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Chemistry of Allene Sulfoxides: a New Synthesis of 1-Aryl-3,4-dihydro-1*H*-[1]benzothieno[3,2-*c*]pyrans

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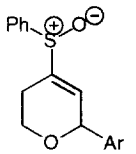
Abstract: A novel synthesis of 1-aryl-3,4-dihydro-1*H*-[1]benzothieno[3,2-*c*]pyrans has been developed, utilising the acid-catalysed cyclisation of 5,6-dihydro-4-phenylsulfinyl-2*H*-pyrans. Both ring systems could be isolated from suitably substituted allene sulfoxides upon exposure to *p*-toluenesulfonic acid in refluxing tetrahydrofuran, the nature of the product depending on the reaction time.

INTRODUCTION

Allene sulfoxides are extremely versatile intermediates in organic synthesis,[2-4] and we have demonstrated their wide applicability for the construction of carbocyclic[5] and heterocyclic[6,7] systems. We now wish to report our recent findings, extending the use of allene sulfoxide chemistry to the synthesis of substituted dihydropyrans (**1**), which have been further elaborated to provide a novel method for the preparation of 1-aryl-3,4-dihydro-1*H*-[1]benzothieno[3,2-*c*]pyrans (**2** R=Ar).



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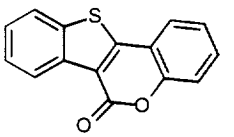
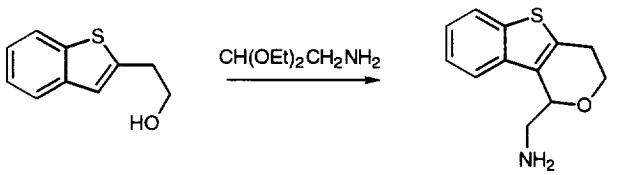


3

To date, the benzothieno[3,2-*c*]pyran system (**2**) has only been reported by Dobson,[8] and related ring systems of type (**3**) have also been described, containing a fused aromatic ring at the 3,4-position.[9,10] The heterocycle (**2**) was formed by closure of the oxygen-containing ring as illustrated in Scheme 1, whereas our new procedure relies on closure of the central sulfur-containing ring.

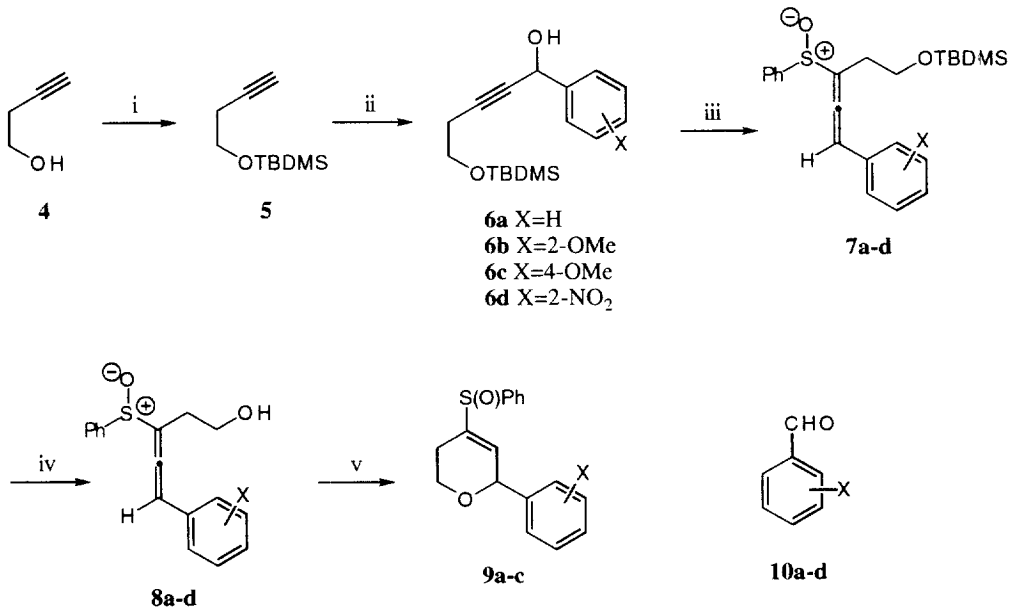


Scheme 1

RESULTS & DISCUSSION

Our initial targets were 2-aryl-substituted 5,6-dihydro-2*H*-pyrans (**9a-c**), which were synthesised using our previously developed procedures.[11] The general route employed to obtain these dihydropyrans is outlined in Scheme 2.

