

3-BROMO-2-t-BUTYLSULFONYL-1-PROPENE.
A VERSATILE MULTI-COUPLING REAGENT
Part 1

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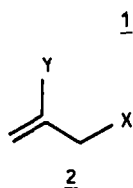
Summary -

The 3-bromo-2-t-butylsulfonyl-1-propene **3** was prepared in two steps from allyl-t-butylthioether in 70% overall yield. This reagent reacts selectively with a broad range of nucleophiles (amine, thiolate, lithium ester- and keto- enolates, magnesium, zinc and lithium organometallics) to furnish the unsaturated sulfones of type **4** in typical yields of 80-90%. The sulfone **3** reacts also in the presence of zinc with various electrophiles (aldehydes, ketones, nitriles and an imine) to afford the functionalized unsaturated sulfones of type **7** in good yields.

A - Introduction

Convergent synthesis is one of the most useful strategy in organic synthesis. In such an approach, there is a need of highly reactive and selective reagents of type **1** which are able to form sequentially two new bonds with two different reagents A and B. (see scheme 1). To be of general utility and versatility, the carbon skeleton of **1** must be simple, so that it can be found in many retrosynthetic approaches.

Reagents of type **1** which satisfy these conditions were



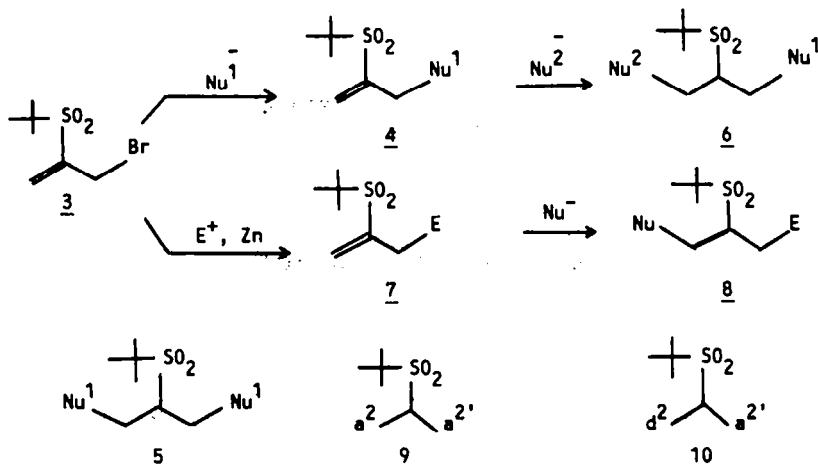
called multi-coupling reagents^{2,3}. Functionalized allylic compounds of type **2** are a class of such reagents which are synthetically very useful. The groups X and Y can be :
Y=COOR, X=Br⁴ or ZnBr⁵ ; Y=CONR¹R², X=Li or ZnBr^{5b,6} ;
Y=COR, X=OH⁷ ; Y=OR, X=Hal⁸ ; Y=P(O)(OR)₂, X=Br⁹ or
X=ZnBr^{5b,10}, X and Y=Hal¹¹ ; Y=CH₂SiMe₃,
X=OR¹² ; Y=SR, X=OR¹³, Y=SiMe₃, X=Br, I¹⁴ or MgBr, ZnBr^{15,5b} ; Y=SePh, X=Br¹⁶ ; Y=SOR, X=Br or
ZnBr^{5b,17} ; Y=SO₂R, X=Br^{5b,17,18,19} and ZnBr²⁰.

We describe here the preparation and reactions of 3-bromo-2-t-butylsulfonyl-1-propene **3** (preliminary reports : ref. 19 and 20a).

The reactivity pattern of the sulfone **3** is shown in scheme 2. It reacts with a nucleophile Nu¹ to give selectively the unsaturated sulfone **4** without any bis-addition of Nu¹ (which

would lead to the saturated sulfone 5. By reaction with a different nucleophile Nu², a sulfone of type 6 is obtained (see accompanying paper).

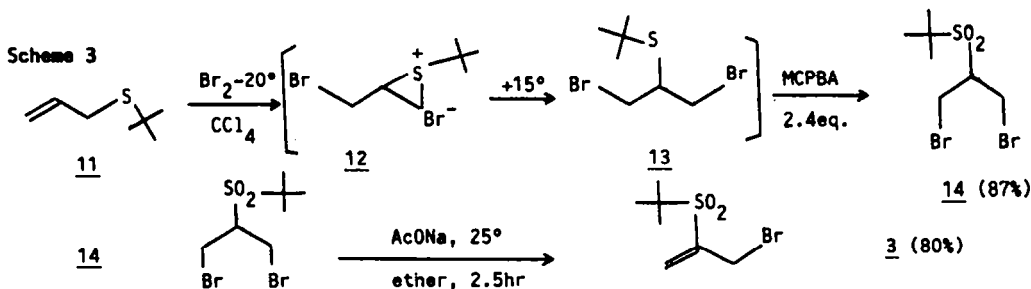
Scheme 2



The 3-bromo-2-tert-butylsulfone 3 reacts also readily with electrophiles E in the presence of zinc and affords mono-coupling products of type 7 which can react with a nucleophile Nu to furnish the highly functionalized sulfones 8. The sulfone 3 is a multi-coupling reagent which is synthetically equivalent to the a²/a^{2'} synthon 9 and to the d²/a^{2'} synthon 10 (see ref. 21 for this nomenclature). The scope of the reactions of 3 with nucleophiles and electrophiles will be indicated.

B - Preparation of 3-bromo-2-tert-butylsulfone-1-propene 3

The sulfone 3 is easily available in 2 steps from tert-butylthioether²² 11 with an overall yield of 70% (see scheme 3). The addition of one equivalent of bromine to a carbon tetrachloride solution of the thioether 11 furnishes a yellow precipitate of the episulfonium salt 12 which, by warming to 15°, gives the unstable²³ dibromo thioether 13. This thioether was directly oxidized to the dibromo sulfone 14 with meta-chloroperoxybenzoic acid (2.4 equiv.) with an isolated yield of 87%. The elimination of HBr occurs smoothly by stirring an ethereal solution of 14 with 1.5 eq. of dry sodium acetate for 2.5hr at 25° to afford the desired sulfone 3 as a crystalline solid (m.p. 43°; purity: 96%; 80% yield).



All these reactions can easily be performed on a 50 gr scale, making the reagent 3 readily available in large quantities. The sulfone 3 can be stored many months in a refrigerator without any decomposition.

C - Reaction of the sulfone 3 with nucleophiles

The simultaneous presence of an allylic bromine atom and of a vinylic sulfone confers an exceptional electrophilicity on 3 (as compared to an allylic bromide or to a vinylic sulfone). Various nucleophiles Nu¹ react rapidly with 3 and afford the highly functionalized

sulfones of type 4 (see scheme 2 and table 1). Thus even an amine like aniline reacts at -50° within 0.5 hr (see entry 2 of table 1); other soft nucleophiles like lithium thiophenolate or a malonate type enolate react also smoothly (see entry 1 and 3 of table 1). More reactive nucleophiles like lithium enolates furnish the desired addition products in good yield providing that the sulfone 3 is slowly added as a THF solution at a low temperature (-80°); see entries 4-6 of table 1 and the experimental part. Very reactive nucleophiles like lithium or magnesium reagents can also be added (entries 7-14 of table 1). The best yields are obtained by adding the organometallics to a THF solution of the sulfone 3 at -90° and then warming up to the temperature indicated in the table. Under these conditions a large variety of organometallics (alkynyl, aryl, vinylic, primary, secondary and tertiary alkyl) afford the unsaturated sulfones (4g - 4n) in 60 to 94% yields (see table). An exception was dimethylphenylsilyllithium²³ which gives low yields of the desired coupling product 4m under various conditions; but the corresponding cyanocuprate^{24,25} generated by adding one equivalent of CuCN (0.5 hr at -40°) to dimethylphenylsilyllithium gives a clean substitution reaction which furnishes the allylsilane 4m in 74% yield (see entry 13 of table 1). The reactivity of 4m was shortly investigated: pivaloyl chloride in the presence of $TiCl_4$ (compare with ref. 26) did not react with 4m and the reaction of 4m with dimethyl maleate in the presence of tetrabutylammonium fluoride only gives 2-propenyl-*t*-butylsulfone; no cyclic^{20b} product could be detected. Finally even an activated zinc reagent like allylzinc bromide was able to add to 3 although after a longer reaction time (24 hr at 25°) to yield in 85% the 1,5-dienylsulfone 4c (see entry 15 of table 1).

