# **934.** *The Direct Introduction of the Diazonium Group into Aromatic Nuclei. Part VIII.*[1] *The Preparation of Diazonium Salts from Tertiary Amines.*

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*NN*-Dialkylanilines, in which both the *ortho*- and the *para*-position are unsubstituted, can be converted into *p*-dialkylaminobenzenediazonium salts in moderate-to-good yields by treatment with an excess of buffered nitrous acid in a homogeneous solution. An *ortho*-substituent greatly hinders the reaction and a mixture of products is obtained including the *p*-alkylaminobenzenediazonium salt, the *N*-alkyl-*p*-nitrosoaniline, and the *NN*-dialkyl-*p*-nitroaniline. A *para*-substituent completely inhibits the formation of a diazonium salt, but nitration occurs rapidly in buffered nitrous acid.

THE first paper in the present series showed that the direct introduction of the diazonium group into aromatic nuclei by nitrous acid was a general reaction.[2] Included among the examples was the preparation of diazonium salts from *NN*-dimethyl- and *NN*-diethylaniline. Although the preparation of *para*-nitroso-derivatives is well known, it was shown that if the tertiary aromatic amines were treated with nitrous acid solutions of low acidity the reaction went further to yield the corresponding diazonium salt. This preparation of diazonium salts from tertiary aromatic amines was not studied in detail and it is the purpose of the present paper to describe such an investigation.

The previous results were confirmed and in general tertiary aromatic amines in which both the *ortho*- and the *para*-position are unsubstituted can be converted into diazonium salts in good yield (see Table 1).

TABLE 1.

Yields of azo-2-naphthol dyes from *NN*-dialkylanilines unsubstituted in the *ortho*- and *para*-positions.

Amine (1 mol.) + $NaNO_2$ (15 mol.) + HCl (10 mol.) in aqueous acetone at 0—5°.

| Amine | Reaction time (hr.) | Yield (%) |
|---|---|---|
| *NN*-Dimethylaniline | 14 | 55 |
| *NN*-Diethylaniline | 48 | 56 |
| *N*-Benzyl-*N*-ethylaniline | 64 | 33 |
| *N*-Ethyl-*N*-2-hydroxyethylaniline | 24 | 82 |
| *NN*-Diethyl-*m*-toluidine | 41 | 54 |
| *N*-Benzyl-*N*-ethyl-*m*-toluidine | 48 | 49 |

No attempt has been made to investigate the effect of changing the reaction conditions; the object of the work has been solely concerned with the effect of changing the structure of the tertiary amine. The buffered nitrous acid solutions (see Table heading) were the same as those previously developed for the preparation of diazonium salts from phenols.[3] This was done for convenience only and there is good reason to believe that these yields can be

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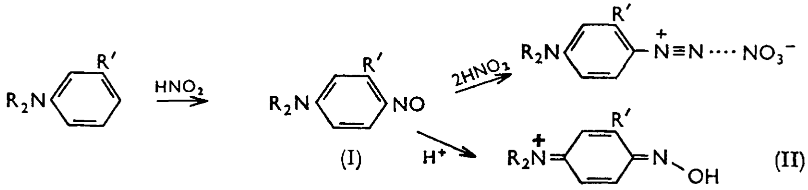
[1] Part VII, Tedder and Webster, *J.*, 1960, 4417.
[2] Tedder, *J.*, 1957, 4003.
[3] Tedder and Theaker, *J.*, 1958, 2573.