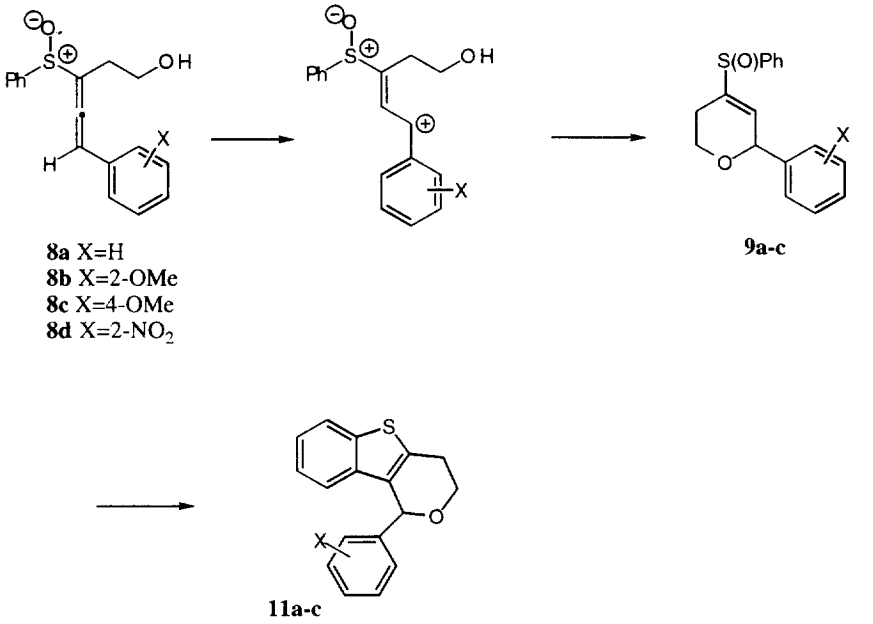
Protection of the acetylenic alcohol (**4**) as the corresponding *tert*-butyldimethylsilyl (TBDMS) ether (**5**) was readily accomplished using the procedure reported by Corey and Venkateswarlu (TBDMSCl, imidazole, DMAP, DMF).[12] The acetylenic Grignard reagent was prepared from (**5**) by exchange with ethylmagnesium bromide, and subsequent reaction with commercially available aldehydes (**10a-d**) afforded the propargylic alcohols (**6a-d**) in 42-64 % yield. Treatment of (**6a-d**) with benzenesulfenyl chloride[13] in the presence of triethylamine gave the protected allene sulfoxides (**7a-d**), and deprotection with acetic acid in aqueous THF[14] smoothly provided alcohols (**8a-d**) in 14-33 % overall yield for both steps.



Scheme 2. *Reagents & Conditions*: i, TBDMSCl, imid, DMAP, DMF; ii, EtMgBr, Et_2O, 4 h then (**10**); iii, PhSCl, Et_3N, Et_2O; iv, AcOH, H_2O, THF (13:7:3); v, *p*-TsOH, THF, reflux.

Alcohols (**8a-c**) cyclised under acid-catalysed conditions (refluxing THF, 5 h) to provide substituted dihydropyrans (**9a-c**) in 29-59 % yield. In all successful cases, the aromatic group contained either no substituent (X=H) or an electron-donating substituent (X=OMe). No cyclisation product was observed when the 2-nitrophenyl allene sulfoxide (**7d** X=2-NO_2) was treated with acid, even under forcing conditions. This result was expected, and agrees with our proposed mechanism for the cyclisation reaction (Scheme 3). The first step involves protonation of the central allene carbon atom leading to a benzylic carbocation; further stability is conferred upon this intermediate by the presence of an electron-donating methoxy substituent, at either the

ortho- or *para*-position (X=2-MeO, 4-MeO). This extra resonance-stabilising effect manifests itself in terms of a higher chemical yield (44 and 59 %), as compared with the unsubstituted phenyl (X=H) analogue (29 %).



8a X=H
8b X=2-OMe
8c X=4-OMe
8d X=2-NO_2

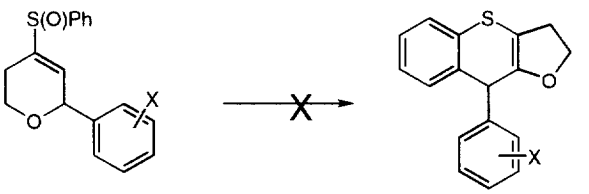
9a-c

11a-c

Scheme 3

Alcohols (**8a-c**) underwent an entirely unprecedented cyclisation sequence upon prolonged exposure to *p*-toluenesulfonic acid in refluxing THF, to give 1-aryl-substituted 3,4-dihydro-1*H*-[1]benzothieno[3,2-*c*]pyrans (**11a-c**) presumably *via* the intermediacy of dihydropyrans (**9a-c**).

