

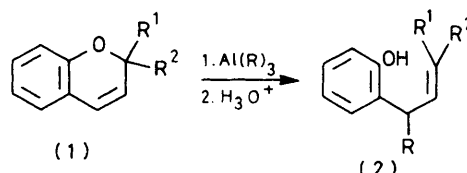
The Behaviour of 2*H*-1-Benzopyrans Towards Trialkylaluminium Reagents

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2*H*-1-Benzopyrans react with trialkylaluminium compounds by alkyl- and hydrogen-transfer to C-2 and C-4 to give the *o*-allylphenols (2), (3), and the (*E*)-*o*-propenylphenols (4) and (5). The site of attack and the ratio of alkyl- to hydrogen-transfer depend on the alkylaluminium used and on the size of the substituent at C-2 of the pyran. A mechanism involving reaction of the alkylaluminium with the quinone methide (6), which is in equilibrium with the pyran (1), is in accord with all experimental results.

It has been reported¹ that 2,2-diethyl-2*H*-1-benzopyran (1e) reacts with triethylaluminium leading to 2-(1,3-diethylpent-2-enyl)phenol (2e) in high yield. As the reaction, which is analogous to reductions of (1) with lithium aluminium hydride² or magnesium,³ may be of synthetic interest, we have studied the behaviour of 2*H*-1-benzopyran towards



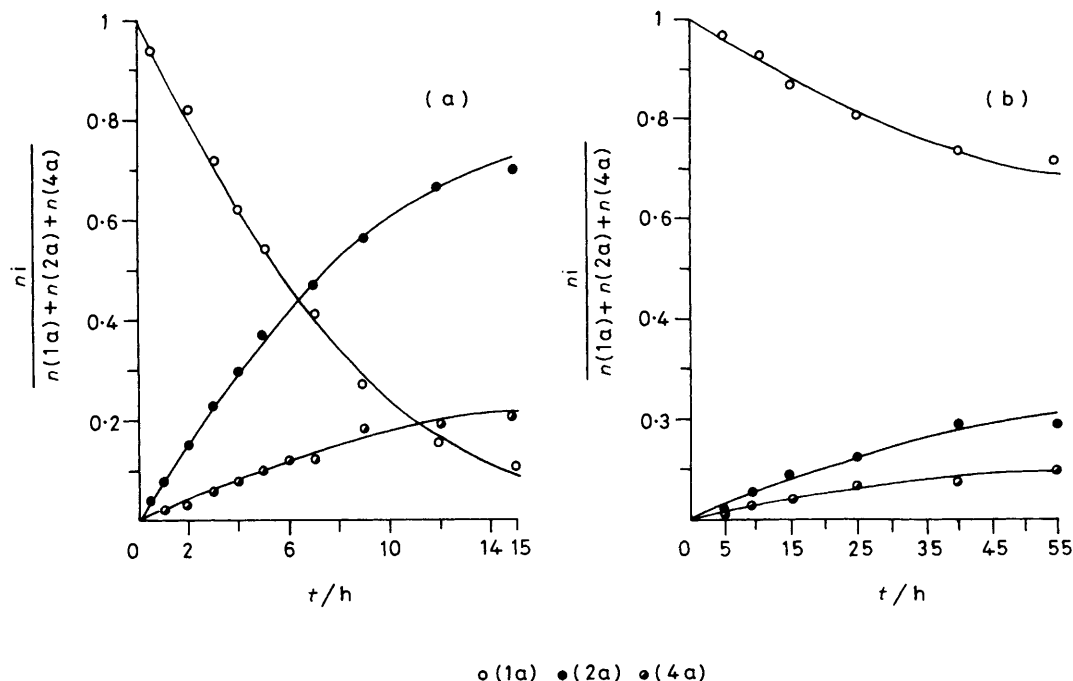
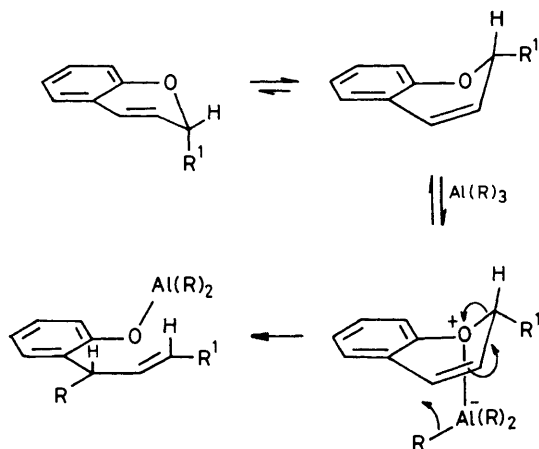


