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Studies in Alkylation of 3-Methyl-3-Sulfolene and Thermolysis of Resulting 2-Alkyl-3-Sulfolenes: Convenient Synthesis of 1,2-Disubstituted-1,3-Dienes

Shailesh R. Desai, Vinayak K. Gore, T. Mayelvaganan, R. Padmakumar and Sujata V. Bhat*

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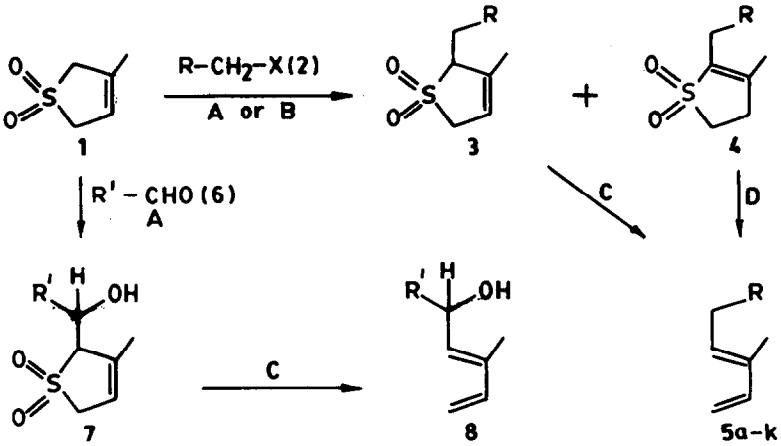
Department of Chemistry, Indian Institute of Technology, Powai, Bombay-400 076, India.

Abstract: Various 1,2-disubstituted-1,3-dienes have been synthesised through the alkylation of 3-methyl-3-sulfolene (1) followed by thermolysis of the resulting 2-alkyl-3-methyl- 3-sulfolene (3,7). The alkylations with bulky iodides, particularly, containing ethylene ketal or phenyl sulfide moiety yield considerable amounts of rearranged 2-alkyl-3-methyl-2-sulfolene (4). The sulfolenes 3,4 & 7 have been desulfonylated under mild conditions to yield corresponding 1,3-dienes.

The conjugated dienes are versatile building blocks in the synthesis of organic natural products, especially as a component of the Diels-Alder reaction[1]. Moreover, wide variety of biological activities are associated with conjugated diene derivatives, the prominent among them are insect sex pheromone[2] and organoleptic[3] properties.

In recent years large number of methods for the synthesis of conjugated dienes have been reported. Among others, the methods utilising organometallic reagents,[4] modified Wittig reagents[5] and thermal ring opening of cyclobutenes[6] or sulfolenes[7] have received considerable interest. The reaction of 3-sulfolene with alkyl halides or aldehydes followed by thermal desulfonylation provides a facile stereoselective method for synthesising (E), (E,Z) and (E,E) conjugated dienes. The study of using 3-sulfolenes as anionic and cationic butadienyl equivalents in organic synthesis has drawn increasing attention. These reactions have been applied in the synthesis of several natural products.[7a,b,c]



5a) R=-OMe
b) R=-SPh
c) R=-Ph
d) R=-C6H3(2',5'-OMe2)
e) R=-Me
f) R=-H
5g) R=-CH2-O-Me
h) R=-CH2-SPh
i) R=-CH2-CH
j) R=-CH2-C-Me
k) R=-CH-CH2
8a) R'=-CH2-C-Me
b) R'=-CH2-CH2-C6H5

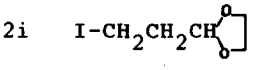
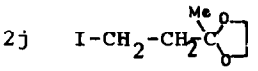
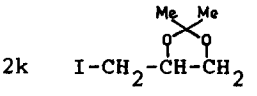
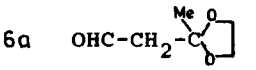
REAGENTS AND CONDITIONS A,B,C AND D ARE GIVEN IN TABLE-1

SCHEME-1

We report herein our studies on the alkylation reaction of 3-sulfolene with alkyl halides, aldehydes and subsequent smooth desulfonylation of the resulting sulfolene derivatives to provide convenient synthesis of substituted 1,3-dienes (5a-k,8a,b).

