Tetrahedron Vol. 48, No. 24, pp. 5179-5190, 1992
Printed in Great Britain

0040-4020/92 \$5.00+.00

2-(Chloromethyl)-3-tosylpropene: An Useful Reagent for the Synthesis of Allyl Sulfones

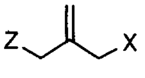
Carmen Nájera* and José M. Sansano

Departamento de Química Orgánica, Facultad de Ciencias,
Universidad de Alicante, E-03080 Alicante, Spain

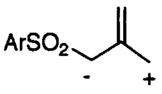
(*Received in UK* 27 *March* 1992)

Abstract: 2-(Chloromethyl)-3-tosylpropene (5) prepared directly from commercially available 3-chloro-2-(chloromethyl)propene reacts with a variety of heteronucleophiles and Grignard derivatives to afford allyl sulfones 7 and 8 respectively. It reacts also with electrophiles such as carbonyl compounds in the presence of zinc metal under Barbier conditions to give functionalized allyl sulfones of the type 12.

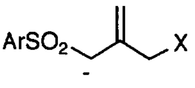
Isobutene derivatives with two functional groups at the allylic positions **1** are adequate synthons for the preparation of cyclopentane derivatives through transition-metal-catalyzed [3+2] cycloaddition reactions[1]. The corresponding sulfone derivatives **1** ($Z=ArSO_2$) are specially interesting compounds because they can be used as multicoupling reagents : (a) as the synthon **2** either *via* the above mentioned palladium catalyzed reactions (**1**, $Z=ArSO_2$, $X=OCO_2Et$[1a,2a], $X=Cl$[2b]) or *via* the organolithium derivative (**1**, $Z=PhSO_2$, $X=Br$)[3], (b) as the synthon **3** by allylic deprotonation of the corresponding allyl sulfones ($X=Cl$)[2b], ($X=SiMe_3$)[4] and (c) as the synthon **4** (X=alkyl) in the regioselective γ-substitution of the arylsulfonyl group by means, for instance, of lithium dialkylcuprates[5], organoaluminium compounds in the presence of aluminium chloride[6] or transition-metal-catalyzed alkylation reactions[7]. This type of allyl sulfones **1** ($Z=ArSO_2$) has been prepared generally from 2-methylene-1,3-propanediol ($X=OCO_2Et$)[1a], methallyl phenyl sulfone ($X=Cl$, OCO_2Et)[2a] ($X=Br$)[3] or 2-(bromomethyl)prop-2-enyl acetate ($X=OAc$)[8]. We describe here that 2-(chloromethyl)-3-tosylpropene (**5**)[9], easily prepared from 3-chloro-2-(chloromethyl)propene, is an useful starting compound for the general preparation of allyl sulfones working as synthon **6a** or **6b**.



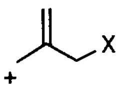
1



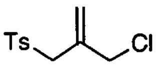
2



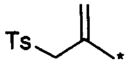
3



4



5

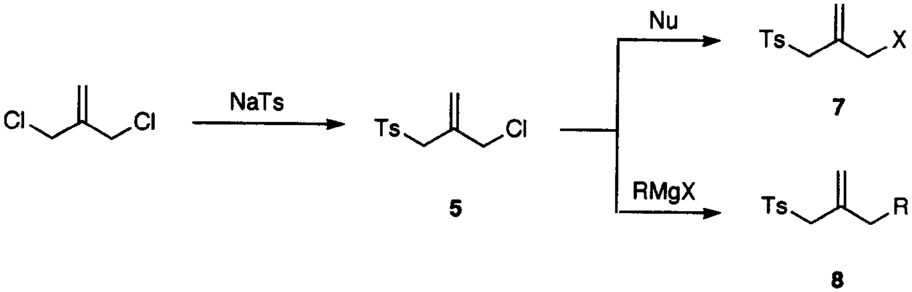


6a, * = +
6b, * = -

Ts= p-$CH_3C_6H_4SO_2$

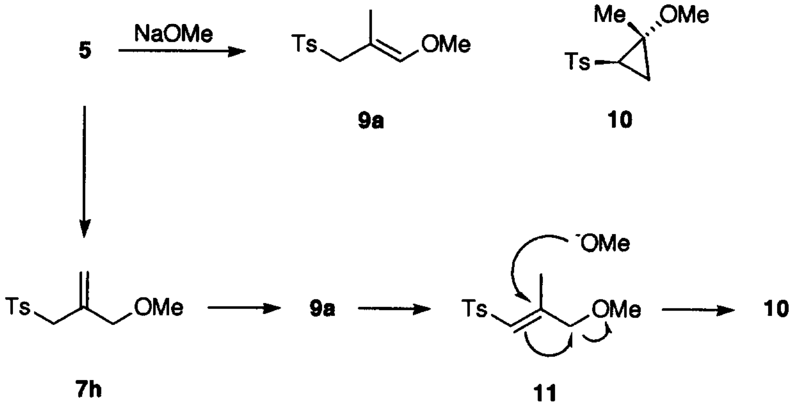
RESULTS AND DISCUSSION

The reaction of commercially available 3-chloro-2-(chloromethyl)propene with sodium *p*-toluenesulfinate under methanol reflux in 1:1.1 molar ratio provides the reagent **5** in 78% yield . The chlorine atom of compound **5** reacts with different heteronucleophiles under the appropiate reaction conditions to afford the corresponding functionalized allyl sulfones **7** in good yields (Scheme 1 and Table 1).



Scheme 1

The substitution process takes place in all cases regioselectively and only in two cases further isomerization of the double bond to the corresponding functionalized methallyl sulfones **9** has been observed. When sodium methoxide was used as nucleophile (Table 1, entry 8) reacts with compound **5** to afford under methanol reflux a 1:1 mixture of compounds **9a** and **10** and mainly ($>98\%$) the cyclopropane derivative **10** after 3 days at 80°C in 84% yield (Scheme 2). It means that first at all compound **9a** was formed by isomerization of compound of the type **7** (X=OMe), a second isomerization process of **9a** to the vinyl sulfone **11** followed by Michael addition of methoxide anion and γ-elimination gives compound **10**. The phosphonium salt derivative **9b** (Table 1, entry 12) is the other case of isomerization of the precursor **7m** ($X=Ph_3P^+$).



Scheme 2

Table 1. Synthesis of Allyl Sulfones **7**, **8** and **9**.

Entry	Reaction conditions				Product		
	Nu or RM (equiv.)	Solvent	T	Time	No.	X or R	Yield (%)[a]
1	Bu^{n}NH$_2$ (2.5)	THF	reflux	14h	**7a**	NHBu^n	94
2	PhNH$_2$ (3.0)	THF	reflux	1d	**7b**	NHPh	83
3	Pyrrolidine (4.0)	THF	rt	17h	**7c**	N-(CH$_2$)$_4$	91
4	Morpholine (4.0)	CH$_2$Cl$_2$	rt	19h	**7d**		85
5	NaN$_3$ (5.0)	H$_2$O/MeOH	reflux	1d	**7e**	N$_3$	89
6	NaNO$_2$ (2.0)	DMSO[b]	rt	6h	**7f**[c]	OH	88
7	NaOAc (6.0)	AcOH	reflux	3d	**7g**[d]	OAc	97
8	NaOMe (3.0)	MeOH[b]	reflux	7d	-[e]		95
9	NaSPh (1.5)	THF[b]	reflux	1d	**7i**	SPh	94
10	NaTs (3.0)	MeOH	reflux	2d	**7j**	Ts	67[f]
11	NaI (2.0)	Me$_2$C=O	reflux	1d	**7k**	I	92
12	AgNO$_2$ (1.5)	Ether[b]	rt	4d	**7l**	NO$_2$	82[g]
13	PPh$_3$ (1.2)	PhCH$_3$	reflux	2d	**9b**		55[g]
14	MeMgCl (4.0)[h]	THF[b]	reflux	3d	**8a**	Me	95

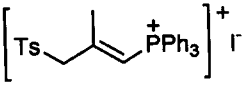
Table 1. Cont.

