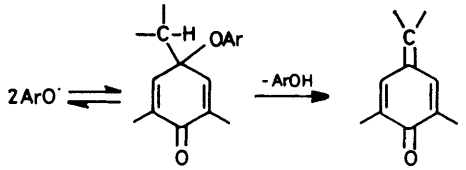
Acid-catalysed Rearrangement of 2,3,4,5-Tetrahydrobenz[*b*]oxepin-2-spirocyclohexa-2′,5′-dien-4′-one and 3′,5′,7,9-Tetra-t-butyl-2,3,4,5-tetrahydrobenz[*b*]oxepin-2-spirocyclohexa-2′,5′-dien-4′-one. Evidence for a Quinone Methide Intermediate

By **Matti Karhu**, Department of Chemistry, University of Helsinki, Vuorikatu 20, SF–00100 Helsinki 10, Finland

The title compounds have been obtained in 29 and 43% yield, respectively, by ferricyanide oxidation of the appropriate diphenols. Acid hydrolysis of the unsubstituted dienone leads to dienone–phenol rearrangement or ring opening depending on the concentration of the acid used in the hydrolysis. Under similar conditions the t-butylated dienone rearranges to a chroman which provides strong evidence for a quinone methide intermediate in this reaction.

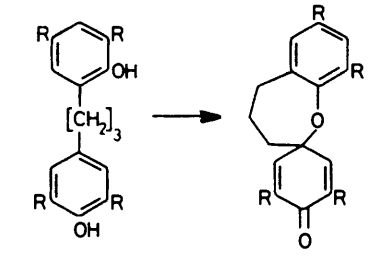
QUINONE methides of type (B) have been postulated [1] to arise from phenoxyl radicals *via* quinol ethers (A) in



(A) (B)

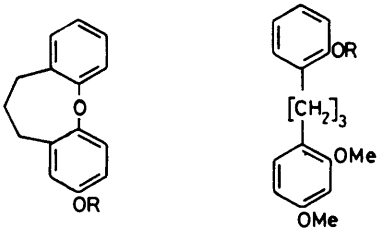
enzymatic and other phenol oxidations. Previous studies have shown that spirocyclic dienones undergo dienone–phenol rearrangement [2] or ring opening [3] under acidic conditions. To test the possible effect of substituents on the formation of quinone methides the spirocyclic dienones (3) [4] and (4) have been prepared and subjected to acid hydrolysis.

The aldehyde (9) was prepared from 2,4-di-t-butylphenol by hydroxymethylation with formaldehyde, followed by oxidation over active manganese dioxide.



(1) R = H
(2) R = Bu^t

(3) R = H
(4) R = Bu^t

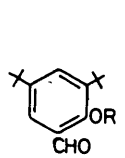


(5) R = Me
(6) R = COMe

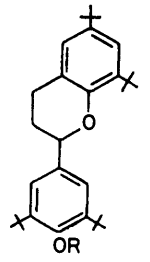
(7) R = H
(8) R = Me

Treatment of the potassium salt of this aldehyde with benzyl chloride gave the benzyl ether (10), which was condensed with 3,5-di-t-butyl-4-hydroxyacetophenone to 2-benzyloxy-4′-hydroxy-3,3′,5,5′-tetra-t-butylchalcone.

Catalytic reduction of the chalcone over Raney nickel gave a mixture of products which showed aliphatic t-butyl groups in the n.m.r. Obviously the basic catalyst converts the chalcone to a sodium salt which is



(9) R = H
(10) R = PhCH$_2$



(11) R = H
(12) R = COMe

reduced to a substituted cyclohexanone through the tautomeric dienone form of the salt. When palladised charcoal was used as catalyst the chroman (11) was formed through ring–chain tautomerism of the dihydrochalcone. By increasing the temperature the chalcone could be reduced to the desired diphenol (2).

