# The Rearrangement of Some N-Substituted Hydrazobenzenes.

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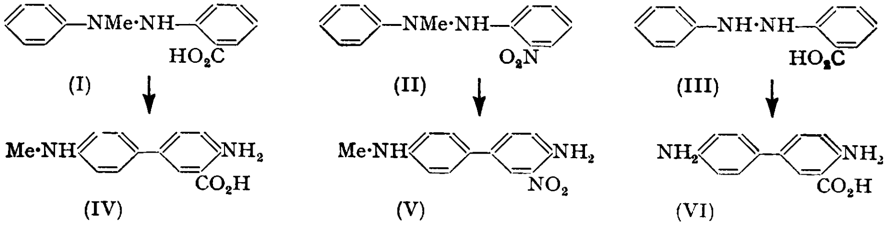
Some unsymmetrical *N*-substituted hydrazobenzenes have been prepared and their rearrangements studied.

Although the benzidine transformation has been extensively studied, particularly in the early days by Jacobsen, it is curious to find that the transformation of hydrazobenzenes of the type Ar·NMe·NHAr′ (Ar $\neq$ Ar′) has not been investigated. Such hydrazobenzenes were prepared by condensing *as*-methylphenylhydrazine with the corresponding *o*-bromobenzenes and copper powder as a catalyst. In the preparation of *N*′-methylhydrazobenzene-2-carboxylic acid (I) an inert atmosphere is needed or the product is almost exclusively azobenzene-2-carboxylic acid. This easy demethylation of the *N*-methyl group is surprising. If phenylhydrazine itself is used in the condensation in the presence of air azobenzene-2-carboxylic acid is again formed. In the condensation of methylphenylhydrazine and *o*-bromonitrobenzene *N*-methyl-2′-nitrohydrazobenzene (II) is obtained even in the presence of air.

The rearrangements of the hydrazobenzenes (I), (II), and (III) to the benzidines (IV), (V), and (VI) were effected by means of warm dilute hydrochloric acid.

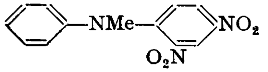


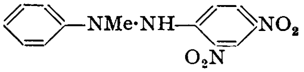
When the amino-acid (IV) was basified with sodium hydroxide the sparingly soluble sodium salt was formed, from which the free acid was isolated by acetic acid. The *N*-

methyl-3′-nitrobenzidine (V) easily forms a monohydrochloride and on reduction the corresponding diamine. This forms a benziminazole with formic acid and a quinoxaline with benzil.

When 1-chloro-2 : 4-dinitrobenzene is used instead of the mononitro-compound *N*-methyl-2 : 4-dinitrodiphenylamine (VII) is obtained. If, however, this condensation is carried out in the absence of copper but with potassium acetate, a mixture of this product (VII) and *N*-methyl-2′ : 4′-dinitrohydrazobenzene (VIII) is obtained. The latter does not rearrange under conditions which convert (I) into (IV).

(VII)





(VIII)

## EXPERIMENTAL

N′-*Methylhydrazobenzene*-2-*carboxylic acid*.—Freshly distilled *as*-methylphenylhydrazine (2 g.), freshly precipitated copper (2 g.), and fused potassium carbonate (2 g.) in absolute alcohol (10 c.c.) were placed in a flask, flushed with nitrogen, a solution of *o*-bromobenzoic acid (2 g.) in absolute alcohol (10 c.c.) was run in, and the mixture refluxed with stirring for 4 hr. in a nitrogen atmosphere. After removal of the alcohol the residue was extracted with water, the copper filtered off, the filtrate carefully neutralised (dilute acetic acid), and the *hydrazobenzene* which was precipitated as a yellow solid was filtered off and recrystallised as soon as possible from methanol–water, giving pale yellow needles (1·4 g.), m. p. 157—158° (Found : C, 69·3; H, 6·0. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%).

*Azobenzene*-2-*carboxylic Acid*.—By the same method and from reactants in air, the brown azo-compound was obtained on addition of dilute acetic acid. This crystallised from light petroleum (b. p. 60—80°) in orange crystals, m. p. 90° (Found : C, 69·0; H, 4·6. Calc. for $C_{13}H_{10}O_2N_2$ : C, 69·0; H, 4·4%).

