

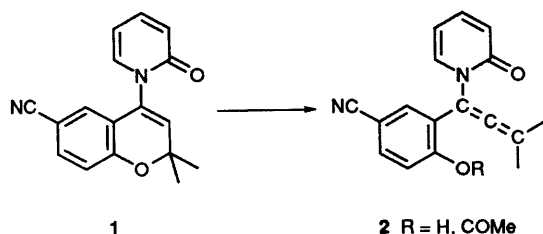
Allenes from 3-Bromo-2*H*-1-benzopyrans

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The anionic cleavage of 2*H*-1-benzopyrans results in the formation of allenes.

A variety of synthetic routes is available for the synthesis of allenes,¹ notable amongst which are the use of dihalogenocarbenes,² rearrangement of acetylenes,³ Wittig reaction of ketenes,⁴ 1,4-addition of alkyl lithium reagents to conjugated enynes⁵ and elimination of halogen or hydrogen halide from suitably functionalised halogeno-alkanes and -alkenes.⁶

The chemistry of the 4*H*-1-benzopyran-4-ones is dominated by their facile ring opening under basic conditions, as is that of their 2,3-dihydro analogues, although to a lesser extent.⁷ The ring opening of 2*H*-1-benzopyrans has been achieved photochemically,⁸ a feature which has attracted attention in the search for photochromic materials.⁹ More recently, C-3 directed metallation of the 2*H*-1-benzopyran **1** with lithium diisopropylamide in tetrahydrofuran (THF) at -70°C afforded the allenyl phenol **2** ($\text{R} = \text{H}$) which recycled in solution to **1**. However, conversion into the acetate **2** ($\text{R} = \text{COMe}$) and subsequent thermal cyclisation gave a benzo[*b*]-furan.¹⁰ Allenyl phenols have previously been obtained by the silver catalysed dienone-phenol rearrangement of allenyl dienones derived from aryl prop-2-ynyl ethers.¹¹



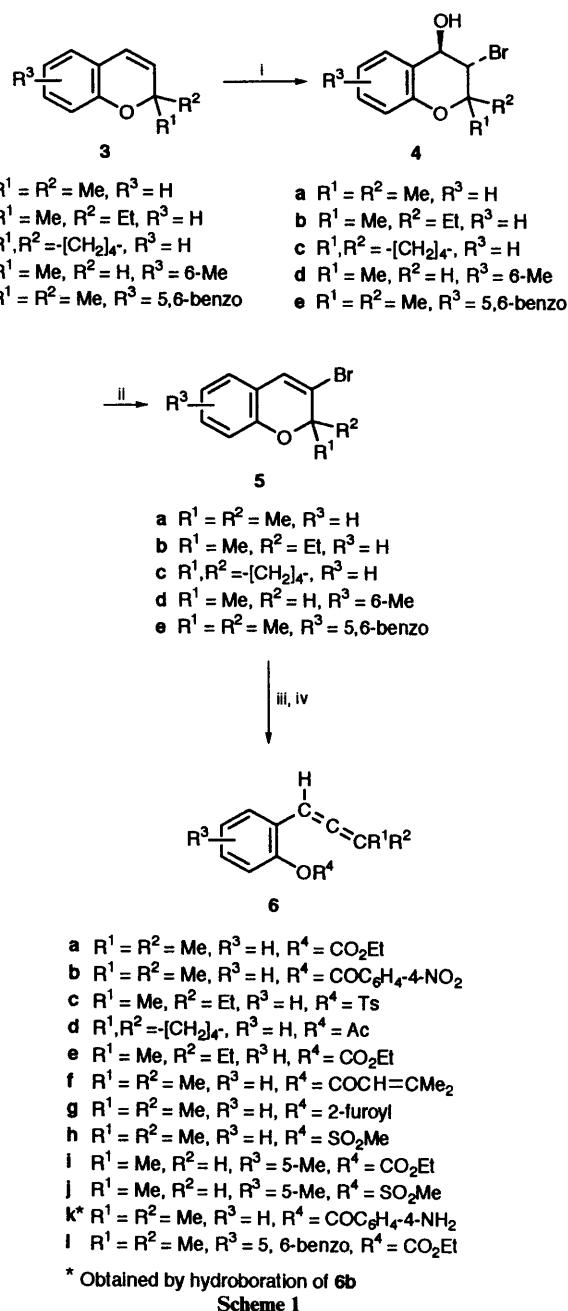
The ring cleavage of 3-bromo-2,5-diarylfurans on reaction with butyllithium to give 2,5-diarylfurans and allenes or acetylenes has been shown to be markedly dependent upon both solvent and temperature.¹² The ring opening of many other five-membered heterocycles has also been studied.¹³

We now describe a versatile and expedient allene synthesis accomplished by the anionic cleavage of a benzopyran ring, which relies on metal halogen exchange rather than directed metallation group methodology.

Discussion

The key compounds in the sequence are the 3-bromo-2*H*-1-benzopyrans **5**, which are obtained from 2*H*-1-benzopyrans **3** in excellent yield by a two step sequence involving the reaction with *N*-bromosuccinimide (NBS) in moist dimethyl sulfoxide¹⁴ to afford the *trans*-3-bromo-3,4-dihydro-2*H*-1-benzopyran-4-ols **4** and subsequent facile elimination of water by refluxing these bromohydrins in toluene containing a catalytic amount of toluene-4-sulfonic acid (4-TsOH) (Scheme 1).

