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Dilithiated 2-(Chloromethyl)-3-tosylpropene: A New γ-Chlorinated Allyl Sulfone Dianion in Organic Synthesis

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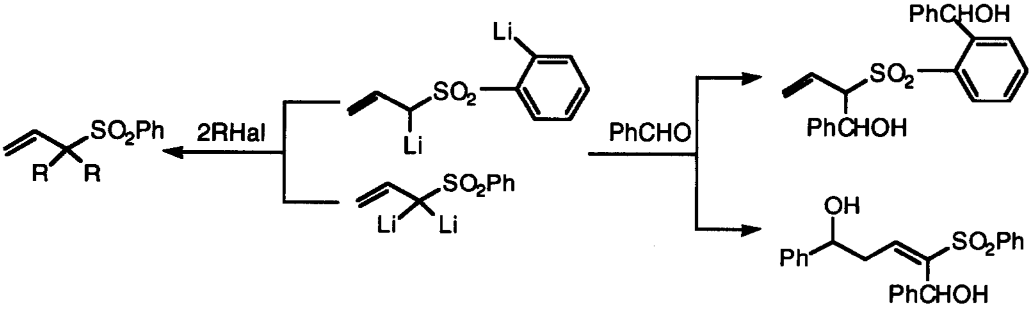
Abstract: Dilithiation of 2-(chloromethyl)-3-tosylpropene (**1**) with n-butyllithium at -90°C in the presence of DMPU affords the allylic dianion **2** which reacts with deuterium oxide or very reactive alkylating agents to give α,α-disubstituted products **3** or **4**, respectively. Monoalkylation at the α-position followed by cyclopropanation reaction takes place with n-alkyl bromides to provide tosylated methylenecyclopropanes **5**. The reaction of dianion **2** with aldehydes or electrophilic olefins occurs at the α-position followed by the corresponding annulation process obtaining tosylated 2,5-dihydrofurans **6** or cyclopentenes **8**, respectively. When ketones are used as electrophiles, dianion **2** reacts at the γ-position yielding 3-(tosylmethylene)tetrahydrofurans **7**. Reductive desulfonylation of compounds **5-8** with sodium amalgam or samarium(II) iodide to afford the corresponding desulfonylated derivatives **22-26** has been also studied.

INTRODUCTION

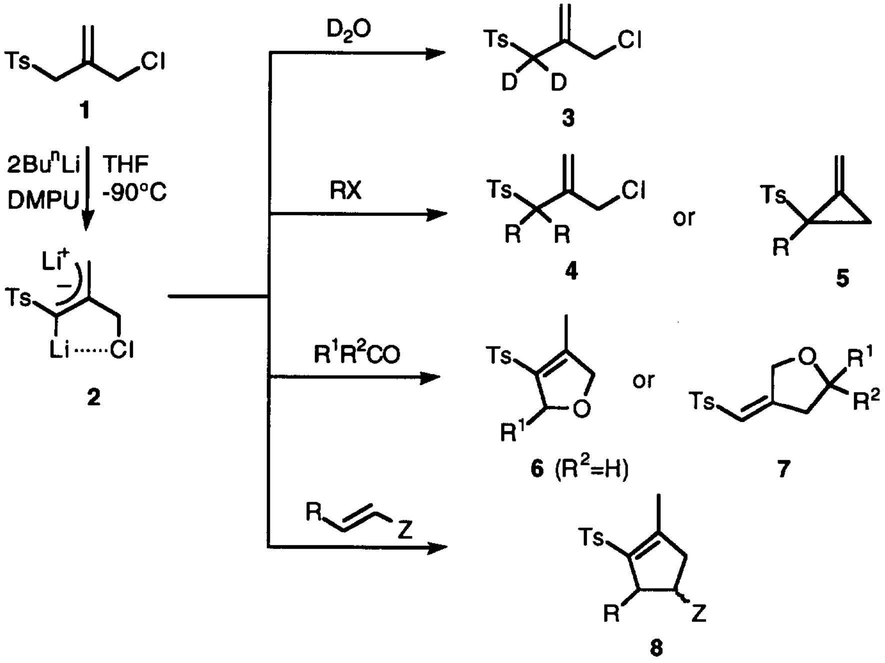
The utility of sulfones as building blocks is mainly based in their ability to stabilize carbanions. Specially useful are monolithio derivatives of allylic sulfones which have been used in regioselective carbon-carbon bond formation mainly in the synthesis of various isoprenoid structures due to their general tendency to undergo α- rather than γ-alkylation[1]. Dilithiated allyl phenyl sulfone is the only dilithio derivative described[2], which has been used in the synthesis of carba-prostacyclins[2b]. The dilithiation of allyl phenyl sulfone at -50°C takes place in the α- and *ortho*-positions, however, double alkylation reaction of this dianion occurs only at the α-position, in contrast with benzaldehyde reacts at the α- and *ortho*-positions. At 50°C the α,*ortho*-dianion is converted into the thermodynamically more stable α,α-dilithio intermediate which suffers dialkylation reaction also at the α-position and reacts with benzaldehyde at the α and γ-positions of the allyl moiety[2a] (Scheme 1). We have studied the dilithiation of 2-(chloromethyl)-3-tosylpropene (**1**), a γ-chlorofunctionalized allyl sulfone with isobutene structure[3], and the reactivity and synthetic applications of these new allyl sulfone dianion as bifunctional conjunctive reagent[4].



Scheme 1

RESULTS AND DISCUSSION

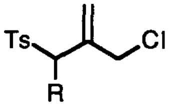
When 2-(chloromethyl)-3-tosylpropene (**1**) was treated with two equivalents of n-butyllithium[5] in THF at -90°C in the presence of *N,N'*-dimethylpropyleneurea (DMPU, two equivalents)[7] over 15 min the corresponding dianion **2** was formed. This intermediate is stable at -90°C for one hour, decomposes at higher temperatures to give an intractable mixture of products and reacts with different electrophiles regioselectively depending on the kind of electrophilic reagent (Scheme 2). The structure for dianion **2** has been proposed according to the chemical behaviour of this intermediate in comparison with the monolithium derivative.[3b,6] The treatment of intermediate **2**



(Ts=p-$CH_3C_6H_4SO_2$)

Scheme 2

with deuterium oxide afforded the α,α-dideuterated compound **3** in 72% yield and 90% of deuterium incorporation corresponding to two atoms of deuterium (^{1}H and ^{13}C NMR) (Scheme 2). We never observe deuterolysis at the *ortho*-position in the aromatic ring as in the case of allyl phenyl sulfone[2]. By reaction of dianion **2** with very reactive alkylating agents, α,α-dialkylated **4** and or monoalkylated **9** compounds were obtained (Scheme 2 and Table 1). In the case of α-bromoacetonitrile and ethyl α-bromoacetate monoalkylated products **9f** and **9g**, respectively, were isolated, probably due to the transformation of the organolithium compound **10** into intermediates **11**. When less reactive alkyl bromides or benzyl chloride were allowed to react with dianion **2** only tosylated methylenecyclopropanes **5**[8] were obtained, even with a large excess of electrophile (Scheme 2 and Table 1). The monoalkylated monoanion **10** suffers γ-elimination[9], better than the second alkylation reaction between -30°C and room temperature to give compounds **5**. This cyclization was never observed when dianion **2** was allowed to warm till room temperature.



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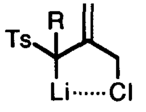

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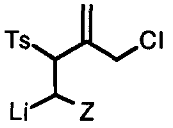

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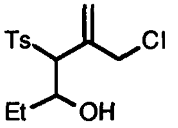
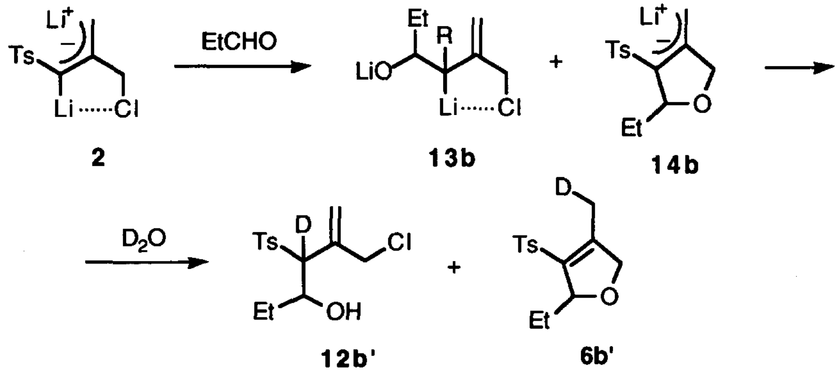


12b

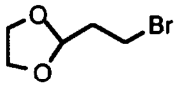
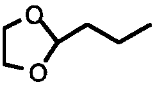
The reaction of intermediate **2** with aldehydes took place at the α-position to give, after intramolecular etherification, tosylated 2,5-dihydrofurans **6**[10] (Scheme 2 and Table 2). However, with ketones it reacted also regiospecifically at the less hindered γ-position to afford tosylated methylenetetrahydrofurans **7**, whose stereochemistry was assigned according to the positive nOe effect between the vinylic proton and the methylene group in β respect to the oxygen atom (Scheme 2 and Table 2).

