"*Syn-Effect*" in the Desulfonylation Reaction of α,α-Dialkylated (*E*)-Allylic Sulfones

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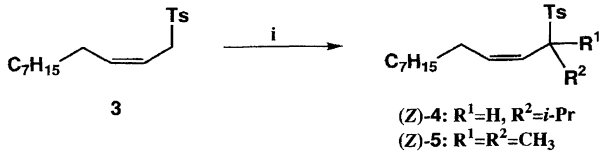
It was found that the desulfonylation reaction of α,α-dialkylated (*E*)-allylic sulfones with a base preferentially affords the sterically unfavorable (*Z*)-alkadienes. The relative degree of the "*syn-effect*", which is herein defined as an effect which stabilizes the *syn*-conformation, leading to (*Z*)-products, in the transition state against the steric hindrance, was revealed for various substituents at the δ-position of the (*E*)-allylic sulfones to be as follows: RO–≫CH_3– > RS– > –CH_2– > $(CH_3)_2CH$–≫$(CH_3)_3C$– > C_6H_5–. This finding is in accord with a previously found tendency in the conversion of (*E*)-vinylic sulfones to the corresponding allylic sulfones under basic conditions.

In the previous papers[1,2] we reported on the stereochemistry of the conversion of vinylic sulfones to the corresponding allylic sulfones by a treatment with a base under mild conditions; that is, (*E*)-vinylic sulfones preferentially afforded (*Z*)-allylic sulfones as kinetically-controlled products, while (*Z*)-vinylic sulfones and α-alkylated vinylic sulfones gave (*E*)-allylic sulfones exclusively. The former experimental results were rationalized by a new concept, "*conformational acidity*",[1,2] which essentially implies the "*syn-effect*".[3]

On the other hand, Otera and his co-workers have reported[4] an interesting phenomenon in which (*E*)-allylic sulfone (**1**) underwent a desulfonylation reaction due to a treatment with a base, giving (*E,Z*)-alkadiene (**2**) in preference to its (*E,E*)-isomer, as shown in Scheme 1.

In order to confirm the propriety to apply the concept of the "*syn-effect*" to this desulfonylation reaction, the above result was first compared with a case utilizing (*Z*)-allylic sulfone as a substrate. (*Z*)-2-Methyl-3-tosyl-4-tridecene [(**Z**)-**4**] was prepared from (*Z*)-1-tosyl-2-undecene (**3**), which is readily available by our original method,[5] via α-alkylation, as illustrated in Scheme 2. The abbreviation Ts in the Scheme hereafter means the *p*-tolylsulfonyl (=tosyl, *p*-$CH_3C_6H_4SO_2$–) group.

When compound (**Z**)-**4** was treated with excess amounts of *t*-BuOK under similar conditions to those employed by Otera and co-workers,[4] the isomerization of (**Z**)-**4** to the thermodynamically more stable (*E*)-isomer [(**E**)-**4**] took place prior to the expected desulfonylation reaction. It may have proceeded through an initial formation of α-carbanion (**4a**) of (**Z**)-**4** due to the remaining acidic α-methine proton, followed by equilibrium between vinylic sulfone intermediate (**4b**), as shown in Scheme 3. It is noteworthy that the intermediary anion (**4b**) of vinylic sulfone cannot revert to **4a**, but is selectively converted to (**E**)-**4** via **4c** by a steric demand, as has been observed previously.[1,2]



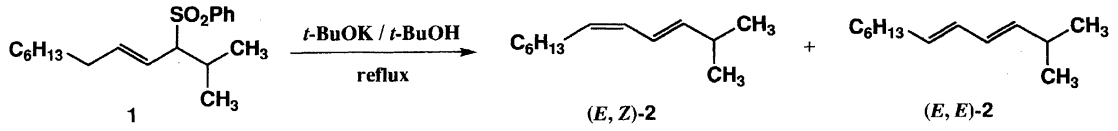
3

(**Z**)-**4**: R^1=H, R^2=*i*-Pr
(**Z**)-**5**: R^1=R^2=CH_3

(i) for (**Z**)-**4**, *n*-BuLi (1 molar amount) /*i*-PrI (1.09 molar amount); for (**Z**)-**5**, *n*-BuLi (2 molar amounts) / MeI (2 molar amounts).

Scheme 2.

