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DIMERIZATION OF (E)-2-BENZENESULFONYL-1,3-ALKADIENES. THE BENZENESULFONYL GROUP EXERTS ACYCLIC STEREOCONTROL.

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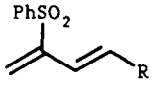
Abstract. Mild dehydration of 2-benzenesulfonyl allylic alcohols **8** afforded a series of (E)-2-benzenesulfonyl-1,3-alkadienes **1** which dimerized to functionalized vinylcyclohexenes **3** in regio- and stereodefined manner. The configuration at C-3 in **3e** was determined by X-ray crystallography.

Introduction. 2-Benzenesulfonyl-1,3-alkadienes **1** have hardly been investigated. Recently, Chou and his coworkers[1] have obtained parent **1a** (R = H)



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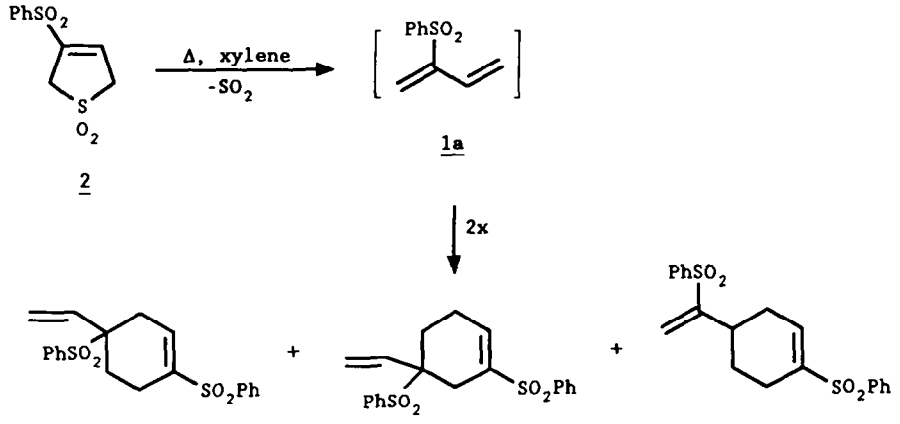
from 3-sulfolene **2** and shown that it dimerizes *in situ*, affording three isomers, assigned structure **3a** (*para* isomer), **4** (*meta* isomer) and **5** (Scheme 1). Bäckvall et al. have prepared inter al. **1b**[2a] (R = Me) *via* sulfonylmercuration of 1,3-pentadiene and described one dimerization product (*para*, stereochemistry unknown).[2b] We here report a new approach to 2-benzenesulfonyl-1,3-alkadienes (**1**). The compounds are of interest in

stereoselective cycloadditions and because of the synthetic versatility c the benzenesulfonyl group.[3]

Scheme 1.



	3a	4	5	
	3a	4	5	Ref.
Yield	6	2	1	1
Ratios	6	1	traces	this work

Results. Phenyl vinyl sulfone (**6**) and aldehydes **7** were coupled to 2-ben zenesulfonyl substituted allylic alcohols **8** in the presence of 1,4-diaza bicyclo[2.2.2]octane[4-6] (DABCO) (Scheme 2 and Table 1).

Scheme 2. Preparation of Benzenesulfonyl Substituted Allyl Alcohols **8**

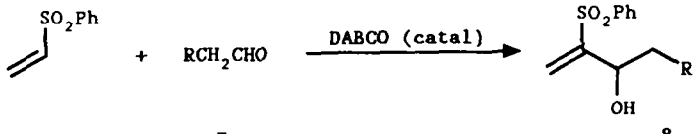
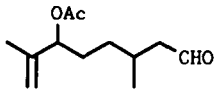


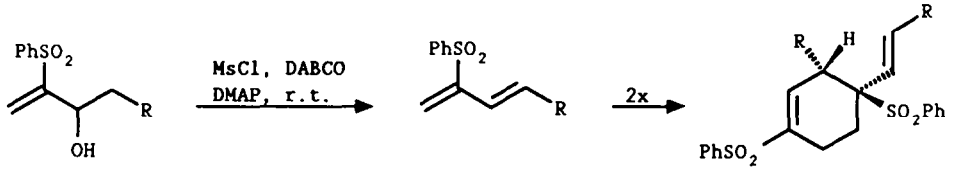
Table 1. 2-Benzenesulfonyl-3-hydroxy-1-alkenes (**8a-f**) Prepared

	Aldehyde[a] RCH_2CHO (**7**)	Reaction time	Isolated Yield[b] [%]
a	CH_3CHO	10d	81
b	CH_3CH_2CHO	11d	66[c]
c	$CH_3(CH_2)_2CHO$	4w	60
d	$(CH_3)_2CHCH_2CHO$	11w	65
e	$Ph(CH_2)_2CHO$	3w	46[d]
f		8w	47

[a]1 - 5 eq of aldehyde **7** was used with respect to phenyl vinyl sulfone **6**. [b]Alcohols **8b-f** were purified by column chromatography, alcohol **8a** was distilled (Kugelrohr). [c]Refers to 50% conversion of **6**. [d]Refers to 78% conversion of **6**.