The reaction between a molar equivalent of NBS and the 2*H*-1-benzopyran **3a** results in a good yield of the bromohydrin but accompanied by some unchanged starting material. Attempts to achieve complete conversion to the bromohydrin **4a** by using a slight excess of NBS and temperatures above $\sim 10^{\circ}\text{C}$ invariably

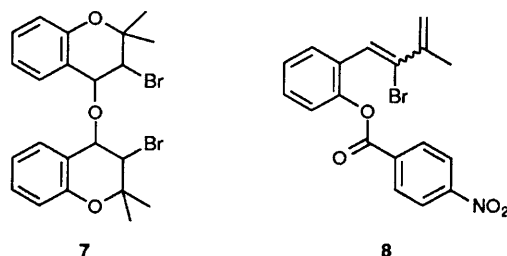


Reagents and conditions: i, *N*-Bromosuccinimide, DMSO, H_2O ; ii, 4-TsOH, PhMe, heat; iii, BuLi, Et_2O , 0°C –room temp.; iv, electrophile, H_2O . Note: only relative stereochemistry shown for the *trans*-bromohydrins **4**.

gave a small amount of 3,6-dibromo-3,4-dihydro-2*H*-1-benzopyran-4-ol in addition to the desired product. This compound presumably results from electrophilic aromatic

substitution in the activated 6-position of the ring. The structure of this dibromo compound was evident from the ^1H NMR spectrum of the crude reaction product. The signals for the geminal dimethyl group and 3- and 4-H are all duplicated, but only three extra aromatic signals are present and these are in a pattern which is characteristic of a 6-substituted chroman unit.

It is of interest to note that the benzopyrans **3b** and **3d** which are unsymmetrically substituted at C-2 give rise to diastereoisomeric mixtures of the bromohydrins. The diastereofacial preference is more significant in the case of **3d** than of **3b**, in keeping with the greater difference in spatial requirements of H and CH_3 compared with those of CH_3 and CH_2CH_3 .



The initial dehydration experiments on **4a** used short reflux times (10–20 min) in toluene containing 4-TsOH whereupon varying amounts of the ether **7**, apparently as a single epimer, were isolated. The configuration about the ether linkage has not been established, since the magnitude of the single vicinal coupling constant $J_{3,4}$ 6.2 Hz lies between those observed for the *trans*-bromohydrins **4b**, **4d** and others¹⁵ ($J_{3,4}$ ~ 8–10 Hz) and the related *cis*-bromohydrins ($J_{3,4}$ ~ 3–5 Hz).^{15,16} However, it seems likely that in **7** the bromine substituents and the ether function possess a *trans* disposition since this compound presumably results from interception of the heteroatom stabilised cation derived from **4a** by second molecule of *trans*-bromohydrin.

Treatment of an ethereal solution of the 3-bromo-2*H*-1-benzopyrans **5** with BuLi and subsequent addition of an electrophile gave the allenes **6** in good yield, together with a small amount of the 2*H*-1-benzopyrans **3**.

The allenes all display the characteristic 1945–1960 cm^{-1} band in the IR spectrum¹⁷ and a low field signal at $\sim\delta$ 205 together with signals at $\sim\delta$ 100 and $\sim\delta$ 86 for the central (C-2), dialkyl (C-3) and aryl (C-1) substituted allene carbons respectively in the ^{13}C NMR spectrum.¹⁸ The signal for the allenyl proton appears as a multiplet (5J ~ 2.9 Hz) in all the examples as a result of long range coupling to the alkyl substituents and resonates in the range δ 6.04–6.30 in the ^1H NMR spectrum. The ^1H and ^{13}C NMR spectra of the allenes **6i** and **6j** derived from the C-2 monosubstituted 3-bromo-2*H*-1-benzopyran **5d** are slightly different, the distinguishing feature being the presence of a multiplet at $\sim\delta$ 5.5 assigned to the additional allene proton. The monoalkyl substituted allene carbon atom (C-3) now resonates at $\sim\delta$ 89, shifted upfield in comparison to those of the dialkyl substituted allenes.

Treatment of the bromoalkene **5e** with BuLi followed by the addition of ethyl chloroformate gave an inseparable mixture of the allene **6l** and an unidentified compound. The allenic structure of **6l** was indicated by the presence of a characteristic septet at δ 6.51 (J 2.8 Hz) and a doublet at δ 1.88 assigned to the allenyl and methyl group protons respectively in the ^1H NMR spectrum and by the lowfield signal at δ 206.2 for C-2 in the ^{13}C NMR spectrum. The $\text{C}=\text{C}=\text{C}$ stretching vibration at 1958 cm^{-1} in the IR spectrum is a feature of this and the other allenes prepared in this work.

It is noteworthy that a broad range of substituents can be introduced into the allene function because of the ready

availability of substituted 2*H*-1-benzopyrans¹⁹ from either Claisen rearrangement of aryl prop-2-ynyl ethers²⁰ or reduction and dehydration of 3,4-dihydro-2*H*-1-benzopyran-4-ones¹⁵ which are easily obtained by the Kabbe route.²¹ Furthermore a diverse range of electrophiles may be used to trap the intermediate phenoxide ion.