The alkylation of 3-methyl-3-sulfolene (1) with alkyl bromides (2a-e, Table 1) was achieved in the presence of lithium hexamethyldisilazane (LiHMDS) in THF at -90°C (Scheme 1). However, the alkylation with iodides (2g-k) other than methyl iodide required the presence of HMPA as cation trapping agent. The alkylation of (1) with bulky iodides containing phenylsulphide group (2h) and ethylene ketal moiety (2j,k) yielded considerable amounts of rearranged sulfolenes 4h,4j and 4k respectively.

Table-1. Alkylation of 3-methyl-3-sulfolene & thermolysis to yield dienes 5 & 8

Entry	electrophile alkyl halide or aldehyde		Reaction condition	Product (yield)	Desulfonylation condition	Diene (yield)
1	2a	$Br-CH_2-OMe$	A	3a(88)	E	-
2	2b	$Br-CH_2-SPh$	A	3b(27)	C	5b(85)
3	2c	$Br-CH_2Ph$	A	3c(82)	C	5c(80)
4	2d	$BrCH_2-C_6H_3(OMe)_2$	A	3d(80)	C	5d(80)
5	2e	Cyclogeranyl bromide	A	3e(70)	C	5e(75)
6	2f	I-Me	A	3f(85)	E	-
7	2g	$I-CH_2-CH_2OMe$	B	3g(89)	E	-
8	2h	$I-CH_2-CH_2-SPh$	B	3h(37) 4h(35)	C D	5h(74) 5h(60)
9	2i		B	3i(85)	C	5i(88)
10	2j		B	4j(78)	D	5j(60)
11	2k		B	4k(80)	D	5k(65)
12	6a		A	7a(56)	C	8a(68)
13	6b	$OHC-CH_2-CH_2-Ph$	A	7b(80)	C	8b(74)

A = -90°C, LiHMDS (1eq), THF, 1/2 hr
B = -90°C, LiHMDS (1eq), THF, HMPA (3eq), 1/2 hr
C = Pyridine, reflux, 1-2 hr
D = Pyridine, DBU (3eq), reflux, 12-24 hr
E = Toluene (containing trace amount of pyridine), reflux; the product identified as Diels-Alder adduct

Various conditions for thermolysis of alkyl sulfolene **3** and **4** were studied. The sulfolene **3** underwent smooth desulfonylation in refluxing pyridine (1-2 hr) to yield diene **5**. On the other hand, the rearranged sulfolene **4** could not be desulfonylated under the same conditions. The desulfonylation of sulfolene **4** could be achieved in pyridine solution containing DBU (3 eq) at 100-110°C (24 hr). Obviously

under this condition the sulfolene **4** underwent desulfonylation after isomerisation of double bond. It is noteworthy that earlier workers had reported failure in isomerisation of double bond of rearranged 2-alkyl-3-methyl-2-sulfolene, and hence had to be discarded during total synthesis of α-eudesmol[7a].

The alkylation of sulfolene **1** with aldehyde **6a,b** yielded the diastereomeric mixture of 2-hydroxyalkyl-3-methyl-3-sulfolene(**7a-b**) respectively. The diastereomeric mixture of **7** was not further separated as one chiral centre would be eliminated after desulfonylation. The hydroxydienes **8a** & **8b** were obtained from sulfolenes **7a** & **7b** respectively after heating in refluxing pyridine. Similarly, chiral diene **5k** was obtained by alkylation of sulfolene **1** with (S)2,3-isopropylidene-dioxypropyl iodide (**2k**) followed by thermolysis of the resulting rearranged sulfolene **4k**.

In summary, we have obtained convenient synthetic route to several 1,2-disubstituted-1,3-dienes, some of which had applications in the synthesis of natural products[8]. Our further studies in utility of these dienes in Diels-Alder reaction will be the subject of separate communication.

