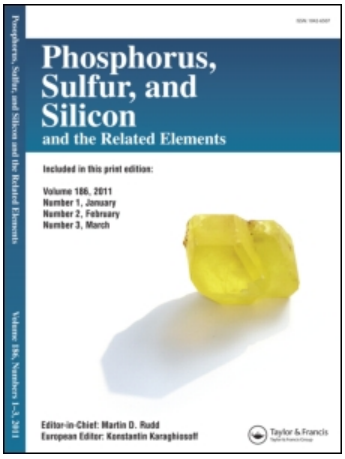

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HALOGENOVINYL SULFONES 5[1]. SYNTHESIS OF A DIBENZOPYRAN DERIVATIVE FROM AN INTRAMOLECULAR DIELS-ALDER REACTION

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HALOGENOVINYL SULFONES 5[1]. SYNTHESIS OF A DIBENZOPYRAN DERIVATIVE FROM AN INTRAMOLECULAR DIELS-ALDER REACTION

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Reaction of o-(1,3-pentadienyl)-phenol **3** with 1,3-dichloro-2-phenylsulfonylpropane **2** in the presence of triethylamine gave o-(1,3-pentadienyl)-phenyl (2-phenylsulfonyl)-2-propenyl ether **4** in 91–100% yields, which underwent intramolecular Diels-Alder reactions to afford dibenzopyran derivatives.

Keywords: Diels-alder reaction; stereoselective; vinylsulfone; intramolecular reaction

INTRODUCTION

Vinyl sulfones are known to be good dienophiles and many examples have been published[2]. Although the use of vinyl sulfones in bimolecular Diels-Alder reactions has ample precedent, examples of the corresponding intramolecular process are rare[3–5].

On the other hand, the o-dienylphenyl allyl ethers would be expected to be valuable building blocks in a variety of interesting polycyclic systems such as tetrahydrocannabinol skeleton via intramolecular cycloadditions. As an extension of our studies on synthetic application of halogenovinylsulfones, we wish to report the synthesis and the intramolecular Diels-Alder reaction of sulfonyltriene **4**.

*Corresponding author.

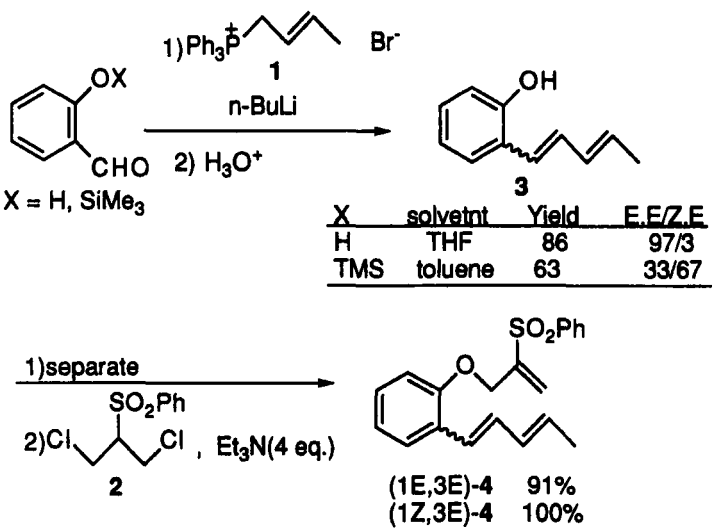
RESULTS AND DISCUSSIONS

The starting o-(1,3-pentadienyl)-phenyl (2-phenyl-sulfonyl)-2-propenyl ether **4**(sulfonyltriene) was prepared according to the Scheme 1. o-(1,3-Pentadienyl)phenol **3**, which was obtained from the Wittig reactions of salicylaldehydes with phosphonium salt **1** in the presence of n-BuLi as geometrical isomer, reacted with 1,3-dichloro-2-phenylsulfonylpropane **2** in the presence of 4 equivalents of triethylamine to give **4** in good yield.

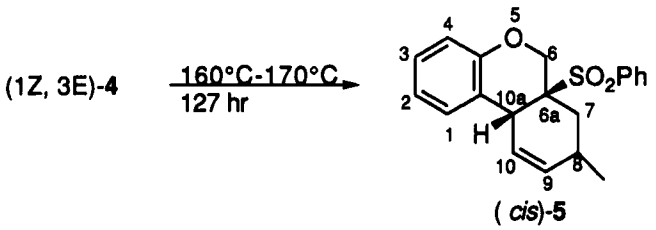
Heating a toluene solution of (1Z,3E)-**4** at 160°C–170°C in an autoclave for 127 hr gave *dl*-6aβ,7,8,10aβ-tetrahydro-8-methyl-6a-phenyl-sulfonyl-dibenzo-[b,d]pyran, (*cis*)-**5** in 71% yield as only isolable products (Scheme 2). The structure of (*cis*)-**5** was determined by spectral data, and the configuration was confirmed by X-ray crystallography (Fig. 1).

