Thiele–Winter Acetoxylation of Quinones.† Part IV.[1] Quinones containing One or More t-Butyl Groups

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The acetoxylation of many 1,4- and 1,2-benzoquinones and two diphenoquinones containing one or more t-butyl groups has been studied; also most of the relevant earlier work has been repeated. The results show that acetoxylation rarely occurs *ortho* to a t-butyl group. In eight of the quinones studied the reaction resulted in replacement of a t-butyl by an acetoxy-group. A mechanism for this acetoxyde-t-butylation is proposed. One of the *ortho*-benzoquinones (5-methyl-3-t-butyl) reacted partly as such and partly in its tautomeric quinone methide form to give 1,2,4-triacetoxy-5-methyl-3-t-butylbenzene (20%) and 1,2-diacetoxy-5-acetoxymethyl-3-t-butylbenzene (14·5%).

WHEN a quinone undergoes the Thiele–Winter reaction to give a triacetoxy-compound, two of the acetoxy-groups are derived by reaction at the two quinonoid oxygen atoms and the third is normally produced by replacement of a hydrogen atom in the nucleus of the original quinone. However, four examples have been reported in which the entering acetoxy-group replaces a t-butyl group. We have repeated nearly all the previous work on 1,2- and 1,4-benzoquinones containing either one or two t-butyl groups, and we have studied eleven other t-butylated quinones. We have also re-investigated the Thiele–Winter reaction of the spiro-1,1′-bi-indanediquinone (14). Our own and previous results are summarised in the Table. One of the quinones studied is a new compound and three of the other quinones have been made by new methods; details are given in the Experimental section.

1,4-Benzoquinones.—Musso and Maassen [3] found that Thiele–Winter acetoxylation of 2-t-butyl-1,4-benzoquinone gave 1,2,4-triacetoxy-5-t-butylbenzene (1; R = Ac) (46%) and an oil, which they suggested contained the isomer (2; R = Ac). We have confirmed these results but were unable to purify the oily product. However, after the oil had been hydrolysed and methylated, then fractionally distilled, a combination of t.l.c. and n.m.r. spectroscopy showed the presence of all three isomers (1—3; R = Me). Hence acetoxylation of the quinone must have given all three triacetates (1—3; R = Ac) in *minimum* yields of 52, 3, and 6%, respectively. The apparently larger yield of the more sterically hindered product (3; R = Ac) compared with isomer (2; R = Ac) is not regarded as significant since hydrolysis and methylation of the mixture are unlikely to have occurred quantitatively. Moreover, some loss of material inevitably occurred during purification.

2,5-Di-t-butyl-1,4-benzoquinone was shown by Flaig *et al.*[4] to give the mono-t-butylbenzene (1; R = Ac), by a process involving the replacement of one t-butyl group by an acetoxy-group. Under the same conditions we obtained the same product (50%) together with *ca.* 8% of the triacetoxydi-t-butylbenzene (4; R = Bu^t), identical with the compound which had been made by the reductive acetylation of the monoepoxide of 2,5-di-t-butyl-1,4-benzoquinone.[5] The 2,6-di-t-butyl-quinone behaved like the 2,5-isomer and underwent acetoxyde-t-butylation to give 1,2,5-triacetoxy-3-t-butylbenzene (2; R = Ac),[6,7] identical with the product which had been obtained previously from the acetoxylation of the 3,5-di-t-butyl-1,2-quinone.[4] There was, however, no trace of the triacetoxydi-t-butylbenzene (5; R = Bu^t).

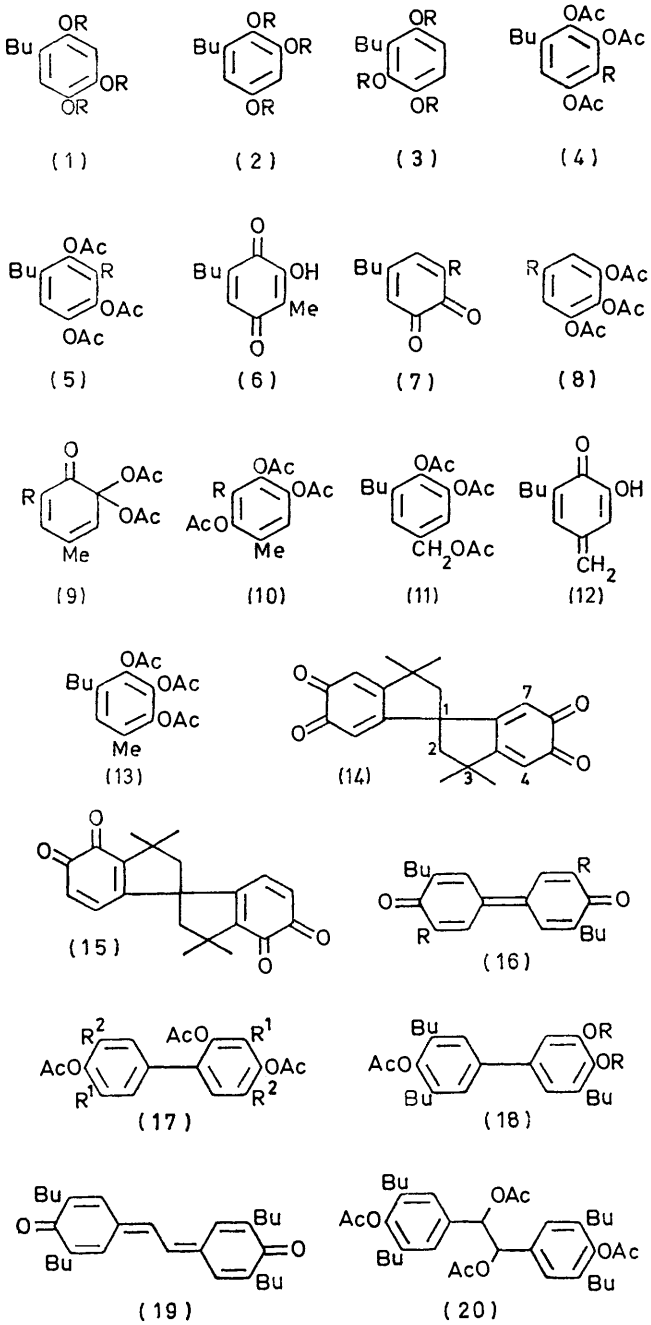
Flaig *et al.*[4] showed that 2-hydroxy-5-t-butyl-1,4-benzoquinone was converted into a mixture of the 2-acetoxy-5-t-butylquinone and 1,2,4,5-tetra-acetoxybenzene, this being the fourth previously recorded example of acetoxyde-t-butylation. Unfortunately, they did not record the respective yields, nor the length of the reaction time. In a 24 h experiment we obtained only the tetra-acetate (5% yield); the low yield of this product may have been due to its rapid hydrolysis when the reaction mixture was diluted with water.

