528. *Aryldihydroresorcinols. Part I. Dihydro-5-α-naphthyl- and 5-(4-Diphenylyl)dihydro-resorcinol.*

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Dihydro-5-α-naphthyl- and 5-(4-diphenylyl)dihydro-resorcinol have been prepared for comparison with dihydro-5-phenyl- and -5-*m*-nitrophenyl-resorcinol. The naphthyl compound is intermediate between the phenyl and the nitrophenyl compound in its reactions with phosphorus chlorides, whilst the diphenylyl compound is comparable with the phenyl compound but somewhat less reactive. This behaviour is correlated with the electron-affinities of the aryl groups.

Whilst dihydro-5-phenylresorcinol behaves similarly to the 5-alkyldihydroresorcinols [1, 2, 3] in its reactions with phosphorus chlorides,[4, 5] dihydro-5-*m*- and -*p*-nitrophenylresorcinol do not.[6] This difference was attributed [6] to the electron-affinity of the nitro-group, and the relative affinities of the phenyl and nitrophenyl groups are indicated by the strengths of the acids: benzoic and *m*- and *p*-nitrobenzoic acid, 10^5K 6·3, 32·1, and 37·6 respectively.[7]

Dihydro-5-α-naphthyl- and 5-(4-diphenylyl)dihydro-resorcinol have been studied since

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[1] Crossley and Le Sueur, *J.*, 1902, **81**, 821; 1903, **83**, 110.
[2] Crossley and Haas, *J.*, 1903, **83**, 494.
[3] Crossley and Pratt, *J.*, 1915, **107**, 171.
[4] Boyd, Clifford, and Probert, *J.*, 1920, **117**, 1383.
[5] Hinkel and Hey, *J.*, 1928, 2786.
[6] Hinkel and Dippy, *J.*, 1930, 1387.
[7] Dippy, *Chem. Rev.*, 1939, **25**, 206.

the two binuclear radicals should both exhibit greater electron-affinity than a phenyl [8] but less than a nitrophenyl radical. The α-naphthyl radical would be intermediate between phenyl and nitrophenyl ($10^5K = 20{\cdot}4$ for 1-naphthoic acid [9]), and the 4-diphenylyl radical between the naphthyl and the phenyl group,[8] although the apparent dissociation constants of benzoic and diphenyl-4-carboxylic acid in aqueous 2-butoxyethanol (pK 5·65 and 5·66 respectively [10]) are virtually identical.

Both dihydroresorcinols gave the corresponding 2-bromo-derivative with bromine and so resemble the phenyl compound,[4] dihydrodimethylresorcinol giving also the 2 : 2-dibromo-derivative.[11] With sodium hypobromite, however, whilst diphenylyldihydroresorcinol was oxidised to diphenylylglutaric acid (cf. ref. 12), the naphthyl compound was oxidised only to the 2-bromo-derivative (cf. ref. 11).

On oxidation with aqueous potassium permanganate, the dihydronaphthylresorcinol yielded a mixture from which naphthylsuccinic acid could be isolated (cf. ref. 4) but the reaction with the diphenylyl compound proceeded further, giving diphenyl-4-carboxylic acid.

In the reactions of the two dihydroresorcinols with phosphorus chlorides, the expectations based on the relative electron-affinities of the aryl groups have been realised. The diphenylyl behaved similarly to the phenyl compound but gave a much smaller yield of arylchloro*cyclo*hexenone (25 compared with 65% [4]), and the corresponding chloro-ketone from the naphthyl compound was only isolated when phosphorus pentachloride was used. The comparative behaviour of these dihydroresorcinols containing the binuclear groups with those containing the phenyl and the nitrophenyl group is summarised in the Table and agrees with the sequence, phenyl < 4-diphenylyl < α-naphthyl < *m*-nitrophenyl, for the electron-affinities of the groups.

