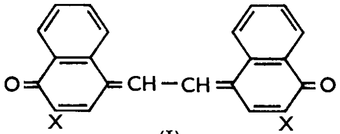
90. *Derivatives of Stilbenequinone.*

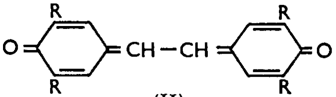
By WILLIAM BRADLEY and JOHN D. SANDERS.

The structures assigned to the product obtained by heating 4-methyl-1-naphthol with azobenzene [1,2-di-(3-anilino-1,4-dihydro-4-oxo-1-naphthylidene)ethane] and to the 3-hydroxy-analogue prepared from it by the action of nitric acid have been confirmed. The mechanism of the formation of the 3-anilino-derivative from 4-methyl-1-naphthol and azobenzene has been studied. Several new derivatives of stilbenequinone have been prepared and their reactions with aniline–sodamide, sodium methoxide, acetyl chloride, sulphuric acid, aluminium chloride, and other reagents have been studied.

ON being heated with azobenzene 4-methyl-1-naphthol forms a green quinone to which structure (I; X = NHPh) was assigned on the grounds of composition, reduction to a tetrahydro-derivative, and hydrolysis to a red dihydroxy-analogue (I; X = OH) which was also prepared by the action of potassium hydroxide on 4-methyl-1,2-naphthaquinone.[1] Further work has shown that the dihydroxy-compound results also on keeping or heating 4-methyl-1,2-naphthaquinone, either alone or with benzaldehyde, and by keeping it with alcoholic potassium hydrogen carbonate. The dianilino-compound (I; X = NHPh) was also formed by the action of nitrosobenzene on 4-methyl-1-naphthol, thus confirming the structure assigned. In addition, the dihydroxy-compound (I; X = OH) resulted from the action of aqueous-alcoholic sodium hydroxide on 4-di(ethoxycarbonyl)methyl-1,2-naphthaquinone, or on heating 4-bromomethyl-1,2-naphthaquinone; this confirms the participation of the 4-substituent [methyl, bromomethyl, or di(ethoxycarbonyl)-methyl] in the formation of the end product (I; X = OH).



(I)



(II)

The structures (I; X = NHPh and OH) having been established, a study was made of some related simpler stilbenequinone derivatives (II). Most of these were readily obtained by the action of silver oxide on 2,6-derivatives of *p*-cresol,[2] as orange or red crystalline compounds amongst which the 3,5,3′,5′-tetra-t-butyl derivative (II; R = Bu^t) was the most interesting. It formed a violet disulphate, $C_{30}H_{42}O_2,2H_2SO_4$, and a paramagnetic green hemisulphate, $C_{30}H_{42}O_2,0{\cdot}5H_2SO_4$. The structurally related dianthrone

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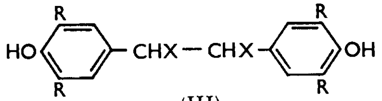
[1] Bradley and Watkinson, *J.*, 1956, 319.

[2] Porter and Thurber, *J. Amer. Chem. Soc.*, 1921, **43**, 1194; Goldschmidt and Bernard, *Ber.*, 1923, **56**, 1963.

also forms a salt with diradical character [3] but, whilst dianthrone and its halogen derivatives pass into diradical forms on being heated,[4] the same behaviour was not observed with any of the simple 3,5,3′,5′-tetrasubstituted stilbenequinones examined. Anhydrous aluminium chloride forms a violet salt with 3,5,3′,5′-tetra-t-butylstilbenequinone but there



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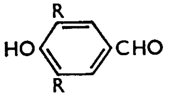
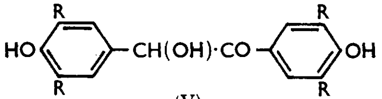


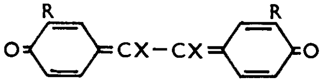
(IV)