The X-ray crystal structure of (**11b**) is shown in Figure 1, and provides unambiguous evidence that products (**11a-c**) are the benzothienopyrans depicted in Scheme 3, rather than the isomeric benzothiopyranofurans (Scheme 4), since on NMR and IR data alone, both isomers could be suggested.



Scheme 4

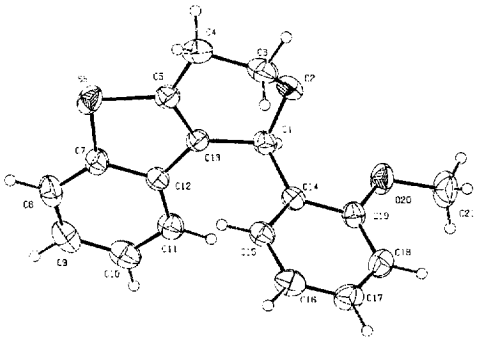
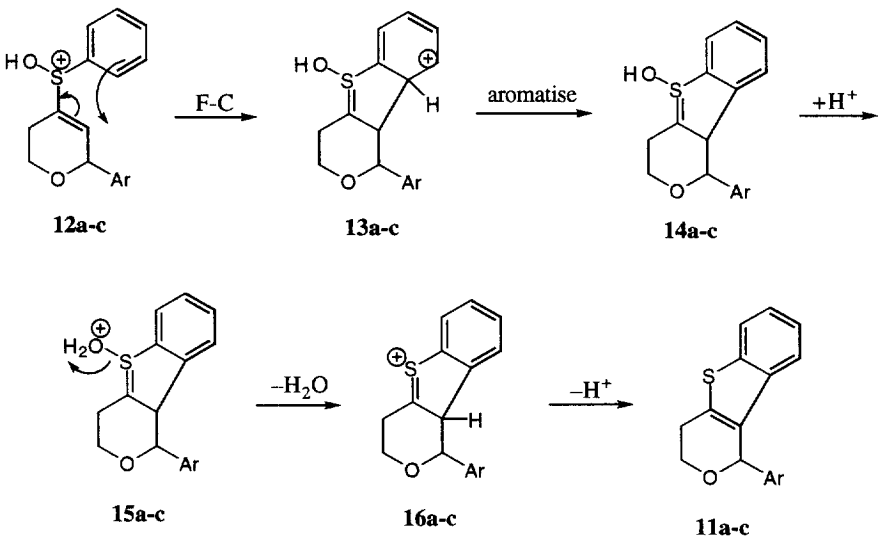


Figure 1. ORTEP plot of (**11b**)

Our proposed mechanism is depicted in Scheme 5. The first step involves protonation of the sulfoxide oxygen atom to give (**12a-c**). A Friedel-Crafts reaction then takes place to produce a carbocation (**13a-c**), which can re-aromatise by loss of a proton, providing intermediate (**14a-c**). Protonation and subsequent dehydration of (**14a-c**) leads to the formation of thionium species (**16a-c**), which then gives the requisite benzothienopyrans (**11a-c**) upon loss of a proton.



Scheme 5

In conclusion, a new synthesis of 1-aryl-substituted 3,4-dihydro-1*H*-[1]benzothieno[3,2-*c*]pyrans (13 % yield for compound (**11b**) over 5 steps) has been developed, which relies on closure of the central sulfur-containing ring as a key step. This tandem double cyclisation (allene sulfoxide–dihydropyran–benzothienopyran) serves to demonstrate the applicability of allene sulfoxide chemistry to the preparation of complex heterocyclic building blocks.

EXPERIMENTAL

All melting points are uncorrected. IR spectra were recorded using a Perkin-Elmer 881 spectrometer. NMR spectra were recorded using Jeol EX400, Bruker WM300, and Bruker WM250 spectrometers. Mass spectra were recorded at the EPSRC Mass Spectrometry Service Centre at the University of Wales, Swansea, and using a VG Micromass 7070F high resolution instrument. Aromatic aldehydes (**10a-d**) were purchased from Aldrich Chemical Co.