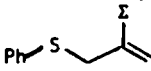
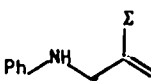
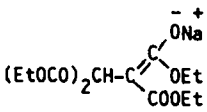
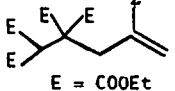

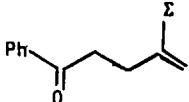
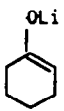
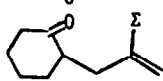
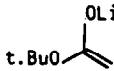
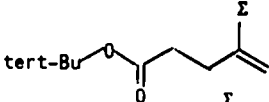
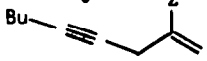
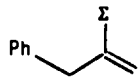
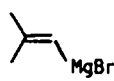
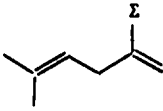
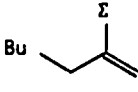
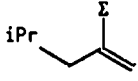
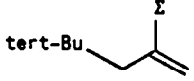
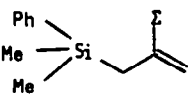
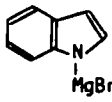
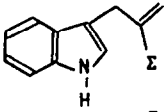
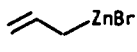
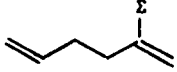
D - Reaction of sulfone 3 with electrophiles

As indicated in scheme 2, the sulfone 3 is also able to react with various electrophiles in the presence of zinc^{20a} or of chromium (II) salts^{20c}. Under previously developed Barbier conditions^{5b} (generation of the organometallic species in the presence of the electrophile), the sulfone 3 reacts readily with aldehydes, ketones and nitriles in the presence of zinc; even some alkynes can be used as electrophiles in this reaction (see ref. 5b). Thus the dropwise addition of a THF solution of 3 to a THF solution of the carbonyl compound containing activated zinc (see experimental part) at 40° - 50° gives, after a reaction time of typically 0.5 hr, the desired addition product of type 7 (see scheme 2 and table 2) in good to excellent yields. The reaction flask was immersed into an ultrasound bath during the reaction. This procedure allows an efficient stirring of the highly concentrated reaction mixture and an additional activation of the zinc²⁷. Aldehydes and ketones give a very fast addition and high yields (see entries 1-10 of table 2); the zinc salt of α -hydroxyacetone is an exception and the desired diol is only isolated in 40% (see entry 11 of table 2). Unsaturated ketones or aldehydes react specifically in a 1,2 fashion and even the sensitive β -ionone (entry 9 of table 2) furnishes the corresponding unsaturated tertiary alcohol in 83% yield. Nitriles give an imine which is easily hydrolysed (1 NHCl, 0° , 0.5 hr) to afford the corresponding ketone in 64% yield to 70% yield (see entries 12-14 of table 2); even a moderately electrophilic imine reacts with 3 and zinc, leading to the unsaturated aminosulfone 7o in 65% yield (see entry 15 of table 2).

Conclusion

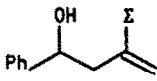
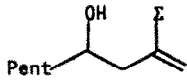
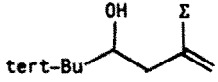
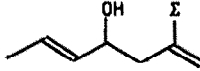
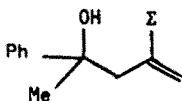
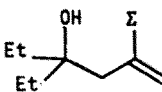
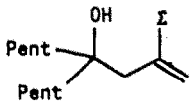
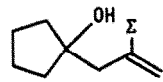
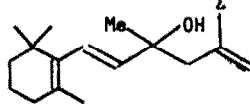
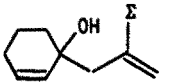
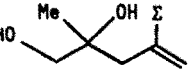
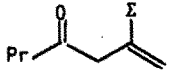
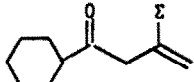
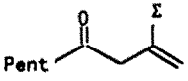
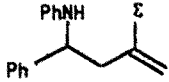
In this article we have shown the great versatility of reagent 3 to form new carbon-carbon bonds with various substrates (electrophiles and nucleophiles); we have thus demonstrated the multicoupling ability of this reagent.

Table 1. Products of type 4 obtained by the reaction of 3-bromo-2-tert-butylsulfonyl-1-propene with nucleophiles

Entry	Nucleophile	Product of type 4 (a)	Reaction conditions	Yield %
1	PhSLi	<u>4a</u> 	0.25hr at -78°	84
2	PhNH ₂	<u>4b</u> 	0.5 hr at -50°	92
3		<u>4c</u> 	1 hr at -50°	65
4		<u>4d</u> 	1 hr at -80° ; 0.25hr at -40°	84
5		<u>4e</u> 	1 hr at -70° ; then 0.25hr at -60°	94
6		<u>4f</u> 	1 hr at -80°	86
7	Bu≡-Li	<u>4g</u> 	0.5 hr at -78° ; then 0.25hr at -70°	80
8	Ph-MgBr	<u>4h</u> 	0.5 hr at -78° ; then 1.5 hr at -50°	89
9		<u>4i</u> 	0.5 hr at -78° ; then 1 hr at -45°	93
10	BuMgBr	<u>4j</u> 	0.5 hr at -78° ; then 1 hr at -65°	85
11	i-Pr-MgCl	<u>4k</u> 	0.5 hr at -78° ; then 1 hr at -65°	90
12	tert-Bu-MgCl	<u>4l</u> 	0.5 hr at -90° ; then 0.5 hr at -75°	94
13	Ph-SiCuCNLi Me ₂	<u>4m</u> 	0.5 hr at -80°	74
14		<u>4n</u> 	0.5 hr at -60° ; then 1.5 hr at -50° (solvent : toluene)	60
15		<u>4o</u> 	24 hr at 25°	85

(a) Σ stands for 50₂-tert-Butyl

Table 2. Products of type 7 obtained by the reaction of 3-bromo-2-tert-butylsulfonyl-1-propene with aldehydes, ketones, nitriles and an imine

Entry	Electrophile	Product of type 7	Yield %
1	Benzaldehyde	<u>7a</u> 	85
2	Hexanal	<u>7b</u> 	85
3	Pivalaldehyde	<u>7c</u> 	85
4	Crotonaldehyde	<u>7d</u> 	88
5	Acetophenone	<u>7e</u> 	86
6	3-pentanone	<u>7f</u> 	88
7	6-undecanone	<u>7g</u> 	82
8	Cyclopentanone	<u>7h</u> 	84
9	β-ionone	<u>7i</u> 	83
10	Cyclohexenone	<u>7j</u> 	80
11	α-hydroxyacetone	<u>7k</u> 	40
12	Butyronitrile	<u>7l</u> 	64
13	Cyclohexyl cyanide	<u>7m</u> 	65
14	Hexanenitrile	<u>7n</u> 	70
15	Benzalanilin	<u>7o</u> 	65

EXPERIMENTAL PART -

THF and ether were distilled from sodium/benzophenone. Infrared spectra were recorded on a Perkin Elmer 457G spectrometer. Proton NMR spectra were obtained at 100MHz with a Jeol MH100 and at 250MHz with a Bruker AM 250. ^{13}C NMR spectra were obtained with a Jeol FX90. Chemical shifts in CDCl_3 solution are reported in ppm relative to tetramethylsilane as an internal standard. Gas chromatography was carried out with a Carlo Erba 2150 model equipped with an OV 101 (20 m) column. Merck 60 (70-230 mesh) silica gel was used for the flash chromatography.²⁸

1,3-Dibromo-2-t-butylsulfonylpropane 14

In a dry three-neckflask, equipped with mechanical stirring, a pressure equilibrating dropping funnel and a thermometer, is placed a solution of allyl, tert butyl thioether²² 7.35 g (56.5 mmol) in 50 ml CCl_4 . To this solution, cooled at -20°C , is added dropwise, a solution of 9.03 g bromine (56.5 mmole) in 25 ml CCl_4 , so that temperature never exceeds -15°C . A yellow precipitate of the episulfonium bromide separates out. The temperature is then allowed to raise up to $+15^\circ\text{C}$ (the precipitates dissolves to give an orange solution of 13), the mixture is stirred over 5 min and poured out in the dropping funnel of a second device, analogous to the former one, where a suspension of 29.5 g (135 mmol) of metachloroperbenzoic acid in 80 ml CH_2Cl_2 has been prepared in the flask. The solution of 13 is then added dropwise at -20° within 15 min, and the mixture 13 allowed to warm up to room temperature and stirred over 3 hrs. 300 ml CH_2Cl_2 and 600 ml CHCl_3 are then added, the organic layer is washed with water (300 ml) and a 20% sodium hydrogensulfite solution (3 x 150 ml). The aqueous phase thus obtained is extracted once more (150 ml of CH_2Cl_2). The joined organic phases are then washed successively with a sodium carbonate solution (3 x 150 ml), water (2 x 150 ml) and sat. NaCl (150 ml). After drying over MgSO_4 and evaporation of solvents under reduced pressure, 17.3 g of crude 14 are obtained. They are purified by filtration on a silica gel column (CH_2Cl_2) to give 15.8 g (87%) of 14 used as such for the next step.

