742. *Synthetic and Oxidative Studies in the Polyhydroxydiphenyl Series. Part II.*[1] 5 : 6-*Dichloro*-2 : 3-*dihydroxydiphenyl.*

By J. MALCOLM BRUCE and F. K. SUTCLIFFE.

Nitration of 4 : 5-dichloroveratrole yields the 3-nitro-derivative, and this has been converted into 4 : 5-dichloro-3-iodoveratrole which, with iodobenzene and copper, affords both 5 : 6-dichloro-2 : 3-dimethoxy- and 5 : 6 : 5′ : 6′-tetrachloro-2 : 3 : 2′ : 3′-tetramethoxy-diphenyl. However, the former diphenyl is more conveniently prepared by treatment of 2 : 3-dimethoxydiphenyl[1] with sulphuryl chloride. It is readily demethylated, and the resulting dihydric phenol is converted by mild oxidants into the corresponding diphenoquinone.

IN Part I[1] the preparation, from 3-lithioveratrole and *cyclo*hexanone, of 2 : 3-dihydroxydiphenyl was described. On oxidation in anhydrous solution this yielded 2 : 3-diphenoquinone, but in aqueous media dark amorphous products were formed, most probably by polymerisation involving the 5- and the 6-position. In order to investigate the possibility of ring fission in 2 : 3-diphenoquinones it is necessary to suppress this polymerisation by the introduction of blocking groups, and in the present paper the synthesis of 5 : 6-dichloro-2 : 3-dihydroxydiphenyl is described.

4 : 5-Dichloroveratrole (I) was prepared by chlorination of veratrole with an excess of sulphuryl chloride; even after prolonged refluxing, the dichloro-compound is the sole product. Peratoner and Ortoleva[2] have reported the preparation of this compound by use of exactly two equivalents of chlorinating agent.

In an attempt to prepare 4 : 5-dichloro-3-lithioveratrole, the compound (I) was treated in ethereal solution with one equivalent of *n*-butyl- and phenyl-lithium severally, and the resulting mixtures were carboxylated. No pure product was isolated from the former reaction, but phenyl-lithium afforded, probably, 4 : 5-diphenylveratrole (II). This

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[1] Part I, Bruce and Sutcliffe, *J.*, 1955, 4435. Throughout this paper, " diphenylbenzoquinone," wherever it occurs, should read " diphenoquinone."

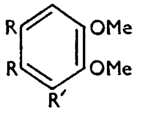
[2] Peratoner and Ortoleva, *Gazzetta*, 1898, **28**, I, 232.

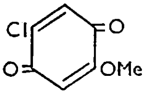
[3] Wittig and Fuhrmann, *Ber.*, 1940, **73**, 1197.

structure is supported by the ultraviolet absorption spectrum and by an analogous reaction of 3-chloroanisole, giving 3-methoxydiphenyl, described by Wittig and Fuhrmann.[3]

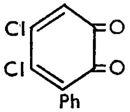
In view of these results, alternative routes to the dichlorodimethoxydiphenyl (III) were sought. Nitration of 4 : 5-dichloroveratrole afforded the 3-nitro-derivative, m. p. 111·5°, together with the quinone (IV); Cousin [4] prepared *x* : *y*-dichloro-3-nitroveratrole, m. p. 110—111°, by chlorination of 3-nitroveratrole, and the present work indicates that his product was the 5 : 6-dichloro-isomer. Reduction of 4 : 5-dichloro-3-nitroveratrole yielded the corresponding amine, which was converted *via* the diazonium chloride into 4 : 5-dichloro-3-iodoveratrole. The latter, with iodobenzene and copper in the Ullmann reaction, afforded both the required diphenyl (III) and 5 : 6 : 5′ : 6′-tetrachloro-2 : 3 : 2′ : 3′-tetramethoxydiphenyl.