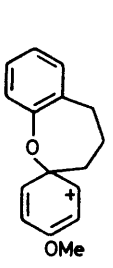
The diphenol (1) was obtained from the dibenzyl ether of the corresponding chalcone by catalytic reduction over Raney nickel.

Oxidation of the diphenols (1) and (2) with alkaline potassium ferricyanide gave the spirodienones (3) and (4) in 29 and 43% yield, respectively.

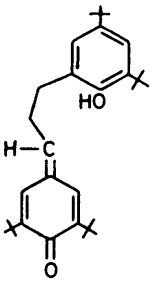
In 30% methanolic sulphuric acid the dienone (3) underwent dienone–phenol rearrangement with alkyl group migration to give (5), whereas in 3% acid it gave the ring-opened product (7). The structure of (5) was confirmed by a combination of ^{13}C and ^1H n.m.r. analysis,[5] and that of the methylated ring-opened product (8) by synthesis.

In dilute methanolic sulphuric acid the cation (13), which seems to be the primary intermediate for both pathways, undergoes nucleophilic addition of the solvent, followed by cleavage of the ether linkage.[6] The foregoing results and the rearrangement in acetic anhydride,

described later, indicate that these two modes of rearrangement of the unsubstituted dienone depend on the nucleophilicity of the solvent and the concentration of the acid used in the hydrolysis.



(13)



(14)

Rearrangement of the t-butylated dienone (4) in methanol with *ca.* 10% sulphuric acid gave the chroman (11).

In acetic anhydride with a trace of concentrated sulphuric acid the dienone (3) rearranged nearly quantitatively to 2-acetoxy-11,12-dihydro-10*H*-dibenz[*b*,*g*]-oxocin (6), which gave (5) by hydrolysis and methylation.

Under similar conditions the dienone (4) afforded the acetate (12) in 45% yield. The structure assigned to the rearrangement product is based on mixed m.p. determination and comparison of spectra with those of 2-(4-acetoxy-3,5-di-t-butylphenyl)-6,8-di-t-butylchroman obtained by acid-catalysed acetylation of the chroman (11).

These results clearly show that dienone–phenol rearrangement and ring-opening are inhibited in the t-butyl substituted dienone. The structures of the rearrangement products (11) and (12) strongly suggest the quinone methide (14) as an intermediate, formed from the dienone (4) by acid-catalysed elimination. The free phenol then reacts intramolecularly with the methine group to give (11) in methanol or (12) in acetic anhydride. The formation of the quinone methide is obviously due to the steric hindrance by the bulky alkyl groups at the 2- and 6-positions in the dienone ring.

EXPERIMENTAL

M.p.s were determined with a m.p. microscope (Zeiss), and are uncorrected. I.r. spectra were recorded with a Perkin-Elmer 125 spectrophotometer and n.m.r. spectra with a JEOL JMN-PMX60 spectrometer for solutions in deuteriochloroform. Mass spectra were obtained with a JEOL JMS-01SG-2 instrument. Precoated, 2-mm thick plates (Merck Kieselgel 60 F_{254}) were used for preparative t.l.c. Light petroleum had boiling range 40—60 °C.

2,4′-*Dibenzyloxychalcone*.—To a stirred suspension of 2-benzyloxybenzaldehyde [7] (14.9 g) and 4-benzyloxyacetophenone [8] (15.8 g) in methanol (100 ml) was added a solution of sodium (0.5 g) in methanol (10 ml). Stirring was continued overnight at room temperature, the precipitate collected, washed with methanol (40 ml), and dried to give the *chalcone* (25.7 g, 87.4%) as pale yellow crystals, m.p. 96—98° (from ethanol), δ 7.37 (10 H, s, Ar-H), 7.9—6.8 (10 H, m, Ar-H and CH=CH), and 5.1 (4 H, s, 2 × OCH_2Ar); *m/e* 420 (M^+, 2.6%) (Found: C, 83.2; H, 5.5. $C_{29}H_{24}O_3$ requires C, 82.8; H, 5.8%).