*General Procedure for the Preparation of Propargylic Alcohols (**6a-d**)*

A solution of 1-[(*tert*-butyldimethylsilyl)oxy]-3-butyne[15] (33 mmol) in distilled THF (5 ml) was added to an ice-cooled solution of ethylmagnesium bromide (3 M soln in ether, Aldrich, 36 mmol), and the resulting mixture stirred at 0 °C for 4 h. A solution of the aromatic aldehyde (**10a-d**) (33 mmol, 1 equiv) in distilled THF (5 ml) was then added dropwise, and the resulting mixture stirred for a further 2 h at 0 °C. The reaction mixture was allowed to warm to room temperature, and then quenched with satd. aq. ammonium chloride soln. The mixture was poured into further satd. aq. ammonium chloride soln. which was extracted with ether (4 x 50 ml). The combined organic extracts were washed with brine and dried over sodium sulfate, before concentrating to a residue at water aspirator pressure.

*1-[(tert-Butyldimethylsilyl)oxy]-5-phenyl-3-pentyn-5-ol (**6a**).* The product was purified by flash column chromatography eluting with 3:1 petrol/ether (3.16 g, 33 %).ν_{max} (film) 3369 (OH), 2952, 2927, 2855, 1603 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.08 (6H, s), 0.90 (9H, s), 2.45 (1H, d *J*=2.0 Hz), 2.50 (2H, td *J*=2.0, 7.0 Hz), 3.77 (2H, t *J*=7.0 Hz), 5.40-5.48 (1H, m), 7.29-7.59 (5H, m) ppm; δ_C (63 MHz, $CDCl_3$) –5.29, –3.58, 18.33, 22.68, 25.60, 25.66, 26.21, 61.78, 64.78, 81.09, 84.47, 126.66, 128.24, 128.55, 141.09 ppm; CIMS 308 (M^++NH_4, 17 %), 290, 273, 263, 250, 233, 215, 202, 189, 185, 159; HRMS Calcd for $C_{17}H_{30}NO_2Si$ (M^-+NH_4) 308.2046, Found. 308.2046

*1-[(tert-Butyldimethylsilyl)oxy]-5-(2-methoxyphenyl)-3-pentyn-5-ol (**6b**).* The crude oil was purified by flash column chromatography eluting with 2:1 petrol/ether to afford the title compound (7.92 g, 75 %). ν_{max} (film) 3420 (OH), 2980, 2935, 2880, 1600,1580 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 0.09 (6H, s), 0.91 (9H, s), 2.53 (2H, td *J*=2.0, 7.0 Hz), 2.96 (1H, br s), 3.79 (2H, t *J*=7.0 Hz), 3.89 (3H, s), 5.73 (1H, d *J*=2.0 Hz), 6.89-7.03 (2H, m), 7.27-7.60 (1H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.68, –5.11, 18.20, 23.20, 25.57, 25.63, 25.94, 55.40, 61.77, 80.27, 83.77, 110.69, 120.78, 127.86, 129.01, 129.49, 156.64 ppm; EIMS 303 (M^+–OH, 2 %), 245, 230, 218, 201, 185, 171, 158; HRMS Calcd for $C_{18}H_{27}O_2Si$ (M^+–OH) 303.1780, Found. 303.1780

*1-[(tert-Butyldimethylsilyl)oxy]-5-(4-methoxyphenyl)-3-pentyn-5-ol (**6c**).*The product was obtained after flash column chromatography eluting with 2:1 petrol/ether (4.65 g, 44 %). ν_{max} (film) 3420 (OH), 3000, 2952, 2928, 2855,1611,1512 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.08 (6H, s), 0.85 (9H, s), 2.11 (1H, br s), 2.42 (2H, td *J*=2.0, 7.0 Hz), 3.68 (2H, t *J*=7.0 Hz), 3.72 (3H, s), 5.33 (1H, s), 6.78-7.40 (4H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.29, –5.01, 18.33, 23.23, 25.27, 25.79, 25.88, 55.30, 61.89, 64.34, 81.25, 84.18, 113.86, 128.99,

133.45, 159.56 ppm; CIMS 321 (MH^+, 28 %), 305, 303, 279, 263, 222, 205, 189, 159, 154, 151; HRMS Calcd for $C_{18}H_{27}O_2Si$ (M^+–OH) 303.1780, Found. 303.1780

