Thiele–Winter Acetoxylation of Quinones. Part V.[1] Structures of the Major Triacetate Product from 5-Methyl-3-t-butyl-1,2-benzoquinone and of the By-product from 2-Methyl-6-t-butyl-1,4-benzoquinone

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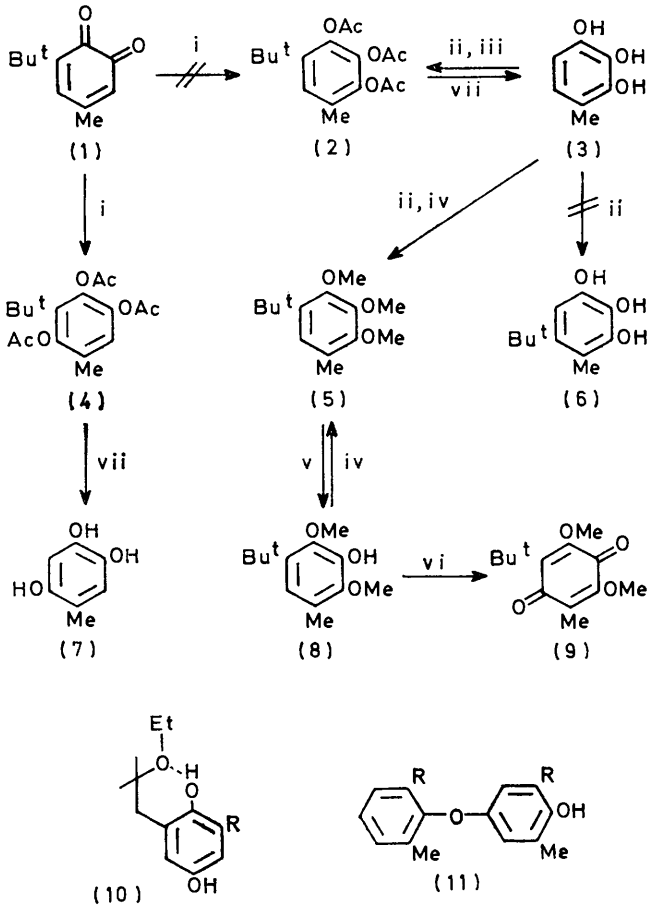
It has been confirmed that Thiele–Winter acetoxylation of 5-methyl-3-t-butyl-1,2-benzoquinone gives 1,2,4-triacetoxy-5-methyl-3-t-butylbenzene. The by-product from 2-methyl-6-t-butyl-1,4-benzoquinone has been shown to be 2-(2-ethoxy-2-methylpropyl)-6-methylhydroquinone (10), formed by photoreaction in ethanol.

RECENTLY we reported that Thiele–Winter acetoxylation of 5-methyl-3-t-butyl-1,2-benzoquinone (1) gave a mixture of 1,2-diacetoxy-5-acetoxymethyl-3-t-butylbenzene (14·5%) and a triacetate (20%) which could have structure (2) or structure (4).[1] Earlier, Takacs had studied the reaction and had obtained one product only which he had assumed to have structure (4).[2] We considered that structure (2) was more probable because an acetoxy-group entering at position 6 of the

[1] Part IV, J. M. Blatchly, R. J. S. Green, and J. F. W. McOmie, *J.C.S. Perkin I*, 1972, 2286.
[2] F. Takacs, *Monatsh.*, 1964, **95**, 961.

quinone is less sterically hindered than it would be at position 4. We have now prepared 4-methyl-6-t-butylpyrogallol and thence the triacetate (2). The m.p., and the i.r. and n.m.r. spectra of the latter are different from those of the Thiele–Winter product which must therefore have structure (4) as suggested by Takacs.