I.R. (neat, KBr) : 1315, 1295, 1260, 110, 1085, 865, 845, 690

RMN ^{13}C (CDCl_3) : 57.47, 28.3, 23.39 ppm

RMN ^1H (CDCl_3) : 4.0 (m,5H), 1.43 (s,9H)

3-Bromo-2-t-butyl sulfonyl-1-propene 3

14.5 g (45 mmol) of 14, 120 ml THF, 5.6 g (67.5 mmol) of AcONa (previously dried under a vacuum, 5 hr at 100°C) are placed in a flask immersed in an ultrasound laboratory cleaner (48kHz, 30 w), and allowed to react for 2.5 hrs at room temperature. The white fine suspension is then filtrated, the precipitate is washed (2 x 30 ml CH_2Cl_2), the filtrate is partly concentrated under a vacuum to evaporate THF, and diluted with 150 ml CH_2Cl_2 , then washed with water (3 x 30 ml), then a sat. NaCl solution (2 x 30 ml) and dried over magnesium sulfate. After evaporation of solvents, under reduced pressure, 9.9 g of 3 are obtained (purity 93% according to VPC). This product can be used as such, or chromatographed on silica gel (cyclohexane/ethylacetate = 80/20) to give 80% of 3 (purity 96%). m.p. : 43°C

I.R. (KBr, neat) : 3100, 3040, 2970, 1480, 1460, 1435, 1395, 1284, 1118, 1098, 972, 800, 760, 720

RMN ^{13}C (CDCl_3) : 143.76, 134.55, 60.51, 27.14, 23.39

RMN ^1H (CDCl_3) : 6.63 (s,2H), 4.38 (s,2H), 1.46 (s,9H).

General procedure for the addition of a nucleophile to the sulfone 3

Method A : direct addition (addition of a solution of 3 to the nucleophile)

This procedure has been used with keto- and ester- enolates. A dry three-neck flask equipped with a pressure-equilibrating dropping funnel, a magnetic bar, a thermometer and a rubber septum was flushed with Ar. Diisopropylamine (7.5 mmol) and 21 ml of dry THF were added through the rubber septum. The stirred mixture was cooled to -78° (acetone/dry ice) and 6.4 mmol of BuLi (2.1N in ether) were added through the dropping funnel. After 0.5 hr at -78°C , a solution of the ketone or ester (6.35 mmol) in 3 ml of THF was slowly added to the LDA solution. The lithium enolate was formed after 1-1.5 hr stirring at -78°C . Then a solution of 3 (6.22 mmol) in 25 ml of THF was added within 20 min. After the time indicated in the table 1 (determined by taking aliquots and controlling the progress of the reaction by t.l.c. or g.c.), the reaction mixture was diluted with 150 ml of ether and aq. NH_4Cl (40 ml). The two layers were separated and the aq. layer was extracted with ether (2 x 30 ml). The combined organic phases were washed with aq. NH_4Cl (30 ml), H_2O (2 x 30 ml) and brine (40 ml), dried (MgSO_4) and filtered. The solvent was evaporated and the residue was purified by flash-chromatography.

Method B : inverse addition (addition of the nucleophile to a solution of the sulfone 3)

The same apparatus as in method A was used. A stirred solution of 10 mmol of the sulfone 3 in 50 ml of THF was cooled to -90° and an ether or THF solution of the organometallics (10 mmol) was slowly added within 10 min. The reaction was then stirred as indicated in the table 1 (time and temperature) and worked up as above.

2-t-Butylsulfonyl-3-thiophenyl-1 propene 4a

Method B : A solution of 3.33 ml of BuLi (1.83N ; 6.10 mmol) was added at -78° to 671 mg (6.10 mmol) of thiophenol in 20 ml of THF, followed, after 5 min, by a solution of 1.5 g (5.98 mmol) of the sulfone 3 in 20 ml of THF. After 0.25 hr at -78° , the reaction was worked up and purified by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/55:35:5) to give 1.35 g (84%) of a solid m.p. 89°C . See table 4 for the spectroscopic data.

Found : C, 57.60 ; H, 6.75%. Calcd. for $\text{C}_{13}\text{H}_{18}\text{S}_2\text{O}_2$: C, 57.74 ; H, 6.71%.

2-t-Butylsulfonyl-3-(N-phenylamino)-1-propene 4b

A solution of 800 mg (8.6 mmol) of aniline in 5 ml THF is added to a solution of 1 g (4.15 mmol) of sulfone 3 in 5 ml THF at -78° .

The temperature is allowed to raise to -50°C . After stirring for 30 min at -50°C , the reaction is over (check by t.l.c) and 20 ml of aq. sat. NH_4Cl and 50 ml CH_2Cl_2 are added. The organic phase is washed with brine (20 ml), dried over MgSO_4 , and the solvents are evaporated under vacuum. The residue is chromatographed on silicagel (solvent Hexane : CH_2Cl_2 : ether/70:30:2) to give 960 mg (91.5%) of amine 4b. m.p.: 124.5°C (CH_2Cl_2 , pentane); see Table 3 for spectroscopic data.

Found : C, 61.41 ; H, 7.90%. Calcd. for $\text{C}_{13}\text{H}_{19}\text{NSO}_2$: C, 61.63 ; H, 7.56%.

Ethyl-1,1,2,2-tetracarboxylate-4-t-Butylsulfonyl-4-pentene 4c

Method A : The reagent is prepared from 105 mg NaH (4.37 mmol) freed of oil by washing with THF, dispersed in 15 ml of THF. A solution of 1.32 g (4.15 mmol) of ethyl ethane tetracarboxylate in 10 ml THF is added dropwise at 0°C to this suspension and the mixture is then stirred over 1 hr at 0°C .

The solution is then added to a solution of 3 (1 g, 4.15 mmol) in 10 ml THF at -78° . The temperature is allowed to raise to -50°C . After 1 hr, a copious white precipitate is formed. 20 ml of sat. NH_4Cl solution are added, the organic layer is separated, washed with water (3 x 5 ml) dried over magnesium sulfate and solvents are evaporated under a vacuum. The remaining crude oil is chromatographed on silica gel (solvent : hexane : CH_2Cl_2 : ether/70:30:5) to give 1.88 g (95%) of ester 4c. m.p. : 64°C , see table 3 for spectroscopic data.

Found : C, 52.30 ; H, 7.26%. Calcd. for $\text{C}_{21}\text{H}_{34}\text{S}_4\text{O}_{10}$: C, 52.70 ; H, 7.16%.

4-t-Butylsulfonyl-1-oxo-1-phenyl-4-pentene 4d

Method A : The lithium enolate of acetophenone was generated as indicated in the general procedure with the following quantities : 750 mg (7.4 mmol) of diisopropylamine in 21 ml of THF, 3.05 ml (6.40 mmol) of BuLi 2.1N in ether, 762 mg (6.35 mmol) of acetophenone. After 1.5 hr at -70° , 1.5 g (6.2 mmol) of the sulfone 3 in 25 ml of THF was added at -80° within 20 min and after 1 hr at -80° , the reaction mixture was warmed up to -40° and worked up after 15 min at this temperature to give after a purification by flash chromatography (solvent : CH_2Cl_2 :hexane/6:1) 1.46 g of white crystals (m.p. 110° ; 84% yield). See table 3 for the spectroscopic data.

Found : C, 64.05 ; H, 7.12%. Calcd. for $\text{C}_{15}\text{H}_{20}\text{SO}_3$: C, 64.25 ; H, 7.19%.

