232. *Derivatives of* 3 : 5-*Dihalogen-substituted Anilines.*

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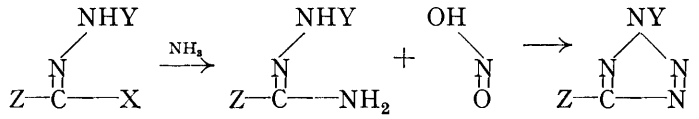
AMONG the disubstituted anilines those having halogen atoms in the 3 : 5-positions have been least studied. During the past few years in the course of other investigations many derivatives of 3 : 5-dichloro- and 3 : 5-dibromo-aniline and of the more highly substituted anilines obtained from them have been prepared, and their properties are here briefly recorded.

The bases themselves are comparatively easily prepared from *p*-nitro-aniline by introduction of halogen in both *o*-positions, removal of the amino-group, and subsequent reduction of the nitro-group. Both can be further halogenated, in the *p*- and one *o*-position when the acetanilides are acted upon, and in the 2-, 4-, and 6-positions when the anilines themselves are used.

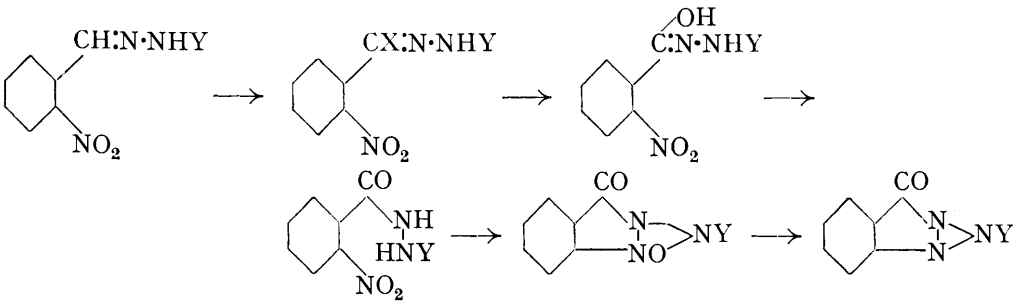
The resulting anilines are readily diazotised and the diazonium salts yield hydrazines on reduction, and couple and condense in a normal manner. The hydrazines form stable and well-crystallised hydrazones, which react with halogens much as other halogen-substituted hydrazones do, the ω-hydrogen of the aldehyde residue being replaced by halogen, which also enters the hydrazine residue in positions *o*- and *p*- to the nitrogen when these are not already occupied. As in other cases, the action of chlorine is more energetic than that of bromine and carries substitution in the hydrazine residue one stage further. Thus chlorine substitutes in the *p*- and both *o*-positions or such of these as are not already occupied, whereas bromine enters only one of the vacant *o*-positions when both are unoccupied and does not substitute in the remaining *o*-position when one is already occupied.

These ω-substituted hydrazones yield with ammonia hydrazidines, which are converted by nitrous acid into the corresponding tetrazoles :



Among the ω-substituted hydrazones the behaviour of those derived from *o*-nitrobenzaldehyde is peculiar, the action of ammonia upon them yielding not the basic hydr-

azidines but very highly explosive compounds, *iso*diazole oxides, which on reduction yield *iso*diazoles :



The 3 : 5-phenyldiazonium salts couple readily with acetoacetic ester to form ethyl 3 : 5-dibromo- or 3 : 5-dichloro-phenylazoacetoacetates, which when acted upon by bromine in an acetic acid solution of sodium acetate yield the corresponding ethyl α-bromoglyoxylate 3 : 5-dibromo- or 3 : 5-dichloro-phenylhydrazone, or, when glacial acetic acid alone is the solvent, ethyl 3 : 5-dichloro- or 3 : 5-dibromo-phenyl-γ′-bromo- or -γγ′-dibromo-azoacetoacetates :

$$\begin{array}{ccccc} \mathrm{Y{\cdot}NH{\cdot}N{:}C(CO{\cdot}CH_2Br)(CO{\cdot}CHBr_2){\cdot}CO_2Et} & \longleftarrow & \mathrm{Y{\cdot}NH{\cdot}N{:}C(CO{\cdot}CH_3){\cdot}CO_2Et} & \longrightarrow & \mathrm{Y{\cdot}NH{\cdot}N{:}C(Br){\cdot}CO_2Et} \end{array}$$

These on treatment with sodium ethoxide undergo ring closure and form the corresponding 4-hydroxy-3-carbethoxy-1-(3′ : 5′-dichloro- or 3′ : 5′-dibromo-phenyl)-pyrazoles or -5-bromopyrazoles, $\begin{array}{l} \mathrm{C(CO_2Et){:}N} \\ \mathrm{|\quad\quad >NY} \\ \mathrm{C(OH){=}CH\ (or\ CBr).} \end{array}$

Experimental.

