38. *The Preparation of* 2 : 2′-*Diaminodiphenylamines and* 2 : 2′-*Diacetamidodiphenylamines and their Behaviour on Oxidation.*

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2 : 2′-*Diaminodiphenylamine* and its 4-*methoxy*-, 4 : 4′-*dimethyl*-, 4 : 4′-*dimethoxy*-, and 4-methoxy-4′-methyl-derivatives have been prepared. Each of these substances can be converted into its diacetyl derivative by the action of cold acetic anhydride and into the corresponding 1-phenyl-2-methylbenziminazole with acetic anhydride on heating. Oxidation of the base yields the corresponding phenazine. Mild oxidising agents do not affect 2 : 2′-*diacetamidodiphenylamine* or its 4 : 4′-*dimethyl* derivative, but 2 : 2′-*diacetamido*-4 : 4′-*dimethoxydiphenylamine* and 2 : 2′-*diacetamido*-4-*methoxy*-4′-*methyldiphenylamine* are converted into *quinoneimines* with the loss of a methyl group.

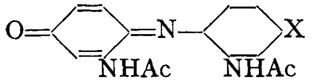
ECKERT and STEINER (*Monatsh.*, 1914, **35**, 1154) reduced 2 : 2′-dinitrodiphenylamine with stannous chloride and obtained phenazine by oxidising the resulting solution with hydrogen peroxide, but neither 2 : 2′-*diaminodiphenylamine* nor its methyl or methoxy-derivatives appear to have been described.

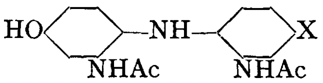
2 : 2′-Diaminodiphenylamine, 2 : 2′-*diamino*-4 : 4′-*dimethyldiphenylamine*, 2 : 2′-*diamino*-4 : 4′-*dimethoxydiphenylamine*, 2 : 2′-*diamino*-4-*methoxydiphenylamine*, and 2 : 2′-diamino-4-methoxy-4′-methyldiphenylamine have now been prepared by the reduction of the corresponding dinitro-compounds with zinc dust and acetic acid, and with the exception of the last they were all obtained as colourless crystalline substances which rapidly darkened on exposure. Treatment of these diaminodiphenylamines with cold acetic anhydride leads to the formation of the corresponding diacetamido-compound, and the action of boiling acetic anhydride converts them into the 1-(2′-*acetamidophenyl*)-2-*methylbenziminazole*.

Oxidation of 2 : 2′-diaminodiphenylamines with mild oxidising agents such as ferric chloride or hydrogen peroxide leads to the production of phenazines and in this way phenazine itself was obtained from 2 : 2′-diaminodiphenylamine, 2 : 7-dimethylphenazine from the 4 : 4′-dimethyl compound, 2-*methoxyphenazine* from the 4-methoxy-compound, 2 : 7-dimethoxyphenazine from the 4 : 4′-dimethoxy-derivative, and 2-*methoxy*-7-*methylphenazine* from the 4-methoxy-4′-methyldiphenylamine. The methoxymethyl compound, in particular, is readily oxidised and an aqueous acetic acid solution of this substance deposits crystals of the phenazine when exposed to air. Addition of the oxidising agent to acid solutions of the diamines produces an intense coloration, which fades on standing and in the case of the 2 : 2′-diamino-4 : 4′-dimethoxydiphenylamine the solution becomes deep purple and deposits crystals resembling copper-bronze. This substance is highly unstable and is rapidly converted into the phenazine. It is considered probable that in all cases the primary product of oxidation is a free radical, which would account for the colour produced, and that in this case the free radical is stable enough to crystallise from the solution. It was not, however, possible to obtain it in a pure state.

Oxidation of 2 : 2′-*diacetamido*-4 : 4′-*dimethoxydiphenylamine* with such reagents as ferric chloride, nitrous acid or hydrogen peroxide yields a black, crystalline substance with a green metallic lustre which appears to be 3-*acetamido*-N-(2′-*acetamido*-4′-*methoxyphenyl*)-*quinoneimine* (I, X = OMe). It forms an intense crimson solution in organic solvents.

(I.)

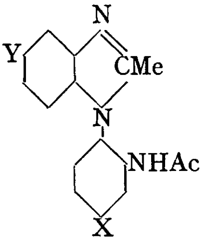




(II.)