Dihydroresorcinol	Product with PCl_3	Product with PCl_5	
		2 mol.	4 mol.
Ph	Chloro-ketone [4]	Hexadiene and dichlorodiphenyl [5]	
p-C_6H_4Ph	Chloro-ketone (small yield)	Hexadiene and dichloroterphenyl	
α-$C_{10}H_7$	—	Chloro-ketone	Dichlorophenyl derivative
m-$NO_2{\cdot}C_6H_4$	—	—	Hexadiene [6]

The absence of dichloro(naphthyl)*cyclo*hexadiene from the phosphorus pentachloride reaction is probably due to use of an excess of pentachloride, since 1 : 3-dichloro-5 : 5-dimethyl*cyclo*hexa-1 : 3-diene is converted into 3 : 5-dichloro-*o*-xylene when heated with phosphorus pentachloride for several hours.[13]

Dihydro-5-α-naphthylresorcinol was prepared in good yield from 4-α-naphthylbut-3-en-2-one by the procedure described by Crossley and Renouf [14] for dihydrophenylresorcinol. With 4-phenylbenzylideneacetone, however, only a poor yield of 5-*p*-diphenylyldihydroresorcinol was obtained : a better yield resulted when benzene was substituted for ethanol as the reaction medium. Condensation of ethyl 4-phenylcinnamate or ethyl 4-phenylbenzylidenemalonate with ethyl acetoacetate also gave the diphenylyldihydroresorcinol but neither yield was as good as that from 4-phenylbenzylideneacetone.

EXPERIMENTAL

Dihydro-5-α-naphthylresorcinol.—4-α-Naphthylbut-3-en-2-one [15] was prepared both from α-naphthaldehyde and, more conveniently, from the aldehyde bisulphite compound which is isolated during the preparation of the aldehyde by the procedure described by Hinkel, Ayling,

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[8] Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 427.
[9] Bethmann, *Z. phys. Chem.*, 1890, **5**, 399.
[10] Berliner and Blommers, *J. Amer. Chem. Soc.*, 1951, **73**, 2479.
[11] Vorländer and Kohlmann, *Annalen*, 1902, **322**, 257.
[12] *Idem*, *Ber.*, 1899, **32**, 1879.
[13] Crossley and Le Sueur, *J.*, 1902, **81**, 1533.
[14] Crossley and Renouf, *J.*, 1915, **107**, 608.
[15] Gibson, Hariharan, Menon, and Simonsen, *J.*, 1926, 2259

and Beynon.[16] The bisulphite compound (12·25 g.), acetone (20 g.), sodium hydroxide (12·9 g.), and water (950 c.c.) were boiled for 3 min., then cooled, a further 20 g. of acetone in water (100 c.c.) added, and the whole was shaken for 3 days. Extraction with ether, drying, and distillation yielded the ketone, b. p. 210°/21 mm. (Found : C, 85·2; H, 6·3. Calc. for $C_{14}H_{12}O$: C, 85·7; H, 6·2%) (Gibson *et al.*[15] record b. p. 200—201°/10 mm.; Wilds *et al.*[17] record b. p. 167—173°/0·9 mm.). The oxime crystallised from benzene as colourless prisms, m. p. 138° (Found : C, 79·3; H, 6·2. Calc. for $C_{14}H_{13}ON$: C, 79·6; H, 6·2%) (Gibson *et al.*[15] record m. p. 136—137°).

To this ketone (1·1 g.) in ether (10 c.c.) was added bromine (0·9 g.) in ether (5 c.c.); 3 : 4-*dibromo*-4-α-*naphthylbutan*-2-*one* separated and crystallised from chloroform as needles, m. p. 110° (Found : Br, 45·1. $C_{14}H_{12}OBr_2$ requires Br, 44·9%).