Reagents: i, Ac_2O–H_2SO_4; ii, Bu^tOAc–H_2SO_4; iii, Ac_2O–pyridine; iv, Me_2SO_4–OH^-; v, MeMgI; vi, AcO·OH or $ON(SO_3K)_2$; vii, $F_3C{\cdot}CO_2H$

Formylation [3] of pyrogallol with ethyl orthoformate followed by reduction [4] of the pyrogallol 4-aldehyde with zinc and hydrochloric acid gave 4-methylpyrogallol (3). When the latter was warmed with t-butyl acetate containing sulphuric acid as catalyst it gave 4-methyl-6-t-butylpyrogallol. This was converted into the acetate (2) by treatment with acetic anhydride, with pyridine as catalyst, rather than an acid, in order to prevent an acid-catalysed rearrangement of the t-butyl group in the desired triacetate.

Since the synthetic triacetate, m.p. 117°, was not identical with the Thiele–Winter product, m.p. 144°, it was necessary to prove that t-butylation of 4-methylpyrogallol, followed by acetylation, had given compound (2) and not the isomer (6) whose triacetate would have been different from the Thiele-Winter product. The butylated methylpyrogallol was converted into the trimethyl ether (5), which was identical with the product obtained by methylation of the dimethoxyphenol (8). The latter was made by t-butylation of 2,6-dimethoxy-3-methylphenol and its orientation was proved by oxidation with peracetic acid or with potassium nitrosodisulphonate to give the tetrasubstituted quinone (9). If t-butylation of 2,6-dimethoxy-3-methylphenol had occurred *ortho* instead of *meta* to the methyl group, either oxidation would have failed to occur or else the t-butyl group would have been displaced. The possibility that the t-butyl group might have migrated during oxidation to give the quinone (9) is considered highly unlikely. Such a migration has apparently never been observed in any of the many studies on the oxidation of t-butylated phenols.

During the foregoing work some related reactions were studied. Partial demethylation of pyrogallol trimethyl ether and of 1,2,3,6,7,8-hexamethoxybiphenylene by heating with methylmagnesium iodide in toluene is known to give 2,6-dimethoxyphenol [5] and 2,7-dihydroxy-1,3,6,8-hexamethoxybiphenylene,[6] respectively, *i.e.* the central of the three adjacent methoxy-groups is preferentially demethylated in each case. When this reaction was applied to the pyrogallol trimethyl ether (5) it gave a mixture containing the phenol (8) together with a lesser amount of one of the other two possible isomers. Reductive acetylation of the quinone (9) gave a monoacetate which is considered to be 4-acetoxy-3,5-dimethoxy-2-methyl-6-t-butylphenol, the sterically hindered hydroxy-group situated between the t-butyl and the methyl groups having escaped acetylation; *cf.* acetylation of 2-methyl-6-t-butylhydroquinone which gave the monoacetate, 4-acetoxy-2-methyl-6-t-butylphenol.[1]

After some attempts to hydrolyse the triacetate (2) had proved unsatisfactory we tried using trifluoroacetic acid at the suggestion of Dr. G. I. Fray.[7] When the triacetate (2) was boiled with 70% trifluoroacetic acid, de-t-butylation as well as hydrolysis occurred and the reaction gave a 96% yield of 4-methylpyrogallol (3). We have described elsewhere [8] the extension of this reaction as a general method for the de-t-butylation of t-butylphenols and for the hydrolysis of aryl acetates. In particular it has provided a simple proof of the structure of Takacs' triacetate, since when this was heated with trifluoroacetic acid it gave the hydroxytoluhydroquinone (7), which must have come from the triacetate (4). Of course, the hydroxyhydroquinone (7) might be produced by de-t-butylation and hydrolysis of 1,2,5-triacetoxy-4-methyl-3-t-butylbenzene, but the formation of this from the quinone (1) would involve

[3] H. Gross, A. Rieche, and G. Matthey, *Chem. Ber.*, 1963, **96**, 308.
[4] R. Majima and Y. Okazaki, *Ber.*, 1916, **49**, 1482.
[5] C. D. Hurd and H. E. Winburg, *J. Amer. Chem. Soc.*, 1942, **64**, 2086.
[6] W. Baker, N. J. McLean, and J. F. W. McOmie, *J. Chem. Soc.*, 1964, 1067.
[7] D. Bryce-Smith, B. Vickery, and G. I. Fray, *J. Chem. Soc.* (*C*), 1967, 390.
[8] J. F. W. McOmie and S. A. Saleh, *Tetrahedron*, 1973, **29**, in the press.

an unprecedented migration of a t-butyl group. Attempts to t-butylate the hydroxyhydroquinone (7) with t-butyl acetate in the presence of concentrated sulphuric acid gave an inseparable mixture.