E-selective dehydration of **8** was accomplished with methanesulfonyl chloride and DABCO[7] at room temperature in the presence of catalytic 4-dimethylaminopyridine (DMAP)[8], yielding the desired 1,3-alkadienes **1**, which partially dimerized to **3** under the conditions of the reaction and even during workup (Scheme 3). However, chromatographic separation of the respective pairs of **1b-e** and **3b-e** was feasible (silica gel), giving the series of monomers **1b-e** (Table 2), which were characterized in full by ^1H

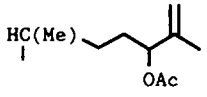
Scheme 3. Dehydration of 2-Benzenesulfonyl Allylic Alcohols **8**



8 **1** **3**

and ^{13}C NMR (Table 3). Preparation of bulky monomer **1f**, derived from isopulegol (**7f**) succeeded without formation of dimer **3f**. However, complete dimerization ensued when **1f** (neat) was kept for 3 weeks at room temperature.

Table 2. Isolation of 2-Benzenesulfonyl-1,3-alkadienes (**1a-f**) and their Dimers (**3a-f**)

	R	1 [%]	3 [%]	Total Yield [%]
a	H	46[a]	32[a]	78
b	CH_3	39	39	78
c	CH_2CH_2	36	45	81
d	$CH(CH_3)_2$	53	18	71
e	CH_2Ph	56	14	70
f		86	--	86

[a] Facile dimerization (see text).

Table 3. NMR Data of 2-Benzenesulfonyl-1,3-alkadienes (**1**) ($CDCl_3$, TMS, δ ppm)

1	H-1_{cis}-Σ	H-1_{trans}-Σ	H-3	H-4(Z)	H-4(E)	H-5	H-6
a	6.37	6.01	6.35	5.68	5.32	-	-
b	6.23	5.87	6.02	6.17	-	1.73	-
c	6.23	5.88	5.99	6.18	-	2.08	0.95
d[a]	6.20	5.88	5.97	6.10	-	2.46	0.92
e	6.27	5.87	6.06	6.26	-	3.37	-
f	6.26	5.88	5.98[b]		-	[c]	[c]

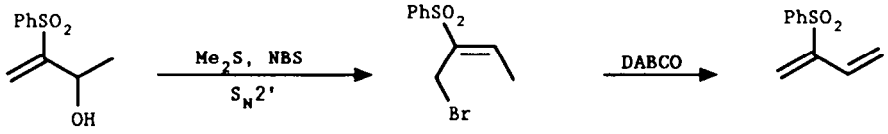
[a] In CD_2Cl_2 [b] AB part of ABX [c] No assignment Σ = $PhSO_2$

1	C-1	C-2	C-3	C-4	C-5	C-6
b	121.80	148.20	133.72	121.92	18.64	-
c	121.73	148.36	138.93	119.76	26.01	12.81
d[a]	122.02	148.91	145.85	118.33	31.90	22.97
e	122.36	147.92	137.01	121.95	39.01	-
f	122.22	148.18	143.89	119.72	37.11	30.07

[a] In CD_2Cl_2

In accord with the report of Chou[1] parent **1a** could only be handled in *dilute* solution, dimerization to **3a**, **4** and **5** being fast at room temperature. 2-Benzenesulfonyl-1,3-butadiene (**1a**) was also prepared from **8a** *via* **9** (Scheme 4).

Scheme 4. Alternative Route to **1a**



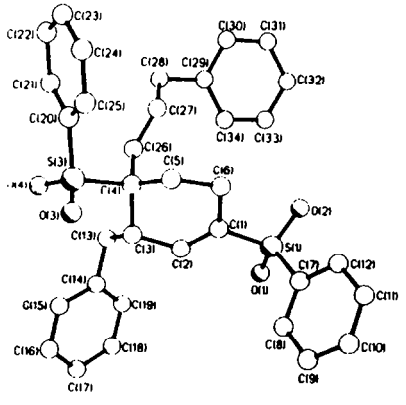
8a 9 1a

A somewhat higher regioselectivity in favour of *para* oriented dimer **3a** was obtained in our work (Scheme 1) by using the milder method for preparing **1**.