The reaction of dianion **2** with aldehydes took place between -90°C and room temperature. When the reaction with propanal was quenched with water at different temperatures, mixtures of compounds **6b** and **12b** (as mixture *erythro/threo*:1/2, deduced by ^{1}H NMR[11]) were obtained. If deuterium oxide was added at -40°C a mixture of deuterated compounds **6b'** and **12b'** (*ca.* 1:3 molar ratio; 32% yield) was isolated (Scheme 3). It



Scheme 3

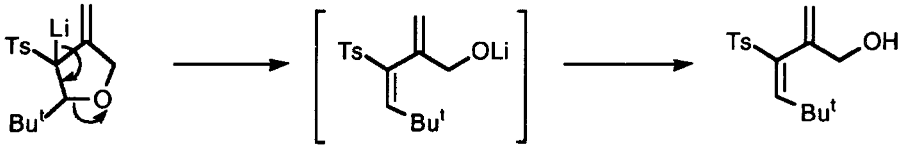
Table 1. Alkylation Reactions of Dianion **2**.

	Product			
Electrophile[a]	No.	R	yield (%)[b]	mp. (°C)[c] or R_f[d]
Me_2SO_4	**4a, 9a**	Me	47, 31[e]	0. 51, 0.46
$CH_2{=}CHCH_2Br$	**4b, 9b**	$CH_2{=}CHCH_2$	46, 38[e]	0.62, 0.53[f]
$HC{\equiv}CCH_2Br$	**4c**	$HC{\equiv}CCH_2$	62	141-142
$PhCH_2Br$	**4d, 9d**	$PhCH_2$	38, 31[e]	0.60, 0.50
$I(CH_2)_3I$[g]	**4e**	-[h]	20	0.56
$BrCH_2CN$	**9f**	CH_2CN	52	130-131
$BrCH_2CO_2Et$	**9g**	CH_2CO_2Et	63	101-102
EtBr	**5a**	Et	54	0.50
n-BuBr	**5b**	n-Bu	45	0.53
Me_3SiCH_2Br	**5c**	Me_3SiCH_2	51	0.52
$THPOCH_2CH_2Br$	**5d**	$THPOCH_2CH_2$	33	0.30
$EtOCH(Me)OCH_2CH_2Br$	**5e**	$HOCH_2CH_2$[i]	60	0.42[j]
	**5f**		52	0.15
$PhCH_2Cl$	**5g**	$PhCH_2$	33	59-60

[a] Two equivalents were added. [b] Isolated yield based on compound **1**, after column chromatography on silica gel. [c] Hexane/ether. [d] Hexane/ether: 1/1. [e] Compounds **4** and **9** were separated by column chromatography. [f] Lit.[6] oil. [g] 1.2 Equivalents. [h] R-R=$(CH_2)_3$. [i] Deprotection of the ketal took place during chromatography. [j] Ether.

means that the precursor of compounds **12** is the β-oxido organolithium compound **13b**, which cyclizes slowly to give the less stable intermediate **14b**[12] precursor of dihydrofuran **6b** (Scheme 3).

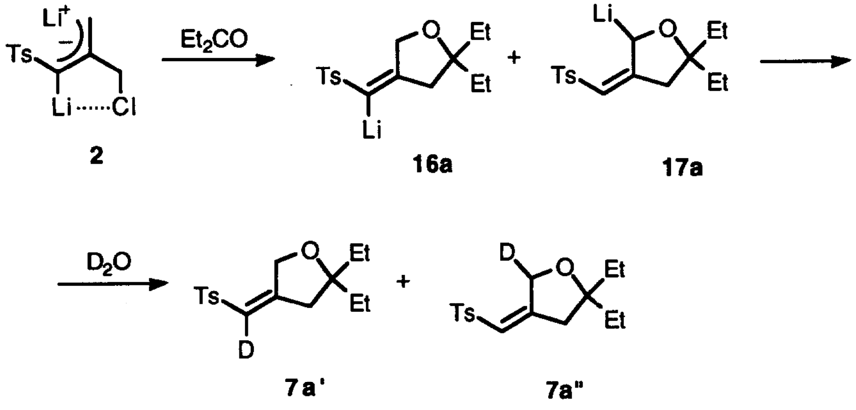
Only in the case of the reaction of dianion **2** with pivalaldehyde the 2-tosyl-1,3-diene **15**[13] was exclusively obtained due to the β-elimination reaction of the corresponding β-alkoxido organolithium compound **14d** (Scheme 4). The *E*-configuration of compound **15** was determined from ^1H NMR data for vinylic protons in β-position respect to the sulfone group in such type of sulfonyl dienes[14].



14d **15**

Scheme 4

The reaction of dianion **2** with ketones takes place at temperatures ranging between -90° and -15°C to lead to 3-(tosylmethylene)tetrahydrofurans **7**. The addition to the carbonyl group and the cyclization processes occur simultaneously since when the reaction of intermediate **2** with 3-pentanone was quenched with water at different temperatures only compound **7a** and starting chlorosulfone **1** were obtained. When this reaction was quenched with deuterium oxide at -40°C compounds **7a'** and **7a"** (*ca.* 3:7 molar ratio; 47% yield) were obtained. At -15°C compound **7a"** was the only one isolated in 52% yield. Monoanions **16a** and **17a** seem to be in this case the intermediates, monolithium compound **17a** being the most thermodynamically stable one (Scheme 5).



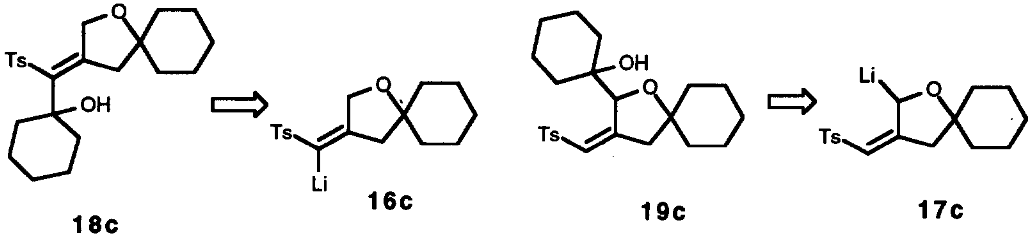
Scheme 5

Table 2. Reaction of Dianion **2** with Carbonyl Compounds. Synthesis of Furan Derivatives **6** and **7**.

Carbonyl compound[a]	Product				
	No.	R1	R2	Yield (%)[b]	mp. (°C)[c] or R_f[d]
MeCHO	**6a**	Me	H	62	85-86
EtCHO	**6b**	Et	H	68	0.47
Pr^iCHO	**6c**	Pr^i	H	59	0.48
Bu^tCHO	**15**	-	-	55	72-73
PhCHO	**6e**	Ph	H	67	109-110[e]
Et_2CO	**7a**	Et	Et	52	0.35
$(c\text{-}C_3H_5)_2CO$	**7b**	$c\text{-}C_3H_5$	$c\text{-}C_3H_5$	75	0.40
$(CH_2)_5$-C=O	**7c**[f]	$(CH_2)_5$-C		40[g]	0.74[h]
PhCOMe	**7d**	Ph	Me	61	107-109
Ph_2CO	**7e**	Ph	Ph	84	148-150

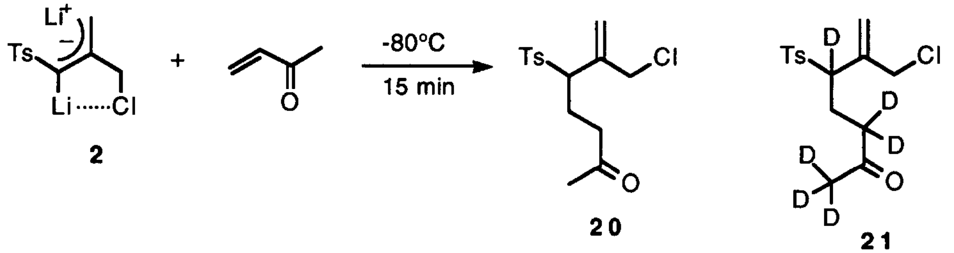
[a] 1.2 Equivalents were added. [b] Isolated yield based on compound **1** after flash chromatography (silica gel). [c] Hexane/ether. [d] Hexane/ether: 1/1. [e] Lit.[10] 110-112°C (hexane/dichloromethane). [f] Compounds **18c** and **19c** were also obtained, the molar ratio being *ca.* 1:3:3 (^{1}H RMN). [g] Overall yield for compounds **7c**, **18c**, and **19c**. [h] R_f for compounds **7c**, **18c**, and **19c**, hexane/ether: 1/3.

The reaction of dianion **2** with cyclohexanone afforded a mixture of compounds **7c**, **18c** and **19c** in *ca.* 1: 3: 3 molar ratio. The formation of diaddition products **18c** and **19c** is due to the reaction of cyclohexanone with carbanions **16c** and **17c**, respectively (Scheme 6 and Table 2).



Scheme 6

When electrophilic olefins reacted with intermediate **2**, a Michael-induced ring closure[15] process took place, and the corresponding tosylated cyclopentenes **8** were obtained (Scheme 1 and Table 3) after quenching at room temperature or at 0°C (see Table 3). In these cases dianion **2** reacted regioselectively at the α-position giving, with β-substituted olefins, a *cis/trans*-mixture of diastereomeric cyclopentenes **8b,c** (deduced by ^{1}H NMR) or only the *trans* one for compound **8d**, derived from cinnamonitrile. The configuration of compounds **8** was assigned according to nOe experiments. In the case of the reaction of dianion **2** with methyl vinyl ketone quenching was also carried out with water after 15 min at -80°C and the Michael adduct **20** was isolated in 85% yield (Scheme 7). When the quenching was carried out with deuterium oxide the hexadeuterated derivative **21** was obtained in 76% yield. The same Michael-type addition occurs in the reaction of monolithium derivative of the benzenesulfonyl homologue **1** with cycloalkenones but not ring closure was observed[16]. Following by TLC the reaction it can be observed that the cyclization process yielding compounds **8** starts at -20°C.