improved. Certainly, more detailed experiments with dimethylaniline have shown that so large an excess of nitrous acid is not necessary. The essential requirements for the preparation of diazonium salts, are, first, that the amount of nitrous acid be sufficient to convert the nitroso-compound formed initially into the diazonium salt and, secondly, that the acidity be sufficiently low for the nitroso-compound to be unprotonated and not in the quinone imine oxime structure (II) normally present in mineral acid solution. There is a patent claiming a process for the preparation of diazonium salts directly from tertiary aromatic amines,[4] to the effect that tertiary amines in which at least one of the *N*-alkyl groups contains more than three carbon atoms yield diazonium salts on treatment with nitrous acid. In so far as it goes this statement is true since direct treatment of dimethylaniline with nitrous acid yields about 1% of diazonium salt.[2] Long alkyl chains reduce the stability of the quinone imine oxime (II), probably as a result of steric hindrance, and this is presumably the justification of the patent claims. However, the yields obtained under the conditions described are very poor and the suggestion made in the patent that the reaction involves reduction of a nitroso-group to an amino-group by nitrous acid, is clearly wrong. In the present work, the formation of the unreactive quinone imine oxime for *any* tertiary amine was kept to a minimum by the low acidities used and the free nitroso-compound was kept in solution by the addition of acetone. Alternatively an imiscible organic solvent such as benzene or ethyl acetate was found suitable. Under these conditions the nitroso-compound collected in the organic layer until it reacted to form the diazonium salt which then passed into the aqueous layer. In the absence of a solvent the nitroso-compound formed a dark oil and the yields were much poorer.



(I)

(II)

According to text-books, *ortho*-substituted tertiary amines do not react with nitrous acid. The lack of reactivity of these amines is due to steric hindrance which prevents the dialkylamino-group from attaining the planar structure necessary for it to exert its full ($+M$) electron-donating effect. In the present work it was found that *ortho*-substituted *NN*-dialkylanilines reacted extremely slowly with the buffered nitrous acid. In more acidic media [amine (1 mole) + HCl (10 moles) + $NaNO_2$ (10 moles)] the reaction was still very slow and a mixture of products was isolated. These included the *p*-monoalkylaminobenzenediazonium salt, the corresponding dealkylated nitroso-compound, and the *NN*-dialkyl-*p*-nitroaniline in which both 4-*N*-alkyl groups remained intact (see Table 2). The dealkylation may involve an $S_E2$ replacement in which the nitrosonium ion attacks the tertiary nitrogen atom, and the *N*-nitrosoamine formed by elimination of one of the alkyl groups then undergoes a Fischer–Hepp rearrangement to yield the *para*-nitroso-compound

TABLE 2.

Products of reaction of nitrous acid with *ortho*-substituted *NN*-dialkylanilines

A = $p$-Alk·NH·$C_6H_4$·$N_2^+X$. B = $p$-ON·$C_6H_4$·NHAlk. C = $p$-$O_2N$·$C_6H_4$·$NAlk_2$.

| | A (%) | B (%) | C (%) |
|---|---|---|---|
| *NN*-Dimethyl-*o*-toluidine, 24 hr. at 5° .................. | 8 | 42 | 5 |
| *NN*-Diethyl-*o*-toluidine, 48 hr. at 15° .................. | 2 | 8? | 7 |
| *NN*-Dimethyl-*o*-anisidine, 15 hr. at 15° ............... | 3 | — | 69 |
| *NN*-Dimethyl-α-naphthylamine,* 4 hr. at 15° ......... | 36 | — | 7 |

* Two-phase system (benzene–water).

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[4] Hinman and Hollmann, U.S.P. 2,178,585/1939.

(and hence the diazonium salt). However, the fact that neither free secondary amine nor *N*-nitrosoamine was isolated suggests that dealkylation and substitution are concerted. The striking difference in reactivity between *NN*-dimethyl- and *NN*-diethyl-*o*-toluidine is in accord with this concept. Dealkylation of *ortho*-substituted dialkylanilines by nitrous acid has previously been reported by Sveshnikov, Levkoev, and Krasnova, who used much more acidic media than employed in the present work.[5]