Figure. Reaction of the 2H-1-benzopyran (1a) with triethylaluminium (a) under u.v. irradiation and (b) in darkness



Scheme 2.

anism of the stereoselective formation of *o*-allylphenols, a possible route which is consistent with the observations^{4,5} is shown in Scheme 2.

However, a similar transformation, which involves 1,2-addition and the subsequent *Z*-*E* isomerization of the double bond, would not explain the formation of (*E*)-*o*-propenylphenols.^{1,4}

The formation of (2), (3) and the *E*-isomers of (4) and (5), could easily be interpreted as being due to the action of trialkylaluminium compounds on the quinone methanide (6) which is in photochemically induced⁶ equilibrium with compound (1) (Scheme 3). This equilibrium could also explain the reactions of 2H-1-benzopyrans with various reducing agents^{7,8} and Grignard compounds.^{9,10}

Experimental

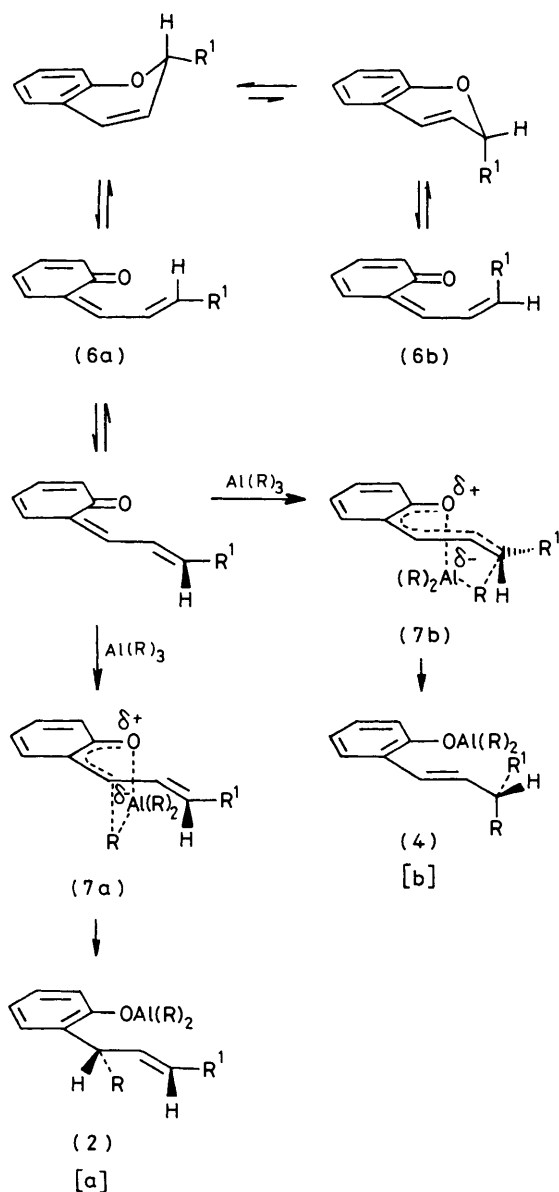
All m.p.s are uncorrected. I.r. spectra were recorded with a Pye-Unicam SP-1100 instrument, and ¹H n.m.r. were obtained

on either a Perkin-Elmer R-24 or a Varian T-60A spectrometer at 60 MHz, using SiMe₄ as internal reference. G.l.c. was carried out on a Hewlett-Packard 5710-A chromatograph using nitrogen as the carrier gas and a column packed with DEGS (20%) on chromosorb W-HMDS 80/100. Mass spectra were performed on a Hewlett-Packard 5930-A spectrometer.