Although the allenyl phenol prepared by Gericke and Lues¹⁰ appears to be unstable, the allenes described herein are generally stable. Thus they can be distilled or crystallised and can be stored at 5 °C for several weeks. Nevertheless, they are reactive compounds and, for instance, hydrolysis of **6a** proceeds smoothly in refluxing THF containing aqueous NaOH to afford the 2*H*-1-benzopyran **3a**.

Allenes are readily hydroborated, but the results are often difficult to interpret because both mono- and di-adducts are usually formed and subsequent oxidation yields alcohols, ketones, diols and alkenes.²² 9-Borabicyclo[3.3.1]nonane (9-BBN) has been shown to be particularly selective for the hydroboration of several simple allenes affording allylboranes which lead to homoallylic alcohols as the major products when acetone is added to the reaction mixtures prior to oxidation with alkaline hydrogen peroxide.²³

The hydroboration of **6b** with 9-BBN in THF was investigated. After several hours at room temperature, TLC investigation showed that the allene remained unchanged. However, when the reaction mixture was refluxed, a new component gradually formed, which reached a constant concentration (TLC) after ~3.5 h at reflux, whereupon the reaction mixture was cooled, diluted with acetone and then oxidised with alkaline hydrogen peroxide. Elution of the crude product from silica gave 1-[2-(4-aminobenzoyloxy)phenyl]-3-methylbuta-1,2-diene **6k** arising from reduction of the aromatic nitro group. Although the signal for the amino group in the ^1H NMR spectrum centred at δ 4.2 was extremely broad, its presence was confirmed by exchange with D_2O and supported by NH stretching absorptions in the IR spectrum. The preferential reduction of the nitro group is surprising in view of the usually facile reactivity of 9-BBN towards allenes,²³ and the observation that 9-BBN reacts slowly with ester functions at 25 °C to afford alcohols.²⁴

The reaction of allenes with halogens has been comprehensively discussed.²⁵ Frequently mixtures of mono-addition products are isolated which result from indiscriminate attack by the halogen at the allenic double bonds.²⁶ The addition of iodine to a range of simple substituted allenes has been shown to afford 1,3-dienes by way of an addition–elimination sequence, together with mono-addition products.²⁷ Reaction of one equivalent of bromine with **6b** gave the diene **8** in excellent yield. The formation of this product can be rationalised by either the addition of bromine across the C-2–C-3 double bond followed by the 1,2-elimination of HBr or by addition of bromine across the C-1–C-2 double bond followed by the 1,4-elimination of HBr. The latter is favoured in view of the benzylic nature of the intermediate carbocation.

Experimental

Melting points were determined in capillary tubes and are uncorrected. Distillations were performed using a Kugelrohr (Buchi GKR-50 Glass Tube Oven) and all boiling points quoted relate to the oven temperature at which the distillation commenced. Fourier transform infrared spectra were recorded on a Mattson Polaris spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker WM 250 instrument for solutions in CDCl_3 , J values are given in Hz. Flash chromatographic separations were performed on Crossfields Sorbsil C60 silica gel (M.P.D. 60 Å, 40–60 μ , activated) according to the literature procedure.²⁸ The 2*H*-1-benzopyrans

3a,²⁹ **3b**,³⁰ **3c**,¹⁵ **3d**¹⁶ and **3e**³¹ had identical physical and spectroscopic properties to those reported in the literature, as did the *trans*-3-bromo-3,4-dihydro-2*H*-1-benzopyran-4-ols **4a**³² and **4c**¹⁵ and the 2-bromo-2,3-dihydro-1*H*-naphtho[2,1-*b*]pyran-1-ol **4e**.³³

General Method for the Preparation of the Bromohydrins 4.—*N*-Bromosuccinimide (25 mmol) was added portionwise over 45 min to a magnetically stirred solution of the 2*H*-1-benzopyran (14 mmol) in dimethyl sulfoxide (25 cm³) and water (2 cm³) at ~5 °C. On completion of the addition, the pale brown solution was stirred for a further 1 h at room temp. and then poured into water (500 cm³). The mixture was extracted with ethyl acetate (5 × 50 cm³) and the combined extracts were washed with brine (5 × 50 cm³) and water (100 cm³). Removal of the dried (Na₂SO₄) solvent gave the crude bromohydrins accompanied by some unchanged 2*H*-1-benzopyran. Purification was effected by elution from silica followed by distillation.

3-Bromo-2-ethyl-3,4-dihydro-2-methyl-2*H*-1-benzopyran-4-ol 4b. 95% from **3b** as a mixture of diastereoisomers (~ratio 1:1)* as a colourless oil after elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 130 °C/0.2 mbar; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3410; $\delta_{\text{H}}(\text{mixture})$ 0.95 (3 H, t, *J* 7.4, 2-CH₂CH₃), 1.04 (3 H, t, *J* 7.4, 2-CH₂CH₃), 1.38 (3 H, s, 2-Me), 1.54 (3 H, s, 2-Me), 1.73 (2 H, m, 2-CH₂CH₃), 1.92 (2 H, m, 2-CH₂CH₃), 3.03 (2 H, br s, OH), 4.17 (1 H, d, *J* 9.4, 3-H), 4.21 (1 H, d, *J* 10.0, 3-H), 4.95 (2 H, m, 4-H), 6.85 (2 H, m, Ar-H), 6.99 (2 H, m, Ar-H), 7.20 (2 H, m, Ar-H) and 7.46 (2 H, m, Ar-H); $\delta_{\text{C}}(\text{mixture})$ 6.66, 7.13, 18.8, 24.3, 24.4, 33.3, 60.0, 63.4, 70.1, 70.3, 80.3, 80.5, 117.0, 117.1, 121.0, 121.2, 122.4, 122.8, 127.5, 127.8, 129.6, 129.7, 151.9 and 152.3 (Found: C, 53.0; H, 5.4; Br, 29.4. C₁₂H₁₅BrO₂ requires C, 53.1; H, 5.6; Br, 29.5%).