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Experimental

^{1}H NMR were recorded with Hitachi R-600 (60 MHz) and Varian XL-300 (300 MHz) NMR spectrometer in $CDCl_3$ using TMS as internal standard, J values are given in Hz. Mass spectra were recorded with Shimadzu GC MS-QP 1000 spectrometer at 70 eV. IR spectra were recorded with a Perkin Elmer 681 spectrometer. The microanalysis was done on Carlo Erba strumentazione 1106 elemental analyser. Usual work up refers to the extraction with ethyl acetate, washing the organic extracts with water, brine, drying over anhydrous Na_2SO_4 and evaporation of the solvent under reduced pressure. Column chromatography was done on silica gel (100-200 mesh), slurry packed, employing increasing amounts of ethyl acetate in petroleum ether (b.p. 60-80^o) as eluting solvent. Alkylated sulfolene derivatives which are not solids were obtained as viscous liquid, whereas all the dienes were colourless oil.

Alkylation of 1 : General procedure A

To a mixture of 3-methyl-3-sulfolene (1, 50 mmol) and alkyl halide (2a, 100 mmol) in THF (100 mL) at -98°C, was added dropwise a solution of LiHMDS (50 mmol) in THF (30 mL) under an atmosphere of argon. The resulting mixture was allowed to warm up gradually to 0°C (1/2 hr) and then quenched with saturated aqueous NH_4Cl (75 mL). After the removal of THF in vacuo, the residue was extracted repeatedly with ethyl acetate. The combined extracts were then washed successively with water, brine and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was chromatographed over silica gel column to furnish the 2-alkyl-3-methyl-3-sulfolene (3).

Alkylation of 1 : General procedure B

To a mixture of 3-methyl-3-sulfolene (50 mmol) and alkyl halides (100 mmol) and HMPA (150 mmol) in THF (100 mL) at -98°C was added dropwise a solution of LiHMDS (50 mmol) in THF (30 mL) during a period of 15 min under the atmosphere of argon. The resulting mixture was allowed to warm up gradually to 0°C and then quenched with ethyl acetate (100 mL). The solution was then filtered, the filtrate on evaporation in vacuo gave the crude reaction mixture, which was purified on silica gel column to furnish the 2-alkyl-3-methyl-3-sulfolene (3), sometimes accompanied by rearranged 2-alkyl-3-methyl-2-sulfolene (4, see Table 1).

2-Methoxymethyl-3-methyl-3-sulfolene (3a)

m.p. 46-47° (chloroform-petroleum ether)

ν_{max}(nujol) : 2930, 1650, 1460, 1310 1130 cm^{-1}.

^{1}H NMR (300 MHz): δ 5.72 (1H,m), 3.76 (2H,m,), 3.65 (2H,m), 3.57 (1H,m), 3.35 (3H,s), 1.85 (3H,bs). MS : m/e 177 (M^++1), 112 (M^+-SO_2).

Anal. calc. for $C_7H_{12}SO_3$, C,47.71; H,6.86; S,18.19; found, C, 47.94; H,6.6.74; S,18.38.

2-Phenylthiomethyl-3-methyl-3-sulfolene (3b)

ν_{max}(nujol) : 3020, 2930, 1600, 1490, 1440, 1320,1140, cm^{-1}.

^{1}H NMR (60 MHz): δ 7.22 (5H,m,), 5.70 (1H,bs),3.68 (3H,m), 3.35 (2H,d,J=7Hz), 1.74 (3H,bs). MS : m/e 255 (M^++1), 190 (M^+-SO_2).

Anal. calc. $C_{12}H_{14}S_2O_2$: C,56.66; H,5.55; S,25.21; found: C,56.82; H,5.72; S,25.06.

2-Benzyl-3-methyl-3-sulfolene (3c)

ν_{max}(nujol) : 2940, 1650, 1610, 1500, 1460, 1320,1140 cm^{-1}.

^{1}H NMR (300 MHz): δ 7.20-7.31 (5H,m), 5.64 (1H,m), 3.75 (1H,bt,J=6.8), 3.48-3.68 (2H,m), 3.28,2.95 (1H each,dd,J=6.8,14.6), 1.69 (3H,bs).

