Thiele acetylation of substituted benzoquinones

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The treatment of substituted quinones with acetic anhydride under acid catalysis gives substituted triacetoxybenzenes. Previous work on this reaction is summarized, and the reaction has been extended to include quinones having electron-withdrawing groups, and two quinones which had previously been reported as inactive.

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The sulfuric acid catalyzed reaction of acetic anhydride with quinone to give 1,2,4-triacetoxybenzene was reported by Thiele in 1898 (1). Since that time, other workers have reported results with various quinones, occasionally employing boron trifluoride in place of sulfuric acid. Their work and the results reported in this paper are summarized in the accompanying tables. Table I lists the quinones which gave only one product, and Table II lists the quinones which gave isomers. Reactions not included in Table I are the formation of 1,2,4-triacetoxynaphthalene in an 81% yield by the boron trifluoride catalyzed acetylation of 1,4-naphthoquinone (2), and in a 78% yield by the sulfuric acid catalyzed acetylation of 1,2-naphthoquinone (2). 2-Methyl-1,4-naphthoquinone has been reported as being inert to the Thiele reaction (2). However, we have found that boron trifluoride catalysis gives a 27% yield of 2-methyl-1,3,4-triacetoxynaphthalene with a reaction period of 18 h, and a 52% yield with a reaction period of 120 h.

Trimethylquinone has also been reported as being inert (2) to this reaction, but we have obtained the triacetoxy derivative in a good yield with boron trifluoride as the catalyst (see Table I).

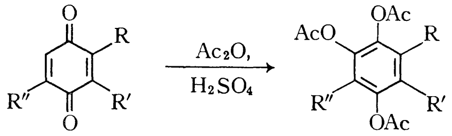
None of the quinones previously studied contained an electron-withdrawing substituent, and in only one case, 5-isopropyltoluquinone (3), was more than one isomer reported.

The acetylation product from 5-hydroxytoluquinone has been corrected to that shown in Table I on the following basis. The compound was first prepared as an unidentified isomer by Thiele and Winter (4). Erdtman (3) erroneously assigned a 2,3,4,5-tetraacetoxy structure on the basis of the acetylation of 5-methoxytoluquinone. He converted what he thought was 2,3,5-triacetoxy-4-methoxytoluene into the tetramethoxy derivative, which he found to be identical with that of the compound originally obtained by Thiele and Winter. However, Anslow *et al.* (5) found that the acetylation of 5-methoxytoluquinone gave 2,3,6-triacetoxy-4-methoxytoluene. Therefore, the product of the acetylation of 5-hydroxytoluquinone is the other isomer, 2,3,4,6-tetraacetoxytoluene.

Vapor-phase chromatography (v.p.c.) of the reaction product from toluquinone showed two isomers instead of the one reported by Thiele (4). Neither compound could be identified by nuclear magnetic resonance (n.m.r.). These compounds were identified as the 2,3,5-triacetoxy isomer (a known compound) and the 2,4,5-triacetoxy isomer by an independent synthesis from 6-hydroxytoluquinone (6), as described in the Experimental.

The sulfuric acid catalyzed reaction product from phenylquinone, when analyzed by v.p.c., showed four peaks: 19% starting material, 21.4% 2,3,6-triacetoxybiphenyl, 7.1% 2,5-diacetoxybiphenyl, and 52.4% 2,4,5-triacetoxybiphenyl. Only the latter 2,4,5-isomer, a known compound, was reported by Fieser (7). The 2,3,6-isomer could not be isolated as a solid or as an oil of purity higher than 89%. The n.m.r. spectrum of this compound was not helpful, since all of the aromatic protons fell under the same peak. The isomer was identified by conversion into its trimethoxy derivative and subsequent n.m.r. analysis.