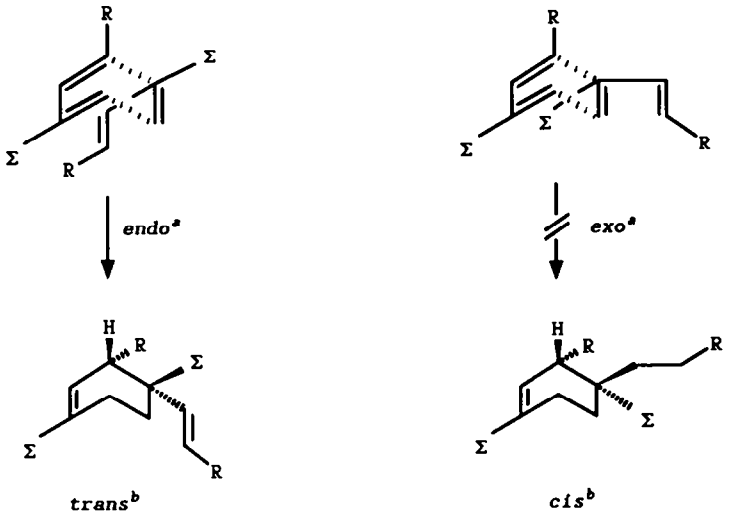
Regioselectivity and Stereochemistry of Dimerization. Unlike the dimerization of parent **1a** which was regiorandom (Scheme 1), 4-alkylated 2-benzenesulfonyl-1,3-dienes **1b-e** dimerized to *para* isomers **3b-e** exclusively, which crystallized on standing at -20°C. Crystallization of dimer **3f** was not successful.

Dimerization was not only regioselective. The ^{13}C spectra showed just *one* of two possible *diastereomeric* dimers. Spectroscopic data did not allow clear assignment of the configuration at C-3. However, the X-ray crystal structure determination of **3e** revealed the bulky benzenesulfonyl group to be *trans* to the vicinal benzyl group (Fig. 1). Therefore, all members of the series **3b-f** have been formed in an *endo* sense, irrespective of the size of the alkyl group R (Scheme 5).

Figure 1. X-ray Crystal Structure of **3e**



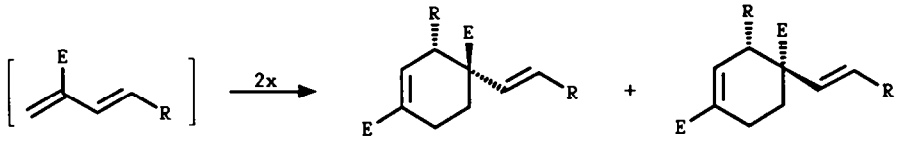
Scheme 5. *Endo* versus *Exo* Dimerization



Σ = SO_2Ph

[a] *endo* and *exo* refer to position of alkenyl group with respect to roof-lil transition state of Diels-Alder dimerization.
[b] *trans* and *cis* refer to the relationship of benzenesulfonyl group at C- and alkyl group R at C-3.

Previously, we have shown[7a] that a series of 2-methylene-3-alkenoic este: **10** (E = CO_2Me), which were generated at room temperature, dimerized spo



10 *trans*-**11** *cis*-**11**

taneously to *trans*- and *cis*-**11**. Similarly, the related group of acet activated dienes **10** (E = COMe) dimerized to a mixture of diastereomers. Both classes of compounds (**10**, E = CO_2Me and COMe) were *more* reactive th sulfonyl acivated dienes **1**, whereas the steric course of dimerization w *less* selective (Table 4).

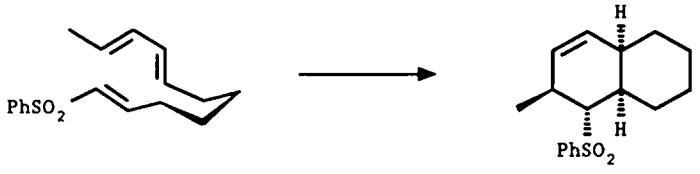
Complete diastereocontrol in the self-dimerization of sulfonyl dienes **1** **3** appears to be the consequence of the bulk of the benzenesulfonyl gro (A value 2.50)[9a] and the diminished reactivity of **1** compared with este **10** (E = CO_2Me, COMe).

Table 4. Diastereocontrol of Dimerization as a Function of Acceptor Group

Diene	Acceptor Group E	A value of Acceptor	Diastereoselectivity *trans* : *cis*
1	$PhSO_2$	2.50[a]	**3**; 100%
10	CO_2Me	0.60[b]	**11**; ~5:1 to 10:1[c]
10	COMe	Me(1.70) > MeO(0.60)[b]	**11**; 2:1 to 4:1[d]

[a]Ref. 9a. [b]Ref. 9b. [c]Ref. 7a. [d]Ref. 7d.