Whereas the *ortho*-substituted *NN*-dialkylanilines reacted extremely slowly with buffered nitrous acid, the *para*-substituted dialkylanilines (*NN*-dimethyl-*p*-toluidine and -*p*-anisidine) reacted quite rapidly; however, the product of the reaction was neither a nitroso-compound nor a diazonium salt, but the corresponding 2-nitro-derivative. Nitric oxide was evolved during the reaction, in the approximate proportion of two moles per mole of amine. The overall stoicheiometry of the reaction can therefore be represented:

$$\mathrm{ArH + 3HNO_2 \longrightarrow ArNO_2 + 2H_2O + 2NO}$$

The direct nitration of *para*-substituted aromatic tertiary amines by nitrous acid had previously been reported by Hodgson and his co-workers.[6,7] The striking feature of the present results is that this nitration occurs in solutions of very low acidity (pH 3—4).[3]

## EXPERIMENTAL

N-*Dimethylaniline.*—Sodium nitrite (17·25 g.) in water (35 c.c.) was added to dimethylaniline (6·05 g.) in ethyl acetate (50 c.c.). Then 4N-hydrochloric acid (62·5 c.c.) was added with stirring gradually during 1 hr. The vessel was surrounded by a water-bath (15—20°) for 7 hr. Ether was added, the layers were separated, and the aqueous layer was re-extracted with more ether. Residual ether was removed by suction, and zinc chloride (3·5 g. in 3 c.c. of water) was added. Sodium chloride was added in sufficient quantity to make the overall salt concentration 10%. The solution was set aside for 40 hr., whereafter *p*-dimethylaminobenzenediazonium chloride zinc double salt (6·38 g.) was isolated by filtration. (Preparation of 1-*p*-dimethylaminophenylazo-2-naphthol by direct introduction of the diazonium group into *NN*-dimethylaniline in homogeneous solution has been described previously.[2])

N-*Diethylaniline.*—Diethylaniline (1·6 c.c.) was dissolved in acetone (60 c.c.) and 2N-hydrochloric acid (50 c.c.), and the solution cooled to 0°. Sodium nitrite (10·35 g.) in water (20 c.c.) was added and the mixture was kept at 5° for 48 hr. The acetone was then evaporated under reduced pressure and the residual solution filtered and treated with β-naphthol (2·16 g.) in 2N-sodium hydroxide (100 c.c.). After 2 hr. the azo-dye (1·8 g.) was isolated by filtration and recrystallised from acetone to give dark red crystals of 1-*p*-diethylaminophenylazo-2-naphthol, m. p. and mixed m. p. 118—119°.[2]

N*N-Dimethyl*-m-*toluidine.*—2N-Hydrochloric acid (100 c.c.) was added gradually to a cooled solution of *NN*-dimethyl-*m*-toluidine (3·26 g.) and sodium nitrite (20·7 g.) in aqueous acetone (acetone 180 c.c., water 45 c.c.). The mixture was kept at 5° for 41 hr., being then still dark green; it was therefore kept for a further 9 hr. at 18—20°. Half the solution was then kept for a further 38 hr. while the other half was worked up. Acetone was removed under reduced pressure and the residual solution was extracted with chloroform. The aqueous layer was treated with an alkaline solution of β-naphthol Next morning the dye (1·8 g. from the first portion and 1·6 g. from the second portion) was recrystallised twice from acetone, to yield 1-(4-*dimethylamino*-2-*methylphenylazo*)-2-*naphthol* as needles with a green sheen, m. p. 118°, $\lambda_{max.}$ (in EtOH) 515·6 mμ (ε 36,800) (Found: C, 75·3; H, 6·8; N, 12·6. $C_{21}H_{23}N_3O$ requires C, 75·6; H, 6·9; N, 12·6%).

N-*Benzyl*-N-*ethylaniline.*—2N-Hydrochloric acid (100 c.c.) was added to a solution of *N*-benzyl-*N*-ethylaniline (4·22 g.) and sodium nitrite (20·7 g.) in a cooled mixture of acetone (180 c.c.) and water (50 c.c.). The reaction mixture was left at 5° for 40 hr., then further 2N-hydrochloric acid (50 c.c.) and acetone (50 c.c.) were added. After a further 24 hr. at 5° acetone was evaporated under reduced pressure from the now yellow mixture. The aqueous

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[5] Sveshnikov, Levkoev, and Krasnova, *Zhur. obshchei Klim.*, 1952, **22**, 1170; *Chem. Abs.*, 1953, **47**, 6363.