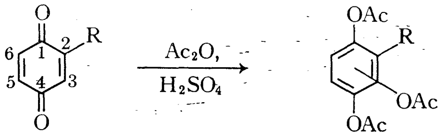
TABLE I

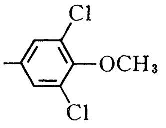


R	R′	R″	Yield (%)	Reference
H	H	H	?	1
H	OCH_3	H	98	3
H	OCH_3	OCH_3	Not reported	3
OCH_3	H	OCH_3	Not reported	3
OCH_3	OCH_3	H	63	3
OCH_3	H	C_6H_5	38*	8
C_6H_5	OCH_3	OCH_3	Not reported*	8
Br	OCH_3	OCH_3	Not reported	8
OCH_3	H	CH_3	100*	5
CH_3	H	CH_3	96	3
CH_3	H	CH_3	91*	10
H	CH_3	CH_3	92	3
H	CH_3	CH_3	Not reported*	10
CH_3	CH_3	H	90*	Experimental
OH†	H	CH_3	60 (4)	‡
H	H	$COCH_3$	92	Experimental
H	H	$COCH_3$	78*	Experimental
H	H	$COOCH_3$	34	Experimental
CH_3	CH_3	CH_3	Not reported	10
CH_3	CH_3	CH_3	62*	Experimental
H	Cl	Cl	Not reported	10

*Boron trifluoride was used in place of sulfuric acid.
†This group becomes acetylated during the reaction.
‡See the text.

TABLE II



	Isomeric yield (%) for substitution at position:			
R	3	5	6	Reference
CH_3	—	78*	15	Experimental
CH_3	—	89†	11†	Experimental
$(2\text{-}CH_3)\text{-}5\text{-}CH(CH_3)_2$	38	—	57	3
$4'\text{-}C_6H_4NO_2$	18	56	19	Experimental
	—	65	35	Experimental
C_6H_5	21	52	—	Experimental
C_6H_5	31†	62†‡	—	Experimental

*Only the 2,4,5-triacetoxy isomer was previously reported (4) (in a "good" yield).
†Boron trifluoride was used in place of sulfuric acid.
‡Only the 2,4,5-triacetoxy was previously reported (7, 8) (in a 41% yield).

4′-Nitrophenylquinone gave products which could not be analyzed by v.p.c. Conversion into the trimethoxy derivative by hydrolysis and methylation, followed by v.p.c. and subsequent n.m.r. analysis, showed all three isomers to be present in the yields shown.

The reaction of 4′-methoxyphenylquinone gave a tar. A similar result was obtained by Blatchly and McOmie (8) when 5-methoxy-2-(2′-methoxy)phenylquinone was treated, with boron trifluoride as the catalyst. By blocking the positions ortho to the methoxy group with chlorine atoms to prevent a Friedel–Crafts reaction on this aromatic nucleus, the reaction of 4′-methoxy-3′,5′-dichlorophenylquinone proceeded smoothly to give both the 2,4,5- and the 2,3,5-triacetoxy isomers, identified by n.m.r.

Fieser and Fieser (2) have indicated that boron trifluoride is a weaker catalyst than sulfuric acid in this reaction. We have found two cases in which reaction occurred when boron trifluoride was used as the catalyst, but in which starting material was recovered when sulfuric acid was used. In two cases (phenylquinone and toluquinone) when isomers were obtained, the use of boron trifluoride had little effect on the ratio of isomers.

The possibility of conversion of one isomer into another under our reaction and work-up conditions was excluded by the following experiments. Pure 2,4,5-triacetoxybiphenyl was shown by v.p.c. analysis to be unchanged after the same treatment as described in the Experimental for the reaction of phenylquinone. Treatment of a mixture of 76% 2,3,6-triacetoxybiphenyl and 24% 2,4,5-triacetoxybiphenyl for 18 h with the same reactants, followed by the same work-up, gave 74% and 26% of the isomers, respectively, as shown by v.p.c.

From the data it is apparent that some generalizations can be made. The choice of the catalyst may be important in determining whether a reaction will occur. Strong electron-donating groups direct primarily para and secondarily meta; the entering group will not enter the ortho position. Weak electron-donating groups direct both para and meta. When two electron-donating groups are in the same quinone ring, the effect of the stronger electron-donating group predominates. Electron-withdrawing groups direct ortho. A bulky group will show some steric effect by inhibiting the reaction at the ortho position. In general, the same orientation effects apply here as in the addition of mercaptans to quinones (9). However, caution must be exercised, since 4′-nitrophenylquinone unexpectedly gave a large amount of the para isomer, and phenylquinone gave some ortho isomer and no meta isomer.

