

937. *Aryldihydroresorcinols. Part II.* The Influence of the Nitro-group in Dihydro-5-o-nitrostyrylresorcinol.*

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Dihydro-5-styrylresorcinol resembles an alkyl- rather than an aryl-dihydroresorcinol.

The influence of the nitro-group in dihydro-5-o-nitrostyrylresorcinol is much less marked than that in dihydronitrophenylresorcinols, the nitrostyryl being comparable with the styryl and the phenyl compound but a little less reactive.

DIHYDRO-5-STYRYLRESORCINOL behaves as a typical dihydroresorcinol in its reactions with phosphorus halides. With phosphorus trichloride and tribromide 3-chloro- and 3-bromo-5-styrylcyclohex-2-en-1-one respectively are obtained, in yields comparable with but slightly less than those of the corresponding halogeno-ketones given by dihydrophenylresorcinol.^{1,2} With two molecular proportions of phosphorus pentachloride the dihydroresorcinol yields 1:3-dichloro-5-styrylcyclohexa-1:3-diene and with four molecular proportions 3:5-dichlorostilbene. Dihydrostyrylresorcinol appears to be somewhat more reactive towards phosphorus pentachloride than is dihydrophenylresorcinol³ but not quite so reactive as dihydrodimethylresorcinol,⁴ the respective yields of the corresponding dichlorocyclohexadienes being 79, 62, and 85%. With phosphorus pentabromide only a tribromo-derivative could be isolated, apparently 2-bromo-5- $\alpha\beta$ -dibromophenethyldihydroresorcinol, the formation of which is probably due to the tendency of phosphorus pentabromide to behave as a mixture of bromine and phosphorus tribromide in this type of reaction,⁵ the 2-position and the ethylene bond being attacked.

With bromine, dihydrostyrylresorcinol behaves as an alkyl- rather than as an aryl-dihydroresorcinol since it yields 2:2-dibromo-5- $\alpha\beta$ -dibromophenethyldihydroresorcinol, thus resembling dihydrodimethylresorcinol (which gives the 2:2-dibromo-derivative),⁶ rather than dihydrophenylresorcinol (which only gives the 2-bromo-derivative¹).

* Part I, *J.*, 1956, 2679.

¹ Boyd, Clifford, and Probert, *J.*, 1920, **117**, 1383.

² Hinkel and Hey, *J.*, 1928, 1202.

³ Hinkel and Hey, *J.*, 1928, 2789.

⁴ Crossley and Le Sueur, *J.*, 1902, **81**, 826.

⁵ Crossley and Le Sueur, *J.*, 1903, **83**, 113.

⁶ Vorländer and Kohlmann, *Annalen*, 1902, **322**, 257.

Whilst dihydronitrophenylresorcinols differ considerably from dihydrophenylresorcinol in their reactions with phosphorus chlorides,⁷ the influence of the nitro-group in dihydro-5-*o*-nitrostyrylresorcinol is much less marked. The dihydroresorcinol yields 3-chloro- and 3-bromo-5-*o*-nitrostyrylcyclohex-2-en-1-one with the appropriate phosphorus trihalide, although in slightly smaller yield than is obtained from the styryl compound. With either two or four molecular proportions of phosphorus pentachloride the only product isolated was 3 : 5-dichloro-2'-nitrostilbene. This was unexpected and was probably due to an easy conversion of the expected dichlorocyclohexadiene into the stilbene derivative under these conditions.⁸ An excess of bromine yielded only a dibromo-derivative, with no apparent addition at the ethylenic bond of the nitrostyryl group, probably owing to a deactivating influence of the nitro-group.

The reactivity of 5-aryldihydroresorcinols has been correlated⁷ with the electron affinity of the aryl group (cf. also Part I) and the resemblance of the styryl compound to an alkyl rather than an aryl compound would be expected, the relative affinities of the phenyl, styryl, and methyl groups being indicated by the strengths of the acids : benzoic, cinnamic, and acetic acids, 10^5K 6.27, 3.65, and 1.75 respectively.⁹ With dihydro-5-*o*-nitrostyrylresorcinol, the electron affinity of the nitrophenyl group should not be transmitted through the ethylenic bond to any marked extent but the electron-donating properties of the aralkyl group would be weakened, and the strength⁹ of *o*-nitrocinnamic acid (10^5K 7.07) indicates that the dihydroresorcinol should resemble, but be somewhat less reactive than, the phenyl compound.