was no evidence of rearrangement after 3 weeks at the room temperature in nitrobenzene. In contrast, even after 3 days 2,6-di-t-butyl-*p*-benzoquinone was rearranged in part into the 2,5-derivative. Hydrogen iodide reduced 3,5,3′,5′-tetra-t-butylstilbenequinone to the quinol, but reaction with hydrogen bromide formed αβ-dibromo-4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylbibenzyl (III; R = Bu^t, X = Br).[5] On being heated with aniline, then cooled, acidified, and distilled in steam, 3,5,3′,5′-tetra-t-butylstilbenequinone gave 4-hydroxy-3,5-di-t-butylbenzaldehyde (IV; R = Bu^t). In this reaction it is probable that αβ-dianilino-4,4′-dihydroxy-3,5,3′,5′-di-t-butylbibenzyl (III; R = Bu^t, X = NHPh) is formed at the first stage (Zincke and Fries [6] have described compounds of this type) and that this undergoes scission after being dehydrogenated by the parent quinone. The aldehyde was characterised as the 2,4-dinitrophenylhydrazone and synthesised from 4-methyl-2,6-di-t-butylphenol by reaction with *N*-bromosuccinimide and subsequent hydrolysis. On being heated with phenylhydrazine the quinone was in part reduced to the quinol and in part decomposed to form the aldehyde already described.

3,5,3′,5′-Tetra-t-butylstilbenequinone reacted easily with sodium methoxide at the room temperature under nitrogen. The first product isolated (4-hydroxy-α-methoxy-3,5-di-t-butylbenzyl 4-hydroxy-3,5-di-t-butylphenyl ketone) had m. p. 119° and formed



(V)



(VI)

a mono-2,4-dinitrophenylhydrazone. Aeration of this in sodium methoxide solution gave the benzoin (V; R = Bu^t), which gave an osazone with 2,4-dinitrophenylhydrazine and 3,5,3′,5′-tetra-t-butylbenzil on being oxidised with chromium trioxide, from which the same osazone was prepared and also a quinoxaline derivative. The same benzoin derivative (V) was formed when the quinone was refluxed under nitrogen with alcoholic sodium hydroxide and then aerated.

On being heated with methanol 3,5,3′,5′-tetra-t-butylstilbenequinone gave αβ-dimethoxy-3,5,3′,5′-tetra-t-butylstilbenequinone (VI; R = Bu^t, X = OMe), the expected simple adduct [5] of the quinone (1 mol.) and methanol (2 mol.) having been dehydrogenated.

Thiele acetylation [6] during 36 hours gave a tetra-acetyl derivative (VII; R = Bu^t, X = OAc), in which only two of the *O*-acetyl groups were readily hydrolysed. Short treatment with acetic anhydride and sulphuric acid gave a diacetyl derivative which was converted into the tetra-acetate (VII; R = Bu^t, X = OAc) on further treatment. The diacetyl derivative was not hydrolysed by hot 20% sulphuric acid and it appears probable that it has structure (VIII; R = Bu^t). With acetic anhydride and sodium acetate a brown product resulted, changed into αβ-diacetoxy-3,5,3′,5′-tetra-t-butylstilbenequinone (VI; X = OAc) on treatment with chromium trioxide in dilute acetic acid. Refluxing

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[3] Hirshon, Gardner, and Fraenkel, *J. Amer. Chem. Soc.*, 1953, **75**, 4115.

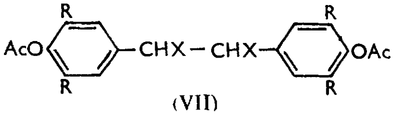
[4] Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419; Thielacker, Kortüm, and Friedheim, *Chem. Ber.*, 1950, **83**, 508.

[5] Zincke and Münch, *Annalen*, 1904, **335**, 168.

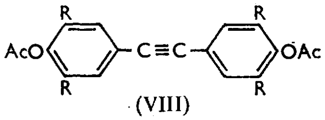
[6] Zincke and Fries, *Annalen*, 1902, **325**, 46.

with acetic acid containing sodium acetate gave the same derivative. Acetyl chloride, used alone, reduced 3,5,3′,5′-tetra-t-butylstilbenequinone to the quinol but after a small proportion of acetic acid had been added αβ-dichloro-4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylbibenzyl (III; R = Bu^t, X = Cl) was formed.

Other 3,5,3′,5′-tetrasubstituted stilbenequinones showed similar properties, so far as they were studied, except in the following respects.