3-Bromo-3,4-dihydro-2,6-dimethyl-2*H*-1-benzopyran-4-ol 4d. 86% from **3d** as a mixture of diastereoisomers (~ratio 14:1)† as a colourless oil after elution from silica with 20% ethyl acetate in hexane and distillation, b.p. 90 °C/0.4 mbar; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3418; δ_{H} major isomer 1.45 (3 H, d, *J* 6.6, 2-Me), 2.27 (3 H, s, 6-Me), 2.64 (1 H, br s, OH), 4.98 (1 H, dq, *J* 6.6, 3, 2, 2-H), 5.67 (1 H, dd, *J* 9.8, 3, 2, 3-H), 6.37 (1 H, d, *J* 9.8, 4-H), 6.72 (1 H, d, *J* 7.9, 8-H), 6.81 (1 H, d, *J* 1.9, 5-H) and 6.93 (1 H, dd, *J* 7.8, 1, 9, 7-H) (Found: C, 51.2; H, 5.0; Br, 31.1. C₁₁H₁₃BrO₂ requires C, 51.4; H, 5.1; Br, 31.1%).

General Method for the Preparation of 3-Bromo-2*H*-1-benzopyrans and 2-Bromo-3*H*-naphtho[2,1-*b*]pyran 5.—A solution of the bromohydrin **4** (10 mmol) in toluene (150 cm³) containing a catalytic quantity of toluene-4-sulfonic acid was heated under reflux until TLC examination of the reaction mixture indicated that none of the starting material remained (*ca.* 80 min). The cooled solution was diluted with ethyl acetate (100 cm³) and washed with water (3 × 50 cm³). Removal of the dried (Na₂SO₄) solvent gave the crude product which was purified by elution from silica and distillation or recrystallisation. The following compounds were obtained in this manner.

3-Bromo-2,2-dimethyl-2*H*-1-benzopyran 5a. 88% from **4a** as a colourless oil after elution from silica with 10% ethyl acetate in hexane, b.p. 105 °C/0.4 mbar (lit.,³⁴ b.p. 126–128 °C/10 mmHg); δ_{H} 1.60 (6 H, s, 2-Me), 6.74 (1 H, s, 4-H), 6.83–6.98 (3 H, m, Ar-H) and 7.19 (1 H, m, Ar-H); δ_{C} 26.6 (2 × C), 80.0, 116.5, 121.4, 122.1, 125.2, 125.5, 125.8, 129.4 and 151.6.

3-Bromo-2-ethyl-2-methyl-2*H*-1-benzopyran 5b. 80% from **4b** as a colourless oil after elution from silica with 10% ethyl acetate in hexane, b.p. 110 °C/0.4 mbar; δ_{H} 1.03 (3 H, t, *J* 6.2, 2-

CH₂CH₃), 1.54 (3 H, s, 2-Me), 1.89 (2 H, q, *J* 6.2, 2-CH₂CH₃), 6.76 (1 H, s, 4-H), 6.78–6.81 (3 H, m, Ar-H) and 6.90 (1 H, m, Ar-H); δ_{C} 7.88, 25.1, 32.4, 82.8, 116.1, 121.0, 121.6, 122.9, 125.5, 126.8, 129.4 and 152.0 (Found: C, 57.0; H, 5.1; Br, 31.8. C₁₂H₁₃BrO requires C, 56.9; H, 5.2; Br, 31.6%).

3-Bromospiro(2*H*-1-benzopyran-2,1'-cyclopentane) 5c. 76% from **4c** as a colourless oil after elution from silica with 10% ethyl acetate in hexane, b.p. 140 °C/0.4 mbar, which decomposed on standing at room temp.; δ_{H} 1.73–2.15 (8 H, m, –[CH₂]₄–), 6.77 (1 H, s, 4-H), 6.79–6.92 (3 H, m, Ar-H) and 7.15 (1 H, m, Ar-H); δ_{C} 24.1 (2 × C), 37.4 (2 × C), 90.4, 116.5, 121.4, 121.7, 122.7, 124.4, 126.7, 129.2 and 151.5. Satisfactory elemental analyses could not be obtained for this compound.

3-Bromo-2,6-dimethyl-2*H*-1-benzopyran 5d. 47% from **4d** as a colourless oil after elution from silica with 5% ethyl acetate in light petroleum (b.p. 40–60 °C), b.p. 85 °C/0.07 mbar (lit.,³⁵ b.p. 66–68 °C/0.05 mbar); δ_{H} 1.49 (3 H, d, *J* 6.7, 2-Me), 2.28 (3 H, s, 6-Me), 5.01 (1 H, q, *J* 6.7, 2-H), 6.72–6.76 (2 H, m, Ar-H) and 6.97 (1 H, d, *J* 2.1, 5-H); δ_{C} 18.7, 20.5, 79.9, 116.2, 120.3, 121.7, 125.3, 126.3, 129.9, 130.8 and 146.6 (Found: C, 55.2; H, 4.5; Br, 33.2. C₁₁H₁₁BrO requires C, 55.2; H, 4.6; Br, 33.4%).

