929. *Chrom-3-en-6-ols. The Action of Pyridine on Alk-2-enylbenzoquinones*

By D. McHale and J. Green

Allylbenzoquinones are converted by treatment with pyridine into quinols and chrom-3-en-6-ols. The tendency for the latter reaction to occur increases as the benzoquinone ring becomes more highly substituted.

In an earlier Paper,[1] the pyridine-catalysed cyclisation of ubiquinone 30 (I; R = OMe, $n = 6$) to ubichromenol 30 (II; R = OMe, $n = 5$) was described. We now report an extension of this work to other alk-2-enylbenzoquinones.

The allylbenzoquinones, not previously described, were prepared by Claisen rearrangement of the appropriate 4-allyloxyphenol and subsequent oxidation of the resulting allylquinol with silver oxide. Although the 4-allyloxyphenols derived from symmetrically substituted quinols could be obtained directly from the quinol by Williamson synthesis, 3-methyl-4-allyloxyphenol was not readily obtained in this manner and was best prepared from the allyl ether of 4-acetoxy-2-methylphenol. An alternative procedure for the preparation of the allylbenzoquinones, which gave satisfactory yields of 2-allyl-6-methylbenzoquinone, 3-allyl-2,5-dimethylbenzoquinone, and 5-allyl-2,3-dimethylbenzoquinone, involved the oxidation of the appropriate *o*-allylphenol with Frémy's salt by the method of

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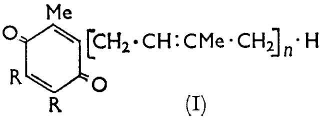
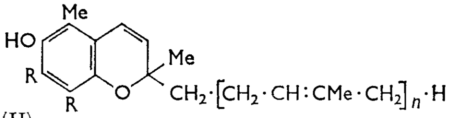
[1] D. McHale and J. Green, *Chem. and Ind.*, 1962, 1867.

Teuber and Jellinek.[2] The γγ-disubstituted allylbenzoquinones were all derived from trimethylquinol by condensation with an α-hydroxyalkene and oxidation of the resulting quinol.

Apart from allylbenzoquinone, all the benzoquinones examined gave chromenols when heated in solution in pyridine although the yields were lower than with the ubiquinones.



(I)



(II)

With allylbenzoquinone, the solution in pyridine darkened rapidly at room temperature and charred when heated. Allylquinol was the only product identified in the reaction mixture. 2-Allyl-6-methylbenzoquinone behaved similarly and gave 2-allyl-6-methylquinol, but thin-layer chromatography (t.l.c.) of the crude product indicated that some chromenol was also present. The tendency for the benzoquinones to undergo cyclisation to chromenols rather than reduction to quinols increases as the benzoquinone ring becomes more highly substituted. Thus, 5-allyl-2,3-dimethylbenzoquinone gives approximately equal yields of 5-allyl-2,3-dimethylquinol and 7,8-dimethylchrom-3-en-6-ol whereas allyltrimethylbenzoquinone gives 5,7,8-trimethylchrom-3-en-6-ol as major product.

The ultraviolet spectra (Table) of the chromenols show a typical pattern which differs markedly from that of the quinones.

Ultraviolet spectra of chromenols ($\lambda_{max.}$ in mμ, ε in parentheses)

5,8-Dimethylchromenol *	233 (16,100)		273 (6800)	*281* (6700)	340 (3200)
7,8-Dimethylchromenol *	232 (22,100)		270 (5700)	*278* (5000)	334 (4200)
5,7,8-Trimethylchromenol * ...	233 (17,200)		273 (7900)	*281* (6700)	333 (2800)
(II; R = Me, n = 1) †	236 (19,700)	*264*	274 (8900)	284 (8200)	340 (3500)
(II; R = Me, n = 2) †	235 (18,900)	*263*	273 (8600)	284 (7900)	339 (3400)
(II; R = Me, n = 3) †	235 (18,500)	*264*	274 (8700)	284 (8100)	340 (3400)
(II; R = Me, n = 3) †‡	235 (19,100)	*265*	273 (8300)	283 (7400)	339 (3200)

Inflections in italics.

* In ethanol. † In hexane. ‡ Double bonds saturated.

Chromen-6-ols unsubstituted at C-5 or C-7 do not couple with diazonium salts. In this respect they are unlike the chroman-6-ols, where the coupling reaction[3] differentiates between substitution at C-5 and C-7.

EXPERIMENTAL

Ultraviolet light absorption was measured with a Uvispek spectrophotometer. Pressures cited for short-path distillations are Pirani-gauge measurements. Light petroleum refers to the fraction of b. p. 60—80°. Alumina is Peter Spence type 0.