(VII)



(VIII)

Whilst most of the substituted stilbenequinones were red, derivatives containing allyl groups as 3,3′-substituents were orange: these were also less stable towards storage. Redox potentials in alcohol could not be determined with accuracy but it was observed that the values for the 3,5,3′,5′-tetrabromo, 3,5,3′,5′-tetramethyl, and 3,5,3′,5′-tetra-t-butyl derivatives formed a diminishing sequence. With acetyl chloride, the 3,5,3′,5′-tetramethyl derivative gave 4,4′-diacetoxy-αβ-dichloro-3,5,3′,5′-tetramethylbibenzyl (VII; R = Me, X = Cl), analogous to the product obtained by Zincke and Münch[5] from 3,5,3′,5′-tetrabromostilbenequinone. In the reaction with aniline 3,5,3′,5′-tetramethylstilbenequinone gave less of the aldehyde (IV; R = Me), but reduction of the quinone occurred accompanied by oxidation of the aniline to nitrobenzene. With methanol or sodium methoxide 3,5,3′,5′-tetramethylstilbenequinone gave 4,4′-dihydroxy-αβ-dimethoxy-3,5,3′,5′-tetramethylbibenzyl (III; R = Me, X = OMe).

EXPERIMENTAL

1,2-*Di*-(1,4-*dihydro*-3-*methyl*-4-*oxo*-1-*naphthylidene*)*ethane*.—A solution of 1,4-dimethyl-1-naphthol (2·0 g.) in dry benzene (100 ml.) was shaken for 5 hr. at 50° with dry, freshly prepared silver oxide (5 g.) and anhydrous sodium sulphate (7·5 g.). The resulting suspension was filtered, the residue was washed with benzene, and the combined washings and filtrate were concentrated, then chromatographed on alumina. Two bands were formed. The less mobile was orange and on being eluted with benzene afforded 1,2-*di*-(1,4-*dihydro*-3-*methyl*-4-*oxo*-1-*naphthylidene*)*ethane* as orange needles (0·24 g.), m. p. 265° (decomp.) (Found: C, 85·2; H, 5·2. $C_{24}H_{18}O_2$ requires C, 85·2; H, 5·3%).

The same procedure was employed in the preparation of several other derivatives of stilbenequinone (see Table).

Deriv. of phenol oxidised	Wt. (g.)	Ag_2O used (g.)	Deriv. of stilbenequinone formed	Yield (g.)	Found (%)		Formula	Required (%)		M. p.
					C	H		C	H	
2-Allyl-4,6-dimethyl	5·8	30	3,3′-Diallyl-5,5′-dimethyl	0·6	82·5	7·0	$C_{22}H_{22}O_2$	83·0	6·9	189—190°
2,4-Dimethyl-6-propyl	4·0	20	3,3′-Dimethyl-5,5′-dipropyl	0·5	82·1	7·8	$C_{22}H_{26}O_2$	82·0	8·1	120
2 Allyl-3,4,6-trimethyl	4·9	18	5,5′-Diallyl-3,6,3′,6′-tetramethyl	1·0	82·9	7·1	$C_{24}H_{26}O_2$	83·3	7·1	138—139
2,4,5-Trimethyl-6-propyl	5·5	20	3,6,3′,6′-Tetramethyl-5,5′-dipropyl	0·96	82·4	8·6	$C_{24}H_{30}O_2$	82·3	8·6	188—189

Solutions of 3,3′-diallyl-5,5′-dimethylstilbenequinone were orange; on being warmed they became almost colourless.

1,2-*Di*-(1,4-*dihydro*-3-*hydroxy*-4-*oxo*-1-*naphthylidene*)*ethane*.—(a) 4-Methyl-1,2-naphthaquinone, when kept in a closed bottle for 14 weeks, acquired a red-violet lustre. Extraction with benzene and then with acetone left a dark red solid which on being crystallised from 1,2,4-trichlorobenzene afforded maroon crystals, m. p. 345°, identical with the derivative prepared from 1,2-di-(3-anilino-1,4-dihydro-4-oxo-1-naphthylidene)ethane by the action of nitric acid. The same derivative resulted when 4-methyl-1,2-naphthaquinone was heated on the steam bath for 5 hr., or when 4-methyl-1,2-naphthaquinone (0·4 g.) was dissolved in cold ethanol (150 ml.) and shaken overnight with dry potassium hydrogen carbonate (2 g.). The dark brown precipitate (0·22 g.) which was formed in this preparation was collected and acidified, and the maroon product was crystallised from 1,2,4-trichlorobenzene to give the above dihydroxy-derivative, m. p. 345°. The same dihydroxy-derivative was formed together with sodium benzoate when 5N-sodium hydroxide (0·5 ml.) was added to 4-methyl-1,2-naphthaquinone (0·5 g.) and benzaldehyde (3 ml.) in 95% alcohol (10 ml.) and the reactants were shaken for 24 hr.

