795. *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part II.*[1] *Diazonium Salts from Aromatic Sulphonic Acids, Carboxylic Acids, and Nitro-compounds prepared by use of Mercuric Ions as Catalyst.*

By J. M. Tedder and G. Theaker.

A method for introducing a diazonium group directly into deactivated aromatic nuclei has been developed. The aromatic compound, dissolved in sulphuric acid, is treated with nitrosylsulphuric acid and a catalytic amount of mercuric sulphate. Moderate yields of diazonium salts have been prepared from aromatic sulphonic acids, carboxylic acids, and nitro-compounds by this method.

The preceding paper described the formation of diazonium salts directly from aromatic compounds containing activating groups, probably by electrophilic attack of a nitrosonium ion on the aromatic nucleus, to yield a nitroso-derivative which then reacts further to yield the diazonium salts. If this mechanism is correct, the simple reaction is unlikely to be extended to unactivated aromatic nuclei, because there is strong evidence to show that the nitrosonium ion is not sufficiently reactive.[2] There are, however, other possible ways of introducing a nitroso-group into an aromatic nucleus under conditions such that it will be able to react further to yield a diazonium salt. The first approach we have made involves the preliminary mercuration of the aromatic nucleus. Reaction of diphenylmercury compounds with dinitrogen trioxide to yield nitroso-compounds and diazonium salts was first reported by Bamberger[3] and various similar reactions have since been described.[4] Mercuration followed by nitrosation and formation of diazonium salts was

---

[1] Part I, preceding paper.

[2] Ingold, " Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., 1953, p. 287; Tedder, *Chem. Rev.*, 1955, **55**, 816.

[3] Bamberger, *Ber.*, 1897, **30**, 506.

[4] Kunz, *Ber.*, 1898, **31**, 1528; Smith and Taylor, *J. Amer. Chem. Soc.*, 1935, **57**, 2460; Makarova and Nesmejanov, *J. Gen. Chem.* (*U.S.S.R.*), 1939, **9**, 771 (*Chem. Abs.*, 1940, **34**, 391).

also studied in connection with " oxynitration," [5] and very much earlier a peculiar oxidation accompanied by diazonium salt formation is described in a patent.[6] On these foundations we have attempted to develop a practical method of preparing diazonium salts.

The process involves the initial mercuration of the aromatic compound under acid conditions.[7] The mercuric ion is then replaced by the nitrosonium ion to form the aromatic nitroso-compound, which reacts as before to form the diazonium salt:

$$\begin{aligned} \mathrm{ArH} + \mathrm{Hg^{++}} &\longrightarrow \mathrm{ArHg^{+}} + \mathrm{H^{+}} \\ \mathrm{ArHg^{+}} + \mathrm{NO^{+}} &\longrightarrow \mathrm{Ar{\cdot}NO} + \mathrm{Hg^{++}} \\ \mathrm{Ar{\cdot}NO} + \mathrm{NO^{+}} &\longrightarrow \mathrm{Ar{\cdot}N_2^{+}} + 2[\mathrm{O}] \end{aligned}$$

The important feature of these reactions is that the mercuric ion (shown unhydrated, no evidence being at present available as to its form in concentrated sulphuric acid) is regenerated in the second stage of the reaction, so that only catalytic amounts of mercury are required.

This reaction was first attempted with benzene, which was treated with excess of nitrosylsulphuric acid and one mole of mercuric oxide dissolved in concentrated sulphuric acid. Diazonium salts were certainly formed under conditions which would have left benzene unaffected in the absence of mercury. However, instead of simply benzenediazonium sulphate, the coupling products indicated the presence of at least four salts. These were believed to be the *o*- and *p*-nitro-derivatives, a bisdiazonium salt, and the expected benzenediazonium salt, but only the *o*-nitro-derivative was fully characterised. The bisdiazonium salt was formed even under conditions which left a large portion of the benzene unchanged. These results were attributed to the fact that phenylmercuric sulphate, nitrosobenzene, and benzenediazonium sulphate are all soluble in concentrated sulphuric acid and can undergo further substitution more rapidly than the undissolved benzene. However, the catalytic effect of mercury was confirmed and, secondly, phenylmercuric sulphate treated with nitrosylsulphuric acid in concentrated sulphuric acid solution yielded benzenediazonium sulphate extremely rapidly at 0°. Attention was then turned to deactivated molecules which are soluble in concentrated sulphuric acid.