*1-[(tert-Butyldimethylsilyl)oxy]-5-(2-nitrophenyl)-3-pentyn-5-ol (**6d**).* The product was obtained by flash column chromatography eluting with 3:1 and then 2:1 petrol/ether (3.43 g, 31 %) as an unstable oil. ν_{max} (film) 3394 (OH), 2954, 2929, 2857, 1610,1528 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.05 (6H, s), 0.86 (9H, s), 2.44 (2H, td *J*=2.0, 7.0 Hz), 3.22 (1H, d *J*=2.0 Hz), 3.74 (2H, t *J*=7.0 Hz), 5.95-6.02 (1H, m), 7.42-8.18 (4H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.40, –5.32, 18.31, 23.17, 25.60, 25.66, 25.79, 61.36, 61.56, 78.99, 85.06, 124.91, 129.15, 129.48, 133.65, 135.81, 148.13 ppm

*General Procedure for the Preparation of Allene Sulfoxides (**7a-d**)*

A solution of benzenesulfenyl chloride[13] (3.7 mmol) in diethyl ether (10 ml) was slowly added at 0 °C to a solution of propargylic alcohol (**6a-d**) (3.25 mmol) in diethyl ether (10 ml) containing triethylamine (4.9 mmol). The reaction mixture was stirred for 3 h whilst slowly warming to room temperature. Water was added to the mixture, and after separating the layers, the aqueous phase was extracted with ether (3 x 50 ml). The combined organic extracts were then washed with brine, and dried over sodium sulfate before concentrating at reduced pressure to a residue.

*1-[(tert-Butyldimethylsilyl)oxy]-5-phenyl-3-phenylsulfinyl-3,4-pentadiene (**7a**).* The compound was obtained by flash column chromatography eluting with 2:1 hexane/ether (0.52 g, 40 %).ν_{max} (film) 3061, 2953, 2928, 2856, 1941 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 0.01 (6H, s), 0.80 (9H, s), 2.20-2.67 (2H, m), 3.66 (2H, m), 6.59-6.68 (1H, m), 7.22-7.71 (10H, m) ppm; δ_C (63 MHz, $CDCl_3$) –5.29, –3.58, 18.36, 25.64, 25.82, 26.01, 29.54, 60.14, 100.95, 116.37, 124.54, 127.45, 128.58, 128.71, 129.00, 129.26, 139.74, 143.81, 213.03 ppm; CIMS 399 (MH^+, 90 %), 291, 233; HRMS Calcd for $C_{23}H_{31}O_2SSi$ (MH^+) 399.1814, Found. 399.1814

*1-[(tert-Butyldimethylsilyl)oxy]-5-(2-methoxyphenyl)-3-phenylsulfinyl-3,4-pentadiene (**7b**).* The product was obtained after flash column chromatography eluting with 3:1 cyclohexane/ether (0.90 g, 65 %). ν_{max} (film) 2960, 2930, 2860, 1940, 1600, 1580 cm^{-1}; δ_H (300 MHz, $CDCl_3$) –0.03 (6H, s), 0.81 (9H, s), 2.18-2.38 (1H, m), 2.50-2.64 (1H, m), 3.55-3.73 (2H, m), 3.85 (3H, s), 6.85-7.06 (3H, m), 7.18-7.30 (2H, m), 7.38-7.54 (3H, m), 7.60-7.70 (2H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.15, –4.27, 18.44, 25.94, 26.09, 26.31, 27.39, 55.86, 61.55, 96.17, 111.22, 112.64, 121.02, 124.71, 129.08, 129.22, 129.51, 136.20, 143.99, 144.21, 156.75, 203.97 ppm; EIMS 428 (M^+, 4 %), 371, 353, 303, 279, 263, 241, 231, 217, 202, 189, 171, 161; HRMS Calcd for $C_{24}H_{32}O_3SSi$ (M^+) 428.1841 Found. 428.1885

*1-[(tert-Butyldimethylsilyl)oxy]-5-(4-methoxyphenyl)-3-phenylsulfinyl-3,4-pentadiene (**7c**).* The product was purified by flash column chromatography eluting with 2:1 ether/petrol (0.88 g, 63 %). ν_{max} (film) 2954, 2929, 2855, 1939, 1698, 1607 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 0.09 (6H, s), 0.84 (9H, s), 2.23-2.70 (2H, m), 3.62-3.78 (2H, m), 3.86 (3H, s), 6.60-6.71 (1H, m), 6.85-7.91 (9H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.40, 18.20, 25.84, 27.69, 55.36, 61.36, 101.32, 114.35, 124.49, 128.75, 129.06, 130.83, 132.00, 143.89, 159.73, 202.47 ppm; CIMS 429 (MH^+, 67 %), 407, 371, 348, 332, 315, 297, 268, 222, 207, 189; HRMS Calcd for $C_{24}H_{32}O_3SSi$ (M^+) 428.1841 Found. 428.1885.