4-*Allyloxy*-2,3-*dimethylphenol*.—A solution of sodium (1·2 g.) in ethanol (150 ml.) was treated with 2,3-dimethylquinol[4] (6·9 g.) and heated to reflux. Allyl bromide (6·5 g.) was added over 5 min. and the solution heated under reflux for 4 hr. The supernatant layer was decanted and the bulk of the ethanol evaporated. The resulting slurry was extracted into ether and washed with water, dilute hydrochloric acid, and water. Evaporation of the ether gave a solid (9·6 g.) which was adsorbed from light petroleum on to alumina and eluted with 30% v/v benzene in light petroleum followed by 50% v/v benzene in light petroleum. The solid (2·7 g.) obtained from the latter fraction was crystallised from light petroleum and gave the *allyloxyphenol* (0·6 g.), m. p. 99—100° (Found: C, 73·8; H, 8·1. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%).

4-*Allyloxy*-2,5-*dimethylphenol*.—In a similar manner, 2,5-dimethylquinol[5] (6·9 g.) gave 4-allyloxy-2,5-dimethylphenol (0·4 g.), m. p. 61—62° (previously[6] described as an oil) (Found: C, 74·1; H, 7·8%).

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[2] H. J. Teuber and G. Jellinek, *Chem. Ber.*, 1952, **85**, 95.

[3] J. Green and S. Marcinkiewicz, *Analyst*, 1959, **84**, 297.

[4] L. I. Smith and F. L. Austin, *J. Amer. Chem. Soc.*, 1942, **64**, 530.

[5] L. I. Smith, J. W. Opie, S. Wawzonek, and W. W. Pritchard, *J. Org. Chem.*, 1939, **4**, 318.

[6] F. Bergel, A. Jacob, A. R. Todd, and T. S. Work, *J.*, 1938, 1375.

4-*Allyloxy*-3-*methylphenol*.—4-Acetoxy-2-methylphenol[7] (5 g.), potassium iodide (2·7 g.) anhydrous potassium carbonate (4·5 g.), allyl bromide (4·6 g.), and acetone (50 ml.) were heated under reflux with stirring for 7 hr. The reaction mixture was filtered and the solvent evaporated. The residual oil (5·8 g.) when taken up in light petroleum deposited plates (1 g.), m. p. 94—96° (undepressed on admixture with 4-acetoxy-2-methylphenol). The oil (4·7 g.) recovered from the mother-liquors was refluxed in ethanol (20 ml.) and potassium hydroxide (2·3 g.) was added. After 20 min., 2N-hydrochloric acid (35 ml.) was added to the refluxing solution. The inorganic salt was dissolved in water and the organic layer was diluted with ether. The aqueous layer was separated and the organic layer was washed with water, dried, and evaporated. The residual oil (3·4 g.) was extracted with boiling light petroleum (3 × 30 ml.) and the combined extract left at 0°. 4-*Allyloxy*-3-*methylphenol* separated as needles (2·6 g.) which, after recrystallisation from light petroleum, had m. p. 34—35° (Found: C, 72·7; H, 7·8. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%).

General Claisen Rearrangement Procedure.—A solution of the 4-allyloxyphenol (0·5 g.) in decalin (10 ml.) was heated at 190—200° for 2½ hr. The white solid that separated on cooling was collected and washed with light petroleum and recrystallised.

This method gave: 5-*allyl*-2,3-*dimethylquinol* (70%), m. p. 135—136° (from light petroleum) (Found: C, 74·1; H, 7·7. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%); 3-*allyl*-2,5-*dimethylquinol* (50%), m. p. 139° (from benzene) (Found: C, 74·6; H, 7·8%); 2-*allyl*-6-*methylquinol* (69%), m. p. 70° (from light petroleum) (Found: C, 73·2; H, 7·4. $C_{10}H_{12}O_2$ requires C, 73·1; H, 7·4%); and allylquinol (68%), m. p. 88° (from benzene–light petroleum) (lit.,[8] 92°).

General Oxidation Procedure.—A solution of the quinol (0·3 g.) in ether (10 ml.) was shaken with silver oxide (1·0 g.) for 2 hr. After filtration, evaporation of the solvent and distillation of the residual oil gave the quinone. Ultraviolet spectra were determined in ethanol.