(*b*) 4-Di(ethoxycarbonyl)methyl-1,2-naphthaquinone (0·5 g.) was refluxed for 24 hr. with sodium hydroxide (2 g.) in 50% aqueous alcohol (30 ml.). A blue-green solution was formed. On the addition of dilute sulphuric acid a maroon precipitate was formed, and this on being crystallised from 1,2,4-trichlorobenzene afforded 1,2-di-(1,4-dihydro-3-hydroxy-4-oxo-1-naphthylidene)ethane, m. p. 345°, identical with the products described above.

(*c*) 4-*Bromomethyl*-1,2-*naphthaquinone* was prepared by refluxing 4-methyl-1,2-naphthaquinone (0·5 g.) with *N*-bromosuccinimide (1·0 g.) in chloroform (150 ml.) for 2 hr. A brown precipitate was formed. This was dissolved in benzene and the filtered solution was allowed to evaporate. Red-brown crystals, m. p. >360° (Found: C, 52·6; H, 3·0; Br, 31·7. $C_{11}H_7BrO_2$ requires C, 52·6; H, 2·8; Br, 31·9%), were obtained. On being heated in benzene solution 4-bromomethyl-1,2-naphthaquinone readily gave a crystalline precipitate of 1,2-di-(1,4-dihydro-3-hydroxy-4-oxo-1-naphthylidene)ethane, m. p. 345°. The same derivative was formed with ease when the bromomethyl compound was warmed with dilute sodium hydroxide or sodium acetate.

1,2-*Di*-(3-*anilino*-1,4-*dihydro*-4-*oxo*-1-*naphthylidene*)*ethane*.—This derivative (Found: C, 82·8; H, 4·7; N, 5·45. Calc. for $C_{34}H_{24}N_2O_2$: C, 82·9; H, 4·9; N, 5·7%) was prepared by Bradley and Watkinson's method [1] and also by the following means.

(*a*) 4-Methyl-1,2-naphthaquinone (0·2 g.) and aniline (0·17 ml.) were dissolved in dry ether (117 ml.), and the brown solution was allowed to evaporate at the room temperature. The residue was chromatographed in benzene on alumina. Aniline passed through the column first, then 2-anilino-1,4-naphthaquinone 4-anil, m. p. and mixed m. p. 182—183°. Following were a brown band and a green zone; when the last was eluted with benzene 1,2-di-(3-anilino-1,4-dihydro-4-oxo-1-naphthylidene)ethane was obtained, identical with the compound prepared from 4-methyl-1-naphthol and azobenzene.

(*b*) 4-Methyl-1-naphthol (6 g.), nitrosobenzene (4 g.), and anhydrous sodium carbonate (4·5 g.) in acetone (45 ml.) were shaken for 15 min. at 0°. Benzene was then added to the red-brown suspension and this was filtered and the filtrate chromatographed on alumina. The most mobile band was orange: elution with benzene gave 2-anilino-1,4-naphthaquinone 4-anil, m. p. 180—182°. A second orange zone followed, then a green band and this was eluted with benzene. The eluate rapidly afforded a precipitate which on being crystallised from 1,2,4-trichlorobenzene gave 1,2-di-(3-anilino-1,4-dihydro-4-oxo-1-naphthylidene)ethane.

Properties of Stilbenequinone Derivatives.—(a) On being heated in acetophenone, 1,2,4-trichlorobenzene, 2-methylnaphthalene, or anthracene 3,5,3′,5′-tetra-t-butylstilbenequinone [7] showed no change in colour indicative of thermochromism.

(b) *Salts*. The same derivative (1 g.) was shaken for 30 min. with 98% "AnalaR" sulphuric acid (50 ml.). The suspension was filtered and the filtrate added to ice (400 g.). The dark green precipitate which was formed was collected, washed with water, and dried (0·5 g.; m. p. 185°) (Found: C, 74·7; H, 9·0; S, 3·3. $C_{30}H_{42}O_2,0{\cdot}5H_2SO_4$ requires C, 74·5; H, 8·9; S, 3·3%). The *hemisulphate* was dissociated to tetra-t-butylstilbenequinone on contact with hot water, alcohol, acetone, acetic acid, or aqueous sodium carbonate.

On being shaken with an excess of concentrated sulphuric acid in acetic acid the same quinone gave a crystalline violet *disulphate*, m. p. >360° (Found: C, 56·9; H, 7·2; S, 10·3. $C_{30}H_{42}O_2,2H_2SO_4$ requires C, 57·2; H, 7·3; S, 10·2%).