15	MeMgCl (1.5)	THF[b]	rt	2d	**8a**	Me	93[g]
16	$Bu^{sec}MgCl$ (4.0)[h]	THF[b]	rt	1d	**8b**	Bu^{sec}	75
17	$Bu^{tert}MgCl$ (1.5)	THF[b]	rt	4h	**8c**	Bu^{tert}	86
18	$CH_2=CHMgCl$ (1.5)	THF[b]	reflux	9h	**8d**	$CH=CH_2$	87[i]
19	$CH_2=CHCH_2MgBr$ (4.0)[j]	THF[b]	rt	1d	**8e**	$CH_2CH=CH_2$	77[i]
20	$CH_2=CHCH_2MgBr$ (1.5)	THF[b]	rt	4h	**8e**	$CH_2CH=CH_2$	89[g]
21	$PhCH_2MgCl$ (1.5)	THF[b]	rt	2.5h	**8f**	CH_2Ph	78[g]
22	PhMgCl (1.5)	THF[b]	rt	1d	**8g**	Ph	93
23	$PhC\equiv CMgBr$ (3.0)[k]	THF[b]	reflux	4d	**8h**	$C\equiv CPh$	50
24	$(MeO_2C)_2CHMgBr$ (3.0)[k,l]	THF[b]	reflux	4d	**8i**	$CH(CO_2Me)_2$	72
25	$(MeO_2C)_2CHNa$ (1.5)[m]	THF[b]	rt	6h	**8i**	$CH(CO_2Me)_2$	72[g]

[a] Isolated yield based on compound **5**. [b] Anhydrous. [c] This product has been prepared starting from 2-methylene-1,3-propanediol[1a] and the homologous phenylsulfonyl from methallyl phenyl sulfone[2a]. [d] The homologous phenyl sulfonyl has been recently prepared from 2-(bromomethyl)prop-2-enyl acetate[8]. [e] A 1:1 mixture of compounds **9a** and **10** was obtained. [f] Referred to the starting 2-(chloromethyl)-3-chloro-1-propene. [g] Based on compound **7k**. [h] In the presence of cooper(I) bromide (2.0 equiv.). [i] About 10% of methallyl tosyl sulfone was also obtained. [j] In the presence of cooper(I) iodide (2.0 equiv.). [k] In the presence of cooper(I) bromide (1.5 equiv.). [l] Prepared from dimethyl malonate and isopropylmagnesium bromide in THF. [m] Prepared from dimethyl malonate and sodium hydride in THF.

Compounds **9** are stereoselectively obtained with *E*-configuration deduced from the positive NOE effect between the vinylic proton and the methylene group. The cyclopropyl sulfone **10** seems to be the *trans* isomer according to the negative NOE effect between methyl and methyne protons.

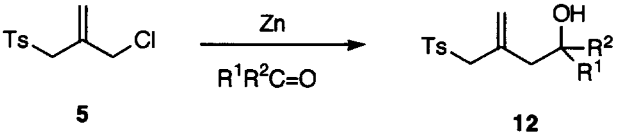
The nitrosulfone **7l** ($X=NO_2$) and the phosphonium salt **9b** has been prepared starting from the more reactive iodide **7k** (X=I) (Table 1, entries 12 and 13, respectively). On the other hand, disulfone **7j** (X=Ts) is directly obtained from 3-chloro-2-(chloromethyl)propene (Table 1, entry 10).



9b

The γ-chlorosulfone **5** reacts also with carbon nucleophiles such as alkyl, allyl, vinyl, aryl, alkynyl and malonate as well as primary, secondary and tertiary Grignard derivatives to give allyl sulfones **8** (Scheme 1 and Table 1). The carbon-carbon coupling reaction needs in same cases (Table 1, entries 14, 16, 23 and 24) cooper(I) bromide or iodide (2 or 1.5 equiv.) and the corresponding double amount of the organomagnesium compound under THF reflux in order to obtain the desired sulfone **8**. However, starting from the iodide **7k** (Table 1, entries 15, 20, 21 and 25) the reaction takes place at room temperature with only 1.5 equivalents of Grignard reagent. When dimethyl malonate was used as nucleophile the magnesium derivative needs cooper(I) bromide and the sodium one reacts with the iodide **7k**. Only when vinyl- or allyl-magnesium bromide (Table 1, entries 18 and 19) are used as nucleophiles about 10% of methallyl *p*-tolyl sulfone is also formed, probably due to the formation of the organomagnesium derivative of compound **5** which is reduced by proton-abstraction from the α-hydrogens of the sulfone group.

Attempts to prepare the corresponding carbanion **6b** with lithium, magnesium or copper[10], derived from compound **5** failed, even in the presence of benzaldehyde under typical Barbier conditions[11], methallyl *p*-tolyl sulfone was the only product formed (see above). However, when zinc, activated by 1,2-dibromoethane and trimethylchlorosilane[12], in anhydrous THF is allowed to react with 2-(chloromethyl)-3-tosylpropene (**5**) and carbonyl compounds[13] the corresponding addition products **12** are obtained (Scheme 3 and Table 2).

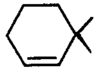


Scheme 3

Zinc foil or powder give the same results, but the second works under mild conditions and less excess of metal. When the reaction is carried out with the corresponding iodide **7k** methallyl tosyl sulfone was mainly obtained. In the case of α,β-unsaturated carbonyl compounds only 1,2-addition was observed (Table 2, entries 5 and 8).

We conclude that 2-(chloromethyl)-3-tosylpropene is an excellent multicoupling reagent working as

Table 2. Synthesis of Tosylated Homoallylic Alcohols **12**.

Entry	Reaction conditions			Product			
	Zn (equiv.)	T	Time	No.	R^1	R^2	Yield[a], %
1	Foil (5.0)	reflux	1d	**12a**	Pr^i	H	96[b]
2	Powder (2.5)	rt	1d	**12a**	Pr^i	H	97[b]
3	Foil (5.0)	reflux	1d	**12b**	Ph	H	76
4	Powder (2.5)	rt	1d	**12b**	Ph	H	77
5	Powder (2.5)	rt	2d	**12c**	$CH_3CH{=}CH$[c]	H	85
6	Powder (2.5)	reflux	2d	**12d**	Et	Et	73
7	Powder (2.5)	reflux	1d	**12e**	Pr^n	Me	69
8	Powder (2.5)	reflux	2d	**12f**			73
9	Powder (2.5)	reflux	2d	**12g**	Ph	CH_3	80

[a] Isolated yield after column chromatography, based on compound **5**. [b] Crude pure compound (300MHz, ^{1}H-RMN). [c] *Z*/*E* mixture.

cationic or anionic synthon **6a** or **6b** respectively useful for the general synthesis of allyl sulfones.