This method gave: 5-*allyl*-2,3-*dimethylbenzoquinone*, b. p. 35°/0·03 mm. (Found: C, 75·2; H, 7·0. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%), $\lambda_{max.}$ 256 mμ (ε 17,300), $\lambda_{infl.}$ 260 mμ; 3-*allyl*-2,5-*dimethylbenzoquinone*, b. p. 40—45°/0·1 mm. (Found: C, 75·0; H, 6·8%), $\lambda_{max.}$ 256 mμ (ε 21,000) $\lambda_{infl.}$ 260 mμ; 2-*allyl*-6-*methylbenzoquinone*, b. p. 35—40°/0·05 mm. (Found: C, 73·7; H, 6·2. $C_{10}H_{10}O_2$ requires C, 74·0; H, 6·2%), $\lambda_{max.}$ 255 mμ (ε 18,500) $\lambda_{infl.}$ 252 and 261 mμ; and allylbenzoquinone, b. p. 35°/0·05 mm. (lit.,[8] 102—103°/18 mm.), $\lambda_{max.}$ 247 mμ (ε 16,400) $\lambda_{infl.}$ 251 mμ.

3-*Allyloxy*-1,2-*xylene*.—2,3-Xylenol (10 g.), allyl bromide (9·9 g.) anhydrous potassium carbonate (11·3 g.), and acetone (50 ml.) were heated under reflux with stirring for 6 hr. The inorganic salt was filtered off and the filtrate evaporated. The residual oil was dissolved in Claisen's alkali (50 ml.) and extracted wih light petroleum (4 × 20 ml.). The combined extract was washed with water and evaporated to an oil (8·3 g.). Distillation gave the *ether* (6·5 g.) b. p. 54°/0·05 mm. (Found: C, 81·8; H, 8·9. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%).

2-Allyloxy-1,4-xylene, b. p. 46°/0·05 mm. (lit.,[9] 63—64°/1 mm.) and 2-allyloxytoluene, b. p. 40°/0·05 mm. (lit.,[10] 85°/12 mm.) were obtained in a similar manner.

6-*Allyl*-2,3-*xylenol*.—A solution of 3-allyloxy-1,2-xylene (6·5 g.) in decalin (20 ml.) was heated at 190—200° for 2½ hr. Claisen's alkali (20 ml.) was added to the cooled mixture and the decalin extracted into light petroleum (3 × 20 ml.). The alkaline layer was acidified with hydrochloric acid and extracted with ether. The combined ether extracts were washed, dried, and evaporated. The resulting oil (6·5 g.) was adsorbed from light petroleum on to Decalso F (150 g.) (column packed dry and washed with light petroleum). Elution with light petroleum gave 6-*allyl*-2,3-*xylenol* (4·5 g.), b. p. 50°/0·05 mm. (Found: C, 81·2; H, 8·8. $C_{11}H_{14}O$ requires C, 81·4; H, 8·7%). Continued elution with 10% v/v benzene in light petroleum gave 4-*allyl*-2,3-*xylenol* (0·7 g.), b. p. 50°/0·05 mm., m. p. 36° (Found: C, 81·4; H, 8·7%).

6-*Allyl*-2,5-*xylenol*.—In a similar manner 2-allyloxy-1,4-xylene (9 g.) gave 6-allyl-2,5-xylenol (6·2 g.), b. p. 57°/0·05 mm. (lit.,[9] 75—77°/1 mm.) and 4-*allyl*-2,5-*xylenol* (0·8 g.), b. p. 57°/0·05 mm. (Found: C, 81·6; H, 8·9%).

6-Allyl-2-methylphenol, b. p. 45°/0·05 mm. (lit.,[10] 106—107°/12 mm.) was also obtained by this method.

Oxidations with Frémy's Salt.[11]—The phenol (1·3 g.) in methanol (10 ml.) was added with

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[7] B.P. 900,217.

[8] L. I. Smith, H. H. Hoehn, and A. G. Whitney, *J. Amer. Chem. Soc.*, 1940, **62**, 1863.

[9] C. S. Marvel and N. A. Higgins, *J. Polymer Sci.*, 1948, **3**, 448.

[10] L. Claisen and O. Eisleb, *Annalen*, 1913, **401**, 21.

[11] G.P. 942,562.

stirring to a solution of Frémy's salt (4·8 g.) in water (240 ml.) and N-sodium acetate (8 ml.). After 2 hr. the yellow oil that had separated was extracted into ether and the extract washed and dried. Evaporation and distillation of the residue gave the quinone identical in infrared and ultraviolet spectra with those prepared from the quinol.

