m. p., which was probably a mixture of the arylazo-β-naphthol and its acetate, since, after hydrolysis with alcoholic hydrochloric acid, it gave the arylazo-β-naphthol.

The yield of arylazo-β-naphthol obtained from the precipitate (or tar), together with the amount of acetoxy-compound previously removed from the solution, corresponds almost quantitatively with the amount of arylazo-β-naphthylamine initially decomposed.

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