3,5,3′,5′-Tetra-t-butylstilbenequinone (0·5 g.) was recovered unaltered after being kept for 3 weeks with anhydrous aluminium chloride (6·9 g.) in dry nitrobenzene (50 g.), and the violet solution which was formed was added to dilute hydrochloric acid. Addition of titanium tetrachloride to a solution of the quinone in nitrobenzene gave a blue colour; with stannic chloride the hue was dark green.

(c) *Reaction with hydriodic and hydrobromic acid.* 3,5,3′,5′-Tetra-t-butylstilbenequinone

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[7] Cook, *J. Org. Chem.*, 1953, **18**, 261.

(0·4 g.) was dissolved in glacial acetic acid (20 ml.), and a solution of hydriodic acid (*d* 1·9; 25 ml.) in acetic acid (25 ml.) was added. The dark red solution was shaken at the room temperature for 30 min. and then added to water (100 ml.). The pale yellow precipitate had m. p. 234—235° after crystallisation from acetic acid and was identified as 4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylstilbene. Similar treatment of 3,5,3′,5′-tetramethylstilbenequinone[2] gave the analogous 4,4′-dihydroxy-3,5,3′,5′-tetramethylstilbene.

Dry hydrogen bromide was passed into a solution of 3,5,3′,5′-tetra-t-butylstilbenequinone (0·1 g.) in benzene (50 ml.), affording after 15 min. a colourless precipitate (0·12 g.) of αβ-dibromo-4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylbibenzyl, m. p. 159°. 3,5,3′,5′-Tetramethylstilbenequinone gave analogously αβ-dibromo-4,4′-dihydroxy-3,5,3′,5′-tetramethylbibenzyl, m. p. 176°.

(d) 3,5,3′,5′-*Tetra-t-butylstilbenequinhydrone.* 4,4′-Dihydroxy-3,5,3′,5′-tetra-t-butylstilbene (0·1 g.) and 3,5,3′,5′-tetra-t-butylstilbenequinone (0·1 g.) were dissolved in 95% alcohol, and the solution was concentrated to 15 ml. On being cooled in ice, green-brown needles, m. p. 245—246° (Found: C, 82·8; H, 9·9. $C_{60}H_{86}O_4$ requires C, 82·8; H, 9·9%), of the *quinhydrone* separated.

(e) αβ-*Diacetoxy*-3,5,3′,5′-*tetra-t-butylstilbenequinone.* Sodium acetate (0·4 g.) and tetra-t-butylstilbenequinone (0·5 g.) were refluxed in acetic anhydride (50 ml.) for 7 days. The brown solution was added to water (150 ml.) and after the excess of acetic anhydride had been hydrolysed the light brown precipitate (0·072 g.) was collected and a portion (0·04 g.) was shaken for 12 hr. with chromium trioxide (0·5 g.) in water (3 ml.) and acetic acid (14 ml.). Addition to water gave αβ-*diacetoxy*-3,5,3′,5′-*tetra-t-butylstilbenequinone* as orange needles, m. p. 136—138° (Found: C, 74·0; H, 6·5. $C_{34}H_{46}O_6$ requires C, 74·2; H, 6·6%). The same compound resulted when the quinone (0·4 g.) was refluxed for 7 days with sodium acetate (0·4 g.) in glacial acetic acid (50 ml.).

(f) αβ-*Dichloro*-4,4′-*dihydroxy*-3,5,3′,5′-*tetra-t-butylbibenzyl and* 4,4′-*diacetoxy*-αβ-*dichloro*-3,5,3′,5′-*tetramethylbibenzyl.* (1) A solution of 3,5,3′,5′-tetra-t-butylstilbenequinone (0·4 g.) in "AnalaR" acetyl chloride (10 ml.) was shaken at the room temperature for 30 min. On the addition of acetic acid (2 ml.) to the resulting brown solution a crystalline precipitate of (0·09 g.) αβ-*dichloro*-4,4′-*dihydroxy*-3,5,3′,5′-*tetra-t-butylbibenzyl* was formed (Found: C, 67·5; H, 8·5; Cl, 13·9. $C_{30}H_{44}Cl_2O_2$ requires C, 67·8; H, 8·7; Cl, 14·0%). In contact with water the bibenzyl derivative quickly lost hydrogen chloride with formation of the original quinone.

(2) In a parallel experiment 3,5,3′,5′-tetramethylstilbenequinone (0·5 g.) and acetyl chloride (10 ml.) gave 0·11 g. of 4,4′-*diacetoxy*-αβ-*dichloro*-3,5,3′,5′-*tetramethylbibenzyl* (Found: C, 62·0; H, 5·7; Cl, 16·9. $C_{22}H_{24}Cl_2O_4$ requires C, 62·4; H, 5·7; Cl, 16·8%).