Thiele–Winter acetoxylation of 2-methyl-5-t-butyl-1,4-benzoquinone proceeded normally and gave the triacetate (4; R = Me). The structure of the product was shown by the fact that when it was hydrolysed and then oxidised it gave the hydroxy-quinone (6). The n.m.r. spectrum of the latter did not show long-range coupling between the ring proton and the side-chain methyl group. Such long-range coupling would be expected if the acetoxy-group had entered the ring adjacent to the t-butyl group. In the n.m.r. spectra of eight toluquinones reported by others [8-10] and a further eight measured by us the methyl group always showed long-range coupling with the adjacent proton (J 1·5—1·8 Hz). Corbett [11] reported that he had made the

† The general title of this series has been changed from 'Thiele Acetylation of Quinones' to that given above, which acknowledges the contribution made by E. Winter and focuses the attention on the most important feature of the reaction for synthetic purposes. The amended title is used in the comprehensive review on this reaction.[2]

[1] Part III, J. M. Blatchly, R. J. S. Green, J. F. W. McOmie, and J. B. Searle, *J. Chem. Soc.* (*C*), 1969, 1353.
[2] J. F. W. McOmie and J. M. Blatchly, *Org. Reactions*, 1972, **19**, 199.
[3] H. Musso and D. Maassen, *Annalen*, 1965, **689**, 93.
[4] W. Flaig, T. Ploetz, and H. Biergans, *Annalen*, 1955, **597**, 196.
[5] F. R. Hewgill and S. L. Lee, *J. Chem. Soc.* (*C*), 1968, 1549.
[6] H. Musso and R. Zunker, *Annalen*, 1968, **717**, 64.
[7] U. Cuntze, D. Maassen, and H. Musso, *Chem. Ber.*, 1969, **102**, 2851.
[8] R. K. Norris and S. Sternhell, *Austral. J. Chem.*, 1966, **19**, 617.
[9] G. R. Allen, C. Pidacks, and M. J. Weiss, *J. Amer. Chem. Soc.*, 1966, **88**, 2536.
[10] M. F. Ansell, B. W. Nash, and D. A. Wilson, *J. Chem. Soc.*, 1963, 3012.
[11] J. F. Corbett, *J. Chem. Soc.* (*C*), 1970, 1912.

quinone (6) by the oxidation of 3-methyl-6-t-butylpyrocatechol with potassium nitrosodisulphonate. Although this synthesis is ambiguous, he assigned structure (6) to



Bu = t-butyl throughout

his product because of the similarity of its behaviour to that of 2-hydroxy-6-t-butyl-1,4-benzoquinone on autoxidation. The hydroxy-quinone (6) reacted with acetic anhydride and sulphuric acid, under mild conditions, to give the corresponding acetoxy-quinone, but when the reaction mixture was kept at 65—70° for 138 h some reduction and acetylation occurred to give 1,3,4-triacetoxy-2-methyl-5-t-butylbenzene (4; R = Me) in low yield.

Our attempts to make 2-methyl-6-t-butyl-1,4-benzoquinone from 2-methyl-6-t-butylphenol by oxidation with potassium nitrosodisulphonate, chromic acid, or peracetic acid were unsuccessful, and the synthesis *via* hydrolysis of the nitrosated phenol gave low yields. The best method involved the reduction of the nitrosated phenol with sodium dithionite followed by oxidation of the resulting amino-phenol with chromic acid. The quinone has since been made in good yield by the oxidation of 2-methyl-4,6-di-t-butylphenol and of 4-bromo-2-methyl-6-t-butylphenol.[12] Thiele–Winter acetoxylation of 2-methyl-6-t-butyl-1,4-benzoquinone gave a triacetate (8% yield) which was identical with the product obtained by the similar acetoxylation of 3-methyl-5-t-butyl-1,2-benzoquinone (7; R = Me); the product must therefore be the triacetate (5; R = Me). The aqueous-ethanolic mother liquor yielded another compound, $C_{13}H_{20}O_3$ (3% yield), which has not yet been identified.

2-Bromo-5-t-butyl-1,4-benzoquinone did not react with acetic anhydride in the presence of boron trifluoride, and with perchloric acid as catalyst intractable tars were formed. However, with sulphuric acid as catalyst under various conditions (see Table) two products were obtained. One was the corresponding hydroquinone diacetate, and the other a triacetate which is probably the less sterically hindered isomer (4; R = Br). The n.m.r. spectrum of the diacetate shows peaks at τ 2·72 and 2·88 for H-3 and H-6, respectively. The triacetate has a peak at τ 2·90 which is intermediate between the τ values (3·01 and 2·85) calculated [13] for the aromatic proton in compound (4; R = Br) and in the other possible isomer, respectively, so that no reliable conclusion can be drawn. Our attempts to prove the orientation by reactions involving debromination were unsuccessful.

1,2-*Benzoquinones*.—Thiele–Winter acetoxylation of 1,4-quinones almost certainly involves the stepwise 1,4-addition of acetic anhydride (or acetic acid) to the enone system. Most 1,2-quinones react similarly to give products of 1,4-addition,[2] but 4,5-disubstituted 1,2-quinones can only undergo 1,6-addition unless one of the substituents is displaced. Thus 4,5-dimethyl-1,2-benzoquinone [14] and the diquinone (14) [15] (see later) are known to give pyrogallol triacetate derivatives whereas 5-t-butyl-4-methoxy-1,2-benzoquinone gives a 6% yield of 1,2,4-triacetoxy-5-methoxybenzene together with black tarry products.