(I) R = Cl, R′ = H
(II) R = Ph, R′ = H
(III) R = Cl, R′ = Ph





(IV)



(V)

5 : 6-Dichloro-2 : 3-dimethoxydiphenyl was more conveniently prepared by refluxing 2 : 3-dimethoxydiphenyl [1] with a large excess of sulphuryl chloride. On being demethylated it gave the corresponding dihydroxydiphenyl, which with silver oxide in ether afforded 5 : 6-dichloro-2 : 3-diphenoquinone (V). This quinone was also obtained by effecting the oxidation with sodium iodate in aqueous media, from which it separated in an anhydrous state.

5 : 6-Dichloro-2 : 3-diphenoquinone is more soluble in organic solvents than is the parent 2 : 3-diphenoquinone [1] and, as expected, it is also much more stable. Thus it remains unchanged for several hours at 20° in 2% aqueous sodium carbonate, sodium hydrogen carbonate, or disodium hydrogen phosphate; 2 : 3-diphenoquinone dissolved to a brown solution. At 100°, dichlorodiphenoquinone dissolves completely. Both quinones are rapidly decomposed by cold 2% aqueous sodium hydroxide.

EXPERIMENTAL

Reactions with organolithium compounds were carried out under oxygen-free nitrogen. Sulphuryl chloride was distilled through a short Dufton column immediately before use and had b. p. 68·5°. Solutions in organic solvents were dried with sodium sulphate. Absorption spectra were measured in dioxan in a Unicam S.P. 500 spectrophotometer. M. p.s are corrected.

4 : 5-*Dichloroveratrole* (I).—Sulphuryl chloride (284 c.c.) was added during 1 hr. to stirred veratrole (207 g.) at 15—20°, and stirring was continued at this temperature for 1 hr. and then at 75—80° for 2 hr. The excess of chloride was removed at 30 mm. and the residue, after being washed with a little cold light petroleum (b. p. 40—60°), was crystallised from ethanol, to give dichloroveratrole (249 g., 80%) as needles, m. p. 83·5° (Peratoner and Ortoleva [2] report m. p. 85·5—86·5°) (Found : Cl, 34·2. Calc. for $C_8H_8O_2Cl_2$: Cl, 34·3%).

4 : 5-*Diphenylveratrole* (II).—Phenyl-lithium, from bromobenzene (9 g.) and lithium (0·9 g.), in ether (35 c.c.) was stirred at 0° whilst 4 : 5-dichloroveratrole (8·3 g.) in ether (80 c.c.) was added during 30 min. After being stirred at 20° for 2½ hr. the brown suspension was added to solid carbon dioxide (75 g.), the mixture was decomposed with water, and the ethereal phase was separated, washed with water, and dried; acidification of the aqueous phase failed to yield a precipitate. Removal of the ether and distillation of the residue gave a fore-run of dichloroveratrole (1·1 g.) and then a yellow viscous oil, b. p. 180—210°/0·3 mm., from which, by trituration with cold light petroleum (40 c.c.; b. p. 60—80°), a solid (1·4 g.) was obtained. Crystallisation of this from ethanol gave 4 : 5-*diphenylveratrole* as rhombic plates, m. p. 147° (Found : C, 82·7; H, 6·1. $C_{20}H_{18}O_2$ requires C, 82·8; H, 6·2%). Light absorption : $\lambda_{max.}$ 238, 283 mμ (log ε 4·43, 4·09). 1 : 2-Diphenylbenzene has $\lambda_{max.}$ 232 mμ (log ε 4·44).

In an experiment with ethereal *n*-butyl-lithium, an acidic fraction was obtained, but no pure material could be isolated from it.