Therefore, an α,α-dimethylated allylic sulfone, (*Z*)-2-methyl-2-tosyl-3-dodecene [(**Z**)-**5**], was prepared (Scheme 2) so as to avoid the isomerization of (*Z*)-allylic sulfone to (*E*)-isomer via α-carbanion. It was proved that a treatment of (**Z**)-**5** with *t*-BuOK in a similar manner affords only (*E*)-2-methyl-2,4-dodecadiene (**6**, Scheme 4) in accord with the previous result observed in the conversion of (*Z*)-vinylic sulfone to the corresponding allylic sulfone,[1,2] due to a steric congestion excluding the *syn*-conformation [(**Z**)-**5b**] in the



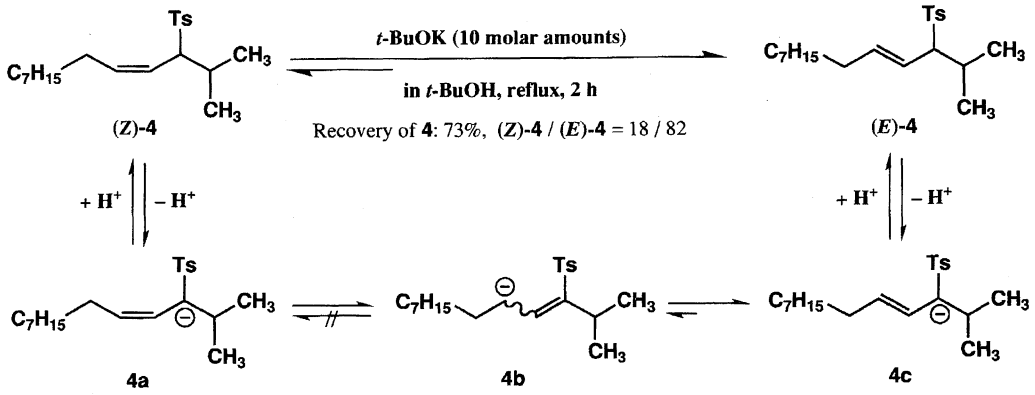
1

(*E*, *Z*)-**2**

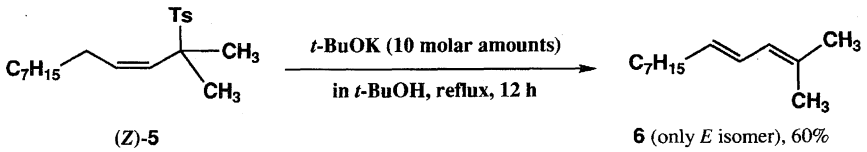
(*E*, *E*)-**2**

(*E*, *Z*) : (*E*, *E*) = 81 : 19

Scheme 1.



Scheme 3.



Scheme 4.

transition state (Fig. 1).

Toward the elucidation of the origin of the "*syn-effect*", we describe herein the detailed results concerning an investigation of the stereochemistry for the desulfonylation reaction of various α,α-dialkylated (*E*)-allylic sulfones, including the time-course of the reaction.

Results and Discussion

Preparation of α,α-Dialkylated (*E*)-Allylic Sulfones. The stereochemically pure α,α-dialkylated (*E*)-allylic sulfones used in the present investigation were prepared according to the procedures shown in Schemes 5, 6, and 7.

The stereoselective preparation of α,α-dialkylated (*E*)-allylic sulfones (**11a—e**) was achieved by applying our original methodology[2a,2b] through the regioselective iodosulfonization of 1-alkenes (**7a—d**) and the stereoselective isomerization of α-monoalkylated (*E*)- and/or (*Z*)-vinylic sulfones (**9a—e**)[6] to the corresponding (*E*)-allylic sulfones (**10a—e**), as shown in Scheme 5.

α,α-Dialkylated (*E*)-allylic sulfones (**11f,g**), having an isopropyl or *t*-butyl substituent at the δ-position, were prepared starting from (*E*)-allylic alcohols (**12a,b**) via allylic sulfides (**13a,b**), followed by oxidation to the sulfones (**14a,b**) and subsequent dialkylation (Eq. 1 of Scheme 6). The preparation of (*E*)-1-phenyl-4-propyl-4-tosyl-2-heptene (**11h**) was accomplished by using 3-buten-1-ol as a starting material according to the procedure expressed in Eq. 2 of Scheme 6, since the desulfonylation reaction of **11h** took place very easily under basic conditions, as shown later.

α,α-Dialkylated (*E*)-allylic sulfones (**20a—d,f—h**) possessing an alkoxy or an alkylthio group at the δ-position were derived from the corresponding homoallylic alcohols (**17a—d**) through iodosulfonization, a subsequent treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) leading to (*E*)-allylic sulfones (**18a—d**), and dialkylation, followed by ether or thioether formation, as shown in Eq. 1 of Scheme 7.