In contrast to 4-methyl-1,2-benzoquinone, which yields 2,4,5-triacetoxytoluene [16] by a 1,4-addition, 4-t-butyl-1,2-benzoquinone yields 1,2,3-triacetoxy-5-t-butylbenzene (8; R = Bu^t) by a 1,6-addition reaction.

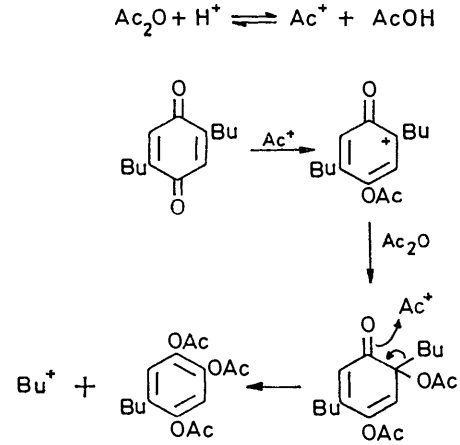
[12] D. G. Hewitt, *J. Chem. Soc.* (*C*), 1971, 2967.
[13] K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1968, **28**, 89.
[14] L. Horner and K. Sturm, *Annalen*, 1955, **597**, 1.
[15] W. Baker and J. C. McGowan, *J. Chem. Soc.*, 1943, 486.
[16] H. Budzikiewicz, W. Metlesics, and F. Wesseley, *Monatsh.* 1960, **91**, 117.

4-(1,1,3,3-Tetramethylbutyl)-1,2-benzoquinone likewise yields the pyrogallol derivative (8; R = $Me_3C{\cdot}CH_2{\cdot}CMe_2$).[17] In these three monoalkyl-1,2-benzoquinones the electronic effects of the substituents are closely similar but if the butyl and the tetramethylbutyl quinone underwent 1,4-addition reactions the products would be severely sterically hindered. Thiele–Winter acetoxylation of 3,5-di-t-butyl-1,2-benzoquinone (7; R = Bu^t) and of 3-bromo-5-t-butyl-1,2-benzoquinone (7; R = Br) proceeded with displacement of the 5-t-butyl group to give 1,2,5-triacetoxy-3-t-butylbenzene (2; R = Ac) (64% yield) [4] and 1,2,5-triacetoxy-3-bromobenzene (5%) respectively. Surprisingly the acetoxylation of 3-methyl-5-t-butyl-1,2-benzoquinone (7; R = Me) gave a low yield (12%) of t-butyl compound (5; R = Me). 3-Hydroxy-4,6-di-t-butyl-1,2-benzoquinone did not undergo the Thiele–Winter reaction but gave only the corresponding 3-acetate.[4] 5-Methoxy-3-t-butyl-1,2-benzoquinone was rapidly decomposed by acids and no reaction products were isolated.

Takacs [18] found that the Thiele–Winter reaction of 5-methyl-3-t-butyl-1,2-benzoquinone gave the same product, m.p. 144—145°, as that obtained from the acid-catalysed rearrangement of the dienone (9; R = Bu^t). He assumed the product was the triacetate (10; R = Bu^t) by analogy with earlier work [16] which had shown that the corresponding reactions with 3,5-dimethyl-1,2-benzoquinone and the dienone (9; R = Me) both gave the same triacetate (10; R = Me). The latter is also obtained by acetoxylation of 2,6-dimethyl-1,4-benzoquinone and thus its structure is firmly established. In our hands, acetoxylation of 5-methyl-3-t-butyl-1,2-benzoquinone gave the same triacetate as that described by Takacs together with a product (14·5%), m.p. 94—95°, which is shown by its analysis and its n.m.r. spectrum to be the acetoxymethyl compound (11). The 1,2-quinone had evidently reacted partly as such and partly as the tautomeric *para*-quinone methide (12). The related quinone, 4-methyl-1,2-naphthoquinone, undergoes Thiele–Winter acetoxylation entirely in the quinone methide form to give 1,2-diacetoxy-4-acetoxymethylnaphthalene (79%).[19] We have investigated the structure of the triacetate, m.p. 144—145°, obtained by Takacs since the two reactions he used could both give either 1,2,4-triacetoxy-5-methyl-3-t-butylbenzene (10; R = Bu^t) or its isomer, 2,3,4-triacetoxy-1-methyl-5-t-butylbenzene (13). If structure (10; R = Bu^t) is correct then hydrolysis of it, followed by oxidation would be expected to give a hydroxy-1,4-quinone isomeric with the stable, yellow quinone (6) which we had obtained in almost quantitative yield by the same sequence starting from the triacetate (4; R = Me). However, we obtained only an unstable red oil; this suggests that Takacs's triacetate has structure (13). Our attempts to make the latter compound by t-butylation of 4-methylpyrogallol followed by acetylation were unsuccessful.

The diquinones (14) and (15) may be regarded as derivatives of 4,5- and 3,4-di-t-butyl-1,2-benzoquinone, respectively. The diquinone (14) undergoes the Thiele–Winter reaction to give a mixture of two hexa-acetates, the major product being the symmetrical (and least hindered) compound, 5,6,7,5′,6′,7′-hexa-acetoxy-3,3,3′,3′-tetramethylspiro-1,1′-bi-indane.[15] The n.m.r. spectrum of this compound shows a singlet at τ 3·35 while the tetra-acetate, obtained by reducing and then acetylating the diquinone (14) shows two singlets at τ 3·05 and 3·36 (each 2 ArH). The minor product shows two singlets at τ 3·07 and 3·34 (each 1 ArH) and hence must be the unsymmetrical (4,5,6,5′,6′,7′) hexa-acetate. Recently Taimr and Pospíšil have shown that acetoxylation of the isomeric diquinone (15), gives the 4,6,7,4′,6′,7′-hexa-acetoxyspirobi-indane, *i.e.* the product of 1,4-additions.[20]

Other Quinones.—3,3′-Dimethyl-5,5′-di-t-butyldiphenoquinone (16; R = Me),[21] like 3,3′,5,5′-tetramethyldiphenoquinone,[22] undergoes a 1,4-addition in the Thiele–Winter reaction to give a triacetate which is assumed to be (17; R^1 = Me, R^2 = Bu^t) rather than the more hindered isomer (17; R^1 = Bu^t, R^2 = Me). 3,3′,5,5′-Tetra-t-butyldiphenoquinone (17; R^1 = R^2 = Bu^t), however, undergoes a 1,8-addition, with displacement of a t-butyl group, to give 3,4,4′-triacetoxy-3′,5,5′-tri-t-butylbiphenyl (18; R = Ac). Hydrolysis of this triacetate, followed by methylation, gave an acetoxydimethoxybiphenyl which almost certainly has the structure (18; R = OMe), the highly hindered acetoxy-group at position 4′ having been protected from hydrolysis by the two adjacent t-butyl groups.