2-Bromo-3,3-dimethyl-3*H*-naphtho[2,1-*b*]pyran 5e. 97% from **4e** as a pale brown solid from ethyl acetate and hexane, m.p. 78.5–79.5 °C; δ_{H} 1.63 (6 H, s, 3-Me), 7.08 (1 H, d, *J* 8.1, Ar-H), 7.37 (1 H, m, Ar-H), 7.42 (1 H, s, 1-H), 7.51 (1 H, m, Ar-H), 7.69–7.79 (2 H, m, Ar-H) and 7.90 (1 H, d, *J* 8.0, Ar-H); δ_{C} 26.3 (2 × C), 79.9, 114.6, 118.1, 121.1, 121.9, 123.8, 124.0, 126.8, 128.5, 128.9, 129.3, 129.7 and 149.7 (Found: C, 62.0; H, 4.3; Br, 27.9. C₁₅H₁₅BrO requires C, 62.3; H, 4.5; Br, 27.6%).

Using the aforementioned general method, but refluxing the reaction mixture of **4a** for 10 min gave, after elution of the crude reaction mixture from silica with 10% ethyl acetate in hexane: fraction 1, 3-bromo-2,2-dimethyl-2*H*-1-benzopyran **5a** (12%) identical in all aspects to that prepared above; fraction 2, bis(*trans*-3-bromo-3,4-dihydro-2,2-dimethyl-2*H*-1-benzopyran-4-yl) ether **7** (32%) as colourless needles from ethyl acetate and hexane, m.p. 218.5–220.0 °C; δ_{H} 1.57 (6 H, s, 2-Me), 1.62 (6 H, s, 2-Me), 4.52 (2 H, d, *J* 6.2, 3-H), 5.57 (2 H, d, *J* 6.2, 4-H), 6.85 (2 H, dd, *J* 8.1, 1.4, 8-H), 7.04 (2 H, m, 6-H), 7.28 (2 H, m, 7-H) and 7.58 (2 H, dd, *J* 8.0, 1.4, 5-H); δ_{C} 23.8 (2 × C), 27.0 (2 × C), 59.1 (2 × C), 77.2 (2 × C), 78.0 (2 × C), 117.4 (2 × C), 120.4 (2 × C), 120.9 (2 × C), 129.5 (2 × C), 129.9 (2 × C) and 152.5 (2 × C) (Found: M⁺, 494.0103; C, 53.4; H, 4.9; Br, 32.0. C₂₂H₂₄Br₂O₃ requires M⁺, 494.0093; C, 53.5; H, 4.9; Br, 32.2%); and fraction 3 unchanged bromohydrin **4a** (9%).

General Method for the Preparation of Allenes 6.—Butyllithium (10 mmol) was added to a cold (0 °C) stirred solution of the 3-bromo-2*H*-1-benzopyran **5** (10 mmol) in anhydrous diethyl ether (25 cm³) under N₂. The resulting pale yellow solution was stirred at room temp. for 1 h and then cooled to 0 °C. The electrophile (10 mmol) was added in a single portion and the reaction mixture was stirred and warmed to room temp. over 1 h. The reaction mixture was diluted with water (70 cm³) and extracted with ethyl acetate (3 × 50 cm³). Removal of the combined, dried (Na₂SO₄) solvent gave a pale yellow oil which was eluted from silica to give two fractions, the latter being identified as the original 2*H*-1-benzopyran **3** which results from protonation of the unchanged anion on aqueous work-up.

1-(2-Ethoxycarbonyloxyphenyl)-3-methylbuta-1,2-diene 6a. 67% as a colourless oil from **5a** and ethyl chloroformate after elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 150 °C/0.4 mbar; $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1955 and 1763; δ_{H} 1.41 (3 H, t, *J* 6.9, CH₂CH₃), 1.83 [6 H, d, *J* 2.9, C(CH₃)₂], 4.34 (2 H, q, *J* 6.9, OCH₂CH₃), 6.12 (1 H, septet, *J* 2.9, ArCH=C), 7.13–7.23 (3 H, m, Ar-H) and 7.39 (1 H, m, Ar-H);

* Ratio based upon comparison of the relative integrals for the 2-Me signals at δ 1.38 and 1.54.

† Ratio based upon comparison of the relative integrals for the 6-Me signals at δ 2.27 and 2.31.

δ_{C} 14.2 (CH_2CH_3), 20.1 [$\text{C}(\text{CH}_3)_2$], 64.8 (OCH_2CH_3), 86.3 ($\text{ArCH}=\text{C}$), 98.8 [$\text{C}=\text{C}(\text{CH}_3)_2$], 122.2, 126.2, 127.3, 128.2, 128.4, 147.9 ($\text{ArC}=\text{O}$), 153.6 ($\text{C}=\text{O}$) and 204.3 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 233.1178; C, 72.3; H, 7.0. $\text{C}_{14}\text{H}_{16}\text{O}_3$ requires MH^+ , 233.1177; C, 72.4; H, 7.0%).