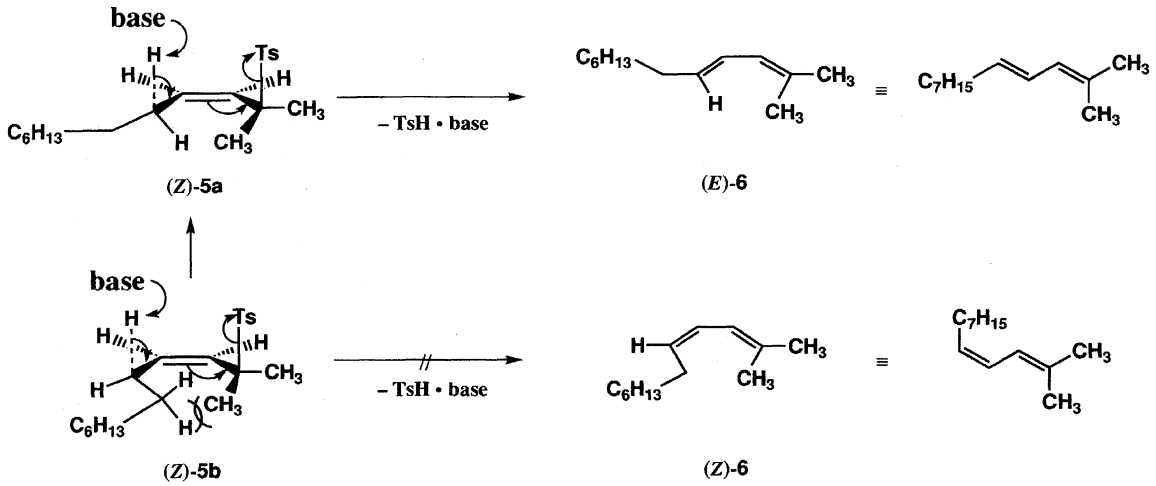
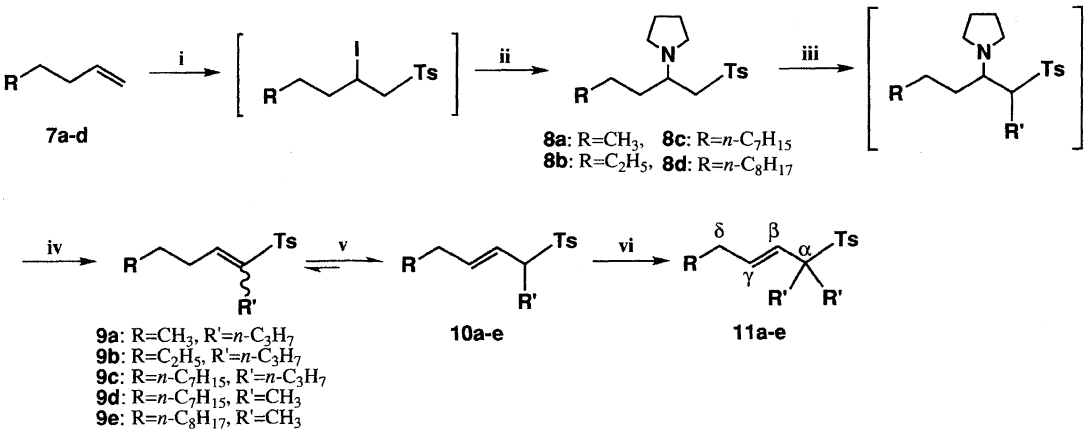
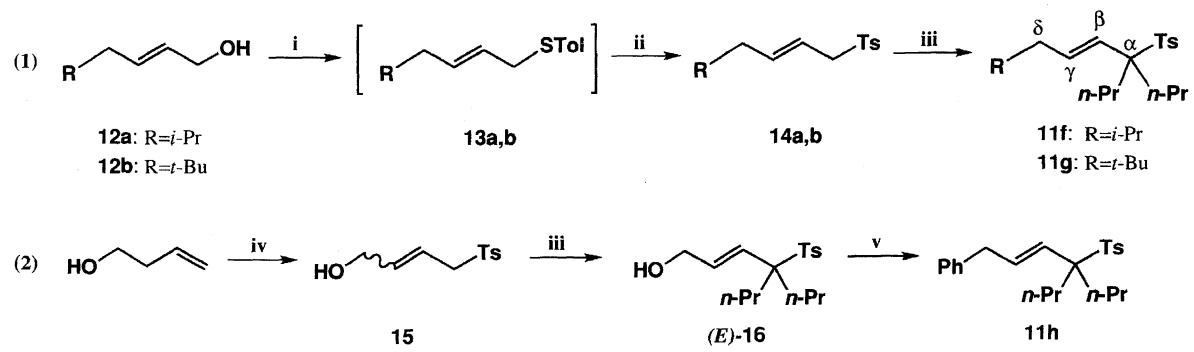


Fig. 1.