SCHEME

3,3′,5,5′-Tetra-t-butylstilbenoquinone (19) behaves as a 1,4-methylenequinone and, when treated with acetic anhydride in presence of sulphuric acid, undergoes two 1,6-additions to give the tetra-acetoxybibenzyl (20).[23]

Mechanism of the De-t-butylation.—From the eight

[17] J. Pospíšil and V. Ettel, *Coll. Czech. Chem. Comm.*, 1959, **24**, 729.
[18] F. Takacs, *Monatsh.*, 1964, **95**, 961.
[19] L. F. Fieser and C. K. Bradsher, *J. Amer. Chem. Soc.*, 1939, **61**, 417.
[20] L. Tamir and J. Pospíšil, *Chem. and Ind.*, 1969, 456.
[21] A. Rieker and H. Kessler, *Chem. Ber.*, 1969, **102**, 2147.
[22] H. Erdtman, *Proc. Roy. Soc. Ser. A*, 1934, **143**, 177.
[23] W. Bradley and J. D. Sanders, *J. Chem. Soc.*, 1962, 480.

examples of acetoxyde-t-butylation in the Table it can be seen that this type of reaction only occurs when the normal reaction would involve acetoxylation adjacent to a t-butyl group, *i.e.* at a position subject to marked steric hindrance. The mechanism of the debutylation has not been established but since the t-butyl group is the only group which is known to be displaced during the Thiele–Winter reaction, it is probable that it is detached as the carbonium ion. A possible reaction sequence is shown in the Scheme, for 2,5-di-t-butyl-1,4-benzoquinone. Admittedly this mechanism does not explain the observation of Flaig *et al.*[4] that in the Thiele–Winter acetoxylation of 3,5-di-t-butyl-1,2-benzoquinone approximately 1 mol of sulphuric acid is reduced for each mol of quinone which reacts. However this result may have been fortuitous. We have found that some samples of commercial acetic anhydride darken and give off sulphur dioxide when they are warmed with concentrated sulphuric acid. For this reason it is advisable always to check the purity of acetic anhydride before using it for Thiele–Winter acetoxylations.

Thiele–Winter acetoxylation of t-butyl- and related quinones

1,4-Benzoquinone derivative	mmol	Catalyst (ml)	Ac_2O (ml)	Time (h)	Temp. (°C)	Substituents in benzene *	M.p. (°C)	Yield (%)	Ref.
2-But	97·5	BF_3-Et_2O (5)	70	2 +0·5	20 100	1,2,4-$(OAc)_3$-5-But	119—121	46	3
	73	BF_3-AcOH (4)	50	12	20	1,2,4-$(OAc)_3$-5-But 1,2,4-$(OAc)_3$-3-But 1,2,5-$(OAc)_3$-3-But	105—110 and 121—122 Oil Oil	52 6 [a] 3 [a]	
2,5-$(But)_2$	20	H_2SO_4	40	(48 days)	20 [b]	1,4,x-$(OAc)_3$-3-But	110—111 and 121—122	52	24
	47·5	H_2SO_4 (50)	300	24	20	1,2,4-$(OAc)_3$-5-But	116—122	40	4
	13·6	H_2SO_4 (6)	90	24	20	1,2,4-$(OAc)_3$-5-But 1,3,4-$(OAc)_3$-2,5-$(But)_2$	105—110 and 121—122 166—168 [c]	50 8	
2,6-$(But)_2$		H_2SO_4 H_3PO_4				1,2,5-$(OAc)_3$-3-But 1,2,5-$(OAc)_3$-3-But		40 [d] 50 [d]	6 7
	9·1	H_2SO_4 (15) BF_3-AcOH	60	24	20	1,2,5-$(OAc)_3$-3-But	91—92 and 106—107	61 Low	
2-Br-5-But [25]	2	H_2SO_4 [e] (0·5)	10	68	20	1,4-$(OAc)_2$-2-Br-5-But 1,3,4-$(OAc)_3$-2-Br-5-But [g]	78—79·5 [f] 104—105	8·5 7	
	20	H_2SO_4 (5)	80	42	60—65	Same products	78—79·5 104—105	9·6 13	
	6	H_2SO_4 (1·5)	25	69	60	1,4-$(OAc)_2$-2-Br-5-But 1,2,4-$(OAc)_3$-5-Br	78—79 114—116 [h]	3·5 1	
2-OH-5-But	5·6	H_2SO_4 (1)	25	?	20	1,2,4,5-$(OAc)_4$ 2-(OAc)-5-(But)-1,4-BQ	226 93—94		4
	3	H_2SO_4 (1)	10	24	20	1,2,4,5-$(OAc)_4$	223—225	5	
2-Me-5-But	56	H_2SO_4 [j] (2)	50	24	20	1,3,4-$(OAc)_3$-2-Me-5-But [i]	103—104 and 113—114	71	
2-Me-6-But	8·4	H_2SO_4 (1)	25	12	20	1,2,4-$(OAc)_3$-3-Me-5-But [k] $C_{13}H_{20}O_3$ [l]	125—126 172—173	7·7 3	
3-OH-2-Me-5-But	2·2	H_2SO_4 (0·1)	5	(10 min)	22	3-(OAc)-2-Me-5-But-1,4-BQ [m]	53—54·5	72	
	3·1	H_2SO_4 (0·4)	10	73	50—55	3-(OAc)-2-Me-5-But-1,4-BQ 1,3,4-$(OAc)_3$-2-Me-5-But	53—54 Impure	59 1	
	3·1	H_2SO_4 (0·4)	10	138	65—70	1,3,4-$(OAc)_3$-2-Me-5-But	114—115	15	
1,2-Benzoquinone derivative									
4-But [26]	14·8	H_2SO_4 (0·3)	30	(6 min)	20	1,2,3-$(OAc)_3$-5-But [n]	105—106	77	
3,5-$(But)_2$	22·7	H_2SO_4 (1·6)	150	0·5	5—10	1,2,5-$(OAc)_3$-3-But	105·5—106·5	64	4
5-Me-3-But	1·7	H_2SO_4				1,2,4-$(OAc)_3$-5-Me-3-But	144—145	27	18
	11·2	H_2SO_4 (0·2)	20	(6 min)	20	1,2,4-$(OAc)_3$-5-Me-3-But 1,2-$(OAc)_2$-5-$(AcO{\cdot}CH_2)$-3-But	143—144 94—95	20 14·5	
3-Me-5-But	11·2	H_2SO_4 (0·2)	35	(6 min)	20	1,2,4-$(OAc)_3$-3-Me-5-But	125—126	12	
5-MeO-3-But		BF_3-AcOH, H_2SO_4, or $HClO_4$				Viscous red tars			
4-MeO-5-But	2·6	H_2SO_4 (0·01)	20	(5 min) +12	100 20	1,2,4-$(OAc)_3$-5-(MeO) [p]	138—139	6	
	1	BF_3-AcOH (0·03)	5	48	22	Black tar			
3-Br-5-But	14·4	H_2SO_4 (0·5)	30	1	20	1,2,5-$(OAc)_3$-3-Br [q]	73—74	5	
3-OH-4,6-$(But)_2$	4·2	H_2SO_4 (3)	25			3-(OAc)-4,6-(But)-1,2-BQ	189	45	4
Other quinones									
3,3′-Me_2-5,5′-$(But)_2$-diphenoquinone	9·3	BF_3-AcOH (1)	20	(6 min)	20	2,4,4′-$(OAc)_3$-3,3′-Me_2-5,5′-$(But)_2$-BP [r]	187	76	
3,3′,5,5′-$(But)_4$-diphenoquinone	4·9	BF_3-AcOH (2)	20	3	45	3,4,4′-$(OAc)_3$-3′,5,5′-$(But)_3$-BP [s]	168—169·5	90	
3,3′,5,5′-$(But)_4$-stilbenoquinone	2·3	H_2SO_4 (0·5)	20	0·5	21	x,β.4,4′-$(OAc)_4$-3,3′,5,5′-$(But)_4$-BB	244—245	126 (crude)	23
Compound (15)		H_2SO_4 (trace)	(1 : 1 Ac_2O–AcHO)	3	20	4,4′,6,6′,7,7′-$(OAc)_6$BI	231—235 (decomp.)	34	20
Compound (14)	5·9	H_2SO_4 (0·2)	22	20	20	5,5′,6,6′-7,7′-$(OAc)_6$BI 4,5,5′,6′,7′-(OAc)-BU [u]	245—246 200	5·6 [t] 5·9	15