Dihydro-5-*o*-nitrostyrylresorcinol was only obtained in poor yield from 6-*o*-nitrophenylhexa-3 : 5-dien-2-one, considerable polymerisation still occurring even when ether was substituted for ethanol or benzene as the reaction medium. It was more satisfactory to isolate and then hydrolyse the ethyl dihydronitrostyrylresorcyrate rather than to hydrolyse the ester without isolating it.¹⁰ Alternative routes *via* diethyl *o*-nitrocinnamylidene-malonate or β -(*o*-nitrostyryl)acrylic acid were even less fruitful.

EXPERIMENTAL

Action of Phosphorus Trichloride on Dihydro-5-styrylresorcinol.—Dihydrostyrylresorcinol¹¹ (5 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus trichloride (1.6 g., 1 mol.) for 3 hr. The chloroform was evaporated and crushed ice added to the residue, the mixture then being extracted with ether. The extract was washed with 4% sodium hydroxide solution and water, and dried (Na_2SO_4). Evaporation of the ether yielded 3-chloro-5-styrylcyclohex-2-en-1-one (3.2 g., 59%) as a pale yellow oil, which solidified when frozen, and crystallised from aqueous methanol as a microcrystalline powder, m. p. 44° (Found : Cl, 15.1. $\text{C}_{14}\text{H}_{13}\text{OCl}$ requires Cl, 15.2%).

Action of Phosphorus Pentachloride on Dihydro-5-styrylresorcinol.—(a) The dihydroresorcinol (10 g., 1 mol.) was suspended in dry chloroform (25 c.c.), phosphorus pentachloride (19.5 g., 2 mol.) added in small quantities, and the mixture heated under reflux for 3 hr. The above procedure gave 1 : 3-dichloro-5-styrylcyclohexa-1 : 3-diene (9.3 g., 79%), b. p. 140°/0.23 mm., which solidified and crystallised from aqueous ethanol in plates, m. p. 83° (Found : C, 67.5; H, 5.0. $\text{C}_{14}\text{H}_{12}\text{Cl}_2$ requires C, 67.0; H, 4.8%).

(b) The dihydroresorcinol (5 g., 1 mol.) was suspended in dry chloroform (15 c.c.), phosphorus pentachloride (19.5 g., 4 mol.) gradually added, and the mixture heated on a water-bath for 3 hr. Subsequent procedure as above yielded 3 : 5-dichlorostilbene as a reddish-yellow oil (5 g., 86%), b. p. 164—166°/0.7 mm., which solidified when frozen and crystallised from aqueous methanol in short needles, m. p. 80°, depressed by ~25° when mixed with the above dichlorostyrylcyclohexadiene (Found : C, 67.6; H, 4.3. $\text{C}_{14}\text{H}_{10}\text{Cl}_2$ requires C, 67.5; H, 4.0%).

Action of Phosphorus Tribromide on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (5 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus tribromide (3.1 g.,

⁷ Hinkel and Dippy, *J.*, 1930, 1387.

⁸ Crossley and Le Sueur, *J.*, 1902, 81, 1534.

⁹ Dippy, *Chem. Rev.*, 1939, 25, 206.

¹⁰ Crossley and Pratt, *J.*, 1915, 107, 173.

¹¹ Vorländer and Erig, *Annalen*, 1897, 294, 312.

1 mol.) for 3 hr. The above procedure gave 3-bromo-5-styrylcyclohex-2-en-1-one (3.5 g., 54%) which solidified and crystallised from aqueous ethanol in white needles, m. p. 69° (Found: C, 60.4; H, 4.8; Br, 28.9. $C_{14}H_{13}OBr$ requires C, 60.7; H, 4.7; Br, 28.8%).

Action of Phosphorus Pentabromide on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (5 g., 1 mol.) was suspended in dry chloroform (15 c.c.), and phosphorus pentabromide (20.1 g., 2 mol.) added in small quantities. The mixture was heated for 3 hr. and, by following the usual procedure, a red oil (7.25 g.) was obtained. Cooling and addition of ether yielded a pink solid (2.9 g.), which was dissolved in methanol, treated with charcoal, heated to boiling, and then filtered. Addition of water to the filtrate precipitated 2-bromo-5- $\alpha\beta$ -dibromophenethyldihydroresorcinol as a white solid which, crystallised from ethanol, had m. p. 155° (Found: C, 37.0; H, 2.8. $C_{14}H_{13}O_2Br_3$ requires C, 37.1; H, 2.9%). The ether solution yielded a red oil which decomposed when distillation under reduced pressure was attempted.