2,4-*Di-t-butylphenol*.—Phenol (188 g) was alkylated by the method described earlier [9] until t.l.c. [cyclohexane–ethyl acetate (8 : 1)] showed a trace of 2,4,6-tri-t-butylphenol; the mixture was then poured into a stirred solution of sodium hydroxide (100 g) in water (2 800 ml). The sodium salt of 4-t-butylphenol was filtered off. The organic layer was separated, stirred with 2M-hydrochloric acid (800 ml), and separated again. Drying ($MgSO_4$) and evaporation yielded a yellow oil. Distillation under vacuum gave 2,4-di-t-butylphenol as an oil (291 g, 72%), b.p. 128—129° at 10 mmHg (lit.,[10] 120—130.5° at 10 mmHg), which solidified, m.p. 54—55° (lit.,[9] 54—55°), δ 7.28 (1 H, d, *J* 2 Hz, 3-H), 7.05 (1 H, dd, *J* 2 and 8 Hz, 5-H), 6.47 (1 H, d, *J* 8 Hz, 6-H), 4.53 (1 H, s, OH), and 1.43 and 1.30 [9 H, s, $C(CH_3)_3$].

3,5-*Di-t-butyl*-2-*hydroxybenzyl Alcohol*.—The method of Claus *et al.*[11] was slightly modified. Arsenic trioxide (0.3 g) in 2% sodium hydroxide (15 ml) and 35% formalin (67 ml) were added to a stirred solution of 2,4-di-t-butylphenol (103 g), 20% aqueous potassium hydroxide (160 ml), and methanol (70 ml). Methanol (180 ml) was then added until the mixture turned to a clear brownish solution and the stirring was continued for 48 h at room temperature. The reaction mixture was poured into water (700 ml) and the resulting suspension acidified with 2M-hydrochloric acid. Filtration and recrystallisation from n-hexane gave the benzyl alcohol as needles (71.6 g, 60.7%), m.p. 99—100° (lit.,[11] 99—100°).

3,5-*Di-t-butyl*-2-*hydroxybenzaldehyde* (9).—3,5-Di-t-butyl-2-hydroxybenzyl alcohol (49.6 g) in ether (70 ml) was added to a vigorously stirred suspension of active manganese dioxide [12] (120 g) in ether (300 ml). After stirring at room temperature for 4 h the oxidant was removed by filtration and the filtrate evaporated to give a green oil (54.1 g), which partly solidified on standing at room temperature. Recrystallisation from ethanol afforded the benzaldehyde as pale yellow prisms (37.3 g, 76%), m.p. 60—61° (lit.,[13] 61.5—63.0°), δ 11.7 (1 H, s, OH), 9.88 (1 H, s, CHO), 7.62 and 7.35 (1 H, d, *J* 2 Hz, Ar-H), and 1.43 and 1.35 [9 H, s, $C(CH_3)_3$].

2-*Benzyloxy*-3,5-*di-t-butylbenzaldehyde* (10).—3,5-Di-t-butyl-2-hydroxybenzaldehyde (35.2 g) was dissolved in a solution of potassium hydroxide (9.8 g) in 99.5% ethanol (150 ml). Evaporation of the solution under vacuum at 60° afforded a yellow solid. Toluene (200 ml) was added and the suspension was evaporated as before to give the potassium salt of the aldehyde (9) as a yellow powder.

To the suspension of this salt in dimethylformamide (150 ml) was added benzyl chloride (20 ml). After stirring at 50° for 5 h the yellow solution was poured into water (1 000 ml). The precipitate was filtered off, washed with water, and recrystallised from ethanol to give the *benzyl ether* as crystals (41.5 g, 85.4%), m.p. 96—97°, $\nu_{max.}$ (KBr) 1 680 cm^{-1}; δ 10.38 (1 H, s, CHO), 7.80 and 7.68 (1 H, d, *J* 3 Hz, Ar-H), 7.55—7.30 (5 H, m, Ar-H), 5.05 (2 H, s, OCH_2Ar), and 1.47 and 1.35 [9 H, s, $C(CH_3)_3$]; *m/e* 324 (M^+, 15%) (Found: C, 81.6; H, 8.4. $C_{22}H_{28}O_2$ requires C, 81.4; H, 8.7%).

