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SYNTHESES WITH SULFONES XLVIII : STEREOSELECTIVE SYNTHESIS OF 2-ISOPROPYL 1,4-DIENES THROUGH THE IRON-CATALYSED CROSS-COUPLING REACTION OF 2-BENZENESULFONYL 1,4-DIENES AND ISOPROPYLMAGNESIUM CHLORIDE.

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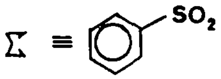
Abstract : *The stereoselective synthesis of 2-isopropyl 1,4-dienes through the cross-coupling reaction of 2-benzenesulfonyl 1,4-dienes and isopropylmagnesium chloride under transition-metal catalysis is described. Iron salts, which were better catalysis than palladium or nickel ones, led to substitution of the sulfonyl group with >97% stereospecificity and without isomerisation of the isopropyl Grignard moiety to the n-propyl derivative. Notable amounts of the compound resulting from reduction of the sulfonyl group were also formed.*

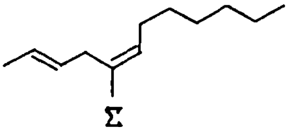
The stereoselective synthesis of vinylsulfones is readily achieved by condensation of α-sulfonyl carbanions with aldehydes, acetylation of the intermediate β-hydroxysulfones and β-elimination of acetic acid [1]. Vinylsulfones are stereospecifically converted into disubstituted olefins by hydrogenolysis with sodium dithionite [2]. This latter transformation has also been achieved with n-alkylmagnesium halides under nickel or palladium catalysis in 97% or 98% stereospecificity, respectively [3]. Recently, these techniques have been applied to the preparation of 1,3- and 1,4-dienes from 2-benzenesulfonyl 1,3- and 2-benzenesulfonyl 1,4-dienes [4]. Reduction of the sulfonyl group of E 2-benzenesulfonyl 1,3-dienes with Grignard reagents in the presence of nickel or palladium complexes led to 1,3-dienes >97% EE [5,6]. In the case of 2-benzenesulfonyl 1,4-dienes, sodium dithionite was recommended for the hydrogenolysis of the sulfonyl moiety and yielded 1,4-dienes >97% EE [6].

During this latter study, the unexpected formation of a mixture of cross-coupling and hydrogenolysis products was observed in the reaction of 2-benzenesulfonyl 1,4-dienes with Grignard reagents under nickel or palladium catalysis. Purification of the substitution products (>4 isomers) on a silica gel column containing 10% of $AgNO_3$ afforded a fraction containing 1-2% of an isopropyl 1,4-diene according to ^1H NMR analysis. Phenylmagnesium halides are known to couple with vinylsulfones under nickel or iron catalysis [7] while only nickel salts catalyse the cross-coupling reaction of these compounds with methylmagnesium halides [7b]. The iron-catalysed cross-coupling reaction of n-alkyl Grignard reagents with vinylsulfones is an efficient technique for preparing trisubstituted olefins [8]. However, even in the presence of iron salts, sec-alkyl Grignard reagents lead almost exclusively to hydrogenolysis products. The present paper reports the study of the isopropylation of 2-benzenesulfonyl 1,4-dienes whereas the application of this technique to the synthesis of the pheromone of Yellow Scale is described in the following paper.

E 2-Benzenesulfonyl 1,4-dienes were prepared according to literature procedures [1,4b]. Thus EE 4-benzenesulfonyl 2,5-dodecadiene <u>1</u> was obtained in 71% yield, >98% EE, according to HPLC, ^1H- and ^{13}C NMR analyses as previously described [4b]. 1-Benzenesulfonyl 4-methyl 3-pentene <u>2</u> was prepared from 1-bromo 4-methyl 3-pentene [9] and sodium benzenesulfinate (DMF, 18h, 20°, 74%) [10]. Treatment of <u>2</u> with n-butyllithium at -78°C (THF, 0.5h) followed by heptanal at -35°C

FORMULAE





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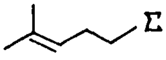

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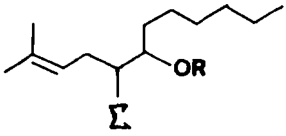

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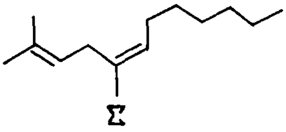

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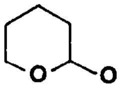

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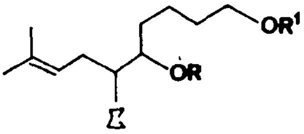

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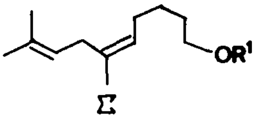
a $R=R^1=H$
b $R=H$, $R^1=Si(Me)_2tBu$
c $R=H$, $R^1=CPh_3$
d $R=R^1=Ac$
e $R=Ac$, $R^1=Si(Me)_2tBu$
f $R=Ac$, $R^1=CPh_3$