EXPERIMENTAL

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. Spectra were recorded on the following instruments: IR, Pye Unicam SP3-200; NMR, Bruker AC-300, recorded in $CDCl_3$ with TMS as internal standard, ^{13}C NMR assignments were done on the basis of DEPT experiments; MS, Hewlett-Packard 5988A (EI, 70eV). Microanalyses were performed by the Microanalyses Service of the University of Alicante. T.l.c. analyses were carried out on pre-coated Merck Silicagel 60F-254 plates (visualization by UV) and column chromatography was performed on Merck Silicagel 60 (70-230 mesh). Solvents were dried as usually. Organomagnesium compounds were comercially available (Aldrich and Fluka) in THF and also zinc foil or powder (99.999%, Aldrich).

Synthesis of 2-(Chloromethyl)-3-tosylpropene (5). A solution of 3-chloro-2-(chloromethyl)propene (2.9 ml. 25 mmol) and sodium *p*-toluenesulfinate (4.45 g, 25 mmol) in methanol (50 ml) was heated under reflux. After 1d the solvent was evaporated (15 torr) and the residue was dissolved in water (40 ml) and extracted with dichloromethane (2 x 25 ml). The organic layer was dried (Na_2SO_4) and evaporated to give crude product **5** which after recrystallization from hexane/ether affords 4.83 g of white crystalls: mp 83-84°C; ν (Nujol) 1640, 880 (C=CH), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.44 (s, 3H, CH_3), 3.92 (s, 2H, CH_2S), 4.19 (s, 2H, CH_2Cl), 5.00, 5.44 (2s, 1H, C=CH_2), 7,35 and 7,74 (2d, J=8.0Hz, 4H, ArH); δ_C 21.45 (CH_3), 46.81 (CH_2Cl), 59.30 (CH_2S), 124.04, 133.49 (CH_2=C), 128.24, 129.67, 134.97 and 144.90 (ArC); *m/z* 246 (M^++2, 1%), 244 (M^+, 2), 209 (41), 180 (11), 155 (76), 139 (21), 105 (11), 92 (26), 91 (100), 89 (61), 77 (13), 65 (79), 63 (31), 53 (75) and 51 (23). Anal. calcd. for $C_{11}H_{13}ClO_2S$: C, 53.98; H, 5.35. Found: C, 54.5; H, 5.4.

Synthesis of Allyl Sulfones 7 and 9 and Derivatives. General Procedure. A mixture of compound **5** (0.5 mmol) and nucleophile (see Table 1) in the corresponding solvent (ca. 5 ml) was stirred under the conditions indicated in Table 1. The recation was followed by t.l.c. and after extractive work-up compounds **7**, **9** and **10** were isolated and purified by column chromatography or and by recrystallization.

Butyl[2-(tosylmethyl)-2-propenyl]amine (**7a**): R_f 0.2 (hexane/ether:1/10); ν (film) 3050, 1630, 910 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.82 (t, J=7.0Hz, 3H, CH_3CH_2), 1.29 (m, 4H, $\mathit{CH}_2\mathit{CH}_2CH_3$), 2.08 (broad s, 1H, NH), 2.36 (s, 3H, CH_3Ar), 2.43 (t, J=7.0Hz, 2H, $CH_2\mathit{CH}_2N$), 3,82 (s, 2H, CH_2S), 4.85, 5.18 (2s, 2H, C=CH_2), 7,25 and 7,68 (2d, J=8.0 Hz, 4H, ArH); δ_C 13.86 ($\mathit{C}H_3CH_2$), 20.27 ($\mathit{C}H_2CH_3$), 21.51 ($\mathit{C}H_3Ar$), 31.81 ($\mathit{C}H_2CH_2N$), 48.64 ($CH_2\mathit{C}H_2N$), 53.64 ($\mathit{C}H_2NBu$), 60.37 (CH_2S), 120.58, 135.77 (CH_2=C), 128.39, 129.51, 135.52 and 144.52 (ArC); *m/z* 281 (M^+, 1%), 238 (38), 145 (12), 139 (28), 126 (78), 125 (22), 91 (100), 82 (74), 68 (29) and 65 (48). Anal. calcd. for $C_{15}H_{23}NO_2S$: C, 64.02; H, 8.24; N, 4.98. Found: C, 64.1; H, 8.4; N, 5.0.

Phenyl[2-(tosylmetyl)-2-propenyl]amine (**7b**): mp 73-74°C (hexane/ether); ν (film) 3400 (NH), 3080, 1640, 875 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.42 (s, 3H, CH_3), 3.83, 3.89 (2s, 4H, CH_2N, CH_2S), 4.10 (broad s, 1H, NH), 4.91, 5.32 (2s, 2H, CH_2=C), 6.56 (d, J=8.1Hz, 2H, 2x*o*-Ph), 6.68 (t, J=7.3Hz, 1H, *p*-Ph), 7.13 (t, J=7.7Hz, 2H, 2x*m*-Ph), 7.31 and 7.35 (2d, J=8.1Hz, 4H, *p*-TolH); δ_C 21.49 (CH_3), 48.16 (CH_2N), 60.19 (CH_2S), 120.63, 135,14 (CH_2=C), 112.68, 117.40, 128.27, 129.06, 129.60, 135.24, 144.71 and 147.53 (ArC); *m/z* 301 (M^+, 19%), 148 (21), 147 (12), 146 (100), 145 (23), 144 (85), 130 (15), 106 (83), 104 (16), 91 (42), 77 (39), 71 (20) and 65 (22). Anal. calcd. for $C_{17}H_{19}NO_2S$: C, 67.74; H, 6.35; N, 4.65. Found: C, 67.7; H, 6.3; N, 4.5.

N-*[2-(tosylmetyl)-2-propenyl]pyrrolidine* (**7c**): R_f 0.3 (hexane/ether:1/10); ν (film) 3075, 1635, 880 (CH=C), 1300 and 1145 cm^{-1} (SO_2); δ_H 1.73 (m, 4H, 2xCH_2CH_2N), 2.43 (s, 7H, CH_3, 2x$CH_2\mathit{CH}_2N$), 3.11 (s, 2H, CH_2N), 3.96 (s, 2H, CH_2S), 4.93, 5.27 (2s, 2H, CH_2=C), 7.33 and 7.75 (2d, J=8.0Hz, 4H, ArH); δ_C 21.32 (CH_3), 23.24 (2x$\mathit{C}H_2CH_2N$), 53.55 (2x$CH_2\mathit{C}H_2N$), 59.63, 60.19 (CH_2S, $N\mathit{C}H_2C$), 121.17, 135.06 (CH_2=C), 128.18, 129.30, 135.46 and 144.28 (ArC); *m/z* 280 (M^++1, 0.5%), 279 (M^+, 2), 155 (18), 125 (11), 124 (100), 123 (33), 122 (33), 108 (23), 95 (24), 94 (23), 91 (65), 89 (11), 84 (93), 70 (14), 65 (34), 55 (27) and 42 (29). Anal. calcd. for $C_{15}H_{21}NO_2S$: C, 64.48; H, 7.58; N, 5.01. Found: C, 61.5; H, 7.1; N, 5.0.