[6] Hodgson and Kershaw, *J.*, 1930, 277.

[7] Hodgson and Crook, *J.*, 1932, 1812.

layer was decanted from an oil which separated and was extracted three times with chloroform (50 c.c.). The final almost colourless aqueous phase contained no diazonium salt, but the chloroform extracts were found to do so. The combined chloroform extracts were washed with 0·5N-hydrochloric acid (3 × 120 c.c.). The combined acid washings were treated with an alkaline solution of β-naphthol. Next morning the azo-dye was collected in chloroform. The extract was washed twice each with 0·5N-sodium hydroxide and hydrochloric acid and water, dried ($Na_2SO_4$), and evaporated to yield the dye (2·5 g.) which was chromatographed on activated alumina and so proved to be almost pure. Recrystallisation from aqueous acetone gave 1-[p-(N-*benzyl*-N-*ethylamino*)*phenylazo*]-2-*naphthol* as dark needles with a metallic lustre, m. p. 136—137°, $\lambda_{max.}$ (in EtOH) 507 mμ (ε 32,700) (Found: C, 78·6; H, 6·1; N, 11·2, $C_{25}H_{23}N_3O$ requires C, 78·8; H, 6·0; N, 11·1%).

N-*Benzyl*-N-*ethyl*-m-*toluidine*.—2N-Hydrochloric acid (100 c.c.) was added to a solution of *N*-benzyl-*N*-ethyl-*m*-toluidine (4·5 g.) and sodium nitrite (20·7 g.) in acetone (175 c.c.) and water (50 c.c.). The mixture was kept for 24 hr. at 5°, then further hydrochloric acid (50 c.c.) and acetone (50 c.c.) were added. After a further 24 hr. at 5°, all the nitrous acid had reacted or evaporated, yet the solution was still dark green, so more sodium nitrite (6·9 g.) and 2N-hydrochloric acid (40 c.c.) were added. After another 24 hr., the acetone was evaporated under reduced pressure and the residual solution was extracted with ether. The aqueous layer was treated with an alkaline solution of β-naphthol; next morning the dye (3·85 g.) was collected, chromatographed on activated alumina, and eluted with benzene–light petroleum. This showed that there was very litle impurity. The eluted material recrystallised from aqueous acetone to yield dark red 1-[4-(*N-benzyl-N-ethylamino*)-2-*methylphenylazo*]-2-*naphthol*, m. p. 121—122°, $\lambda_{max.}$ (in EtOH) 515·5 mμ (ε 24,600) (Found: C, 78·9; H, 6·4; N, 10·6. $C_{26}H_{25}N_3O$ requires C, 79·0; H, 6·3; N, 10·6%).

N-*Ethyl*-N-2-*hydroxyethylaniline*.—2N-Hydrochloric acid (100 c.c.) was added to a solution of *N*-ethyl-*N*-2-hydroxyethylaniline (3·3 g.) and sodium nitrite (20·7 g.) in acetone (175 c.c.) and water (50 c.c.). The mixture was kept for 24 hr. (the green colour had almost disappeared). Acetone was evaporated under reduced pressure and the residual solution was extracted with chloroform. The aqueous layer was treated with an alkaline solution of β-naphthol. After 2 hr. the dye (5·5 g.) was collected and chromatography on activated alumina showed that it was almost pure. Recrystallisation from aqueous acetone yielded dark red 1-[4-(N-*ethyl*-N-2-*hydroxyethylamino*)*phenylazo*]-2-*naphthol*, m. p. 119—120°, $\lambda_{max.}$ (in EtOH) 500 mμ (ε 30,700) (Found: C, 71·8; H, 6·5; N, 12·2. $C_{20}H_{21}N_3O_2$ requires C, 71·6; H, 6·3; H, 12·5%).