*1-[(tert-Butyldimethylsilyl)oxy]-5-(2-nitrophenyl)-3-phenylsulfinyl-3,4-pentadiene (**7d**).* The product was purified by flash column chromatography eluting with 1:1 petrol/ether (0.32 g, 22 %) and was obtained as an unstable oil. ν_{max} (film) 3064, 2953, 2928, 2884, 2856, 1962, 1672, 1651, 1600 cm^{-1}; δ_H (250 MHz, $CDCl_3$) –0.06 (6H, s), 0.83 (9H, s), 2.21-2.69 (2H, m), 3.63-3.78 (2H, m), 7.30-8.18 (10H, m) ppm; δ_C (100 MHz, $CDCl_3$) –5.41, –3.58, 18.16, 25.64, 25.75, 25.82, 33.61, 60.83, 101.23, 118.82, 121.91, 124.58, 127.56, 128.78, 129.44, 131.42, 133.67, 136.61, 139.89, 162.50 ppm

*General Procedure for the Removal of the Silyl Protecting Group (**8a-d**)*

The allene sulfoxide (**7a-d**) (3.2 mmol) was dissolved in a mixed solvent system containing glacial acetic acid, water and THF in the ratio 13:7:3 respectively (23 ml), and the solution stirred for 18 h at room temperature. The reaction mixture was then poured into water (100 ml), and the cloudy solution was neutralised by careful addition of solid potassium bicarbonate with vigorous stirring. The crude product was extracted into ether (3 x 100 ml) and the combined organic extracts washed with brine, dried over magnesium sulfate and concentrated to a residue.

*5-Phenyl-3-phenylsulfinyl-3,4-pentadien-1-ol (**8a**).* The product was obtained by flash column chromatography eluting with 5:1 ethyl acetate/petrol (0.61 g, 67 %). ν_{max} (film) 3397, 3061, 2951, 2927, 2855, 1940 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 1.72 (1H, br s), 2.41-2.54 (2H, m), 3.60-3.86 (2H, m), 6.64-6.73 (1H, m), 7.17-7.71 (10H, m) ppm; δ_C (63 MHz, $CDCl_3$) 29.54, 61.18, 100.95, 116.40, 124.54, 127.58, 128.69, 129.00, 129.06, 131.13, 139.77, 143.58, 215.13 ppm; CIMS 285 (MH^+, 33 %), 267, 252, 232, 195, 194, 177; HRMS Calcd for $C_{17}H_{17}O_2S$ (MH^+) 285.0948, Found. 285.0949

*5-(2-Methoxyphenyl)-3-phenylsulfinyl-3,4-pentadien-1-ol (**8b**).* The product was obtained as a white solid by recrystallisation from diethyl ether (0.51 g, 51 %) m.p. 110.9-112.1 °C. ν_{max} ($CHCl_3$) 3405, 2935, 2839, 1939, 1736, 1598, 1583 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.30-2.51 (2H,m), 3.64-3.79 (2H, m), 3.92 (3H, s), 6.86-7.03 (3H, m), 7.17-7.42 (2H, m), 7.46-7.61 (3H, m), 7.63-7.73 (2H, m) ppm; δ_C (100 MHz, $CDCl_3$) 29.54, 55.35, 60.89, 95.51, 110.96, 112.59, 119.72, 120.76, 124.37, 128.97, 129.03, 129.87, 130.79, 142.54, 156.75, 205.97 ppm; EIMS 314 (M^+, 18 %), 296, 283, 269, 252, 241, 226, 208, 189, 175, 161; HRMS Calcd for $C_{18}H_{18}O_3S$ (M^+) 314.0977, Found. 314.0983

*5-(4-Methoxyphenyl)-3-phenylsulfinyl-3,4-pentadien-1-ol (**8c**).* The product was obtained by flash column chromatography eluting with 3:1 ethyl acetate/petrol (0.52 g, 52 %). ν_{max} (film) 3403, 2933, 2836, 1937, 1722, 1607 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.39-2.50 (2H, m), 3.60-3.79 (2H, m), 3.80 (3H, s), 6.60-6.69 (1H, m), 6.83-7.69 (9H, m) ppm; δ_C (100 MHz, $CDCl_3$) 29.57, 55.39, 61.14, 100.60, 114.50, 123.50, 124.52, 128.75, 128.89, 131.16, 142.57, 159.95, 203.81 ppm; CIMS 315 (MH^+, 58 %), 297, 285, 267, 208, 207, 189, 175; HRMS Calcd for $C_{18}H_{19}O_3S$ (M^+) 315.1055, Found. 315.1055