* Unless otherwise indicated; BQ = benzoquinone, BP = biphenyl, BB = bibenzyl, BI = 3,3,3′,3′-tetramethylspiro-1,1′-bi-indane.

[a] Yields were estimated after hydrolysis and methylation (see Experimental section). [b] With occasional brief periods of warming on a steam-bath. [c] Lit.,[5] m.p. 168—170°. [d] This is the overall yield after the initial product had been hydrolysed and then oxidised to 2-hydroxy-6-t-butyl-1,4-benzoquinone. [e] With BF_3-AcOH there was no reaction; $HClO_4$ gave tars. [f] Lit., m.p. 75—77° (D. F. Bowman and F. R. Hewgill, *J. Chem. Soc.* (*C*), 1969, 2164). [g] Found: C, 49·5; H, 4·9. $C_{16}H_{19}BrO_6$ requires C, 49·6; H, 4·95%. [h] Lit., m.p. 116·5—117·5° (J. M. Blatchly, J. F. W. McOmie, and J. B. Searle, *J. Chem. Soc.* (*C*), 1969, 1350). [i] Found: C, 63·4; H, 6·85. $C_{17}H_{22}O_6$ requires C, 63·3; H, 6·9%. [j] BF_3-AcOH gave a low yield of the same product. [k] No depression of m.p. when mixed with product from the acetoxylation of 3-methyl-5-t-butyl-1,2-benzoquinone. [l] See Experimental section. [m] Found: C, 66·2; H, 6·7. $C_{13}H_{16}O_4$ requires C, 66·1; H, 6·8%. [n] Identified by comparison with an authentic sample (see Experimental section). [p] Lit., m.p. 138—140° (S. L. Fries, A. H. Soloway, B. K. Morse, and W. C. Ingersoll, *J. Amer. Chem. Soc.*, 1952, **74**, 1305). [q] Found: C, 43·5; H, 3·2. $C_{12}H_{11}BrO_6$ requires C, 43·5; H, 3·4%. [r] Found: C, 71·7; H, 7·85. $C_{28}H_{36}O_6$ requires C, 71·8; H, 7·7%. [s] Found: C, 72·6; H, 8·3. $C_{30}H_{40}O_6$ requires C, 72·55; H, 8·1%. [t] Total yield was 97% but fractional crystallisation involved great loss of material. [u] The orientation of this isomer was determined in the present work.

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EXPERIMENTAL

The identity of compounds was checked by i.r. and n.m.r. (in $CDCl_3$ at 100 or 60 MHz) spectra and, where appropriate, by mixed m.p.s. Quinones were made by literature methods (see Table), except for those now described.

2-t-Butyl-1,4-benzoquinone.—Oxidation of 2-t-butylhydroquinone by potassium bromate and sulphuric acid (Vogel's method [27]) gave the quinone, m.p. 59° in quantitative yield.