(i) $TsNa \cdot 4H_2O / I_2$ in AcOEt / H_2O; (ii) pyrrolidine in CH_3CN; (iii) *n*-BuLi in HMPA / THF, then R'I; (iv) *m*-CPBA / Na_2CO_3 in CH_2Cl_2; (v) *t*-BuOK in *t*-BuOH; (vi) *n*-BuLi in THF, then R'I

Scheme 5.



(i) MsCl / Et_3N, then *p*-TolSLi; (ii) OXONE; (iii) *n*-BuLi / *n*-PrI, [**(*E*)-16** was separated by TLC]; (iv) $TsNa \cdot 4H_2O / I_2$, then DBU; (v) MsCl / Et_3N, then Ph_2CuLi

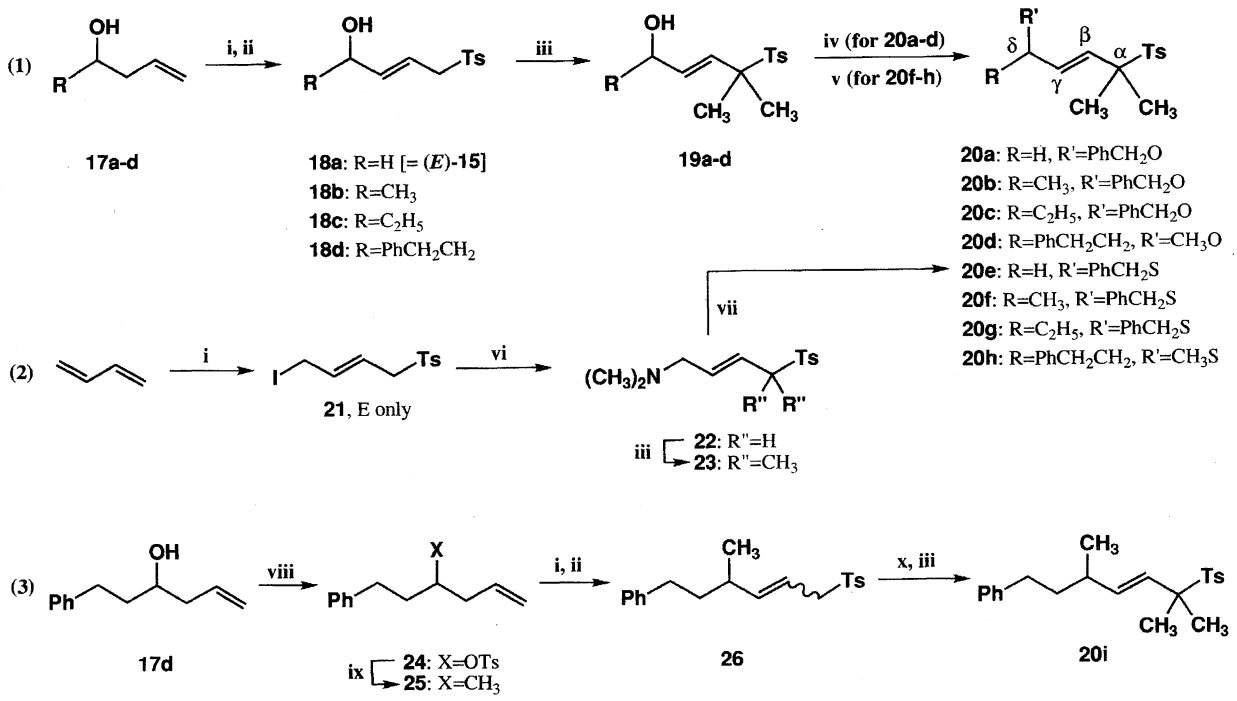
Scheme 6.

(*E*)-1-Benzylthio-4-methyl-4-tosyl-2-pentene (**20e**) and (*E*)-2,5-dimethyl-7-phenyl-2-tosyl-3-heptene (**20i**) were prepared from 1,3-butadiene and 1-phenyl-5-hexen-3-ol (**17d**), respectively, as illustrated in Eqs. 2 and 3 of Scheme 7.

Desulfonylation Reaction of α,α-Dialkylated (*E*)-Allylic Sulfones. Desulfonylation reactions of the (*E*)-allylic sulfones prepared as mentioned above to the corresponding alkadienes were carried out by utilizing *t*-BuOK as a base for determining the relative degree of the "*syn-effect*" for various substituents at the δ-position.