*5-(2-Nitrophenyl)-3-phenylsulfinyl-3,4-pentadien-1-ol (**8d**).* The product was obtained by flash column chromatography eluting with 3:1 ethyl acetate/petrol as a very unstable oil (0.67 g, 64 %). ν_{max} (film) 3409, 3068, 2932, 2883, 1965, 1672, 1602 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.65-2.77 (2H, m), 3.68-3.81 (2H, m), 7.28-

7.37 (1H, m), 7.45-7.71 (6H, m), 8.09-8.13 (2H, m), 8.40-8.44 (1H, m) ppm; δ_C (100 MHz, $CDCl_3$) 34.16, 61.32, 118.93, 121.78, 124.72, 128.44, 128.53, 129.74, 131.33, 134.05, 136.78, 139.92, 162.90 ppm

*General Procedure for the Preparation of Dihydropyrans (**9a-c**)*

A solution of allene sulfoxide (**8a-c**) (0.73 mmol) in THF (20 ml) containing a catalytic quantity of *p*-toluenesulfonic acid was heated at reflux temperature for 3-5 h. The reaction mixture was then cooled to room temperature and poured into dilute potassium carbonate solution. The crude product was extracted into ether (3 x 100 ml), and the combined organic extracts washed with brine and dried over magnesium sulfate, before concentrating to a residue.

*2-Phenyl-4-phenylsulfinyl-5,6-dihydro-2H-pyran (**9a**).* The product was obtained by flash column chromatography eluting with 2:1 ether/petrol (60 mg, 29 %). ν_{max} (film) 3418, 3057, 2924, 1687, 1658, 1608 cm^{-1}; δ_H (250 MHz, $CDCl_3$) 2.73 (2H, t *J*=6.0 Hz), 3.85 (2H, t *J*=6.0 Hz), 6.20 (1H, d *J*=12.0 Hz), 6.92 (1H, d *J*=12.0 Hz), 7.01-7.75 (10H, m) ppm; δ_C (100 MHz, $CDCl_3$) 29.60, 42.13, 45.16, 58.11, 77.20, 125.02, 126.16, 128.44, 128.91, 129.32, 134.15, 135.05, 141.34, 143.51 ppm

*2-(2-Methoxyphenyl)-4-phenylsulfinyl-5,6-dihydro-2H-pyran (**9b**).* The product was purified by flash column chromatography eluting with 3:1 ether/cyclohexane (101 mg, 44 %). ν_{max} (film) 2915, 2840, 1600 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.60-2.71 (2H, m), 3.73-3.85 (2H, m), 3.85 (3H, s), 6.20 (1H, d *J*=15.0 Hz), 6.85-7.01 (3H, m), 7.11 (1H, d *J*=15.0 Hz), 7.24-7.69 (6H, m) ppm; δ_C (75 MHz, $CDCl_3$) 41.90, 55.85, 58.31, 71.20, 111.13, 120.85, 124.95, 126.61, 128.73, 129.50, 132.00, 135.24, 139.01, 158.04 ppm; EIMS 315 (MH^+, 38 %), 297, 267, 241, 207, 189, 175; HRMS Calcd for $C_{18}H_{19}O_3S$ (MH^+) 315.10549, Found. 315.10444

*2-(4-Methoxyphenyl)-4-phenylsulfinyl-5,6-dihydro-2H-pyran (**9c**).*The product was purified by flash column chromatography eluting with 1:1 ether/hexane then 5:1 ether/hexane (135 mg, 59 %). ν_{max} (film) 3054, 2957, 2933, 2836, 1602 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 1.85-2.32 (2H, m), 3.69-4.10 (5H, m), 5.23 (1H, d *J*=15.0 Hz), 6.76 (1H, d *J*=15.0 Hz), 6.83-6.92 (2H, m), 7.18-7.30 (2H, m), 7.44-7.75 (5H, m) ppm; δ_C (100 MHz, $CDCl_3$) 19.41, 21.00, 55.29, 61.97, 63.25, 75.59, 76.07, 113.92, 114.02, 114.27, 124.38, 124.51, 124.90, 127.04, 127.38, 127.53, 128.88, 129.23, 129.96, 130.93, 131.22, 142.05, 143.22, 159.59 ppm; CIMS 314 (M^+, 14 %), 297, 189; HRMS Calcd for $C_{18}H_{18}O_3S$ (M^+) 314.0977, Found. 314.0977