It is also of interest that the intramolecular Diels-Alder reaction of **12** affords diastereomer **13**, in which the sterically demanding benzenesulfonyl group adopts the equatorial position *trans* to the neighbouring methyl group.[10] Presumably, the alternative *cis* transition state entails unfavourable repulsion of these two groups.



12 **13**

In conclusion, because of its size and electronic properties the benzenesulfonyl group exerts useful regio and stereo control in a pericyclic reaction. Starting from conformationally mobile, acyclic reactants **1** we have obtained functionalized cyclohexenes **3** with 100% regio- and 100% diastereocontrol, even before recrystallization. Diastereocontrol is lost partially if benzenesulfonyl is replaced by an ester grouping (**10**; E = CO_2Me)[7a] and even more so, by an acetyl group (**10**; E = COMe)[7b].

EXPERIMENTAL

For the preparation and spectral data of α-hydroxyalkylated vinylsulfones (**8a-e**) see ref. 4c.

8-Acetoxy-2-benzenesulfonyl-5,9-dimethyl-3-hydroxy-1,9-decadiene (8f). Aldehyde **7f**[11] (3.3 g, 15.5 mol) and sulfone (**6**) (2.6 g, 15.5 mmol) were mixed and 1,4-diazabicyclo[2.2.2]octane (170 mg, 1.55 mmol) was added. After 8 w at room temperature, the crude product was purified by flash chromatography on silica (ether/ light petroleum, 2 : 1) to give **8f** (2.8 g,

47%, diastereomeric mixture), as a viscous oil. IR ($CHCl_3$) ν 3540, 3020 2960, 1730, 1450, 1370, 1305, 1250, 1140, 1080, 1025, 965, 910, 710, 690 590 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.98 - 7.51 (m, 5 H, H_{arom}), 6.41 6.39 (d, ^2J = 0.75 Hz, 1 H, $PhSO_2C=CH_{cis}$), 6.14/6.12 (bs, 1 H, $PhSO_2C$ CH_{trans}), 5.09/5.07 (t, ^3J = 7 Hz, 1 H, CHOAc), 4.89 (m, 2 H, $CH_3C=CH_2$) 4.42 (m, 1 H, CHOH), 3.21 (bs, 1 H, OH), 2.06/ 2.05 (s, 3 H, $COCH_3$), 1.70 1.68 (s, 3 H, CCH_3), 1.64 - 0.87 (m, 7 H), 0.82/0.76 (d, ^3J = 6 Hz, 3 H $CHCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.39/170.32 (s, C=O), 154.40/153.9 (s, $PhSO_2C=$), 143.04 (s, $CH_3C=CH_2$), 139.45/139.39 (s, C_{arom}), 133.73 129.33, 129.23 (d, C_{arom}), 124.58/124.37 (t, $PhSO_2C=CH_2$), 113.01/112.9 (t, $CH_3C=CH_2$), 66.99/66.57 (d, CHOH), 43.71/43.45 (d, CHOAc), 32.94 31.56, 29.16 (t, 3 CH_2), 29.86 (d, $CHCH_3$), 21.17 (q, $COCH_3$), 19.89/19.7 (q, CCH_3), 18.00/17.96 (q, $CHCH_3$); mass spectrum (70 eV, 130°C), *m/* (relative intensity) 380 (0, M^+), 348 (1), 333 (2), 319 (5), 196 (25), 17 (39), 178 (33), 161 (34), 125 (62), 109 (50), 108 (50), 93 (57), 81 (49) 77 (71), 44 (100). Exact mass calcd for $C_{12}H_{20}O_2$ 196.1464, Found 196.1462

General Procedure for the Dehydration of 2-Benzenesulfonyl-3-hydroxy-1-al kenes (8a-f). 1,4-Diazabicyclo[2.2.2]octane (3 eq) and a catalytic amour of *p*-(dimethylamino)pyridine were added to a solution of allylic alcohol (1 eq) in dry CH_2Cl_2 (1.5 mL/mmol **8**) under nitrogen. The mixture wa cooled to 0°C and methanesulfonyl chloride (1.2 eq in 1.5 mL CH_2Cl_2/mmc **8**) was dropped in slowly by syringe. The formation of a colorless precipi tate was observed after a short time. The mixture was stirred at room tem perature for the indicated reaction time, diluted with CH_2Cl_2, washed wit water (3x), and dried ($MgSO_4$). After filtration and evaporation of th solvent the residue was flash chromatographed on silica gel as detailed.