NN-*Dimethyl*-o-*toluidine*.—A solution of the amine (2·7 g.) in 2N-hydrochloric acid (50 c.c.) was added to sodium nitrite (6·9 g.) in ice-cold water (50 c.c.). The resultant solution was left at 5° for 24 hr. The little remaining nitrous acid was destroyed by sulphamic acid, and the solution was extracted with chloroform. The extract was dried ($Na_2SO_4$) and evaporation left an oil (3·08 g.) which was taken up in 6N-hydrochloric acid. This acidic mixture was extracted with ether; the ether layer was evaporated to yield an oil (0·6 g.) which was not investigated further. The acidic layer was neutralised with sodium hydrogen carbonate, a green precipitate (1·25 g.) separating. Two recrystallisations from benzene–light petroleum gave green *N*-methyl-4-nitroso-*o*-toluidine, m. p. 141° [8] (Found: C, 63·7; H, 6·2; N, 19·1. Calc. for $C_8H_{10}N_2O$: C, 64·0; H, 6·7; N, 18·7%). The original aqueous mother-liquor was rendered alkaline and re-extracted with chloroform. The extract was dried ($Na_2SO_4$). Evaporation left an oil (0·55 g.) which was taken up in 2N-hydrochloric acid. This acidic solution was extracted with ether, and the ether layer was evaporated to yield an oil (0·01 g.) which was not investigated further. The acidic layer was neutralised and the crude yellow product (0·2 g.) was purified by chromatography to yield a yellow oil which solidified. Two recrystallisations from aqueous methanol afforded yellow *NN*-dimethyl-4-nitro-*o*-toluidine, m. p. 41° [9] (Found: C, 59·8; H, 6·1; N, 15·1. Calc. for $C_9H_{12}N_2O_2$: C, 60·0; H, 6·6; N, 15·1%). The original mother-liquor was treated with an alkaline solution of β-naphthol. The dye (0·46 g.) was isolated in chloroform and purified by two recrystallisations from aqueous methanol. The red needles of 1-(4-*methylamino*-m-*tolylazo*)-2-*naphthol* had m. p. 76—77°, $\lambda_{max.}$ (in EtOH) 438 mμ (ε 17,400) (Found: C, 74·1; H, 5·9; N, 14·2. $C_{18}H_{17}N_3O$ requires C, 74·3; H, 5·8; N, 14·4%).

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[8] Kock, *Annalen*, 1888, **243**, 308.
[9] Bernthsen, *Ber.*, 1892, **25**, 3133.

NN-*Diethyl*-o-*toluidine*.—A solution of *NN*-diethyl-*o*-toluidine (4·89 g.) in 2N-hydrochloric acid (150 c.c.) was added to sodium nitrite (20·7 g.) in water (150 c.c.). The mixture was left at 5° for 24 hr., then further sodium nitrite (20·7 g. in 50 c.c. of water) and 2N-hydrochloric acid (150 c.c.) were added. The mixture was set aside at 5° for an additional 24 hr., then treated with an excess of sulphamic acid. The solution was extracted with chloroform, then rendered alkaline with sodium hydrogen carbonate, and extracted again. Both extracts yielded oils on evaporation (1·47 g. from the acidic and 2·10 g. from the alkaline solution); these were combined and chromatographed on alumina. The column was eluted with light petroleum (b. p. 60—80°). The first material eluted was unchanged *NN*-diethyl-*o*-toluidine (0·79 g.), which was identified by its infrared spectrum. The next fraction was a yellow oil (0·28 g.) which was characterised by its conversion into a picrate and proved to be *NN*-diethyl-*p*-nitro-*o*-toluidine. The *picrate* had m. p. 205—206° (Found: C, 46·5; H, 4·6; N, 16·2. $C_{17}H_{19}N_5O_9$ requires C, 46·7; H, 4·3; N, 16·0%). Further elution of the column yielded a third fraction, a greenish-yellow oil (0·4 g.) which failed to give a picrate and was not characterised. An orange band adhered to the column and was separated by extrusion and extraction with benzene–chloroform. Evaporation of this solvent left a viscous red oil (0·11 g.) which was not identified. The original mother-liquor was treated with an alkaline solution of β-naphthol. The crude dye (0·15 g.) was isolated in chloroform; it was presumed to be 1-(4-ethylamino-*o*-tolylazo)-2-naphthol but an attempt to recrystallise it from aqueous methanol was unsuccessful.