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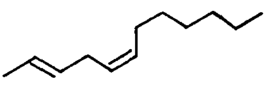
a $R^1=Ac$ b $R^1=Si(Me)_2tBu$
c $R^1=CPh_3$



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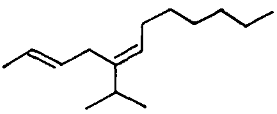

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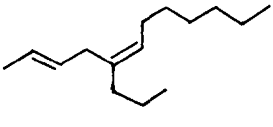

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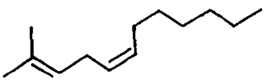

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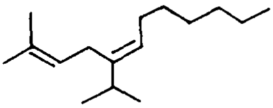

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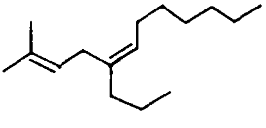

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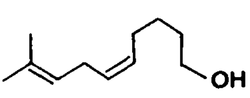

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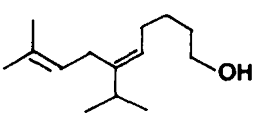

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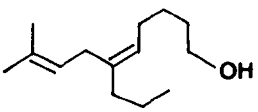

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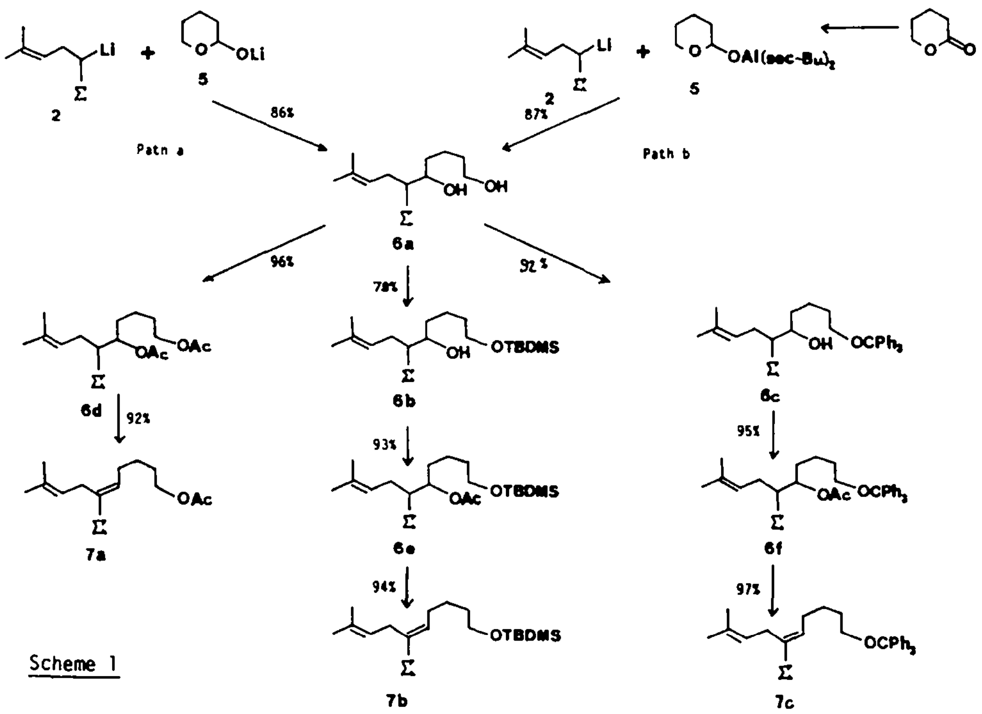
(15h) afforded 85% of 3a (threo/erythro [11] : 56/44). Acetylation with acetic anhydride (CH_2Cl_2, Et_3N, DMAP, 4h) [12] yielded 96% of β-acetoxysulfones 3b (threo/erythro : 56/44) which were converted into dienesulfone 4 (Et_2O, NaOH powder, 5h, 95%). After chromatography, dienesulfone 4 was >99% E according to HPLC and ^1H NMR analyses.

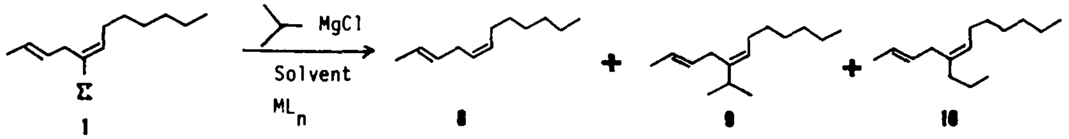
Functionalised dienesulfones, model compounds for yellow scale, were prepared according to the two methods indicated in scheme 1. Sulfone 2 (pKa~30) was metalated with n-butyllithium while alkoxide 5 (pKa~18) was obtained upon treatment of the hemiacetal with either n-butyllithium or LDA, Path a, or controlled reduction of δ -valerolactone with DIBAH [13], Path b. Both condensation reactions. Paths a and b (20°C, 18h) yielded 86-87% of a mixture (threo/erythro : 52/48) of hydroxysulfones 6. Selective silylation of the primary alcohol by a known method [14a] (TBDMS-Cl, DMAP, Et_3N, CH_2Cl_2, 0°C, 18h) followed by chromatography furnished 79% of compounds 6b along with 10% of disilylated derivatives and 5% of unchanged 6a. In a similar way diols 6a were selectively tritylated (Ph_3CCl, DMAP, Et_3N, CH_2Cl_2, 20°C, 18h) [14b] at the primary alcohol to furnish 6c in 92% yield. Acetylation of 6a, 6b and 6c in the usual way (CH_2Cl_2, Et_3N, DMAP, 4h) [12] followed by elimination of acetic acid (Et_2O, NaOH powder, 5h) completed the syntheses of dienesulfones 7a, 7b and 7c.HPLC and ^1H NMR analyses indicated dienesulfones 7b and 7c were >99% E whereas 7a contained 2% of another isomer.



