XXVIII.—*Studies in Adjacent Substitution. Part I. Some Reactions of 3-Chloro-2-aminoanisole.*

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REACTIONS already described of 3-halogeno-2-nitrophenols (Hodgson and Moore, J., 1925, **127**, 2260; 1926, 155; 1927, 1141) and 3-chloro-2-nitroanisole (Hodgson and Handley, J., 1926, 542) showed peculiarities which were tentatively ascribed to adjacent substitution. The results of the present investigation support that supposition.

3-*Chloro*-2-*aminoanisole* forms stable salts with hydrochloric, hydrobromic, and nitric acids (compare the stable hydrates of 3-chloro-2-nitrophenol, *loc. cit.*) and the sulphate, in marked contrast to aniline sulphate, is very soluble in water. The diazonium salts are stable even in boiling aqueous hydrochloric or sulphuric acid over a wide range of concentrations (compare Meldola, Woolcott, and Wray, J., 1896, **69**, 1327) and replacement of the diazo-group by hydroxyl has not yet been effected. Its replacement by halogens and cyanogen, however, takes place normally in the Sandmeyer reaction. 3-*Chloro*-2-*cyanoanisole* cannot be hydrolysed to the acid by the usual methods.

The colours of the hydrazones formed from 3-chloroanisyl-2-hydrazine and *o*-, *m*-, and *p*-nitrobenzaldehydes and the colours developed by products in alcoholic alkali are very similar to those given by the respective *o*-, *m*-, and *p*-nitrobenzaldehyde-2-chlorophenylhydrazones (Chattaway and Clemo, J., 1923, **123**, 3041).

The dyes formed by coupling diazotised 2-chloro-3-aminoanisole with Schäffer, R-, and N.W. salts give on wool colours which are more reddish-orange than those given by the corresponding unsubstituted aniline azo-dyes and exhibit the powerful hypsochromic effect of chlorine in the *o*-position with respect to the azo-group (compare Hodgson and Handley, this vol., p. 165). The differences in shade between the scarlet-red colours produced by the corresponding *o*-anisidine azo-dyes and the reddish-orange colours mentioned above are much greater than the differences in the case of the azo-dyes formed from aniline and from *o*-chloroaniline, the bathochromic effect of the methoxy-group being almost completely inhibited in the presence of the *o*-substituted chlorine.

EXPERIMENTAL.

3-*Chloro*-2-*aminoanisole*.—Iron powder (20 g.) was slowly added to a mixture of 50% acetic acid (140 g.) and 3-chloro-2-nitroanisole (30 g.) on the water-bath. After the vigorous reaction had abated, the mixture was heated for 1 hour and made slightly alkaline with sodium hydroxide solution, and 3-*chloro*-2-*amino*-

anisole was then obtained by steam-distillation in excellent yield as a colourless oil, b. p. 246° (slight decomp.) (Found : Cl, 22·4. C_7H_8ONCl requires Cl, 22·5%). It has a pleasant odour and is almost insoluble in water. It gives a brown coloration with bleaching powder after a few minutes, and a dark brown precipitate with bromine water. The carbylamine reaction only takes place with difficulty. The *hydrochloride* crystallises from water, in which it is only sparingly soluble, in long, colourless needles, m. p. 211° (Found : Cl, 36·5. C_7H_8ONCl,HCl requires Cl, 36·6%), the *hydrobromide* in colourless needles which sublime at 250° (0·0932 g. gave 0·1313 g. of silver halides. Calc.: 0·1296 g.), and the *nitrate*, which is much more soluble, in colourless needles, m. p. 137° (Found: Cl, 16·3. C_7H_8ONCl,HNO_3 requires Cl, 16·1%). The *monoacetyl* derivative, prepared from the amine (2 g.) and acetic anhydride (2·5 g.) on the water-bath, crystallises from 60% alcohol in colourless prisms, m. p. 123° (Found : Cl, 17·5. $C_9H_{10}O_2NCl$ requires Cl, 17·8%). The *diacetyl* derivative, formed by heating the amine with excess of acetyl chloride in glacial acetic acid, crystallises from dilute acetic acid in large, colourless plates, m. p. 145·5° (Found : Cl, 15·0. $C_{11}H_{12}O_3NCl$ requires Cl, 14·7%). The *benzoyl* derivative separates from alcohol in fine, colourless needles, m. p. 135° (Found : Cl, 13·9. $C_{14}H_{12}O_2NCl$ requires Cl, 13·6%).