MS : m/e 223 (M^++1), 158 (M^+-SO_2).
Anal. calc. for $C_{12}H_{14}SO_2$: C, 64.84; H, 6.35; S, 14.42; found, C, 64.63; H, 6.19; S, 14.52.

2-(2',5'-Dimethoxyphenyl)-3-methyl-3-sulfolene (3d)

ν_{max} (nujol) : 2940, 1650, 1610, 1500, 1320, 1140 cm^{-1}.
^1H NMR (500 MHz): δ 6.87-6.75 (3H,m), 5.64 (1H,m), 3.78 (3H,s), 3.74 (3H,s) 3.17, 2.93 (1H each, dd, J=5.5, 14), 1.70 (3H,s). MS : m/e 283 (M^++1), 218 (M^+-SO_2). Anal. calc. for $C_{14}H_{18}SO_4$: C, 59.55; H, 6.43; S, 11.35; found, C, 59.89; H, 6.32; S, 11.52.

2-(2',6',6'-trimethylcyclohexenyl)-3-methyl-3-sulfolene (3e)

ν_{max} (neat): 2970, 2980, 1570, 1310, 1160, 1110 cm^{-1}
^1H NMR (60 MHz): δ 5.7 (1H,bs) 3.7 (3H,m), 2.71 (1H,dd,J=14.5,5.5), 2.54 (1H,dd,J=14.5,12), 1.94 (2H,t,J=6.4), 1.80 (3H,d,j=1.2), 1.59 (3H,m), 1.59, 1.09, 1.02 (3H each,s). MS : m/e 269 (M^++1), 204 (M^+-SO_2).
Anal. calc. for $C_{15}H_{24}SO_2$: C, 67.12; H, 9.01; S, 11.94; found, C, 66.86, H, 9.24, S, 11.82.

2,3-Dimethyl-3-sulfolene (3f)

ν_{max} (neat): 1450, 1310, 1250, 1230 1130 cm^{-1}.
^1H NMR (60 MHz): δ 5.62 (1H,bs), 3.68 (2H,s), 3.54 (1H,q,J=7), 1.82 (3H,s) and 1.4 (3H,d,J=7). The NMR data was identical with those reported[7b].
MS : m/e 147 (M^++1), 82 (M^+-SO_2).
Anal. calc. for $C_6H_{10}SO_2$: C, 49.29; H, 6.89; S, 21.93; found, C, 49.58; H, 7.08; S, 21.70.

2-(2'-Methoxyethyl)-3-methyl-3-sulfolene (3g)

ν_{max} (neat): 2940, 1460, 1400, 1320, 1130 cm^{-1}.
^1H NMR (300 MHz): δ 5.68 (1H,m), 3.70-3.73 (3H,m), 3.60 (2H,m), 3.37 (3H,s), 2.09 (2H,m), 1.86 (3H,bs). MS : m/e 191 (M^++1), 126 (M^+-SO_2).
Anal. calc. for $C_8H_{14}SO_3$: C, 50.50; H, 7.42; S, 16.85; found, C, 50.19; H, 7.55; S, 16.97.

2-(2'-Phenylthioethyl)-3-methyl-3-sulfolene (3h)

ν_{max} (neat): 3070, 2930, 1600, 1490, 1440, 1320 1140^1 cm.
^1H NMR (60 MHz): δ 7.22 (5H,m), 5.70 (1H,bs), 3.68 (3H,m), 3.35 (2H,d,J=7), 1.74 (3H,bs). MS : m/e 269 (M^++1), 204 (M^+-SO_2). Anal. calc. for $C_{13}H_{16}S_2O_2$: C, 58.18; H, 6.01; S, 23.89; found, C, 58.29; H, 6.10; S, 24.11.

2-(3'-Ethylenedioxy-propyl)-3-methyl-3-sulfolene (3i)

ν_{max} (neat): 2940, 2900, 1450, 1420, 1310, 1130 cm^{-1}.
^1H NMR (60 MHz): δ 5.68 (1H,m), 4.93 (1H,m), 3.84-4.01 (4H,m), 3.66-3.71

(2H,m), 3.61 (1H,m), 1.87-2.01 (4H,m), 1.86 (3H,bs). MS : m/e 233 (M^++1), 168 (M^+-SO_2). Anal. calc. for $C_{10}H_{16}SO_4$: C, 51.71; H, 6.94; S, 13.80; found, C, 51.98; H, 6.76; S, 14.01.