In the thermal reaction of (1E, 3E)-4, *dl*-6aβ,7,8,10aα-tetrahydro-8-methyl-6a-phenyl-sulfonyl-dibenzo[b,d]pyran (*trams*-**5**), 2-ethyl-8-(2-phenylsulfonylpropenyl)-3-chromene **6**, 8-methyl-dibenzopyran **7**, and diphenyl-disulfide were obtained in 20%, 30%, 15% and 8% yields, respectively (Scheme 3).

The cromene **6** would be formed by Claisen rearrangement of 2-(2-phenylsulfonyl)-propenyl group followed by proton migration and cyclyzation as illustrated in Scheme 4.



SCHEME 1



SCHEME 2

Treatment of (*cis*)-**5** with 6% sodium amalgam in a mixture of THF/MeOH(3/5) at room temperature afforded an unexpected product **8** in 79% yield along with a normal desulfonylated compound **9** in 16% yield. The product **8** would come from a radical cleavage of pyran ring via a following pathway (Scheme 5).

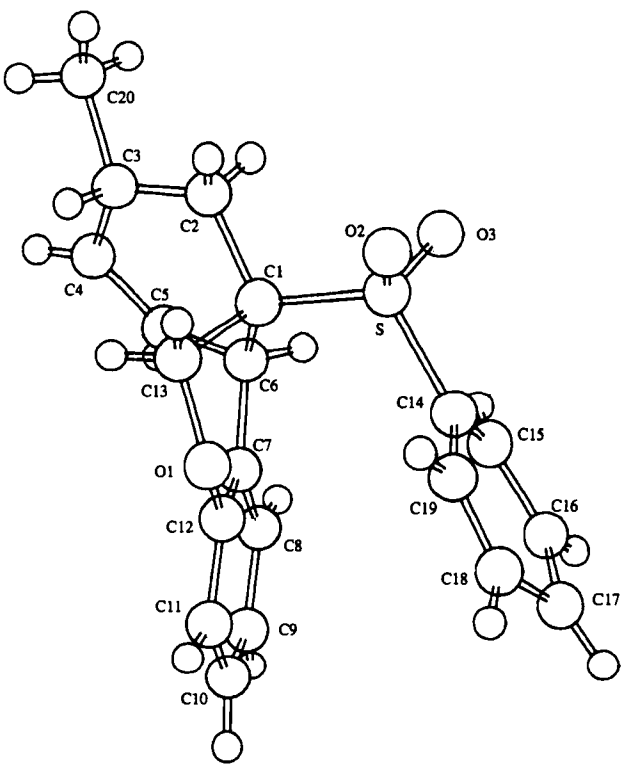
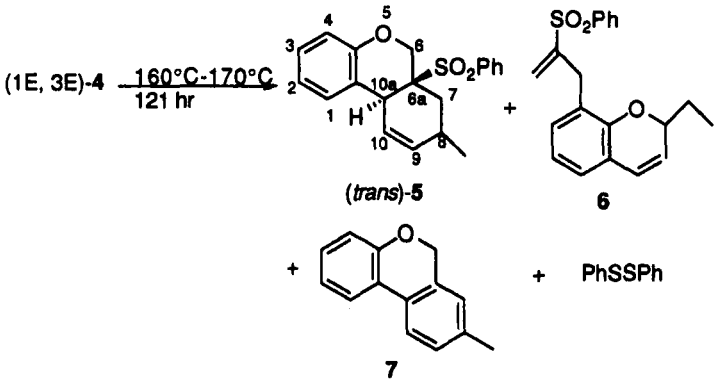
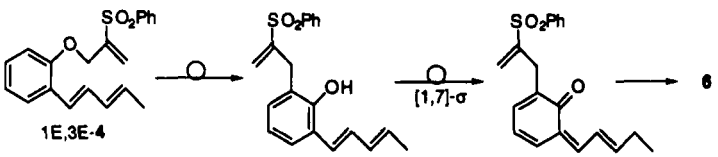


FIGURE 1 X-ray crystal structure of cis-**5**.