Scheme 7

The different behaviour of dianion **2** in cyclization process, depending on the type of electrophiles, is due to the stability of the corresponding cyclic compound. In the case of the reaction with alkyl halides to give cyclopropanes **5**, no isomerization of the double bond took place because methylenecyclopropanes are more stable than the isomeric methylcyclopropenes. In the reaction with aldehydes or electrophilic olefins the most stable dihydrofurans **6** or cyclopentenes **8** were, respectively, obtained and the isomerization of the *exo* double bond to the *endo* position favours also the cyclization process.

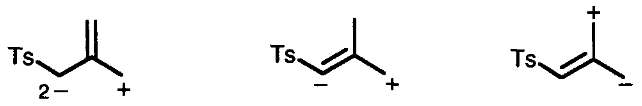
Table 3. Reaction of Dianion **2** with Electrophilic Olefins. Synthesis of Cyclopentenes **8**.

Electrophilic Olefin[a]	Product				
	No.	R	Z	Yield (%)[b]	mp. (°C)[c] or R_f[d]
CH_2=CHCOMe	**8a**	H	COMe	76	0.51[e]
(*E*)-MeCH=CHCOMe[f]	**8b**	Me	COMe	78	0.24[g]
(*E*)-MeCH=$CHCO_2Me$[h]	**8c**	Me	CO_2Me	62	0.26[i]
(*E*)-PhCH=CHCN[h]	**8d**	Ph	CN	51	143-144[j]

[a] 1.2 Equivalents were added. [b] Isolated yield based on compound **1** after column chromatography on silica gel. [c] Hexane/ether. [d] Hexane/ether : 1/1. [e] Ether. [f] The reaction was quenched after 1 h at room temperature. [g] *Cis/trans* : 1/3. [h] The reaction was quenched at 0°C. [i] *Cis/trans* : 1/4. [j] Only *trans*.

Reductive desulfonylation of representative compounds **5-8** was carried out with *ca.* 6% sodium amalgam[17] in methanol in the presence of 4 equiv. of Na_2HPO_4 (Table 4). Tosylated methylenecyclopropane **5f** afforded a *ca.* 1:1 mixture of methylenecyclopropane **22**[19] and cyclopropene **23** after 1 h at 0°C. The dihydrofuran **24** which was obtained by hydrogenolysis of compound **6c** after 2h at 0°C, decomposed by chromatography or distillation. The reduction of methylenetetrahydrofurans **7d** was carried out with freshly prepared samarium(II) iodide[20] in THF-HMPA at -20°C during 1.5 h, affording the homoallylic alcohol **25** in 72% yield. The reduction of tetrahydrofurans **7** with sodium amalgam or sodium dithionite[21] gave complex mixture of products or no reduction, respectively. Finally, the tosylated cyclopentene **8a** was reduced with sodium amalgam at room temperature for 1d to give a 1:1 mixture of diastereomeric cyclopentenylethanols **26**.

We can conclude that this chlorinated allyl sulfone dianion reacts regioselectively with electrophiles being specially useful in cycloannulation reactions acting as: (a) synthon **I** with alkyl halides, (b) synthon **II** with aldehydes and electrophilic olefins, and (c) synthon **III** with ketones (Scheme 8).



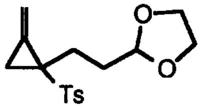
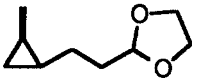
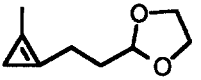
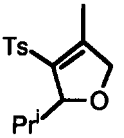
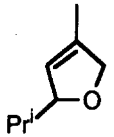
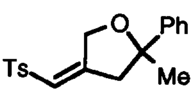
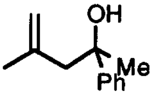
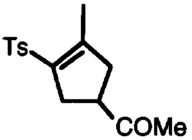
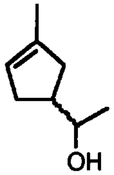
I **II** **III**

Scheme 8

EXPERIMENTAL

General. Melting points were obtained with a Reichert Thermovar apparatus and are uncorrected. IR spectra were obtained as films in a Pye Unicam SP3-200 spectrophotometer as neat liquids. ^{1}H and ^{13}C spectra were recorded on a Bruker AC-300 spectrometer with $SiMe_4$ as internal standard and using $CDCl_3$ as solvent. ^{13}C-NMR assignments were made on the basis of DEPT experiments. MS spectra were measured in a Hewlett-

Table 4. Reduction of Compounds **5-8** with Sodium Amalgam.

Starting Compound	No.	Reaction conditions T (°C)	Reaction conditions Time	Product Structure	Product No.	Product Yield(%)[a]	Product R_f[b]
	**5f**	0	1 h		**22**	94[c]	0.75
					**23**		0.75
	**6c**	0	2 h		**24**	92[d]	-[e,f]
	**7d**[g]	-20	1.5 h		**25**	72	0.40
	**8a**	25	1 d		**26**[h]	90[d]	0.30[i]

[a] Based on starting compound. [b] Hexane/ether:4/1. [c] Compounds **22** and **23** were obtained in 42:58 molar ratio (GLC) and could not be separated. [d] Crude pure compound. [e] T_r 4.05 (see Experimental). [f] Lit.[18]. [g] The reduction was carried out with SmI_2 in THF-HMPA. [h] Mixture of diastereomers 1:1 deduced by GLC. [i] Hexane/ether: 1/1.

Packard 5988A (EI, 70eV). High resolution mass spectra were measured in the corresponding Service at the University of Zaragoza. Elemental analyses were performed by the Microanalyses Service of the University of Alicante. Chromatographic analysis (GLC) were determined with a Hewlett-Packard HP-5890 instrument equipped with a 25 m WCOT capillary column (0.22 mm diam., 0.2μm film thickness OV-101 stationary phase) using nitrogen (2 ml/min) as the carrier gas, $T_{injector}$=270°C, T_{column}=60°C, and 60-270 (15°C/min). Thin layer chromatography (TLC) was carried out on Schleicher &Schuell F1500/LS 254 plates coated with a 0.2 mm layer of silica gel and UV visualization. Column chromatography was performed using silica gel 60 of 70-270 mesh and hexane/ether as eluant. All starting materials were commercially available (Aldrich, Fluka, Janssen) of the best grade and were used without further purification. THF was dried with $LiAlH_4$ under argon atmosphere. Methanol was dried with magnesium turnings and stored under argon.

Reaction of Dianion 2 with Electrophiles. General Procedure.

To a solution of 2-(chloromethyl)-3-tosylpropene (1) (98 mg, 0.4 mmol) and *N,N*-dimethylpropyleneurea (106 μl, 0.88 mmol) in THF (3 ml) cooled at -90°C was added a 1.6M solution of *n*-butyllithium (550 μl, 0.88 mmol) in hexane. After 15 min stirring at the same temperature the electrophile was aded (1.2 or 2.2 mmol, see tables 1-3) and the reaction was warmed up to room temperature (see tables 1-3)[22]. The reaction was hydrolyzed with 3M hydrochloric acid (4 ml) and extracted with ether (2x10 ml). The organic layer was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* (15 torr). The crude product was purified by column chromatography and by recrystallization to afford compounds **3-9**, **12**, **15** and **18-21**. Yields and physical data are included in tables 1-3, spectral and analytical data follow:

2-(Chloromethyl)-3,3-dideuterio-3-tosyl-1-propene (**3**): mp 85-86°C (hexane/ether); ν (Nujol) 1640, (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.44 (s, 3H, CH_3Ar), 4.19 (s, 2H, CH_2Cl), 5.01, 5.44 (2s, 2H, CH_2=C), 7.35 and 7.74 (2d, J=8.0 Hz, 4H, ArH); δ_C 21.47 (CH_3Ar), 46.82 (CH_2Cl), 58.72 (quint., J=21.8 Hz, CD_2), 124.00, 133.38 (CH_2=C), 128.25, 129.66, 134.95 and 144.91 (ArC); *m/z* 246 (M^+, 0.3%), 211 (25), 155 (44), 147 (12), 91 (100), 65 (17) and 55 (10). Anal. calcd. for $C_{11}H_{11}ClD_2O_2S$: C, 53.54; H, 4.49; and S, 12.99. Found: C, 53.51; H, 4.50; and S, 13.54.

2-(Chloromethyl)-3-methyl-3-tosyl-1-butene (**4a**): ν 3090, 1620, (HC=C), 1290 and 1140 cm^{-1} (SO_2); δ_H 1.51 [s, 6H, $(CH_3)_2$CS], 2.37 (s, 3H, CH_3Ar), 4.25 (s, 2H, CH_2Cl), 5.15, 5.58 (2s, 2H, CH_2=C), 7.26 and 7.59 (2d, J=8.2 Hz, 4H, ArH); δ_C 21.61 (CH_3Ar), 21.81 [$(CH_3)_2$CS], 44.84 (CH_2Cl), 66.19 (CS), 124.00, 141.95 (CH_2=C), 129.12, 130.71, 131.27 and 144.86 (ArC); *m/z* 236 (M^+-Cl, 2%), 157 (14), 119 (27), 117 (89), 92 (16), 91 (25), 81 (100), 79 (38), 67 (12), 65 (26), 53 (16) and 41 (16). Anal. calcd. for $C_{13}H_{17}ClO_2S$: C, 53.57; H, 6.28; and S, 11.75. Found: C, 53.58; H, 6.98; and S, 11.40.