Synthesis of 2H-1-Benzopyrans.—The following 2H-1-benzopyran (1a)¹¹ (24%), b.p. 49–50 °C at 1 Torr; 2-methyl-2H-1-benzopyran (1b)¹² (31%), b.p. 45–46 °C at 0.5 Torr; 2,2-dimethyl-2H-1-benzopyran (1d)¹² (45%), b.p. 84–85 °C at 1.5 Torr; and 2,2-diethyl-2H-1-benzopyran (1e)¹³ (64%), b.p. 99–100 °C at 2.8 Torr.

2-Isobutyl-2H-1-benzopyran (1c).—(*Z*)-2-(3-Hydroxy-5-methylhex-1-enyl)phenol was distilled at 160 °C/3 Torr with nitrogen flushing. The distillate (5 g) was purified in a chromatographic column using Merck silica gel (70–230 mesh) and dry n-hexane as solvent, to give crude (1c) (3 g); this yielded on distillation pure compound (2.5 g, 30%), colourless oil, b.p. 84–86 °C at 1.2 Torr (Found: C, 83.2; H, 8.15. C₁₃H₁₅O requires C, 83.40; H, 8.02%); δ (CCl₄) 0.9 (6 H, d), 1.1–2.1 (3 H, m), 4.85 (1 H, m), 5.35 (1 H, c), 6.1 (1 H, d), and 6.5–7.1 (5 H, m).

The (*Z*)-2-(3-hydroxy-5-methylhex-1-enyl)phenol¹ was prepared in the following way: to a solution of tri-isobutylaluminium (17.3 g, 0.68 mol) in anhydrous benzene (150 ml) was added, under nitrogen at 0 °C, coumarin (25 g, 0.17 mol) in the same solvent (100 ml). The mixture was stirred for 24 h at room temperature, and poured into ice-water. The resulting solution was acidified by addition of hydrochloric acid until aluminium hydroxide just dissolved, and then extracted with diethyl ether. The extracts were washed with water and dried (MgSO₄). The solvents were evaporated off, and the residue fractionated by column chromatography (silica gel and methylene dichloride); the products, in order of elution, were 1-(*o*-hydroxyphenyl)-5-methylhexan-3-one (ca. 30%) and



Scheme 3.

(*Z*)-2-(3-hydroxy-5-methylhex-1-enyl)phenol (9 g) (m.p. 56 °C from benzene-*n*-hexane, lit.,¹ 56 °C).

General Procedure.—To a solution of the organoaluminium compound (0.09 mol) in dry benzene (50 ml), under nitrogen, was added 2*H*-1-benzopyran (0.03 mol) in benzene (50 ml). The mixture was stirred during 24 h at room temperature, and heated for an additional hour at 80 °C. The solution was cooled, poured into ice-water, and acidified until aluminium hydroxide just dissolved. The organic layer was washed with water and dried (MgSO_4). The products were obtained by elution of the reaction mixtures (after removal of solvent) through a silica-gel column, using benzene-*n*-hexane (3 : 1) as eluant, and purified by distillation; only spectroscopic evidence for the presence of the minor products could be obtained. When the reaction of compound (1) with organoaluminium compounds was carried out at higher temperatures (in benzene under reflux, 6 h) by-products formed by transformation of the allylic groups were obtained (e.g. formation of

chroman, indan, and dihydrofuran derivatives by transposition at the *para*-position, etc.).

The irradiated reactions were carried out in a quartz flask 25 cm from the light source (quartz lamp, 125 W), and monitored by g.l.c. and ^1H n.m.r. spectroscopy. The following compounds were obtained in this way: 2-(1-ethylprop-2-enyl)phenol (2a), colourless liquid, b.p. 68–70 °C at 0.3 Torr; δ (CDCl_3) 0.85 (3 H, t), 1.75 (2 H, q), 3.45 (1 H, c), 4.70–5.25 (2 H, m), 6.0 (1 H, m), and 6.8–7.2 (4 H, m). Phenylurethane, m.p. 84–85 °C (Found: C, 76.7; H, 6.75; N, 4.8. $\text{C}_{18}\text{H}_{19}\text{NO}_2$ requires C, 76.87; H, 6.76; N, 4.98%).