3′,5′-*Di-t-butyl*-4′-*hydroxyacetophenone*.— 2,6-Di-t-butylphenol (62 g) in carbon disulphide (50 ml) was added during 0.5 h at 0° to a stirred mixture of aluminium chloride (48 g) and acetyl chloride (27 ml) in carbon disulphide (180 ml). Stirring was continued for a further 1 h at 0°. Isolation of

the product in the usual manner and recrystallisation from light petroleum (b.p. 80—110°) afforded the acetophenone as crystals (33.0 g, 44.4%), m.p. 150—151° (lit.,[14] 147—148°), δ 7.87 (2 H, s, Ar-H), 5.73 (1 H, s, OH), 2.57 (3 H, s, $COCH_3$), and 1.48 [18 H, s, $C(CH_3)_3$].

2-Benzyloxy-4'-hydroxy-3,3',5,5'-tetra-t-butylchalcone.— 2-Benzyloxy-3,5-di-t-butylbenzaldehyde (16.2 g) and 3,5-di-t-butyl-4-hydroxyacetophenone (12.4 g) were dissolved in a solution of potassium t-butoxide (8.4 g) in t-butyl alcohol (130 ml). The mixture was heated at 70° for 3 h and allowed to stand at room temperature overnight. The dark red precipitate was filtered off and washed with t-butyl alcohol (30 ml) to give the potassium salt of the chalcone as a red powder, $\nu_{max.}$ (KBr) 1 625 and 1 590 cm^{-1}. This salt was suspended in water (400 ml). Acidification of the orange suspension with concentrated hydrochloric acid, followed by filtration and drying yielded the *chalcone* as pale yellow crystals (22.8 g, 82.3%), m.p. 180—181° (from ethanol), $\nu_{max.}$ (KBr) 3 545, 1 650, 1 645, and 1 595 cm^{-1}; δ 8.1—7.25 (6 H, m, Ar-H and CH=CH), 5.73 (1 H, s, OH), 4.93 (2 H, s, OCH_2Ar), 1.48 [27 H, s, $C(CH_3)_3$], and 1.38 [9 H, s, $C(CH_3)_3$]; *m/e* 554 (M^+, 6%) (Found: C, 82.6; H, 8.9. $C_{38}H_{50}O_3$ requires C, 82.3; H, 9.1%).

1-(2-Hydroxyphenyl)-3-(4-hydroxyphenyl)propane (1).—A solution of 2,4'-dibenzyloxychalcone (12.6 g) in tetrahydrofuran (THF) (90 ml) and ethanol (90 ml) was stirred with Raney nickel (*ca.* 5 g) at room temperature and 1 atm H_2 for 20 h. The catalyst was removed by filtration and the filtrate evaporated under vacuum to give the diphenol as an oil (7.2 g), which t.l.c. [cyclohexane–ethyl acetate (1 : 1)] showed to consist of a single compound, δ 7.2—6.6 (8 H, m, Ar-H), 4.55 (2 H, s, 2 × OH), 2.62 and 2.60 (2 H, t, $ArCH_2$), and 2.1—1.75 (2 H, m, $CH_2CH_2CH_2$). This oil was used directly for oxidation.