3-Allyl-2-(chloromethyl)-3-tosyl-1,5-hexadiene (**4b**): ν 1300 and 1140 cm^{-1} (SO_2); δ_H 2.39 (s, 3H, CH_3Ar), 2.69 (dd, J=15.2 and 7.2 Hz, 2H, CH_2CS), 2.87 (dd, J=15.2 and 6.5 Hz, 2H, CH_2CS), 4.28 (s, 2H, CH_2Cl), 5.00-5.15 (m, 5H, 2xCH_2=CH and 1H of CH_2=C), 5.68 (s, 1H, CH_2=C), 5.80 (m, 2H, 2xCH=CH_2), 7.25 and 7.60 (2d, J=8.1 Hz, 4H, ArH); δ_C 21.57 (CH_3Ar), 34.48 (CH_2CS), 44.28 (CH_2Cl), 71.56 (CS), 119.64, 124.60, 130.99, 131.43 (3xC=C), 129.01, 130.72, 139.83 and 145.00 (ArC); *m/z* 169 (M^+-Ts, 5%), 133 (40), 119 (16), 105 (36), 93 (12), 92 (12), 91 (100), 79 (47), 77 (32), 65 (30) and 41 (24). Anal. calcd. for $C_{17}H_{21}ClO_2S$: C, 62.85; H, 6.52; and S, 9.87. Found: C, 63.02; H, 6.56; and S, 10.18.

5-(Chloromethyl)-4-propargyl-4-tosyl-5-hexen-1-yne (**4c**): R_f 0.62 (hexane/ether:1/1)); ν (Nujol) 3290, 2120 (C≡CH), 3090, 1625 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.05 (dt, J=4.0 and 2.5 Hz, 2H, HC≡C), 2.40 (s, 3H, CH_3Ar), 2.97, 3.15 (2dd, J=17.3 and 2.5 Hz, 4H, CH_2C≡C), 4.35 (s, 2H, CH_2Cl), 5.13, 5.80 (2s, 2H, CH_2=C), 7.29 and 7.66 (2d, J=8.2 Hz, 4H, ArH); δ_C 21.62 (CH_3Ar), 22.36 (CH_2C≡C), 44.12 (CH_2Cl), 69.85 (CS), 72.80, 77.31 (C≡C), 124.30, 130.94 (CH_2=C), 129.33, 130.78, 138.13 and 145.69 (ArC); *m/z* 321 (M^+, 0.2%), 157 (35), 139 (29), 130 (13), 129 (55), 128 (100), 127 (38), 116 (14), 115 (52), 92 (14), 91 (49), 89 (14), 77 (19), 65 (31), 63 (15) and 51 (11). Anal. calcd. for $C_{17}H_{17}ClO_2S$: C, 63.63; H, 5.34; and S, 9.99. Found: C, 63.65; H, 5.26; and S, 9.90.

3-Benzyl-2-(chloromethyl)-4-phenyl-3-tosyl-1-butene (**4d**): ν 3085, 1620 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.39 (s, 3H, CH_3Ar), 3.10, 3.72 (2d, *J*=16.0 Hz, 4H, 2xCH_2Ph), 4.31 (s, 2H, CH_2Cl), 5.14, 5.75 (2s, 2H, CH_2=C), 7.05-7.39 (m with d at 7.24, *J*=8.1 Hz, 12 H, 2xPh and 2H *p*-Tol), and 7.65 (d, *J*=8.1 Hz, 2H, *p*-TolH); δ_C 21.62 (CH_3Ar), 34.87 (CH_2Ph), 45.02 (CH_2Cl), 74.44 (CS), 125.44, 131.57 (CH_2=C), 126.64, 127.91, 129.05, 130.43, 131.03, 135.18, 140.11 and 144.98 (ArC); *m/z* 389 (M^+-35, 1%), 233 (10), 232 (10), 165 (10), 91 (100), 77 (10) and 65 (10).

3-Chloro-2-(1-tosylcyclopentyl)-1-propene (**4e**): ν 3075, 1640 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 1.45-2.20 [m, 6H, $(CH_2)_3$CS)], 2.13-2.48 (m with s at 2.43, 5H, CH_2CS and CH_3Ar), 4.19 (s, 2H, CH_2Cl), 5.07, 5.62 (2s, 2H, CH_2=C), 7.28 and 7.64 (2d, *J*=8.0 Hz, 4H, ArH); δ_C 21.62 (CH_3Ar), 24.38, 32.54 (CH_2CH_2CS), 45.26 (CH_2Cl), 77.61 (CS), 124.55, 132.31 (CH_2=C), 129.07, 130.49, 141.76 and 144.68 (ArC); *m/z* 198 (M^+-SO_2-Cl, 7%), 157 (19), 145 (17), 144 (13), 143 (67), 139 (15), 107 (100), 91 (92), 79 (93), 77 (40), 65 (58) and 47 (27).

1-Ethyl-1-tosyl-2-methylenecyclopropane (**5a**): ν 1300 and 1140 cm^{-1} (SO_2); δ_H 0.78 (t, *J*=7.5 Hz, 3H, CH_3CH$_2$), 1.45 (dt, *J*=10.0 and 2.1 Hz, 1H, CH_2C=C), 1.82 (m, 2H, CH_2CH$_3$), 2.21 (m, 1H, CH_2C=C), 2.39 (s, 3H, CH_3Ar), 5.52, 5.60 (2t, *J*=2.3 Hz, 2H, CH_2=C), 7.30 and 7.71 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 9.87 (CH_3CH_2), 13.26 (CH_2C=C), 21.48 (CH_3Ar), 22.87 (CH_2CH_3), 44.74 (CS), 107.36, 129.44 (CH_2=C), 128.77, 129.50, 135.39 and 144.32 (ArC); *m/z* 236 (M^+, 13%), 157 (27), 143 (18), 140 (15), 139 (100), 105 (21), 92 (24), 91 (51), 81 (24), 79 (53), 77 (20), 65 (36) and 53 (28). High resolution mass spectrum required for $C_{13}H_{16}O_2S$: *m/z* 236.0871. Found: 236.0876.

1-Butyl-1-tosyl-2-methylenecyclopropane (**5b**): ν 1300 and 1150 cm^{-1} (SO_2); δ_H 0.76 (deform. t, 3H, CH_3CH$_2$), 1.15 (m, 4H, CH_2CH_2CH$_3$), 1.45, 2.21 (2dt, *J*=10.0 and 2.5 Hz, 2H, CH_2C=C), 1.75 (m, 2H, CH$_2$CH_2CS), 2.40 (s, 3H, CH_3Ar), 5.52, 5.60 (2t, *J*=2.5 Hz, 2H, CH_2=C), 7.30 and 7.71 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 13.59 (CH_3CH_2), 13.94 (CH_2C=C), 21.45 (CH_3Ar), 22.36 (CH_2CH_3), 27.68 ($CH_2CH_2CH_3$), 29.52 (CH_2CH_2CS), 44.00 (CS), 107.27, 129.77 (CH_2=C), 128.74, 129.46, 135.34 and 144.28 (ArC); *m/z* 264 (M^+, 0.3%), 157 (19), 143 (30), 142 (11), 140 (13), 139 (100), 109 (30), 93 (21), 92 (21), 91 (51), 79 (27), 77 (20), 67 (55), 65 (39), 55 (20) and 41 (30). Anal. calcd. for $C_{15}H_{20}O_2S$: C, 68.14; H, 7.62; and S, 12.13. Found: C, 68.37; H, 8.07; and S, 12.56.

1-(Trimethylsilylmethyl)-1-tosyl-2-methylenecyclopropane (**5c**): ν 3075, 1640, (CH=C), 1300, 1150 cm^{-1} (SO_2); δ_H -0.05 [s, 9H, $(CH_3)_3$Si], 1.28 (d, *J*=7.6 Hz, 2H, CH_2Si), 1.50, 2.28 (2d, *J*=10.0 Hz, 2H, CH_2C=C), 2.43 (s, 3H, CH_3Ar), 5.60, 5.65 (2s, 2H, CH_2=C), 7.33 and 7.79 (2d, *J*=7.9 Hz, 4H, ArH); δ_C -0.52 [$(CH_3)_3$Si], 15.05 (CH_2C=C), 15.26 (CH_2Si), 21.54 (CH_3Ar), 42.34 (CS), 107.91 (CH_2=C), 129.08, 129.44, 131.22, 134.78 and 144.19 (ArH and *C*=CH_2); *m/z* 293 (M^+, 0.7%), 279 (2), 157 (37), 149 (37), 142 (44), 139 (33), 91 (19), 75 (12), 73 (100), 65 (18) and 41 (16).

1-(2-Tetrahydropyranoxyethyl))-1-tosyl-2-methylenecyclopropane (**5d**): ν 3085, 1640 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.40-2.10 (m, 9H, 3xCH_2CO, CH_2CCO and 1H of CH_2C=C), 2.13 (d, *J*=7.0 Hz, 1H, CH_2C=C), 2.34 (s, 3H, CH_3Ar), 3.35-3.65 (m, 4H, 2xCH_2O), 4.40 (deform. d, *J*=13.5 Hz, 1H, CHO), 5.59

(d, *J*=2.2 Hz, 1H, CH$_2$=C), 5.67 (s, 1H, CH$_2$=C), 7.34 and 7.77 (2d, *J*=8.0 Hz, 4H, ArH); δ_C 14.80 (CH$_2$C=C), 19.41 (CH$_2$CCO), 21.57 (CH$_3$Ar), 25.29, 29.95, 30.49 (3xCH$_2$CCO), 42.23 (CS), 62.23, 64.34 (2xCH$_2$O), 98.85 (CHO), 107.75, 129.47 (CH$_2$=C), 128.91, 129.62, 135.25 and 144.47 (ArC); *m/z* 253 (M^++2-THP, 0.5%), 251 (M^+-THP, 0.6), 2.35 (12), 157 (11), 149 (14), 139 (43), 92 (15), 91 (65), 85 (100), 79 (24), 78 (10), 77 (39), 67 (29), 65 (58), 63 (16), 57 (30), 56 (18), 55 (35), 53 (20), 52 (17), 43 (29) and 41 (85).