(*E*)-2-(1-Ethylbut-2-enyl)phenol (2b), colourless liquid, b.p. 105–106 °C at 2.5 Torr; δ (CDCl_3) 0.85 (3 H, t), 1.65 (5 H, m), 5.5 (2 H, m), and 6.4–7.2 (4 H, m). Aryloxyacetic acid, m.p. 90–91 °C (Found: C, 71.75; H, 7.7. $\text{C}_{14}\text{H}_{18}\text{O}_3$ requires C, 71.79; H, 7.69%).

(*E*)-2-(1-Ethyl-5-methylhex-2-enyl)phenol (2c), colourless liquid, b.p. 96–98 °C at 1 Torr; δ (CDCl_3) 0.9 (6 H, d), 1.0 (3 H, t), 1.7 (1 H, m), 1.8 (2 H, m), 2.0 (2 H, m), 3.4 (1 H, m), 5.7 (2 H, m), and 6.4–7.3 (4 H, m). Phenylurethane, m.p. 89–90 °C (Found: C, 78.6; H, 7.9; N, 4.35. $\text{C}_{22}\text{H}_{27}\text{NO}_2$ requires C, 78.34; H, 8.01; N, 4.15%).

2-(1,3-Diethylpent-2-enyl)phenol (2e), colourless liquid, b.p. 106–110 °C at 3 Torr; δ (CDCl_3) 0.9 (6 H, t), 1.0 (3 H, t), 1.7 (2 H, m), 2.05 (2 H, c), 2.15 (2 H, c), 3.75 (1 H, c), 5.3 (1 H, d), and 6.5–7.3 (4 H, m). Phenylurethane, m.p. 128–129 °C (Found: C, 78.2; H, 7.9; N, 4.15. $\text{C}_{22}\text{H}_{27}\text{NO}_2$ requires C, 78.34; H, 8.01; N, 4.15%).

2-(1-Isobutylprop-2-enyl)phenol (2f), colourless liquid, b.p. 87–88 °C at 0.8 Torr; δ (Cl_3CD) 0.9 (6 H, d), 1.3–1.8 (3 H, m), 3.7 (1 H, c), 4.7–5.25 (2 H, m), 6.0 (1 H, oct.), and 6.7–7.2 (4 H, m). Phenylurethane, m.p. 113–114 °C (Found: C, 77.65; H, 7.45; N, 4.4. $\text{C}_{20}\text{H}_{23}\text{NO}_2$ requires C, 77.67; H, 7.44; N, 4.53%).

(*E*)-2-(1-Isobutylbut-2-enyl)phenol (2g), colourless liquid, b.p. 118–119 °C at 3 Torr; δ (CDCl_3) 0.85 (6 H, m), 1.2–1.9 (3 H, m), 1.6 (3 H, m), 3.5 (1 H, m), 5.45 (2 H, m), and 6.4–7.1 (4 H, m) [Found: 204 (M^+). $\text{C}_{14}\text{H}_{20}\text{O}$ requires M , 204].

(*E*)-2-(1-Isobutyl-5-methylhex-2-enyl)phenol (2h), colourless liquid, b.p. 103–106 °C at 1 Torr; δ (Cl_3CD) 0.9 (12 H, m), 1.95 (2 H, m), 3.6 (1 H, m), 5.6 (2 H, m), and 6.6–7.3 (4 H, m). Phenylurethane, m.p. 109–110 °C (Found: C, 79.1; H, 8.35; N, 3.75. $\text{C}_{24}\text{H}_{31}\text{NO}_2$ requires C, 78.90; H, 8.49; N, 3.84%).