Aromatic sulphonic acids, nitro-compounds, and carboxylic acids all yielded diazonium salts when treated with nitrosylsulphuric acid and catalytic amounts of mercuric sulphate in concentrated sulphuric acid. The Table lists the best yields (estimated by titration of the diazonium salt), obtained by use of 0·01 mol. of mercuric oxide, in 3—4 experiments, but no exhaustive investigation of all the variables was attempted. The results provide evidence for the basic mechanism. From *p*-nitroanisole and *p*-anisic acid appreciable yields of nitroso-compounds were isolated and the latter were converted by fresh nitrosylsulphuric acid into more diazonium salt. However, a variety of side reactions are possible as indicated by the annexed scheme. Aromatic nitro-compounds could be formed by oxidation of the intermediate nitroso-compound or by direct nitration of the starting aromatic compound (cf. Part I). In fact, only benzene yielded nitrated products under

Aromatic compound	$NaNO_2$ (mols.)	Conditions (time in hr.)	Yield (%)
$Ph{\cdot}SO_3H$	2·1	$2\frac{3}{4}$, 75°	20
1-$C_{10}H_7{\cdot}SO_3H$	2·1	$2\frac{1}{4}$, 60°	29
p-$C_6H_4Me{\cdot}SO_3H$	2·1	3, 60° *	53
p-$C_6H_4Me{\cdot}NO_2$	3·1	7, 70°	37
o-$C_6H_4Me{\cdot}NO_2$	2·1	3, 70°	24
p-$NO_2{\cdot}C_6H_4{\cdot}OMe$	5·0	3, 20° *	75
1-$C_{10}H_7{\cdot}NO_2$	2·1	$2\frac{1}{4}$, 30°	7
p-$C_6H_4Me{\cdot}CO_2H$	2·1	3, 70°	21
1-$C_{10}H_7{\cdot}CO_2H$	2·1	$5\frac{1}{4}$, 20°	17
p-$MeO{\cdot}C_6H_4{\cdot}CO_2H$	2·1	$\frac{1}{2}$, 20° *	13

* Nitrosylsulphuric acid added during 3—6 hr.

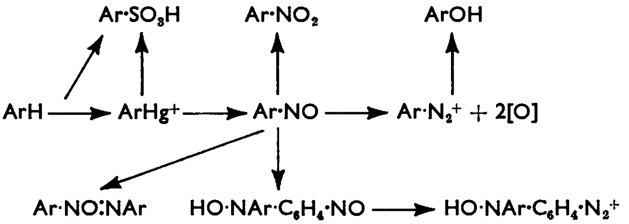
---

[5] Westheimer, Segel, and Schramm, *J. Amer. Chem. Soc.*, 1947, **69**, 773; Carmack, Baizer, Handrick, Kissinger, and Specht, *ibid.*, p. 785.

[6] Bayer Farb., B.P. 27,373.

[7] Schramm, Klapproth, and Westheimer, *J. Phys. Colloid Chem.*, 1951, **55**, 843.

mild conditions, though under forcing conditions a nitrated diazonium salt was obtained from *p*-nitrotoluene. In the conditions which gave the maximum yields of diazonium salts from *p*-nitroanisole and *p*-nitrotoluene, no nitrated product could be detected and in the former case the bulk of the starting material not accounted for by the diazonium salt was recovered as nitroso- and azoxy-compounds.



Further work is being devoted to the individual stages of the reaction.

EXPERIMENTAL

Reaction of Benzene with Nitrosylsulphuric Acid in the presence of Mercuric Salts.—Benzene (1·76 g.) was added at 20° to a solution of yellow mercuric oxide (4·88 g.) and sodium nitrite (9·36 g.) in concentrated sulphuric acid (65 ml.) through which a stream of nitrogen was passing. After 2 hr. the mixture was poured on ice (1 kg.), neutralised with sodium hydrogen carbonate (207 g.), then filtered to remove mercuric oxide. 1% Sodium β-naphthoxide solution was added to the filtrate until no more diazonium salt was present. The dye was isolated by extracting the mixture with chloroform, the extract being washed with alkali before drying (Na_2SO_4) and evaporation. This gave crude dye (1·5 g., 27%), as a green powder, m. p. 110—130°.