2,5-Di-t-butyl-1,4-benzoquinone.—Nitric acid (35%; 20 ml) was added to a solution of 1,4-dimethoxy-2,5-di-t-butylbenzene [28] (5 g) in ethanol (20 ml) and the (vigorous) reaction was initiated by addition of a crystal of sodium nitrite. The mixture was kept at 40° for 10 min, and was then diluted with water. The precipitated solid (4 g) was chromatographed in benzene on an alumina column to give the quinone (3·0 g, 68%), m.p. 150—151° (lit.,[29] 151—153°) and 1,4-dimethoxy-2-nitro-5-t-butylbenzene (1·0 g, 21%), m.p. 98—99° (lit.,[30] 96—97°).

Under the conditions used by Hewgill and Kennedy [31] (HNO_3–AcOH–Ac_2O) the nitro-compound only was formed.

2-Methyl-5-t-butyl-1,4-benzoquinone.—Oleum (40 ml) was added gradually to a solution of toluhydroquinone (25 g) in acetic acid (200 ml) and t-butyl alcohol (28 ml), with the temperature kept below 20°. Next day the mixture was poured into a large volume of water and the oil was collected in ether. The oil was dissolved in methanol and oxidised with an excess of hydrated iron(III) chloride. The quinone (7 g), m.p. 97—98° (lit.,[32] 99—100°) was collected in chloroform.

3-Hydroxy-2-methyl-5-t-butyl-1,4-benzoquinone.— The Thiele acetylation product (8·0 g) from 2-methyl-5-t-butyl-1,4-benzoquinone was dissolved in a mixture of aqueous 25% sodium hydroxide (17·5 ml) and ethanol, under nitrogen. After 20 min, the mixture was acidified with concentrated hydrochloric acid (16 ml) in water (40 ml). It was then heated to 50° and iron(III) chloride hexahydrate (14 g) in water (25 ml) was added. The precipitated quinone, m.p. 198—199° (from methanol–acetic acid, 9 : 1) (lit.,[11] 202°) was obtained in almost quantitative yield (Found: C, 67·8; H, 7·2. Calc. for $C_{11}H_{14}O_3$: C, 68·0; H, 7·3%).

The same quinone was obtained, in low yield, when the same triacetoxy-compound was hydrolysed and methylated, then treated with 35% nitric acid in methanol.

2-Methyl-6-t-butyl-1,4-benzoquinone.—Nitrosation [33] of 2-methyl-6-t-butylphenol gave *2-methyl-6-t-butyl-1,4-benzoquinone oxime* (87%) as yellow needles (from benzene), m.p. 164—165° (Found: C, 68·0; H, 8·0. $C_{11}H_{15}NO_2$ requires C, 68·4; H, 7·8%). Treatment of the oxime with acetic anhydride containing boron trifluoride gave only the corresponding *oxime acetate* as yellow plates (from light petroleum), m.p. 69—70° (Found: C, 66·4; H, 7·5. $C_{13}H_{17}NO_3$ requires C, 66·4; H, 7·3%).

The oxime (4·0 g) in water (70 ml) containing sodium hydroxide (2·0 g) was reduced at 80° by addition of sodium dithionite (20 g). The oily product was washed by decantation, then it was dissolved in acetic acid (35 ml) and oxidised at 10° by addition of chromic oxide (6·0 g) in water (100 ml). The mixture was steam-distilled, and the crude product (2 g) gave 2-methyl-6-t-butyl-1,4-benzoquinone (1·4 g, 38% overall) as yellow rhombs (from methanol), m.p. 31—32° (lit.,[12] yellow oil) (Found: C, 74·2; H, 7·7. Calc. for $C_{11}H_{14}O_2$: C, 74·1; H, 7·9%).

When the quinone was reduced with sodium dithionite and then treated with acetic anhydride it gave a monoacetate, which is assumed to be *4-acetoxy-2-methyl-6-t-butylphenol*, m.p. 124—125° [from petroleum (b.p. 60—80°)] (Found: C, 70·7; H, 8·2. $C_{13}H_{18}O_3$ requires C, 70·2; H, 8·2%), τ 3·26, and 3·37 (2 ArH, dd), 5·18 (ArOH), 7·80 (OAc), 7·93 (ArMe), and 8·65 (Bu^t), $J_{3,5}$ 2·2 Hz.

3-Bromo-5-t-butyl-1,2-benzoquinone.—Bromination of 4-t-butylpyrocatechol gave 3-bromo-5-t-butylpyrocatechol,[34] m.p. 86°, which was characterised as the *diacetate*, m.p. 96° (from methanol) (Found: C, 51·1; H, 5·2. $C_{14}H_{17}BrO_4$ requires C, 51·1; H, 5·2%). Oxidation of the catechol (3·5 g) in ether (50 ml) with lead dioxide (7·7 g) gave the quinone, m.p. 98—99° (lit.,[34] 98—100°) in almost quantitative yield.

Thiele–Winter Acetoxylation of Quinones: General Procedure.—The acetylations were carried out as indicated in the Table. The reaction mixtures were poured onto crushed ice and hydrolysis of the excess of acetic anhydride was allowed to proceed for 2 h or more. The number of products obtained was checked by t.l.c. Where a single compound was indicated, crystallisation from methanol (with charcoal treatment if necessary) and sometimes finally from light petroleum (b.p. 60—80°) was sufficient to give the pure product. Mixtures of products were separated either by fractional crystallisation or, more usually, by column chromatography in benzene on silica gel.

Thiele–Winter Acetoxylation of 2-t-Butyl-1,4-benzoquinone.—The quinone (12 g) in acetic anhydride (30 ml) containing boron trifluoride–ether complex (4 ml) was stirred at room temperature for 2 h then warmed on a boiling water-bath for 30 min. The mixture was added to ice–water (300 g) and the products were collected in ether. Crystallisation of the mixed products from methanol gave 1,2,4-triacetoxy-5-t-butylbenzene (6·2 g, 27·5%), m.p. 120°. The mother liquor was treated with dimethyl sulphate and alkali (*cf.* ref. 1). The resulting mixture of methoxy-compounds (*ca.* 10 g) was examined by n.m.r. spectroscopy (solutions in $CDCl_3$). The major component was clearly 1,2,4-trimethoxy-5-t-butylbenzene: τ 3·20 (H-6, s), 3·54 (H-3, s), 6·21, 6·24, and 6·26 (3 OMe), and 8·69 (Bu^t). The two minor components were 1,2,5-trimethoxy-3-t-butylbenzene, τ 3·75 and 3·82 (2 ArH, dd), and 8·70 (Bu^t), $J_{4,6}$ 3·0 Hz, and 1,2,4-trimethoxy-3-t-butylbenzene, τ 3·47 and 3·65 (2 ArH, dd) and 8·60 (Bu^t), $J_{5,6}$ 9·0 Hz. The peaks due to the methoxy-groups were all superimposed in the region τ 6·30—6·40. The ratio of the three components was 10 : 1 : 2.