2-(2'-phenylthioethyl)-3-methyl-2-sulfolene (4h)

m.p. 65-67°C (ethyl acetate-petroleum ether)

ν_{max}(Nujol): 1590,1470,1380,1290,1130,740 cm^{-1}.

^{1}H NMR (60 MHz): δ 7.10-7.45 (5H,m), 3.05-3.50 (3H,m), 2.50-3.00 (4H,m), 1.8 (3H,s). MS : m/e 269 (M^++1). Anal. calc. for $C_{13}H_{16}S_2O_2$: C, 58.18; H, 6.01; S, 23.89; found, C, 58.34; H, 6.17; S, 23.98.

2-(3'-Ethylenedioxy-butyl)-3-methyl-2-sulfolene (4j)

ν_{max} (neat): 2940, 2900, 1455, 1420, 1312, 1130 cm^{-1}.

^{1}H NMR (60 MHz): δ 3.95 (4H,s), 3.2 (2H,t,J=7), 2.5-2.8 (4H,m), 2.0 (2H,t,J=7), 1.90 (3H,s), 1.35 (3H,s). MS : m/e 247 (M^++1).

Anal. calc. for $C_{11}H_{18}SO_4$: C, 53.64; H, 7.36; S, 13.02; found, C, 53.73; H, 7.52; S, 12.91.

2-(2',3'-Isopropylidenedioxypropyl)-3-methyl-2-sulfolene(4k)

ν_{max} (neat): 3030, 1400, 1390, 1310, 1240 cm^{-1}.

^{1}H NMR (60 MHz): δ 4.44 (1H,m), 4.10 (1H,dd), 3.67 (1H,dd), 3.25 (3H,t,J=7), 2.78 (2H,m), 2.65 (2H,m), 1.96 (3H,s), 1.44 (3H,s), 1.33 (3H,s). MS : m/e 247 (M^++1). $[\alpha]_D^{25}$ -12.86 (C,4.2,$CHCl_3$). Anal. calc. for $C_{11}H_{18}SO_4$: C, 53.64; H, 7.36; S, 13.02; found: C, 53.81; H, 7.23; S, 13.14.

Thermolysis of 2-alkyl-3-methyl-3-sulfolene (3) in refluxing pyridine: General procedure C

A solution of 2-alkyl-3-methyl-3-sulfolene (3,10 mmol) in pyridine (25 mL) was refluxed for 1-2 hr under an atmosphere of argon. The solvent was removed in vacuo and the residue was purified over silica gel column chromatography to yield the diene (5).

Thermolysis of 2-alkyl-3-methyl-2-sulfolene (4) in refluxing pyridine containing DBU, General procedure D

A mixture of sulfolene 4 (10 mmol) and DBU (30 mmol) in pyridine (10 ml) was refluxed for 24-36 hrs. The solvent was removed under reduced pressure and the crude product was purified by column chromatography over silica gel to yield the diene.

(E)-1-Phenylthio-3-methyl-2,4-pentadiene (5b)

ν_{max}(neat): 3060, 2930, 1640, 1610, 1590, 1480, 1440,1000, 910, 740, cm^{-1}.

^{1}H NMR (60 MHz): δ 7.25 (5H,m), 6.38 (1H,dd,J=11,17), 5.60 (1H,t,J=7), 5.10 (1H,d,J=17), 4.98 (1H,d,J=11), 3.6 (2H,d,J=7), and 1.62 (3H,bs).

MS : m/e 190 (M^+). Anal. calc. for $C_{12}H_{14}S$: C,75.74; H , 7.41; S, 16.85; found, C,75.98; H,7.55, S,16.72

(E)-3-Methyl-5-phenyl-1,3-pentadiene (5c)

ν_{max}(neat): 2920, 1630, 1610, 1500, 1440, 1000, 910, 750 cm^{-1}.
^1H NMR (60 MHz): δ 7.23 (5H,bs), 6.45 (1H,dd,J=10 & 17), 5.7 (1H,t,J=7), 5.15 (1H,d,J=17), 5.0 (1H,d,J=10), 3.5 (2H,d,J=7) and 1.86 (3H,s).
MS : m/e 158 (M^+). Anal. calc. for $C_{12}H_{14}$: C, 91.08; H, 8.92; found, C,91.01; H,9.08.