This method gave: 5-allyl-2,3-dimethylbenzoquinone (1 g.); and 3-allyl-2,5-dimethylbenzoquinone (1 g.). The product from 6-allyl-2-methylphenol (1·6 g.) showed a strong hydroxyl absorption in its infrared spectrum. Adsorption from light petroleum on to Decalso F (30 g.) and elution with light petroleum gave an oil (0·7 g.) which showed both hydroxyl and quinonoid absorption. Continued elution with 10% v/v benzene in light petroleum gave 6-allyl-2-methylbenzoquinone (0·3 g.).

Geranyltrimethylbenzoquinone (I; R = Me, *n* = 2).—Trimethylquinol (5 g.), linalool (5 g.) and redistilled boron trifluoride etherate (2·0 ml.) in dry ether (50 ml.) were left for 72 hr. at room temperature. The product was diluted with ether and washed with water, N-sodium hydroxide, and water. Evaporation of the dried organic layer gave an oil which was taken up in light petroleum (b. p. 40—60°) and allowed to crystallise. *Geranyltrimethylquinol* (3·0 g.) separated as a waxy solid, m. p. 114° (Found: C, 79·0; H, 9·5. $C_{19}H_{28}O_2$ requires C, 79·1; H, 9·8%) and was dissolved in ether (50 ml.) and shaken with silver oxide (8·0 g.) for 2 hr. The product was filtered and the solvent evaporated. Short-path distillation of the residual oil gave *geranyltrimethylbenzoquinone* (2·0 g.) [110° (bath)/0·01 mm.] (Found: C, 79·8; H, 8·9. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·2%), $\lambda\lambda_{max.}$ 259 and 267 mμ (ε 17,000 and 17,700) in ethanol.

In a similar manner: nerolidol gave *farnesyltrimethylbenzoquinone* (I; R = Me, *n* = 3) [145° (bath)/0·02 mm.] (Found: C, 81·6; H, 9·6. $C_{24}H_{34}O_2$ requires C, 81·4; H, 9·6%), $\lambda\lambda_{max.}$ 259 and 267 mμ (ε 17,800 and 18,100) in ethanol; phytol gave phytyltrimethylbenzoquinone[12] [150° (bath)/0·01 mm.] (Found: C, 81·6; H, 11·8. Calc. for $C_{29}H_{48}O_2$: C, 81·3; H, 11·3%), $\lambda\lambda_{max.}$ 261 and 267 mμ (ε 18,500 and 18,500) in ethanol.

Action of Pyridine on Allylbenzoquinone.—A solution of allylbenzoquinone (0·8 g.) in pyridine (20 ml.) was heated to reflux; it darkened immediately. After 2½ hr. the product was cooled, diluted with ether, and washed with water, 2N-hydrochloric acid, and water. The organic layer was filtered and evaporated. Crystallisation of the residue from benzene gave a solid (0·15 g.), m. p. 88° (undepressed with allylquinol).

Action of Pyridine on 2-Allyl-6-methylbenzoquinone.—2-Allyl-6-methylbenzoquinone (0·5 g.), treated as above, gave a solid (0·1 g.), m. p. 60° (undepressed with 2-allyl-6-methylquinol). T.l.c. of the mother-liquors on Merck silica gel G (in which 25 p.p.m. of sodium fluorescein was incorporated during the preparation of the plates) with ether–light petroleum (1 : 1) as eluant showed a quenching spot under ultraviolet light (254 mμ) at R_F 0·37. This spot gave a positive reaction with Emmerie and Engel's reagent[13] and when eluted into ethanol had $\lambda\lambda_{max.}$ 275 and 340 mμ.

7,8-Dimethylchrom-3-en-6-ol.—A solution of 5-allyl-2,3-dimethylbenzoquinone (1·3 g.) in pyridine (20 ml.) was refluxed for 5 hr. The product, worked up in the usual way, gave a black oil (0·9 g.), which was extracted with boiling light petroleum (3 × 20 ml.). The combined extract was evaporated to low volume (20 ml.) and left to crystallise. The solid (0·2 g.) that separated was recrystallised from light petroleum and had m. p. 133° (undepressed with 5-allyl-2,3-dimethylquinol). The combined mother-liquors were evaporated to a low bulk and then adsorbed on to Decalso F (30 g.). Elution with benzene gave the *chromenol* (0·2 g.), m. p. 100—101° from light petroleum (Found: C, 74·6; H, 6·7. $C_{11}H_{10}O_2$ requires C, 75·0; H, 6·9%).

5,8-Dimethylchrom-3-en-6-ol.—In a similar manner, 3-allyl-2,5-dimethylbenzoquinone (1·2 g.) gave 3-allyl-2,5-dimethylquinol (0·2 g.) and the *chromenol* (0·3 g.), m. p. 95—96°, from light petroleum (Found: C, 74·8; H, 6·5%).