1-(2-Hydroxyethyl)-1-tosyl-2-methylenecyclopropane (5e): ν 3450 (OH), 1300 and 1150 cm^{1} (SO$_2$). δ_H 1.65 (dt, *J*=10.0 and 2.1 Hz, 1H, CH$_2$C=C), 2.00 (m, 2H, CH$_2$CH$_2$O), 2.31 (dt, *J*=10.0 and 2.3 Hz, 1H, CH$_2$C=C), 2.39 (s, 3H, CH$_3$Ar), 2.75 (br. s, 1H, OH), 3.72 (m, 2H, CH$_2$O), 5.63 (m, 2H, CH$_2$=C), 7.37 and 7.76 (2d, *J*=8.0 Hz, 4H, ArH); δ_C 15.55 (CH$_2$C=C), 21.55 (CH$_3$Ar), 33.57 (CH$_2$CH$_2$O), 42.64 (CS), 59.99 (CH$_2$O), 107.90, 129.55 (CH$_2$=C), 128.89, 129.70, 134.59 and 144.79 (ArC); *m/z* 251 (M^+-1, 0.5%), 221 (18), 157 (26), 149 (90), 143 (38), 142 (29), 141 (18), 141 (21), 139 (100), 129 (10), 121 (16), 105 (23), 97 (60), 92 (51), 91 (91), 89 (25), 85 (31), 79 (16), 77 (56), 67 (24), 65 (78), 63 (26), 55 (14), 53 (18), 51 (23), 43 (23) and 41 (37).

2-[2-(2-Methylene-1-tosylcyclopropyl)ethyl]-1,3-dioxolane (5f): ν 1300 and 1145 cm^{1} (SO$_2$); δ_H 1.47 (d, *J*=10.0 Hz, 1H, CH$_2$C=C), 1.64 (m, 2H, CH$_2$CH$_2$CO), 1.86 (m, 2H, CH$_2$CO), 2.25 (d, *J*=10.0 Hz, 1H, CH$_2$C=C), 2.41 (s, 3H, CH$_3$Ar), 3.76 (m, 4H, 2xCH$_2$O), 4.73 (t, *J*=4.2 Hz, 1H, CHO), 5,55, 5.60 (2s, 2H, CH$_2$=C) 7.30 and 7.70 (2d, *J*=7.9 Hz, 4H, ArH); δ_C 14.31 (CH$_2$C=C), 21.50 (CH$_3$Ar), 24.24 (CH$_2$CH$_2$CO), 30.16 (CH$_2$CH$_2$CO), 43.43 (CS), 64.67 (CH$_2$O), 103.24 (CHO), 107.54, 129.61 (CH$_2$=C), 128.79, 129.57, 135.19 and 144.42 (ArC); *m/z* 308 (M^+, 0.2%), 153 (12), 139 (18), 91 (25), 86 (12), 81 (13), 79 (15), 77 (11), 73 (100), 65 (18) and 45 (22). High resolution mass spectrum required for $C_{16}H_{20}O_4S$: *m/z* 308.1083. Found: 308.1036.

1-Benzyl-1-tosyl-2-methylenecyclopropane (5g): ν 1300 and 1145 cm^{-1} (SO$_2$); δ_H 1.13, 2.16 (2dd, *J*=10.0 and 2.1 Hz, 2H, CH$_2$C=C), 2.39 (s, 3H, CH$_3$Ar), 3.17 (s, 2H, CH$_2$Ph), 5.51 (m, 2H, CH$_2$=C), 6.92 (m, 2H, Ph), 7.12 (m, 3H, Ph), 7.27 and 7.69 (2d, *J*=7.9 Hz, 4H, *p*-Tol); δ_C 13.13 (CH$_2$C=C), 21.53 (CH$_3$Ar), 34.98 (CH$_2$Ph), 44.36 (CS), 108.38, 134.83 (CH$_2$=C), 126.82, 127.91, 128.52, 128.89, 129.50, 129.90, 135.21 and 144.37 (ArC); *m/z* 298 (M^+, 0.5%), 143 (67), 142 (65), 141 (71), 139 (24), 129 (15), 128 (76), 127 (14), 115 (34), 92 (12), 91 (100), 65 (37) and 62 (10).

2,4-Dimethyl-3-tosyl-2,5-dihydrofuran (6a): R_f 0.32 (hexane/ether:1/1); ν 3070, 1640 (CH=C), 1300 and 1150 cm^{-1} (SO$_2$); δ_H 1.36 (d, *J*=6.4 Hz, 3H, CH$_3$CO), 2.12 (s, 3H, CH$_3$CCH$_2$), 2.41 (s, 3H, CH$_3$Ar), 4.55, 4.64 (2dd, *J*=14.2 and 6.9 Hz, 2H, CH$_2$O), 4.98 (m, 1H, CHO), 7.35 and 7.77 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 11.16 (CH$_3$CCH$_2$), 21.34, 21.50 (CH$_3$CO and CH$_3$CO), 78.17 (CH$_2$O), 82.96 (CHO), 128.31, 129.81, 135.45, 138.46, 144.47 and 149.69 (ArC and C=C); *m/z* 237 (M^+-15, 11), 97 (17), 92 (15), 91 (100), 89 (66), 67 (20), 65 (72), 63 (31), 53 (70), 51 (23), 43 (39) and 41 (31).

2-Ethyl-4-methyl-3-tosyl-2,5-dihydrofuran (6b): ν 3070, 1640 (CH=C), 1300 and 1150 cm^{1} (SO$_2$); δ_H 0.82 (t, *J*=7.3 Hz, 3H, CH$_3$CH$_2$), 1.66, 1.85 (2m, 2H, CH$_2$CH$_3$), 2.13 (s, 3H, CH$_3$C=CH$_2$), 2.40 (s, 3H, CH$_3$Ar), 4.56 (dd, *J*=14.5 and 2.0 Hz, 1H, CH$_2$O), 4.62 (dd, *J*=14.5 and 5.5 Hz, 1H, CH$_2$O), 4.90 (m, 1H, CHO), 7.33

and 7.76 (2d, J=8.0 Hz, 4H, ArH); δ_C 8.43 (CH_3CH_2), 11.17 (CH_3CCH_2), 21.49 (CH_3Ar), 27.65 (CH_2CH_3), 78.97 (CH_2O), 87.64 (CHO), 127.15, 129.79, 133.56, 138.32, 144.46 and 150.38 (ArC and C=C); *m/z* 238 (M^++1-Et, 11%), 237 (M^+-Et, 73), 236 (13), 139 (17), 92 (17), 91 (100), 79 (11), 77 (14), 69 (13), 67 (11), 65 (37), 53 (20) and 43 (47). Anal. calcd. for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81; and S, 12.04. Found: C, 63.07; H, 6.79; and S, 11.99.

2-Ethyl-4-(deuteriomethyl)-3-tosyl-2,5-dihydrofuran (6b'): R_f 0.47 (hexane/ether:1/1); ν 3070, 1640, (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.82 (t, J=7.3 Hz, 3H, CH_3CH_2), 1.66, 1.85 (2m, 2H, CH_2CH_3), 2.13 (m, 2H, CH_2D), 2.40 (s, 3H, CH_3Ar), 4.56 (dd, J=14.5 and 2.0 Hz, 1H, CH_2O), 4.62 (dd, J=14.5 and 5.5 Hz, 1H, CH_2O), 4.90 (m, 1H, CHO), 7.33 and 7.76 (2d, J=8.0 Hz, 4H, ArH); δ_C 8.43 (CH_3CH_2), 10.99 (t, J=19.5 Hz, CD), 21.49 (CH_3Ar), 27.65 (CH_2CH_3), 78.97 (CH_2O), 87.64 (CHO), 127.15, 129.79, 133.56, 138.82, 144.46 and 150.38 (ArC and C=C); *m/z* 238 (M^+-Et, 5%), 237 (41), 155 (19), 139 (11), 92 (13), 91 (100), 89 (17), 77 (11), 65 (42), 53 (32), 51 (14) and 41 (21).

2-Isopropyl-4-methyl-3-tosyl-2,5-dihydrofuran (6c): ν 3070, 1640 (CH=C), 1300 and 1150 cm^{1} (SO_2); δ_H 0.64, 0.98 [2d, J=7.0 Hz, 6H, $(CH_3)_2CH$], 2.10-2.20 (m with s at 2.14, 4H, CHCH= and CH_3CCH_2), 2.39 (s, 3H, CH_3Ar), 4.60 (deform. d, J=14.5 Hz, 2H, CH_2O), 4.83 (m, 1H, CHO), 7.34 and 7.77 (2d, J=8.1 Hz, 4H, ArH); δ_C 11.22 (CH_3CCH_2), 14.16, 19.85 [$(CH_3)_2CH$], 21.57 (CH_3Ar), 31.99 (CHCHO), 79.96 (CH_2O), 127.31, 129.83, 133.15, 138.27, 144.52 and 150.50 (ArC and C=C); *m/z* 237 (M^+-Pr^i, 38%), 128 (13), 92 (12), 91 (98), 77 (16), 70 (13), 67 (13), 65 (53), 55 (26), 43 (99) and 41 (100).