(2'-t-Butylsulfonyl-2'-propenyl)-1-cyclohexanone 4e

Method A : The lithium enolate of cyclohexanone was indicated in the general procedure with the same quantities as for the synthesis of 4d and 622 mg (6.35 mmol) of cyclohexanone. After 1.5 hr at -40° , 1.5 g (5.98 mmol) of the sulfone 3 in 20 ml of THF was added at -80° within 20 min and after 1 hr at -70° , the reaction mixture was warmed up to -60° and worked up after 15 min at this temperature to give after a purification by flash chromatography (solvent : CH_2Cl_2 :hexane/9:1) 1.45 g of white crystals (m.p. 86° ; 94% yield). See table 3 for the spectroscopic data.

t-Butyl 4-t-butylsulfonyl-4-pentenoate 4f

Method A : The lithium enolate of t-butyl acetate was generated as indicated in the general procedure with the same quantities as for the synthesis of 4d and 737 mg (6.35 mmol) of t-butyl acetate. After 1 hr at -80° , 1.5 g (5.98 mmol) of the sulfone 3 in 30 ml of THF was added within 20 min. After 1 hr at -78° the reaction was worked up and the residue was purified by flash chromatography (solvent : CH_2Cl_2 and CH_2Cl_2 : ether/97:3) to give 1.41 g of an oil which crystallizes (m.p. 43° (ether/hexane) : 86% yield). See table 3 for the spectroscopic data.

Found : C, 56.29 ; H, 8.70%. Calcd. for $\text{C}_{13}\text{H}_{24}\text{SO}_4$: C, 56.49 ; H, 8.75%.

2-t-Butylsulfonyl-1-nonen-4-yne 4g

Method B : A solution of hexynyllithium (prepared by the addition of 3.9 ml of BuLi (7.5 mmol) 1.98N in ether to 738 mg (9.0 mmol) of 1-hexyne in 10 ml of THF at -30° ; after 15 min at 25° , the solution is ready for use) was added to a stirred solution of 1.5 g (5.98 mmol) of the sulfone 3 dissolved in 25 ml of THF at -90° . After 0.5 hr at -78° , the mixture was warmed up to -70° and worked up after 0.25 hr at this temperature to give after a purification of the residue by flash chromatography (solvent : hexane : ether : CH_2Cl_2 /15:1:15) 1.15 g (80% yield) of an oil; See table 3 for the spectroscopic data.

2-t-Butylsulfonyl-3-phenyl-1-propene 4h

Method B : A solution of phenylmagnesium bromide (6.6 mmol) in 10 ml of THF was added to a solution of 1.5 g (5.98 mmol) of the sulfone 3 in 30 ml of THF at -90° . The reaction mixture was stirred 0.5 hr at -78° and was then warmed up to -50° and worked up after 1.5 hr at this temperature to give, after a purification by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/40:40:3), 1.26 g of an oil which crystallizes readily (m.p. 72° , 89% yield). See table 3 for the spectroscopic data.

Found : C, 65.21 ; H, 7.70%. Calcd. for $\text{C}_{13}\text{H}_{18}\text{SO}_2$: C, 65.51 ; H, 7.70%.

2-t-Butylsulfonyl-5-methyl-1,4-hexadiene 4i

Method B : A solution of 2-methyl-1-propenylmagnesium bromide 8 ml (6.6 mmol) 0.84N in THF was added at -85° to a solution of 1.5 g (5.98 mmol) of the sulfone 3 in 20 ml of THF. After 0.5 hr at -78° , the reaction mixture was stirred 1 hr at -45° to give, after work-up, a residue which was purified by flash chromatography (solvent : hexane : ether : CH_2Cl_2 /40:4:40) to furnish 1.20 g of a pure oil (93% yield); See table 3 for the spectroscopic data.

2-t-Butylsulfonyl-1-heptene 4j

Method B : A solution of 6 mmol of butylmagnesium bromide (1.82N in ether) was added at -90° to a stirred solution of 1.5 g (5.98 mmol) of the sulfone 3. After 0.5 hr at -78° , the reaction mixture was stirred 1 hr at -65° and then worked up. The residue was purified by flash chromatography (solvent : CH_2Cl_2 : hexane : ether/8:4:1) to furnish 1.11 g (85% yield) of a pure oil; See table 3 for the spectroscopic data.

2-t-Butylsulfonyl-4-methyl-1-pentene 4k

Method B : A solution of isopropylmagnesium chloride (6.6. mmol of a 1.56N solution in THF) in 10 ml of THF was slowly added within 15 min at -90° to a solution of 1.5 g (5.98 mmol) of the sulfone 3 in 30 ml of THF. After 0.5 hr at -78° , the reaction was stirred 1 hr at -65° and worked up; The residue was purified by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/8:8:1) to afford 1.12 g of an oil (90% yield). See table 3 for the spectroscopic data.²

2-t-Butylsulfonyl-4,4-dimethyl-1-pentene 4l

Method B : A solution of 4.2 ml (6.6 mmol) of t-butylmagnesium chloride 1.56N in THF was dissolved in 10 ml of THF and added within 15 min to a cooled solution (-90°) of 1.5 g (5.98 mmol) of the sulfone 3. After 0.5 hr at -90° , the reaction mixture was stirred 0.5 hr at -75° and worked up; The residue was purified by flash chromatography (solvent : CH_2Cl_2 : hexane : ether/8:8:1) 1.25 g of an oil which crystallizes readily to give white crystals (m.p. 91° ; 94% yield); See table 3 for the spectroscopic data.

Found : C, 60.50 ; H, 10.25%. Calcd. for $\text{C}_{11}\text{H}_{22}\text{SO}_2$: C, 60.51 ; H, 10.25%.

(2-t-Butylsulfonyl-2-propenyl)-dimethylphenylsilane 4m

Method B : A solution of dimethylphenylsilyllithium in THF²⁴ (6 mmol) was added at -60° to a suspension of 532 mg (5.95 mmol) of copper cyanide in 25 ml of THF. The reaction mixture was then stirred at -40° for 0.5 hr after which time the copper cyanide was dissolved. This solution was cooled to -80° and cannulated to a cooled solution (-9°) of 1.5 g (5.98 mmol) of the sulfone 3 dissolved in 20 ml of THF. After 0.5 hr at -20° the reaction mixture was worked up to give a residue which, after flash chromatography (solvent : hexane : CH_2Cl_2 : ether/40:60:1) gives an oil (1.30 g ; 74% yield). This compound had only a purity of 85%. See table 3 for the spectroscopic data.

3-(2-t-Butylsulfonyl-2-propenyl)-indole 4n

Method B : A solution of 3 ml of ethylmagnesium bromide (6.10 mmol) 2.05N in ether was added at -40° to a solution of 702 mg (6.0 mmol) of indole in 10 ml of toluene. This solution was stirred 0.5 hr at 25° and then cooled to -30° and cannulated to a solution of 1.5 g (5.98 mmol) of the sulfone 3 in 30 ml of dry toluene at -90° . After 0.5 hr at -60° , the reaction mixture was stirred 1.5 hr at -50° and worked up. A flash chromatography of the residue (solvent : hexane : CH_2Cl_2 : ether/3:5:1) yields 0.99 g of an oil which crystallizes readily (m.p. 180° ; 60% yield). See table 3 for the spectroscopic data.

Found : C, 65.05 ; H, 6.85%. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NSO}_2$: C, 64.95 ; H, 6.90%.

2-t-Butylsulfonyl-1,5-hexadiene 4o

Method B : A solution of allylzinc bromide³⁰ (7.2 mmol) prepared from 470 mg (7.2 mmol) of zinc and 880 mg (7.2 mmol) of allyl bromide in 4 ml of THF was added at -85° to a cooled solution of 1.5 g (5.98 mmol) of the sulfone 3 in 30 ml of THF. The reaction mixture was then stirred 24 hr at 25° and worked up. The residue was purified by flash chromatography (solvent : hexane : CH_2Cl_2 : ether/35:65:3) to furnish 1.0 g of a pure oil (85% yield). See table 3 for the spectroscopic data.

General procedure for the reaction of the sulfone 3 with an electrophile in the presence of zinc
In a three neck flask fitted with a pressure-equilibrating dropping funnel, a magnetic bar, a thermometer, are placed 1 g (15.4 mmol) of Zinc foil 99.995% cut in pieces and a small quantity (about 0.1 g) of crushed glass. The flask is flushed with argon. 1,2-dibromoethane (460 mg) in 2.5 ml THF are added. The flask is heated to start boiling and stirring is continued at $30-35^{\circ}$ for 15-20 min. The flask is immersed in a laboratory ultra sound cleaner (48kHz, 30W) containing water at 55°C . The suspension in the flask being at a temperature of 45° , part of the electrophile (3 mmol) is added, the remaining part (3.3 mmol) is admixed with 1.5 g (6.2 mmol) of bromosulfone 3 in 4.5 ml of THF and sequentially added over a period of 15 min (the temperature may raise up to 52°C in some cases. Sonication is better than magnetic stirring. After 15-60 min (check by t.l.c. or g.c.) the reaction is over. The flask is cooled to 0°C and 20 ml of a sat. NH_4Cl solution and 50 ml CH_2Cl_2 are added under stirring. Zinc metal is filtrated, the two phases are separated and the aqueous one is extracted with CH_2Cl_2 (2 x 30 ml). The joined organic phases are washed with water (2 x 30 ml), $\text{HCl}2\text{N}$ (30 ml) and brine (30 ml), dried over magnesium sulfate. The solvents are evaporated under a vacuum. The crude product is purified by flash chromatography³⁶. In one case, (7g), the reaction was performed on a 25 mmol scale with analogous yields.