From this mixture the following products were obtained by fractional crystallisation from ethyl alcohol: (*a*) A dark product, m. p. 160—170°, not very soluble in ethanol, which dissolved in concentrated sulphuric acid to give a blue-purple solution ($\lambda_{max.}$ in $CHCl_3$, 505—510 mμ), probably bisazo-compound. (*b*) Orange needles, m. p. 206—207°, which dissolved in concentrated sulphuric acid to give a purple-red solution (Found: C, 64·95; H, 3·9; N, 14·0. Calc. for $C_{16}H_{11}O_3N_3$: C, 65·5; H, 3·8; N, 14·3%), mixed m. p. with *o*-nitrophenylazo-β-naphthol[8] 207°, $\lambda_{max.}$ (in $CHCl_3$) 496—500 mμ (authentic dye 498 mμ). (*c*) A very small quantity of orange needles (from benzene), m. p. *ca.* 246° (Hewitt and Mitchell[9] describe *p*-nitrophenylazo-β-naphthol, m. p. 247°). (*d*) Phenylazo-β-naphthol contaminated with some β-naphthol, identified by its absorption.

In a control experiment benzene (1·76 g.) was added at 20° to a solution of sodium nitrite (9·36 g.) in concentrated sulphuric acid (65 ml.) through which nitrogen was passing. The mixture quickly became a red-brown but no diazonium salt was detected after 2 hr.

Reaction of Phenylmercuric Sulphate with Nitrosylsulphuric Acid.—Benzene (1·76 g.) was added to a solution of yellow mercuric oxide (1·22 g.) in concentrated sulphuric acid (25 ml.) at 20°. The mixture became clear in ½ hr. It was then cooled to 0—2° and sodium nitrite (5·45 g.) in concentrated sulphuric acid (35 ml.) was added all at once with stirring. After 2 min. the mixture was poured on ice (800 g.), neutralised with sodium hydrogen carbonate, filtered, and coupled with β-naphthol. The dye was isolated by chloroform as above (0·35 g., 6·2%; m. p. 115—120°). The crude product crystallised from acetone in red needles, m. p. 128° alone or mixed with phenylazo-β-naphthol. The colour in concentrated sulphuric acid was bright pink-red.

Reaction between Nitrosylsulphuric Acid and Deactivated Aromatic Compounds in the Presence of Mercuric Ions.—*Titration procedure.* In the following experiments, the yields of diazonium salt were determined by diluting aliquot parts of the mixtures in ice-water, removing the excess of nitrous acid with sulphamic acid solution, neutralising the whole with sodium acetate solution and coupling with standard 3-methyl-1-*p*-sulphophenyl-5-pyrazolone solution containing sodium acetate. After a suitable period for completion of coupling, the excess of pyrazolone was back-titrated with standard *p*-nitrobenzenediazonium chloride solution with the sodium salt of H-acid as external indicator.

---

[8] Meldola and Hughes, *J.*, 1891, **59**, 374.

[9] Hewitt and Mitchell, *J.*, 1906, **89**, 1170.

Benzenesulphonic acid. Sodium benzenesulphonate (3·60 g.) was added to a solution of mercuric oxide (0·043 g.) and sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) at 20°. The mixture was heated to 75° in 15 min., then kept at this temperature. Every half-hour aliquot samples were withdrawn and the yield of diazonium salt estimated by titration. This yield was a maximum of 20% after 2¾ hr. and thereafter fell slightly. In a similar experiment at 90° a maximum yield of 14% was obtained after 1¼ hr. and then fell rapidly. The identity of the diazonium salt was established by repeating the conditions of the first experiment and after 2¾ hr. pouring the whole mixture on ice (400 g.). The mixture was partly neutralised with 10% sodium hydroxide solution, the final pH being adjusted by completing the neutralisation with sodium carbonate. The diazonium salt was coupled wth β-naphthol and the dye isolated as the sodium salt by salting out with sodium chloride and filtration. The dye was obtained fairly free from salt by extraction with methanol and evaporation of the extract and was identified by absorption spectrometry in aqueous solution ($\lambda_{max.}$ 481 mμ).

Naphthalene-1-*sulphonic acid.* Sodium naphthalene-1-sulphonate (4·60 g.) was dissolved in a solution of mercuric oxide (0·043 g.) and sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) at 20°. The mixture was heated at 60° while the reaction was followed as before. A maximum yield of 29% was obtained after 2¼ hr. In a similar experiment the diazonium salt was coupled with β-naphthol and the sodium salt of the dye isolated as before. Paper chromatography indicated the presence of more than one dye and the product was not investigated further.