(g) *Reductive acetylation.* 3,5,3′,5′-Tetra-t-butylstilbenequinone (0·25 g.) with zinc (0·8 g.) and refluxing acetic anhydride (50 ml.) gave, after addition of the resulting suspension to water (200 ml.), 4,4′-dihydroxy-3,5,3′,5′-tetra-t-butylstilbene, m. p. 236° (from acetic acid).

Similar treatment of 3,5,3′,5′-tetramethylstilbenequinone (0·45 g.) gave 4,4′-diacetoxy-3,5,3′,5′-tetramethylstilbene, m. p. 237—238° (0·48 g.).

(h) *Thiele acetylation.* 3,5,3′,5′-Tetramethylstilbenequinone (0·8 g.) was shaken for 8 hr. at the room temperature with acetic anhydride (50 ml.) and sulphuric acid (1 ml.). The red quinone dissolved slowly, forming a pale yellow solution. On addition to water a precipitate was formed and this crystallised from acetic acid as colourless needles of α,β,4,4′-tetra-acetoxy-3,5,3′,5′-*tetramethylstilbene*, m. p. 187—188° (Found: C, 66·3; H, 6·4; Ac, 36·2. $C_{26}H_{30}O_8$ requires C, 66·4; H, 6·4; 4Ac, 36·6%).

Analogous treatment of 3,5,3′,5′-tetra-t-butylstilbenequinone (1 g.) with acetic anhydride (20 ml.) and concentrated sulphuric acid (0·5 ml.) gave first a violet and after 30 min. a brown solution. Addition to water after 36 hr. and hydrolysis of the excess of acetic anhydride afforded a colourless precipitate (1·85 g.) which on crystallisation from acetic acid gave α,β,4,4′-*tetra-acetoxy*-3,5,3′,5′-*tetra-t-butylbibenzyl*, m. p. 244—245° (Found: C, 71·2; H, 8·5. $C_{38}H_{54}O_8$ requires C, 71·5; H, 8·5%).

When the above stilbenequinone (7 g.) was shaken with acetic anhydride (125 ml.) and sulphuric acid (2 ml.) for 6 hr. and the product was isolated as in the preceding experiment, it afforded a colourless precipitate (4 g.). Crystallisation from alcohol and then from acetic acid gave 4,4′-*diacetoxy*-3,5,3′,5′-*tetra-t-butyltolane*, m. p. 160° (Found: C, 78·7; H, 8·9. $C_{34}H_{46}O_4$ requires C, 78·8; H, 8·9%).

(i) *Reaction with aniline and phenylhydrazine.* 3,5,3′,5′-Tetra-t-butylstilbenequinone

(1·5 g.) was refluxed with " AnalaR " aniline (30 ml.) for 15 min. The pale yellow solution was cooled, mixed with an excess of dilute sulphuric acid, and distilled in steam. Pale yellow crystals were formed in the condenser and these were collected and crystallised from alcohol as needles, m. p. 188—189° (Found: C, 74·6; H, 9·1. $C_{15}H_{22}O_2$ requires C, 74·4; H, 9·4%), consisting of 4-*hydroxy*-3,5-*di-t-butylbenzaldehyde*. The 2,4-*dinitrophenylhydrazone*, crystallised from acetic acid, had m. p. 235—236° (Found: C, 60·4; H, 6·7; N, 13·2. $C_{21}H_{26}N_4O_5$ requires C, 60·8; H, 6·3; N, 13·6%). The non-volatile part of the steam-distilled suspension gave 4,4'-dihydroxy-3,5,3',5'-tetra-t-butylstilbene (0·8 g.; m. p. 235°).

(j) *Reaction with aniline and sodamide*. Sodamide (2·5 g.) was heated with aniline (25 ml.) until ammonia evolution ceased and then the solution was cooled. 3,5,3',5'-Tetra-t-butylstilbenequinone (2 g.) was added and the solution stirred in a current of nitrogen at the room temperature for 2 days. It was then added to water, and the suspension which was formed was steam distilled. The distillate contained aniline and azobenzene. The non-volatile portion was filtered and the filtrate extracted with benzene; the solution so obtained gave 4-hydroxy-3,5-di-t-butylbenzaldehyde (0·01 g.; m. p. 188°). The water-insoluble part (1·05 g.) was dissolved in benzene and chromatographed on alumina, giving the unchanged quinone, the related quinhydrone, and a yellow band containing 4-hydroxy-3,5-di-t-butylbenzaldehyde (0·015 g.), m. p. 185—186° (from alcohol).