NN-*Dimethyl*-1-*naphthylamine*.—Treatment of *NN*-dimethyl-1-naphthylamine with buffered nitrous acid or with a homogeneous nitrous acid solution containing equal parts of hydrochloric acid and sodium nitrite failed to yield a diazonium salt. However, in a two-phase system an appreciable yield of diazonium salt was obtained. A solution of *NN*-dimethyl-1-naphthylamine (3·42 g.) in benzene (30 c.c.), floating on a solution of sodium nitrite (6·9 g.) in water (25 c.c.), was stirred mechanically. N-Hydrochloric acid (100 c.c.) was added during 2 hr.; the mixture was stirred for a further 4 hr. at 15—18°. The excess of nitrous acid was destroyed with sulphamic acid and the two layers were separated. The aqueous phase was extracted, first, with more benzene and then with ether. The residues (1·38 g.) from both the extracts were combined and chromatographed on activated alumina. Elution with benzene gave two fractions, one eluted (0·7 g.) and one retained on the column. The latter fraction was isolated by extrusion and extraction with methanol. A total of 0·13 g. was extracted from which a very small yield of unidentified red crystals was obtained (Found: C, 44·1; H, 3·0; N, 12·2%) (m. p. 300°). The eluted fraction was rechromatographed on activated alumina. The product (0·3 g.) eluted from the second column was recrystallised from aqueous methanol, to yield *NN*-dimethyl-4-nitro-1-naphthylamine, m. p. 58° (Found: C, 65·9; H, 5·4; N, 13·2. Calc. for $C_{12}H_{12}N_2O_2$: C, 66·7; H, 5·5; N, 13·0%). The original aqueous mother-liquor was treated with an alkaline solution of β-naphthol. Next morning the dye (2·38 g.) was isolated by filtration and was recrystallised from methanol to give dark red needles of 1-(4-*methylamino*-1-*naphthylazo*)-2-*naphthol*, m. p. 128—129°, $\lambda_{max.}$ (in EtOH) 518 mμ (ε 19,100) (Found: C, 77·3; H, 5·4; N, 12·7. $C_{21}H_{17}N_3O$ requires C, 77·0; H, 5·2; N, 12·8%).

NN-*Dimethyl*-o-*anisidine*.—2N-Hydrochloric acid (150 c.c.) was added to a cooled solution of *NN*-dimethyl-*o*-anisidine (4·5 g.) and sodium nitrite (31·1 g.) in acetone (240 c.c.) and water (150 c.c.). The mixture was kept at 10—15° for 15 hr. during which yellow crystals separated. These (1·89 g.) were filtered off and the filtrate was treated with sulphamic acid; evaporation under reduced pressure precipitated further solid (0·22 g.). The aqueous mother-liquor was extracted with chloroform, to yield an orange solid (2·97 g.), and then rendered alkaline with sodium hydrogen carbonate and extracted again to yield further yellow solid (1·12 g.). The principal component of these extracts was *NN*-dimethyl-4-nitro-*o*-anisidine, of which the total yield (pure) was 2·76 g. (m. p. 99—100° [5]) (Found: N, 14·0. Calc. for $C_9H_{12}N_2O_3$: N, 14·3%). The remaining oil still contained a high proportion of the nitro-compound, as shown by the formation of the *picrate*, m. p. 117—118° (Found: C, 42·8; H, 3·8; N, 16·6. $C_{15}H_{15}N_5O_{10}$ requires C, 42·4; H, 3·5; N, 16·5%). The main aqueous solution was treated with an alkaline solution of β-naphthol. After 2 hr. the dye (0·3 g.) was isolated by chloroform-extraction and recrystallised from aqueous methanol to yield dark needles of 1-(3-*methoxy*-4-*methylaminophenylazo*)-2-*naphthol*, m. p. 91—92° (Found: C, 70·6; H, 6·1; N, 13·5. $C_{18}H_{17}N_3O_2$ requires C, 70·4; H, 5·5; N, 13·7%), $\lambda_{max.}$ (in EtOH) 489 mμ (ε 19,200).