The spectroscopic data of the following compounds are collected in table 4.

1-Phenyl-3-tert butylsulfonyl-3-buten-1-ol 7a

(from benzaldehyde). See general procedure

Eluent for flash chromatography : CH_2Cl_2 : hexane : ether/70:30:10, obtained 1.1 g (85%) of 7a.

m.p. : 97°C (CH_2Cl_2 /Pentane).

Found : C, 62.56 ; H, 7.42%. Calcd. for $\text{C}_{14}\text{H}_{20}\text{SO}_3$: C, 62.66 ; H, 7.51%.

2-tert-Butylsulfonyl-1-nonan-4-ol 7b

(from Hexanal). See general procedure. Obtained 1.34 g (85%) of 7b. Same eluent as above for chromatography.

m.p. : 25°C (from : CH₂Cl₂/Pentane)

2,2-Dimethyl-5-tert butylsulfonyl-5-hexen-3-ol 7c

(from pivalaldehyde). See general procedure. Obtained 1.27 g (85%) of 7c. Same eluent for chromatography as above.

m.p. : 83°C (from : CH₂Cl₂/Pentane)

Found : C, 58.10 ; H, 9.64%. Calcd. for C₁₂H₂₄SO₃ : C, 58.03 ; H, 9.73%.

2-tert-Butylsulfonyl-1,5-hexadien-4-ol 7d

(from crotonaldehyde). See general procedure. Obtained 1.21 g of 7d (88%). Eluent for chromatography : CH₂Cl₂:Hexane: ether/70:30:30. Oil.

1-Phenyl-1-methyl-3-tert butylsulfonyl-3-buten-1-ol 7e

(from acetophenone). See general procedure. Obtained 1.46 g of 7e (86%). Eluent for chromatography : CH₂Cl₂: hexane : ether/70:30:10. m.p. : 127°C (from : CH₂Cl₂/pentane).

2-tert-Butylsulfonyl-4-ethyl-1-hexen-4-ol 7f

(from 2-pentanone). See general procedure. Obtained 1.35 g of 7f (88%). Eluent for chromatography : same as preceding case. m.p. : 61°C (from : CH₂Cl₂/pentane).

Found : C, 57.88 ; H, 9.60%. Calcd. for C₁₂H₂₄SO₃ : C, 58.03 ; H, 9.73%.

2-tert-Butylsulfonyl-4-pentyl-1 nonen-4-ol 7g

(from 6-undecanone, on 25 mmol). See general procedure. Obtained 6.8 g of 7g (82%). Eluent, same as the preceding case. m.p. : 51°C (from CH₂Cl₂/pentane).

1-(2-tert-Butylsulfonyl-1-propen-3-yl) cyclopentan-1-ol 7h

(from cyclopentanone). See general procedure. Obtained 1.28 g (84%). Eluent for chromatography : CH₂Cl₂:hexane:ether/ 70:30:15. m.p. : 87°C (from CH₂Cl₂/pentane).

5-tert-Butylsulfonyl-3-methyl-1-(2,6,6-trimethyl-1-cyclohexenyl)1,5 hexadien-3-ol 7i

(from -ionone). See general procedure. Obtained : 1.77 g of 7i (83%). Same eluent as in the case of 7e. m.p. : 87°C (from : pentane/CH₂Cl₂).

1-(2-ter-Butylsulfonyl-1-propen-3-yl)-2-cyclohexen-1-ol 7j

(from cyclohexenone). See general procedure. Obtained 1.24 g (80%). Same eluent as for 7e.

m.p. : 81°C (from CH₂Cl₂/pentane).

Found : C, 60.52 ; H, 8.54%. Calcd. for C₁₃H₂₂SO₃ : C, 60.43 ; H, 8.58%.

2-tert-Butylsulfonyl-4-methyl-1-penten-4,5-diol 7k

(from -hydroxyacetone). See general procedure but on a 12.4 mmol scale. Zinc is activated as indicated, then the mixture is cooled at -35°C, and hydroxyacetone (0.92 g, 12.4 mmol) is added, then 8.03 ml of a 1.55 N solution of allyl zinc bromide (12.45 mmol) is added. The temperature is raised to 35°C, then the bromosulfone 3 is added and the general procedure is followed. Obtained : 0.59 g (40%). Eluent for chromatography : 1.5% MeOH in Et₂O. m.p. : 89°C.

2-tert-Butylsulfonyl-1-hepten-4-one 7l

(from butyronitrile). See the general procedure. The obtained imine is hydrolysed by stirring the crude product with a 1N HCl solution at 0°C for 15 min. Obtained : 0.9 g (64%) of 7l. Eluent for chromatography : CH₂Cl₂ : hexane : ether/70:30:5. m.p. : 51°C (from CH₂Cl₂/pentane).

Found : C, 56.96 ; H, 8.67%. Calcd. for C₁₁H₂₀SO₃ : C, 56.86 ; H, 8.67%.

2-tert-Butylsulfonyl-4 cyclohexyl-1-buten-4-one 7m

(from cyclohexylcyanide). Same hydrolysis as for 7l. Obtained : 1.06 g of 7m (65%)

Eluent for chromatography : CH₂Cl₂:hexane:ether/70:30:5. m.p. : 23° (from CH₂Cl₂/pentane).

2-tert-Butylsulfonyl-1-nonen-4-one 7n

(from hexane nitrile). See the general procedure. Same hydrolysis as for 7l. Obtained : 1.1 g (70%) of 7n. Eluent : same mixture as for 7l. m.p. : 49°C (from CH₂Cl₂/hexane).

2-tert-Butylsulfonyl-4-phenyl-4(N-phenylamino)-1-butene 7o

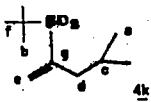
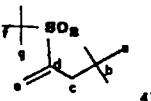
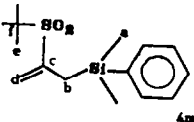
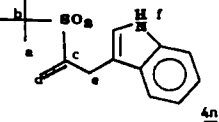
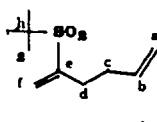
(from benzalanilin). See the general procedure. Obtained : 1.34 g of 7o (65%).

Eluent for chromatography : CH₂Cl₂:hexane:ether/70:30:10. m.p. : 143°C (from ether/pentane).

Found : C, 70.05 ; H, 7.20%. Calcd. for C₂₀H₂₅NSO₂ : C, 69.94 ; H, 7.33%.

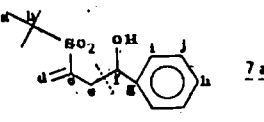
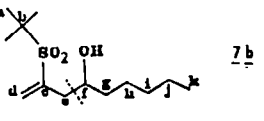
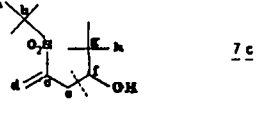
Table 3. Spectroscopic data of compounds 4a-4o