(E)-3-Methyl-(2',5'-dimethoxyphenyl)-1,3-pentadiene (5d)

ν_{max}(neat): 2920, 1630, 1610, 1510, 1440, 1230, 1185, 910 750 cm^{-1}.
^1H NMR (60 MHz): δ 6.8 (3H,bs), 6.4 (1H,dd,J=10,17), 5.6 (1H,t,J=7), 5.15 (1H,d,J=17), 5.0 (1H,d,J=10), 3.78 (3H,s), 3.74 (3H,s), 3.3 (2H,d,J=7) and 1.75 (3H,s). MS : m/e 218 (M^+).
Anal. calc. for $C_{14}H_{18}O_2$: C,77.03; H,8.31; found, C,77.24; H,8.49.

(E)-3-Methyl-2-(2',6',6'-trimethyl-cyclohexenyl)-penta-1,3-diene (5e)

ν_{max}(neat): 2980, 1630, 1600, 1460, 1380, 1300, 1100, 890, 760 cm^{-1}.
^1H NMR (300 MHz): δ 6.38 (1H,dd,J=17.4, 10.6), 5.35 (1H,bt,J=6.5), 5.05 (1H,d,J=17.4), 4.9 (1H,d,J=10.6), 2.83 (2H,d,J=6.4), 1.92 (2H,bt,5.95), 1.78 (3H,d,J=1.22), 1.6 (2H,m), 1.53 (3H,s), 1.42 (2H,m) and 0.96 (3H,s).
MS : m/e 204 (M^+).
Anal. calc. for $C_{15}H_{24}$: C,88.16; H,11.84; found, C,89.01; H,11.93.

(E)-1-Phenylthio-4-methyl-3,5-hexadiene (5h)

ν_{max} (neat): 2920, 1630, 1610, 1590, 1480, 1440, 990, 900, 740 cm^{-1}.
^1H NMR (60 MHz): δ 7.0-7.5 (5H,m), 6.38 (1H,dd,J=11, 17) , 5.6 (1H,t,J=7), 5.10 (1H,d,J=17), 4.98 (1H,d,J=11), 2.80-3.10 (2H,m), 2.50 (2H,m) and 1.70 (3H,s). MS : m/e 205 (M^++1).
Anal. calc. for $C_{13}H_{16}S$: C,76.42; H,7.89, S,15.69; found, C, 76.26, H, 7.99; S,15.96.

(E)-1-Ethylenedioxy-5-methyl-4,6-heptadiene (5i)

ν_{max}(neat): 2950, 1650, 1610, 1420, 1150, 910 cm^{-1}.
^1H NMR (300 MHz): δ 6.37 (1H,dd,J=10.7 & 17.4), 5.52 (1H,t,J=7.3), 5.1 (1H,dd,J=17.4 & 1.2), 4.94 (1H,d,J=10.68), 4.87 (1H,m), 3.85-3.98 (4H,m), 2.24-2.32 (2H,m) and 1.67-1.78 (5H,m). MS : m/e 168 (M^+).
Anal. calc. for $C_{10}H_{16}O_2$: C,71.39; H,9.59; found, C,71.56; H,9.47.

(E)-2-Ethylenedioxy-6-methyl-5,7-octadiene (5j)

ν_{max}(neat): 2950, 1650, 1610, 1420, 1150 & 915 cm^{-1}.
^1H NMR (60MHz): δ 6.4 (1H,dd,J=10 & 17), 5.5 (1H,t,J=7), 5.15 (1H,d,J=17),

4.9 (1H,d,J=10), 3.9 (4H,s), 2.2 (2H,m), 1.75 (5H,bs) & 1.3 (3H,s).
MS : m/e 182 (M^+).
Anal. calc. for $C_{11}H_{18}O_2$: C,72.49; H,9.95, found, C,72.88; H,10.16.