NN-*Dimethyl*-p-*toluidine*.—2N-Hydrochloric acid (100 c.c.) was added to a solution of *NN*-dimethyl-*p*-toluidine (2·7 g.) and sodium nitrite (20·7 g.) in acetone (100 c.c.) and water (100 c.c.).

The mixture was left at 5° but after 0·5 hr. started to separate into two liquid phases, so further acetone (75 c.c.) was added. After 24 hr. sulphamic acid was added and the acetone was evaporated under reduced pressure. The residue was extracted with chloroform, to yield an oil (3·2 g.), and the aqueous solution was rendered alkaline with sodium hydrogen carbonate and extracted again, to yield further red oil (0·5 g.). The combined oils were chromatographed on activated alumina. The first fraction eluted was *NN*-dimethyl-2-nitro-*p*-toluidine (2·66 g.) which was characterised as picrate, m. p. 128—129° [6] (Found: C, 43·7; H, 3·5; N, 17·6. Calc. for $C_{15}H_{15}O_9N_5$: C, 44·0; H, 3·7; N, 17·1%). The main aqueous mother-liquor contained no detectable diazonium salt.

NN-*Dimethyl*-p-*anisidine*.—2N-Hydrochloric acid (75 c.c.) was added to a solution of *NN*-dimethyl-*p*-anisidine (2·25 g.) and sodium nitrite (15·5 g.) in acetone (120 c.c.) and water (75 c.c.). The mixture was left at 5° for 18 hr. (in the early stages of the reaction slow effervescence was observed), then treated with sulphamic acid, and evaporated under reduced pressure. A yellow solid (0·10 g.) separated and was recrystallised from light petroleum (b. p. 40—60°) to yield yellow *NN*-dimethyl-2,6-dinitro-*p*-anisidine, m. p. 90—91° [7] (Found: C, 44·6; H, 4·6; N, 17·8. Calc. for $C_9H_{11}N_3O_5$: C, 44·8; H, 4·6; N, 17·4%). The aqueous filtrate was rendered alkaline with sodium hydrogen carbonate and extracted with chloroform. The chloroform extract yielded an oil (2·83 g.) which was chromatographed on activated alumina. Elution with light petroleum gave a trace of unidentified material. The main fraction, a red oil (2·1 g.), was eluted with benzene. Treatment of this with picric acid in ethanol yielded *NN*-dimethyl-2-nitro-*p*-anisidine picrate, m. p. 143° [7] (Found: C, 42·2; H, 3·7; N, 16·3. Calc. for $C_{15}H_{15}N_5O_{10}$: C, 42·4; H, 3·5; N, 16·5%). The main aqueous mother-liquor contained no detectable diazonium salt. The experiment was repeated in an atmosphere of carbon dioxide with a continuous stream of carbon dioxide passing over the reactants. The carbon dioxide was led into a conventional nitrometer in which a colourless non-acidic gas was collected. This gas, which gave brown fumes in the air, was identified as nitric oxide by its infrared spectrum. After 6 hours' reaction, just over 1·8 moles of nitric oxide per mole of anisidine had been collected.

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