3-Methyl-1-[2-(4-nitrobenzoyloxy)phenyl]buta-1,2-diene 6b. 55% as pale yellow needles from **5a** and 4-nitrobenzoyl chloride after elution from silica with 15% ethyl acetate in hexane and recrystallisation from ethyl acetate and hexane, m.p. 81.0–82.5 °C; $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 1950, 1737 and 1598; δ_{H} 1.64 [6 H, d, J 2.6, $\text{C}(\text{CH}_3)_2$], 6.05 (1 H, septet, J 2.6, $\text{ArCH}=\text{C}$), 7.16 (1 H, m, $\text{Ar}-\text{H}$), 7.26–7.29 (2 H, m, $\text{Ar}-\text{H}$), 7.42 (1 H, m, $\text{Ar}-\text{H}$) and 8.37–8.42 (4 H, m, nitrobenzoyl $\text{Ar}-\text{H}$); δ_{C} 20.1 [$\text{C}(\text{CH}_3)_2$], 86.7 ($\text{ArCH}=\text{C}$), 98.8 [$\text{C}=\text{C}(\text{CH}_3)_2$], 122.5, 123.6 ($2 \times \text{C}$), 126.6, 127.5, 127.9, 128.9, 131.3 ($2 \times \text{C}$), 134.8, 147.4 ($\text{ArC}=\text{O}$), 150.9, 163.0 ($\text{C}=\text{O}$) and 204.5 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 310.1079; C, 69.9; H, 4.9; N, 4.5. $\text{C}_{18}\text{H}_{15}\text{NO}_4$ requires MH^+ , 310.1091; C, 69.9; H, 4.9; N, 4.5%).

3-Methyl-1-(2-tosyloxyphenyl)penta-1,2-diene 6c. 86% as a pale yellow oil from **5b** and tosyl chloride after elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 200 °C/0.5 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1951 and 1597; δ_{H} 0.96 (3 H, t, J 6.8, CH_2CH_3), 1.74 (3 H, d, J 2.9, $\text{C}=\text{CCH}_3$), 2.01 (2 H, m, CH_2CH_3), 2.44 (3 H, s, $\text{Ar}-\text{Me}$), 6.04 (1 H, m, $\text{ArCH}=\text{C}$), 7.13–7.17 (3 H, m, $\text{Ar}-\text{H}$), 7.29–7.35 (3 H, m, $\text{Ar}-\text{H}$) and 7.71–7.74 (2 H, m, $\text{Ar}-\text{H}$) (Found: MH^+ , 329.1211; C, 69.5; H, 6.2; S, 9.7. $\text{C}_{19}\text{H}_{20}\text{O}_3\text{S}$ requires MH^+ , 329.1211; C, 69.4; H, 6.2; S, 9.9%).

1-(2-Acetoxyphenyl)-2-cyclopentylideneethene 6d. 48% as a colourless oil from **5c** and acetic anhydride after elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 170 °C/0.3 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1950, 1763 and 1594; δ_{H} 1.75–1.80 (4 H, m, $-\text{[CH}_2\text{]}_2-$), 2.34 (3 H, s, OAc), 2.50–2.55 (4 H, m, $-\text{[CH}_2\text{]}_2-$), 6.15 (1 H, quintet, J 2.8, $\text{ArCH}=\text{C}$), 7.05 (1 H, m, $\text{Ar}-\text{H}$), 7.19–7.22 (2 H, m, $\text{Ar}-\text{H}$) and 7.41 (1 H, m, $\text{Ar}-\text{H}$) (Found: C, 78.9; H, 7.1. $\text{C}_{15}\text{H}_{16}\text{O}_2$ requires C, 78.9; H, 7.1%).

1-(2-Ethoxycarbonyloxyphenyl)-3-methylpenta-1,2-diene 6e. 84% as a colourless oil from **5b** and ethyl chloroformate after elution from silica with 15% ethyl acetate in hexane and distillation, b.p. 160 °C/0.4 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1951, 1762 and 1597; δ_{H} 1.07 (3 H, t, J 6.7, CH_2CH_3), 1.41 (3 H, t, J 6.9, OCH_2CH_3), 1.82 (3 H, d, J 2.7, CCH_3), 2.09 (2 H, m, CH_2CH_3), 4.33 (2 H, q, J 6.9, OCH_2CH_3), 6.21 (1 H, m, $\text{ArCH}=\text{C}$), 7.10–7.20 (3 H, m, $\text{Ar}-\text{H}$) and 7.41 (1 H, m, $\text{Ar}-\text{H}$); δ_{C} 12.1, 14.2, 18.6, 27.0, 64.8 (OCH_2CH_3), 88.0 ($\text{ArCH}=\text{C}$), 105.2 [$\text{C}=\text{C}(\text{Me})\text{Et}$], 122.2, 126.2, 127.2, 128.1, 128.3, 147.7 ($\text{ArC}=\text{O}$), 153.5 ($\text{C}=\text{O}$) and 203.5 ($\text{C}=\text{C}=\text{C}$) (Found: C, 73.0; H, 7.4. $\text{C}_{15}\text{H}_{18}\text{O}_3$ requires C, 73.1; H, 7.4%).