2-(3,5-Di-t-butyl-4-hydroxyphenyl)-6,8-di-t-butylchroman (11).— 2-Benzyloxy-4'-hydroxy-3,3',5,5'-tetra-t-butylchalcone (2.8 g) in toluene was hydrogenated over Pd–C (0.3 g; Koch–Light; 10% Pd) in a rocking autoclave (500 ml) at 120—125° and 100 atm H_2 for 8 h. The catalyst was filtered off and the solvent evaporated under vacuum. Crystallisation from ethanol afforded the *chroman* (11) as needles (2.1 g, 93.3%), m.p. 138—139°, $\nu_{max.}$ (KBr) 3 625 cm^{-1}; δ 7.28 (2 H, s, Ar-H), 7.20 and 6.79 (1 H, d, *J* 2 Hz, Ar-H), 5.17 (1 H, s, OH), 4.97 (1 H, dd, *J* 3 and 9 Hz, ArCHROAr), 3.15—2.85 (2 H, m, $ArCH_2$), 2.3—1.9 (2 H, m, $ArCH_2CH_2$), 1.47 [18 H, s, $C(CH_3)_3$], and 1.43 and 1.32 [9 H, s, $C(CH_3)_3$]; *m/e* 450 (M^+, 100%) (Found: C, 82.5; H, 10.0. $C_{31}H_{46}O_2$ requires C, 82.6; H, 10.3%).

1-(3,5-Di-t-butyl-2-hydroxyphenyl)-3-(3,5-di-t-butyl-4-hydroxyphenyl)propane (2).—(a) *Reduction over* Pd–C. 2-Benzyloxy-4'-hydroxy-3,3',5,5'-tetra-t-butylchalcone (4.2 g in ethanol (100 ml) was hydrogenated at 145—150° and 120 atm H_2 over Pd–C (0.2 g) (Fluka AG; 5% Pd) in a rocking autoclave for 8 h. Filtration and evaporation of the filtrate under vacuum gave the diphenol (2) as an oil (3.5 g), δ 7.15 (1 H, d, *J* 2 Hz, Ar-H), 7.05—7.0 (3 H, s, Ar-H), 5.02 and 4.58 (1 H, s, OH), 2.8—2.45 (4 H, m, $ArCH_2$), 2.15—1.9 (2 H, m, $CH_2CH_2CH_2$), 1.42 [27 H, s, $C(CH_3)_3$], and 1.30 [9 H, s, $C(CH_3)_3$], which t.l.c. showed to contain a small amount of the chroman (11). This oil was used for oxidation without purification.

(b) *Reduction over* Pd–$BaSO_4$. The chalcone (1.4 g) in THF (70 ml) was hydrogenated at 165—170° and 150 atm H_2 over Pd–$BaSO_4$ (0.3 g) (Koch–Light; 5% Pd) for 9 h. Isolation as before gave the diphenol (2) as an oil (1.15 g). According to n.m.r. the diphenol contained a small amount of a compound which had been reduced to a substituted cyclohexanol.

2,3,4,5-Tetrahydrobenz[b]oxepin-2-spirocyclohexa-2',5'-dien-4'-one (3).—The diphenol (1) (4.8 g) in 2M-sodium hydroxide (200 ml) and water (400 ml) was added dropwise during 2.5 h to a vigorously stirred mixture of potassium ferricyanide (26.3 g), water (1 000 ml), and light petroleum (1 800 ml) under nitrogen. The organic layer was separated, dried ($MgSO_4$), and evaporated at 40° under vacuum to afford a pale yellow solid. Recrystallisation from light petroleum gave the *spirodienone* (3) as needles (1.4 g, 29.2%), m.p. 85—86°, $\nu_{max.}$ (KBr) 1 690, 1 665, 1 630, and 1 605 cm^{-1}; δ 7.2—6.7 (6 H, m, Ar-H and C*H*=CH), 6.1 (2 H, d, *J* 11 Hz, α-' dienone ' H), 3.1—2.7 (2 H, m, $ArCH_2$), and 2.0—1.6 (4 H, m, CH_2CH_2); *m/e* 226 (M^+, 25%) (Found: C, 79.8; H, 6.5. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