N-*[2-(tosylmethyl)-2-propenyl]morpholine* (**7d**): mp 87-88°C (hexane/ether); ν ($CHCl_3$) 3040, 1630, 910 (CH=C), 1300 and

1140 cm^{-1} (SO_2); δ_H 2.21 (m, 4H, 2xCH_2CH_2N), 2.35 (s, 3H, CH_3), 2.85 (s, 2H, CCH_2N), 3.55 (m, 4H, 2xCH_2O), 3.86 (s, 2H, CH_2S), 4.86, 5.14 (2s, 2H, CH_2=C), 7.25 and 7.67 (2d, J=8.0Hz, 4H, ArH); δ_C 21.35 (CH_3), 53.00 (2xCH_2CH_2N), 59.24 (CCH_2N), 62.93 (CH_2S), 66.71 (CH_2O), 121.94, 134.15 (CH_2=C), 128.18, 129.35, 135.53 and 144.35 (ArC); *m/z* 295 (M^+, 1%), 141 (12), 140 (100), 139 (20), 124 (13), 110 (36), 109 (44), 108 (43), 100 (71), 94 (22), 91 (64), 86 (13), 82 (19), 80 (18), 65 (41), 56 (24) and 55 (22). Anal. calcd. for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.17; N, 4.74. Found: C, 60.9; H, 7.1; N, 4.4.

3-Azido-2-(tosylmethyl)propene (7e): mp 40-41°C (hexane/ether); ν (film) 3040, 1640, 880 (CH=C), 2090 (N_3), 1300 and 1135 cm^{-1} (SO_2); δ_H 2.44 (s, 3H, CH_3), 3.83, 3.94 (2s, 4H, CH_2N, CH_2S); 5.01, 5.35 (2s, 2H, CH_2=C), 7.35 and 7.74 (2d, J=8.0Hz, 4H, ArH); δ_C 21.39 (CH_3), 54.67 (CH_2N), 60.02 (CH_2S), 122.77, 131.80 (CH_2=C), 128.20, 129.60, 134.80 and 144.87 (ArC); *m/z* 210 (M^+-42, 97%), 155 (15), 145 (52), 139 (22), 130 (19), 129 (13), 117 (27), 105 (45), 92 (12), 91 (100), 77 (11) and 65 (37). Anal. calcd. for $C_{11}H_{13}N_3O_2S$: C, 52.57; H, 5.21; N, 16.72. Found: C, 53.1; H, 5.3; N, 16.7.

2-(Tosylmethyl)-2-propen-1-ol (7f)^{1a}: mp 83-84°C (hexane/ether); ν (film) 3480 (OH), 3050, 1630, 880 (CH=C), 1290 and 1140 cm^{-1} (SO_2); δ_H 2.44 (s, 3H, CH_3), 2.65 (broad s, 1H, OH), 3.88 (s, 2H, CH_2S), 4.19 (s, 2H, CH_2O), 4.93, 5.33 (2s, 2H, CH_2=C), 7.35 and 7.76 (2d, J=8.1Hz, 4H, ArH); δ_C 21.53 (CH_3), 59.94 (CH_2S), 64.81 (CH_2O), 120.31, 136.50 (CH_2=C), 128.33, 129.66, 135.04 and 144.86 (ArC); *m/z* 210 (M^+-16, 15%), 209 (100), 155 (19), 145 (59), 139 (22), 117 (30), 105 (42), 92 (16), 91 (97), 77 (12) and 65 (36).

2-(Tosylmethyl)-2-propenyl acetate (7g): mp 48-49°C (hexane/ether); ν (film) 3040, 1640, 880 (CH=C), 1730 (C=O), 1300 and 1050 cm^{-1} (SO_2); δ_H 2.06 (s, 3H, CH_3CO), 2.44 (s, 3H, CH_3Ar), 3.86 (s, 2H, CH_2S), 4.62 (s, 2H, CH_2O), 5.01, 5.35 (2s, 2H, CH_2=C), 7.35 and 7.75 (2d, J=8.1Hz, 4H, ArH); δ_C 20.57 (CH_3CO), 21.41 (CH_3Ar), 59.84 (CH_2S), 65.42 (CH_2O), 122.51, 132.07 (CH_2=C), 128.30, 129.54, 134.90, 144.75 (ArC) and 170.06 (C=O); *m/z* 225 (M^+-43, 1%), 139 (11), 113 (100), 91 (44), 65 (19) and 43 (77). Anal. calcd. for $C_{13}H_{16}O_4S$: C, 59.19; H, 6.01. Found: C, 58.4; H, 6.0.

Phenyl [2-(tosylmethyl)-2-propenyl] thioether (7i): R_f 0.36 (hexane/ether: 1/1); ν (film) 3050, 1640, 870 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.41 (s, 3H, CH_3), 3.68, 3.94 (2s, 4H, 2xCH_2S), 4.79, 5.08 (2s, 2H, CH_2=C), 7.20-7.31 (m, 7H, Ph and 2H of *p*-Tol) and 7.71 (d, J=8.0Hz, 2H, *p*-TolH); δ_C 21.47 (CH_3), 39.87 (CH_2SPh), 60.20 (CH_2SO), 122.79 (CH_2=C), 126.66, 127.32, 128.26, 128.74, 128.91, 129.56, 130.57, 132.71 and 144.66 (ArC and C=CH_2); *m/z* 319 (M^++1, 1%), 318 (M^+, 3), 164 (11), 163 (100), 161 (29), 135 (29), 130 (28), 129 (34), 91 (33), 77 (10) and 65 (21). Anal. calcd. for $C_{17}H_{18}O_2S_2$: C, 64.12; H, 5.70. Found: C, 64.1; H, 5.8.

3-Tosyl-2-(tosylmethyl)propene (7j): mp 117-118°C (hexane/ether); ν (Nujol) 3060, 1640 (CH=C), 1310, 1290 and 1140 cm^{-1} (SO_2); δ_H 2.45 (s, 6H, 2xCH_3), 3.99 (s, 4H, 2xCH_2S), 5.17 (s, 2H, CH_2=C), 7.34 and 7.72 (2d, J=8.0Hz, 8H, ArH); δ_C 21.62 (2xCH_3), 61.51 (2xCH_2S), 125.67, 129.54 (CH_2=C), 128.37, 131.82, 135.14 and 145.09 (ArC); *m/z* 364 (M^+, 1%), 210 (12), 209 (100), 155 (12), 145 (48), 139 (16), 130 (15), 129 (12), 117 (22), 105 (34), 91 (65) and 65 (25). Anal. calcd. for $C_{18}H_{20}O_4S_2$: C, 59.32; H, 5.53. Found: C, 59.0; H, 5.5.

2-(Tosylmethyl)-2-propenyl iodide (7k): R_f 0.42 (hexane/ether: 1/1); ν (film) 3040, 1630, 900 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.45 (s, 3H, CH_3), 3.93, 4.09 (2s, 4H, CH_2I, CH_2S), 4.91, 5.50 (2s, 2H, CH_2=C), 7.35 and 7.75 (2d, J=8.2Hz, 4H, ArH); δ_C 8.75 (CH_2I), 21.56 (CH_3), 60.68 (CH_2S), 122.89 (CH_2=C), 128.31, 129.72, 135.08, 135.15 and 144.97 (ArC, C=CH_2); *m/z* 336 (M^+, 1%), 210 (13), 209 (100), 181 (19), 155 (18), 145 (26), 139 (30), 130 (16), 129 (12), 117 (22), 105 (38), 92 (19), 91 (96), 89 (16), 71 (12) and 65 (41). Anal. calcd. for $C_{11}H_{13}IO_2S$: C, 39.30; H, 3.90. Found: C, 40.3; H, 4.3.