Structure	¹ H NMR spectra (a)	¹³ C NMR spectra (a)	I.R. (b)
	1.42(s, 9H, (a)); 4.08(s, 2H, (b)); 6.55(m, 2H, (c)); 7.55(m, 5H, arom., (H))	23.6(a); 34.7(b); 60.5(d) 127.0; 129.2; 129.9; 131.6 134.5; 143.5	3095, 3050, 2960, 1475, 1440, 1400, 1282, 1125, 1110, 990, 800, 750, 725, 695
	1.40(s, 9H(a)); 4.20(m, 3H, (e, NH)); 3.16(s, 1H, (d) trans/SO ₂); 3.25(s, 1H, (d), cis/SO ₂); 6.66 and 7.20 (m, 5H, phenyl)	23.54(a); 45.14(e); 60.18 (b); 118.11(i); 112.9 and 129.31(g, h); 129.76(d); 144.65(c); 146.59(f)	3415, 3370, 3100, 3080, 3050, 3015, 2985, 2965, 2925, 2890, 1920, 1820, 1730, 1605, 1555, 1510, 1475, 1460, 1450, 1435, 1285, 1160, 1120, 1030, 1015, 995, 960, 800, 755, 710, 695
	1.32(m, 12H, (k, m)); 1.38(s, 9H, (a)); 3.24(s, 2H, (e)); 4.26(m, 8H, (j, l)); 6.36(s, 2H, (d))	13.70 and 13.91(k, m); 23.48(a); 34.20(e); 56.55 (f); 58.90(g); 60.35(b); 62.21 and 61.88((j, l); 142.84(c); 131.93(d); 168.07 and 166.70(h, i)	2960, 1735, 1460, 1390, 1295, 1210, 1105, 1030, 860, 800, 740, 700
	1.45(s, 9H, (a)); 2.96(t, J=7Hz, 2H, (b)); 3.41(t, J=7Hz, 2H, (c)); 6.10(s, 1H, (d) cis-SO ₂ -t-Bu); 6.31 (s, 1H, (d) trans-SO ₂ -t-Bu); 7.64(m, 3H, arom. H); 8.09 (m, 2H, arom. H)	23.7(a); 27.1(c); 37.9(b); 60.4(e); 128.0; 128.7; 129.4; 133.3; 136.5; 146.7; 198.0(f)	3098, 3060, 2990, 1688, 1600, 1560, 1450, 1430, 1318, 1281, 1218, 1160, 1100, 970, 926, 815, 802, 750, 701, 690
	1.42(s, 9H, (a)); 2.57-1.51 (m, 9H); 2.93(m, 2H); 6.00 (s, 1H, (b) cis SO ₂ -t-Bu); 6.28(s, 1H, (b) trans SO ₂ -t-Bu)	23.7(a); 25.2; 28.1; 32.6; 33.9; 42.3; 49.7; 60.4; 130.3(b); 145.4(c); 211.4 (d)	2990, 2940, 1705, 1480, 1462, 1440, 1400, 1280, 1130, 1006, 980, 950, 840, 800, 750, 698, 625
	1.43(s, 9H, (a)); 1.51(s, 9H, (b)); 2.70(m, 4H, (c, d)); 6.13(s, 1H, (e) cis SO ₂ -t-Bu); 6.41(s, 1H, trans SO ₂ -t-Bu)	23.6(a); 27.5(d); 30.0(b); 33.9(c); 60.2(f); 80.7(g); 128.6(e); 146.5(h); 171.0 (i)	2990, 2940, 1730, 1480, 1393, 1370, 1292, 1160, 1106, 960 850, 801, 738
	0.97(t, J=6Hz, 3H, (a)); 1.43(s, 9H, (j)); 1.32-1.63 (m, 4H, (b, c)); 2.26(m, 2H, (d)); 3.46(m, 2H, (g)); 6.46(s, 1H, (i) cis SO ₂ -t-Bu); 6.60(s, 1H, (i) trans SO ₂ -t-Bu)	13.6(a); 18.4; 21.9; 23.0; 23.5(j); 30.9; 60.2(k); 74.0 and 85.4(e, f); 130.2 (i); 143.9(h)	2960, 2938, 2870, 1630, 1480, 1460, 1295, 1160, 1102, 955, 801, 749
	1.48(s, 9H, (a)); 3.91(s, 2H, (b)); 5.77(s, 1H, (c) cis SO ₂ -t-Bu); 6.43(s, 1H, (c) trans SO ₂ -t-Bu); 7.49(m, 5H, arom. H)	23.8(a); 38.2(b); 60.4(d); 127.1; 128.8; 129.4; 130.4 136.8; 147.8	3060, 2980, 1620, 1600, 1500, 1472, 1450, 1432, 1390, 1360, 1285, 1192, 1150, 1092, 950, 800, 765, 735, 710, 700
	1.42(s, 9H, (i)); 1.69(s, 3H, (b)); 1.84(s, 3H, (a)); 3.23(d, J=7.5Hz, 2H, (e)); 5.34(t, J=7.5Hz, 1H, (d)); 6.10(s, 1H, (g) cis SO ₂ -t-Bu); 6.34(s, 1H, (g) trans SO ₂ -t-Bu)	17.8 and 25.6(a, b); 23.7 (i); 30.6(e); 60.0(h); 118.9 (d); 128.7(g); 135.8(c); 146.9(f)	2980, 2960, 1480, 1450, 1290, 1100, 950, 800, 740
	0.93(t, J=6Hz, 3H, (a)); 1.2-1.84(m, 6H, (g, h, i)); 1.42(s, 9H, (b)); 2.52(t, J=7.8Hz, 2H, (f)); 6.13(s, 1H, (d) cis SO ₂ -t-Bu); 6.37 (s, 1H, (d) trans SO ₂ -t-Bu)	13.9(a); 22.4; 23.7(b); 28.4; 31.2; 31.9; 60.0(c) 128.0(d); 147.9(e)	2970, 2930, 2860, 1460, 1361, 1290, 1110, 950, 801, 740, 700

	1.02(d, J=6.9Hz, 6H, (a)); 1.42(s, 9H, (b)); 2.08(m, 1H, (c)); 2.42(d, J=6.3Hz, 2H, (d)); 6.13(s, 1H, (c) cis SO ₂ -t-Bu; 6.43(s, 1H, (e) trans SO ₂ -t-Bu	23.5(a); 23.7(b); 27.8(c); 41.1(d); 60.0(f); 129.2 (e); 146.4(g)	2980, 1470, 1390, 1370, 1290, 1110, 800, 760, 700
	1.02(s, 9H, (a)); 1.39(s, 9H, (g)); 2.43(s, 2H, (c)); 6.22(s, 1H, (e) cis SO ₂ - t-Bu; 6.42(s, 1H, (e) ^z trans SO ₂ -t-Bu)	23.5(g); 29.4(a); 32.3(c) 44.1(b); 60.1(f); 130.8(e) 145.0(d)	3100, 2980, 2961, 2950, 2865, 1480, 1392, 1365, 1295, 1282, 1270, 1140, 1108, 979, 803, 750
	0.42(s, 6H, (a)); 1.42(s, 9H, (f)); 2.20(s, 2H, (b)); 5.64(s, 1H, (d) cis SO ₂ - t-Bu; 6.04(s, 2H, (d) ^z trans SO ₂ -t-Bu; 7.42- 7.49(m, 5H, arom.H)	3.2(a); 21.7(b); 23.6(f) 60.0(e); 126.1; 127.8; 129.3; 133.6; 137.4; 144.4 (c)	3060, 3040, 2960, 1612, 1480, 1460, 1430, 1395, 1365, 1290, 1250, 1195, 1110, 1090, 940, 930, 840, 800, 738, 700
	1.51(s, 9H, (a)); 4.47(s, 2H, (e)); 5.89(s, 1H, (d) 6.34(s, 1H, (d) trans SO ₂ - t-Bu; 7.21-7.82(m, 5H, arom.H); 8.48(s, 1H, (f)	23.9(a); 28.4(e); 60.3(b) 110.9; 111.5; 118.8; 119.7 122.3; 123.4; 126.8; 130.0 136.5; 146.9(c)	3330, 3100, 3058, 2980, 2910, 1640, 1620, 1572, 1460, 1430, 1340, 1270, 1232, 1200, 1145, 1090, 1070, 1010, 975, 970, 910, 828, 800, 780, 760, 742, 703, 660
	1.40(s, 9H, (g)); 2.41- 2.72(m, 4H, (c, d)); 5.04- 5.29(3s, 2H, (a)); 5.85(m, 1H, (b)); 6.07(s, 1H, (f) cis SO ₂ -t-Bu; 6.28(s, 1H, (f) trans SO ₂ -t-Bu)	23.6(g); 31.2(c); 32.5(d) 60.0(h); 116.1(a); 128.7(f); 136.4(b); 146.8(e)	2990, 1640, 1480, 1450, 1390, 1365, 1290, 1101, 1000, 915, 800, 740

(a) All spectra were obtained in CDCl₃ with tetramethyl silane as an internal standard
 (b) Infrared spectra were recorded as film (liquids) or KBr plates (solids)