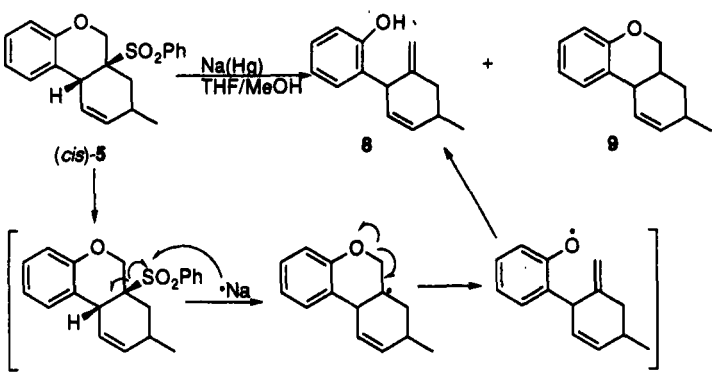
SCHEME 3



SCHEME 4

EXPERIMENTAL

Melting points were taken using a Yanagimoto micro-melting point apparatus. IR spectra were obtained on a JASCO A-100 spectrometer. ^{1}H-NMR spectra were recorded on either a JEOL PMX-60SI, Bruker AC250 spectrometers and ^{13}C-NMR spectra were recorded on a Bruker AC250 spectrometer. All chemical

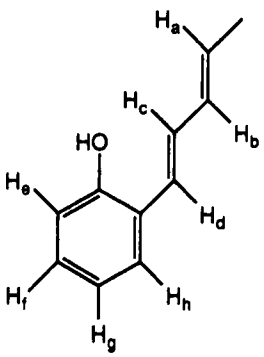


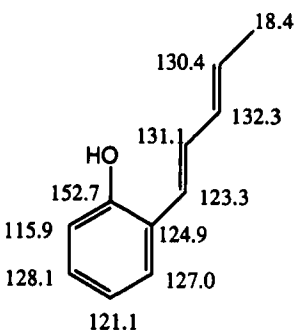
SCHEME 5

shifts were reported in ppm using tetramethylsilane as the internal standard. Mass spectra were obtained with a HITACHI M-80B spectrometer. High resolution mass spectra were taken with a HITACHI M-80B or JEOL JMS-DX300 spectrometers. Gas chromatography was performed on a Hewlett-Packard 5890A gas chromatography using a DB-1 megapore column (30 m × 0.53 mm). Elemental analysis was performed on a PERKIN-ELMER MODEL 240B apparatus. X-ray crystal structure analysis was performed using a RIGAKU AFC5S.

Preparation of 3

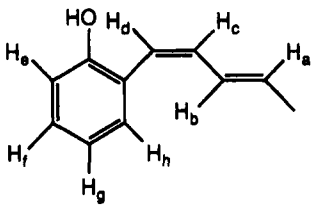
To a suspension of phosphonium salt **1**, obtained from a reaction of crotyl bromide with triphenyl phosphine, in THF (40 ml) was added dropwise a solution of butyllithium(1.5M in n-hexane, 15.2 ml, 24.2 mmol) at −13°C. After 30min., a solution of salicylaldehyde(1.46g, 12 mmol) in THF (20 ml) was added dropwise to the red solution at −13°C and stirred for 1hr. at this temperature and for 12 hr at room temperature. Then an aqueous saturated solution of ammonium chloride (30 ml) was added, and the mixture was concentrated in vacuo. The residue was extracted dichloromethane, and the organic layer was washed with saturated sodium chloride solution, dried over anhydrous Na_2SO_4. Then the solvent was evaporated in vacuo to give yellow oil which was chromatographed on silica gel using chloroform as an eluent to give a geometrical isomer mixture of **3**(1.65g, 86%). The ratio of (1E,3E)-**3**/(1Z,3E)-**3** was 97/3 which was measured by gas chromatography. The mixture was chromatographed again to give pure (1E,3E)-**3** and (1Z,3E)-**3**.

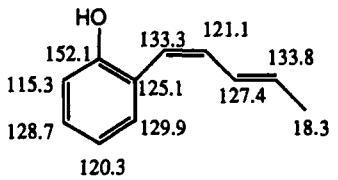




(1E,3E)-**3**; mp. 60.0–60.8°C; IR $^{\nu}$(cm^{-1}) 3420, 1600, 1480, 1460; ^{1}H NMR($CDCl_3$) $^{\delta}$1.82(d, 3H, J = 6.75Hz, CH_3), 5.07(br.s, 1H, OH), 5.82(dq, 1H, J-6.75, 15.0, H_a), 6.23(dd, 1H, J = 15.0, 12.3Hz, H_b), 6.63(d, 1H, J = 15.8Hz, H_d), 6.70–6.80(m, 2H, H_e and H_c), 6.88(m, 1H, H_g), 7.08(m, 1H, H_f), 7.37(dd, 1H, J = 7.20, 1.50Hz, H_h).