(k) *Reaction with sodium methoxide*. 3,5,3',5'-Tetra-t-butylstilbenequinone (1 g.) was shaken in a stoppered flask with 40 ml. of sodium methoxide solution, prepared from sodium (75 g.) and methanol (1 l.), air having been displaced by nitrogen. After 15 min. the quinone had dissolved, forming a violet solution, and this was kept for 36 hr. In contact with air and water this afforded a colourless precipitate which crystallised from 50% alcohol as colourless needles, m. p. 119° (Found: C, 77·4; H, 10·0; MeO, 5·9. $C_{31}H_{46}O_4$ requires C, 77·2; H, 9·6; MeO, 6·4%). This derivative formed a 2,4-*dinitrophenylhydrazone*, m. p. 180—182° (Found: C, 66·9; H, 7·6; N, 8·8. $C_{37}H_{50}N_4O_7$ requires C, 67·1; H, 7·6; N, 8·5%). The compound, m. p. 119°, was insoluble in dilute sodium hydroxide; it was identical with 4-*hydroxy*-α-*methoxy*-3,5-*di-t-butylbenzyl* 4-*hydroxy*-3,5-*di-t-butylphenyl ketone* prepared as described below. Further aeration of the derivative, m. p. 119° (0·05 g.), as a suspension in the sodium methoxide solution (10 ml.) for 30 min. afforded a blue solution. This was added to water, the suspension was filtered, and the filtrate acidified with hydrochloric acid. A pale yellow precipitate was formed and this crystallised from benzene–light petroleum (b. p. 40—60°) as colourless needles, m. p. 168—170°, of 4,4'-*dihydroxy*-3,5,3',5'-*tetra-t-butylbenzoin* (Found: C, 77·0, 77·1; H, 9·5, 9·7. $C_{30}H_{44}O_4$ requires C, 76·9; H, 9·5%).

The same benzoin derivative, m. p. 168—170°, was formed when the quinone (1 g.) was refluxed under nitrogen for 4 hr. with a solution of sodium hydroxide (4 g.) in ethanol (40 ml.).

The *O*-methyl compound, m. p. 119°, was also obtained under the following conditions. 3,5,3',5'-Tetra-t-butylstilbenequinone (2·0 g.) was refluxed under nitrogen with the sodium methoxide solution (50 ml.). The quinone dissolved, forming a violet solution which became green after 45 min. After 1 hr. a portion (10 ml.) of the solution was separated and aerated. A pale greenish-blue solution was formed and this was added to water. The colourless, flocculent precipitate which was obtained crystallised from alcohol as colourless needles, m. p. 119—120°, identical with the material of the same m. p. described above.

The compound, m. p. 168—170° (0·03 g.), was mixed with chromium trioxide (0·05 g.) in acetic acid (10 ml.), and the solution so obtained was added to water. A precipitate (0·03 g.) was formed that crystallised from alcohol as needles, m. p. 54° (Found: C, 77·3; H, 9·0. $C_{30}H_{42}O_4$ requires C, 77·1; H, 9·0%), consisting of 4,4'-*dihydroxy*-3,5,3',5'-*tetra-t-butylbenzil*. This, with *o*-phenylenediamine in acetic acid, formed 2,3-*di*-(4-*hydroxy*-3,5-*di-t-butylphenyl*)-*quinoxaline*, m. p. 296—298° (Found: C, 80·1; H, 8·6. $C_{36}H_{46}N_2O_2$ requires C, 80·3; H, 8·6%), and it gave a *bis*-2,4-*dinitrophenylhydrazone*, m. p. 195—196° (Found: C, 60·7; H, 6·2; N, 13·8. $C_{42}H_{50}N_8O_{10}$ requires C, 61·0; H, 6·1; N, 13·6%), which was also prepared directly from the benzoin derivative.

3,5,3',5'-Tetra-t-butylstilbenequinone (1 g.) and methanol (15 ml.) were heated together for 60 hr. at 100° in a sealed tube. The colourless product was cooled, then poured into a beaker; it rapidly became yellow and after 5 min. brown. This solution was added to cold water; the brown solid which was formed crystallised from 95% alcohol, giving orange needles of αβ-*dimethoxy*-3,5,3',5'-*tetra-t-butylstilbenequinone*, m. p. 140—141° (Found: C, 77·4; H, 9·1. $C_{32}H_{46}O_4$ requires C, 77·7; H, 9·3%).