(Z)-2,2-Diethyl-4-(tosylmethylene)tetrahydrofuran (7a): ν 3070, 1620 (CH=C), 1300 and 1150 cm^{1} (SO_2); δ_H 0.85 (t, J=7.5 Hz, 6H, 2xCH_3CH_2), 1.39-1.96 (m, 4H, 2xCH_2CH_3), 2.40 (s, 3H, CH_3Ar), 2.52 (s, 2H, CH_2CO), 4.44 (s, 2H, CH_2O), 6.05 (s, 1H, CH=C), 7.32 and 7.77 (2d, J=8.1 Hz, 4H, ArH); δ_C 7.72 (CH_3CH_2), 21.56 (CH_3Ar), 30.70 (CH_2CH_3), 42.15 (CH_2CO), 57.30 (CH_2O), 75.20 (CO), 122.14, 128.81 (CH=C), 128.28, 129.59, 135.91 and 144.73 (ArC); *m/z* 209 (M^+-Et_2CO, 34%), 155 (16), 145 (21), 139 (21), 109 (15), 91 (100), 89 (74), 87 (47), 69 (17), 65 (57), 57 (70), 53 (37), 45 (61), 43 (22) and 41 (33).

(Z)-5-Deuterio-2,2-diethyl-4-(tosylmethylene)tetrahydrofuran (7a"): R_f0.35 (hexane/ether:1/1); ν3070, 1620 (CH=C), 1300 and 1150 cm^{-1} (SO_2); δ_H 0.85 (t, J=7.5 Hz, 6H, 2xCH_3CH_2), 1.39-1.96 (m, 4H, 2xCH_2CH_3), 2.40 (s, 3H, CH_3Ar), 2.52 (s, 2H, CH_2CO), 4.44 (s, 1H, CHD), 6.05 (s, 1H, CH=C), 7.32 and 7.77 (2d, J=8.1 Hz, 4H, ArH); δ_C 7.72 (CH_3CH_2), 21.56 (CH_3Ar), 30.70 (CH_2CH_3), 42.15 (CH_2CO), 57.04 (t, J=21.0 Hz, CHD), 75.20 (CO), 122.14, 128.81 (CH=C), 128.28, 129.59, 135.91 and 144.73 (ArC); *m/z* 210 (M^+-Et_2CO, 7%), 209 (6), 155 (17), 139 (15), 92 (21), 91 (100), 87 (37), 77 (10), 69 (13), 65 (52), 57 (68), 55 (12), 53 (14), 45 (48) and 41 (23).

(Z)-2,2-Dicyclopropyl-4-(tosylmethylene)tetrahydrofuran (7b): ν 3080, 1625 (CH=C), 1300 and 1150 cm^{1} (SO_2); δ_H 0.29-0.41 (m, 8H, 4xCH_2CH), 0.71-0.79 (m, 2H, 2x$CHCH_2$), 2.40 (s, 3H, CH_3Ar), 2.59 (s, 2H, CH_2CO), 4.38 (s, 2H, CH_2O), 6.09 (s, 1H, CH=C), 7.32 and 7.76 (2d, J=8.1 Hz, 4H, ArH); δ_C -0.23, 0.73 (CH_2CH), 18.59 ($CHCH_2$), 21.52 (CH_3Ar), 45.07 (CH_2CO), 57.84 (CH_2O), 71.46 (CO), 122.34, 128.36, 129.52, 129.53, 135.75 and 144.67 (C=C and ArC); *m/z* 318 (M^+, 0.1%), 111 (100), 91 (27), 89 (10), 69 (81), 65 (15), 63 (14) and 41 (42).

(Z)-*2-Phenyl-2-methyl-4-(tosylmethylene)tetrahydrofuran* (7d): ν (Nujol) 1300 and 1140 cm^{1} (SO_2); δ_H 1.56 (s, 3H, CH_3CO), 2.40 (s, 3H, C*H*$_3$Ar), 2.78, 2.92 (2d, *J*=14.5 Hz, 2H, CH_2CO), 3.80, 4.13 (2d, *J*=13.7 Hz, 2H, CH_2O), 5.89 (s, 1H, CH=C), 7.20-7.39 (m, 7H, Ph and 2x*p*-Tol) and 7.67 (d, *J*=8.0 Hz, 2H, *p*-TolH); δ_C 21.52 (CH_3Ar), 30.30 (CH_3CO), 47.31 (CH_2CO), 57.06 (CH_2O), 74.49 (CO), 123.42, 124.64, 126.86, 127.69, 128.19, 128.29, 129.50, 135.59, 144.69 and 146.35 (ArC and C=C); *m/z* 209 (*M*$^+$-PhCOMe, 4%), 155 (12), 121 (77), 105 (14), 91 (68), 89 (22), 77 (24), 65 (38) and 43 (100). Anal. calcd. for $C_{19}H_{20}O_3S$: C, 69.48; H, 6.14; and S, 9.76. Found: C, 69.60; H, 5.97; and S, 9.86.

(Z)-*2,2-Diphenyl-4-(tosylmethylene)tetrahydrofuran* (7e): ν (Nujol) 1620 (CH=C), 1300 and 1150 cm^{1} (SO_2); δ_H 2.41 (s, 3H, C*H*$_3$Ar), 3.39 (s, 2H, CH_2CO), 3.90 (s, 2H, CH_2O), 5.82 (s, 1H, CH=C), 7.21-7.38 (m, 12H, 2xPh and 2x*p*-Tol), 7.68 (d, *J*=8.1 Hz, 2H, 2x*p*-TolH); δ_C 21.56 (CH_3Ar), 45.13 (CH_2CO), 57.14 (CH_2O), 77.81 (CO), 124.11, 125.83, 126.01, 126.97, 127.17, 128.08, 128.11, 128.18, 128.32, 129.56, 129.73, 135.70, 144.73 and 145.83 (ArC and C=C); *m/z* 313 (*M*$^+$-Ph, 4%), 235 (12), 183 (100), 157 (14), 105 (99), 91 (39), 89 (12), 77 (54), 65 (16) and 51 (11). Anal. calcd. for $C_{24}H_{22}O_3S$: C, 73.82; H, 5.68; and S, 8.21. Found: C, 74.00; H, 5.47; and S, 8.20.

4-Acetyl-1-methyl-2-tosylcyclopentene (8a): ν 3060, 1640 (CH=C), 1710 (C=O), 1300 and 1150 cm^{-1} (SO_2); δ_H 2.12 (s, 3H, CH_3CO), 2.16 (t, *J*=1 Hz, 3H, C*H*$_3$CCH$_2$), 2.40 (s, 3H, C*H*$_3$Ar), 2.68-2.92 (m, 4H, 2xCH_2CO), 3.17-3.24 (m, 1H, CHCO), 7.33 and 7.75 (2d, *J*=8.1 Hz, 4H, ArH); δ_C 14.99 (CH_3CCH_2), 21.51 (CH_3Ar), 28.24 (CH_3CO), 35.84, 41.92 (2xCH_2CO), 47.01 (CHCO), 127.19, 129.77, 132.29, 137.82, 144.18, 151.99 (ArC and C=C) and 207.38 (CO); *m/z* 278 (*M*$^+$, 0.8%), 235 (15), 157 (12), 139 (18), 123 (18), 91 (26), 79 (39), 77 (24), 65 (18) and 43 (100). High resolution mass spectrum required for $C_{15}H_{18}O_3S$: *m/z* 278.0977. Found: 278.0965.

cis/trans-*4-Acetyl-1,3-dimethyl-2-tosylcyclopentene* (8b): ν 3050, 1630 (CH=C), 1705 (CO), 1300 and 1145 cm^{-1} (SO_2); δ_H *(cis/trans)* 0.87, 1.23 (2d, *J*=6.5 Hz, 3H, C*H*$_3$CH), 1.98 (s, 3H, CH_3CO), 2.05 (s, 3H, C*H*$_3$CCH$_2$), 2.20-2.45 (m with s at 2.35, 4H, C*H*$_3$Ar and C*H*CH$_3$), 2.65 (s, 2H, CH_2), 3.07 (m, 1H, CHCO), 7.23 and 7.65 (2d, *J*=8.1 Hz, 4H, ArH); δ_C *(trans)* 15.41 (CH_3CCH_2), 21.03 (CH_3CH), 21.42 (CH_3Ar), 27.91 (CH_3CO), 39.98 (CH_2), 44.51 ($CHCH_3$), 56.00 (CHCO), 126.87, 129.54, 137.10, 138.74, 143.84, 152.64 (ArC and C=C) and 207.03 (CO); δ_C *(cis)* 14.80, 15.63 (CH_3CCH_2, CH_3CH), 21.43 (CH_3Ar), 29.45 (CH_3CO), 38.27 (CH_2), 42.60 ($CHCH_3$), 54.18 (CHCO), 126.98, 129.68, 137.96, 138.87, 143.92, 153.30 (ArC and C=C) and 206.28 (CO); *m/z* 292 (*M*$^+$, 1%), 250 (28), 249 (19), 157 (13), 139 (27), 137 (25), 95 (14), 94 (12), 93 (60), 92 (11), 91 (44), 79 (23), 78 (11), 77 (35), 65 (23), 53 (11) and 43 (100).

cis/trans-*1,3-Dimethyl-4-(methoxycarbonyl)-2-tosylcyclopentene* (8c): ν 3080, 1630 (CH=C), 1730 (CO), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.28 (d, *J*=6.5 Hz, 3H, C*H*$_3$CH), 2.15 (t, *J*=0.8 Hz, 3H, C*H*$_3$CCH$_2$), 2.43 (s, 3H, C*H*$_3$Ar), 2.61 (qd, *J*=6.5 and 4.7 Hz, 1H, C*H*CH$_3$), 2.79 (m, 2H, CH_2), 3.22 (m, 1H, CHCO), 3.60 (s, 3H, CH_3O), 7.31 and 7.74 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 15.38 (CH_3CCH_2), 20.34 (CH_3CH), 21.36 (CH_3Ar), 41.24 (CH_2), 45.75 ($CHCH_3$), 48.19 (CHCO), 51.77 (CH_3O), 127.07, 129.57, 129.62, 137.35, 138.63, 143.87