*Hydrazobenzene*-2-*carboxylic Acid*.—Freshly distilled phenylhydrazine (2 g.), in place of the *N*-methylphenylhydrazine, gave hydrazobenzene-2-carboxylic acid, which crystallised from ethanol–water in white needles (1·6 g.), m. p. 166—168° (Found : C, 68·5; H, 5·4; N, 12·4. Calc. for $C_{13}H_{12}O_2N_2$ : C, 68·4; H, 5·3; N, 12·3%).

N′-*Methylbenzidine*-3-*carboxylic Acid* (IV).—*N*-Methylhydrazobenzene-2′-carboxylic acid (1 g.) was shaken in dilute hydrochloric acid (50 c.c.; 1 : 4) overnight. The suspension was heated for 1 hr. in a boiling-water bath, then basified with sodium carbonate, and the sodium salt, which is fairly insoluble in water, was filtered off and recrystallised from water. The free *acid* was liberated by suspending the salt in water, adding a few drops of glacial acetic acid, till the solution was almost neutral to litmus, and recrystallising the precipitate from methanol–water (yield, 0·8 g.; m. p. 202—204°) (Found : C, 69·6; H, 6·0. $C_{14}H_{14}O_2N_2$ requires C, 69·4; H, 5·8%).

*Benzidine*-3-*carboxylic Acid*.—Hydrazobenzene-2-carboxylic acid (2 g.) was suspended in dilute hydrochloric acid (1 : 4; 70 c.c.), left overnight, and heated for 1 hr. in a boiling-water bath. The filtered solution was then basified, basic impurities were removed by extraction with ether and the aqueous solution was acidified with dilute acetic acid. The white benzidine-3-carboxylic acid was centrifuged off, the supernatant liquid decanted, and the benzidine purified by dissolution in 3N-hydrochloric acid (charcoal) and precipitation as a white micro-crystalline solid by the addition of excess of sodium acetate (yield, 1 g.; m. p. 209—211°) (Found : N, 12·5. Calc. for $C_{13}H_{12}O_2N_2$ : N, 12·3%).

N-*Methyl*-2′-*nitrohydrazobenzene*.—To a solution of *o*-bromonitrobenzene (10 g.) in absolute alcohol (30 c.c.) were added freshly precipitated copper (1 g.), fused potassium carbonate (4 g.), and a solution of freshly distilled *as*-methylphenylhydrazine (7 g.) in absolute alcohol (20 c.c.). The mixture was refluxed for 13 hr., the copper and potassium carbonate were filtered off from the hot solution, and the alcohol was removed under reduced pressure without heating. The N-*methyl*-2′-*nitrohydrazobenzene* was obtained crystalline, together with a dark oil. The oil was decanted and the product recrystallised from light petroleum (b. p. 60—80°) as orange prisms (4·7 g.), m. p. 90° (Found : C, 64·3; H, 5·4. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·7%).

N-*Methyl*-3′-*nitrobenzidine*.—*N*-Methyl-2′-nitrohydrazobenzene (1 g.) was suspended in dilute hydrochloric acid (1 : 1, 25 c.c.) and shaken overnight. The suspension was then heated for 1 hr. in a boiling-water bath, and the clear solution decanted from oily starting material. On cooling, a yellow hydrochloride crystallised and was filtered off and the free base liberated (sodium carbonate) and recrystallised from methanol in purple needles (0·4 g.), m. p. 180—181° (Found : C, 64·2; H, 5·7. $C_{13}H_{13}O_2N_3$ requires C, 64·2; H, 5·4%). The yellow *monohydro-*

*chloride*, crystallised from methanol, had m. p. 217—220° (Found: C, 56·4; H, 5·3. $C_{13}H_{13}O_2N_3,HCl$ requires C, 55·8; H, 5·0%).