(1Z,3E)-**3**; bp. 50–60°C(0.1 Torr); IR(neat) $^{\nu}$(cm^{-1}) 3420, 1600, 1480; ^{1}H NMR($CDCl_3$) $^{\delta}$1.76(d, 3H, J = 6.70, CH_3), 5.12(br.s, 1H, OH), 5.91(dq, 1H, J = 14.0, 6.80Hz, Ha), 6.16–6.27(m, 2H, H_c and H_b), 6.36(d, 1H, J = 11.4Hz, H_d), 6.87–6.93(m, 2H, H_e and H_g), 7.14–7.24(m, 2H, H_f and H_h).





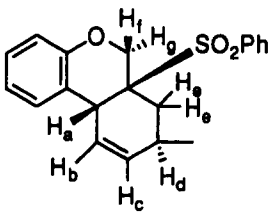
Typical Procedure: Preparation of (Z.E)-4

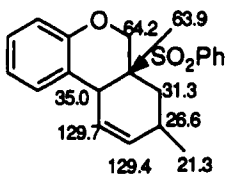
To a solution of triethylamine(0.41g, 4 mmol), 2-(1Z,3E-pentadienyl)-phenol(0,31g, 1.93 mmol) **3** and catalytic amounts of hydroquinone in THF (7ml) was added a solution of 2-(phenylsulfonyl)-propane 2(0.49g, 1.93 mmol) in THF(3 ml) at room temperature. After the mixture was stirred for 6hr, the solvent was evaporated in vacuo, and the residue was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, and concentrated to give a crude mixture which was chromatographed over silica gel to give pure (Z,E)-**4** quantitatively as colorless syrup. IR(neat) $^{\nu}$(cm^{-1}) 1600, 1490, 1320, 1240, 1140; UV($CHCl_3$) $^{\lambda}$max(nm) 274; ^{1}H NMR($CDCl_3$) $^{\delta}$ 1.78(dd, 3H, J = 6.52, 1.52Hz, CH_3), 4.72(m, 2H, CH_2), 5.83(dq, 1H, J = 6.77, 14.9Hz, CH), 6.13–6.20(m, 2H, CHx2), 6.16(m, 1H, $=CH_2$), 6.37–6.44(m, 1H, CH), 6.54(m, 1H, $=CH_2$), 6.62–7.94(m, 9H, Ar); MS m/z 340(M^+).

(*E,E*)-**4**; 91% yield; mp. 59.8–62.0(colorless plates); IR(KBr) $^{\nu}$(cm^{-1}) 1600, 1490, 1310, 1230, 1140; UV($CHCl_3$) $^{\lambda}$max(nm) 281($^{\epsilon}$ 10651), 305($^{\epsilon}$ 7394), 315($^{\epsilon}$ 7205); ^{1}H NMR($CDCl_3$) $^{\delta}$ 1.61(d, 3H, J = 6.76Hz, CH_3), 4.75(m, 2H, CH_2), 5.79(dd, 1H, J = 6.76, 14.9Hz, CH), 6.15(dd, 1H, J = 15.0, 9.4Hz, CH), 6.17(s, 1H, $=CH_2$), 6.42(d, 1H, J = 15.8Hz, CH), 6.58(s, 1H, $=CH_2$) 6.67(dd, 1H, J = 15.7, 10.1Hz, CH), 6.87–7.95(m, 9H, Ar); MS m/z 340(M^+)

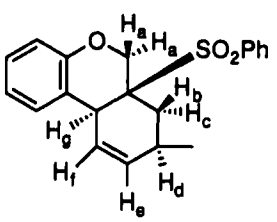
Preparation of cis-5;

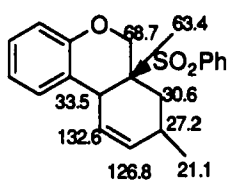
A solution of (Z,E)-4(2.57g, 7.55 mmol) in toluene(30 ml) was heated at 170°C for 127hr in a stainless autoclave. After cooling, the solvent was evaporated and residue was chromatographed on silica gel to give cis-5 in 71%(1.82g) yield. mp. 170.5–172.4°C; IR(KBr) $\nu(cm^{-1})$ 1600, 1500, 1300, 1230, 1150, 1070; UV($CHCl_3$) λmax(nm) 274(ε 2562); ^1H NMR($CDCl_3$) δ 1.10(d, 3H, J = 6.36Hz, CH_3), 1.98–2.26(m, 3H, H_e and H_d), 3.98(br.s, 1H, H_a), 4.05(d, 1H, J = 12.3Hz, H_g), 4.54(dd, 1H, J = 1.78, 12.3Hz, H_f), 5.48(d, 1H, J = 10.0Hz, H_b), 5.63(ddd, 1H, J = 9.94, 2.30, 2.30Hz, H_c), 6.28–7.77(m, 9H, Ph); MS m/z 340(M^+). Anal. Calcd for $C_{20}H_{20}O_3S$: C 70.56, H 5.92. Found: C 70.68, H 5.88.