4-α-Naphthylbut-3-en-2-one was condensed with ethyl malonate according to the modified procedure described by Crossley and Renouf[14] for dihydrophenylresorcinol, the dihydroresorcylic ester first produced being hydrolysed without isolation, and a viscid mass was obtained which solidified (70%). Crystallisation from aqueous ethanol yielded *dihydro*-5-α-*naphthylresorcinol monohydrate* as needles, m. p. 93° (Found : C, 74·5; H, 6·4. $C_{16}H_{14}O_2,H_2O$ requires C, 75·0; H, 6·3%). Storage in a vacuum yielded the anhydrous *compound*, m. p. 140° (Found : C, 80·5; H, 6·1. $C_{16}H_{14}O_2$ requires C, 80·6; H, 5·9%), also obtained by precipitation from ethanol by light petroleum (b. p. 40—60°) and used in subsequent reactions.

Ethyl dihydro-α-*naphthylresorcylate*, isolated by acidification before hydrolysis with sodium hydroxide in following the above procedure, crystallised from aqueous ethanol as needles, m. p. 116° (Found : C, 73·8; H, 5·4. $C_{19}H_{18}O_4$ requires C, 73·5; H, 5·8%).

2-*Bromodihydro*-5-α-*naphthylresorcinol*.—The dihydroresorcinol (2·23 g.) dissolved in chloroform (17 c.c.) when bromine (1·5 g.) in chloroform (10 c.c.) was added with shaking during 30 min. After 2 hr. the chloroform was evaporated, leaving an oil which solidified when stirred with light petroleum (b. p. 40—60°). Crystallisation from ethanol yielded 2-*bromodihydro*-5-α-*naphthylresorcinol* as needles, m. p. 156° (Found : Br, 24·7. $C_{16}H_{13}O_2Br$ requires Br, 25·2%).

Action of Phosphorus Pentachloride on Dihydro-5-α-*naphthylresorcinol*.—(*a*) The dihydroresorcinol (2·38 g., 1 mol.) and phosphorus pentachloride (4·2 g., 2 mol.) in dry chloroform (15 c.c.) were heated under reflux for 2 hr. The chloroform was removed under reduced pressure and the residual dark brown oil was poured into water and extracted with ether. The extract was washed with aqueous sodium hydroxide and water and dried (Na_2SO_4). Removal of the ether and distillation gave a yellow oil, b. p. 265°/20 mm., which partly solidified. Crystallisation from light petroleum (b. p. 40—60°)–acetone yielded 3-*chloro*-1-α-*naphthyl*cyclo*hex*-2-*en*-1-*one* as needles, m. p. 82° (Found : Cl, 13·4. $C_{16}H_{13}OCl$ requires Cl, 13·8%).

(*b*) The dihydroresorcinol (2·38 g., 1 mol.) and phosphorus pentachloride (8·4 g., 4 mol.) in chloroform (20 c.c.) were heated under reflux and the product was treated as described above. Removal of the ether yielded an oil, b. p. 236°/22 mm., which solidified. 1-(3 : 5-*Dichlorophenyl*)*naphthalene* crystallised from light petroleum (b. p. 60—80°) as needles, m. p. 96° (Found : C, 70·2; H, 3·6. $C_{16}H_{10}Cl_2$ requires C, 70·3; H, 3·7%).

Oxidation of Dihydronaphthylresorcinol.—The dihydroresorcinol (5 g.) was suspended in water (150 c.c.), and hot 4% aqueous potassium permanganate gradually added, with stirring, until the permanganate was no longer decolorised (about 5 hr.). The manganese dioxide was removed and the solution acidified and extracted with ether. Evaporation of the ether and fractional crystallisation of the residual solid from aqueous ethanol yielded a small amount of α-naphthylsuccinic acid, m. p. 204° (Wislicenus, Butterfass, and Koken[18] record m. p. 206°).