The following compounds were prepared by suitable modifications of ordinary methods : 3 : 5-*dibromodiacetanilide*, $C_6H_3Br_2{\cdot}NAc_2$, long colourless prisms from alcohol, m. p. 142° (Found : Br, 47·7. $C_{10}H_9O_2NBr_2$ requires Br, 47·85%); 2 : 3 : 4 : 5-*tetrachloroacetanilide*, colourless silky needles from acetic acid, m. p. 165° (Found : Cl, 51·35. $C_8H_5ONCl_4$ requires Cl, 51·45%); 3 : 4 : 5 : 6-*tetrabromoacetanilide*, colourless elongated prisms from alcohol, m. p. 264° (Found : Br, 70·95. $C_8H_5ONBr_4$ requires Br, 70·9%); 2 : 3 : 4 : 5 : 6-*pentabromodiacetanilide*, by acetylation of pentabromoaniline, colourless rhombic plates from alcohol, m. p. 198° (Found : Br, 60·7. $C_{10}H_6O_2NBr_5$ requires Br, 60·7%); 3 : 5-*dichloro*-o-*nitrobenzanilide*, short, pale yellow, flattened prisms, m. p. 202° (Found : Cl, 22·8. $C_{13}H_8O_3N_2Cl_2$ requires Cl, 22·8%); 3 : 5-*dichloro*-m-*nitrobenzanilide*, pale yellow prisms, m. p. 195° (Found : Cl, 22·8%); 3 : 5-*dichloro*-p-*nitrobenzanilide*, pale yellow prisms, m. p. 221° (Found : Cl, 22·9%); 3 : 5-*dibromo*-o-*nitrobenzanilide*, slender yellow prisms, m. p. 228° (Found : Br, 40·3. $C_{13}H_8O_3N_2Br_2$ requires Br, 40·2%); 3 : 5-*dibromo*-m-*nitrobenzanilide*, pale yellow prisms, m. p. 220° (Found : Br, 40·1%); 3 : 5-*dibromo*-p-*nitrobenzanilide*, pale yellow prisms, m. p. 240° (Found : Br, 40·15%). These nitro-compounds were all crystallised from glacial acetic acid.

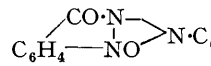
3 : 5-*Dichlorobenzeneazo*-2′-*phenol*, $C_6H_3Cl_2{\cdot}N_2{\cdot}C_6H_4{\cdot}OH$, was prepared by slow addition of a cold solution of 3 : 5-dichlorobenzenediazonium chloride (from 3 g. of 3 : 5-dichloroaniline) to a cooled solution of 10 g. of phenol and 30 g. of sodium hydroxide in 150 c.c. of water, followed by acidification with acetic acid and steam-distillation. The *o*-compound separated from the distillate as a yellow solid very easily soluble in hot alcohol, from which it crystallised in orange needles, m. p. 142° (Found : C, 53·4; H, 3·1; N, 10·35. $C_{12}H_8ON_2Cl_2$ requires C, 53·9; H, 3·0; N, 10·5%). 3 : 5-*Dichlorobenzeneazo*-4′-*phenol* remained in the distilling flask; it formed brick-red prisms from alcohol, m. p. 138° (Found : Cl, 24·4. $C_{12}H_8ON_2Cl_2$ requires Cl, 26·6%). The following were obtained similarly : 3 : 5-*dibromobenzeneazo*-2′-*phenol*, lemon-yellow needles from alcohol, m. p. 161° (Found : Br, 44·8. $C_{18}H_8ON_2Br_2$ requires Br, 44·9%); 3 : 5-*dibromobenzeneazo*-4′-*phenol*, light reddish-brown plates from toluene, m. p. 162° (Found : Br, 44·8%); 3 : 5 : 3′ : 5′-*tetrachloro*-2 : 4-*bisbenzeneazophenol*, brown needles from glacial acetic acid, m. p. 236° (Found : Cl, 31·8. $C_{18}H_{10}ON_4Cl_4$ requires Cl, 32·0%); 3 : 5 : 3′ : 5′-*tetrabromo*-2 : 4-