The fact that Thiele–Winter acetoxylation of the quinone (1) gives the more hindered triacetate (4) instead of the possible alternative triacetate (2) shows that in this particular instance electronic effects predominate over the unfavourable steric effect.

By-product from 2-Methyl-6-t-butyl-1,4-benzoquinone.—In Part IV[1] we recorded that the Thiele–Winter acetoxylation of 2-methyl-6-t-butyl-1,4-benzoquinone gave 1,2,4-triacetoxy-3-methyl-5-t-butylbenzene and a compound $C_{13}H_{20}O_3$ (3% yield). We are indebted to Dr. R. W. Alder for suggesting structure (10; R = Me) for the latter. Structure (10) is in complete agreement with the i.r., n.m.r., and mass spectral evidence. Our attempts to prepare the compound $C_{13}H_{20}O_3$ by acid-catalysed addition of ethanol to the benzoquinone were unsuccessful but the product was formed when an ethanolic solution of 2-methyl-6-t-butyl-1,4-benzoquinone was exposed to sunlight or, better, to u.v. light. Evidently the compound $C_{13}H_{20}O_3$ had not been formed during the Thiele–Winter reaction but must have been formed by reaction of some unchanged quinone with solvent during recrystallisation. The photochemical reaction of 2,6-di-t-butyl-1,4-benzoquinone with ethanol gives compound (10; R = Bu^t),[9] whose properties are closely similar to those of our product (10; R = Me).

Contrary to our earlier report[1] we were able to oxidise 2-methyl-6-t-butylphenol to the benzoquinone (78% yield) with potassium nitrosodisulphonate. Oxidation of the phenol with chromic acid gave the benzoquinone (11%), 3,3′-dimethyl-5,5′-di-t-butyldiphenoquinone (29%), and the diphenyl ether (11; R = Bu^t) (2%). The formation of simple diphenyl ethers by the intermolecular oxidation of phenols is uncommon,[10] the closest analogy being the oxidation of 2,6-dimethylphenol by silver oxide to give the diphenyl ether (11; R = Me) in 15% yield.[11]

EXPERIMENTAL

The identity of compounds was checked by i.r. and n.m.r. spectra (solvent $CDCl_3$; 100 MHz) and by comparison of R_F values (t.l.c.). Silica gel (MFC) was used for column chromatography and kieselgel G or H (usually mixed with a fluorescent reagent) for t.l.c. and for preparative t.l.c.

t-Butylation of 4-Methylpyrogallol (3).—A mixture of 4-methylpyrogallol (4·25 g), t-butyl acetate (15 ml), and concentrated sulphuric acid (0·75 ml) was warmed at 65—68° for 3 h, cooled, and poured into ice–water. The crude product (5·3 g) was collected in ether and chromatographed on a column of silica gel (200 g) (chloroform as eluant) to give *4-methyl-6-t-butylpyrogallol* (4·70 g, 79%) as a viscous oil which was further purified by sublimation at 80—85° and 0·10 mmHg (Found: C, 67·45; H, 8·2. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%), τ 3·37 (ArH), 4·03br (OH, s), 4·33br (2 × OH, s), 7·90 (ArMe), and 8·67 (Bu^t).