Reduction of (I, X = OMe) yields (II, X = OMe), which can be reconverted into (I, X = OMe) by oxidation.

The compound (II, X = OMe) on methylation with methyl sulphate in air-free potassium hydroxide solution gives 2 : 2′-diacetamido-4 : 4′-dimethoxydiphenylamine. When (II, X = OMe) is treated with acetic anhydride, an *iminazole* is produced and this must be either (III; X = OMe, Y = OAc) or (III; X = OAc, Y = OMe). From a



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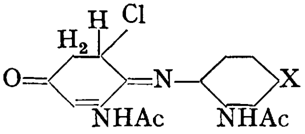

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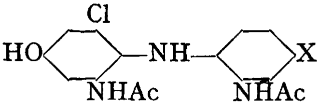

(V.)

consideration of the inductive effects of the two groups involved, the latter appears to be more probable. Hydrolysis of the compound (III) gives the corresponding *aminohydroxyiminazole*. Hydrochloric acid rapidly decolorises (I, X = OMe) and converts it into a *chlorinated iminazole*. It appears that the initial reaction is the addition of hydrogen chloride to the quinonoid nucleus to give (IV, X = OMe), which then rearranges to give (V, X = OMe). This is followed by iminazole formation and hydrolysis.

Oxidation of 2 : 2′-*diacetamido*-4-*methoxy*-4′-*methyldiphenylamine* produces (I, X = Me), which is orange-brown and has a slight green lustre and can be reduced to (II, X = Me). A series of compounds analogous to those described above, *viz.*, (III, X = OAc, Y = Me) or (III; X = Me, Y = OAc), an *aminohydroxyiminazole* by hydrolysis of this *diacetyl* compound, and a *chloro-iminazole* by the action of hydrochloric acid on (I, X = Me), have been obtained. Both (I, X = OMe) and (I, X = Me) give *mononitro*-compounds with nitric acid.

2 : 2′-*Diacetamidodiphenylamine* and its 4 : 4′-*dimethyl* derivative are not affected by mild oxidising agents and, although a deep brown colour is produced in the solution when 2 : 2′-*diacetamido*-4-*methoxydiphenylamine* is treated with ferric chloride, no crystalline oxidation product has been isolated.

EXPERIMENTAL.

2 : 2'-Dinitrodiphenylamine (Eckert and Steiner, *loc. cit.*) and its analogues were reduced to the corresponding 2 : 2'-diamino-compounds by the gradual addition of zinc dust to a suspension of the amine (2 g.) in glacial acetic acid (30 c.c.) with vigorous shaking. When the solution became almost colourless, the excess of zinc dust was removed, and the filtrate diluted with water (300 c.c.). The acetic acid was partially neutralised with ammonia, and crystalline sodium acetate added to precipitate the amine.

2 : 2'-Diacetamidodiphenylamine and its analogues separated when cold solutions of the amines in dilute acetic acid were treated with a slight excess of acetic anhydride.

2 : 2'-*Diaminodiphenylamine* crystallised from light petroleum (b. p. 60—80°) in almost colourless prisms, m. p. 101°, which darkened on exposure (yield, about 60%) (Found : C, 72·6; H, 6·6. $C_{12}H_{13}N_3$ requires C, 72·4; H, 6·5%).

2 : 2'-*Diacetamidodiphenylamine* crystallised from dilute acetic acid in colourless plates, m. p. 199° (Found : C, 67·6; H, 6·4. $C_{16}H_{17}O_2N_3$ requires C, 67·9; H, 6·0%).

1-(2'-*Acetamidophenyl*)-2-*methylbenziminazole*.—The above diacetyl compound (1 g.) was boiled under reflux with acetic anhydride (10 c.c.) for 30 minutes. The solution was diluted with water and rendered alkaline with ammonia. The precipitate crystallised from aqueous alcohol in colourless prisms, m. p. 220° (Found : C, 72·3; H, 5·5. $C_{16}H_{15}ON_3$ requires C, 72·5; H, 5·7%).

2 : 2'-*Dinitro*-4 : 4'-*dimethyldiphenylamine*.—4-Iodo-3-nitrotoluene (5 g.), 3-nitro-*p*-toluidine (2·5 g.), potassium carbonate (1 g.), and copper powder (1 g.) were intimately mixed and heated together at 160° until the mass was solid (2 hours). The mixture was pulverised and extracted with hot acetic acid, from which 2 : 2'-dinitro-4 : 4'-dimethyldiphenylamine separated in orange plates, m. p. 195° (yield, about 50%) (Found : C, 58·8; H, 4·5; N, 14·6. Calc. : C, 58·6; H, 4·5; N, 14·6%).