trans-5; pale yellow oil; IR(neat) 1590, 1500, 1310, 1230, 1150 cm^{-1}; ^1H NMR($CDCl_3$) δ 1.00(3H, d, J = 7.15Hz, CH_3), 1.64(1H, dd, J = 14.9, 9.64Hz, H_c), 2.35(1H, dd, J = 14.8, 6.06, H_b), 2.69–2.82(1H, m, H_d), 4.01(1H, d, J = 10.9, H_a), 4.05(1H, d, J = 10.9Hz, H_a), 4.11(1H, br.s, H_g), 5.66(1H, ddd, J = 9.92, 1.53, 2.52, H_e), 5.90(1H, ddd, J = 9.94, 4.04, 9.94Hz, H_f), 6.66–7.91(9H, m, Ph); MS m/z 340(M^+). Anal. Calcd for $C_{20}H_{20}O_3S$ mw: 340.1161. Found, M^+: 340.1164.



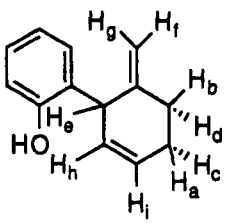


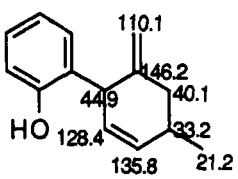
Compound **6**: pale yellow syrup; IR(neat) $\nu(cm^{-1})$ 1590, 1500, 1310, 1230, 1150; ^1H NMR($CDCl_3$)$^\delta$ 0.80(t, 3H, J = 7.41, CH_3), 1.52(m, 2H, CH×2), 3.51(m, 2H, CH_2), 4.56(m, 1H, CH), 5.43(m, 1H, one of $=CH_2$), 5.60(dd, 1H, J = 9.87, 3.24Hz, CH), 6.32(dd, 1H, J = 9.89, 1.70Hz, CH), 6.37(m, 1H, one of $=CH_2$), 6.72–7.92(m, 8H, Ph); ^{13}C NMR($CDCl_3$) δ 9.18, 28.4, 29.8, 76.5,

120.6, 124.0, 124.3, 125.6, 125.7, 130.8, 149.4, 151.3 and other aromatic carbons on phenylsulfonyl group; MS m/z 340(M^+). Anal. Calcd for $C_{20}H_{20}O_3S$, mw: 340.1161. Found, M^+: 340.1164.

Compound **7**: colorless oil; IR(neat) $^{\nu}$(cm^{-1}) 1610, 1600, 1520, 1490, 1230; ^{1}H NMR($CDCl_3$) $^{\delta}$ 2.34(s, 3H, CH_3), 5.06(s, 2H, CH_2), 6.92–7.68(m, 8H, Ph); ^{13}C NMR($CDCl_3$) $^{\delta}$ 21.3, 68.5, 117.3, 122.0, 122.1, 123.0, 123.1, 125.3, 127.3, 129.0, 129.2, 131.4, 137.5; MS m/z 196(M^+).

Compound **8**: pale yellow oil; IR(neat) $^{\nu}$(cm^{-1}) 3470, 1590, 1490; ^{1}H NMR($CDCl_3$) $^{\delta}$ 1.09(d, 3H, J = 6.87, CH_3), 2.03(dd, 1H, J = 11.7, 3.38Hz, Hb), 2.46–2.52(m, 1H, Hc), 2.58(dd, 1H, J = 12.1, 6.89Hz, Hd), 4.19(br.d, 1H, J = 2.21Hz, He), 4.52(s, 1H, Hf), 4.86(s, 1H, Hg), 5.33(br.s, 1H, OH), 5.68(ddd, 1H, J = 9.75, 2.40, 2.47Hz, Hh), 5.71(ddd, 1H, J = 2.22, 9.75, 2.03Hz, Hi), 6.61–7.20(m, 4H, Ph); MS m/z 201(M^+ + 1).





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