*General Procedure for the Preparation of Benzothienopyrans (**11a-c**)*

A solution of allene sulfoxide (**8a-c**) (0.3 mmol) in THF (100 ml) containing a catalytic quantity of *p*-toluenesulfonic acid was heated at reflux temperature for 24 h. After cooling, solid potassium carbonate was added and the mixture stirred vigorously. After filtration, the solvent was removed at reduced pressure to give a crude residue.

*3,4-Dihydro-1-phenyl-1H-[1]benzothieno[3,2-c]pyran (**11a**).* The product was purified by recrystallisation from ether to give a bright yellow solid (14 mg, 18 %) m.p. 118-122 °C. ν_{max} ($CHCl_3$) 1578 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.90-3.04 (2H, m), 3.84-3.90 (1H, m), 4.01-4.06 (1H, m), 5.85 (1H, s), 6.89-7.72 (9H, m) ppm; δ_C (100 MHz, $CDCl_3$) 26.60, 61.70, 76.74, 121.87, 122.23, 123.72, 123.92, 127.41, 127.81,

127.98, 128.18, 135.93, 137.23, 138.23, 139.83 ppm; EIMS 266 (M^+, 100 %), 234, 189, 161; HRMS Calcd for $C_{17}H_{14}OS$ (M^+) 266.0765, Found. 266.0765

*3,4-Dihydro-1-(2-methoxyphenyl)-1H-[1]benzothieno[3,2-c]pyran (**11b**).* The product was purified by recrystallisation from *tert*-butyl methyl ether to give a colourless solid (45 mg, 51 %) m.p. 122-124 °C. ν_{max} ($CHCl_3$) 1600, 1580 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 3.04-3.12 (2H, m), 3.97-4.16 (5H, m), 6.48 (1H, s), 6.72-7.81 (8H, m) ppm; δ_C (100 MHz, $CDCl_3$) 26.58, 55.95, 61.32, 70.10, 111.04, 120.36, 121.86, 122.36, 123.83, 124.03, 127.64, 129.50, 129.93, 130.26, 135.97, 137.39, 138.36, 157.91 ppm; EIMS 296 (M^+, 100 %), 281, 265, 250, 235, 221, 208, 189; HRMS Calcd for $C_{18}H_{16}O_2S$ (M^+) 296.0871, Found. 296.0871

*3,4-Dihydro-1-(4-methoxyphenyl)-1H-[1]benzothieno[3,2-c]pyran (**11c**).* The product was purified by flash column chromatography eluting with 1:1 petrol/ether (7 mg, 8 %). ν_{max} (film) 1604, 1579 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 2.95-3.10 (2H,m), 3.78 (3H, s), 3.91-4.15 (2H, m), 6.98 (1H, s), 7.17-7.80 (8H, m) ppm; δ_C (100 MHz, $CDCl_3$) 26.45, 55.24, 61.58, 76.47, 113.85, 114.42, 123.71, 125.50, 127.55, 128.77, 129.05, 129.41, 135.74 ppm; CIMS 296 (M^+, 5 %), 218, 205, 185, 154; HRMS Calcd for $C_{18}H_{16}O_2S$ (M^+) 296.0871, Found. 296.0871

*X-Ray Structural Analysis of **11b**.* Crystal data was collected using the MARresearch Image Plate System with MoKα radiation (λ=0.71070 Å). The crystal was positioned at 75 mm from the Image Plate and 95 frames were measured at 2° intervals with a counting time of 2 mins. $C_{18}H_{16}O_2S$, FW=296.37, monoclinic crystals in a P21/n space group, a=13.489 (12), b=7.994 (9), c=14.753 (14) Å, β=112.47 (1)°, U=1470 (3) $Å^3$, Z=4, dc=1.339 Mgm^{-3}, F(000)=642.4472, T=293 K. Of the 4472 reflections collected, 2564 were independent, R_{int}=0.0407. Data analysis was carried out with the XDS program.[16] The structure was solved by direct methods with the Shelx86 program.[17] The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structure was then refined using Shelxl[18] to R1=0.0570, wR2=0.1442 on 1862 reflections with I>2σ(I). All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Data have been deposited at the Cambridge Crystallographic Data Centre.

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