2 : 2'-*Diamino*-4 : 4'-*dimethyldiphenylamine* was prepared from this dinitro-compound in about 70% yield. On addition of the sodium acetate a sticky precipitate separated and it was extracted with dilute hydrochloric acid. The required amine separated on further treatment with sodium acetate and crystallised from light petroleum (b. p. 80—100°) in colourless prisms, m. p. 104° (Found : C, 74·0; H, 7·5. $C_{14}H_{17}N_3$ requires C, 74·0; H, 7·5%).

Treatment of the amine with acetic anhydride yielded 2 : 2'-*diacetamido*-4 : 4'-*dimethyldiphenylamine*, which separated from benzene in colourless needles, m. p. 215° (Found : C, 69·1; H, 6·9; N, 13·6. $C_{18}H_{21}O_2N_3$ requires C, 69·45; H, 6·8; N, 13·5%).

1-(2'-*Acetamido*-4'-*methylphenyl*)-2 : 5-*dimethylbenziminazole* was obtained when this diacetamido-compound (1 g.) was refluxed with acetic anhydride (10 c.c.) for 30 minutes. It crystallised from aqueous alcohol in colourless prisms, m. p. 217° (Found : C, 73·5; H, 6·3. $C_{18}H_{19}ON_3$ requires C, 73·7; H, 6·5%).

2 : 2'-*Diamino*-4 : 4'-*dimethoxydiphenylamine* was prepared from 2 : 2'-dinitro-4 : 4'-dimethoxydiphenylamine (Robinson and Tomlinson, J., 1934, 1529), the solution finally becoming colourless. The product crystallised from light petroleum (b. p. 80—100°) or from aqueous alcohol in colourless prisms, m. p. 100° (Found : C, 64·9; H, 6·5; N, 16·4. $C_{14}H_{17}O_2N_3$ requires C, 64·9; H, 6·6; N, 16·2%).

2 : 2'-*Diacetamido*-4 : 4'-*dimethoxydiphenylamine* was prepared by treating this amine with acetic anhydride. It crystallised from aqueous alcohol in colourless plates, m. p. 233° (Found : C, 63·2; H, 5·8; N, 12·2. $C_{18}H_{21}O_4N_3$ requires C, 63·0; H, 6·1; N, 12·2%).

5-*Methoxy*-1-(2'-*acetamido*-4'-*methoxyphenyl*)-2-*methylbenziminazole* was obtained when the diacetamido-compound was refluxed with acetic anhydride. It separated from aqueous alcohol in colourless prisms, m. p. 236° (Found : C, 66·8; H, 6·3; N, 12·8. $C_{18}H_{19}O_3N_3$ requires C, 66·5; H, 5·8; N, 12·9%).

When this substance was boiled with hydrochloric acid for ten minutes and the resulting solution was diluted and rendered alkaline, 5-*methoxy*-1-(2'-*amino*-4'-*methoxyphenyl*)-2-*methylbenziminazole* was obtained. It separated from aqueous alcohol in faintly yellow prisms, m. p. 148°. It was diazotisable (Found : C, 68·1; H, 6·4; N, 15·1. $C_{16}H_{17}O_2N_3$ requires C, 67·9; H, 6·0; N, 14·8%).

2 : 2'-*Dinitro*-4-*methoxy*-4'-*methyldiphenylamine*.—4-Iodo-3-nitrotoluene (5 g.), *m*-nitro-*p*-anisidine (2·5 g.), potassium carbonate (1 g.), and copper powder (1 g.) were mixed and heated together at 120° until the mass was solid. It was then pulverised and extracted with glacial acetic acid, from which the *dinitro*-compound crystallised in orange-red plates, m. p. 188° (yield, 50%) (Found : C, 55·5; H, 4·3; N, 13·4. $C_{14}H_{13}O_5N_3$ requires C, 55·4; H, 4·3; N, 13·9%).