4 : 5-*Dichloro*-3-*nitroveratrole*.—Nitric acid (305 c.c., *d* 1·45) was cooled to 0° and added to

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[4] Cousin, *Compt. rend.*, 1902, **135**, 969; *Ann. Chim. Phys.*, 1903, **29**, 87.

stirred, freshly distilled, acetic anhydride (560 c.c.) at $\ngtr$5° (ice–salt). 4 : 5-Dichloroveratrole (166 g.) was added with stirring at 0—2° during 40 min., stirring was continued for 30 min., and the yellow suspension was poured on ice (8 kg.). After being kept overnight, the solid was collected, washed with water, and extracted at 20° with benzene (1·5 l.); sublimation of the insoluble material (26·5 g., 20%) at 180°/25 mm. and crystallisation of the sublimate from butan-1-ol afforded 2-chloro-5-methoxy-1 : 4-benzoquinone as bright yellow needles, m. p. 175·5° (lit.,[5] 172°, 172—173°, 173°) (Found : C, 48·8; H, 2·9; Cl, 20·4. Calc. for $C_7H_5O_3Cl$: C, 48·7; H, 2·9; Cl, 20·6%). Light absorption : $\lambda_{max.}$ 270, 370 mμ (log ε 4·21, 2·76). The benzene extract was washed with 10% aqueous sodium hydroxide, then with water, dried, and concentrated to 500 c.c., and the solution was chromatographed on alumina (200 × 45 mm.). Elution with benzene, removal of the solvent, and crystallisation of the residue from benzene–light petroleum (b. p. 60—80°) afforded the *nitro-compound* (94 g., 47%) as almost colourless needles, m. p. 111·5° (Found : C, 38·3; H, 3·0; N, 5·5; Cl, 28·2. $C_8H_7O_4NCl_2$ requires C, 38·1; H, 2·8; N, 5·6; Cl, 28·2%).

3-*Amino*-4 : 5-*dichloroveratrole*.—4 : 5-Dichloro-3-nitroveratrole (88 g.), granulated tin (100 g.), acetic acid (250 c.c.), concentrated hydrochloric acid (380 c.c.), and water (380 c.c.) were heated together under reflux until a vigorous reaction set in. This was moderated by water-cooling, and, after 10 min., the mixture was refluxed for 30 min., cooled, and basified below 20° with 40% aqueous sodium hydroxide. The suspension was extracted with benzene, the extract was washed with water and dried, and the solvent was removed. Distillation of the residue gave an oil (65 g., 84%), b. p. 102°/0·25 mm., which solidified and, on crystallisation from light petroleum (b. p. 60—80°), afforded the stable *amine* as needles, m. p. 79° (Found : C, 43·6; H, 4·2; N, 6·5; Cl, 32·5. $C_8H_9O_2NCl_2$ requires C, 43·2; H, 4·1; N, 6·3; Cl, 32·0%). The NN-*diacetate* forms prisms [from benzene–light petroleum (b. p. 60—80°)], m. p. 119·5° (Found : C, 47·3; H, 4·3; N, 4·8; Cl, 23·3; Ac, 27·5. $C_{12}H_{13}O_4NCl_2$ requires C, 47·1; H, 4·3; N, 4·6; Cl, 23·2; Ac, 28·1%). The β-*naphthol azo-derivative* forms orange needles [from light petroleum (b. p. 100—120°)], m. p. 149° after sintering at 145° (Found : C, 57·4; H, 3·8; N, 7·7; Cl, 18·7. $C_{18}H_{14}O_3N_2Cl_2$ requires C, 57·3; H, 3·7; N, 7·4; Cl, 18·8%).

4 : 5-*Dichloro*-3-*iodoveratrole*.—3-Amino-4 : 5-dichloroveratrole (11·1 g.) in concentrated hydrochloric acid (50 c.c.) and water (125 c.c.) was diazotised at 0—5° with 20% aqueous sodium nitrite, and to the orange solution was added potassium iodide (11 g.) in water (25 c.c.). The suspension was kept at 20° for 30 min., and then heated on the boiling-water bath for 1 hr.; a dense brown oil separated. The aqueous phase was decanted, boiling water (250 c.c.) was added to the residue, and the mixture was basified with 10% aqueous sodium hydroxide. After cooling, the solid was extracted with benzene, and the extract was washed successively with 5% aqueous sodium hydroxide, water, 5% hydrochloric acid, and water, and dried. Removal of the solvent and distillation of the residue gave an oil, b. p. 107°/0·04 mm., which solidified and afforded the *iodo-compound* (12·4 g., 74%) as needles, m. p. 82·5°, from ethanol (Found : C, 28·7; H, 2·1; AgHal., 156. $C_8H_7O_2Cl_2I$ requires C, 28·8; H, 2·1; AgHal., 157%).