3-Methyl-1-[2-(3-methylbut-2-enyloxy)phenyl]buta-1,2-diene 6f. 62% as a colourless oil, which darkened on standing at room temp., from **5a** and 3-methylbut-2-enoyl chloride after elution from silica with 15% ethyl acetate in hexane and distillation, b.p. 150 °C/0.1 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1950, 1737 and 1591; δ_{H} 1.80 [6 H, d, J 2.6, $\text{C}(\text{CH}_3)_2$], 2.01 (3 H, m, Me), 2.26 (3 H, m, Me), 5.98 (1 H, m, $\text{alkenyl}-\text{H}$), 6.07 (1 H, septet, J 2.6, $\text{ArCH}=\text{C}$) and 7.06–7.39 (4 H, m, $\text{Ar}-\text{H}$); δ_{C} 20.1 ($2 \times \text{C}$), 20.4, 27.5, 86.7 ($\text{ArCH}=\text{C}$), 98.6 [$\text{C}=\text{C}(\text{CH}_3)_2$], 115.1, 122.9, 125.7, 127.1, 128.0, 128.3, 147.5 ($\text{ArC}=\text{O}$), 159.7, 164.7 ($\text{C}=\text{O}$) and 204.1 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 243.1385. $\text{C}_{16}\text{H}_{18}\text{O}_2$ requires MH^+ , 243.1384). Satisfactory elemental analyses could not be obtained for this compound.

1-[2-(2-Furoyloxy)phenyl]-3-methylbuta-1,2-diene 6g. 46% as a pale yellow oil, which darkened on standing at room temp., from **5a** and 2-furoyl chloride after elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 180 °C/0.1 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1954, 1741 and 1594; δ_{H} 1.70 [6 H, d, J 2.9, $\text{C}(\text{CH}_3)_2$], 6.10 (1 H, septet, J 2.9, $\text{ArCH}=\text{C}$), 6.61 (1 H, dd, J 3.7, 1.9, furan-H), 7.16–7.44 (5 H, m, $4 \times \text{Ar}-\text{H}$, furan-H) and 7.69 (1 H, dd, J 3.6, 2.0, furan-H); δ_{C} 20.0 ($2 \times \text{C}$), 86.8 ($\text{ArCH}=\text{C}$),

98.7 [$\text{C}=\text{C}(\text{CH}_3)_2$], 112.1, 119.3, 122.8, 126.3, 127.3, 128.2, 128.7, 131.2, 144.1, 147.0 ($\text{ArC}=\text{O}$), 156.7 ($\text{C}=\text{O}$) and 204.4 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 255.1021. $\text{C}_{16}\text{H}_{14}\text{O}_3$ requires MH^+ , 255.1020). Satisfactory elemental analyses could not be obtained for this compound.

3-Methyl-1-(2-methylsulfonyloxyphenyl)buta-1,2-diene 6h. 49% as a yellow oil from **5a** and methanesulfonyl chloride on elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 170 °C/0.1 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1954 and 1589; δ_{H} 1.83 [6 H, d, J 2.5, $\text{C}(\text{CH}_3)_2$], 3.21 (3 H, s, SO_2Me), 6.28 (1 H, septet, J 2.5, $\text{ArCH}=\text{C}$) and 7.21–7.35 (4 H, m, $\text{Ar}-\text{H}$); δ_{C} 20.0 ($2 \times \text{C}$), 37.7 (SO_2Me), 86.2 ($\text{ArCH}=\text{C}$), 99.6 [$\text{C}=\text{C}(\text{CH}_3)_2$], 122.7, 127.2, 127.6, 128.7, 129.1, 146.0 ($\text{ArC}=\text{O}$) and 204.7 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 239.0742; C, 60.6; H, 5.9; S, 13.4. $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$ requires MH^+ , 239.0741; C, 60.5; H, 5.9; S, 13.5%).

1-(2-Ethoxycarbonyloxy-5-methylphenyl)buta-1,2-diene 6i. 53% as a yellow oil from **5d** and ethyl chloroformate on elution from silica with 10% ethyl acetate in hexane and distillation, b.p. 130 °C/0.7 mbar; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1951, 1761 and 1589; δ_{H} 1.41 (3 H, t, J 7.2, OCH_2CH_3), 1.80 [3 H, dd, J 7.1, 3.2, $\text{C}=\text{CH}(\text{CH}_3)$], 2.34 (3 H, s, 5-Me), 4.34 (2 H, q, J 7.2, OCH_2CH_3), 5.54 [1 H, m, $\text{C}=\text{CH}(\text{CH}_3)$], 6.18 (1 H, m, $\text{ArCH}=\text{C}$), 7.01 (2 H, m, $\text{Ar}-\text{H}$) and 7.21 (1 H, m, $\text{Ar}-\text{H}$); δ_{C} 13.9, 14.2, 20.8, 64.7 (OCH_2CH_3), 87.7, 89.1, 121.9, 126.8, 128.3, 128.6, 135.8, 145.8 ($\text{ArC}=\text{O}$), 153.6 ($\text{C}=\text{O}$) and 206.9 ($\text{C}=\text{C}=\text{C}$) (Found: C, 72.3; H, 6.7. $\text{C}_{14}\text{H}_{16}\text{O}_3$ requires C, 72.4; H, 7.0%).