Scheme 1

The results of the reaction of dienesulfone 1 with isopropylmagnesium chloride in the presence of various transition-metal complexes are collected in Table 1. Nickel and palladium catalysts afforded mixtures of dodecadiene 8, 5-isopropyl 2,5-dodecadiene 9, and n-propylation products 10. In all cases >90% conservation of the double bond configuration was observed. Iron salts led to mixtures of olefins 8 and 9 with excellent, >96%, stereospecificity. Moreover, the n-propylation product, 10 could only be detected in the experiment in which a phosphine ligand was added to the iron salt, entry 12. Smith and Kochi [15] have pointed out that using iron salts instead of nickel ones leads to the suppression of alkyl rearrangement of the Grignard moiety in the cross-coupling reaction of alkenyl halides with Grignard reagents. Ether proved to be the best solvent and led to acceptable yields of 9 with either $FeCl_3$ or $Fe(acac)_3$, entries 11 and 14. An experiment with n-propylmagnesium chloride, entry 15, furnished a mixture of 8 and 10 which confirmed that isomerisation of the Grignard reagent was negligible under these conditions.
Lehmkuhl and coll. [16] have shown that η^1-η^2-4-alkenylnickel complexes are stable to β-hydride elimination. It is possible that a similar interaction between this double bond and the

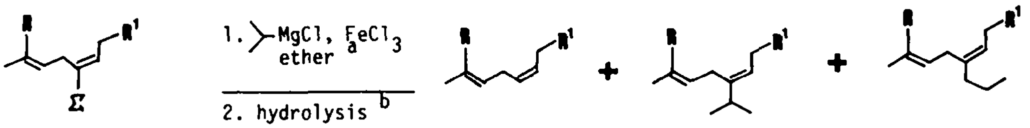
TABLE I : Reaction of dienesulfone 1 with isopropylmagnesium chloride catalysed by various transition-metal complexes.



Entry	Conditions [a]			Products %(EZ/EE)[c]		
	ML_n	Solvent	RMgCl [b]	8	9	10
1	$Ni(acac)_2$	THF	A	63 (90/10)	13	5 products
2	$NiCl_2DPPP$	"	B	19 (92/8)	5	"
3	"	Et_2O	"	25 (95/5)	5	"
4	$Pd(acac)_2$	THF	"	70 (90/10)	2	10 (90/10)
5	$Pd(acac)_2$ + 2 nBu_3P	"	"	63 (92/8)	3	17 (93/7)
6	" "	"	A	50 (90/10)	2	19 (92/8)
7	" "	Et_2O	"	23 (90/10)	5	37 (90/10)
8	" "	C_6H_6	"	30 (90/10)	4	38 (90/10)
9	$Fe(DBM)_3$	THF	B	40 (96/4)	5	-
10	"	Et_2O	"	35 (96/4)	10 (97/3)	-
11	$Fe(acac)_3$	"	"	39 (98/2)	27 (97/3)	1
12	$Fe(acac)_3$ + nBu_3P	"	"	48 (97/3)	6	8
13	$FeCl_3$	THF	"	62 (98/2)	8 (98/2)	-
14	"	Et_2O	"	37 (98/2)	28 (98/2)	-
15	"	"	"	27 (99/1)	-	60 (98/2) [d]

[a] 1 mmol of 1.5ml of solvent ; 16h at 20°C. [b] A iPrMgCl 0.8-1.2M in ether ; B iPrMgCl 0.9M in THF. [c] Capillary GLC (n-tridecane-internal standard). [d] n-PrMgCl 1M in ether.

TABLE II : Reaction of dienesulfones 1, 4, 7b and 7c with isopropylmagnesium chloride catalysed by $FeCl_3$.