3',5',7,9-Tetra-t-butyl-2,3,4,5-tetrahydrobenz[b]oxepin-2-spirocyclohexa-2',5'-dien-4'-one (4).—The diphenol (2) (0.9 g) in light petroleum (200 ml) was added dropwise during 3 h to a vigorously stirred mixture of potassium ferricyanide (2.6 g), water (300 ml), 2M-sodium hydroxide (40 ml), and light petroleum (300 ml) under nitrogen. Evaporation of the dried ($MgSO_4$) light petroleum layer at room temperature under vacuum gave a dark red oil. Preparative t.l.c. (cyclohexane) gave the *dienone* (4) as a solid (390 mg, 43.3%), m.p. 40° (starts to decomp.), $\nu_{max.}$ (KBr) 1 665, 1 640, and 1 618 cm^{-1}; δ 7.2 and 7.0 (1 H, d, *J* 3 Hz, Ar-H), 6.62 (2 H, s, ' dienone ' H), 3.0—2.7 (2 H, m, $ArCH_2$), 2.0—1.6 (4 H, m, CH_2CH_2), 1.30 and 1.23 [9 H, s, $C(CH_3)_3$], and 1.13 [18 H, s, $C(CH_3)_3$]; *m/e* 450 (M^+, 58%) (Found: C, 82.5; H, 10.3. $C_{31}H_{46}O_2$ requires C, 82.6; H, 10.3%). All attempts to crystallise this dienone failed.

Rearrangement of the Dienone (3).—(a) *In 30% methanolic sulphuric acid.* The dienone (450 mg) was dissolved with stirring at room temperature in a mixture of concentrated sulphuric acid (9 ml) and methanol (21 ml). The solution was stirred for a further 5 min, then poured onto crushed ice, and extracted with ether (3 × 30 ml). The extracts were washed with saturated sodium hydrogencarbonate solution (2 × 40 ml) and water (40 ml) and dried ($MgSO_4$). Evaporation of the solvent gave the *methyl ether* (5) as a yellowish oil (420 mg, 87.9%), which showed a single compound on t.l.c. [cyclohexane–ethyl acetate (4 : 1)], $\nu_{max.}$ (neat film) 3 060, 2 040, 1 610, 1 580, 1 480, 1 220, 1 035, and 740 cm^{-1}; δ 7.3—6.5 (7 H, m, Ar-H), 3.73 (3 H, s, OCH_3), 2.78 and 2.73 (2 H, t, $ArCH_2$), and 2.0—1.7 (2 H, m, $CH_2CH_2CH_2$) (Found: C, 80.2; H, 6.8. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%).

(b) *In 3% methanolic sulphuric acid.* Concentrated sulphuric acid (2 ml) was added to a solution of the dienone (1.2 g) in methanol (60 ml) and the mixture was stirred at room temperature overnight. Isolation as above gave a yellow oil (1.3 g) which was purified by preparative t.l.c. (two plates) in cyclohexane–ethyl acetate–methanol (7 : 1 : 1) to give the *dimethyl ether* (7) as an oil (1.06 g, 74.2%), $\nu_{max.}$ (neat film) 3 410 cm^{-1}; δ 7.2—6.3 (7 H, m, Ar-H), 5.07 (1 H, s, OH), 3.77 (6 H, s, 2 × OCH_3), 2.63 (4 H, t, 2 × $ArCH_2$), and 2.15—1.75 (2 H, m, $CH_2CH_2CH_2$) (Found: C, 74.6; H, 7.4. $C_{17}H_{20}O_3$ requires C, 75.0; H, 7.4%). Methylation of the product (500 mg) with dimethyl sulphate in 2M-sodium hydroxide gave the trimethyl ether (8) (400 mg), which had identical i.r. and n.m.r. spectra with those of synthetic (8).