3-Nitro-2-(tosylmethyl)propene (7l): mp 114-115°C (hexane/ether); ν ($CHCL_3$) 3060, 1645, 870 (CH=C), 1550, 1265 (NO_2), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.45 (s, 3H, CH_3), 3.99 (s, 2H, CH_2S), 5.16 (s, 2H, CH_2N), 5.30, 5.57 (2s, 2H, CH_2=C), 7.37 and 7.75 (2d, J=8.0Hz, 4H, ArH); δ_C 21.55 (CH_3), 60.18 (CH_2S), 78.77 (CH_2N), 127.41, 129.85 (CH_2=C), 128.39, 129.96, 134.90 and 145.38 (ArC); *m/z* 255 (M^+, 0.1%), 209 (12), 155 (81), 139 (12), 105 (14), 100 (30), 92 (11), 89 (12), 69 (12) and 65 (34). Anal. calcd. for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49. Found: C, 51.6; H, 5.9; N, 6.0.

(Z)-*1-Methoxy-2-methyl-3-tosylpropene* (**9a**): R_f 0.35 (hexane/ether:1/1); δ_H 1.67 (d, J=1.0Hz, 3H, $CH_3C{=}CH$), 2.39 (s, 3H, CH_3Ar), 3.11 (s, 3H, CH_3O), 3.83 (s, 2H, CH_2S), 5.82 (br s, 1H, CH=C), 7.31 and 7.75 (2d, J=8.0Hz, 4H, ArH); δ_C 16.81 ($CH_3C{=}CH$), 21.34 (CH_3Ar), 54.27 (CH_3O), 56.84 (CH_2S), 101.03, 147.56 (C=CHO), 128.37, 128.89, 136.09 and 143.88 (ArC).

(E)-*(2-Methyl-3-tosyl-1-propenyl)triphenylphosphonium iodide* (**9b**): mp 222-223°C (CH_2Cl_2/ether); ν ($CHCl_3$) 3040, 1685 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.93 (d, J=2.2Hz, 3H, CH_3CCP), 2.38 (s, 3H, CH_3Ar), 4.70 (s, 2H, CH_2), 6.89 (d, J=20.1Hz, 1H, CHP), 7.33 (d, J=8.1Hz, 2H, *p*-TolH), 7.70-7.93 (m with d at 7.92, J=8.1Hz, 17H, 2x*p*-TolH, 3xPh); δ_C 21.48 (CH_3Ar), 24.69 (d, J=7.5Hz, CH_3CCP), 66.70 (d, J=18.2Hz, CH_2), 112.51 (d, J=8.7Hz, CHP), 118.3 (d, J=90.0, 3xC_i-Ph), 128.24, 129.84, 135.23, 145.18 (*p*-TolC), 130.52 (d, J=12.9Hz, 6xC_m-Ph), 133.43 (d, J=10.9Hz, 6xC_o-Ph), 135.02 (d, J=3.05Hz, 3xC_p-Ph) and 159.11 (d, J=3.0Hz, C=CP); *m/z* 598 (M^+, 0.1%), 278 (39), 277 (100), 263 (14), 262 (75), 218 (17), 201 (17), 199 (20), 184 (17), 183 (91), 152 (23), 139 (26), 127 (15), 108 (32), 107 (26), 92 (27), 91 (67), 77 (37), 65 (34) and 51 (30). Anal. calcd. for $C_{29}H_{28}IO_2PS$: C, 58.20; H, 4.72. Found: C, 58.0; H, 4.7.

trans-*1-Methoxy-1-methyl-2-tosylcyclopropane* (**10**): mp 67-68°C (hexane/ether); ν (film) 1300 and 1150 cm^{-1} (SO_2); δ_H 1.45, 1.46 (2d, J=9.1, 7.5Hz, 2H, CH_2), 1.65 (s, 3H, CH_3CO), 2.39 (s, 3H, CH_3Ar), 2.50 (dd, J=9.1, 7.5Hz, 1H, CHS), 3.13 (s, 3H, CH_3O), 7.30 and 7.74 (2d, J=8.2Hz, 4H, ArH); δ_C 14.28 (CH_3CO), 20.76 (CH_2), 21.46 (CH_3Ar), 44.21 (CHS), 56.91 (CH_3O), 64.12 ($COCH_3$), 127.16, 129.74, 138.34 and 144.18 (ArC); *m/z* 240 (M^+, 2%), 225 (M^+-15, 2), 91 (13), 85 (100), 65 (11), 55 (31) and 43 (20). Anal. calcd. for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71; S, 13.34. Found: C, 60.1; H, 6.9; S, 14.0.

Synthesis of Allyl Sulfones 8. General Procedure.

a) Without Cooper Halides. To a solution of compound **5** or **7k** (0.4 mmol) in dry THF (3 ml) was added a solution of organomagnesium compound (see Table 1) in THF under argon. The reaction mixture was stirred at the temperature and for the time shown in Table 1 and monotorized by t.l.c.. Then, the reaction was hydrolyzed with a saturated solution of NH_4Cl (10 ml) and extracted with ether (2x10 ml). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and evaporated in vacuo (15 torr). The resulting residue was purified by column chromatography or and by recrystallization to afford compounds **8**.

b) By means of Cooper Halides. To a suspension of cooper halide (see Table 1) in THF (1 ml) was added a solution of the Grignard reagent (see Table 1) in THF at 0°C. After 30 min stirring a solution of compound **5** (98 mg, 0.4 mmol) in THF (2 ml) was dropwise added. The resulting suspension was stirred under argon in the conditions shown in Table 1. After extractive work-up compounds **8** were obtained and purified as before.

2-(Tosylmethyl)-1-butene (**8a**): R_f 0.40 (hexane/ether: 1/1); ν (film) 3070, 1640, 810 (CH=C), 1300 and 1145 cm^{-1} (SO_2); δ_H 1.00 (t, J=7.3Hz, 3H, CH_3CH_2), 2.14 (deform. q, 2H, CH_2CH_3), 2.44 (s, 3H, CH_3Ar), 3.77 (s, 2H, CH_2S), 4.77, 5.03 (2s, 2H, $CH_2{=}C$), 7.33 and 7.74 (2d, J=7.9Hz, 4H, ArH); δ_C 11.73 (CH_3CH_2), 21.45 (CH_3Ar), 28.44 (CH_2CH_3), 63.03 (CH_2S), 118.17, 138.79 ($CH_2{=}C$), 128.33, 129.44, 135.35 and 144.46 (ArC); *m/z* 224 (M^+, 2%), 157 (23), 145 (10), 140 (10), 139 (21), 92 (23), 91 (76), 89 (14), 69 (100), 65 (46), 63 (12) and 41 (67). Anal. calcd. for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19. Found: C, 64.2; H, 7.7.

4-Methyl-2-(tosylmethyl)-1-hexene (**8b**): R_f 0.50 (hexane/ether:1/1); ν (film) 3070, 1640, 810 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.80 (d, J=6.6Hz, 3H, CH_3CH), 0.85 (t, J=7.5Hz, 3H, CH_3CH_2), 1.2, 1.31 (2m, 2H, CH_2CH_3), 1.89, 2.17 (2dd, J= 14.1, 8.4Hz, 2H, $CH_2C{=}C$), 2.44 (s, 3H, CH_3Ar), 3.74 (s, 2H, CH_2S), 4.80, 5.00 (2s, 2H, $CH_2{=}C$), 7.33 and 7.75 (2d, J=8.0Hz, 4H, ArH); δ_C 11.23, 18.74 (CH_3CH_2, CH_3CH), 21.54 (CH_3Ar), 29.12 (CH_2CH_3), 32.29 (CH), 42.87 ($CH_2C{=}C$), 62.46 (CH_2S), 120.75, 135.54 ($CH_2{=}C$), 128.49, 129.51, 136.38 and 144.51 (ArC); *m/z* 266 (M^+, 1%), 157 (14), 155 (17), 146 (15), 139 (19), 131 (20), 111 (37), 110 (69), 95 (28), 92 (12), 91 (50), 69 (100), 65 (21), 55 (35) and 41 (24).