The mixture was distilled at 104—110° and 0·9 mmHg and the oily distillate was crystallised from petroleum (b.p. 30—40°). This gave 1,2,4-trimethoxy-5-t-butylbenzene (2·2 g) as needles, m.p. 53·5—55° (lit.,[35] 54—55°). Chromatography of the concentrated mother liquors on silica gel gave more of this compound (1·1 g) but it was not possible to separate the two minor components.

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Thiele–Winter Acetoxylation of 2-Methyl-6-t-butyl-1,4-benzoquinone.—A solution of the quinone (2 g) in acetic anhydride (25 ml) and concentrated sulphuric acid (1 ml) was kept for 12 h at room temperature. The mixture was poured on ice and, after 2 h, the oily product was separated by decantation. The oil was warmed with ethanol and water (9 : 1) and then kept overnight at 0° after adding a seed crystal. Next day the crystalline 1,2,4-*triacetoxy*-3-*methyl*-5-*t*-*butylbenzene* (0·2 g, 8%) was collected; m.p. and mixed m.p. 125—126° (from light petroleum) (Found: C, 63·0; H, 6·7. $C_{17}H_{22}O_6$ requires C, 63·3; H, 6·9%). After 2 more days at 0°, the mother liquor deposited a compound as needles (0·1 g, 3%), m.p. 172—173° (from benzene) (Found: *m/e* 224·241, 178·099, and 163·077. Calc. for $C_{13}H_{20}O_3$, $C_{11}H_{14}O_2$, and $C_{10}H_{11}O_2$: 224·141, 178·099, and 163·076, respectively).

Thiele–Winter Acetoxylation of 5-Methyl-3-t-butyl-1,2-benzoquinone.—The experimental conditions are given in the Table. The mixture of products was dissolved in 95% methanol and left at 0° overnight. The solution first deposited 1,2-diacetoxy-5-acetoxymethyl-3-t-butylbenzene, m.p. 92—93° then, after 2 days at 0°, the triacetoxy-t-butyltoluene, m.p. 143—144°. Both products were recrystallised from petroleum (b.p. 60—80°). The pure *acetoxymethyl compound* had m.p. 94—95° (Found: C, 63·4; H, 6·7. $C_{17}H_{22}O_6$ requires C, 63·3; H, 6·9%), τ 2·76 and 2·88 (2 ArH, dd), 4·98 ($ArCH_2$), 7·72, 7·80, and 7·95 (3 × OAc), and 8·69 (Bu^t), $J_{4,6}$ 2·0 Hz).

1,2,3-*Triacetoxy*-5-*t*-*butylbenzene.*— 5-*t*-*Butylpyrogallol* [36] (1·74 g) was heated with acetic anhydride (4 ml) and sodium acetate (1·2 g) at 100° for 10 min. On dilution with water the *triacetoxy-compound* (68%) formed needles (from ethanol), m.p. 105—106° (Found: C, 62·3; H, 6·8. $C_{16}H_{20}O_6$ requires C, 62·3; H, 6·5%).

4-*Acetoxy*-3′,4′-*dimethoxy*-3,5,5′-*tri*-*t*-*butylbiphenyl.*— Aqueous 50% potassium hydroxide (20 ml) was added dropwise to a stirred solution of 3,4,4′-triacetoxy-3,5,5′-tri-t-butylbiphenyl (see Table) (2 g) in methanol (10 ml) and dimethyl sulphate (10 ml). Dilution with water then gave the *dimethoxy-compound* (1·2 g, 68%) as needles (from methanol), m.p. 135—136° (Found: C, 76·25; H, 9·3. $C_{28}H_{40}O_4$ requires C, 76·3; H, 9·1%).

N.m.r. Spectra of Quinones.—(a) 1,4-*Benzoquinones.* 2-t-Butyl-: τ 3·36 (H-5, H-6, unresolved m), 3·43 (H-3, d), and 8·74 (Bu^t). 2,5-Di-t-butyl-: τ 3·53 (H-3, H-6) and 8·76 (Bu^t). 2,6-Di-t-butyl-: τ 3·53 (H-3, H-5) and 8·75 (Bu^t). 2-Bromo-5-t-butyl-: τ 2·80 (H-3), 3·21 (H-6), and 8·73 (Bu^t), $J_{3,6}$ 0 Hz. 2-Methyl-5-t-butyl- τ 3·44 (H-6), 3·50 (H-3, q), 8·03 (Me, d), and 8·75 (Bu^t), $J_{Me,H}$ 1·6 Hz. 2-Methyl-6-t-butyl-: τ 3·48br (H-3, H-5), 7·95br (Me), and 8·72 (Bu^t). 3-Hydroxy-2-methyl-5-t-butyl-: τ 2·86 (OH), 3·49 (H-6), 8·13 (Me), and 8·75 (Bu^t). 3-Acetoxy-2-methyl-5-t-butyl: τ 3·41 (H-6), 7·70 (OAc), 8·13 (Me), and 8·75 (Bu^t).