Entry	Dienesulfone [c]	Products [d]							
		Hydrogenolysis			Isopropylation			n-Propylation	
1 [e]	1 (99)	8	37	(98/2)	9	28	(98/2)	-	
2 [f]	4 (99/1)	11	22	(98/2)	12	32	(98/2)	13	1
3 [g]	7a (98/2)	14	42	(97/3)	15	17	(98/2)	16	0.3
4	7b (99/1)	14	43	(98/2)	15	36	(98/2)	16	0.5
5	7c (99/1)	14	40	(90/10)	15	32	(92/8)	16	0.3

[a] 1 mmol of dienesulfone, 3% of $FeCl_3$, 2 mmol of iPrMgCl, Et_2O, 20°C, 1h.
[b] Removal of the primary alcohol group protector. [c] Hplc. [d] Capillary glc. [e] 2% of $FeCl_3$.
[f] 18% of [(3-methyl 2-butenyloctyl)sulfonyl]benzene were also recovered. [g] 4 mmol of iPrMgCl.

transition metal promotes the cross- coupling reaction of 2-benzenesulfonyl 1,4-dienes with alkylmagnesium halides with regard to the hydrogenolysis.

In the presence of 3% of $FeCl_3$ in ether, all of the dienesulfones except the acetoxy compound 7a gave acceptable yields of isopropylated 1,4-dienes, Table II. Some reduction of the double bond α to the sulfonyl group took place with dienesulfone 4. This secondary reaction has been reported in the cross-coupling reaction of vinylsulfones with n-alkyl Grignard reagents in the presence of iron salts[8]. Slight loss of olefinic purity was observed with the tritylated derivative 7c possibly due to the conditions used for removal of the protecting group. Thus the t-butyldimethylsilyl moiety appeared to be the most efficient protecting group for primary alcohols in this reaction.

The cross-coupling of Grignard reagents with vinylhalides catalysed by nickel[17] or iron[18-20] salts is a well-known reaction. However, the starting materials are not always readily available with high olefinic purity[21]. Various vinyl substrates such as enolethers[22], enol silylethers[23], enolphosphates[24], phosphates[25], vinylsulfides[26] and vinylselenides[27] also undergo this nickel-catalysed cross-coupling reaction.

Financial help from the UA 1110 is gratefully acknowledged. We thank Miss Michon, Miss Derouet and Mrs Morin for recording NMR and GLC- mass spectra and Mr Mulot for skillful technical assistance.

EXPERIMENTAL

Elemental analyses (see Table V) were conducted at Paris VI, Centre de Spectrochimie. Spectra were recorded on the following : Cameca 250 or Bruker AM 400 for ^1H NMR, Bruker WH-90 or Bruker AM 400 for ^{13}C NMR, Perkin-Elmer 599 for IR and Varian-Mat CH7 or Riber Nermag R10-10/B for m/z. Analytical GLC were performed on a Girdel 30 equipped with a capillary Chrompack column (CP Sil 8 CB). Preparative GLC was conducted on a Fractovap 4200 (Carlo Erba) equipped with a pyrex column (3m x 7mm, 15% OV 101 on chromosorb W DMCS-AW 60-80 mesh). Flash chromatography was performed according to ref. 28 using Merck silica gel (0.063-0.2 mm or 540 µm, Art. 7734 or 7736) with a pentane/ether gradient unless stated otherwise. Basic silica gel was prepared by treating 200g of Merck silica gel with 500ml of a saturated aqueous solution of $NaHCO_3$, filtering, washing (successively with water, methanol, ethyl acetate, ether and pentane) and drying. Silver nitrate-charged silica gel was prepared according to a known procedure[29]. Analytical HPLC was conducted on a Du Pont 850 Liquid Chromatograph equipped with a Du Pont B 1500 Zorbax Sil (4.6mm x 25cm) column.

After workup all organic layers were dried over anhydrous magnesium sulfate. All solvents were distilled over appropriate reagents : benzophenonesodium (THF, dioxane, ether), P_2O_5 (pentane), calcium hydride (dichloromethane, chloroforme), sodium (benzene, toluene, xylene) magnesium (methanol, ethanol). Grignard reagents and n-BuLi were titrated with a 0.5M solution of 2-butanol in xylene using 2,2'-biquinoline[30] as the indicator. All reactions were run under a positive pressure of dry nitrogen.

IR, m/z and ^1H NMR data for all sulfones are collected in Table III whereas the date for olefinic compounds are given in Table IV.

[(4-Methyl 3-pentenyl)sulfonyl] benzene 2. 8.2g (50mmol) of 1-bromo 4-methyl 3-pentene[9] and 10g (62mmol) of sodium benzenesulfinate dissolved in 50ml of DMF were stirred at 20°C for 18h and then poured over a mixture of 300ml of ice and water. Extraction with dichloromethane, workup and flash chromatography (pentane/AcOEt) yielded 8.2g (74%) of 2[31] as a colourless oil.