2-(1-Isobutyl-3-methylbut-2-enyl)phenol (2i), colourless liquid, b.p. 104–106 °C at 1 Torr; δ (CCl_4) 0.85 (6 H, d), 1.3–1.8 (3 H, m), 1.6 (6 H, s), 3.85 (1 H, m), 5.3 (1 H, d), and 6.5–7.3 (4 H, m) [Found: 218 (M^+). $\text{C}_{15}\text{H}_{22}\text{O}$ requires M , 218].

2-(3-Ethyl-1-isobutylpent-2-enyl)phenol (2j), colourless liquid, b.p. 115–117 °C at 3 Torr; δ (CDCl_3) 1.0 (12 H, m), 1.3–1.7 (3 H, m), 2.05 (2 H, c), 2.15 (2 H, c), 3.75 (1 H, c), 5.3 (1 H, d), and 6.5–7.3 (4 H, m). Phenylurethane, m.p. 131–132 °C (Found: C, 78.8; H, 8.55; N, 3.9. $\text{C}_{24}\text{N}_3\text{NO}_2$ requires C, 78.90; H, 8.49; N, 3.84%).

2-Prop-2-enylphenol (3a), colourless liquid, b.p. 78–80 °C at 3.5 Torr; δ (CDCl_3) 3.3 (2 H, d), 4.8–5.3 (2 H, m), 5.6–6.3 (1 H, m), and 6.5–7.2 (4 H, m). Phenylurethane, m.p. 106 °C (lit.,¹⁴ 106 °C).

(*E*)-2-But-2-enylphenol (3b), colourless liquid, b.p. 74–76 °C at 1 Torr; δ (CDCl_3) 1.65 (3 H, m), 3.25 (2 H, m), and 6.5–7.2 (4 H, m). Aryloxyacetic acid, m.p. 135–136 °C (from water (lit.,¹⁵ 135–136 °C).

(*E*)-2-(5-Methylhex-2-enyl)phenol (3c), colourless liquid, b.p. 93–95 °C at 0.8 Torr (lit.,¹⁶ 100 °C at 1 Torr). Phenylurethane, m.p. 91–92 °C (Found: C, 77.1; H, 6.95; N, 5.0. Calc. for $\text{C}_{18}\text{H}_{19}\text{NO}_2$: C, 76.87; H, 6.76; N, 4.98%).

2-(3-Ethylpent-2-enyl)phenyl (3e), colourless liquid, b.p. 97–100 °C at 3 Torr; δ (CDCl₃) 1.0 (6 H, t), 2.05 (2 H, c), 2.15 (3 H, c), 3.35 (2 H, d), 5.25 (1 H, t), and 6.7–7.2 (4 H, m) [Found: 190 (*M*⁺); C₁₃H₁₈O requires *M*, 190].

(*E*)-2-Prop-1-enylphenol (5a), m.p. 37–38 °C (lit.,¹⁷ 37–38 °C); δ (CDCl₃) 1.85 (3 H, d), 6.15 (1 H, oct.), 6.60 (1 H, d), and 6.6–7.3 (4 H, m).

(*E*)-2-But-1-enylphenol (5b), m.p. 0 °C; δ (CDCl₃) 1.05 (3 H, t), 2.15 (2 H, m), 5.95 (1 H, s), 6.50 (1 H, d), and 6.3–7.2 (4 H, m). Aryloxyacetic acid, m.p. 101–102 °C (lit.,¹⁵ 102 °C).

For the following two compounds we have spectroscopic evidence only: (*E*)-2-pent-1-enylphenol (4a), δ (CDCl₃) 0.9 (3 H, t), 1.2–1.8 (4 H, m), 2.15 (2 H, c), 6.1 (1 H, s), 6.6 (1 H, d), and 6.6–7.4 (4 H, m).

(*E*)-2-(3-Methylpent-1-enyl)phenol (4b), δ (CDCl₃) 1.0 (6 H, m), 1.25 (2 H, m), 2.1 (1 H, m), 5.85 (1 H, c), 6.4 (1 H, d), and 6.6–7.4 (4 H, m).

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