Action of Sodium Hypobromite on Dihydronaphthylresorcinol.—The dihydroresorcinol (5 g.) was dissolved in 4N-sodium hydroxide solution, and sodium hypobromite solution was added until excess was present. The solution, on acidification, yielded a precipitate which when crystallised from alcohol had m. p. 156°, unchanged by admixture with the above 2-bromodihydro-5-α-naphthylresorcinol, m. p. 156°.

4-*Phenylbenzylideneacetone*.—Diphenyl-4-aldehyde[19] (9 g., 1 mol.) was dissolved in acetone (250 c.c.; excess) and water (125 c.c.), 4N-sodium hydroxide (5 c.c.) added, and the mixture shaken for 24 hr. Separation of solid began after 0·5 hr. and was completed at the end of the reaction by addition of water. The 4-*phenylbenzylideneacetone* (10·5 g., 95%) was collected, washed with dilute acetic acid and water, and dried. Crystallised from ethanol it was pale

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[16] Hinkel, Ayling, and Beynon, *J.*, 1936, 342.

[17] Wilds, Beck, Close, Djerassi, Johnson, Johnson, and Shunk, *J. Amer. Chem. Soc.*, 1947, **69**, 1994.

[18] Wislicenus, Butterfass, and Koken, *Annalen*, 1924, **436**, 82.

[19] Hey, *J.*, 1931, 2476.

yellow, melted at 137°, and sublimed at 100°/1 atm. to give small plates (Found : C, 86·6; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·3%). The pale yellow *semicarbazone*, crystallised from methanol, had m. p. 229° (Found : N, 14·8. $C_{17}H_{17}ON_3$ requires N, 15·0%). The 2 : 4-*dinitrophenylhydrazone* crystallised from benzene in deep red needles, m. p. 242° (Found : C, 66·0; H, 4·6. $C_{22}H_{18}O_4N_4$ requires C, 65·6; H, 4·5%).

Ethyl 4-*Phenylcinnamate*.—To diphenyl-4-aldehyde (9 g., 1 mol.) in alcohol-free ethyl acetate (20 c.c.), sodium wire (1·5 g., 1 atom) was added. After 16 hr. sufficient dilute acetic acid was added to decompose any remaining sodium, and the whole was extracted with ether. The extract was washed with dilute sodium hydroxide solution and water and dried (Na_2SO_4). Removal of ether and residual ethyl acetate under reduced pressure and crystallisation of the residue (4·7 g., 37%) from methanol gave yellow plates, m. p. 87° (Hey [19] records m. p. 87°).

Ethyl 4-*Phenylbenzylidenemalonate*.—Diphenyl-4-aldehyde (18 g., 1 mol.) was dissolved in ether, and malonic ester (14·8 c.c., 1 mol.) and piperidine (0·4 c.c.) were added. After 24 hr. at room temperature and 12 hr. on a water-bath the solution was washed with dilute acetic acid and water, and dried (Na_2SO_4). Removal of ether and distillation yielded unchanged ethyl malonate and diphenyl-4-aldehyde and a fraction, b. p. 255—270°/15 mm., consisting of ethyl 4-phenylbenzylidenemalonate (7·4 g., 23%), which, when redistilled at 15 mm., had b. p. 250—270°. The ester was hydrolysed with 5% methanolic potassium hydroxide to give 4-phenylbenzylidenemalonic acid, which crystallised from aqueous ethanol as yellow needles, m. p. 215° (decomp.) [Hey [19] records m. p. 215° (decomp.)].

5-(4-*Diphenylyl*)*dihydroresorcinol*.—(1) *From* 4-*phenylbenzylideneacetone*. (*a*) In ethanol. The procedure followed was similar to that described above for dihydronaphthylresorcinol. 4-Phenylbenzylideneacetone (11 g.) yielded 5-(4-*diphenylyl*)*dihydroresorcinol* (2·8 g., 21%) which, crystallised from acetone, had m. p. 234° (Found : C, 81·4; H, 6·0. $C_{18}H_{16}O_2$ requres C, 81·8; H, 6·1%). Heating the reaction mixture for 19 hr. instead of the usual 7 hr. increased the yield slightly to 25%.