Table 1 gives the time-course of the desulfonylation reactions of α,α-dialkylated (*E*)-allylic sulfones (**11a—h**). From the fact that the isolated total yield of the alkadienes (**27a—h**) and the recovered (*E*)-allylic sulfones were quantitative for all of the experiments examined, it is obvious that the desulfonylation reaction proceeded very cleanly without any other side reactions. The *E*/*Z*-ratios of the resulting alkadienes (**27c,d**) were affected to some extent by the difference in the bulkiness of the α-substituents of the substrates [**11c** ($R' = n\text{-}C_3H_7$), **11d** ($R' = CH_3$)], even though the (*Z*)-isomers predominated in both cases. To our surprise, not only **11a—e**, in which R is a primary alkyl group, but also **11f** ($R = i\text{-}C_3H_7$), afforded (*Z*)-alkadiene (**27f**) in preference to the sterically more favorable (*E*)-isomer. Only **11g** ($R = t\text{-}C_4H_9$) was preferentially converted to (*E*)-alkadiene (**27g**), but still along with significant amounts (about 25%) of the (*Z*)-isomer.

In our previous investigation,[1,2] (*E*)-4,4-dimethyl-1-tosyl-1-pentene as an (*E*)-vinylic sulfone, corresponding to **11g**, was exclusively transformed to (*E*)-allylic sulfone by a treatment with DBU under mild conditions. This stereochemical outcome, which was different from the present one, must have been brought about by the involvement of a further isomerization of (*Z*)-allylic sulfones, which were initially formed, in part, through equilibrium between the vinylic and allylic sulfones, resulting in the exclusive formation of thermodynamically more stable (*E*)-allylic sulfones. Thus, the present results appear to reflect the direct degree of the "*syn-effect*" for various substituents by considering that the proportion of the (*E*)-isomer of the resulting alkadienes to the (*Z*)-isomer were not very much changed during the course of the reaction time, except for the case of α,α-dialkylated (*E*)-



(i) $TsNa \cdot 4H_2O$ / I_2, (ii) DBU; (iii) *n*-BuLi / CH_3I; (iv) Ag_2O / R'X in DMF; (v) PBr_3 / pyridine in CH_2Cl_2, then R'SH / *n*-BuLi or NaH (vi) $(CH_3)_2NH$; (vii) CH_3I, then $LiSCH_2Ph$; (viii) *n*-BuLi / TsCl; (ix) Me_2CuLi; (x) Separation of *(E)*-form.

Scheme 7.

allylic sulfones (**20a—d**) possessing an alkoxy group at the δ-position, as shown later. Ultimately, it has been now confirmed that the "*syn-effect*" works even for relatively bulky substituents, such as the isopropyl and *t*-butyl groups at the δ-position of the starting (*E*)-allylic sulfones in the desulfonylation reaction.

Several explanations for the "*syn-effect*" have been proposed:[2c,3b] (1) 6π-electrons homoaromaticity, (2) a σ-orbital interaction, (3) a dipole–dipole interaction, (4) chelation, and (5) hydrogen bonding.[3e] We have so far been discussing 6π-electrons homoaromaticity as one of the most probable explanations among them for the "*syn-effect*" observed in our experimental investigation.[1,2] Figure 2 illustrates this consideration for the desulfonylation reaction of **11a—e**. Namely, the *syn*-conformation (III) is favored over the *anti*-conformation (IV) due to a stabilizing interaction between the developing charge at the β-position and the CH_2-group at the ε-position. It naturally requires that the four carbon atoms ($C_{\beta-\varepsilon}$ in Fig. 2) participating in the homoaromaticity lie on the same plane in order to get their p-orbitals and pseudo p-orbital of allylic CH_2 to overlap most effectively. In the case of bulky substituents, such as the *t*-butyl group, however, it appears to be quite difficult not only to take such a congested eclipsed conformation in the transition state without widening the angle of C_γ–C_δ–C_ε (and/or C_β–C_γ–C_δ), but also to consider a pseudo p-orbital on the *t*-butyl group participating in the 6π-electrons homoaromaticity, as in the case of a methyl or methylene group. Therefore, the interaction between the σ-orbital of the allylic C–H or C–R bond and the *anti*-bonding orbital (π^*) of an olefin; namely, the $\sigma \rightarrow \pi^*$ interaction (**11g-I** and **11g-II** in Fig. 3), as a sort of hyperconjugation in the transition state, should not be excluded as a possible origin of the "*syn-effect*". It is plausible that the "*conformational acidity*"[2a] of both of the allylic protons is increased to some extent to afford significant amounts (about 25%) of (*Z*)-**27g** due to an effective overlap of the σ-orbitals of allylic CH_2 and the π^*-orbital by widening the C_γ–C_δ–C_ε angle in the eclipsed conformation (**11g-I**), compared with the sterically more favorable transition state **11g-II** leading to a major product, (*E*)-**27g**.