1-(5-Methyl-2-methylsulfonyloxyphenyl)buta-1,2-diene 6j. 55% as a pale yellow oil from **5d** and methanesulfonyl chloride on elution from silica with 7.5% ethyl acetate in hexane. Attempted distillation of the oil resulted in its decomposition; $\nu_{\text{max}}(\text{neat})/\text{cm}^{-1}$ 1950 and 1595; δ_{H} 1.82 [3 H, dd, J 7.4, 3.2, $\text{C}=\text{CH}(\text{CH}_3)$], 2.32 (3 H, s, 5-Me), 3.13 (3 H, s, SO_2Me), 5.57 [1 H, m, $\text{C}=\text{CH}(\text{CH}_3)$], 6.30 (1 H, m, $\text{ArCH}=\text{C}$), 7.03 (1 H, dd, J 7.9, 1.2, $\text{Ar}-\text{H}$) and 7.20–7.29 (2 H, m, $\text{Ar}-\text{H}$); δ_{C} 14.0, 20.8, 37.9 (SO_2Me), 87.7, 89.9, 122.4, 127.8, 128.6, 128.8, 137.0, 143.9 ($\text{ArC}=\text{O}$) and 205.9 ($\text{C}=\text{C}=\text{C}$) (Found: M^+ , 238.0664; C, 60.4; H, 5.9; S, 13.2. $\text{C}_{12}\text{H}_{14}\text{O}_3\text{S}$ requires M^+ , 238.0663; C, 60.5; H, 5.9; S, 13.5%).

Hydroboration of 3-Methyl-1-[2-(4-nitrobenzoyloxy)phenyl]buta-1,2-diene 6b.—A solution of 9-borabicyclo[3.3.1]nonane (9-BBN) [10 mmol, 0.5 mol dm^{-3} in tetrahydrofuran (THF)] was added *via* syringe to a cold (5 °C) stirred solution of the allene **6b** (10 mmol) in anhydrous THF (40 cm^3) under a N_2 atmosphere. The solution was refluxed until the amount of unchanged allene remained constant by TLC ~ 3.5 h. The solution was cooled (ice-water) and acetone (10 mmol) was added in a single portion and the solution stirred for 1 h. Sodium hydroxide (3 mol dm^{-3} ; 3 cm^3) and hydrogen peroxide (30%, 3 cm^3) were added sequentially and the solution was then maintained at 60 °C for 1 h. The cooled solution was poured into water (300 cm^3) and extracted with ethyl acetate (3 \times 50 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated to afford a pale yellow sticky solid which was eluted from silica with 25% ethyl acetate in hexane to afford two fractions; fraction 1, the unchanged allene **6b**, (12%) identical in all aspects with authentic material, and fraction 2 1-[2-(4-aminobenzoyloxy)phenyl]-3-methylbuta-1,2-diene **6k** (75%) as a pale brown solid from ethyl acetate and hexane, m.p. 161.0–162.0 °C; $\nu_{\text{max}}(\text{Nujol})/\text{cm}^{-1}$ 3457, 3369, 1947, 1691 and 1588; δ_{H} 1.67 [6 H, d, J 2.5, $\text{C}(\text{CH}_3)_2$], 4.2 (2 H, vbr s, NH_2), 6.09 (1 H, septet, J 2.5, $\text{ArCH}=\text{C}$), 6.74 (2 H, m, $\text{Ar}-\text{H}$), 7.13–7.43 (4 H, m, $\text{Ar}-\text{H}$) and 8.05 (2 H, m, $\text{Ar}-\text{H}$); δ_{C} 21.1 ($2 \times \text{C}$), 88.9, 98.5, 118.1, 119.3, 123.8, 125.8, 126.7 ($2 \times \text{C}$), 127.2, 128.4, 128.8, 132.4 ($2 \times \text{C}$), 148.0, 164.9 and 204.2 ($\text{C}=\text{C}=\text{C}$) (Found: MH^+ , 280.1338; C, 77.6; H, 6.0; N, 4.8. $\text{C}_{18}\text{H}_{17}\text{NO}_2$ requires MH^+ , 280.1337; C, 77.4; H, 6.1; N, 5.0%).

Bromination of 3-Methyl-1-[2-(4-nitrobenzoyloxy)phenyl]-buta-1,2-diene 6b.—A solution of bromine (50 mmol) in chloroform (30 cm³) was added dropwise over 30 min to a cold (5 °C) stirred solution of the allene **6b** (50 mmol) in chloroform (50 cm³). On completion of the addition, the solution was stirred until the evolution of HBr ceased (~5 h) and then heated to 50 °C for 30 min. The chloroform was removed and the reaction product eluted from silica with 10% ethyl acetate in hexane to give 2-bromo-1-[2-(4-nitrobenzoyloxyphenyl)]-3-methylbuta-1,3-diene **8** (74%) as pale yellow needles from ethyl acetate and hexane, m.p. 132.0–133.5 °C; ν_{\max} (Nujol)/cm⁻¹ 1743 and 1590; δ_{H} 2.16 (3 H, s, Me), 3.80 (1 H, d, *J* 1.0, C=CH₂), 4.31 (1 H, d, *J* 1.0, C=CH₂), 7.09 (1 H, s, Ar-CH=C), 7.32–7.56 (4 H, m, Ar-H) and 8.33–8.43 (4 H, m, O₂NAr-H); δ_{C} 29.2, 41.6, 64.7, 122.0, 123.7 (2 × C), 126.3, 127.0, 129.4, 129.7, 130.1, 131.4 (2 × C), 133.6, 134.6, 147.7, 151.0 and 162.7 (Found: *M* + NH₄⁺, 405.0450. C₁₈H₁₄BrNO₄ requires *M* + NH₄⁺, 405.0449). Satisfactory elemental analyses could not be obtained for this compound.

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