(E)-1,2-Isopropylidene-dioxy-5-methyl-hepta-4,6-diene(5k)
ν_{max}(neat): 2990, 1620, 1600, 1450, 1370, 1360, 1060, 900, 866 cm^{-1}.
^1H NMR (300 MHz): δ 6.40 (1H,dd,J=17.6 & 10.8), 5.47 (1H,bt), 5.15 (1H,d,J=17.6), 4.99 (1H,d,J=10.8), 4.15 (1H,m), 4.03 (1H,dd,J=7.9 & 5.9), 3.56 (1H,dd,7.9 & 7), 2.42 (2H,m), 1.76 (3H,s),& 1.42 (3H,s).
$[\alpha]_D^{25}$ +5.61 (C,4.27,$CHCl_3$). MS : m/e 182 (M^+).
Anal. calc. for $C_{11}H_{18}O_2$: C,72.49; H,9.95; found, C,72.75; H,9.87.

2-[3'-Ethylenedioxy-1'-hydroxy-butyl)-3-methyl-3-sulfolene (7a)
ν_{max}(neat): 3470, 2990, 1630, 1600, 1460, 1380, 1180 cm^{-1}.
^1H NMR (60 MHz): δ 4.5 (1H,m), 4.00 (4H,s), 3.7 (3H,m), 1.95 (5H,bs) and 1.4 (3H,s). MS : m/e 263 (M^++1), 198 (M^+-SO_2).
Anal. calc. for $C_{11}H_{18}SO_5$: C,50:37, H,6.92; S,12.22; found: C, 50.25; H,6.77; S,12.30.

2-(1'-Hydroxy-3'-phenyl-propyl)-3-methyl-3-sulfolene (7b)
ν_{max}(neat): 3460, 2980, 1625, 1450, 1380, 1180 cm^{-1}
^1H NMR (60 HMz): δ 7.3 (5H,s), 5.85 (1H,bs), 4.3 (1H,m), 3.7 (3H,bs), 2.85 (2H,bs), 1.9 (3H,s) and 1.4 (2H,m). MS : m/e 267 (M^++1), 202 (M^+-SO_2)
Anal. calc. for $C_{14}C_{18}SO_3$: C,63.13; H,6.81; S,12.04; found, C,63.49; H, 6.99; S,12.17.

Thermolysis of sulfolenes 7a and 7b

The thermolysis of hydroxy sulfolenes **7a** and **7b** was achieved using procedure C to give dienes 8a and 8b respectively.

(E)-2-Ethylenedioxy-4-hydroxy-6-methyl-5,7-octadiene (8a)
ν_{max}(neat): 3470, 2990, 1630, 1600, 1460, 1380, 1180 cm^{-1}.
^1H NMR (60 MHz): δ 6.4 (1H,dd,J=10,17), 5.3 (1H,d,J=4), 5.15 (1H,d,J=17), 4.95 (1H,d,J=10), 4.6 (1H,m), 4.0 (4H,s), 2.0 (2H,d,J=7), 1.75 (3H,bs) and 1.3 (3H,s). MS : m/e 198 (M^+).
Anal. calc. for $C_{11}H_{18}O_3$: C,66.64; H, 9.15; found, C,66.91; H,9.26.

(E)-3-Hydroxy-5-methyl-1-phenyl-4,6-heptadiene (8b)
ν_{max}(neat): 3460, 2990, 1630, 1600, 1590, 1460, 1380, 1170 cm^{-1}.
^1H NMR (60 MHz): δ 6.4 (1H,dd,J=10,17), 5.3 (1H,d,J=4), 5.15 (1H,d,J=17), 4.95 (1H,d,J=10), 4.6 (1H,t,J=7), 2.7 (2H,t,J=7), 1.75 (3H,d,J=1), 1.3 (2H,m). MS : m/e 202 (M^+).
Anal. calc. for $C_{14}H_{18}O$: C,83.12; H,8.97; found, C,83.02; H 8.83.

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