Toluene-p-*sulphonic acid.* Toluene-*p*-sulphonic acid monohydrate (3·8 g.) and mercuric oxide (0·043 g.) were dissolved in concentrated sulphuric acid (15 ml.) at 20°. A solution of sodium nitrite (2·9 g.) in concentrated sulphuric acid (20 ml.) was added during 4 hr. at 60°. The yield was a maximum of 53% after 3 hr. In another experiment the diazonium salt was coupled with β-naphthol and the sodium salt of the dye isolated as before ($\lambda_{max.}$ 478 mμ in H_2O).

In a control experiment, toluene-*p*-sulphonic acid monohydrate (1·9 g.) was treated with sodium nitrite (1·45 g.) in concentrated sulphuric acid (15 ml.) for 6 hr. at 60°. No diazonium salt was detected.

p-*Toluic acid.* This acid (2·72 g.) was added to mercuric oxide (0·043 g.) and sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) at 20° and the mixture heated to 70°. A maximum yield of diazonium salt (21%) was obtained after 3 hr. The experiment was repeated and the mass poured on ice (600 g.) and after 3 hr. at 70°. The excess of nitrous acid was removed by 10% sulphamic acid solution, the mixture filtered, neutralised with sodium carbonate, and coupled with β-naphthol. The dye was isolated as free acid by just acidifying the mixture (pH 5) with hydrochloric acid and extracting it with ether. To separate the dye from excess of β-naphthol the ethereal solution was shaken with sodium hydrogen carbonate solution and the latter extract re-acidified and extracted with ether. The crude *dye* (m. p. 210—250°) was purified by recrystallising from acetone (m. p. 268°). The solution in concentrated sulphuric acid was red-purple (Found: C, 70·5; H, 5·3. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6%).

1-*Naphthoic acid.* 1-Naphthoic acid (3·44 g.) was added to sodium nitrite (2·9 g.) and mercuric oxide (0·043 g.) in concentrated sulphuric acid (30 ml.) at 20°. The mixture was kept at 20°. Maximum yield of 17% was obtained after 5¼ hr. In a similar experiment the diazonium salt was coupled with β-naphthol and the dye isolated as in the previous example. The crude *dye* (m. p. 260—290°) was purified by crystallisation from acetone as a red amorphous powder [m. p. 332° (decomp.)]: it dissolved in concentrated sulphuric acid to a red-purple solution (Found: C, 74·4; H, 4·4. $C_{21}H_{14}O_3N_2$ requires C, 73·7; H, 4·1%). The dye was not further characterised. There was also obtained a trace of a product which dissolved in concentrated sulphuric acid to a blue-green solution which quickly faded.

p-*Nitrotoluene.* *p*-Nitrotoluene (2·74 g.) was dissolved in concentrated sulphuric acid (15 ml.) containing mercuric oxide (0·043 g.) at 20°, then heated to 70°. Sodium nitrite (4·35 g.) in concentrated sulphuric acid (30 ml.) was added during 5 hr. at 70°. The yield was a maximum (37%) after 7 hr. In a similar experiment the mixture was poured on ice (800 g.), and excess of nitrous acid removed by sulphamic acid. The mixture was extracted with ether, neutralised with sodium carbonate, and coupled with β-naphthol. The dye was isolated by extraction with chloroform, which was then shaken with dilute sodium hydroxide solution. The dye crystallised from benzene as red needles, m. p. 205° (2-methyl-5-nitrophenylazo-β-naphthol,[10] m. p. 204°) (Found: C, 66·6; H, 4·6; N, 13·3. Calc. for $C_{17}H_{13}O_3N_3$: C, 66·45; H, 4·3; N,

---

[10] Leonard and Browne, *Sci. Proc. Roy. Dublin Soc.*, 1920, **16**, 105.

13·7%). In a third experiment, *p*-nitrotoluene (2·74 g.) was added to a solution of mercuric oxide (0·043 g.) and sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) at 20° and the mixture then heated to 95°: a maximum yield of 16% was obtained after 1½ hr. In a similar experiment the diazonium salt was coupled with β-naphthol and the dye isolated as above. In addition to the 2-methyl-5-nitrophenylazo-β-naphthol, there was obtained some dinitrotolylazo-β-naphthol which was less soluble in benzene.

Dinitrotolylazo-β-naphthol crystallised from benzene as red needles, m. p. 246° (Found: N, 15·8. $C_{17}H_{12}O_5N_4$ requires N, 15·9%). The position of the second nitro-group was not established.

o-*Nitrotoluene*. *o*-Nitrotoluene (2·74 g.) was dissolved in concentrated sulphuric acid (15 ml.) containing mercuric oxide (0·043 g.) at 20° and the mixture heated at 70°. Sodium nitrite (2·9 g.) in concentrated sulphuric acid (20 ml.) was added in 3¾ hr. at 70°. Yield was maximum (24%) after 3 hr.