(l) 3,5,3′,5′-Tetramethylstilbenequinone (0·8 g.) and 50 ml. of the sodium methoxide solution were shaken in nitrogen at the room temperature. A pale brown solution was formed in a few minutes and after 30 min. it was added to water and acidified. A colourless precipitate was formed (0·69 g.) and this crystallised from dilute sodium hydroxide as plates, m. p. 160—161° (Found: C, 73·1, 73·6; N, 7·8, 7·8. $C_{20}H_{26}O_4$ requires C, 73·2; H, 7·9%), of 4,4′-*di-hydroxy-αβ-dimethoxy*-3,5,3′,5′-*tetramethylbibenzyl.* It did not react with 2,4-dinitrophenylhydrazine. The same compound, m. p. 159—161°, was formed when the quinone (0·5 g.) was heated in a sealed tube with dry methanol (15 ml.) for 62 hr. at 150° and the precipitate which was formed on addition to water was crystallised from alcohol.

Conversion of 2,6- *into* 2,5-*Di-t-butylbenzoquinone.*—2,6-Di-t-butylbenzoquinone (2·5 g.) was dissolved in dry nitrobenzene (40 ml.) and shaken in a closed bottle with a M-solution (15 ml.) of anhydrous aluminium chloride in nitrobenzene. After 3 days ligroin (b. p. 60—80°) and dilute hydrochloric acid were added and the separated organic layer was washed with water and then chromatographed on alumina. Several bands were formed. The least mobile was separated, and the adsorbed material eluted and again chromatographed. Two bands were formed. The more mobile afforded unchanged 2,6-di-t-butylbenzoquinone; the less mobile gave 0·12 g. of the 2,5-isomer as yellow needles, m. p. 143—146°, not depressed by authentic material.

Preparation of 4-*Hydroxy*-3,5-*di-t-butylbenzaldehyde.*—4-Methyl-2,6-di-t-butyl-4-methylphenol (22 g.), and *N*-bromosuccinimide (40 g.) were refluxed for 90 min. in benzene (500 ml.). The solvent was then evaporated and the residue mixed with a solution of sodium hydroxide (5 g.) in alcohol (60 ml.) and water (30 ml.). On steam distillation, alcohol and benzene were removed and 2,6-di-t-butylbenzaldehyde (4·6 g.) was formed in the condenser. Crystallisation from benzene gave the pure derivative, m. p. 188—189°, identical with that already described.

The same 4-hydroxy-3,5-di-t-butylbenzaldehyde was formed when the tetra-t-butylquinone (1·4 g.) was refluxed for 5 min. with phenylhydrazine (2 ml.), and the product was acidified and steam-distilled. The main product (0·9 g.) was the dihydroxystilbene derivative.

Similar heating of 3,5,3′,5′-tetramethylstilbenequinone (1·5 g.) and aniline (30 ml.) for 10 min. gave an almost colourless solution. This was cooled and neutralised with 15% sulphuric acid, and the suspension which was formed was distilled in steam. The distillate was extracted with benzene and the extract evaporated to small bulk. Needles of 4-*hydroxy*-3,5-*dimethylbenzaldehyde*, m. p. 115—116° (Found: C, 71·9; H, 6·9. $C_9H_{10}O_2$ requires C, 72·0; H, 6·7%) (0·02 g.), and 4,4′-dihydroxy-3,5,3′,5′-tetramethylstilbene (0·7 g.), m. p. 240°, were separated, and a liquid residue of nitrobenzene (1 ml.) was obtained. The nitrobenzene dissolved in dilute hydrochloric acid on the addition of zinc; the aniline was separated by addition of an excess of sodium carbonate and extraction with ether; evaporation of the extract afforded a residue, and this was shaken with an aqueous solution of potassium 1,2-naphthaquinone-4-sulphonate; a red precipitate, m. p. 250°, was formed identified by mixed m. p. as 4-anilino-1,2-naphthaquinone.

The aldehyde, m. p. 115—116°, afforded a red 2,4-*dinitrophenylhydrazone*, m. p. 281—283° (Found: C, 54·3; H, 4·2; N, 16·5. $C_{15}H_{14}N_4O_5$ requires C, 54·6; H, 4·2; N, 16·9%.

Neither of the two quinones was changed in hot dimethylaniline.

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