Action of Bromine on Dihydro-5-styrylresorcinol.—Bromine (2.8 g., >3 mol.) in dry chloroform (24 c.c.) was added during 1 hr. to a suspension of the dihydroresorcinol (1.07 g., 1 mol.) in chloroform (15 c.c.). Next day the suspended solid was filtered off and dried in a vacuum-desiccator over sodium hydroxide. Crystallisation from aqueous acetone yielded 2:2-dibromo-5- $\alpha\beta$ -dibromophenethyldihydroresorcinol, m. p. 185° (decomp.) (Found: Br, 59.2. $C_{14}H_{12}O_2Br_4$ requires Br, 60.1%).

Treatment of the dihydroresorcinol (1 mol.) with bromine (1 or 2 mol.) as above yielded only mixtures from which no pure compound could be isolated.

Action of 2:4-Dinitrophenylhydrazine on Dihydro-5-styrylresorcinol.—The dihydroresorcinol (0.54 g., 1 mol.) and 2:4-dinitrophenylhydrazine (0.92 g., 2 mol.) were heated to boiling in ethanol (50 c.c.). The solution was cooled slightly, concentrated hydrochloric acid (1 c.c.) added, and the solution heated under reflux for 2.5 hr. During the heating dihydrostyrylresorcinol bis-2:4-dinitrophenylhydrazone trihydrate separated as a yellow solid, m. p. 188° (1.36 g., 87%) (Found: C, 50.4; H, 4.2; N, 17.3. $C_{26}H_{22}O_8N_8, 3H_2O$ requires C, 49.7; H, 4.5; N, 17.8%). Crystallisation from aqueous acetone gave the monohydrate as a dark purple solid, m. p. 228°, the change in colour suggesting such a loss of water of crystallisation (Found: C, 53.3; H, 3.9; N, 18.5. $C_{26}H_{22}O_8N_8, H_2O$ requires C, 52.7; H, 4.1; N, 18.9%).

6-o-Nitrophenylhexa-3:5-dien-2-one.—A mixture of *o*-nitrocinnamaldehyde (10 g.), acetone (30 c.c., excess), water (200 c.c.) and 10% aqueous sodium hydroxide (8 c.c.) was shaken for 24 hr. at room temperature. 6-o-Nitrophenylhexa-3:5-dien-2-one separated as a brown solid which crystallised from light petroleum (b. p. 80–100°) in pale yellow needles, m. p. 73.5° (9.1 g., 74%). Diehl and Einhorn¹² record m. p. 73.5°.

Ethyl Dihydro-5-o-nitrostyrylresorcinol-4-carboxylate.—Sodium (2 g., 1 g.-atom) was dissolved rapidly in ethanol, excess of which was then removed under reduced pressure, and to the resulting sodium ethoxide was added ethyl malonate (17 c.c., >1 mol.). As soon as the sodium ethoxide had reacted with the ester, ether was added, a finely divided precipitate of ethyl sodiomalonate being obtained. 6-o-Nitrophenylhexa-3:5-dien-2-one (19.0 g., 1 mol.) was then added gradually with shaking and the mixture heated under reflux for 48 hr. The sodium salt of the dihydroresorcylic ester, which separated during the condensation, was filtered off and dissolved in water, the solution then being shaken with ether until the ether ceased to be coloured yellow. The aqueous solution was acidified and the liquid decanted from the light brown oil which separated. Trituration of this oil with ethyl acetate gave ethyl dihydro-5-o-nitrostyrylresorcinol-4-carboxylate as a light brown solid, which crystallised from aqueous ethanol as a pale yellow powder, m. p. 144° (6.4 g., 22%) (Found: C, 61.8; H, 5.0. $C_{17}H_{17}O_6N$ requires C, 61.6; H, 5.2%).

When ethanol or benzene (cf. Part I) was employed as the reaction medium polymerisation of the unsaturated ketone occurred, and no dihydroresorcylic ester could be isolated. A similar result was obtained when toluene, anisole, dioxan, or light petroleum (b. p. 80–100°) was employed. Substitution of piperidine for sodium ethoxide as the condensing agent in ethanol solution was also unsuccessful.

Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcylic ester (6.4 g.) was heated in 10% aqueous sodium hydroxide for about 15 min. at 70°, until a small portion gave no precipitate when acidified. The bulk of the solution was then acidified and boiled, dihydro-5-o-nitrostyrylresorcinol separating as a dark brown solid, which crystallised from aqueous ethanol as a yellow micro-crystalline powder, m. p. 141° (3 g., 60%) (Found: C, 65.0; H, 5.2; N, 5.2. $C_{14}H_{13}O_4N$ requires C, 64.9; H, 5.1; N, 5.4%).

¹² Diehl and Einhorn, *Ber.*, 1885, 18, 2327.

