# CLXXIX.—*Conversion of Hydroaromatic into Aromatic Compounds. Part IV. The Influence of the Nitro-group in Nitrophenyldihydroresorcinols.*

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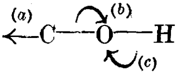
5-m-*Nitro-* and 5-p-*nitro-phenyldihydroresorcinols* exhibit properties in common with all dihydroresorcinols, but show a marked difference in their action with the chlorides of phosphorus.

Neither of the nitrophenyldihydroresorcinols reacts with phosphorus trichloride in the usual manner, whereas alkyl- and aryl-substituted dihydroresorcinols yield the corresponding chloroketone derivatives with both phosphorus trichloride and phosphorus oxychloride (Crossley and Haas, J., 1903, **83**, 494; Crossley and Le Sueur, *ibid.*, p. 110; Crossley and Pratt, J., 1915, **107**, 191; Boyd, Clifford, and Probert, J., 1920, **117**, 1383).

Phosphorus oxychloride is without action upon *m*-nitrophenyldihydroresorcinol, but yields with the *p*-nitro-compound a small amount of 3 : 5-*dichloro*-1-p-*nitrophenyl*-$\Delta^{2:4}$-cyclo*hexadiene*.

Phosphorus pentachloride acts upon *m*-nitrophenyldihydroresorcinol to give 3 : 5-*dichloro*-1-m-*nitrophenyl*-$\Delta^{2:4}$-cyclo*hexadiene* together with a small quantity of 3 : 5-*dichloro*-3′-*nitrodiphenyl*. In order to effect reaction four molecular proportions of the pentachloride are required instead of the usual two.

The low reactivity of the nitrophenyldihydroresorcinols towards the chlorides of phosphorus may be attributed to the recognised electron-affinity of the nitro-group, since, in any hydroxyl compound, intramolecular electron-attraction (*a*) must oppose the separation of hydroxyl (*b*), just as it assists the separation of hydrogen (*c*) :



$\overset{(a)}{\leftarrow}\text{—C—}\overset{\curvearrowright(b)}{\text{—O—}}\underset{\curvearrowleft(c)}{\text{—H}}$ (Allan, Oxford, Robinson, and Smith, J., 1926, 405).

The powerful electron-affinity of the nitro-group is also shown by the great readiness with which the nitrobenzaldehydes condense with acetone: our preparative work has convinced us that the order of facility of the condensation of benzaldehydes with acetone is *m*- and *p*-nitro- ≫ methoxy- and chloro- > unsubstituted benzaldehyde. The position of the nitro-compounds in this sequence is again attributable to the electron-affinity of the nitrophenyl group, since the accepted theory of the aldol reaction involves in its application to the present cases the addition of an anion to aromatic carbonyl carbon.

The effect of the nitrophenyl group upon the properties of the dichlorohexadienes shows no very marked difference from that of the phenyl group. The chlorination of 3 : 5-dichloro-1-*m*-nitrophenyl*cyclo*hexadiene yields 3 : 5-dichloro-3′-nitrodiphenyl and 2 : 3 : 5( ?)-*trichloro-3′-nitrodiphenyl* (compare Hinkel and Hey, J., 1928, 2786). However, in contrast with the case of the phenyl compound, where trichlorodiphenyl is formed with excess of chlorine in hot solution, the formation of the trichloro-3′-nitrodiphenyl is favoured at low temperature.

The constitution of 3 : 5-dichloro-3′-nitrodiphenyl has been established by reduction to the amino-derivative and oxidation of this to 3 : 5-dichlorobenzoic acid.

## EXPERIMENTAL.

m-*Nitrobenzylideneacetone.*—The method described by Baeyer and Becker (*Ber.*, 1883, **16**, 1969) has been so modified as to need redescription. 0·1*N*-Sodium hydroxide (150 c.c.) was added below 0° to a solution of *m*-nitrobenzaldehyde (30 g.) in acetone (300 c.c.) and the mixture was shaken for 20 minutes, slightly acidified, and evaporated. The orange-coloured liquid residue (probably the aldol intermediate compound) was heated for ½ hour at 100° with concentrated hydrochloric acid (0·5 c.c.): from a hot alcoholic solution of the dehydrated product, on cooling, *m*-nitrobenzylideneacetone separated in pale yellow needles (25 g.), m. p. 102° (Vorländer, *Annalen*, 1897, **294**, 291, records m. p. 96°) (Found : C, 62·3; H, 4·7. Calc. : C, 62·8; H, 4·7%).

5-m-*Nitrophenyldihydroresorcinol.*—By condensing *m*-nitrobenzylideneacetone with ethyl malonate by Vorländer's method (*loc. cit.*), ethyl *m*-nitrophenyldihydroresorcylate was obtained, m. p. 169° (decomp.); Vorländer records m. p. 163° (Found : C, 59·1; H, 5·15. Calc. : C, 58·8; H, 5·2%).

A solution of the ester (20 g.) in 4% aqueous sodium hydroxide (400 c.c.) was boiled for 5 minutes and cooled, and dilute hydrochloric acid added until the solution became faintly acid; on stirring, a dark brown impurity separated. The filtered solution was boiled with excess of hydrochloric acid until the liberation of carbon dioxide ceased. The brown solid which separated yielded, on crystallisation from aqueous acetone, 5-m-*nitrophenyldihydroresorcinol* in small plates (14 g.), m. p. 188° (decomp.) (Found : C, 61·8; H, 4·8. $C_{12}H_{11}O_4N$ requires C, 61·8; H, 4·7%).