When the pyrogallol was heated with acetic anhydride containing a catalytic amount of pyridine it gave *2,3,4-triacetoxy-1-methyl-5-t-butylbenzene* (2) (93%) as crystals (from ethanol), m.p. 117—117·5° (Found: C, 63·6; H, 6·9. $C_{17}H_{22}O_6$ requires C, 63·3; H, 6·9%), τ 2·87 (ArH), 7·70, 7·73, and 7·76 (3 × OAc), 7·83 (ArMe), and 8·69 (Bu^t).

2,3,4-Trimethoxy-1-methyl-5-t-butylbenzene (5).—(*a*) Potassium hydroxide (4·17 g) in water (50 ml) was added gradually to a stirred solution of 4-methyl-6-t-butylpyrogallol (3·4 g), sodium dithionite (300 mg), and dimethyl sulphate (37 ml) in methanol (50 ml) during 35 min. The temperature was kept at 22° for the first 10 min then at 42—48° for 25 min. The mixture was stirred for 2 h more, then diluted with water, and the product (3·2 g) was collected in ether, chromatographed in methylene dichloride, and then distilled at 30° and 0·001 mmHg to give the *trimethoxy-compound* as an oil (Found: C, 70·8; H, 9·2. $C_{14}H_{22}O_3$ requires C, 70·6; H, 9·3%), τ 3·18 (ArH), 6·11, 6·13, and 6·17 (3 × OMe), 7·79 (ArMe), and 8·66 (Bu^t).

(*b*) Potassium hydroxide (20 g) in water (30 ml) was added in portions to a stirred mixture of 2,6-dimethoxy-3-methyl-5-t-butylphenol (8) (65 mg), sodium dithionite (25 mg), methanol (15 ml), and dimethyl sulphate (25 ml) kept at room temperature. The mixture was heated for 1 h at 60° then worked up. T.l.c. with benzene as eluant gave the trimethoxy-compound (50 mg, 72%) as an oil, identical with that obtained in (*a*) (R_F value; i.r. and n.m.r. spectra).

3-Hydroxy-2,4-dimethoxybenzaldehyde.—2,6-Dimethoxyphenol (7·7 g) and hexamethylenetetramine (7 g) in trifluoroacetic acid (75 ml) were boiled under reflux for 15 h (method of Smith[12]). The solvent was removed under reduced pressure and the residue was added to ice–water (500 ml). The product was collected in ether and chromatographed on a column of alumina (150 g) [ethyl acetate–chloroform (5 : 95) as eluant]. Preparative t.l.c. with the same solvent then gave the aldehyde (2·75 g, 30%), m.p. 110° (lit.[13] 105°), τ −0·24 (CHO), 2·56 (d, ArH), 3·25 (d, ArH), 4·36 (ArOH), 5·98 (OMe), and 6·04 (OMe), $J_{5,6}$ *ca.* 8 Hz.

Formylation of 2,6-dimethoxyphenol with hexamine in glyceroboric acid[14] is reported to give the *p*-hydroxyaldehyde (m.p. 111—112°), whereas formylation of the same phenol with dichloromethyl methyl thioether gives a 7 : 3 mixture of the *m*- and *p*-hydroxyaldehydes.[13]

2,6-Dimethoxy-3-methylphenol.—The foregoing aldehyde (1·26 g) was heated under reflux with amalgamated zinc (50 g) in concentrated hydrochloric acid (100 ml) and water (100 ml) for about 15 h. The mixture was filtered, diluted to 800 ml, and then extracted with ether. The product was purified by column chromatography and preparative t.l.c. [ethyl acetate–methylene dichloride (5 : 95) as solvent system]. The resulting material (560 mg, 48%) was distilled at 50° and 0·005 mmHg and gave *2,6-dimethoxy-3-methylphenol* as an oil (Found: C, 64·5; H, 7·4. $C_9H_{12}O_3$ requires C, 64·3; H, 7·2%), τ 3·30—3·49 (2ArH, ABq), 4·44 (ArOH), 6·14 (2 × OMe), and 7·78 (ArMe).