Table 4. Spectroscopic data of compounds 7a-7c

Structure	¹ H NMR Spectra ^a	¹³ C NMR Spectra ^a	I.R. ^b
	1.36(s, 9H, (a)); 2.84(d, 2H, J=6.5Hz, (e)); 3.44(d, 1H, J=4.5Hz, OH); 5.08(m, 1H, (f)); 6.20(s, 1H, Hd trans/SO ₂); 6.40(s, 1H, Hd cis/SO ₂); 7.56(s, 5H, (phényl)	143.55(c); 143.28(g); 131.99(d); 128.35(i); 127.55(h); 125.79(j); 72.76(f); 60.30(b); 42.10 (e); 23.50(a)	3520, 3030, 2980, 2930, 2890, 1600, 1495, 1455, 1400, 1370, 1280, 1200, 1150, 1100, 1050, 965, 940, 915, 880, 845, 805, 760, 740, 700, 630
	0.90(t, 3H, J=6.5Hz, (k)); 1.40(Ls, 9H, (a)); 2.60 (m, 2H, (e)); 3.32(La, 1H, OH); 3.92(La, 1H, (f)); 6.38(s, 1H, (Hd trans/SO ₂)) 6.44(s, 1H, (Hd cis/SO ₂))	144.21(c); 131.19(d); 70.32(f); 60.18(b); 39.95 (e); 37.39(g); 31.79; 25.29; 23.57(a); 22.58; 14.06(k)	3500, 2930, 2860, 1620, 1480, 1460, 1400, 1290, 1195, 1160, 1100, 1030, 950, 865, 800, 740, 700
	0.92(s, 9H, (h)); 1.40(s, 9H, (a)); 3.60(m, 1H, (f)); 2.50(m, 3H, (e, OH)); 6.32 (s, 1H, (Hd trans/SO ₂)); 6.44(s, 1H, (Hd cis/SO ₂))	145.25(c); 131.01(d); 78.60 (f); 60.24(b); 34.94(e); 29.88(g); 25.59(h); 23.63 (a)	3460, 2950, 2900, 2860, 1625, 1480, 1390, 1365, 1285, 1190, 1155, 1100, 1060, 1040, 1025, 1005, 950, 900, 865, 805, 780, 740, 690, 625

	<p>1.40(s, 9H, (a)); 1.70(d, 3H, J=6.5Hz, (i)); 2.60(d, 2H, J=7.5Hz, (e)); 3.40(1a, 1H, (OH)); 4.40(m, 1H, (f)); 5.7(m, 2H, (g, h)); 6.3(s, 1H, (Hd trans/SO₂)); 6.4(s, 1H, (Hd cis/SO₂))</p>	<p>140.81(c); 130.35(d); 128.83(g); 124.36(h); 68.38(f); 57.59(b); 37.07(e); 20.89(a); 14.96(i)</p>	<p>3460, 2980, 2920, 1480, 1450, 1395, 1285, 1195, 1155, 1100, 1030, 965, 870, 800, 740</p>
	<p>1.36(s, 9H, (a)); 1.62(s, 3H, (g)); 3.00(s, 2H, (e)); 3.8(1a, 1H, OH); 5.84(s, 1H, (Hd trans/SO₂)); 6.26(s, 1H, (Hd cis/SO₂)); 7.5(m, 5H, (phenyl))</p>	<p>146.83(h); 142.21(c); 133.15(d); 128.09; 126.75(i); 125.11; 73.98(f); 60.42(b); 45.97(e); 30.12(g); 23.57(a)</p>	<p>3450, 3080, 3010, 2980, 2930, 1600, 1490, 1475, 1450, 1385, 1360, 1340, 1270, 1225, 1180, 1000, 1060, 1030, 975, 950, 920, 900, 850, 805, 775, 745, 700</p>
	<p>0.90(t, 6H, J=6.5Hz, (h)); 1.40(s, 9H, (a)); 1.56(q, 4H, J=6.5Hz, (g)); 2.64(s, 2H, (e)); 3.00(s, 1H, OH); 6.37(s, 1H, (Hd trans/SO₂)); 6.43(s, 1H, (Hd cis/SO₂))</p>	<p>143.31(c); 132.74(d); 74.10(f); 60.39(b); 40.73(e); 30.66(g); 23.59(a); 7.89(h)</p>	<p>3430, 3100, 2960, 2940, 2880, 1620, 1455, 1400, 1375, 1350, 1330, 1280, 1270, 1190, 1125, 1095, 1035, 980, 970, 900, 875, 800, 745,</p>
	<p>0.90(t, 6H, J=6.5Hz, (k)); 1.40(1s, 9H, (a)); 2.62(s, 2H, (e)); 3.00(s, 1H, OH); 6.32(s, 1H, (Hd trans/SO₂)); 6.40(s, 1H, (Hd cis/SO₂))</p>	<p>143.34(c); 132.65(d); 73.77(f); 60.36(b); 41.62(e); 38.85(g); 32.36; 23.59(a); 23.24; 22.61; 14.06(k)</p>	<p>3500, 3100, 2950, 2860, 1620, 1480, 1460, 1400, 1370, 1362, 1335, 1270, 1200, 1130, 1095, 1020, 1000, 970, 940, 915, 880, 800, 745, 710, 690, 630</p>
	<p>1.41(s, 9H, (a)); 1.74(1a, 9H, (g, h)); 2.91(m, 3H, (e, OH)); 6.42(m, 2H, (d))</p>	<p>144.09(c); 132.11(d); 81.46(f); 60.33(b); 42.73(e); 39.84(g); 23.66 and 23.48(h and a)</p>	<p>3420, 2950, 2860, 1480, 1430, 1400, 1365, 1275, 1190, 1150, 1090, 1005, 970, 955, 920, 880, 800, 740, 645</p>
	<p>1.00(s, 6H, (p, q)); 1.40(s, 9H, (a)); 1.68(s, 3H, (g)); 2.84(s, 3H, (r)); 3.40(s, 1H, OH); 5.64(d, 2H, J=15Hz, (h, i)); 6.50(s, 2H, (d))</p>	<p>142.81(c); 139.26; 136.85(j); 133.01(d); 127.91; 125.76; 72.88(f); 60.27(b); 44.04(e); 39.39(n); 33.91(o); 32.62(l); 29.17; 28.81; 23.54(a); 21.45(r); 19.25(m)</p>	<p>3500, 2980, 2940, 2880, 1620, 1445, 1390, 1360, 1330, 1280, 1200, 1095, 1030, 970, 960, 910, 800, 750, 740, 685</p>
	<p>1.40(s, 9H, (a)); 1.76(1a, 4H, (i, j)); 2.00(1a, 2H, (k)); 2.74(s, 2H, (e)); 2.86(s, 1H, OH); 5.84(m, 2H, (h, g)); 6.45(s, 1H, (Hd trans/SO₂)); 6.47(s, 1H, (Hd cis/SO₂))</p>	<p>c</p>	<p>3530, 3100, 2900, 2830, 1640, 1620, 1470, 1430, 1380, 1365, 1340, 1280, 1170, 1150, 1100, 1020, 995, 965, 945, 920, 885, 865, 850, 800, 735, 680</p>
	<p>1.2(s, 3H, (g)); 1.4(s, 9H, (a)); 2.7(m, 2H, (e)); 3.4(1a, 4H, (h, 2OH)); 6.36(s, 1H, (Hd trans/SO₂)); 6.41(s, 1H, (Hd cis/SO₂))</p>	<p>142.6(c); 133.67(d); 7.82(f); 68.74(h); 60.61(b); 40.01(e); 23.84(g); 23.54(a)</p>	<p>c</p>
	<p>0.94(t, 3H, J=6.5Hz, (i)); 1.38(s, 9H, (a)); 1.66(hex, 2H, J=6.5Hz, (h)); 2.58(t, 2H, J=6.5Hz, (g)); 3.66(s, 2H, (e)); 6.30(s, 1H, Hd trans/SO₂); 6.52(s, 1H, Hd trans/SO₂)</p>	<p>204.30(f); 140.07(c); 133.51(d); 60.31(b); 44.81(e); 44.45(g); 23.33(a); 16.98(h); 13.58(i)</p>	<p>3090, 2960, 2880, 1715, 1625, 1480, 1415, 1395, 1365, 1290, 1195, 1160, 1100, 1050, 1015, 980, 950, 890, 800, 740, 660</p>