Typical procedure for the hydroxyalkylation of sulfone 2

9-Methyl 6-phenylsulfonyl 8-decen 1,5-diol 6a

Path a. 1.4ml of n-BuLi (1.5M in hexane) were added to a stirred solution of 448mg (2mmol) of sulfone 2 in 10ml of THF at -78°C. The solution was warmed to room temperature for 0.5h and then cooled to -78°C. A solution containing 244 mg (2.4mmol) of lithiated lactol 5 (obtained from 150ml of H_2O, 12.5ml of HCl (35%), and 50g (0.6mol). of 2,4-dihydropyranne ; 93%)[32] in 6ml of THF (obtained upon stirring 5 with 1.8ml of n-BuLi (or LDA) 1.3M in hexane for 15 min. at this temperature) was syphoned into the reaction vessel. The mixture was then stirred at 20°C for 18h. 1ml of saturated solution of aqueous ammonium chloride was added at 0°C and the reaction mixture was extracted with ether. Workup and flash chromatography furnished 568mg (87%) of diols 6a as a yellow oil.

For the preparation of β-hydroxysulfones 3a both condensation and hydrolysis were carried out at -35°C. In the alternative synthesis of 6a, Path b, 3ml of DIBA-H 0.83M in hexane were added dropwise to a stirred solution of 240mg (2.4mmol) of δ-valerolactone in THF at -78°C and this solution was maintained at this temperature prior to condensation. In this case the reaction mixture was hydrolysed with a 2.5M solution of aqueous HCl.

TABLE III : IR, m/z and ^{1}H NMR data of sulfones.