EXPERIMENTAL

Unless specified otherwise, all reagents were Eastman Kodak Company chemicals. Melting points are corrected.

Acetylation of Toluquinone

Toluquinone (36.6 g) was added to a solution of acetic anhydride (150 ml) and concentrated sulfuric acid (3 g). The mixture was stirred at 55–60° for 3 h, cooled, and poured into cold water (450 ml). After the mixture had been stirred for ½ h, the solid was removed by filtration and recrystallized from ethanol, giving 44.6 g of near-white 2,4,5-triacetoxytoluene, m.p. 110–113° (lit. (4) m.p. 114–115°). Further recrystallization gave white crystals, m.p. 115–116°.

The filtrates were combined and condensed, giving a brown oil. A sample of this oil was chromatographed on a silica gel column with 1:6 benzene–ligroin. Elution with 1:2 benzene–ligroin, followed by 2:1 benzene–ligroin, gave two yellow oily fractions, which were combined. Some crystals were observed in this oil after 10 days. These were used to seed the remaining original brown oily fraction. After 4 days, the resulting slurry was filtered with the aid of a small amount of ethanol, and the product was washed briefly with ethanol, giving a white solid. Recrystallization from ethanol–water gave three crops of white rhombic crystals (3.61 g, 1.90 g, and 0.53 g), m.p. 74.5–76°. An n.m.r. spectrum of this compound in dioxane showed no splitting of the two ring protons.

Anal. Calcd. for $C_{13}H_{14}O_6$: C, 58.6; H, 5.5. Found: C, 58.3; H, 5.0.

To determine the amount of each isomer present, the reaction was repeated. The product was concentrated on a rotary evaporator at 50°. The resulting oil was dissolved in ether and extracted with three portions of water. Evaporation of the ether gave the product in a 90% yield. Vapor-phase chromatographic analysis of this sample with an 8 ft silicone rubber column at 199° showed 82% of the 2,4,5-triacetoxy isomer and 15% of the 2,3,5-triacetoxy isomer. Corrected for the 90% yield, these values become 78% and 14.5%.

2,3,5-Triacetoxytoluene from 6-Hydroxytoluquinone

6-Hydroxytoluquinone (6) (1.4 g) was dissolved in water – sulfur dioxide (70 ml) and allowed to stand overnight. Treatment with carbon did not remove the yellow color. The solution was saturated with sodium chloride and extracted three times with ether. The ether extracts were combined and evaporated, giving a brown oil. This oil was warmed for 4 h (~40°) with acetyl chloride (5 ml) and allowed to stand at room temperature overnight. The solvent was removed under vacuum at 50° and the oil mixed with ether. Filtration, followed by the addition of ligroin, gave white crystals, m.p. 72–73°, with softening at 71°. An infrared spectrum was identical with that of the minor product (m.p. 74.5–76.0°) obtained from the acetylation of toluquinone.

Acetylation of Carbomethoxyquinone

Carbomethoxyquinone (5.92 g) was added to a solution of acetic anhydride (25 ml) and concentrated sulfuric acid (0.5 g). An immediate exothermic reaction occurred, which necessitated cooling. The orange solution was stirred for 2 h at 55–60°, and the cooled solution was poured into water (150 ml), with vigorous stirring. After 15 min, the aqueous layer was decanted and the oil dissolved in a small amount of ethanol. Cream-colored crystals (3.30 g) resulted, m.p. 92–94°; with a second crop of 0.30 g, the yield was 33.9%. An n.m.r. spectrum in dioxane gave a coupling constant of 9.1 c.p.s.; thus the ortho structure was assigned to this compound.

Anal. Calcd. for $C_{14}H_{14}O_8$: C, 54.2; H, 4.6. Found: C, 54.3; H, 4.2.