	7a	1.36(1s, 9H, (a)); 1.80(1a, 6H); 2.50(1a, 1H, (g)); 3.68(s, 2H, (e)); 6.18(s, 1H, (Hd trans/SO ₂)); 6.42 (s, 1H, (Hd cis/SO ₂))	206.77(f); 140.04(c); 133.45(d); 59.92(b); 50.29 (e); 42.73(g); 28.33; 25.80; 25.44; 23.24(a)	2970, 2925, 2850, 1715, 1625, 1480, 1450, 1395, 1365, 1320, 1290, 1195, 1140, 1100, 1065, 1000, 950, 875, 800, 735, 690
	7b	0.90(t, 3H, J=6.5Hz) (k); 1.40(1s, 9H, (a)); 2.56(t, 2H, J=6.5Hz, (g)); 3.62 (s, 2H, (e)); 6.26(s, 1H, Hd trans/SO ₂); 6.54(s, 1H, Hd cis/SO ₂)	204.69(f); 139.79(c); 133.51(d); 60.33(b); 44.57 (e); 42.75(g); 31.22; 23.45 (a); 23.29; 22.40; 13.88(k)	c
	7c	1.32(s, 9H, (a)); 2.90(d, 2H, J=6.5Hz, (e)); 4.70(m, 1H, NH); 6.14(s, 1H, (Hd trans/SO ₂)); 6.22(s, 1H, Hd trans/SO ₂); 6.6-7.5(m, 10H, (phenyls))	160.00; 147.34; 143.55; 143.05; 128.98(d); 128.77; 128.59; 128.36; 127.02; 126.48; 125.79; 120.73; 116.38; 112.83; 59.86(b); 57.45(f); 40.36(e); 20.27 (a)	3380, 3060, 3020, 2980, 2960, 2930, 2860, 1620, 1600, 1510, 1450, 1400, 1390, 1360, 1350, 1315, 1280, 1240, 1190, 1180, 1150, 1090, 1020, 985, 945, 910, 870, 800, 760, 750, 720, 700, 690,

- a/ All spectra were obtained in CDCl₃ with tetramethylsilane as an internal standard ;
 b/ Infrared spectra were recorded as film (liquids) or KBr plates (solids) ;
 c/ Not recorded

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References and Notes -

1. Present address : Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48109-1055.
2. P. Knochel and D. Seebach, *Tetrahedron Lett.* **23**, 3897 (1982) ;
 D. Seebach and P. Knochel, *Helv. Chim. Acta* **67**, 261 (1984)
3. The term conjunctive reagent was used in a recent paper : E. Piers and V. Karunaratne, *J. Org. Chem.* **48**, 1774 (1983)
4. D.J. Dunham and R.G. Lawton, *J. Am. Chem. Soc.* **93**, 2074 (1971) ; E.J. Corey and I. Kuwajima, *Tetrahedron Lett.* 487 (1972) ; M.F. Semmelhack, *Org. React.* **19**, 115 (1972) ; R. Baker, *Chem. Rev.* **73**, 487 (1973)
 L.S. Hegedus, *J. Organomet. Chem. Lib.* **1**, 329 (1976)
5. a/ E. Ohler, K. Reininger and U. Schmid, *Ang. Chem.* **82**, 480 (1970) ;
 b/ P. Knochel and J.F. Normant, *J. Organomet. Chem.* **309**, 1 (1986) ;
 c/ N.E. Alami, C. Beland and J. Villieras, *Tetrahedron Lett.* **28**, 59 (1987) ;
 d/ H. Mattes and C. Benezra, *Tetrahedron Lett.* **26**, 5697 (1985)
6. H.W. Gswend, *Organic Synthesis Today and Tomorrow*, 163 (1981) Pergamon Press ; P. Beak and D.J. Kempf, *J. Am. Chem. Soc.* **102**, 4550 (1980) ; D.J. Kempf, *J. Org. Chem.* **51**, 3921 (1986) ; P. Beak and K.D. Wilson, *J. Org. Chem.* **52**, 218 (1987) ; P. Beak and D.A. Bug, *Tetrahedron Lett.* **27**, 5911 (1986)
7. A.B. Smith, III, B.A. Wexler and J.S. Slade, *Tetrahedron Lett.* **21**, 3237 (1980)
8. Y=OSiMe₃, X=I : A. Hosomi, A. Shirabata, Y. Araki and H. Sakurai, *J. Org. Chem.* **46**, 4631 (1981) ; Y=OMe, X=Br : R.M. Jacobson, R.A. Rath and J.H. Mc Donald III, *J. Org. Chem.* **42**, 2545 (1977) ; Y=OP(O)(OEt)₂, X=OR : J.P. Marino and H. Hiroyuki Abe, *J. Org. Chem.* **46**, 5379 (1981) ; Y=OAc, X=Br : T. Mandai, J. Nokami, T. Youro, Y. Yashinaga and J. Otera, *J. Org. Chem.* **49**, 172 (1984) ; Y=OP(O)(OEt)₂ ; X=Cl : S.C. Welch, J.M. Assercq, J.P. Loh and S.A. Glase, *J. Org. Chem.* **52**, 1440 (1987)
9. J.N. Collard and C. Benezra, *Tetrahedron Lett.* **23**, 3725 (1982)
10. P. Knochel and J.F. Normant, *Tetrahedron Lett.* **25**, 1475 (1984)
11. J.F. Le Borgne, *J. Organomet. Chem.* **122**, 129 (1976) ; E. Negishi and F.L. Luo, *J. Org. Chem.* **48**, 2427 (1983)
12. B.M. Trost, *Ang. Chem. Int. Ed. Engl.* **25**, 1 (1986)

13. B.M. Trost and D.M.T. Chan, *J. Am. Chem. Soc.* **101**, 6429, 6432 (1979) ;
B.M. Trost and J.E. Vincent *ibid.* **102**, 5680 (1980) ;
B.M. Trost and D.P. Curran, *ibid.* **103**, 7380 (1981) ;
B.M. Trost and B.R. Adams *ibid.* **105**, 4849 (1983)
14. L.A. Paquette, R.A. Galemno, Jr. and J.P. Springer, *J. Am. Chem. Soc.* **105**, 6975 (1983)
15. Y.K. Han and L.A. Paquette, *J. Org. Chem.* **44**, 3731 (1979) ;
J.G. Duboudin, B. Jousseau and M. Pinet-Vallier, *J. Organomet. Chem.* **172**, 1 (1979) ;
P. Knochel and J.F. Normant, *Tetrahedron Lett.* **25**, 4383 (1984) ;
Y. Morizawa, H. Oda, K. Oshima and H. Nozaki, *Tetrahedron Lett.* **25**, 1163 (1984)
16. S. Halazy and L. Hevesi, *J. Org. Chem.* **48**, 5242 (1983)
17. P.B. Anzeveno, D.P. Matthews, C.L. Barney and R.J. Barbuch, *J. Org. Chem.* **49**, 3134 (1984)
18. R.E. Donaldson, J.C. Saddler, S. Byrn, A.T. Kenzie and P.L. Fuchs, *J. Org. Chem.* **48**, 2167 (1983) ;
E.J. Corey, W. Su and I.N. Houpis, *Tetrahedron Lett.* **27**, 5951 (1986)
19. P. Knochel and J.F. Normant, *Tetrahedron Lett.* **26**, 425 (1985)
20. a/ P. Auvray, P. Knochel and J.F. Normant, *Tetrahedron Lett.* **26**, 2329 (1985)
b/ P. Auvray, P. Knochel and J.F. Normant, *ibid.* **26**, 4455 (1985)
c/ P. Auvray, P. Knochel and J.F. Normant, *ibid.* **27**, 5091, 5095 (1986)
21. D. Seebach, *Ang. Chem.* **91**, 259 (1979) ; *Ang. Chem. Int. Ed. Engl.* **18**, 239 (1979)
22. D.S. Farbell and W.M. Lovett, *J. Am. Chem. Soc.* **78**, 2259 (1956)
23. J.M. Bland and C.H. Stanmer, *J. Org. Chem.* **48**, 4393 (1983)
24. I. Fleming and F. Roessler, *J.C.S. Chem. Comm.* 276 (1980)
25. J.P. Gorlier, L. Hamon and J. Levisalles, *J. Chem. Soc. Chem. Commun.* 88 (1973) ;
L. Hamon and J. Levisalles, *J. Organomet. Chem.* **251**, 133 (1983)
26. A. Hosomi, M. Saito and H. Sakurai, *Tetrahedron Lett.* 429 (1979)
27. For reviews see : J.L. Luche, *L'Actualité Chimique*, 21 (1982) and P. Boutjouk, *Nachr. Chem. Tech. Lab.* **31**, 798 (1983)
28. W.C. Still, M. Kahn and M. Mitra, *J. Org. Chem.* **43**, 2923 (1978)
29. J.B. Brown, H.B. Henbest and E.R.H. Jones, *J. Chem. Soc.* 3172 (1952)
30. M. Gaudemar, *Bull. Soc. Chim. France*, 974 (1962)