1-(2-*Methoxyphenyl*)-3-(2,4-*dimethoxyphenyl*)*propane* (8).—2,2′,4′-Trimethoxychalcone [15] (9.0 g) in THF (70 ml) was hydrogenated over Raney nickel (*ca.* 2 g) in a rocking autoclave (500 ml) at 130—135° and 100 atm H_2 for 4 h. Filtration, evaporation of the filtrate, and distillation of the product under vacuum afforded the *trimethyl ether* (8) as an oil (5.1 g, 59.4%), b.p. 226—227° at 10 mmHg, $\nu_{max.}$ (neat film) 2 990, 2 930, 1 605, 1 580, 1 490, 1 455, 1 280, 1 235, and 1 200 cm^{-1}; δ 7.2—6.3 (7 H, m, Ar-H), 3.77 (6 H, s, 2 × OCH_3), 3.75 (3 H, s, OCH_3), 2.67 and 2.63 (2 H, t, $ArCH_2$), and 2.1—1.7 (2 H, m, $CH_2CH_2CH_2$) (Found: C, 75.1; H, 8.0. $C_{18}H_{22}O_3$ requires C, 75.0; H, 7.7%).

Rearrangement of the Dienone (3) *in Acetic Anhydride.*—A solution of the dienone (3) (250 mg) in acetic anhydride (20 ml) was treated with concentrated sulphuric acid (2 drops) and stirred at room temperature for 4 h, then poured onto crushed ice, and stirred for 2 h. The oil was extracted into ether (3 × 30 ml). The extracts were washed with saturated sodium hydrogencarbonate solution and water, dried ($MgSO_4$), and evaporated to give the *acetate* (6) as crystals (284 mg, 95.6%), m.p. 44—45° (from light petroleum), $\nu_{max.}$ (KBr) 1 745 cm^{-1}; δ 7.3—6.8 (7 H, m, Ar-H), 2.9—2.6 (4 H, m, 2 × $ArCH_2$), 2.27 (3 H, s, $COCH_3$), and 2.1—1.7 (2 H, m, $CH_2CH_2CH_2$); *m/e* 268 (M^+, 40%) (Found: C, 75.9; H, 5.9. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0%). Hydrolysis of the acetate (250 mg) with sodium hydroxide in methanol–water (3 : 1) followed by methylation with dimethyl sulphate gave the methyl ether (5) (210 mg).

Rearrangement of the Dienone (4).—(a) *In methanol.* Sulphuric acid (2 ml) in methanol (3 ml) was added to a stirred solution of the dienone (4) (76 mg) in methanol (10 ml). The mixture was stirred for a further 5 h at room temperature, poured into water (50 ml), and extracted with ether (3 × 30 ml). The extracts were washed with saturated sodium hydrogencarbonate solution and water, dried ($MgSO_4$), and evaporated under vacuum to give a dark red oil, which t.l.c. showed to consist of a single compound and some u.v. fluorescent polymeric material. Two crystallisations from ethanol afforded the chroman (11) as pink needles (32.4 mg, 43.0%), m.p. 137—138°, i.r. and n.m.r. spectra identical to those of the chroman obtained by catalytic hydrogenation, mixed m.p. 136—137°.

(b) *In acetic anhydride.* The dienone (4) (190 mg) in acetic anhydride (15 ml) was treated with concentrated sulphuric acid (3 drops) and stirred at room temperature for 5 h. According to t.l.c. some polymeric material was formed as in the rearrangement in methanol. Isolation as above and recrystallisation of the partly crystalline red oil (183 mg) from ethanol afforded the *acetate* (12) as crystals (93 mg, 44.9%), m.p. 166.5—167.5°, $\nu_{max.}$ (KBr) 1 760 cm^{-1}; δ 7.45 (2 H, s, Ar-H), 7.22 and 6.98 (1 H, d, *J* 2 Hz, Ar-H), 5.07 (1 H, dd, *J* 3 and 10 Hz, $ArCHROAr$), 3.1—2.8 (2 H, m, $ArCH_2$), 2.35 (3 H, s, $COCH_3$), 2.35—2.1 (2 H, m, $ArCH_2CH_2$), 1.45 [9 H, s, $C(CH_3)_3$], 1.37 [18 H, s, $C(CH_3)_3$], and 1.30 [9 H, s, $C(CH_3)_3$]; *m/e* 492 (M^+, 100%) (Found: C, 80.4; H, 9.4. $C_{33}H_{48}O_3$ requires C, 80.4; H, 9.8%).