(ArC and C=C) and 174.30 (CO); *m/z* 249 (M^++1-CO_2Me, 5%), 248 (M^+-CO_2Me, 19), 152 (11), 139 (38), 93 (92), 92 (80), 91 (100), 77 (71), 65 (58), 55 (29) and 41 (46).

trans-*4-Cyano-3-phenyl-1-methyl-2-tosylcyclopentene* (8d): ν ($CHCl_3$) 3050, 1630 (CH=C), 2220 (C≡N), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.33 (t, *J*=0.7 Hz, 3H, CH_3CCH_2), 2.38 (s, 3H, CH_3Ar), 2.89 [ddq, $J_{a\text{-}b}$=17.0 Hz, $J_{a\text{-}c}$=4.0 Hz and $J_{a\text{-}Me}$=0.7 Hz, 1H, CH_2(a)], 2.96 (ddd, $J_{c\text{-}a}$=4.0 Hz, $J_{c\text{-}b}$=8 Hz and $J_{c\text{-}d}$=8.0 Hz, 1H, CHCN), 3.12 [ddq, $J_{b\text{-}a}$=17.0 Hz, $J_{b\text{-}c}$=8.0 Hz and $J_{b\text{-}Me}$=0.7 Hz, 1H, CH_2(b)], 4.46 (m, 1H, CHPh) and 6.93-7.75 (m, 9H, Ph and *p*-TolH); δ_C 15.58 (CH_3CCH_2), 21.44 (CH_3Ar), 34.72 (CHCN), 43.20 (CH_2), 57.94 (CHPh), 120.97 (CN), 127.34, 127.49, 127.79, 128.72, 129.33, 137.11, 137.75, 138.84, 144.03 and 153.37 (ArC and C=C); *m/z* 337 (M^+, 0.1%), 209 (16), 155 (18), 153 (34), 152 (43), 139 (13), 121 (20), 94 (12), 93 (85), 92 (25), 91 (100), 89 (18), 79 (20), 77 (27), 63 (11), 53 (21) and 51 (10). Anal. calcd. for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68; N, 4.15; and S, 9.50. Found: C, 71.17; H, 5.63; N, 4.05; and S, 9.41.

2-(Chloromethyl)-3-tosyl-1-butene (**9a**): ν 3085, 1630 (CH=C), 1300 and 1140 cm^{1} (SO_2); δ_H 1.43 (d, *J*=7.2 Hz, 3H, CH_3CS), 2.39 (s, 3H, CH_3Ar), 3.91 (q, *J*=7.2 Hz, 1H, CHS), 4.06, 4.18 (2d, *J*=12 Hz, 2H, CH_2Cl), 5.18, 5.48 (2s, 2H, CH_2=C), 7.30 and 7.67 (2d, *J*=8.1 Hz, 4H, ArH); δ_C 14.79 (CH_3CS), 21.59 (CH_3Ar), 48.29 (CH_2Cl), 61.88 (CHS), 121.59, 139.01 (CH_2=C), 129.32, 129.55, 133.51 and 144.93 (ArC); *m/z* 223 (M^+-Cl, 4%), 157 (30), 156 (22), 139 (10), 177 (10), 103 (32), 102 (17), 92 (51), 91 (41), 67 (100), 65 (38) and 41 (22).

2-(Chloromethyl)-3-tosyl-1,5-hexadiene (**9b**): ν 3060, 1640 (CH=C), 1300 and 1140 cm^{1} (SO_2); δ_H 2.50-2.35 (m with s at 2.40, 4H, CH_3Ar and 1H CH_2CS), 3.95 (m, 1H, CH_2CS), 3.81 (m, 1H, CHS), 4.05, 4.06 (2d, *J*=12.0 Hz, 2H, CH_2Cl, 5.00-5.14 (m, 2H, CH_2=CH), 5.14, 5.54 (2s, 2H, CH_2=C), 5.56 (m, 1H, CH=CH_2), 7.30 and 7.68 (2d, *J*=8.1 Hz, 4H, ArH); δ_C 21.60 (CH_3Ar), 32.38 (CH_2CS), 48.14 (CH_2Cl), 66.54 (CS), 118.46, 122.26, 138.38, 133.57 (2xC=C), 129.38, 129.58, 136.32 and 145.05 (ArC); *m/z* 249 (M^+-Cl, 3%), 157 (12), 130 (11), 129 (16), 128 (28), 93 (100), 92 (16), 91 (90), 79 (51), 78 (10), 77 (65), 65 (38), 53 (14), 51 (10) and 41 (16).

2-(Chloromethyl)-4-phenyl-3-tosyl-1-butene (**9d**): ν 3085, 1630, 800 (CH=C), 1300 and 1145 cm^{1} (SO_2); δ_H 2.40 (s, 3H, CH_3Ar), 2.94 (dd, *J*=14.0 and 11.4 Hz, 1H, CH_2Ph), 3.46 (dd, *J*=14.0 and 3.5 Hz, 1H, CH_2Ph), 3.72, 3.90 (2d, *J*=12.4 Hz, 2H, CH_2Cl), 4.00 (dd, *J*=11.4 and 3.5 Hz, 1H, CHS), 5.36, 5.51 (2s, 2H, CH_2=C), 7.15-7.40 (m with d at 7.29, *J*=7.9 Hz, 7H, Ph and 2H of *p*-Tol) and 7.71 (d, *J*=7.9 Hz, 2H, *p*-Tol); δ_C 21.66 (CH_3Ar), 34.35 (CH_2Ph), 48.17 (CH_2Cl), 68.16 (CHS), 122.22, 133.91 (CH_2=C), 126.88, 128.40, 129.10, 129.42, 129.65, 135.98, 136.48 and 145.07 (ArC); *m/z* 179 (M^+-Ts, 18%), 157 (12), 144 (12), 143 (100), 142 (31), 141 (13), 129 (59), 128 (73), 127 (16), 115 (27), 91 (86), 77 (13) and 65 (30).

4-(Chloromethyl)-3-tosyl-4-pentenenitrile (**9f**): ν ($CHCl_3$) 2240 (C≡N), 1300 and 1140 cm^{-1} (SO_2); δ_H 2.46 (s, 3H, CH_3Ar), 2.92 (dd, *J*=17.0 and 10.5 Hz, 1H, CH_2CN), 3.08 (dd, *J*=17.0 and 5.0 Hz, 1H, CH_2CN), 4.08 (d, *J*=5.7 Hz, 2H, CH_2Cl), 4.13 (m, 1H, CHS), 5.39, 5.71 (2s, 2H, CH_2=C), 7.38 and 7.71 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 18.23 (CH_2CN), 21.64 (CH_3Ar), 47.37 (CH_2Cl), 61.86 (CHS), 115.20 (CN), 123.42, 132.34 (CH_2=C), 129.28, 130.07, 135.49 and 146.22 (ArC); *m/z* 283 (M^+, 0.5%), 248 (10), 155 (54), 128 (12), 91

(100), 65 (42) and 63 (10). High resolution mass spectrum required for $C_{13}H_{14}ClNO_2S$: *m/z* 283.0434. Found: 283.0424.

Ethyl 4-(Chloromethyl)-3-tosyl-4-pentenoate (**9g**): ν ($CHCl_3$) 1730 (C=O), 1300 and 1140 cm^{-1} (SO_2); δ_H 1.14 (t, *J*=7.1 Hz, 3H, CH_3CH_2), 2.38 (s, 3H, CH_3Ar), 2.72 (dd, *J*=16.2 and 10.1 Hz, 1H, CH_2CO), 3.02 (dd, *J*=16.2 and 5.0 Hz, 1H, CH_2CO), 4.00 (q, *J*=7.1 Hz, 2H, CH_2CH_3), 4.03 (dd, *J*=12.8 and 0.9 Hz, 1H, CH_2Cl), 4.16 (dd, *J*=12.8 and 1.1 Hz, 1H, CH_2Cl), 4.25 (dd, *J*=10.1 and 5.0 Hz, 1H, CHS), 5.13, 5.51 (2s, 2H, CH_2=C), 7.29 and 7.65 (2d, *J*=8.1 Hz, 4H, ArH); δ_C 13.90 (CH_3CH_2), 21.53 (CH_3Ar), 33.93 (CH_2CO), 47.03 (CH_2Cl), 61.21 (CH_2O), 63.43 (CHS), 121.91, 132.96 (CH_2=C), 129.36, 129.62, 137.10, 145.33 (ArC) and 168.91 (CO); *m/z* 331 (M^+, 2%), 177 (32), 175 (100), 149 (10), 147 (29), 139 (22), 133 (25), 105 (16), 92 (13), 91 (39), 67 (33) and 65 (33). Anal. calcd. for $C_{15}H_{19}ClO_4S$: C, 54.46; H, 5.79; and S, 9.69. Found: C, 54.44; H, 5.78; and S, 10.01.