Acetylation of Acetoquinone

Acetoquinone (16.18 g) was mixed with acetic anhydride (70 ml) and concentrated sulfuric acid (30 drops). The mixture was stirred at 55–60° for 1 h and then allowed to stand at room temperature over the weekend. The solution was poured into water (350 ml) and the slurry was stirred until crystallization occurred. The pale-tan crystals were removed by filtration and dried (26.3 g), m.p. 93.5–96.0°. Recrystallization from ethanol gave 23.7 g of cream-colored crystals, m.p. 95.0–97.5°. An n.m.r. spectrum in 30% dioxane solution showed a coupling constant of 8.9 c.p.s., indicating that this was the ortho isomer.

Anal. Calcd. for $C_{14}H_{14}O_7$: C, 57.1; H, 4.8. Found: C, 57.0; H, 4.4.

Acetylation of 3′,5′-Dichloro-4′-methoxyphenylquinone

3′,5′-Dichloro-4′-methoxyphenylquinone (1.0 g) was added to acetic anhydride (15 ml) and concentrated sulfuric acid (2 drops). The mixture was stirred at 60° for 16 h, during which it darkened considerably. The solution was poured into ice water, with stirring. The aqueous layer was decanted and the residual oil dissolved in ethanol. The ethanol was evaporated to dryness on a rotary evaporator and the residue was washed with ether. The product crystallized from ethanol (0.48 g), m.p. 150–152°. Recrystallization from ethanol with Darco G60 gave white crystals, m.p. 150.5–152.5°. An n.m.r. spectrum showed the two sets of phenyl protons with no coupling in the tetra-substituted ring, thus indicating that this was the para isomer.

Anal. Calcd. for $C_{19}H_{16}O_7Cl_2$: C, 53.4; H, 3.8; Cl, 16.6. Found: C, 53.4; H, 4.0; Cl, 16.9.

To determine the yield of this isomer, the preceding reaction was run at 45° for 72 h. The solution was condensed in benzene and extracted with cold 1 *N* sodium hydroxide. The organic layer was washed twice with water and once with a saturated sodium chloride solution. Removal of the benzene gave 1.59 g of a brown oil. Vapor-phase chromatographic analysis with an 8 ft silicone oil column at 250° showed only two fractions (35% and 65%), having retention times of 12 and 23 min, respectively. The major fraction was identified as the para isomer by the matching of retention times.

The identity of the second component was determined by n.m.r. The preceding reaction was rerun. The brown oil was chromatographed rapidly on silica gel with ether–ligroin (3:2), giving a yellow oil whose infrared spectrum showed differences from that of the para isomer. This sample was rechromatographed with ether–ligroin (3.5:6.5) on silica gel, giving a deep-yellow first fraction and a larger second fraction. The column was washed with ether, giving a third fraction. Infrared spectra showed the second and third fractions to be the same. These were combined and shown by v.p.c. to contain 76% of the unknown material and 24% of the para isomer. An n.m.r. spectrum of this sample showed three lines of a quartet with a coupling constant of 4 c.p.s., indicating that the second fraction was the meta isomer. The fourth line of the quartet appeared to fall under the protons of the other phenyl ring.

3′,5′-Dichloro-4′-methoxyphenylquinone

4-Amino-2,6-dichlorophenol hydrochloride (50 g) was dissolved in warm water (500 ml); acetic anhydride (125 ml) was added, with stirring, causing the temperature to rise to 75° and giving a clear solution. After the mixture had stood overnight, the gray crystals were removed by filtration, m.p. 158–160°, with sintering at 148°. The product was dissolved in ethanol (100 ml), treated with Darco G60, and poured into water (2 000 ml) to give 29.9 g, m.p. 155–158°.

A mixture of the preceding product (27 g), methyl iodide (18 g), potassium carbonate (17.2 g), and acetone (150 ml) was stirred and refluxed for 18 h. The potassium carbonate was separated by filtration and the solution condensed to half of its original volume under reduced pressure. The addition of water (400 ml) containing some sodium hydroxide gave white fluffy crystals. The product was collected by filtration, washed with water, and dried, yielding 23.0 g, m.p. 194.5–196.5°.