Dehydration of 8a. Reaction of alcohol **8a** (3.18 g, 15 mmol) with DABC (5.04 g, 45 mmol), cat. DMAP and methanesulfonyl chloride (2.06 g, 1 mmol) in CH_2Cl_2 (45 mL) for 6 h (TLC) gave 2.37 g of crude brown oil Separation of the component with the higher R_F-value by chromatograph (ether/light petroleum, 2 : 1) yielded 1.33 g (46%) of a yellowish oil which consisted of compounds **1a**, **3a**, **4** in a 5 : 10 : 3 ratio by the tim the ^1H NMR spectrum was recorded. The second fraction crystallized to giv 0.93 g (32%) of *para*-dimer **3a**, slightly contaminated with dimer **5**. Fc spectroscopic data of **1a** see ref. 2b, for **3a**, **4**, **5** see ref. 1a. Alterna tively, formation of diene **1a** was followed by ^1H NMR by reaction of brc mide **9**[5] (30 mg, 0.11 mmol in 1 mL of $CDCl_3$) with two equivalents of DABC at room temperature. In solution (0.11 M), diene **1a** was stable for a least 8 h.

2-Benzenesulfonyl-1,3-pentadiene (1b) and 1,4-Bis(benzenesulfonyl)-3-me thyl-4-(1-propenyl)-1-cyclohexene (3f). Alcohol **8b** (230 mg, 1 mmol) wa

dehydrated within 18 h by action of DABCO (340 mg, 3 mmol), cat. DMAP and methanesulfonyl chloride (140 mg, 1.2 mmol) in dry CH_2Cl_2 (3 mL). After aqueous workup, chromatography (ether/ light petroleum, 2 : 1) yielded 80 mg (39%) of monomeric diene **1b** as a colorless liquid (first fraction). For ^1H NMR spectral data see ref. 2b. ^{13}C NMR (50 MHz, APT, subtractive) δ 148.20 (s, *C*=CH_2), 139.42 (s, C_{arom}), 133.72 (d, =C*CH*), 133.40, 129.10, 127.94 (d, C_{arom}), 121.92 (d, CCH=*CH*), 121.80 (t, C=*C*H_2), 18.64 (q, CH_3). The second fraction crystallized from the above solvent mixture to give dimer **3b** (50 mg, 24%), colorless needles, mp 145 - 147°C (ether/light petroleum). For ^1H and ^{13}C NMR spectral data see ref. 2b. IR (KBr) ν 3080, 2960, 1650, 1580, 1450, 1300, 1150, 1090, 1070, 760, 720, 690 cm^{-1}; mass spectrum (70 eV, 160°C), *m/z* (relative intensity) 416 (0, M^+), 275 (36), 259 (6), 150 (11), 149 (11), 133 (41), 125 (100), 105 (20), 91 (20), 77 (36). Exact mass calcd for $C_{16}H_{19}O_2S$ 275.1105, found 275.1104. Anal. Calcd for $C_{22}H_{24}O_4S_2$: C, 63.44; H, 5.81. Found: C, 62.91; H, 5.80.