2 : 2'-Diamino-4-methoxy-4'-methyldiphenylamine was not obtained in a pure state. The oily reduction product on treatment with cold acetic anhydride yielded 2 : 2'-*diacetamido*-4-*methoxy*-4'-*methyldiphenylamine*, which crystallised from dilute acetic acid in colourless prisms, m. p. 181—182° (Found: C, 65·9; H, 6·0; N, 13·1. $C_{18}H_{21}O_3N_3$ requires C, 66·1; H, 6·4; N, 12·8%).

1-[2'-*Acetamido*-4'-*methoxy*(or *methyl*)*phenyl*]-5-*methyl*(or *methoxy*)-2-*methylbenziminazole* was obtained in colourless prisms, m. p. 202° (from aqueous alcohol), by treatment of the above diacetamido-compound with boiling acetic anhydride (Found: C, 70·0; H, 6·4. $C_{18}H_{19}O_2N_3$ requires C, 70·0; H, 6·1%).

2 : 2'-*Dinitro*-4-*methoxydiphenylamine* was prepared by heating *m*-nitro-*p*-anisidine (17 g.), *o*-chloronitrobenzene (16 g.), copper powder (6 g.), and potassium carbonate (6 g.) together as above. The product separated from alcohol in red plates, m. p. 139—141° (Found: C, 53·8; H, 3·6. $C_{13}H_{11}O_5N_3$ requires C, 54·0; H, 3·8%).

2 : 2'-*Diamino*-4-*methoxydiphenylamine*, which was prepared from the dinitro-compound, separated from light petroleum (b. p. 60—80°) in colourless prisms, m. p. 115°, which rapidly darkened on exposure (Found: C, 68·2; H, 6·7. $C_{13}H_{15}ON_3$ requires C, 68·1; H, 6·5%).

2 : 2'-*Diacetamido*-4-*methoxydiphenylamine* separated from aqueous alcohol in colourless needles, m. p. 172° (Found: C, 65·1; H, 6·2. $C_{17}H_{19}O_3N_3$ requires C, 65·2; H, 6·1%).

Oxidation of 2 : 2'-*Diaminodiphenylamine*.—When a solution of the amine in dilute hydrochloric acid was treated with excess of a concentrated solution of ferric chloride, it became purple, then bluish-green after several hours, and a small quantity of dark crystalline matter separated (the nature of this is under investigation). Addition of sodium acetate to the solution gave a yellow precipitate of phenazine, m. p. 171° (Found: C, 72·6; H, 6·6. Calc.: C, 72·4; H, 6·5%).

Oxidation of 2 : 2'-diamino-4 : 4'-dimethyldiphenylamine in the same way gave a purple solution, which became brown after an hour or two, and a precipitate of 2 : 7-dimethylphenazine, m. p. 155°, was formed (Found: C, 80·7; H, 5·4. Calc.: C, 80·8; H, 5·8%).

Similarly, oxidation of 2 : 2'-diamino-4-methoxy-4'-methyldiphenylamine yielded 2-*methoxy*-7-*methylphenazine*; this separated from aqueous alcohol in yellow needles which lost solvent of crystallisation on drying at 100°; m. p. 135° (Found: C, 74·7; H, 5·2; N, 12·6. $C_{14}H_{12}ON_2$ requires C, 75·0; H, 5·4; N, 12·5%).

Oxidation of 2 : 2'-diamino-4-methoxydiphenylamine gave 2-*methoxyphenazine*, which crystallised from water in yellow needles, m. p. 123°, which lost solvent on drying (Found: C, 74·4; H, 5·0. $C_{13}H_{10}ON_2$ requires C, 74·3; H, 4·8%).

Oxidation of 2 : 2'-diamino-4 : 4'-dimethoxydiphenylamine, dissolved in a minimum of dilute hydrochloric acid, with ferric chloride gave a deep purple solution, from which a precipitate resembling copper-bronze separated. On standing, this gave place to a brownish precipitate of 2 : 7-dimethoxyphenazine, m. p. 163°, and the solution became green and finally yellow (Found: C, 69·8; H, 4·8; N, 11·7. Calc.: C, 70·0; H, 5·0; N, 11·7%). It was not possible to obtain the bronze plates in a state of purity owing to the rapidity with which they were converted into the phenazine.

The yields of the phenazines were almost quantitative.