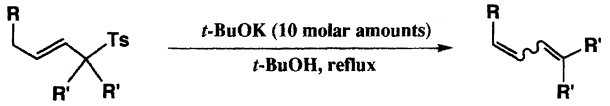
(*E*)-1-Phenyl-4-propyl-4-tosyl-2-heptene (**11h**) readily gave (*E*)-alkadiene (**27h**) almost exclusively (Table 1). This result suggests that the desulfonylation reaction proceeded via the *anti*-periplanar conformation (**11h-II**) to stabilize the developing anion by conjugation with the neighboring double bond and phenyl group, while the ability of the *syn*-conformation (**11h-I**) to keep such a stabilizing conjugation is sterically impossible (Fig. 4).

The experimental results concerning the desulfonylation reaction of (*E*)-1-benzyloxy- and 1-benzylthio-4-methyl-4-tosyl-2-pentenes (**20a,e**) are given in Table 2. (*E*)-Allylic sulfone (**20a**), having a benzyloxyl group at the δ-position, exclusively gave (*Z*)-**28a** in accord with the previous result observed in the conversion of vinylic sulfones to allylic sulfones.

The desulfonylation reaction of **20e** was very fast, and came to completion after 10 min, giving the corresponding diene (**28e**) in quantitative yield ($E/Z = 29/71$).

In order to determine the relative degree of the "*syn-effect*" for various substituents at the δ-position of (*E*)-allylic sulfones, similar experiments were performed for δ,δ-disub-

Table 1.



11a-h 27a-h

	Substrate	Time	Conversion/%	E/Z of **27**[a]
11a	R=CH_3 R′=n-C_3H_7	1 h	2	11/89
		8 h	13	11/89
		12 h	22	10/90
		24 h	42	10/90
		48 h	66[b]	9/91
		96, 144 h	Quant.	10/90
11b	R=C_2H_5 R′=n-C_3H_7	1 h	3	19/81
		8 h	28	19/81
		12 h	41[b]	19/81
		24, 48, 99 h	Quant.	21/79
11c	R=n-C_7H_{15} R′=n-C_3H_7	1 h	7	31/69
		4 h	23	31/69
		8 h	41	32/68
		12 h	56	32/68
		24 h	90[b]	32/68
		48, 96 h	Quant.	31/69
11d[c]	R=n-C_7H_{15} R′=CH_3	1 h	11	19/81
		4 h	35	19/81
		8 h	60	18/82
		12 h	76	18/82
		24 h	Quant.[b,d]	19/81
		48 h	Quant.	20/80
11e	R=n-C_8H_{17} R′=CH_3	1 h	11	18/82
		4 h	42	20/80
		8 h	89[b]	20/80
		12 h	Quant.	20/80
		25 h	Quant.	26/74
11f	R=i-C_3H_7 R′=n-C_3H_7	1 h	Trace	37/63
		8 h	7	35/65
		12 h	8	35/65
		24 h	13	36/64
		48 h	47	35/65
		96, 120,[b] 168, 216 h	Quant.[b]	35/65
11g	R=t-C_4H_9 R′=n-C_3H_7	1 d	Trace	71/29
		8 d	13	73/27
		12 d	29	73/27
		24 d	55	74/26
		36 d	69[b]	74/26
		48 d	89	76/24
		60 d	Quant.	76/24
11 h	R=C_6H_5 R′=n-C_3H_7	8 min	Quant.[b]	92/8

a) The ratios were determined by 400 MHz ^{1}H NMR spectra. b) Isolated total yield of **11** and **27** was quantitative. c) **11d** = (*E*)-**5**. d) (*E*)-**27d** = **6**.

stituted allylic sulfones (Table 2). The relative degree of the "*syn-effect*" for the substituents R^1X and R^2Y was justified by observing the *E*/*Z* ratios of the resulting diene compounds (III and IV in Fig. 5).