5 : 6-*Dichloro*-2 : 3-*dimethoxydiphenyl* (III).—(*a*) 4 : 5-Dichloro-3-iodoveratrole (1·67 g.) and iodobenzene (2·5 g.) were stirred together at 225° whilst activated[6] copper bronze (4 g.) was added during 10 min. The temperature was kept for 15 min. at 225°, raised during 10 min. to 280°, kept for 20 min. at 280°, and was finally raised during 5 min. to 350°. The cooled mixture was repeatedly extracted with boiling light petroleum (b. p. 60—80°), the solvent was removed from the extract, and the residue was distilled to give : (1) a fore-run of iodobenzene; (2) a light yellow oil, b. p. 70—80°/0·05 mm., which solidified, and consisted mainly of diphenyl; (3) an oil, b. p. 115—120°/0·05 mm., which solidified and afforded *dichlorodimethoxydiphenyl* (0·27 g.) as rhombic plates, m. p. 89·5—90°, from light petroleum (b. p. 60—80°) (Found : C, 59·3; H, 4·0; Cl, 25·3. $C_{14}H_{12}O_2Cl_2$ requires C, 59·4; H, 4·2; Cl, 25·1%), light absorption : $\lambda_{max.}$ 292 mμ (log ε 3·36); (4) a yellow oil, b. p. 210°/0·02 mm., which solidified and was triturated with cold light petroleum (10 c.c., b. p. 40—60°); the insoluble solid (0·39 g.) was sublimed at 170°/0·03 mm. and the sublimate was crystallised from methanol, giving 5 : 6 : 5′ : 6′-*tetrachloro*-2 : 3 : 2′ : 3′-*tetramethoxydiphenyl* as prisms, m. p. 172—172·5° (Found : C, 46·6; H, 3·2; Cl, 34·4. $C_{16}H_{14}O_4Cl_4$ requires C, 46·6; H, 3·4; Cl, 34·5%). Light absorption : $\lambda_{max.}$ 294 mμ (log ε 3·76).

(*b*) 2 : 3-Dimethoxydiphenyl[1] (15·5 g.) was refluxed with sulphuryl chloride (135 c.c.) for 8 hr., the excess of chlorinating agent was removed, and the residue was dissolved in ether.

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[5] Asp and Lindberg, *Acta Chem. Scand.*, 1950, **4**, 60; Ioffe and Sukhina, *Zhur. obshchei Khim.*, 1953, **23**, 295, 299.

[6] Kleiderer and Adams, *J. Amer. Chem. Soc.*, 1933, **55**, 4219.

The solution was washed with 10% aqueous sodium hydroxide, then water, and dried, and the solvent was removed. Distillation gave an oil, b. p. 115—135°/0·04 mm., from which, by crystallisation from light petroleum (b. p. 40—60°), 5 : 6-dichloro-2 : 3-dimethoxydiphenyl (15·1 g., 76%) was obtained as rhombic plates, m. p. 90° undepressed on admixture with material prepared by method (*a*) (Found : C, 59·1; H, 4·1; Cl, 24·9%).