bisbenzeneazophenol, brown needles from toluene, m. p. 274° (Found : Br, 60·0. $C_{18}H_{10}ON_4Br_4$ requires Br, 60·1%); 3 : 5-*dichlorobenzeneazo*-β-*naphthol*, scarlet prisms from glacial acetic acid, m. p. 203° (Found : Cl, 22·5. $C_{16}H_{10}ON_2Cl_2$ requires Cl, 22·4%); 2 : 3 : 4 : 5-*tetrachlorobenzeneazo*-β-*naphthol*, scarlet prisms from glacial acetic acid, m. p. 252° (Found : Cl, 36·6. $C_{16}H_8ON_2Cl_4$ requires Cl, 36·8%); 3 : 5-*dibromobenzeneazo*-β-*naphthol*, clusters of orange-red prisms from glacial acetic acid, m. p. 235° (in a sealed tube) (Found : Br, 39·3. $C_{16}H_{10}ON_2Br_2$ requires Br, 39·4%).

Benzaldehyde- and nitrobenzaldehyde-3 : 5-dichloro- and -3 : 5-dibromo-phenylhydrazones react with halogens similarly to other halogen-substituted phenylhydrazones (compare Chattaway and Walker, J., 1925, **127**, 975, 1687, 2407; 1927, 323). The following compounds have been obtained : ω-*chloro*-o-*nitrobenzaldehydepentachlorophenylhydrazone*,

$$NO_2{\cdot}C_6H_4{\cdot}CCl{:}N{\cdot}NH{\cdot}C_6Cl_5,$$

pale yellow plates, m. p. 137° (Found : Cl, 47·3. $C_{13}H_5O_2N_3Cl_6$ requires Cl, 47·5%); ω-*chloro*-m-*nitrobenzaldehydepentachlorophenylhydrazone*, very pale yellow, felted needles, m. p. 198° (Found : Cl, 47·4%); ω-*chloro*-p-*nitrobenzaldehydepentachlorophenylhydrazone*, pale yellow, felted needles, m. p. 208° (Found : Cl, 47·3%); ω-*bromobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazone*, golden-yellow needles from alcohol, m. p. 190° (Found : Br, 67·7. $C_{13}H_7N_3Br_5$ requires Br, 67·5%); ω-*bromo*-o-*nitrobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazone*, pale yellow needles from glacial acetic acid, m. p. 161° (Found : Br, 62·7. $C_{13}H_6O_2N_3Br_5$ requires Br, 62·9%); ω-*bromo*-m-*nitrobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazone*, pale yellow needles from xylene, m. p. 242° (Found : Br, 62·8%); ω-*bromo*-p-*nitrobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazone*, felted yellow needles from xylene, m. p. 268° (Found : Br, 62·7%); ω-*bromobenzaldehydepentabromophenylhydrazone*, colourless needles from toluene, m. p. 179° (Found : Br, 71·5. $C_{13}H_6N_2Br_6$ requires Br, 71·7%); ω-*bromo*-o-*nitrobenzaldehydepentabromophenylhydrazone*, pale yellow needles from toluene, m. p. 240° (Found : Br, 67·0. $C_{13}H_5O_2N_3Br_6$ requires Br, 67·1%); ω-*bromo*-m-*nitrobenzaldehydepentabromophenylhydrazone*, short yellow prisms from acetic anhydride, m. p. 255° (Found : Br, 67·0%); ω-*bromo*-p-*nitrobenzaldehydepentabromophenylhydrazone*, thin yellow needles from toluene, m. p. 265° (Found : Br, 67·0%); m-*nitrobenzaldehydepentachlorophenylhydrazidine*, $NO_2{\cdot}C_6H_4{\cdot}C(NH_2){:}N{\cdot}NH{\cdot}C_6Cl_5$, glistening yellow plates from acetic acid, m. p. 210° (Found : Cl, 41·2. $C_{13}H_7O_2N_4Cl_5$ requires Cl, 41·4%); p-*nitrobenzaldehydepentachlorophenylhydrazidine*, very small, orange needles from acetic acid, m. p. 217° (Found : Cl, 41·2%); *benzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazidine*, small colourless plates from toluene, m. p. 171° (Found : Br, 60·6. $C_{13}H_9N_3Br_4$ requires Br, 60·7%); m-*nitrobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazidine* occurs in two polymorphic forms, separating from xylene in very small, pale orange-yellow crystals, which slowly transform into deep crimson needles, m. p. 218° (Found : Br, 55·7. $C_{13}H_8O_2N_4Br_4$ requires Br, 55·9%); p-*nitrobenzaldehyde*-2 : 3 : 4 : 5-*tetrabromophenylhydrazidine*, deep scarlet needles from xylene, m. p. 248° (Found : Br, 55·7%); *benzaldehydepentabromophenylhydrazidine*, pale blue-coloured, microscopic crystals from benzene, m. p. 106° (Found : Br, 65·9. $C_{13}H_8N_3Br_5$ requires Br, 66·0%); m-*nitrobenzaldehydepentabromophenylhydrazidine*, hexagonal prisms from toluene, m. p. 227° (Found : Br, 61·3. $C_{13}H_7O_2N_4Br_5$ requires Br, 61·4%); p-*nitrobenzaldehydepentabromophenylhydrazidine*, scarlet needles from toluene, m. p. 248° (Found : Br, 61·3%).