5-p-*Nitrophenyldihydroresorcinol.*—The condensation of *p*-nitrobenzylideneacetone with ethyl malonate was conducted in the usual manner and the hydrolysis of the dihydroresorcylate produced was as described above. The solid product when crystallised from aqueous acetone yielded 5-p-*nitrophenyldihydroresorcinol* in faintly brown plates, m. p. 190—191° (decomp.), containing $1H_2O$ (Found :

C, 57·2; H, 5·2; $H_2O$, 7·4. $C_{12}H_{11}O_4N,H_2O$ requires C, 57·2; H, 5·2; $H_2O$, 7·2%).

*Action of Phosphorus Oxychloride on* p-*Nitrophenyldihydroresorcinol.*—A suspension of *p*-nitrophenyldihydroresorcinol (5 g.) in dry chloroform (13 c.c.) was mixed with 10 c.c. of phosphorus oxychloride and heated on a water-bath for 2 hours. The chloroform was then removed, and the residue poured into water and extracted with ether. From the extract, washed with sodium hydroxide solution and with water and dried, a small quantity of 3 : 5-*dichloro*-1-p-*nitrophenyl*-$\Delta^{2:4}$-cyclo*hexadiene* was obtained, which crystallised from aqueous alcohol in colourless prisms, m. p. 81° (Found : Cl, 26·1. $C_{12}H_9O_2NCl_2$ requires Cl, 26·3%).

*Action of Phosphorus Pentachloride on* m-*Nitrophenyldihydroresorcinol.*—*m*-Nitrophenyldihydroresorcinol (30 g.; 1 mol.) was suspended in dry chloroform (80 c.c.), phosphorus pentachloride (90 g.; 4 mols.) gradually added in the cold, and the mixture heated for 1½ hours. The chloroform was removed under reduced pressure, and the residue poured on ice and extracted with ether. From the washed and dried extract, 3 : 5-*dichloro*-1-m-*nitrophenyl*-$\Delta^{2:4}$-cyclo*hexadiene* was obtained, which crystallised from aqueous alcohol in short colourless needles, m. p. 66—68° (Found : Cl, 26·3%), together with a small quantity of 3 : 5-*dichloro*-3'-*nitrodiphenyl*, m. p. 162° (Found : Cl, 26·35. $C_{12}H_7O_2NCl_2$ requires Cl, 26·4%). The separation of the two compounds was effected by fractional crystallisation from methyl alcohol, in which the latter is less soluble.

3 : 5-*Dichloro*-3'-*acetamidodiphenyl.*—3 : 5-Dichloro-3'-nitrodiphenyl (0·9 g.), dissolved in alcohol (10 c.c.), was reduced with stannous chloride (3·3 g.) in absolute alcohol (12 c.c.) saturated with hydrogen chloride. The mixture was heated for 1 hour and, after evaporation, excess of sodium hydroxide was added and the base was extracted with ether. It was obtained as a thick oil, from which, by warming with acetic anhydride, 3 : 5-*dichloro*-3'-*acetamidodiphenyl* was prepared; this crystallised from aqueous alcohol in colourless plates, m. p. 168° (Found : N, 5·0. $C_{14}H_{11}ONCl_2$ requires N, 5·0%).

*Oxidation of* 3 : 5-*Dichloro*-3'-*aminodiphenyl.*—The oil obtained by the reduction of 3 : 5-dichloro-3'-nitrodiphenyl was dissolved in the minimum quantity of glacial acetic acid and heated under reflux with a solution of chromic anhydride in acetic acid. Further additions of chromic anhydride were made until oxidation was complete. On addition of water, 3 : 5-dichlorobenzoic acid, m. p. 183—185° after crystallisation from aqueous methyl alcohol, separated.

*Action of Chlorine on* 3 : 5-*Dichloro*-1-m-*nitrophenyl*-$\Delta^{2:4}$-cyclo*hexadiene*.—(1) *At a low temperature.* Chlorine (1·6 g.; 1 mol.) was passed into a solution of 3 : 5-dichloro-1-*m*-nitrophenyl-$\Delta^{2:4}$-*cyclo*hexadiene (6 g.; 1 mol.) in dry chloroform (16 g.) below 0°. The residue obtained after rapid removal of the chloroform solidified in a vacuum over solid sodium hydroxide and was crystallised from alcohol, 3 : 5-dichloro-3′-nitrodiphenyl (2·5 g.) being obtained in fine colourless needles which, alone or mixed with the aromatic compound obtained from the phosphorus pentachloride reaction, melted at 162°.

(2) *In excess at a low temperature.* Chlorine was slowly passed into a solution of 3 : 5-dichloro-1-*m*-nitrophenyl-$\Delta^{2:4}$-*cyclo*hexadiene (6 g.) in dry chloroform (25 c.c.) kept at − 10°. When chlorine was no longer absorbed, the chloroform was removed and the residue allowed to stand in a vacuum. The sticky mass obtained was dissolved in hot alcohol; on cooling, 2 : 3 : 5(?)-*trichloro*-3′-*nitrodiphenyl* separated, and after crystallisation from alcohol was obtained as fine colourless needles, m. p. 116° (Found : Cl, 32·0. $C_{12}H_6O_2NCl_3$ requires Cl, 35·2%). The low chlorine value is probably due to the presence of a small quantity of 3 : 5-dichloro-3′-nitrodiphenyl.

(3) *In excess at room temperature.* Chlorine was passed into a solution of 3 : 5-dichloro-1-*m*-nitrophenyl-$\Delta^{2:4}$-*cyclo*hexadiene (6 g.) in dry chloroform (16 c.c.) until the copious evolution of hydrogen chloride had ceased. After removal of chloroform and standing in a vacuum, the residue solidified. Crystallisation from alcohol yielded 3 : 5-dichloro-3′-nitrodiphenyl, m. p. 162°.

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