The structures of the (*E*)- and (*Z*)-isomers of the dienes were determined as follows: Diene **28i** was confirmed by a

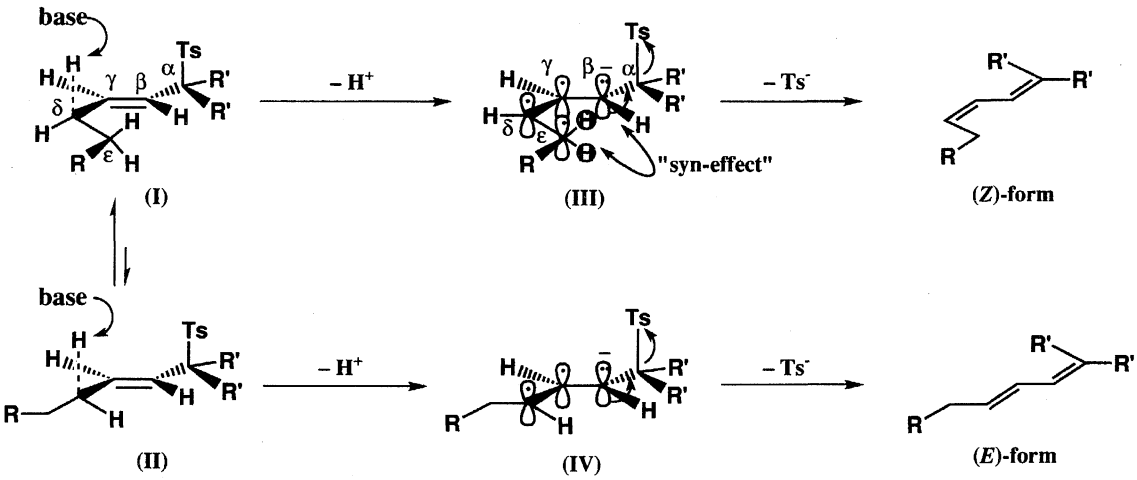


Fig. 2.

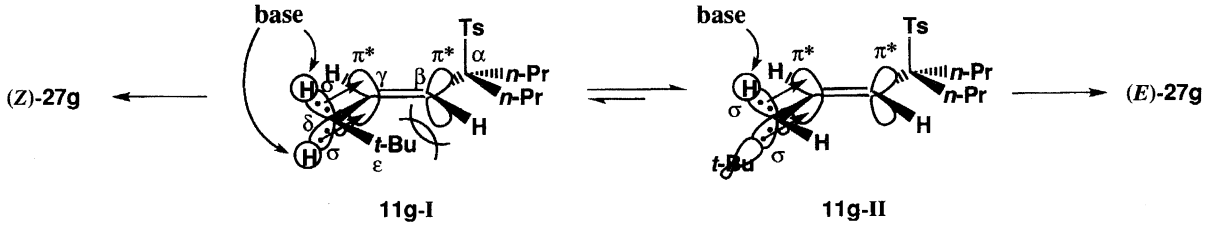


Fig. 3.

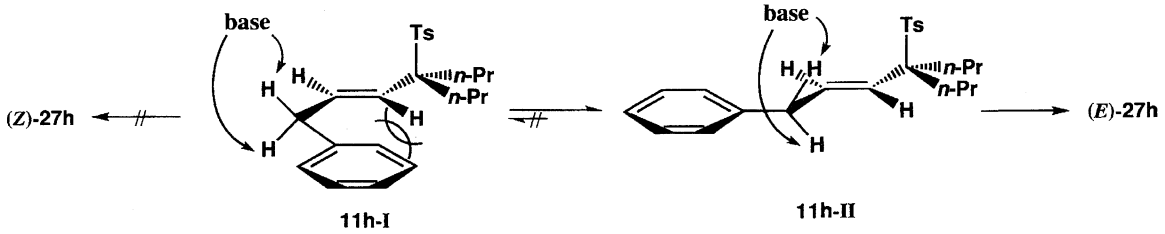


Fig. 4.

comparison with an authentic sample [(*E*)-**28i**] prepared by a stereoselective method (Eq. 1 of Scheme 8).[7] It was quite difficult to discriminate the olefinic protons (Ha and Hb) of the dienylethers (**28b—d**) and thioethers (**28f—h**) based on their coupling patterns in the ^{1}H NMR spectra. Therefore, Ha was partially labeled by deuterium, as shown in Eq. 2 of Scheme 8, in order to assign them with certainty. Based on this assignment of Ha and Hb, the measurement of NOE (for **28d**) or NOESY (for **28g**, (*E*)- and (*Z*)-isomers could not be separated) allowed us to confirm the structures of the (*E*)- and (*Z*)-isomers of the diene products (**28b—d,f—h**), since each olefinic proton of the isomeric products showed the same chemical shifts as those of structually confirmed products (**28d,g**).