5 : 6-*Dichloro*-2 : 3-*dihydroxydiphenyl*.—5 : 6-Dichloro-2 : 3-dimethoxydiphenyl (4·2 g.) was treated in dry chlorobenzene (100 c.c.) with powdered anhydrous aluminium chloride (7 g.), then refluxed for 3 hr., cooled, and poured into ice-cold 15% hydrochloric acid (200 c.c.). The suspension was stirred for 30 min. and extracted with ether, and the extract was washed with water and dried. Removal of the solvent left a dark solid which was washed with light petroleum (b. p. 40—60°) and sublimed at 150°/0·05 mm., to give a colourless microcrystalline powder (3·25 g., 85%); recrystallisation from light petroleum (b. p. 80—100°) afforded the *dihydroxydiphenyl* as needles, m. p. 150·5° (Found : C, 56·6; H, 3·1; Cl, 27·4. $C_{12}H_8O_2Cl_2$ requires C, 56·5; H, 3·1; Cl, 27·9%). Light absorption : $\lambda_{\text{max.}}$ 292 mμ (log ε 3·36) {*diacetate*, rhombic plates [from light petroleum (b. p. 40—60°)], m. p. 76·5° (Found : C, 56·9; H, 3·7; Cl, 20·7; Ac, 25·6. $C_{16}H_{12}O_4Cl_2$ requires C, 56·6; H, 3·5; Cl, 20·9; Ac, 25·4%)}.

5 : 6-*Dichloro*-2 : 3-*diphenoquinone* (V).—(*a*) Silver oxide, prepared[7] from silver nitrate (1 g.), and anhydrous sodium sulphate (2 g.) were suspended in dry ether (25 c.c.), and a solution of 5 : 6-dichloro-2 : 3-dihydroxydiphenyl (0·26 g.) in ether (25 c.c.) was added all at once. After 15 minutes' shaking at 20° the mixture was filtered, the red filtrate was concentrated, at 0°/20 mm., to 10 c.c. and cooled to −75°; the *quinone* (0·15 g., 60%) separated as a red microcrystalline powder, m. p. 127—129° (Found : C, 56·7; H, 2·7; Cl, 27·5. $C_{12}H_6O_2Cl_2$ requires C, 56·9; H, 2·4; Cl, 28·1%). Light absorption : $\lambda_{\text{max.}}$ 415 mμ (log ε 3·34).

(*b*) To 5 : 6-dichloro-2 : 3-dihydroxydiphenyl (128 mg.) in ethanol (10 c.c.) and water (5 c.c.) at 20° was added, all at once, sodium iodate hydrate (220 mg.) in water–ethanol (10 c.c., 5 c.c.). After 1½ hours' stirring at 20° the precipitate was collected, washed with 50% aqueous ethanol, then water, and dried *in vacuo*. The quinone (94 mg., 75%) was obtained as an orange-brown amorphous powder, m. p. 111—117°. Light absorption : $\lambda_{\text{max.}}$ 233, 395, 408 mμ (log ε 4·22, 3·35, 3·36). The mother-liquors, after dilution with water (20 c.c.), gradually deposited deep red platelets (9 mg.), m. p. 127—129° undepressed on admixture with the quinone prepared by method (*a*).

(*c*) The purest specimen of the quinone was obtained by oxidation of dichlorodihydroxydiphenyl (128 mg.) in dioxan (6·5 c.c.) and water (1·5 c.c.) with sodium iodate (55 mg.) in water (2 c.c.) at 20°. After 1 hour's stirring water (10 c.c.) was added, stirring was continued for 30 min., and the mixture was filtered from crude dichlorodiphenoquinone. The filtrate was diluted with water (5 c.c.) and set aside at 20° for several hours; the quinone (12 mg.) separated as deep red platelets with a golden reflex, m. p. 136—137° after sintering at 131°. Light absorption $\lambda_{\text{max.}}$ 224, 415 mμ (log ε 4·13, 3·38).

One of us (J. M. B.) thanks the International Wool Secretariat for financial assistance.

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[*Received, May* 22*nd*, 1956.]

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[7] Willstätter and Müller, *Ber.*, 1908, **41**, 2581.