A solution of methanol (190 ml), water (63 ml), and potassium hydroxide (88 g) was deaerated with nitrogen, and the preceding product (22.0 g) was added under a nitrogen atmosphere. After this solution had been refluxed for 3 h under nitrogen, it was cooled and poured into water (1 200 ml), with stirring. The white crystals were removed by filtration and dissolved in ether. Treatment of the ether solution with dry hydrogen chloride gave 19.7 g of a white solid, melting at 201–231°, with decomposition.

The following diazotization and coupling reactions were run with an unintentional excess of reagents. The preceding product (19.0 g) was mixed with water (160 ml) and concentrated hydrochloric acid (20 ml) to give a slurry at 0–5°. To this was added, with stirring, a solution of sodium nitrite (6.2 g) in water (12 ml). After 45 min, this material was removed by filtration and added, over $\frac{1}{2}$ h, to a mixture of quinone (9.6 g), sodium acetate (25 g), and ice water (750 ml). This mixture was stirred until it reached room temperature, and then filtered; the solid was recrystallized from acetic acid–water to give 13.2 g, m.p. 130–137°. A second recrystallization gave 11.8 g, melting at 134–138°, with sintering at 130°.

Anal. Calcd. for $C_{13}H_8O_3Cl_2$: C, 55.6; H, 2.9; Cl, 24.6. Found: C, 55.2; H, 3,2; Cl, 25.0.

Acetylation of 4′-Nitrophenylquinone

4′-Nitrophenylquinone (16.0 g) was mixed with acetic anhydride (160 ml) and concentrated sulfuric acid (3 ml). The solution was stirred at 45° for 3 days, and the solvents were removed on a rotary evaporator at 45°. The viscous oil was dissolved in chloroform and then extracted twice with a 5% sodium bicarbonate solution. The organic layer was washed twice with water, once with a 5% sodium bisulfite solution, and finally twice with water. The chloroform was evaporated, giving 26.6 g of an oil (95%).

Since previous attempts at v.p.c. had failed, this product was converted into its trimethoxy ether derivative. The preceding oil (13.3 g) was mixed with ethanol (200 ml) into which some dry hydrogen chloride had been bubbled. The resulting solution was heated at 55° for 19 h, after which the solvent was removed under reduced pressure. Acetone (200 ml) was added, followed by methyl iodide (20.5 g) and potassium carbonate (18 g). This mixture was refluxed for 4 h, the potassium carbonate was removed by filtration, and the solvents were removed under reduced pressure. The resulting solid was washed with water and dried (yield 10.2 g). The overall yield from 4′-nitrophenylquinone was 93%.

Vapor-phase chromatography was effected by using a 2 ft silicone rubber column at 228°. The average of six runs showed three peaks of relative areas (corrected for the overall yield) of 18.4 ± 0.5, 19.0 ± 0.6, and 55.7 ± 0.8.

The acetone was removed under reduced pressure and the oil dissolved in ether, from which two crops of yellow crystals were obtained (yield 3.10 g), m.p. 114.5–117.0°, with sintering at 110.5°. This was the major component. An n.m.r. spectrum showed no coupling of the tetra-substituted phenyl protons, indicating that this was the para isomer.

Anal. Calcd. for $C_{15}H_{15}NO_5$: C, 62.3; H, 5.2; N, 4.8. Found: C, 62.4; H, 5.2; N, 4.8.

A third crystalline crop of 1.25 g, having the composition 57:12:31, was obtained from the preceding ether solution. This material was dissolved in acetone, and the acetone was allowed to evaporate until about half of the product had crystallized, whereupon the acetone solution was decanted. Three such recrystallizations gave a sample of a pure (shown by v.p.c.) first fraction as yellow platelets, m.p. 129.5–131.5°, with sintering at 127°. An n.m.r. spectrum showed a coupling constant of 9 c.p.s. for the two phenyl protons, thus identifying this compound as the ortho isomer.

Anal. Found: C, 61.9; H, 5.1; N, 4.8.