(E)-*5,5-Dimethyl-2-methylene-3-tosyl-3-hexen-1-ol* (**15**): ν 3500 (OH), 3080, 1640 (CH=C), 1300 and 1140 cm^{-1} (SO_2); δ_H 1.13 [s, 9H, $(CH_3)_3C$], 2.42 (s, 3H, CH_3Ar), 2.95 (br. s, 1H, OH), 4.25 (s, 2H, CH_2O), 4.45, 5.39 (2s, 2H, CH_2=C), 7.00 (s, 1H, CH=C), 7.28 and 7.66 (2d, *J*=7.9 Hz, 4H, ArH); δ_C 21.47 (CH_3Ar), 29.69 [$(CH_3)_3C$], 34.66 [$C(CH_3)_3$], 65.45 (CH_2O), 120.69, 138.81, 140.24, 151.40 (CH_2=C and CH=C), 128.58, 129.31, 135.01 and 144.05 (ArC); *m/z* 294 (M^+, 2%), 197 (10), 157 (11), 140 (20), 139 (40), 123 (25), 121 (17), 105 (21), 93 (30), 91 (92), 77 (35), 67 (20), 57 (100), 55 (24) and 41 (60). Anal. calcd. for $C_{16}H_{22}O_3S$: C, 65.27; H, 7.53; and S, 10.89. Found: C, 65.07; H, 7.49; and S, 10.98.

6-(Chloromethyl)-5-tosyl-6-hepten-2-one (**20**): R_f 0.65 (ether); ν 3080, 1650 (CH=C), 1710 (C=O), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.90 (m, 1H, CH_2CS), 2.08 (s, 3H, CH_3CO), 2.25 (m, 1H, CH_2CS), 2.40 (s, 3H, CH_3Ar), 2.52 (t, *J*=7.0 Hz, 2H, CH_2CO), 3.89 (dd, *J*=11.5 and 4.0 Hz, 1H, CHS), 4.11 , 4.16 (2d, *J*=16.5 Hz, 2H, CH_2Cl), 5.20, 5.59 (2s, 2H, CH_2=C), 7.35 and 7.77 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 21.55 (CH_3Ar), 22.10 (CH_2CS), 29.76 (CH_3CO), 39.32 (CH_2CO), 48.87 (CH_2Cl), 65.25 (CHS), 122.13, 133.53 (CH_2=C), 129.24, 129.58, 136.71, 145.00 (ArC) and 206.70 (CO); *m/z* 209 (M^+-C_4H_7ClO, 9%), 159 (10), 91 (14), 81 (15), 65 (10) and 43 (100).

6-(Chloromethyl)-1,1,1,3,3,5-hexadeuterio-5-tosyl-6-hepten-2-one (**21**): R_f 0.65 (ether); ν 3080, 1650 (CH=C), 1710 (C=O), 1300 and 1150 cm^{-1} (SO_2); δ_H 1.90, 2.26 (2d, *J*=12.0 Hz, 2H, CH_2D), 2.45 (s, 3H, CH_3Ar), 4.10, 4.14 (2d, *J*=15.5 Hz, 2H, CH_2Cl), 5.20, 5.68 (2d, *J*=0.8 Hz, 2H, CH_2=C), 7.35 and 7.73 (2d, *J*=8.2 Hz, 4H, ArH); δ_C 21.50 (CH_3Ar), 21.95 (CH_2CS), 29.36 (sept, *J*=19.0 Hz, CD_3CO), 39.30 (q, *J*=18.5 Hz, CD_2CO), 48.76 (CH_2Cl), 64.95 (t, *J*=20 Hz, CDS), 122.09 (CH_2=C), 129.19, 129.54, 133.48, 136.62, 144.96 (ArC and *C*=CH_2) and 212.95 (CO); *m/z* 165 (M^+-Ts, 6%), 91 (13), 84 (15), 65 (17), 46 (100), 45 (69), 44 (19) and 43 (10).

Reduction of Compounds 5f, 6c and 8a with Sodiun Amalgam. General Procedure.

To a suspension of anhydrous Na_2HPO_4 (251 mg, 1.75 mmol) and *ca.* 6% sodium amalgam (1.70g, 4.4 mmol) in dry methanol (5ml) was droped at 0°C a solution of the corresponding sulfone (0.44 mmol) in methanol (1.5 ml). The reaction mixture was stirred at the temperature and for the time shown in table 4 and monitorized by TLC and GLC. Then the reaction was hydrolyzed with water and extracted with CH_2Cl_2 (2x10 ml) and the organic layer was dried over anhydrous Na_2SO_4 and evaporated in vacuo (15 torr) yielding crude pure compounds **22-24** and **26**. Yields and physical data are included on the table 4, spectral and analytical data follow:

2-[2-(2-Methylenecyclopopyl)ethyl]-1,3-dioxolane (**22**): ν 3080 and 1640 cm^{-1} (CH=C); δ_H 1.05-1.95 (m, 7H, CH_2CH_2CHO and $CHCH_2C{=}C$), 3.78 (m, 4H, 2xCH_2O), 4.81 (t, J=4.5 Hz, 1H, CHO), 5.26 and 5.33 (2m, 2H, $CH_2{=}C$); δ_C 9.20 ($CH_2C{=}C$), 15.14 (CHC=C), 27.30, 33.34 (CH_2CH_2CO), 64.64 (2xCH_2O), 102.49 ($CH_2{=}C$), 104.02 (CHO) and 136.38 ($C{=}CH_2$); m/z 154 (M^+, 1%), 153 (M^+-1, 4), 99 (13), 81 (16), 79 (13), 73 (100), 45 (35) and 41 (10).

2-[2-(2-Methyl-1-cyclopropenyl)ethyl]-1,3-dioxolane (**23**): ν 3080 and 1640 cm^{-1} (CH=C); δ_H 0.72 (s, 2H, $CH_2C{=}C$), 1.25-1.95 (m, 4H, CH_2CH_2CHO), 1.96 (s, 3H, CH_3), 3.89 (m, 4H, 2xCH_2O) and 4.84 (t, J=4.5 Hz, 1H, CHO); δ_C 8.04 ($CH_2C{=}C$), 11.18 (CH_3), 20.67, 31.59 (CH_2CH_2CO), 64.71 (2xCH_2O), 103.75 (CHO) 105.91 and 108.92 (C=C); m/z 154 (M^+, 1%), 153 (M^+-1, 4), 99 (11), 81 (16), 79 (13), 73 (100), 45 (35) and 41 (10).

2-Isopropyl-4-methyl-2,5-dihydrofuran (**24**):[18] ν 3080 and 1580 cm^{-1} (CH=C); δ_H 0.8, 0.85 [2t, J=6.8 Hz, 6H, $(CH_3)_2$CH], 1.62-1.81 (m with s at 1.71, 4H, CH_3CCH_2 and $CHCH_3$), 4.43 (deform. s, 2H, CH_2O), 4.54 (m, 1H, CHO) and 5.34 (deform. s, 1H, CH=C); δ_C 12.26 ($CH_3C{=}C$), 17.85 [$(CH_3)_2$CH], 33.59 ($CHCH_3$), 78.04 (CH_2O), 91.97 (CHO), 121.79 and 126.72 (C=C); m/z 126 (M^+, 2%), 83 (100), 82 (12), 5 (17) and 43 (5).

erythro/threo-*4-(1-Hydroxymethyl)-1-methylcyclopentene* (**26**): ν 3360 cm^{-1} (OH); δ_H 1.09, 1.10 (2d, J=7.0 Hz, 3H, CH_3CO), 1.63 (s, 3H, $CH_3C{=}C$), 1.95-2.60 (m, 6H, 2x$CH_2C{=}C$, CHCO and OH), 4.11 (m, 1H, CHO) and 5.17 (broad s, 1H, CH=C); δ_C 16.51, 16.57 (CH_3CO), 21.49, 21.52 ($CH_3C{=}C$), 35.02, 35.62, 39.14, 39.73 (2x$CH_2C{=}C$), 45.95, 45.97 (CHCO), 71.83, 71.85 (CO), 123.25, 123.51 (CH=C), 139.41 and 139.70 (C=CH); m/z 126 (M^+, 4%), 108 (9), 93 (100), 91 (20), 82 (10), 79 (30), 77 (20), 67 (17), 53 (14), 45 (18), 43 (16) and 41 (13).

Reduction of Compound 7d with Samarium(II) Iodide. Synthesis of Compound 25.

Over a freshly prepared 0.2M solution of SmI_2[23] (25 ml) was added, at -20°C, first the sulfone **7d** (328 mg, 1.00 mmol) and then HMPA (4 ml), staying the mixture at -20°C during 1.5 hours. The reaction was hydrolyzed with 3M hydrochloric acid (20 ml) and extracted with ether (2x10 ml). The ethereal solution was dried over anhydrous Na_2SO_4 and evaporated *in vacuo* (15 torr). The residue was purified by column chromatography (hexane/ether) yielding the pure compound **25** (see table 4).

4-Methyl-2-phenyl-4-penten-2-ol (**25**): ν 3450 (OH), 3080 and 1640 cm^{-1} (CH=C); δ_H 1.32 (s, 3H, CH_3CO), 1.49 (s, 3H, $CH_3C{=}C$), 2.20 (broad s, 1H, OH), 2.44, 2.57 (2d, J=13.0 Hz, 2H, CH_2), 4.67, 4.82 (2s, 2H, $CH_2{=}C$), 7.15-7.41 (m, 5H, Ph); δ_C 24.18 ($CH_3C{=}C$), 30.66 (CH_3CO), 52.02 (CH_2CO), 76.58 (CO), 115.64 ($CH_2{=}C$), 124.70, 124.77, 126.48. 128.05 and 142.56 ($C{=}CH_2$ and ArC); m/z 174 (M^+-2, 1%), 159 (15), 128 (26), 121 (87), 105 (19), 77 (29), 51 (15) and 43 (100).

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