2 : 3-Dichloroanisole, long, colourless plates, m. p. 33°, from alcohol (Holleman, *Rec. trav. chim.*, 1917, **37**, 96, gives m. p. 31°) (Found : Cl, 39·9. Calc.: Cl, 40·1%), 3-*chloro*-2-*bromoanisole*, long, colourless plates, m. p. 50° (0·1549 g. gave 0·2308 g. of silver halides. Calc.: 0·2318 g.), 3-*chloro*-2-*iodoanisole*, colourless, crystalline clusters, m. p. 53·5° (0·0999 g. gave 0·1424 g. of silver halides. Calc.: 0·1408 g.), and 3-*chloro*-2-*cyanoanisole*, fine, colourless needles, m. p. 114·5°, slowly volatile in steam (Found : Cl, 21·0. C_8H_6ONCl requires Cl, 21·2%), were all obtained in excellent yield by the Sandmeyer method.

3-*Chloro*-2-*thiocyanoanisole* forms colourless needles, m. p. 43° (Found : Cl, 17·9. C_8H_6ONClS requires Cl, 17·8%), volatile in steam.

3-*Chloroanisole*-2-*diazoperbromide* was obtained in bright orange micro-needles, m. p. 115—116° (decomp.), when a slight excess of bromine, dissolved in aqueous potassium bromide, was added to an aqueous solution of 3-chloroanisole-2-diazonium sulphate (0·0726 g. gave 0·1274 g. of silver halides. Calc.: 0·1254 g.). When boiled with glacial acetic acid, it gave 3-*chloro*-2 : 6-*dibromoanisole*, which crystallised from dilute acetic acid or alcohol in fine, colourless needles, m. p. 92° (0·0526 g. gave 0·0920 g. of silver halides. Calc.: 0·0906 g.) and was identified by comparison with a specimen obtained by the sulphonation of *m*-chlorophenol (the *p*-sulphonic acid produced was identified in the form of potassium 3-chloro-6-nitrophenol-4-sulphonate), dibromination, desulphonation, and methylation.

3-*Chloroanisole-2-diazoimide*, obtained by the action of ammonia on the diazoperbromide, was volatile in steam and crystallised from light petroleum in pale yellow prisms, m. p. 35° (Found : Cl, 19·4. $C_7H_6ON_3Cl$ requires Cl, 19·3%).

3-*Chloroanisyl-2-hydrazine hydrochloride*, prepared by the reduction of 3-chloroanisole-2-diazonium chloride with stannous chloride in concentrated hydrochloric acid solution, crystallised from water in colourless needles (Found : Cl, 34·1. $C_7H_9ON_2Cl,HCl$ requires Cl, 34·0%). The following hydrazones were prepared and crystallised from glacial acetic acid; the colours developed in alcoholic potassium hydroxide are recorded after the analysis : *Benzaldehyde*-3-*chloroanisyl*-2-*hydrazone*, pale yellow prisms, m. p. 92° (Found : Cl, 13·4. $C_{14}H_{13}ON_2Cl$ requires Cl, 13·6%). o-*Nitrobenzaldehyde*-3-*chloroanisyl*-2-*hydrazone*, deep crimson rhombs, m. p. 131° (Found : Cl, 11·6. $C_{14}H_{12}O_3N_3Cl$ requires Cl, 11·6%); deep green in the cold, changed to emerald-green on heating. m-*Nitrobenzaldehyde*-3-*chloroanisyl*-2-*hydrazone*, yellow micro-crystals, m. p. 131° (Found : Cl, 11·4%); brown, changed to golden-brown on heating. p-*Nitrobenzaldehyde*-3-*chloroanisyl*-2-*hydrazone*, vermilion micro-prisms, m. p. 105° (Found : Cl, 11·4%); olive-green, changed to bright blue in the cold and to bluish-black on heating.

Dyes.—3-Chloro-2-aminoanisole was diazotised and coupled in the usual way with Schäffer, R- and N.W. acids in alkaline solution. With concentrated sulphuric acid the powdered dyes gave bright red, bluish-red, and violet colours respectively.

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