From the preceding acetone solution, 1 g of a solid having the composition 40:60:1 was isolated. The second fraction was collected by v.p.c. at 285° on silicone rubber. This isomer was obtained as fine yellow needles, m.p. 128.5–130.5°. Vapor-phase chromatography of this sample showed that it contained 3.4% of the ortho isomer. An n.m.r. spectrum showed this sample to have a coupling constant of 3 c.p.s., indicating that it was the meta isomer. The n.m.r. spectrum also showed small amounts of what appeared to be silicone rubber impurities. In view of the impurity of this sample, no combustion analysis was performed. The infrared and n.m.r. spectra for this compound were consistent with those of the ortho and para isomers.

Acetylation of Phenylquinone

Phenylquinone (27.6 g) was mixed with acetic anhydride (250 ml) and concentrated sulfuric acid (3.5 ml). The solution was stirred at 65° for 4 h, and then poured into cold water (700 ml), with stirring. The aqueous layer was decanted and the oil was again washed with water. Ether was added and the resulting white powder separated by filtration with the aid of ether and ligroin; 20.2 g was obtained. Two further crops of this material (0.50 g and 1.73 g) were obtained from the filtrates. An n.m.r. spectrum of this product showed no coupling between the tetra-substituted phenyl protons, indicating that this was the para isomer. An infrared spectrum of this material was identical with that of a sample prepared in a similar run, in which the product was recrystallized from ethanol after treatment with Norit, m.p. 141.0–142.5° (lit. (7) m.p. 135–138°).

The solvents were removed from the filtrates, giving 21.9 g of an oil. In a previous run, v.p.c. analysis had shown that 13% of the reaction product was unreacted phenylquinone. This contaminant was removed by dissolving the oil in ethanol and reducing it with Raney nickel. The catalyst was removed by using a Celite pad, and the ethanol was removed under reduced pressure. The resulting oil was dissolved in ether and extracted with 2% sodium hydroxide. The ether solution was washed with water and then with saturated sodium chloride solution. After the solution was dried over sodium sulfate, the ether was evaporated, giving 16.6 g of an oil. Vapor-phase chromatographic analysis on a 6 ft silicone rubber column at 272° showed this oil to have three components (20.1:60.6:18.8). With a silicone rubber preparative column, the pure first fraction was obtained. An n.m.r. spectrum showed only two methyl groups, indicating a diacetate. The n.m.r. and infrared spectra of this product were identical with those of an authentic sample of 2,5-diacetoxybiphenyl, except for small impurities attributable to silicone rubber contaminants.

Boron Trifluoride Acetylation of Toluquinone

Toluquinone (8.0 g) was added to acetic anhydride

(40 ml) and boron trifluoride etherate (2 ml). The mixture generated heat within 10 min, and was then allowed to stand for 2 h. After the mixture had been poured onto ice, it was stirred for 1 h. The semisolid precipitate was dissolved in benzene (450 ml). This solution was washed with 5% sodium bicarbonate (100 ml) and then with water (100 ml). Evaporation of the solvent gave 17.0 g of an oil. Crystallization from ethanol gave 11.0 g of the 2,5-isomer, melting at 101–103°. The remaining oil (5.9 g) was chromatographed on a 6 ft silicone rubber column at 165°, and showed 31% of the 2,3,5-triacetoxy isomer and 69% of the 2,4,5-triacetoxy isomer.

Boron Trifluoride Acetylation of Phenylquinone

Phenylquinone (6.0 g) was added to acetic anhydride (20 ml) and boron trifluoride etherate (1 ml). The mixture was swirled at room temperature for 15 min, during which a solution was obtained. After the latter had stood for 1.5 h, it was poured onto ice and extracted with ether. The ether solution was treated with Norit and filtered. Evaporation gave a quantitative amount of an oil. Vapor-phase chromatography of this oil on a 6 ft silicone rubber column at 259° showed 6.4% 2,5-diacetoxybiphenyl, 1.3% unknown, 30.8% unknown, and 61.6% 2,4,5-triacetoxybiphenyl.