2-(4-*Acetoxy*-3,5-*di*-*t*-*butylphenyl*)-6,8-*di*-*t*-*butylchroman* (12).—A solution of the chroman (11) (200 mg), acetic anhydride (8 ml), and concentrated sulphuric acid (2 drops) was stirred at room temperature for 1.5 h. The solution was diluted with water (40 ml), stirred for a further 2 h, and extracted with ether (3 × 30 ml). The extracts were washed with saturated sodium hydrogencarbonate solution and water and dried ($MgSO_4$). Evaporation of the solvent yielded a pale yellow oil which was crystallised from ethanol to give the acetate (12) as crystals (117 mg, 55.5%), m.p. 166.5—167.5°, identical n.m.r. spectrum with that of the foregoing rearrangement product, mixed m.p. 166.5—167.5°.

I thank Professor G. Brunow for suggesting the problem and for his continued interest and advice. Financial support from the Research Foundation of Orion Corporation Ltd. and the Magnus Ehrnrooth Foundation is gratefully acknowledged.

[8/475 *Received*, 15*th March*, 1978]

REFERENCES

[1] K. V. Sarkanen, 'Lignins,' eds. K. V. Sarkanen and C. H. Ludwig, Wiley–Interscience, New York, 1971, p. 121; R. D. Parnell and K. E. Russel, *J.C.S. Perkin II*, 1974, 161.
[2] A. M. Choudhury, K. Schofield, and R. S. Ward, *J. Chem. Soc.* (*C*), 1970, 2543.
[3] A. H. Jackson and G. W. Stewart, *Tetrahedron Letters*, 1971, 4941; A. M. Choudhury, *J.C.S. Perkin I*, 1974, 132.
[4] Preliminary communication, G. Brunow and M. Karhu, *J.C.S. Chem. Comm.*, 1976, 753.
[5] M. Karhu and E. J. Rahkamaa, *Finn. Chem. Letters*, 1979, 15.
[6] A. J. Birch, A. H. Jackson, P. V. R. Shannon, and G. W. Stewart, *J.C.S. Perkin I*, 1975, 2492.
[7] M. Miyano, S. Muraki, T. Kusunoki, T. Morita, and M. Matsui, *Nippon Nogeikaguku Kaishi*, 1963, **34**, 683 (*Chem. Abs.*, 1963, **59**, 13,929c).
[8] H. M. Priestley and E. Moness, *J. Org. Chem.*, 1954, **5**, 355.
[9] M. S. Carpenter and W. M. Easter, *J. Org. Chem.*, 1954, **19**, 87.
[10] G. H. Stillson, D. W. Sawyer, and C. K. Hunt, *J. Amer. Chem. Soc.*, 1945, **67**, 303.
[11] P. Claus, P. Schilling, J. S. Gratzl, and K. Gratzl, *Monatsh.* 1972, **103**, 1178.
[12] J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, and T. Walker, *J. Chem. Soc.*, 1952, 1094.
[13] M. Crawford and J. W. Rasburn, *J. Chem. Soc.*, 1956, 2155.
[14] C. D. Cook and N. D. Gilmour, *J. Org. Chem.*, 1960, **25**, 1429.
[15] J. Vandrewalla, *J. Univ. Bombay*, 1948, **16**, 43; see 'Beilsteins Handbuch der Organischen Chemie,' Springer-Verlag, Berlin, vol. VIII, 1970, p. 3712.