2-Benzenesulfonyl-1,3-hexadiene (1c) and 1,4-Bis(benzenesulfonyl)-4-(1-butenyl)-3-ethyl-1-cyclohexene (3c). Conversion of **8c** (240 mg, 1 mmol) with the same amounts of reactants as described for the preparation of **1b** and **3b** afforded, within 18 h, 80 mg (36%) of diene **1c**, colorless liquid after chromatography (ether/light petroleum, 2 : 1). ^1H NMR (200 MHz, $CDCl_3$, subtractive) δ 7.92 - 7.47 (m, 5 H, H_{arom}), 6.23 (s, 1 H, =CHH_{cis}), 6.18 (dt, ^3J = 16 Hz/^3J = 6 Hz, 1 H, CCH=C*H*), 5.99 (dq, ^3J = 16 Hz/^4J = 1 Hz, 1 H, =CC*H*), 5.88 (s, 1 H, CHH_{trans}), 2.08 (dq, ^3J = 6 Hz/^3J = 7 Hz, 2 H, C*H*$_2$CH$_3$), 0.95 (t, ^3J = 7 Hz, 3 H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$) δ 148.36 (s, *C*=CH_2), 138.93 (d, =CCH), 138.87 (s, C_{arom}), 133.86, 129.04, 128.00 (d, C_{arom}), 121.73 (t, C=*C*H_2), 119.76 (d, =CCH*C*H), 26.01 (t, *C*H_2CH$_3$), 12.81 (q, CH_3). Further eluation gave dimer **3c** [(60 mg, 45%, colorless needles, mp 139 - 140°C (ether/light petroleum)] as a second fraction. IR ($CHCl_3$) ν 3040, 2980, 1650, 1450, 1300, 1150, 1080, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.87 - 7.43 (m, 10 H, H_{arom}), 7.01 (m, 1 H, PhSO$_2$C=C*H*), 5.51 (d, ^3J = 16 Hz, 1 H, CC*H*=CH), 5.33 (dt, ^3J = 16 Hz/^3J = 6 Hz, 1 H, CCH=C*H*), 2.98 (m, 1 H, PhSO$_2$C=CHC*H*), 2.47 - 1.98 (m, 4 H, $(CH_2)_2$), 1.96 (m, 4 H, C*H*$_2$CH$_3$), 1.11 (t, ^3J = 7.5 Hz, 3 H, CHCH$_2$C*H*$_3$), 0.83 (t, ^3J = 7.5 Hz, 3 H, =CHCH$_2$C*H*$_3$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 139.67, 139.04 (d, PhSO$_2$C=*C*H, *C*CH=CH), 139.12, 138.03 (s, C_{arom}), 135.40 (s, PhSO$_2$*C*=), 133.83, 133.32, 130.73, 129.11, 128.44, 127.98 (d, C_{arom}), 120.68 (d, CCH=CH), 68.46 (s, *C*CH=CH), 40.86 (d, C-3), 26.14, 25.82 (t, $(CH_2)_2$), 23.53 (t, CH=CHCH$_2$), 20.62 (t, CHCH$_2$CH$_3$), 12.93, 12.03 (q, CH_3); mass spectrum (70 eV, 50°C), *m/z* (relative intensity) 444 (1, M^+), 227 (15), 196 (40), 125 (32), 115 (82), 77 (100), 71 (73). Anal. Calcd for $C_{24}H_{28}O_4S_2$: C, 64.84; H, 6.35. Found: C, 64.03; H, 6.33.

2-Benzenesulfonyl-5-methyl-1,3-hexadiene (1d) and 1,4-Bis(benzenesulfonyl -3-isopropyl-4-[(3-methyl)-1-butenyl]-1-cyclohexene (3d). Reaction c alcohol **8d** (310 mg, 1.2 mmol) with DABCO (400 mg, 3.6 mmol), cat. DMAP an methanesulfonyl chloride (165 mg, 1.44 mmol) in dry CH_2Cl_2 (4 mL) for 24 yielded two fractions on chromatography (ether/light petroleum, 1 : 2) The first fraction was liquid diene **1d** (150 mg, 53%). ^1H NMR (200 MHz CD_2Cl_2, subtractive) δ 7.92 - 7.42 (m, 5 H, H_{arom}), 6.20 (s, 1 H =CH*H*cis), 6.11 (dd, ^3J = 16Hz/^3J = 6 Hz, 1 H, =CCHC*H*), 5.97 (dt, ^3J = 1 Hz/^4J = 1 Hz, 1 H, =CC*H*CH), 5.88 (s, 1 H, CHH_{trans}), 2.46 (m, 1 H, C*H* $(CH_3)_2$), 0.92 (d, ^3J = 7 Hz, 6 H, CH_3); ^{13}C NMR (50 MHz, CD_2Cl_2, subtrac tive) δ 148.91 (s, *C*=CH_2), 145.84 (d, *C*CH=CH), 139.95 (s, C_{arom}), 133.70 129.37, 128.31 (d, C_{arom}), 122.02 (t, C=CH_2), 118.33 (d, CCH=*C*H), 31.9 (d, *C*H$(CH_3)_2$), 21.71 (q, CH_3). Further elution gave 50 mg (18%) of dime **3d** as a colorless oil, which crystallized on standing at -20°C (needles mp 135 - 137°C, ether). IR ($CHCl_3$) ν 3020, 2970, 1445, 1320, 1300, 119C 1150, 910, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.93 - 7.40 (m, 10 H H_{arom}), 7.09 (m, 1 H, $PhSO_2C$=C*H*), 5.71 (dd, ^3J = 17 Hz/^4J = 1.5 Hz, 1 H CC*H*CH), 5.20 (dd, ^3J = 17 Hz/^3J = 7 Hz, 1 H, CCHC*H*), 3.37 (m, 1 H, $PhSO_2$ C=CHC*H*), 2.53 - 2.12 (m, 4 H, $(CH_2)_2$), 1.85 (m, 2 H, C*H*$(CH_3)_2$), 1.21 (d ^3J = 7 Hz), 0.86 (d, ^3J = 6.5 Hz), 0.84 (d, ^3J = 6.5 Hz), 0.72 (d, ^3J = Hz) (each 3 H, CH_3); ^{13}C NMR(50 MHz, $CDCl_3$) δ 142.54 (d, $PhSO_2C$=CH) 139.30 (s, C_{arom}), 136.35 (d, CCH=CH), 134.72 (s, $PhSO_2C$=), 133.78 133.25, 130.65, 129.08, 128.31, 127.93 (d, C_{arom}), 121.89 (d, CCH=CH) 68.16 (s, CCH=CH), 42.58 (d, $PhSO_2C$=CHCH), 31.70, 28.62 (d, CH$(CH_3)_2$) 25.39, 20.30 (t, $(CH_2)_2$), 22.97, 21.91, 21.52, 18.25 (q, CH_3); mass spec trum (70 eV, 180°C), *m/z* (relative intensity) 472 (0, M^+), 331 (23), 28 (36), 287 (35), 275 (10), 263 (16), 189 (100), 125 (89), 91 (40), 78 (45) Exact mass calcd for $C_{18}H_{27}O_2S$ 331.1732, found 331.1731. Anal. Calcd fc $C_{26}H_{32}O_4S_2$: C, 66.07; H, 6.82. Found: C, 65.95; H, 6.83.