2,6-Dimethoxy-3-methyl-5-t-butylphenol (8).—A stirred mixture of 2,6-dimethoxy-4-methylphenol (400 mg), t-butyl

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[11] B. Lindgren, *Acta Chem. Scand.*, 1960, **14**, 1203.
[12] W. E. Smith, *J. Org. Chem.*, 1972, **37**, 3972.
[13] K. Kratzl and F. W. Vierhapper, *Monatsh.*, 1971, **102**, 425.
[14] C. F. H. Allen and G. W. Leubner, *Org. Synth.*, 1951, **31**, 92.

acetate (10 ml), and concentrated sulphuric acid (0·23 ml) was kept at 65—70° for about 15 h. The solvent was removed under reduced pressure and the oily residue dissolved in chloroform was filtered through a column of silica gel (MFC) (150 g). Distillation at 45° and 0·02 mmHg gave the *t-butyl derivative* as an oil (150 mg, 28%) (Found: 69·8; H, 9·1. $C_{13}H_{20}O_3$ requires C, 69·6; H, 9·0%), τ 3·40 (ArH), 4·44 (ArOH), 6·10 (OMe), 6·20 (OMe), 7·77 (ArMe), and 8·65 (Bu^t).

Partial Demethylation of 2,3,4-*Trimethoxy*-1-*methyl*-5-*t-butylbenzene* (5).—A solution of methylmagnesium iodide [from methyl iodide (4·5 ml) and magnesium (1·8 g)] in ether (35 ml) was added to the trimethoxy-compound (3·06 g) in toluene (24 ml). Ether was removed under reduced pressure and was replaced by toluene (35 ml), then the mixture was boiled under reflux for 13 h. The cooled mixture was poured on ice (200 g) and concentrated hydrochloric acid (10 ml), and the product was extracted into ether. The extracts, after being shaken with aqueous 5% sodium hydroxide, gave a dark brown residue (1·5 g) of impure starting material. The alkaline extracts were acidified and were then saturated with sodium chloride before being extracted with ether. Removal of the ether left a mixture which was chromatographed in methylene chloride. The first fraction (44 mg) was sublimed twice at 45° and 0·005 mmHg and gave 2,3,4-*trimethoxy*-1,5-*di-t-butylbenzene*, m.p. 79—80° (Found: C, 72·4; H, 10·1%; M^+, 280. $C_{17}H_{28}O_3$ requires C, 72·8; H, 10·1%; *M*, 280), τ 3·05 (ArH), 6·11 (2 × OMe), 6·16 (OMe), and 8·67 (2 × Bu^t), which was presumably present as an impurity in the material before demethylation. The second fraction (290 mg, 10%) was an oil. It was distilled twice at 40° and 0·08 mmHg, and gave 2,6-dimethoxy-3-methyl-5-t-butylphenol (8) as an oil (Found: C, 69·6; H, 9·0. Calc. for $C_{13}H_{20}O_3$: C, 69·6; H, 9·0%), which had the same i.r. and n.m.r. spectra as the authentic material. The third fraction (120 mg, 4%) was a viscous oil, which was distilled at 40° and 0·08 mmHg, and gave 2,3-dimethoxy-4-(or 6)-methyl-6(or 4)-t-butylphenol, m.p. 55—56° (Found: C, 69·6; H, 9·05. Calc. for $C_{13}H_{20}O_3$: C, 69·6; H, 9·0%), τ 3·21 (ArH), 4·31 (ArOH), 6·14 (2 × OMe), 7·80 (ArMe), and 8·65 (Bu^t).

2,6-*Dimethoxy*-3-*methyl*-5-*t-butyl*-1,4-*benzoquinone* (9).—(*a*) The second fraction from the foregoing demethylation (586 mg), in methanol (50 ml), was treated with a large excess of potassium nitrosodisulphonate (10 g). The mixture was warmed to 60° for 45 min, then cooled to room temperature, diluted with water, and extracted with ether. The crude product was separated by t.l.c. (benzene as eluant) and gave starting material (311 mg) and the *benzoquinone* (275 mg, 44% conversion) as a yellow oil (Found: M^+, 238·121. $C_{13}H_{18}O_4$ requires *M*, 238·121); $\lambda_{max.}$ (EtOH) 277 nm (ε 4230); τ 6·06 and 6·17 (2 × OMe), 8·10 (CMe), and 8·65 (Bu^t).