Condensation of o-Nitrocinnamaldehyde with Ethyl Malonate.—A mixture of ethyl malonate (9 g., 1 mol.), *o*-nitrocinnamaldehyde (10 g., 1 mol.), and piperidine (0.2 c.c.) was kept in a closed flask for 2 days and then heated on a water-bath for 16 hr. Ether was then added and the solution washed with acid and water, and dried (Na_2SO_4). Removal of ether and distillation under reduced pressure yielded unchanged ethyl malonate and then a light yellow oil, of which only a small quantity could be collected, since much charring occurred owing to presence of unchanged aldehyde. The yellow oil solidified and crystallised from aqueous acetone, to give *ethyl 2-nitrocinnamylidenemalonate* as short yellow needles, m. p. 92° (1.8 g., 10%) (Found: C, 60.3; H, 5.2. $\text{C}_{16}\text{H}_{17}\text{O}_6\text{N}$ requires C, 60.2; H, 5.4%).

Action of Phosphorus Trichloride on Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcinol (3 g., 2 mol.) was suspended in dry chloroform (15 c.c.) and heated with phosphorus trichloride (0.8 g., 1 mol.) for 3 hr. The mixture was washed several times with 4% aqueous sodium hydroxide and then water, and the chloroform layer dried (CaCl_2). Evaporation of the chloroform gave a yellow oil (1.75 g., 54%) which solidified and crystallised from aqueous ethanol, to yield *3-chloro-5-o-nitrostyrylcyclohex-2-en-1-one* as yellow needles, m. p. 55° (Found: C, 60.6; H, 4.3. $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NCl}$ requires C, 60.5; H, 4.4%).

If the usual procedure, removal of chloroform and then washing with alkali, was employed, the chloro-ketone was hydrolysed very rapidly to the original dihydroresorcinol.

Action of Phosphorus Pentachloride on Dihydro-5-o-nitrostyrylresorcinol.—(a) The dihydroresorcinol (2 g., 1 mol.) was suspended in dry chloroform (10 c.c.), and phosphorus pentachloride (3.2 g., 2 mol.) added gradually. The mixture was heated for 4 hr. and, by following the usual procedure of evaporating the chloroform and extracting with ether, a yellow oil was obtained. It was passed in ether through a short column of neutralised alumina. The ether eluates yielded *3:5-dichloro-2'-nitrostilbene* (1.45 g., 64%), which crystallised from aqueous ethanol as yellow needles, m. p. 136° (Found: C, 57.5; H, 3.4. $\text{C}_{14}\text{H}_8\text{O}_2\text{NCl}_2$ requires C, 57.2; H, 3.1%).

(b) The dihydroresorcinol (2 g., 1 mol.) was suspended in chloroform (10 c.c.), phosphorus pentachloride (6.4 g., 4 mol.) added in small quantities, and the mixture heated for 4 hr. The usual procedure gave *3:5-dichloro-2'-nitrostilbene* (1.9 g., 84%), which solidified almost immediately and crystallised from aqueous ethanol in small yellow needles, m. p. and mixed m. p. 136° .

Action of Phosphorus Tribromide on Dihydro-5-o-nitrostyrylresorcinol.—The dihydroresorcinol (2 g., 2 mol.) was suspended in chloroform (10 c.c.) and heated with phosphorus tribromide (1.05 g., 1 mol.) for 3 hr. Subsequent procedure yielded a yellow oil which was passed in ether through a column of neutralised alumina (30 g.). On elution with ether *3-bromo-5-o-nitrostyrylcyclohex-2-en-1-one* was obtained. This solidified (1 g., 40%), and crystallised from aqueous methanol in pale yellow plates, m. p. 70° (Found: C, 52.3; H, 3.6. $\text{C}_{14}\text{H}_{12}\text{O}_3\text{NBr}$ requires C, 52.2; H, 3.8%).

Action of Bromine on Dihydro-5-o-nitrostyrylresorcinol.—Bromine (4 g., >3 mol.) in dry chloroform (30 c.c.) was added during 2 hr. to a suspension of the dihydroresorcinol (1.3 g., 1 mol.) in chloroform (15 c.c.), a pasty brown solid separating. Next day the solid was filtered off and dried over sodium hydroxide. Crystallisation from aqueous acetone yielded *2:2-dibromodihydro-5-o-nitrostyrylresorcinol* as a pale yellow microcrystalline powder, m. p. 146° (Found: Br, 39.3. $\text{C}_{14}\text{H}_{11}\text{O}_4\text{NBr}_2$ requires Br, 38.4%).

One of us (D. A. D.) acknowledges a grant from the Swansea Local Education Authority.