2,3,6-Trimethoxybiphenyl

The preceding reaction was repeated twice on a fourfold scale; the products were combined after partial crystallization and separation of the 2,5-isomer from alcohol. The oil was dissolved in benzene and washed successively with 5% sodium bisulfite, 5% sodium bicarbonate, and water. After evaporation of the benzene, v.p.c. of the resulting 35 g of oil showed 2% 2,5-diacetoxybiphenyl, 80% unknown, and 18% of the 2,4,5-triacetoxy isomer. Distillation of the oil gave an 8 g fraction, boiling at 105° and 0.001 mm, whose composition was shown by v.p.c. to be 3% 2,5-diacetoxybiphenyl, 89% unknown, and 8% of the 2,4,5-triacetoxy isomer. The presence of 2,5-diacetoxybiphenyl was due to some phenylhydroquinone impurity in the phenylquinone sample.

The sample was refluxed for 18 h in methanol (250 ml) containing some dry hydrogen chloride. Evaporation to dryness gave a semisolid residue, a sample of which darkened rapidly on exposure to air. This semisolid was refluxed for 18 h in acetone (150 ml) containing methyl iodide (18 g) and potassium carbonate (15 g). Dilution with water (200 ml) and evaporation of the acetone gave a brown solid. Two recrystallizations from alcohol gave 2.2 g of a tan solid, m.p. 91–92°. An additional 1.1 g was obtained from the mother liquors.

An n.m.r. spectrum of this compound in deuteriochloroform showed an AB quartet at 3.26 τ for the two ring protons, with a coupling constant of 9 c.p.s. This compound was therefore the ortho isomer.

Anal. Calcd. for $C_{15}H_{16}O_3$: C, 73.8; H, 6.5. Found: C, 73.6; H, 6.8.

Acetylation of 2,3,5-Trimethylquinone

2,3,5-Trimethylquinone (6.0 g) was dissolved in acetic anhydride (20 ml), and boron trifluoride etherate (1 ml) was added. After the solution had stood at room temperature for 6 days, it was diluted with ice water and allowed to warm for 1 h, with stirring. The pale cream colored solid was removed by filtration and washed well with ethanol to give 7.27 g, m.p. 148.5–151.5°, with sintering at 142.5° (61.6% yield). An infrared spectrum was consistent with the proposed structure, 3,5,6-triacetoxytrimethylbenzene. An analytical sample was prepared by recrystallization from alcohol, m.p. 148–149°.

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.2; H, 6.2. Found: C, 61.0; H, 6.6.

Acetylation of 2,3-Dimethylquinone

2,3-Dimethylquinone (6.0 g) was dissolved in acetic anhydride (20 ml), and boron trifluoride etherate (1 ml) was added. After the solution had stood for 1.5 h at room temperature, it was poured onto ice (200 g) and stirred for 30 min. The solid was collected by filtration and washed with water. Recrystallization from ethanol gave 11.1 g, m.p. 88–90° (90% yield). An infrared spectrum was consistent with the proposed structure, 1,2-dimethyl-3,4,6-triacetoxybenzene.

Anal. Calcd. for $C_{14}H_{16}O_6$: C, 60.0; H, 5.7. Found: C, 59.7; H, 5.5.

2-Methyl-1,3,4-triacetoxynaphthalene

A suspension of 2-methyl-1,4-naphthoquinone (6.0 g) in acetic anhydride (30 ml) containing boron trifluoride etherate (3 ml) was allowed to stand at room temperature for 5 days, with occasional shaking; at the end of the second day the solid material had dissolved. The solution was poured onto ice and stirred for 1 h; then the dark solid material was extracted with ether. The ether extracts were combined, washed with water, with a saturated bicarbonate solution, and with water, dried, and treated with charcoal. Upon evaporation, a tan solid remained, which was dissolved in hot ethanol and chilled, to yield 5.2 g of product (52%), m.p. 142–144°. An infrared spectrum showed only ester carbonyl groups. Recrystallization from ethanol–ligroin gave crystals melting at 144–145°. Infrared analysis of the residue remaining after evaporation of the filtrate showed a mixture of the product and starting material.

Anal. Calcd. for $C_{17}H_{16}O$: C, 64.4; H, 5.4. Found: C, 64.3; H, 5.5.

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