*Nitroso*cyclo*azipentachlorobenztriazone*,  , deep yellow, very small crystals from toluene, explodes at 128° (Found : Cl, 43·0. $C_{13}H_4O_2N_3Cl_5$ requires Cl, 43·1%); *nitroso*cyclo*azitetrabromobenztriazone*, bright yellow, very small crystals from toluene, explodes at 155° (Found : Br, 57·5. $C_{13}H_5O_2N_3Br_4$ requires Br, 57·7%); *nitroso*cyclo*azipentabromobenztriazone*, very small, bright yellow crystals from toluene, explodes at 157° (Found : Br, 62·9. $C_{13}H_4O_2N_3Br_5$ requires Br, 63·1%).

Preparation of 3 : 5-*Dihalogenophenylazoacetoacetates and Derivatives.*—3 : 5-Dichloro- and 3 : 5-dibromo-benzenediazonium chloride couple readily with acetoacetic ester in presence of sodium acetate to form ethyl 3 : 5-dichloro- and 3 : 5-dibromo-phenylazoacetoacetates. Other more highly halogenated benzenediazonium salts behave similarly. These compounds react with halogens in an exactly similar manner to other halogen-substituted phenylazoacetoacetates previously described (Chattaway and Lye, *Proc. Roy. Soc.*, 1932, *A*, **135**, 282).

The following ethyl esters have been prepared : 3 : 5-*dichlorophenylazoacetoacetate*, long, pale yellow prisms from alcohol, m. p. 106° (Found : N, 9·4; Cl, 23·3. $C_{12}H_{12}O_3N_2Cl_2$ requires N, 9·2; Cl, 23·4%); 3 : 5-*dichloro*-4-*bromophenylazoacetoacetate*, long, slender, pale yellow prisms

from alcohol, m. p. 127° (Found : Cl, 18·2; Br, 20·4. $C_{12}H_{11}O_3N_2Cl_2Br$ requires Cl, 18·6; Br, 20·9%); 3 : 5-*dibromophenylazoacetoacetate*, pale yellow needles from alcohol, m. p. 96° (Found : Br, 40·6. $C_{12}H_{12}O_3N_2Br_2$ requires Br, 40·8%); 3 : 4 : 5-*tribromophenylazoacetoacetate*, yellow needles from alcohol, m. p. 146° (Found : Br, 50·8. $C_{12}H_{11}O_3N_2Br_3$ requires Br, 50·95%); α-*bromoglyoxylate*-3 : 5-*dichloro*-4-*bromophenylhydrazone*, long, slender, colourless prisms from alcohol, m. p. 176° (Found : Cl, 16·9; Br, 38·2. $C_{10}H_8O_2N_2Cl_2Br_2$ requires Cl, 16·9; Br, 38·2%); α-*bromoglyoxylate*-3 : 4 : 5-*tribromophenylhydrazone*, colourless needles from alcohol, m. p. 129° (Found : Br, 62·9. $C_{10}H_8O_2N_2Br_4$ requires Br, 63·0%).