(*b*) Hydrogen peroxide (1·5 ml; 34% w/v) was added dropwise to a solution of the phenol (240 mg) in acetic acid (4 ml) containing concentrated sulphuric acid (2 drops). The mixture was stirred overnight at room temperature and was then poured into ice–water; the product was collected in ether. T.l.c. in benzene gave the original phenol (163 mg) and the quinone (77 mg, 30% conversion) as a yellow oil identical with the material already described (i.r. spectrum and t.l.c.).

(*c*) Oxidation as in (*a*) of the phenol made by t-butylation of 2,6-dimethoxy-3-methylphenol gave a mixture which was separated by chromatography with benzene as eluant and then by t.l.c. with methylene chloride. The top band gave 2,6-dimethoxy-3-methyl-5-t-butyl-1,4-benzoquinone (25 mg, 22%), identified by its i.r., n.m.r., and u.v. spectra: the middle band gave starting material (15 mg); the third band gave material identified as 2,6-dimethoxy-3-methyl-1,4-benzoquinone (15 mg, 18%), which formed pale yellow needles, m.p. 122° (lit.,[15] 125°), τ 4·12 (H-5), 6·03 (OMe), 6·20 (OMe), and 8·03 (C–Me). This quinone was probably formed by oxidation of some 2,6-dimethoxy-3-methyl-4-t-butylphenol which n.m.r. spectroscopy indicated was present as a minor component in the partially purified product from the t-butylation of 2,6-dimethoxy-3-methylphenol.

Reductive acetylation of 3,5-dimethoxy-2-methyl-6-t-butyl-1,4-benzoquinone by zinc dust, acetic anhydride, and a few drops of triethylamine gave 4-*acetoxy*-3,5-*dimethoxy*-2-*methyl*-6-*t-butylphenol* (76%) as prisms [from petroleum (b.p. 60—80°)], m.p. 121·5—122° (Found: C, 63·5; H, 7·8%; M^+, 282·146. $C_{15}H_{22}O_5$ requires C, 63·8; H, 7·85%; *M*, 282·147), τ 5·11 (ArOH), 6·30 and 6·33 (2 × OMe), 7·70 (OAc), 7·92 (ArMe), and 8·53 (Bu^t). When this acetoxy-compound was treated with alkali and dimethyl sulphate it gave a trimethoxyphenol, which is assumed to be 3,4,5-*trimethoxy*-2-*methyl*-6-*t-butylphenol*, as an oil (Found: C, 63·5; H, 7·8%; M^+, 254·152. $C_{14}H_{22}O_4$ requires C, 63·8; H, 7·85; *M*, 254·152), τ 4·66 (ArOH), 6·19, 6·20, and 6·40 (3 × OMe), 7·82 (ArMe), and 8·53 (Bu^t).

De-t-butylation and Hydrolysis of Takacs' Triacetate.—The triacetate (4), m.p. 144° (50 mg), sodium dithionite (25 mg), and 70% trifluoroacetic acid were boiled under reflux for 4 h. The solvents were removed under reduced pressure and the residue was purified by t.l.c. [ethyl acetate–chloroform (15 : 85)] and then by sublimation at 85° and 0·2 mmHg. The product was identical (i.r. and n.m.r. spectra) with an authentic specimen of 5-methylbenzene-1,2,4-triol (7) obtained by similar hydrolysis of the corresponding triacetate, itself obtained by Thiele–Winter acetoxylation of toluquinone. As a further proof of identity both trihydroxytoluenes were acetylated and afforded the same triacetate, m.p. 114—115° (lit.[16] 115—116°).