1-*Nitronaphthalene*. 1-Nitronaphthalene (3·46 g.) was added at 20° to a solution of mercuric oxide (0·043 g.) and sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) through which nitrogen was passed. The mixture was kept at 30°. A maximum yield of 7% was obtained after 2¼ hr.

p-*Nitroanisole*. *p*-Nitroanisole (3·06 g.) was dissolved in concentrated sulphuric acid (15 ml.) containing mercuric oxide (0·043 g.) at 20°. A solution of sodium nitrite (6·90 g.) in concentrated sulphuric acid (30 ml.) was added during 3 hr. at 20°. Yield was a maximum (75%) after 3 hr. In a similar experiment the mixture was poured on ice (600 g.); treatment as in preceding cases gave *2-methoxy-5-nitrophenylazo-*β*-naphthol*, which from ethyl methyl ketone formed orange-red needles, m. p. 252—253° (Found: C, 63·0; H, 4·1. $C_{17}H_{13}O_4N_3$ requires C, 63·2; H, 4·05%).

The benzene extract of the diazonium salt solution was evaporated, and the dark residue (39% by wt. of *p*-nitroanisole used) redissolved in acetone. This residue consisted of a little unchanged *p*-nitroanisole (m. p. 50—52°) and a yellow solid (m. p. 114—118°) which melted to a green liquid. This *4-nitro-2-nitrosoanisole* crystallised from aqueous acetic acid as pale yellow plates, m. p. 120° (Found: C, 46·0; H, 3·4. $C_7H_6O_4N_2$ requires C, 46·1; H, 3·3%). Treatment of its solution in acetic acid with aniline at 20° afforded *2-methoxy-5-nitrophenylazobenzene*, pale orange needles (from aqueous ethanol), m. p. 131° (Found: C, 60·4; H, 4·6. $C_{13}H_{11}O_3N_3$ requires C, 60·7; H, 4·3%). To confirm the structure of the nitroso-compound, its solution in concentrated sulphuric acid was treated with sodium nitrite in concentrated sulphuric acid at 20°. After ¼ hr. the diazonium salt obtained was coupled with β-naphthol and the dye isolated as before. The product separated as red needles (from ethyl methyl ketone), m. p. and mixed m. p. 252°. Also obtained was a trace of a dark product (m. p. 194—197°), crystallising from aqueous acetone as cream plates (m. p. 206°) Brand and Eisenmenger [11] report 2 : 2′-dimethoxy-5 : 5′-dinitroazoxybenzene, m. p. 209° (Found: C, 48·5; H, 3·7. Calc. for $C_{14}H_{12}O_7N_4$: C, 48·3; H, 3·5%). *p*-Nitroanisole (1·53 g.) was treated with sodium nitrite (1·45 g.) in concentrated sulphuric acid (22 ml.) for up to 25 hr. at 20°. No diazonium salt was detected.

p-*Anisic acid*. *p*-Anisic acid (3·04 g.) was dissolved in concentrated sulphuric acid (15 ml.) containing mercuric oxide (0·043 g.) at 20°. Sodium nitrite (2·9 g.) in concentrated sulphuric acid (30 ml.) was added during 5 hr. at 20°. Maximum yield (13%) was obtained after ½ hr. In a similar experiment the mixture was poured on ice (600 g.), excess of nitrous acid removed, and the whole extracted with ether. The diazonium salt solution was not investigated further. Evaporating the ethereal solution gave a yellow-brown product (59%), largely nitroso-compound (Liebermann test) and giving with aniline in acetic acid *5-carboxy-2-methoxyazobenzene*, orange needles (from benzene), m. p. 214—215° (Found: C, 65·6; H, 4·9. $C_{14}H_{12}O_3N_2$ requires C, 65·6; H, 4·7%).

No diazonium salt was detected on treatment of anisic acid (1·52 g.) with sodium nitrite (1·45 g.) in concentrated sulphuric acid (22 ml.) at 20° for up to 24 hr.

The authors acknowledge valuable discussions with their colleagues, especially Mr. A. C. Farthing of Imperial Chemical Industries Limited, Dyestuffs Division. They thank Dr. H. Swann for advice on the determination of diazonium salts.

THE UNIVERSITY, SHEFFIELD, 10.

[*Received, May 8th,* 1957.]

---

[11] Brand and Eisenmenger, *J. prakt. Chem.*, 1913, **87**, 487.