(*b*) In benzene. Sodium (3·5 g., 1 atom) was rapidly dissolved in alcohol, excess of which was removed under reduced pressure. To the resulting sodium ethoxide were added ethyl malonate (24 c.c., >1 mol.) and 4-phenylbenzylideneacetone (33 g., 1 mol.) in hot benzene (110 c.c.). The mixture was heated under reflux for 44 hr., then filtered, and the residual sodium salt dissolved in water. Subsequent procedure as above yielded the dihydroresorcinol, m. p. 234° (22 g., 56%).

Ethyl 5-(4-*diphenylyl*)*dihydroresorcylate*, isolated by acidification after removal of the ether in following the above procedure, crystallised from ethanol as needles, m. p. 174—175° (Found : C, 74·9; H, 6·2. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%).

(*c*) In toluene. Following the procedure described under (*b*) but with toluene (120 c.c.) instead of benzene and boiling for 44 hr. gave the dihydroresorcinol (13·2 g., 33%).

(2) *From ethyl* 4-*phenylcinnamate*. Ethyl 4-phenylcinnamate (6 g., 1 mol.) in hot ethanol (60 c.c.) was condensed with ethyl acetoacetate (4·5 c.c., >1 mol.) in the presence of sodium ethoxide (1 mol.) on a water-bath for 22 hr. Subsequent procedure as described above (1*a*) gave the diphenylyldihydroresorcinol, m. p. 234° (1·6 g., 25%).

(3) *From ethyl* 4-*phenylbenzylidenemalonate*. Ethyl 4-phenylbenzylidenemalonate (6·5 g., 1 mol.) in ethanol (5 c.c.) was condensed with ethyl acetoacetate (2·6 g., >1 mol.) in the presence of sodium ethoxide (1 mol.) on a water-bath for 12 hr. The dihydroresorcinoldicarboxylate produced was hydrolysed, etc., as above, to give the diphenylyldihydroresorcinol, m. p. 234° (2·4 g., 46%).

4 : 6-*Diethoxycarbonyl*-5-(4-*diphenylyl*)*dihydroresorcinol* was isolated by acidification before hydrolysis by sodium hydroxide in following the above procedure and crystallised from ethanol as needles, m. p. 198° (Found : C, 70·5; H, 5·9. $C_{24}H_{24}O_6$ requires C, 70·6; H, 5·9%).

5-(4-*Diphenylyl*)*dihydroresorcinol monoxime*. Diphenylyldihydroresorcinol, when treated in ethanol with hydroxylamine hydrochloride (1 or 2 mol.) and sodium hydroxide or heated with hydroxylamine sulphate (>2 mol.) and anhydrous potassium acetate in ethanol under reflux, only gave the *monoxime*, which from methanol formed pale yellow crystals, m. p. 182° (Found : N, 5·0. $C_{18}H_{17}O_2N$ requires N, 5·0%). Although it is possible to obtain the monoximes of dihydroresorcinols,[20,21] the dioxime is usually obtained.

Action of Bromine on Diphenylyldihydroresorcinol.—Bromine (0·8 g., 1 mol.) in chloroform (8 c.c.) was added during 2 hr. to a suspension of diphenylyldihydroresorcinol (1·3 g., 1 mol.) in

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[20] Vorländer and Erig, *Annalen*, 1897, **294**, 316.

[21] Gittel, *Z. Naturwiss.*, 1906, **77**, 145.

chloroform (15 c.c.). Next day the suspended solid was filtered off and dried in a vacuum desiccator over sodium hydroxide. Crystallisation from acetone–pentane gave 2-*bromo*-5-(4-*diphenylyl*)*dihydroresorcinol*, m. p. 228° (Found: Br, 23·5. $C_{18}H_{15}O_2Br$ requires Br, 23·3%). Treatment of the dihydroresorcinol (1 mol.) with bromine (>2 mol.) or the 2-bromo-compound (1 mol.) with bromine (1 mol.) as above did not yield a dibromo-compound.