2-Benzenesulfonyl-5-phenyl-1,3-pentadiene (1e) and 3-Benzyl-1,4-bis(ben zenesulfonyl)-4-(3-phenyl-1-propenyl)-1-cyclohexene (3e). Alcohol **8e** (15 mg, 0.5 mmol) was allowed to react with DABCO (170 mg, 1.5 mmol), cat DMAP and methanesulfonyl chloride (70 mg, 0.6 mmol) in dry CH_2Cl_2 (3 mL) for 21 h, following the general procedure. Chromatography (ether/ligh petroleum, 2 : 1) gave 80 mg (56%) of liquid diene **1e** as first elute compound. IR ($CHCl_3$) ν 3010, 2920, 1445, 1305, 1145, 910, 690 cm^{-1}; ^1H NM (200 MHz, $CDCl_3$, subtractive) δ 7.88 - 7.40 (m, 5 H_{arom}), 7.40 - 6.91 (m 5 H, H_{arom}), 6.27 (s, 1 H, =CHH_{cis}), 6.26 (dt, ^3J = 15.5 Hz/^3J = 6.5 Hz, H, CCH=C*H*), 6.06 (dd, ^3J = 15.5 Hz/^4J = 1 Hz, 1 H, CC*H*=CH), 5.87 (s, 1 H CHH_{trans}), 3.37 (d, ^3J = 6.5 Hz, 2 H, CH_2); ^{13}C NMR (50 MHz, $CDCl_3$, AP subtractive) δ 147.92 (s, *C*=CH_2), 139.15 (s, C_{arom}), 137.01 (d, =CCH

134.35 (s, C_{arom}), 133.27, 128.98, 128.38, 127.92, 126.29 (d, C_{arom}), 122.36 (t, C=CH_2), 121.95 (d, =CCH=CH), 39.01 (t, CH_2); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 284 (0, M^+), 283 (6), 141 (100), 127 (66), 77 (30). The second fraction was oily dimer **3e** (20 mg, 14%), which crystallized from ether on prolonged standing at -20°C (colorless needles, mp 155 - 156°C). IR ($CHCl_3$) ν 3020, 1145, 1305, 1145, 690 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81 - 7.02 (m, 15 H, H_{arom}), 6.78 (m, 1 H, $PhSO_2C$=CH), 5.79 (d, ^3J = 16 Hz, 1 H, CCH=CH), 5.46 (dt, ^3J = 16 Hz/^3J = 7 Hz, 1 H, CCH=CH), 3.83 ((dd, J = 6.5/3 Hz), 3.56 (m, 2 H, diastereotopic, -$CHCH_2$Ph), 3.37 (d, ^3J = 7 Hz, 2 H, =CHCHPh), 2.28 - 1.80 (m, 5 H, $PhSO_2C$=CHCH, $(CH_2)_2$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 138.69, 138.57, 138.26, 138.10 (s, C_{arom}), 138.15, 137.08 (d, $PhSO_2C$=CH, CCH=CH), 134.55 (s, $PhSO_2C$=CH), 133.85, 133.38, 130.73, 129.42, 129.09, 128.86, 128.73, 128.58, 128.40, 128.05, 126.66, 126.55 (d, C_{arom}), 122.66 (d, CCH=CH), 68.11 (s, CCH=CH), 40.97 (d, $PhSO_2C$=CHCH), 39.64, 36.68 (t, CH_2Ph), 25.90, 20.55 (t, $(CH_2)_2$); mass spectrum (70 eV, 210°C), *m/z* (relative intensity) 568 (0, M^+), 427 (14), 335 (47), 285 (11), 209 (14), 194 (32), 171 (28), 125 (29), 117 (17), 91 (100), 77 (29). Exact mass calcd for $C_{28}H_{27}O_2S$ 427.1732, found 427.1732. Anal. Calcd for $C_{34}H_{32}O_4S_2$: C, 72.80; H, 5.67. Found: C, 71.31; H, 5.75.