Compound	IR (KBr)	m/z (relative abondance)	250 MHz ^{1}H NMR (J in Hz ; δ_{TMS} = 0 ppm)
2	1310, 1155	143(5), 125(17), 82(100) 77(35), 67(43)	1.54(br s,3H), 1.63(d,1,3H), 2.32 to 2.45(m,2H), 3.02 to 3.14(m,2H), 4.98(br t, 7,1H), 7.52 to 7.70(m,3H), 7.87 to 7.94(m,2H).
3a	3610, 1310, 1150, 1090	339, 322, 198, 180, 143	0.86(t,6.5, 3x0.44H), 0.89(t,6.5, 3x0.56H), 1.00 to 1.80(m,16H including 4br s : δ 1.40, 3x0.56H ; δ 1.51, 3x0.44H ; δ 1.56, 3x0.44H ; and δ 1.58, 3x0.56H), 2.40(m, 2x0.56H), 2.54(m, 2x0.44H), 3.03(m, 2x0.44H), 3.16(m,0.56H), 3.28(m,0.56H), 4.09(m,0.56H), 4.17(m,0.44H), 4.80 to 4.98(m,1H), 7.51 to 7.73 (m,3H), 7.84 to 7.94(m,2H).
3b	1730, 1310, 1150, 1090	381, 321, 238, 143	0.85(t,6.5, 3x0.44H), 0.89(t,6.5, 3x0.56H), 1.05 to 2.20(m,19H including 4br s : δ 1.50, 3x0.56H ; δ 1.58, 3x0.56H ; δ 1.61, 3x0.44H ; and δ 1.67, 3x0.44H as well as 2s : δ 1.84, 3x0.44H ; δ 1.91, 3x0.56H), 2.32 to 2.83(m,2H), 3.18(m,0.44H), 3.39(m,0.56H), 4.98(br t,7,0.56H), 5.13(br t,7,0.44H), 5.20(m,0.56H), 5.35(m, 0.44H), 7.51 to 7.73(m,3H), 7.84 to 8.00(m,2H).
4a	1310, 1150	195(5), 180(2), 108(100), 93(46), 77(28), 67(26)	0.88(t,6.5,3H), 1.12 to 1.35(m,6H), 1.35 to 1.59(m,8H including 2br s : δ 1.42 and δ 1.47), 2.18(q,7,2H), 2.98(d,6.5,2H), 4.66(br t,6.5,1H), 6.93(t,7.5, 1H), 7.42 to 7.63(m,3H), 7.76 to 7.86(m,2H).
6a	3500, 1300, 1150, 1080	327(18), 251(5), 223(12), 184(90), 167(100)	1.07 to 1.74(m,12H including 2 br s : δ 1.39 and δ 1.46), 2.12 to 2.57(m,4H), 2.95(br t,6,0.48H), 3.11(br q,6,0.52H), 3.60(t,6, 2x0.52H), 3.52(t,6, 2x0.48H), 4.04(m,0.52H), 4.15(m,0.48H), 4.75(br t,6,0.52H), 4.78(br t,6,0.48H), 7.40 to 7.64(m,3H), 7.72 to 7.85(m,2H).
6b	3500, 1300, 1250, 1140, 840	441(0.4), 383(12), 281(17), 241(7), 199(28), 159(40), 149(43), 135(37), 125(33), 75(100)	-0.06(s, 6x0.52H), -0.03(s, 6x0.48H), 0.79(s, 9x0.52H), 0.80(s, 9x0.48H), 1.04 to 1.70(m,12H including 4 br s : δ 1.41, 3x0.48H, δ 1.42, 3x0.52H ; δ 1.49, 3x0.52H ; δ 1.50, 3x0.48H), 2.28 to 2.60(m,2H), 2.97(m,0.52H), 3.06(m,1H), 3.10(m,0.48H), 3.47 to 3.60(m,2H), 4.05(m,0.48H), 4.14(m,0.52H), 4.78 to 4.92 (m,1H), 7.50 to 7.67(m,3H), 7.84 to 7.92(m,2H).
6c	3500, 1300, 1140, 1075	C.I.(NH$_3$) 586(23), 569(100)	1.14 to 1.76(m,12H including 4 br s : δ 1.46, 3x0.48H ; δ 1.48, 3x0.52H ; δ 1.54, 3x0.52H ; δ 1.56, 3x0.48H), 2.34 to 2.66(m,2H), 2.96 to 3.21(m,4H), 4.09(m,0.48H), 4.20(m,0.52H), 4.82 to 4.97(m,1H), 7.19 to 7.72(m,18H), 7.88 to 7.98(m,2H).
6d	1740, 1315, 1250, 1160	411(0.8), 385(1), 225(66), 209(88), 165(33), 149(35), 111(53), 93(48), 82(62), 77(63), 69(85), (100)	1.06 to 2.06(m,18H including 4 br s : δ 1.41, 3x0.48H ; δ 1.49, 3x0.48H ; δ 1.52, 3x0.52H and δ 1.57, 3x0.52H as well as 4s : δ 1.75, 3x0.52H ; 125(82), δ 1.85, 3x0.48H ; δ 1.95, 3x0.52H and δ 1.97, 3x0.48H), 2.22 to 2.73(m,2H), 3.11(m,0.52H), 3.32(m,0.48H), 3.91(t,6.5, 2x0.52H), 3.98(t,6.5, 2x0.48H), 4.8555-(br t,7,0.48H), 5.03(br t,7, 0.52H), 5.19(m,0.48H), 5.32(m,0.52H), 7.47to 7.68(m,3H), 7.78 to 7.91(m,2H).
6e	1740, 1315, 1250, 1160	C.I.(NH$_3$) 500(100), 483 (62)	-0.08(s, 6x0.52H), -0.03(s, 6x0.48H), 0.80(s, 9x0.52H), 0.82(s, 9x0.48H), 1.08 to 2.02(m,15H including 4 br s : δ 1.43, 3x0.48H ; δ 1.51, 3x0.48H ; δ 1.53, 3x0.52H and δ 1.59, 3x0.52H as well as 2 s : δ 1.76, 3x0.52H and δ 1.86, 3x0.48H), 2.27 to 2.76(m,2H), 3.13(m,0.52H), 3.34(m,0.48H), 3.48(t, 6.5, 2x0.52H), 3.55(t,6.5, 2x0.48H), 4.80(br t,7,0.48H), 5.07(br t,7,0.52H), 5.18(m,0.48H), 5.32(m,0.52H), 7.49 to 7.68(m,3H), 7.80 to 7.93(m,2H).
6f	1740, 1300, 1140, 1075	C.I.(NH$_3$) 628(42), 386(100)	1.16 to 1.96(m,15H including 3s : δ 1.49, 3x0.48H ; δ 1.59,3H ; δ 1.66, 3x0.52H ; δ1.83, 3x0.52H and δ 1.90, 3x0.48H), 2.32 to 2.81(m,2H), 3.00(t, 6.5, 2x0.52H), 3.06(t,6.5, 2x0.48H), 3.18(m,0.52H), 3.40(m,0.48H), 4.97(br t,7,0.48H), 5.12(br t,7,0.52H), 5.26(m,0.48H), 5.40(m,0.52H), 7.17 to 7.72(m,18H), 7.88 to 7.99(m,2H).
7a	1300, 1145	C.I.(NH$_3$) 368(100), 351(8)	1.34 to 1.76(m,10H including 2s : δ 1.42 and δ 1.46), 1.99(s,3H), 2.17(q,7, 2H), 2.92(d,6.5,2H), 4.01(t,6,2H), 4.60(br t,6.5,1H), 6.92(t,7,1H), 7.44 to 7.65(m,3H), 7.77 to 7.88(m,2H).
7b	1300, 1146	C.I.(NH$_3$) 440(100), 423(11)	-0.03(s,6H), 0.82(s,9H), 1.38 to 1.54(m,10H including 2 br s : δ 1.42 and δ 1.47), 2.16(q,7,2H), 2.83(d,6.5,2H), 3.56(t,6,2H), 4.61(br t,6.5,1H), 6.93 (t,7,1H), 7.43 to 7.62(m,3H), 7.78 to 7.86(m,2H).
7c	1300, 1140, 1075, 700	C.I.(NH$_3$) 568(100), 551(32)	1.34 to 1.68(m,10H including 2s : δ 1.44 and δ 1.48), 2.14(q,7,2H), 2.82 (d,6.5,2H), 3.08(t,6,2H), 4.62(br t,6.5,1H), 6.86(t,7,1H), 7.20 to 7.64(m,18H), 7,80 to 7.90(m,2H).