Action of Phosphorus Trichloride on 5-(4-*Diphenylyl*)*dihydroresorcinol*.—Diphenylyldihydroresorcinol (2·6 g., 2 mol.) was suspended in dry chloroform (10 c.c.) and heated with phosphorus trichloride (0·7 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 and crystallisation of the residue (0·7 g., 25%) from methanol gave a product of unsharp m. p. which was passed in ether through neutralised alumina; the ether eluates yielded 3-*chloro*-5-p-*diphenylyl*cyclo*hex*-2-*en-one*, which crystallised from ethanol as needles, m. p. 94° (Found: C, 76·2; H, 5·2; Cl, 12·3. $C_{18}H_{15}OCl$ requires C, 76·5; H, 5·4; C, 12·5%).

Action of Phosphorus Pentachloride on 5-*Diphenylyldihydroresorcinol*.—Diphenylyldihydroresorcinol (5·3 g., 1 mol.) was suspended in dry chloroform (12 c.c.), and phosphorus pentachloride (8·4 g., 2 mol.) was added in small quantities. The mixture was heated on a water-bath until hydrogen chloride evolution ceased. The chloroform was then distilled off rapidly and the mixture, after cooling, poured on crushed ice and extracted with ether. The extract was washed with 4% aqueous sodium hydroxide and dried. Removal of ether yielded a brown oil (5·1 g.) which did not solidify and a portion of it was passed in ether through a short column of neutralised alumina. The first ether eluates yielded 1 : 3-*dichloro*-5-(4-*diphenylyl*)cyclo*hexa*-1 : 3-*diene*, which decolorised aqueous potassium permanganate and crystallised from methanol as leaflets, m. p. 70° (Found: C, 71·4; H, 4·5. $C_{18}H_{14}Cl_2$ requires C, 71·8; H, 4·7%). Later eluates yielded 3 : 5-*dichloro*-p-*terphenyl*, which did not decolorise aqueous potassium permanganate and crystallised from methanol as plates, m. p. 120° (Found: Cl, 23·3. $C_{18}H_{12}Cl_2$ requires Cl, 23·7%).

Oxidation of Diphenylyldihydroresorcinol.—(1) *With potassium permanganate*. Diphenylyldihydroresorcinol (1·3 g., 1 mol.) and sodium carbonate (0·5 g.) were dissolved in 12 c.c. of water. To the warm solution was added an excess of a saturated solution of potassium permanganate and the mixture was set aside overnight. The manganese dioxide was filtered off and the solution acidified with sulphurous acid. The resulting precipitate crystallised from ethanol as colourless needles which did not melt sharply, but, when heated at 160°/0·025 mm., the major portion, diphenyl-4-carboxylic acid, sublimed (Found: C, 78·7; H, 5·2. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·1%) (Hey[19] records m. p. 224—225°), m. p. 224° alone or mixed with a specimen, m. p. 224°, prepared from diphenyl-4-aldehyde.

(2) *With sodium hypobromite*. Diphenylyldihydroresorcinol (1·2 g.) in sodium hydroxide solution (1 g. in 50 c.c.) was added to sodium hypobromite solution (from 3·4 g. of bromine). Next day the solution was shaken with ether to remove bromoform and carbon tetrabromide. The aqueous layer was acidified and the precipitated product repeatedly extracted with ether. The dried ethereal extract yielded β-(4-*diphenylyl*)*glutaric acid* (0·8 g., 62%), which crystallised form acetone as needles, m. p. 219° (Found: C, 71·4; H, 5·6. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·7%).

The authors thank Dr. L. E. Hinkel for his continued interest; one (J. H.) was indebted to the Department of Scientific and Industrial Research for a maintenance grant.

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