4,4-Dimethyl-2-(tosylmethyl)-1-pentene (**8c**): mp 77-78°C (hexane/ether); ν (film) 3080, 1640, 810 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 0.87 (s, 9H, 3xCH_3CCH_2), 2.05 (s, 2H, CH_2Bu^t), 2.44 (s, 3H, CH_3Ar), 3.79 (s, 2H, CH_2S), 4.90, 4.99 (2s, 2H, $CH_2{=}C$), 7.33 and 7.73 (2d, J=8.0Hz, 4H, ArH); δ_C 21.48 (CH_3Ar), 29.35 (3xCH_3CCH_2), 31.55 (CCH_3), 48.43 (CH_2Bu^t), 64.27 (CH_2S), 123.08, 135.22 ($CH_2{=}C$), 128.53, 129.41, 134.91 and 144.44 (ArC); *m/z* 267 (M^++1, 0.1%), 266 (M^+, 3), 210 (16), 202

(11), 155 (45), 146 (100), 140 (15), 139 (22), 131 (88), 111 (52), 105 (11), 95 (43), 92 (16), 91 (77), 68 (36), 65 (29), 57 (49), 55 (36) and 41 (30).

2-(Tosylmethyl)-1,4-pentadiene (**8d**): R_f 0.45 (hexane/ether: 1/1); ν (film) 3060, 1630 (CH=C), 1300 and 1145 cm^{-1} (SO_2); δ_H 2.35 (s, 3H, CH_3), 2.81 (d, J=6.7Hz, 2H, CH_2CH), 3.68 (s, 2H, CH_2S), 4.74-5.05 (m, 4H, 2xCH_2=C), 5.60 (m, 1H, CHCH_2), 7.25 and 7.66 (2d, J=7.8Hz, 4H, ArH); δ_C 21.45 (CH_3), 39.98 (CH_2CH), 62.00 (CH_2S), 117.57, 120.65, 134.56, 135.56 (2xCH_2=C), 128.36, 129.47, 135.33 and 144.53 (ArC); *m/z* 236 (M^+, 1.5%), 209 (13), 155 (10), 139 (16), 92 (12), 91 (58), 89 (10), 81 (100), 80 (12), 79 (57), 65 (29), 55 (10), 53 (12) and 41 (14).

2-(Tosylmethyl)-1,5-hexadiene (**8e**): R_f 0.50 (hexane/ether: 1/1); ν (film) 1300 and 1145 cm^{-1} (SO_2); δ_H 2.11-2.37 (m, 4H, 2xCH_2C=C), 2.43 (s, 3H, CH_3), 3.76 (s, 2H, CH_2S), 4.79-5.04 (m, 4H, 2xCH_2=C), 7.33 (m, 1H, CH=CH_2), 7.33 and 7.74 (2d, J=8.0Hz, 4H, ArH); δ_C 21.42 (CH_3), 31.22, 34.52 (2xCH_2C=C), 62.81 (CH_2S), 115.01, 119.68 (2xCH_2=C), 128.30, 129.43, 135.27, 136.58, 137.23 (ArC, CH=CH_2 and C=CH_2); *m/z* 250 (M^+, 0.1%), 157 (46), 139 (32), 85 (82), 94 (100), 93 (27), 92 (21), 91 (89), 79 (72), 77 (19), 67 (48), 65 (41) and 55 (19).

4-Phenyl-2-(tosylmethyl)-1-butene (**8f**): R_f 0.40 (hexane/ether: 1/1); ν (film) 3080, 1635 (CH=C), 1300 and 1145 cm^{-1} (SO_2); δ_H 2.42 (s, 3H, CH_3), 2.44, 2.71 (2t, J=8.0Hz, 4H, CH_2CH_2Ph), 3.73 (s, 2H, CH_2S), 4.80, 5.05 (2s, 2H, CH_2=C), 7.05-7.40 (m, 7H, Ph and 2x*p*-TolH) and 7.71 (d, J=8.0Hz, 2H, *p*-TolH); δ_C 21.46 (CH_3), 33.73, 36.90 (CH_2CH_2Ph), 62.94 (CH_2S), 119.92, 136.70 (CH_2=C), 125.85, 128.20, 128.27, 128.36, 129.48, 135.31, 140.90 and 144.51 (ArC); *m/z* 299 (M^+, 0.6%), 157 (14), 145 (51), 144 (81), 130 (11), 129 (54), 117 (16), 91 (100) and 65 (21).

3-Phenyl-2-(tosylmethyl)propene (**8g**): mp 110-111°C (hexane/ether); ν (film) 3060, 1630, 890 (CH=C), 1300 and 1145 cm^{-1} (SO_2); δ_H 2.42 (s, 3H, CH_3), 3.49, 3.66 (2s, 4H, CH_2Ph, CH_2S), 4.83, 5.04 (2s, 2H, CH_2=C), 7.14-7.27 (m, 5H, Ph), 7.33 and 7.75 (2d, J=8.0Hz, 4H, *p*-TolH); δ_C 21.49 (CH_3), 42.07 (CH_2Ph), 61.55 (CH_2S), 121.29 (CH_2=C), 126.46, 128.37, 128.42, 129.10, 129.53, 135.38, 136.76, 137.86 and 144.60 (ArC and C=CH_2); *m/z* 286 (M^+, 1%), 132 (11), 131 (100), 129 (36), 128 (10), 115 (22), 91 (76) and 65 (28). Anal. calcd. for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34. Found: C, 70.3; H, 6.4.

1-Phenyl-4-(tosylmethyl)-4-penten-1-yne (**8h**): mp 85-86°C (hexane/ether); ν (film) 3075, 1630 (CH=C), 2170 ($C\equiv C$), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.40 (s, 3H, CH_3), 3.30 (s, 2H, $CH_2C\equiv C$), 3.85 (s, 2H, CH_2S), 4.86, 5.42 (2s, 2H, CH_2=C), 7.21-7.34 (m, 7H, Ph, 2x*p*-TolH) and 7.72 (d, J=8.1Hz, 2H, 2x*p*-TolH); δ_C 21.62 (CH_3), 26.70 ($CH_2C\equiv C$), 62.13 (CH_2S), 83.65, 85.56 ($C\equiv C$), 121.45, 132.46 (CH_2=C), 123.25, 124.42, 128.21, 128.52, 129.68, 131.56, 135.18 and 144.81 (ArC and Ph); *m/z* 310 (M^+, 4%), 156 (22), 155 (100), 154 (24), 153 (61), 152 (19), 128 (16), 115 (48), 91 (23) and 65 (14). Anal. calcd. for $C_{19}H_{18}O_2S$: C, 73.52; H, 5.84. Found: C, 72.2; H, 5.6.

Methyl 2-(methoxycarbonyl)-4-(tosylmethyl)-4-pentenoate (**8i**): mp 89-90°C (hexane/ether); ν (film) 3075, 1635, 900 (CH=C), 1735 (C=O), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.40 (s, 3H, CH_3Ar), 2.78 (d, J=8.7Hz, 2H, CH_2CH), 3.61 (t, J=8.8Hz, 1H, CH), 3.67 (s, 6H, 2xCH_3O), 3.75 (s, 2H, CH_2S), 4.79, 5.03 (2s, 2H, CH_2=C), 7.29 and 7.69 (2d, J=8.0Hz, 4H, ArH); δ_C 21.56 (CH_3Ar), 34.22 (CH_2CH), 50.23 (CH), 52.60 (2xCH_3O), 62.75 (CH_2S), 121.94, 133.87 (CH_2=C), 128.43, 129.63, 135.11, 144.79 (ArC) and 168.86 (2xC=O); *m/z* 340 (M^+, 1%), 185 (100), 153 (46), 139 (12), 125 (23), 121 (17), 91 (37) and 65 (17). Anal. calcd. for $C_{16}H_{20}O_6S$: C, 56.46; H, 5.92. Found: C, 56.7; H, 5.9.