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[a] 100MHz ^{13}C J-Modulated NMR spectrum[35] (δ_{CDCl_3} =77.00ppm ; d and q=(+), s and t=(-)) : 13.55(+), 17.27(+), 22.08(-), 24.94(+), 25.16(-), 27.95(-), 28.54(-), 31.11(-), 119.90(+), 127.49(+), 127.60(+), 127.66(+), 128.38(+), 128.48(+), 132.49(+), 132.66(-), 140.13(-).

Typical procedure for protection of the primary alcohol function [13] and acetylation [12]. 1-t-Butyldimethylsilyloxy 9-methyl 6-phenylsulfonyl 8-decen 5-ol 6b

A solution of 166mg (1.1mmol) of t-butyldimethylsilylchloride in 3ml of dichloromethane was added to a solution of 326mg (1 mmol) of sulfonediol 6a, 278 µl (2 mmol) of triethylamine and 5mg (0.04 mmol) of DMAP in 3ml of dichloromethane at 0°C. The mixture was stirred at 0°C for 18h, hydrolysed at this temperature with a saturated aqueous solution of ammonium chloride and extracted with ether. The usual workup and flash chromatography (basic silica gel) yielded 347mg (79%) of monosilylated sulfonediol 6b as a yellow oil along with 10% of disilylated material and 5% of starting sulfonediol 6a.

Acetylations were performed in a similar way using 1.1 equivalents of acetic anhydride. 224mg (2.2 mmol) of acetic anhydride were used for the preparation of diacetoxysulfone 6d and the reaction was conducted at 20°C for 5h. In this latter case flash chromatography was conducted on silica gel.

Typical procedure for the synthesis of vinylsulfones from β-acetoxysulfones. 1-t-Butyldimethylsilyloxy 9-methyl 6-phenylsulfonyl (E)-5,8-decadiene 7b.

40mg (1 mmol) of freshly powdered sodium hydroxide were added to a solution of 193mg (0.4 mmol) of sulfone 6e in ether. The heterogenous reaction mixture was stirred at 20°C for 5h and 0.5ml of a saturated solution of ammonium chloride were added. After extraction with ether and workup, flash chromatography on basic silica gel furnished 159mg (94%) of dienesulfone 7b.

Elimination of acetic acid from β-acetoxysulfone 3b was conducted in THF and flash chromatography was performed on silica gel.

Typical procedure for the reaction of dienesulfones with Grignard reagents in the presence of transition metals.

3ml (0.03 mol)of a 0.01 M solution of catalyst in ether (or in the solvent used for the reaction) were added to 1 mmol of dienesulfone dissolved in 6 ml of ether. The stirred solution was cooled to -78°C and 2 mmol (4 mmol in the case of dienesulfone 7a) of Grignard reagent were

TABLE IV : M/z and ^{1}H-NMR data of olefinic compounds.

Compound	m/z (relative abundance)	250 MHz ^{1}H-NMR (J in Hz ; δ_{TMS} = 0 p.p.m.)
8	166(5), 124(2), 109(3), 95(18), 81(43), 68(100)	0.88(t,6.5,3H), 1.19 to 1.42(m,8H), 1.65(dt, J_1=4.5, J_2=1.5, 3H), 2.03(q,6,2H), 2.70(t,4.5,2H), 5.28 to 5.52(m,4H).
9	208(6), 165(11), 137(12), 123(15), 109(70), 95(47), 81(56), 64(63), 55(100)	0.88 (t,6.5,3H), 0.97(d,7,6H), 1.19 to 1.39(m,8H), 1.63(dt, J_1=5, J_2=1, 3H), 1.98(q,7,2H), 2.20(seven peaks, 7,1H), 2.70(d,5,2H), 5.15(t,7,1H), 5.26 to 5.48(m,2H).
10	208(8), 160(5), 137(12), 123(10), 109(16), 95(50), 81(73), 67(38), 55(100)	0.86(t,7,3H), 0.88(t,6.5,3H), 1.17 to 1.49(m,10H), 1.65(dt, J_1=5, J_2=1, 3H), 1.93(t,7,2H), 1.99(q,7,2H), 2.69(d,5.5,2H), 5.12(t,7,1H), 5.23 to 5.53(m,2H).
11[a]	180(10), 165(10), 95(88), 82(95), 67(100)	0.89(t,6.5,3H), 1.18 to 1.44(m,8H), 1.63(br s,3H), 1.69(br d,1.3, 3H), 2.07(q,6.5,2H), 2.73(t,6.5,2H), 5.09(br t,6.5,1H), 5.26 to 5.46(m,2H-simplifies to an AB system, J_{AB}=10).
12[b]	222(1.5), 179(10), 166(10), 123(55), 109(47), 75(100)	0.88(t,6.5,3H), 0.96(d,6.5,6H), 1.18 to 1.41(m,8H), 1.66(br s,3H), 1.69(br d,1,3H), 1.99(br q,6.5,2H), 2.20(seven peaks, 6.5,1H), 2.71 (d,6.5,2H), 4.98(br t,6.5,1H), 5.12(t,6.5,1H).
13	222(4), 179(5), 166(10), 141(11), 128(26), 123(20), 109(32), 95(100)	0.86(t,7,3H), 0.88(t,6.5,3H), 1.17 to 1.49(m,10H), 1.65(br s,3H), 1.69(br d,1,3H), 1.93(br t,7,2H), 2.00(br q,6.5,2H), 2.68(d,7,2H), 5.02(br tm, J_1=7, J_2=1.4, 1H), 5.10(t,7,1H).
14	168(1.5), 150(2.6), 135(10), 107(16), 93(36), 79(93), 67(100)	1.08 to 2.13(m,13H including 2br s : δ1.60,3H ; δ1.64,3H), 2.68(dd, J_1=6.5, J_2=5.5,2H), 3.60(t,7,2H), 5.08(br t,7,1H), 5.28 to 5.42 (m,2H- simplifies to an AB system, J_{AB}=10).
15	210(19), 137(8), 123(96), 107(41), 91(69), 79(86), 67(100)	0.92(d,6.5,6H), 1.1 to 2.34(m,14H including 2s : δ1.60, 3H and δ1.64,3H), 2.66(d,6.5,2H), 3.61(t,6.5,2H), 4.95(br t,1H), 5.13 (t,7,1H).