*3'-Amino*-N-*methylbenzidine*.—*N*-Methyl-3'-nitrobenzidine (0·1 g.) in glacial acetic acid (50 c.c.) was hydrogenated at room temperature and pressure over palladium charcoal, 1·06 mols. of hydrogen being absorbed in 1 hr. The catalyst was filtered off and the acetic acid was removed under reduced pressure. The residue was basified (10% aqueous sodium hydroxide) and extracted with ether, the ethereal extract dried ($Na_2SO_4$), and the ether removed. The diamine was left as a dark red unstable oil which could not be crystallised. It gave a *hydrochloride* which crystallised from concentrated hydrochloric acid in white needles, m. p. 177—180° after sintering at 160° (Found: C, 49·1; H, 5·9. $C_{13}H_{15}N_3,3HCl$ requires C, 48·6; H, 5·3%).

2 : *3-Diphenyl*-6-p-*toluidinoquinoxaline*.—To a solution of 3'-amino-*N*-methylbenzidine (0·2 g.) in absolute alcohol (2 c.c.) was added a hot solution of benzil (0·2 g.) in glacial acetic acid (2 c.c.). The yellow crystalline condensation product, crystallised from ethanol, had m. p. 196—198° (Found: C, 83·7; H, 6·0; N, 11·2. $C_{27}H_{21}N_3$ requires C, 83·7; H, 5·4; N, 10·9%). The *acetyl* derivative had m. p. 215—217° (from alcohol) (Found: C, 80·8; H, 5·7. $C_{29}H_{23}ON_3$ requires C, 81·1; H, 5·4%).

5-N-*Formyl*-p-*toluidinobenziminazole*.—3'-Amino-*N*-methylbenzidine (0·5 g.) was refluxed with anhydrous formic acid (10 c.c.) for 5 hr. Excess of formic acid and the water formed were removed under reduced pressure, and the white solid residue was dissolved in hot dilute acetic acid (charcoal) and then filtered. The *benziminazole* was precipitated on basification (10% sodium hydroxide) and crystallised from methanol–water. It had m. p. 230—232° (Found: C, 71·7; H, 5·7. $C_{15}H_{13}ON_3$ requires C, 71·7; H, 5·2%). The yellow *picrate* had m. p. 276—279° (Found: C, 52·7; H, 3·6. $C_{15}H_{13}ON_3,C_6H_3O_7N_3$ requires C, 52·5; H, 3·3%).

N-*Methyl-2'* : *4'-dinitrohydrazobenzene*.—(*a*) To a mixture of pure *as*-methylphenylhydrazine (0·5 g.), freshly precipitated copper (0·5 g.), and fused potassium carbonate (0·5 g.) in absolute alcohol (5 c.c.), was added a solution of 1-chloro-2 : 4-dinitrobenzene (1·5 g.) in absolute alcohol (10 c.c.), and the mixture was refluxed for 18 hr. The copper and alcohol were removed. The residue was extracted with hot alcohol and the extract was treated with charcoal; on filtration and cooling, *N*-methyl-2 : 4-dinitrodiphenylamine separated in red needles, m. p. and mixed m. p. 166—167° (Found: C, 57·2; H, 4·0; N, 15·6. Calc. for $C_{13}H_{11}O_4N_3$: C, 57·1; H, 4·1; N, 15·4%).

(*b*) To a solution of 1-chloro-2 : 4-dinitrobenzene (3·2 g.) and sodium acetate (2 g.) in absolute alcohol (30 c.c.) and water (3 c.c.) was added pure *as*-methylphenylhydrazine (2 g.) in absolute alcohol (10 c.c.). The mixture was refluxed for 6 hr., then cooled, and the product was filtered off and fractionally crystallised from alcohol. The *N*-methyl-2' : 4'-dinitrohydrazobenzene, recrystallised in dark red plates, had m. p. 121—123° (Found: C, 54·0; H, 4·6; N, 19·8. $C_{13}H_{12}O_4N_4$ requires C, 54·2; H, 4·2; N, 19·5%). *N*-Methyl-2 : 4-dinitrodiphenylamine recrystallised in orange needles, m. p. 166—167°.

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