3-*Acetamido*-N-(2'-*acetamido*-4'-*methoxyphenyl*)*quinoneimine*.—2 : 2'-Diacetamido-4 : 4'-dimethoxydiphenylamine was finely pulverised, suspended in dilute hydrochloric acid, and treated with excess of ferric chloride or sodium nitrite solution; a purple colour then developed in the solution. When the mixture was shaken, the colourless precipitate was converted almost quantitatively into a black substance (the oxidation was effected more rapidly when the material was dissolved in glacial acetic acid, but the yield was diminished). The *product* crystallised from alcohol in black prisms with a green metallic lustre, m. p. 210° (decomp.) (Found: C, 62·6; H, 5·3; N, 12·8; *M*, in camphor, 340. $C_{17}H_{17}O_4N_3$ requires C, 62·4; H, 5·2; N, 12·8%; *M*, 327).

2 : 2'-*Diacetamido*-4-*hydroxy*-4'-*methoxydiphenylamine*.—The above compound (1 g.) was suspended in acetic acid (15 c.c. of 20%) and shaken with small quantities of zinc dust until the mixture was colourless. The filtered solution was diluted with water (3 vols.) and saturated with salt and the pale pink precipitate produced was crystallised from water. It existed in two different crystalline forms, *viz.*, labile colourless needles, m. p. 186—193°, and almost colourless prisms, m. p. 186° (mixed m. p. 186—191°) (Found: C, 62·1; H, 6·2; N, 12·8; *M*, in camphor, 336. $C_{17}H_{19}O_4N_3$ requires C, 62·0; H, 5·8; N, 12·8%; *M*, 329). This *compound* was very sensitive to oxidising agents and was reconverted into the quinoneimine when solutions of it

were exposed to air. It was insoluble in dilute acid and sodium carbonate solution, but it dissolved in aqueous sodium hydroxide; the alkaline solution became orange on exposure to air.

2 : 2′-Diacetamido-4-hydroxy-4′-methoxydiphenylamine (1 g.) was dissolved in air-free potassium hydroxide solution (30 c.c. of 10%), and methyl sulphate (1·5 g.) added. The mixture was shaken in an atmosphere of coal gas until free from methyl sulphate and the precipitate was crystallised from aqueous alcohol and shown by mixed m. p. determination to be 2 : 2′-diacetamido-4 : 4′-dimethoxydiphenylamine.

5-*Methoxy*(or *acetoxy*)-1-[2′-*acetamido*-4′-*acetoxy*(or *methoxy*)*phenyl*]-2-*methylbenziminazole*.—When 2 : 2′-diacetamido-4-hydroxy-4′-methoxydiphenylamine (1 g.) was refluxed with acetic anhydride (10 c.c.) for 30 minutes and the resulting solution was diluted with water and rendered alkaline, a colourless precipitate separated. The *benziminazole* crystallised from alcohol in needles, m. p. 244° (Found : C, 64·5; H, 5·2; N, 11·5. $C_{19}H_{19}O_4N_3$ requires C, 64·6; H, 5·4; N, 11·9%). It was soluble in dilute acid, insoluble in alkali, and gave no colour with ferric chloride. Hydrolysis was effected by boiling under reflux with either concentrated hydrochloric acid or dilute alcoholic potassium hydroxide. When the resulting solution was diluted, neutralised, and saturated with sodium chloride, 5-*methoxy*(or *hydroxy*)-1-[2′-*amino*-4′-*hydroxy*(or *methoxy*)*phenyl*]-2-*methylbenziminazole* separated. It crystallised from alcohol in colourless prisms, m. p. 278° (decomp.) (Found : C, 67·3; H, 6·0; N, 15·2. $C_{15}H_{15}O_2N_3$ requires C, 66·9; H, 5·6; N, 15·6%). This compound was soluble in dilute acid and in sodium hydroxide solution and was diazotisable. It was also obtained when 2 : 2′-diacetamido-4-hydroxy-4′-methoxydiphenylamine was refluxed with concentrated hydrochloric acid for ½ hour, and the solution diluted with water and rendered alkaline with sodium carbonate; the precipitate which separated crystallised from alcohol in colourless prisms, m. p. 278°, identical with the above.