[a] 100 MHz ^{13}C J-Modulated NMR Spectrum [35] (δ_{CDCl_3} = 77.00ppm ; d and q = (+), s and t=(-) : 14.02(+), 17.75(+), 22.05(+), 22.66(-), 25.65(+), 27.76(-), 28.48(-), 29.09(-), 30.11(-), 31.86(-), 34.57(+), 122.77(+), 124.10(+), 130.61(-), 144.69(-). [b] 100MHz ^{13}C J-Modulated Spectrum -idem- 14.07(+), 17.65(+), 22.65(-), 25.66(+), 26.38(-), 27.22(-), 28.97(-), 29.56(-), 31.76(-), 122.96(+), 128.30(+), 129.80(+), 140.72(-).

added. The homogeneous solution, which was initially the colour of the transition-metal complex, turned black with formation of some insoluble material and this mixture was warmed to 20°C for 1h, whereupon 0.5 ml of a saturated aqueous solution of ammonium chloride were added followed by a solution of the internal standard in toluene (tridecane or heptadecane). The reaction mixture was filtered over 10g of basic silica gel and then this column was rinced 3 times with 20ml of ether. The combined organic layers were washed with a saturated solution of $NaHCO_3$ followed by brine. After the usual workup, removal of the silyl-protecting group ($Bu_4NF \cdot 3H_2O$, THF, 1h, 20°C)[33] or the trityl-protecting group (HCl 5M, $CHCl_3$, 1h, 0°C)[34] was conducted according to literature procedures prior to GLC analysis and the residue was analysed by capillary GLC. The products were separated by preparative GLC prior to ^{1}H-NMR, m/z and elemental analyses.

Compound		Calculated %		Found %		Compound		Calculated %		Found %	
		C	H	C	H			C	H	C	H
2	$C_{12}H_{16}O_2S$	64.25	7.19	64.41	7.15	7c	$C_{36}H_{38}O_3S$	78.51	6.96	78.35	6.89
3a	$C_{19}H_{30}O_3S$	67.42	8.93	66.98	8.87	8	$C_{12}H_{22}$	86.66	13.34	86.48	13.27
3b	$C_{21}H_{32}O_4S$	66.28	8.48	65.95	8.47	9	$C_{15}H_{28}$	86.46	13.54	86.01	13.45
4	$C_{19}H_{28}O_2S$	71.21	8.80	69.56	8.60	10	$C_{15}H_{28}$	86.46	13.54	86.25	13.48
6a	$C_{17}H_{26}O_4S$	62.55	8.03	62.05	7.94	11	$C_{13}H_{24}$	86.58	13.41	86.25	13.28
6b	$C_{23}H_{40}O_4SSi$	62.68	9.15	62.35	8.93	12	$C_{16}H_{30}$	86.40	13.60	86.10	13.57
6c	$C_{36}H_{40}O_4S$	76.02	7.09	75.85	6.98	13	$C_{16}H_{30}$	86.40	13.60	85.99	13.58
6d	$C_{21}H_{30}O_6S$	61.44	7.37	61.15	7.22	14	$C_{11}H_{20}O$	78.52	11.98	78.23	11.95
7a	$C_{19}H_{26}O_4S$	65.11	7.48	65.04	7.39	15	$C_{14}H_{26}O$	79.94	12.46	79.51	12.38
7b	$C_{23}H_{38}O_3SSi$	65.35	9.06	65.74	8.92						

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