Synthesis of Tosylated Homoallylic Alcohols 12. General Procedure. To a suspension of zinc powder (65 mg, 1 mmol) or zinc foil (130 mg, 2 mmol) in dry THF (2 ml) was added successively 1,2-dibromoethane (0.015 ml, 0.038 mmol or 0.030 ml, 0.076 mmol) and chlorotrimethylsilane (0.008 ml, 0.03 mmol) under argon. The reaction mixture was stirred 1h and then a solution of compound **5** (98 mg, 0.4 mmol) and the carbonyl compound (0.48 mmol) in THF (2 ml) was added. The resulting mixture was stirred for the time and at the temperature indicated in Table 2. The suspension was filtered off and to the filtrate was added an aqueous saturated solution of ammonium chloride (10 ml). After extractive work-up the crude product was purified by column chromatography and or by recrystallization to give compounds **12**.

5-Methyl-2-(tosylmethyl)-1-hexen-4-ol (**12a**): R_f 0.50 (hexane/ether:1/10); ν (film) 3520 (OH), 3080, 1640, 800 (CH=C), 1300 and 1150 cm^{-1} (SO$_2$); δ_H 0.86, 0.87 (2d, J=6.8Hz, 6H, 2xCH_3CH), 1.60 (m, 1H, CHCH$_3$), 2.13 (m, 2H, CH$_2$CO), 2.36 (s, 1H, OH), 2.39 (s, 3H, CH_3Ar), 3.44 (m, 1H, CHO), 3.84 (s, 2H, CH$_2$S), 4.83, 5.10 (2s, 2H, CH$_2$=C), 7.29 and 7.70 (2d, J=8.3Hz, 4H, ArH); δ_C 17.32, 18.50 (2xCH$_3$CH), 21.46 (CH$_3$Ar), 33.60 (CHCH$_3$), 40.43 (CH$_2$CO), 62.46 (CH$_2$S), 74.43 (CO), 122.14, 135.41 (CH$_2$=C), 128.35, 129.54, 135.15 and 144.60 (ArC); m/z 282 (M^+, 0.7%), 239 (15), 210 (12), 157 (11), 155 (77), 147 (11), 146 (91), 139 (44), 131 (85), 109 (23), 92 (25), 91 (100), 73 (18), 70 (53), 67 (15), 65 (33), 56 (18), 55 (54) and 43 (41).

1-Phenyl-3-(tosylmethyl)-3-buten-1-ol (**12b**): R_f 0.50 (hexane/ether:1/10); ν (film) 3460 (OH), 3080, 1630, 810 (CH=C), 1300 and 1150 cm^{-1} (SO$_2$); δ_H 2.40 (s, 3H, CH$_3$), 2.56 (m, 2H, CH$_2$CO), 3.40 (br s, 1H, OH), 3.78 (s, 2H, CH$_2$S), 4.80 (m, 1H, CHO), 4.85, 5.10 (2s, 2H, CH$_2$=C), 7.26 (m, 7H, Ph and 2xp-TolH) and 7.68 (d, J=7.5Hz, 2H, p-TolH); δ_C 21.35 (CH$_3$), 44.98 (CH$_2$CO), 62.35 (CH$_2$S), 72.33 (CHO), 122.82 (CH$_2$=C), 127.24, 128.12, 128.18, 129.42, 133.97, 135.07, 143.64 and 144.51 (ArC and C=CH$_2$); m/z 316 (M^+, 3%), 210 (12), 155 (42), 147 (11), 146 (100), 145 (14), 140 (12), 139 (19), 131 (83), 129 (11), 128 (24), 115 (11), 107 (45), 105 (47), 92 (17), 91 (91), 77 (51), 65 (25) and 55 (21).

(Z,E)-*2-(Tosylmethyl)-1,5-heptadien-4-ol* (**12c**): mixture Z/E:1/2; mp 115-116 and 124-126°C (hexane/ether); ν (film) 3550 (OH), 3085, 1630 (CH=C), 1300 and 1150 cm^{-1} (SO$_2$); δ_H 1.68 (m, 3H, CH_3CH), 2.29-2.47 (m with s at 2.42, 5H, CH$_2$CO and CH_3Ar), 2.70 (br s, 1H, OH), 3.87 (s, 2H, CH$_2$S), 4.19 (m, 1H, CHO), 4.86, 5.12 (2s, 2H, CH$_2$=C), 5.41-5.74 (m, 2H, CH=CH), 7.30 and 7.73 (2d, J=8.3Hz, 4H, ArH); δ_C 17.37, 17.64 (CH$_3$CH), 21.35 (CH$_3$Ar), 43.16 (CH$_2$CO), 62.51 (CH$_2$S), 70.79 (CHO), 122.44, 134.00 (CH$_2$=C), 126.56, 133.01 (CH=CH), 128.20, 129.40, 135.10 and 144.49 (ArC); m/z 279 (M^+-1, 4%), 155 (40), 146 (55), 139 (27), 131 (56), 125 (19), 123 (14), 107 (27), 105 (20), 91 (100), 79 (21), 77 (16), 71 (53), 65 (30), 55 (59), 53 (15) and 43 (26).

4-Ethyl-2-(tosylmethyl)-1-hexen-4-ol (**12d**): mp 65-64°C (hexane/ether); ν (film) 3500 (OH), 3080, 1630, 800 (CH=C), 1300 and 1150 cm^{-1} (SO$_2$); δ_H 0.81 (t, J=7.5Hz, 6H, 2xCH_3CH$_2$), 1,39 (q, J=7.5Hz, 4H, 2xCH_2CH$_3$), 2.10 (br s, 1H, OH), 2.32 (s, 2H, CH$_2$CO), 2.39 (s, 3H, CH_3Ar), 4.06 (s, 2H, CH$_2$S), 4.92, 5.03 (2d, J=1Hz, 2H, CH$_2$=C), 7.30 and 7.71 (2d, J=8.2Hz, 4H, ArH); δ_C 7.72 (2xCH$_3$CH$_2$), 21.48 (CH$_3$Ar), 30.70 (2xCH$_2$CH$_3$), 43.90 (CH$_2$CO), 63.02 (CH$_2$S), 74.98 (CO), 123.45, 135.70 (CH$_2$=C), 128.24, 129.52, 134.51 and 144.48 (ArC); m/z 296 (M^+, 0.8%), 267 (15), 211 (36), 147 (11), 146 (100), 139 (30), 131 (86), 111 (10), 92 (14), 91 (74), 87 (39), 65 (23), 57 (50), 55 (23), 45 (19) and 41 (11). Anal. calcd. for $C_{16}H_{24}O_3S$: C, 64.83; H, 8.16; S, 10.82. Found: C, 64.6; H, 8.15; S, 11.3.