Oxidation of 2-*Methyl*-6-*t-butylphenol.*—(*a*) The phenol (3·69 g) in methanol (100 ml) was added to a stirred solution of potassium nitrosodisulphonate (22·9 g) in water (1 l) and 0·17M-potassium dihydrogen phosphate (200 ml). After 1·5 h the product was collected in ether and was purified by column chromatography then t.l.c. with benzene as eluant, thereby giving 2-methyl-6-t-butyl-1,4-benzoquinone (3·11 g, 78%) as a yellow oil. Reduction of this with sodium dithionite gave the hydroquinone, m.p. 96—97° (lit.,[17] 97—98°) (Found: C, 73·0; H, 9·1. Calc. for $C_{11}H_{16}O_2$: C, 73·3; H, 8·95%), τ 3·33 and 3·49 (dd, 2 × ArH), 5·64 and 5·72 (2 × ArOH), 7·79 (ArMe), and 8·62 (Bu^t), $J_{3,5}$ *ca.* 3 Hz.

(*b*) A solution of chromic oxide (2 g) in acetic acid (30 ml) and water (3 ml) was added in portions during 1 h to a stirred solution of the phenol (1 g) in acetic acid (10 ml) at 5°. Stirring was continued overnight. Next day

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[16] H. S. Wilgus and J. W. Gates, *Canad. J. Chem.*, 1967, **45**, 1975.

[17] J. Pospisil and L. Taimr, *Coll. Czech. Chem. Comm.*, 1964, **29**, 381.

the mixture was diluted with water and the organic products were collected in ether and separated by chromatography in methylene chloride to give the original phenol (25 mg) and 2-methyl-6-t-butyl-1,4-benzoquinone (125 mg, 11%). A third component (60 mg) slowly decomposed on silica gel. It was sublimed under reduced pressure and gave *2-methyl-4-(2-methyl-6-t-butylphenoxy)-6-t-butylphenol* (11; R = Bu^t) (20 mg) as a slightly yellow solid, m.p. 145—146° (Found: M^+, 326·226. $C_{22}H_{30}O_2$ requires M, 326·225), τ 2·95—3·21 (3 × ArH, m), 3·55—3·87 (2 × ArH, m), 5·22 (ArOH), 7·81 (ArMe), 8·45 (ArMe), 8·64 (Bu^t), and 8·84 (Bu^t). The fourth fraction consisted of 3,3′-dimethyl-5,5′-di-t-butyldiphenoquinone (59 mg, 29%), which formed deep red needles, m.p. 185—186° (lit.,[18] 196—198°) (Found, M^+, 324. Calc. for $C_{22}H_{28}O_2$: M, 324), identical (i.r. and n.m.r. spectra) with an authentic sample.

Photochemical Addition of Ethanol to 2-Methyl-6-t-butyl-1,4-benzoquinone.—A solution of the quinone (250 mg) in ethanol (25 ml) was exposed to u.v. light from a Gallenkamp high-pressure mercury lamp with Woods-glass filter for 40 h. During this time the yellow colour faded and, after 25 h, plate-like crystals began to separate. The product was purified by chromatography with chloroform as eluant and gave *2-(2-ethoxy-2-methylpropyl)-6-methylhydroquinone* (10) (205 mg, 73%), m.p. 175—176°, which had the same i.r., n.m.r., u.v., and mass spectra as the previously described [1] by-product, $C_{13}H_{20}O_3$ (Found: M^+, 224·241. $C_{13}H_{20}O_3$ requires M, 224·141), τ 1·45 (ArOH), 3·46 and 3·65 (dd, 2 × ArH), 5·70 (ArOH), 6·52 (q, $O{\cdot}CH_2$), 7·26 ($ArCH_2$), 7·78 (ArMe), 8·80 (t, $CH_2{\cdot}CH_3$), and 8·80 (CMe_2), $J_{3,5}$ *ca.* 3, J_{Et} 7·0 Hz; *m/e* 224, 178, 163, 105, and 87.

When the quinone in ethanol was exposed to daylight for 70 h the ether (10), m.p. 174—175°, was obtained in 17% yield.

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