?-*Chloro*-5-*methoxy*(or *hydroxy*)-1-[2′-*amino*-4′-*hydroxy*(or *methoxy*)*phenyl*]-2-*methylbenziminazole*.—The above quinoneimine, $C_{17}H_{17}O_4N_3$, was warmed with concentrated hydrochloric acid until the colour disappeared; the solution was then boiled for 30 minutes and diluted, and sodium acetate added. A precipitate separated and on recrystallisation from alcohol (charcoal) the *chloro-iminazole* was obtained in colourless prisms, m. p. 270°. It was diazotisable and was soluble both in dilute acid and in alkali (Found : C, 59·2; H, 4·3; N, 14·0; Cl, 11·6. $C_{15}H_{14}O_2N_3Cl$ requires C, 59·4; H, 4·6; N, 13·9; Cl, 11·7%).

When the quinoneimine (1 g.) was dissolved in cold nitric acid (10 c.c., *d* 1·43) and the solution was diluted with water, an orange-red crystalline precipitate of a *nitro*-compound was formed. It crystallised from glacial acetic acid in orange-brown prisms which lost solvent on drying (m. p. 215°, decomp.) (Found : C, 54·7; H, 4·0; N, 15·2. $C_{17}H_{16}O_6N_4$ requires C, 54·8; H, 4·3; N, 15·1%).

Both 2 : 2′-diacetamido-4 : 4′-dimethoxydiphenylamine and 2 : 2′-diacetamido-4-hydroxy-4′-methoxydiphenylamine were converted into this nitro-compound when submitted to a similar procedure.

3-*Acetamido*-N-(2′-*acetamido*-4′-*methylphenyl*)*quinoneimine*.—2 : 2′-Diacetamido-4-methoxy-4′-methyldiphenylamine (2 g.) was dissolved in glacial acetic acid (20 c.c.), and excess of ferric chloride solution added. A deep red-brown colour developed and after 10 minutes the solution was diluted with water. The precipitate was recrystallised from alcohol, the *quinoneimine* separating in brown-orange prisms with a slight metallic lustre, m. p. 200° (decomp.) (Found : C, 65·8; H, 5·3; N, 13·6. $C_{17}H_{17}O_3N_3$ requires C, 65·6; H, 5·5; N, 13·5%).

2 : 2′-*Diacetamido*-4-*hydroxy*-4′-*methyldiphenylamine*, obtained by reduction of the above compound by the method described for its methoxy-analogue, crystallised from alcohol in colourless plates, m. p. 222° (Found : C, 65·3; H, 5·8; N, 13·8. $C_{17}H_{19}O_3N_3$ requires C, 65·2; H, 6·1; N, 13·4%).

Treatment of this reduction product (as above) with acetic anhydride yielded 1-[2′-*acetamido*-4′-*acetoxy*(or *methyl*)*phenyl*]-5-*methyl*(or *acetoxy*)-2-*methylbenziminazole*, which was soluble in dilute acid and crystallised from benzene in colourless prisms, m. p. 243° (Found : C, 66·9; H, 5·7; N, 12·7. $C_{19}H_{19}O_3N_3$ requires C, 67·3; H, 5·6; N, 12·5%).

When this benziminazole was hydrolysed as described for the methoxy-analogue, it was converted into 1-[2′-*amino*-4′-*hydroxy*(or *methyl*)*phenyl*]-5-*methyl*(or *hydroxy*)-2-*methylbenziminazole*, which crystallised from alcohol in colourless prisms, m. p. 248°. It was soluble in acid and in dilute sodium hydroxide solution and was diazotisable (Found : C, 70·7; H, 5·3. $C_{15}H_{15}ON_3$ requires C, 71·1; H, 5·9%).

?-*Chloro*-1-[2′-*amino*-4′-*hydroxy*(or *methyl*)*phenyl*]-5-*methyl*(or *hydroxy*)-2-*methylbenziminazole*.—The quinoneimine, $C_{17}H_{17}O_3N_3$ (1 g.), was treated with concentrated hydrochloric acid as described above and this *chloro*-compound was obtained in colourless prisms, m. p. 280°, from alcohol. It was soluble in dilute acid and in alkali and was diazotisable (Found : C, 62·5; H, 5·1; N, 14·8. $C_{15}H_{14}ON_3Cl$ requires C, 62·7;. H, 4·9; N, 14·6%).

Treatment of the quinoneimine, $C_{17}H_{17}O_3N_3$, with nitric acid as above gave a *mononitro*-compound, which crystallised from alcohol in orange prisms, m. p. 203° (decomp.) (Found : C, 57·7; H, 4·8. $C_{17}H_{16}O_5N_4$ requires C, 57·3; H, 4·5%).

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