5,7,8-Trimethylchrom-3-en-6-ol.—A solution of allyltrimethylbenzoquinone (0·8 g.) in pyridine (20 ml.) was refluxed for 5 hr. The product, worked up in the usual way, gave a dark solid (0·8 g.), which was dissolved in hot 40% aqueous ethanol and filtered from an insoluble tarry material. The filtrate on cooling deposited crystals (0·5 g.) of the *chromenol*, which after recrystallisation from light petroleum had m. p. 126—127° (Found: C, 75·5; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%).

2,5,7,8-Tetramethyl-2-(4-methylpent-3-enyl)chrom-3-en-6-ol (II; R = Me, *n* = 1).—A solution

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[12] L. H. Fieser, M. Tishler, and W. L. Sampson, *J. Amer. Chem. Soc.*, 1940, **62**, 996.

[13] A. Emmerie and C. Engel, *Rec. Trav. chim.*, 1939, **58**, 283.

of geranyltrimethylbenzoquinone (1·5 g.) in pyridine (20 ml.) was refluxed for 6 hr. The product was cooled, diluted with light petroleum, and washed in the usual way. The organic layer was filtered and evaporated. The resulting oil (1·3 g.) was adsorbed from light petroleum on to Decalso F (30 g.). After elution with 30% v/v benzene in light petroleum to remove geranyltrimethylbenzoquinone, elution with 60% v/v benzene in light petroleum gave a red oil (0·8 g.), which, after short-path distillation [110° (bath)/0·01 mm.], gave the *chromenol* (Found: C, 79·2; H, 9·1. $C_{19}H_{26}O_2$ requires C, 79·7; H, 9·2%).

The 4-*phenylazobenzoate* had m. p. 118—119° (95% ethanol) (Found: C, 78·0; H, 7·0; N, 5·5. $C_{32}H_{34}N_2O_3$ requires C, 77·7; H, 6·9; N, 5·7%).

In a similar manner: farnesyltrimethylbenzoquinone gave 2-(4,8-*dimethylnona*-3,7-*dienyl*)-2,5,7,8-*tetramethylchrom*-3-*en*-6-*ol* (II; R = Me, $n = 2$), [115° (bath)/0·01 mm.] (Found: C, 81·2; H, 9·9. $C_{24}H_{34}O_2$ requires C, 81·4; H, 9·6%), 4-*phenylazobenzoate*, m. p. 115° (95% ethanol) (Found: C, 78·8; H, 7·3; N, 4·9. $C_{37}H_{42}N_2O_3$ requires C, 79·0; H, 7·5; N, 5·0%); all-*trans*-geranylgeranyltrimethylbenzoquinone gave 2,5,7,8-tetramethyl-2-(4,8,12-trimethyltridec-3,7,11-trienyl)chrom-3-en-6-ol [14] (II; R = Me, $n = 3$) [140° (bath)/0·025 mm.] (Found: C, 82·6; H, 9·6. Calc. for $C_{29}H_{42}O_2$: C, 82·4; H, 10·0%); phytyltrimethylbenzoquinone gave 2,5,7,8-*tetramethyl*-2-(4,8,12-*trimethyltridecyl*)*chrom*-3-*en*-6-*ol* [II; R = Me, $n = 3$ (double bonds saturated)] [130° (bath)/0·015 mm.] (Found: C, 81·0; H, 10·9. $C_{29}H_{48}O_2$ requires C, 81·3; H, 11·3%).

Action of Diazotised o-*Dianisidine on Chromenols and Chromanols.*—7,8-Dimethylchromenol (2·3 mg.) in ethanol (2 ml.) was shaken for 1 hr. with hydrogen in the presence of palladised charcoal. The catalyst was filtered off, and a portion (1 ml.) of the filtrate was made up to 5 ml. with ethanol. This solution and a similar strength solution of the chromenol were treated with 2% sodium carbonate (7·5 ml.) and diazotised *o*-dianisidine (1 ml.) according to the method of Weisler *et al.*[15] and the spectra of the products observed over the range 350—600 mμ. The chromenol showed no absorption, whereas the chromanol derived by hydrogenation showed a band at 393 mμ and a broad but less intense band at 500—505 mμ

When treated in the same manner, neither 5,8-dimethylchromenol nor the chromanol derived from it by hydrogenation showed any absorption.

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[14] P. Schudel, H. Mayer, J. Metzger, R. Rüegg, and O. Isler, *Helv. Chim. Acta*, 1963, **46**, 2517.

[15] L. Weisler, C. D. Robeson, and J. G. Baxter, *Analyt. Chem.*, 1947, **19**, 906.