(b) 1,2-*Benzoquinones.* 4-t-Butyl-: τ 2·81 (H-5, m), 3·65 (H-6, d), 3·77 (H-3, d), and 8·77 (Bu^t), $J_{3,5}$ *ca.* 2, $J_{5,6}$ 10·5 Hz. 3,5-Di-t-butyl-: τ 3·05 (H-4, d), 3·78 (H-6, d), and 8·76 and 9·00 (2 × Bu^t), $J_{4,6}$ 2·6 Hz. 5-Methyl-3-t-butyl-: τ 3·42 (H-4, d), 3·86 (H-6, m), 7·89 (Me, d), and 8·77 (Bu^t), $J_{Me,H}$ *ca.* 1·6 Hz. 3-Methyl-5-t-butyl-: τ 3·08 (H-4, m), 3·82 (H-6, d), 7·99 (Me, d), and 8·78 (Bu^t), $J_{4,6}$ *ca.* 2·0, $J_{Me,H}$ *ca.* 1·5 Hz. 5-Methoxy-3-t-butyl-: τ 3·41 (H-4, d), 4·32 (H-6, d), 6·21 (OMe), and 8·77 (Bu^t), $J_{4,6}$ 3·0 Hz. 4-Methoxy-5-t-butyl-: τ 3·76 (H-6), 4·26 (H-3), 6·16 (OMe), and 8·72 (Bu^t). 3-Bromo-5-t-butyl-: τ 2·44 (H-4, d), 3·73 (H-6, d), and 8·78 (Bu^t), $J_{4,6}$ 2·0 Hz. Bis-spiroquinone (14): τ 3·74 and 3·84 (H-4, H-7, H-4′, H-7′, broad singlets), 7·64 and 7·82 (2 × CH_2, dd), and 8·62 and 8·63 (2 × CMe_2), $J_{4,7} < 1·0$ Hz.

(c) *Diphenoquinone.* 3,3′-dimethyl-5,5′-di-t-butyl-: τ 2·40br (vinyl H), 7·82br (Me), and 8·68br (Bu^t) (probably a mixture of *cis*- and *trans*-isomers, *cf.* ref. 21).

N.m.r. Spectra of Other Compounds.—(a) 1,2,4-*Triacetoxybenzenes.* 6-Bromo-: τ 2·77 (H-5, d), 3·02 (H-3, d), 7·71 (OAc), and 7·78 (2 × OAc), $J_{3,5}$ 2·8 Hz. 3-t-Butyl-: τ 2·91 and 3·13 (2 ArH, dd), 7·74, 7·77, and 7·80 (3 × OAc), and 8·63 (Bu^t), $J_{5,6}$ 9 Hz. 5-t-Butyl-: τ 2·85 (ArH), 3·04 (ArH), 7·75, 7·79, and 7·82 (3 × OAc), and 8·70 (Bu^t). 6-t-Butyl-: τ 3·03 (2 ArH), 7·72, 7·78, and 7·80 (3 × OAc), and 8·68 (Bu^t), $J_{3,5}$ 0 Hz. 5-Methoxy-: τ 3·02 and 3·18 (2 ArH), 6·18 (OMe), 7·70 (2 × OAc), and 7·75 (OAc). 3-Bromo-6-t-butyl-: τ 2·90 (H-5), 7·71 (OAc), 7·74 (2 × OAc), and 8·72 (Bu^t). 3-Methyl-6-t-butyl-: τ 3·02 (H-5), 7·75 (2 × OAc), 7·78 (OAc), 8·10 (ArMe), and 8·72 (Bu^t). 3-Methyl-5-t-butyl-: τ 2·94 (H-6), 7·72, 7·76, and 7·79 (3 × OAc), 8·12 (ArMe), and 8·71 (Bu^t). 5-Methyl-3-t-butyl-: τ 3·01 (H-6), 7·76, 7·78, and 7·83 (3 × OAc), 7·97 (ArMe), and 8·64 (Bu^t). 3,6-Di-t-butyl-: τ 3·12 (H-5), 7·75 (2 × OAc), 7·80 (OAc), and 8·65 and 8·73 (2 × Bu^t).

(b) *Other benzene derivatives.* 1,4-Diacetoxy-2-t-butyl-: τ 2·9—3·05 (3 ArH, m), 7·74 and 7·78 (2 × OAc), and 8·70 (Bu^t). 1,4-Diacetoxy-2-bromo-5-t-butyl-: τ 2·72 (H-3), 2·88 (H-6), 7·70 (2 × OAc), and 8·69 (Bu^t). 1,4-Diacetoxy-2,5-di-t-butyl-: τ 3·03 (ArH), 7·73 (OAc), and 8·70 (Bu^t). 1,2,3-Triacetoxy-5-t-butyl-: 2·92 (2 ArH), 7·79 (3 × OAc), and 8·73 (Bu^t).

(c) *Biphenyls.* 4,4′-Diacetoxy-3,3′,5,5′-tetra-t-butyl-: τ 2·58 (4 ArH), 7·65 (2 × OAc), and 8·60 (4 × Bu^t). 3,4,4′-Triacetoxy-3′,5,5′-tri-t-butyl-: τ 2·64 (H-2′, H-6′), 2·67 (H-2 or H-6, d), 2·84 (H-6 or H-2, d), 7·70 (2 × OAc), 7·78 (OAc), and 8·65 (3 × Bu^t), $J_{2,6}$ 2·2 Hz. 4-Acetoxy-3′,4′-dimethoxy-3,5,5′-tri-t-butyl-: τ 2·66 (H-2, H-6), 3·02 (H-2′ or H-6′, d), 3·14 (H-6′ or H-2′, d), 6·13 (2 × OMe), 7·68 (OAc), 8·60 (Bu^t), and 8·62 (2 × Bu^t), $J_{2',6'}$ 2·2 Hz. 2,4,4′-Triacetoxy-3,3′-dimethyl-5,5′-di-t-butyl-: τ 2·84 (H-6), 2·81 (H-2′ or H-6′, d), 2·99 (H-6′ or H-2′, d), 7·69 (2 ArMe), 7·90, 8·00, and 8·10 (3 × OAc), and 8·67 (2 × Bu^t), $J_{2',6'}$ *ca.* 1·5 Hz.

(d) 3,3,3′,3′-*Tetramethylspiro*-1,1′-*bi*-*indanes.* 5 6,5′,6′-Tetra-acetoxy-: τ 3·05 (H-7), 3·36 (H-4), 7·68 and 7·78 (CH_2, ABq), 7·79 and 7·84 (2 × OAc), and 8·68 and 8·70 (2 × CMe), J_{CH_2} *ca.* 12 Hz. 5,5′,6,6′,7,7′-Hexa-acetoxy-: τ 3·35 (H-4). 4,5,5′,6,6′,7′-Hexa-acetoxy-: τ 3·07 (H-7) and 3·34 (H-4′).

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