8-Acetoxy-2-benzenesulfonyl-5,9-dimethyl-1,3,9-decatriene (1f) and 3-(4-Acetoxy-1,5-dimethyl-5-hexenyl)-4-(6-acetoxy-3,7-dimethyl-1,7-octadienyl)-1,4-bis(benzenesulfonyl)-1-cyclohexene (3f). Alcohol **8f** (220 mg, 0.58 mmol) was dehydrated within 24 h by reaction of DABCO (195 mg, 1.74 mmol), cat. DMAP and methanesulfonyl chloride (80 mg, 0.7 mmol). TLC showed triene **1f** as only product, which was purified by chromatography (ether/light petroleum, 2 : 1) to yield 180 mg (86%) of a colorless oil. IR ($CHCl_3$) ν 2960, 2880, 1730, 1445, 1370, 1320, 1305, 1250, 1145, 1080 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.86 -7.55 (m, 5 H, H_{arom}), 6.26 (s, 1 H, $PhSO_2C$=CHH_{cis}), 5.98 (s, AB-part of ABX-system, 2 H, =CCH=CH), 5.88 (s, 1 H, $PhSO_2C$=CHH_{trans}), 5.05 (t, ^3J = 6 Hz, 1 H, C(H)OAc), 4.87 (m, 2 H, CH_3C=CH_2), 2.22 - 2.06 (m, X-part of ABX-system, 1 H, $CHCH_3$), 2.06 (s, 3 H, $C(=O)CH_3$), 1.64 (s, 3 H, $C(=CH_2)CH_3$), 1.49 - 1.08 (m, 4 H, $(CH_2)_2$), 0.96 (d, $^3J_{5,11}$= 7 Hz, 3 H, $CHCH_3$); ^{13}C NMR (50 MHz, $CDCl_3$, APT) δ 170.21 (s, C=O), 148.16 (s, $PhSO_2C$), 143.89 (d, =CCH=CH), 142.88 (s, CH_3C=CH_2), 139.40 (s, C_{arom}), 133.39, 129.04, 127.90 (d, C_{arom}), 122.22 (t, $PhSO_2C$=CH_2), 119.72 (d, =CCH=CH), 112.72 (t, CH_3C=CH_2), 76.93 (d, OCH), 37.11 (d, $CHCH_3$), 31.83 (t, $OCHCH_2$), 30.07 (t, $OCHCH_2CH_2$), 21.18 (q, $C(=O)CH_3$), 20.08 (q, $C(=CH_2)CH_3$), 18.12 (q, $CHCH_3$); mass spectrum (70 eV, r.t.), *m/z* (relative intensity) 362 (2, M^+), 342 (1), 320 (7), 302 (12), 233 (18), 221 (24), 178 (17), 161 (75), 94 (100), 78 (58), 56 (46), 43 (92). The

dimer **3f** (colorless resin, diasteromeric mixture) was obtained in qu titative yield after keeping neat monomeric triene **1f** at room temperat for about 3 w. IR ($CHCl_3$) ν 3020, 2960, 1730, 1445, 1375, 1320, 13 1250, 1150, 1085, 1025 m^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 -7.40 (m, 10 H_{arom}), 7.00 (m, 1 H, $PhSO_2C=CH$), 5.76 - 5.58 (m, 2 H, $C=CH=CH$), 5.2 4.83 (m, 6 H, OCH, $CH_3C=CH_2$), 3.45-3.29 (m, 1 H, $PhSO_2C=CHCH$), 2.1 0.67 (m, other H); mass spectrum (70 eV, 220°C), *m/z* (relative intensi 724 (0, M^+), 583 (2), 523 (2), 480 (2), 462 (6), 381 (21), 353 (22), (57), 142 (52), 125 (51), 110 (100), 77 (52). Exact mass calcd $C_{34}H_{47}O_6S$ 583.3093, found 583.3092.

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X-Ray Crystallographic Data. Crystal data and lists of X-ray data for sulfone **3e** (Tables 1 - 6) have been deposited at the Cambridge Cryst lographic Data Centre, U.K.