4-Methyl-2-(tosylmethyl)-1-hepten-4-ol (**12e**): mp 56-57°C (hexane/ether); ν (film) 3500 (OH), 3080, 1630, 800 (CH=C), 1300 and 1140 cm^{-1} (SO$_2$); δ_H 0.78-0.92 (m, 3H, CH_3CH$_2$), 1.08 (s, 3H, CH_3CO), 1.11-1.51 (m, 4H, CH_2CH_2CH$_3$), 2.06 (br s, 1H, OH), 2.26, 2.42 (2d, J=14.0Hz, 2H, CH$_2$CO), 2.39 (s, 3H, CH_3Ar), 3.97, 4.10 (2d, J=13.6Hz, 2H, CH$_2$S), 4.92, 5.02 (2s, 2H, CH$_2$=C), 7.28 and 7.70 (2d, J=8.0Hz, 4H, ArH); δ_C 14.46 (CH$_3$CH$_2$), 17.07 (CH$_3$CO), 21.50 (CH$_3$Ar), 26.43 (CH$_2$CH$_3$), 44.90 (CH$_2$CH$_2$CH$_3$), 46.83 (CH$_2$CO), 63.06 (CH$_2$S), 72.84 (CO), 123.53, 135.70 (CH$_2$=C), 128.29, 129.54, 134.56 and 144.50 (ArC); m/z 297 (M^++1, 0.2%), 296 (M^+, 1), 253 (12), 211 (33), 155 (59), 147 (13), 146 (100), 140 (15), 139 (30), 131 (88), 92 (14), 91 (64), 87 (38), 65 (19), 55 (28) and 43 (36). Anal. calcd. for $C_{16}H_{24}O_3S$: C, 64.83; H, 8.16; S, 10.82. Found: C, 65.0; H, 8.4; S, 10.9.

1-[2-(Tosylmethyl)-2-propenyl]-2-cyclohexen-1-ol (**12f**): R_f 0.50 (hexane/ether:1/10); ν (film) 3500 (OH), 3085, 1640, 810 (CH=C), 1300 and 1140 cm^{-1} (SO$_2$); δ_H 1.54-2.06 (m, 6H, CH_2CH_2CH_2CH), 2.34-2.47 (m with s at 2.40, 5H, CH$_3$ and CH$_2$CO), 2.76 (br s, 1H, OH), 3.95 (s, 2H, CH$_2$S), 4.95, 5.06 (2s, 2H, CH$_2$=C), 5.56 (d, J=10.0Hz, 1H, CH=CHCO), 5.79 (2t, J=10.0, 3.7Hz, 1H, CH=CHCO), 7.29, 7.71 (2d, J=8.1Hz, 4H, ArH); δ_C 18.92, 25.09, 35.81 (CH$_2$$CH_2$$CH_2$CO), 21.59 (CH$_3$), 47.21 ($CH_2$CO), 63.10 (CH$_2$S), 69.86 (CO), 123.88, 133.92 (CH$_2$=C), 129.88, 131.98 (CH=CH), 128.42, 129.56, 135.76 and 144.51 (ArC); m/z 288 (M^+-18, 0.8%), 149 (12), 139 (11), 133 (51), 131 (56), 129 (15), 117 (22), 115 (14), 105 (27), 97 (19), 93 (12), 92 (12), 91 (100), 79 (22), 77 (27), 65 (36), 55 (26), 53 (11) and 41 (19). Anal. calcd. for $C_{17}H_{22}O_3S$: C, 66.64; H, 7.24; S, 10.46. Found: C, 66.1; H, 7.1; S, 11.0.

2-Phenyl-4-(tosylmethyl)-3-penten-2-ol (**12g**): R_f 0.60 (hexane/ether:1/10); ν (film) 3470 (OH), 3080, 1630, 800 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.54 (s, 3H, CH_3CO), 2.41 (s, 3H, CH_3Ar), 2.60 (br s, 1H, OH), 2.65, 2.83 (2d, J=14.0 Hz, 2H, CH_2CO), 3.52, 3.70 (2d, J=13.7Hz, 2H, CH_2S), 4.84, 4.98 (2s, 2H, CH_2=C), 7.15-7.40 (m with d at 7.29, J=8.6Hz, 7H, Ph and 2x*p*-TolH), 7.65 (d, J=8.0Hz, 2H, *p*-TolH); δ_C 21.50 (CH_3Ar), 30.33 (CH_3CO), 49.17 (CH_2CO), 62.51 (CH_2S), 74.10 (CO), 124.48, 135.39 (CH_2=C), 124.69, 126.63, 128.07, 128.26, 129.46, 133.75, 144.49 and 146.93 (ArC); *m/z* 330 (M^+, 1%), 155 (11), 146 (12), 131 (15), 121 (100), 105 (12), 91 (24), 77 (11), 55 (13) and 43 (50).

ACKNOWLEDGMENTS. We thank DGICYT (PB88/0287) Spain, for financial support. J. M. S. thanks also to DGICYT for a predoctoral grant.

REFERENCES AND NOTES

1. (a) Shimizu, I.; Ohashi, Y.; Tsuji, J. *Tetrahedron Lett.* **1984**, *25*, 5183. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (c) Trost, B. M.; Bonk, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 8277. (d) Trost, B. M.; Balkovec, J. M.; Angle, S. R. *Tetrahedron Lett.* **1986**, *27*, 1445. (e) Trost, B. M.; King, S. A. *Tetrahedron Lett.* **1986**, *27*, 5971. (f) Trost, B. M.; King, S. A. *Chem. Lett.* **1987**, 15. (g) Trost, B. M.; Mignani, S. M.; Nanninga, T. N. *J. Am. Chem. Soc.* **1988**, *110*, 1602. (h) Trost, B. M.; Seoane, P.; Mignani, S.; Acemoglu, M. *J. Am. Chem. Soc.* **1989**, *111*, 7487. (i) Trost, B. M.; King, S. A. *J. Am. Chem. Soc.* **1990**, *112*, 408. (j) Ishibashi, H.; Okano, M.; Tamaki, H.; Maruyama, K.; Yakuza, T.; Ikeda, M. *J. Chem. Soc., Chem. Commun.* **1990**, 1436.
2. (a) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1987**, *28*, 6053. (b) Breuilles, P.; Uguen, D. *Tetrahedron Lett.* **1988**, *29*, 201.
3. Ghera, E.; Yechezkel, T.; Hassner, A. *Tetrahedron Lett.* **1990**, *31*, 3653.
4. Xiao, X.; Park, S.-K.; Prestwich, G. D. *J. Org. Chem.* **1988**, *53*, 4869.
5. Masaki, Y.; Sakuma, K.; Kaji, K. *J. Chem. Soc., Chem. Commun.* **1980**, 434.
6. Trost, B. M.; Ghadiri, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 1098.
7. (a) Trost, B. M.; Schmuff, N. S.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979. (b) Trost, B. M.; Merlic, C. A. *J. Am. Chem. Soc.* **1990**, *112*, 9590.
8. Magnusson, G.; Lindqvist, F. *J. Chem. Soc., Chem. Commun.* **1990**, 1080.
9. The corresponding phenylsulfonyl derivative[2a] has been used in the preparation of the Tsuji's reagent ($X=OCO_2Et$)[1a] and the bromide (X=Br)[3].
10. Stack, D. E.; Dawson, B. T.; Rieke, R. D. *J. Am. Chem. Soc.* **1991**, *113*, 4672.
11. Knochel, P.; Normant, J. F. *J. Organomet. Chem.* **1986**, *309*, 1.
12. Auvray, P.; Knochel, P.; Normant, J. F. *Tetrahedron* **1988**, *44*, 4495 and 4509.
13. Other electrophiles such as nitriles gave very poor yields (less than 15%).
14. Li, C.J.; Chan, T. H. *Organometallics* **1991**, *10*, 2548.