ββω-*Tribromo*-α-*ketopropaldehyde*-3 : 5-*dichloro*-2 : 4-*dibromophenylhydrazone*, $CHBr_2{\cdot}CO{\cdot}CBr{:}N{\cdot}NH{\cdot}C_6HCl_2Br_2$, forms pale yellow, hair-like prisms from glacial acetic acid, m. p. 223° (Found : Cl, 11·25; Br, 63·5; N, 4·4. $C_9H_3ON_2Cl_2Br_5$ requires Cl, 11·3; Br, 63·9; N, 4·5%).

Ethyl α-*chloroglyoxylate*-2 : 3 : 4 : 5-*tetrachlorophenylhydrazone* forms long colourless prisms from alcohol, m. p. 128° (Found : Cl, 48·4. $C_{10}H_7O_2N_2Cl_5$ requires Cl, 48·5%); *ethyl* α-*aminoglyoxylate*-3 : 5-*dichloro*-4-*bromophenylhydrazone*, slender prisms from alcohol, m. p. 180° (Found : Cl, 19·8; Br, 22·3. $C_{10}H_{10}O_2N_3Cl_2Br$ requires Cl, 20·0; Br, 22·5%); *ethyl* α-*aminoglyoxylate*-2 : 3 : 4 : 5-*tetrachlorophenylhydrazone*, long slender prisms from alcohol, m. p. 148° (Found : Cl, 41·0. $C_{10}H_9O_2N_3Cl_4$ requires Cl, 41·1%).

Ethyl 3 : 5-*dichlorophenylazo*-γ-*bromoacetoacetate* forms long, slender, yellow prisms from alcohol, m. p. 110° (Found : Cl, 18·6; Br, 20·9. $C_{12}H_{11}O_3N_2Cl_2Br$ requires Cl, 18·6; Br, 20·9%); *ethyl* 3 : 5-*dichlorophenylazo*-γγ′-*dibromoacetoacetate*, long yellow prisms from alcohol, m. p. 126° (Found : Cl, 15·2; Br, 34·2. $C_{12}H_{10}O_3N_2Cl_2Br_2$ requires Cl, 15·4; Br, 34·7%); *ethyl* 3 : 5-*dichloro*-4-*bromophenylazo*-γ-*bromoacetoacetate*, long yellow needles from alcohol, m. p. 146° (Found : Cl, 15·3; Br, 34·3%); *ethyl* 3 : 5-*dichloro*-4-*bromophenylazo*-γγ′-*dibromoacetoacetate*, pale yellow prisms from alcohol, m. p. 125° (Found : Cl, 12·9; Br, 43·5. $C_{12}H_9O_3N_2Cl_2Br_3$ requires Cl, 13·1; Br, 44·4%); *ethyl* 3 : 5-*dibromophenylazo*-γ-*bromoacetoacetate*, yellow needles from alcohol, m. p. 134° (Found : Br, 53·6. $C_{12}H_{11}O_3N_2Br_3$ requires Br, 53·7%); *ethyl* 3 : 5-*dibromophenylazo*-γγ′-*dibromoacetoacetate*, long yellow needles from alcohol, m. p. 123° (Found : Br, 60·6. $C_{12}H_{10}O_3N_2Br_4$ requires Br, 60·8%).

4-*Hydroxy*-3-*carbethoxy*-1-(3′ : 5′-*dichlorophenyl*)*pyrazole* forms small colourless prisms from alcohol, m. p. 154° (Found : Cl, 23·3. $C_{12}H_{10}O_3N_2Cl_2$ requires Cl, 23·5%); acetate, m. p. 123°; 5-*bromo*-4-*hydroxy*-3-*carbethoxy*-1-(3′ : 5′-*dichlorophenyl*)*pyrazole*, colourless prisms from alcohol, m. p. 156° (Found : Cl, 18·7; Br, 21·2. $C_{12}H_9O_3N_2Cl_2Br$ requires Cl, 18·7; Br, 21·1%); acetate, m. p. 101°; 4-*hydroxy*-3-*carbethoxy*-1-(3′ : 5′-*dibromophenyl*)*pyrazole*, colourless prisms from alcohol, m. p. 154° (Found : Br, 41·1. $C_{12}H_{10}O_3N_2Br_2$ requires Br, 41·0%); acetate, m. p. 125°.

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