The desulfonylation reaction of (*E*)-2,5-dimethyl-7-phenyl-2-tosyl-3-heptene (**20i**) to the corresponding diene (**28i**) was performed in order to compare the degree of the "*syn-effect*" for the methyl and methylene groups at the δ-position of the substrate (Table 2).

As previously described,[1,2] a steric difference among the linear alkyl substituents R in $RCH_2CH{=}CHCR'_2Ts$ must not be very important when determining the relative degree of the "*syn-effect*" for the δ-substituents. It can therefore be concluded from the results given in Table 2 that the "*syn-effect*" for the methyl group is greater than that for the methylene group.

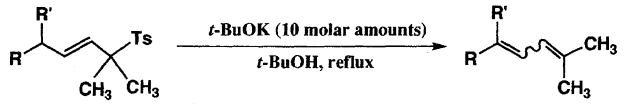
Similar examinations were carried out for the methyl, methylene, alkoxy, and alkylthio groups (Table 2).

From these results and the facts described above (Table 1), the relative degree of the "*syn-effect*" for various δ-substituents of α,α-dialkylated (*E*)-allylic sulfones in the desulfonylation reaction was determined to be as follows:

$$RO{-}\,(R = CH_3, PhCH_2) \gg CH_3{-} > RS{-}\,(R = CH_3, PhCH_2) > {-}CH_2{-} > (CH_3)_2CH{-} \gg (CH_3)_3C{-} > C_6H_5{-}$$

These results are in good accord with previous results,[1,2] and a remarkably strong "*syn-effect*" was again observed for the alkoxy substituents at the δ-position. This is attributable to several causes, as shown in Fig. 5:[1b,2c] (1) effective 6π-electrons homoaromaticity using a pair of non-bonding electrons on an oxygen atom, (2) intramolecular hydrogen bond-

Table 2.



20a-i 28a-i

	Substrate	Time	Conversion/%	E/Z of **28**[a]
20a	R=H R′=OCH_2Ph	1 h	Quant.[b]	0/100
20b	R=CH_3 R′=OCH_2Ph	1 h	6	14/86
		4 h	25	14/86
		12 h	58	16/84
		25 h	85	18/82
		48 h	Quant.[c]	26/74
		144 h	Quant.	87/13
20c	R=C_2H_5 R′=OCH_2Ph	1 h	1	0/100
		4 h	7	4/96
		12 h	23	5/95
		25 h	47	6/94
		48 h	89	10/90
		72 h	Quant.[c]	13/87
		144 h	Quant.[d]	49/51
20d	R=CH_2CH_2Ph R′=OCH_3	1 h	5	0/100
		4 h	14	7/93
		12 h	42	9/91
		25 h	81	10/90
		48 h	Quant.[c]	25/75
		144 h	Quant.	41/59
20e	R=H R′=SCH_2Ph	10 min	Quant.[e]	29/71
20f	R=CH_3 R′=SCH_2Ph	15 min	83[e]	81/19
20g	R=C_2H_5 R′=SCH_2Ph	15 min	86[e]	43/57
20h	R=CH_2CH_2Ph R′=SCH_3	15 min	94[e]	40/60
20i	R=CH_2CH_2Ph R′=CH_3	1 h	2	81/19
		8 h	20	80/20
		24 h	40	77/23
		48 h	66[c]	77/23
		96, 144 h	Quant.	77/23

a) The ratios were determined by 400 MHz ^{1}H NMR spectra. b) Product **28a** was isolated in 75% yield. c) Isolated total yield of **20** and **28** was quantitative. d) Isolated total yield of **20** and **28** was 94%. e) Isolated yields of **28**.

ing, and (3) the relatively high electronegativity of the oxygen atom, which strengthens the $\sigma\rightarrow\pi^*$ interaction of the allylic C–H bond(s) with the π^*-orbital of the olefin in the transition state in consequence of an increase in the acidity of the allylic proton(s), whereas the $\sigma\rightarrow\pi^*$ interaction of the allylic C–OR″ bond is very unlikely, since $R''O^+$ must be considered in the no-bond resonance structure.

Though it is still an open question why the alkylthio group lies between the methyl and methylene groups, the following should be considered: (a) the difference in the p- or pseudo p-orbital size and bond length in connection with 6π-electrons homoaromaticity, (b) the possibility of hydrogen bonding, (c) the polarizability and electronegativity, and (d) the participation of 3d-orbital of sulfur atom to stabilize the developing anion at the neighboring carbon atom, which may reduce the $\sigma\rightarrow\pi^*$ interaction between allylic C–H and π^*-

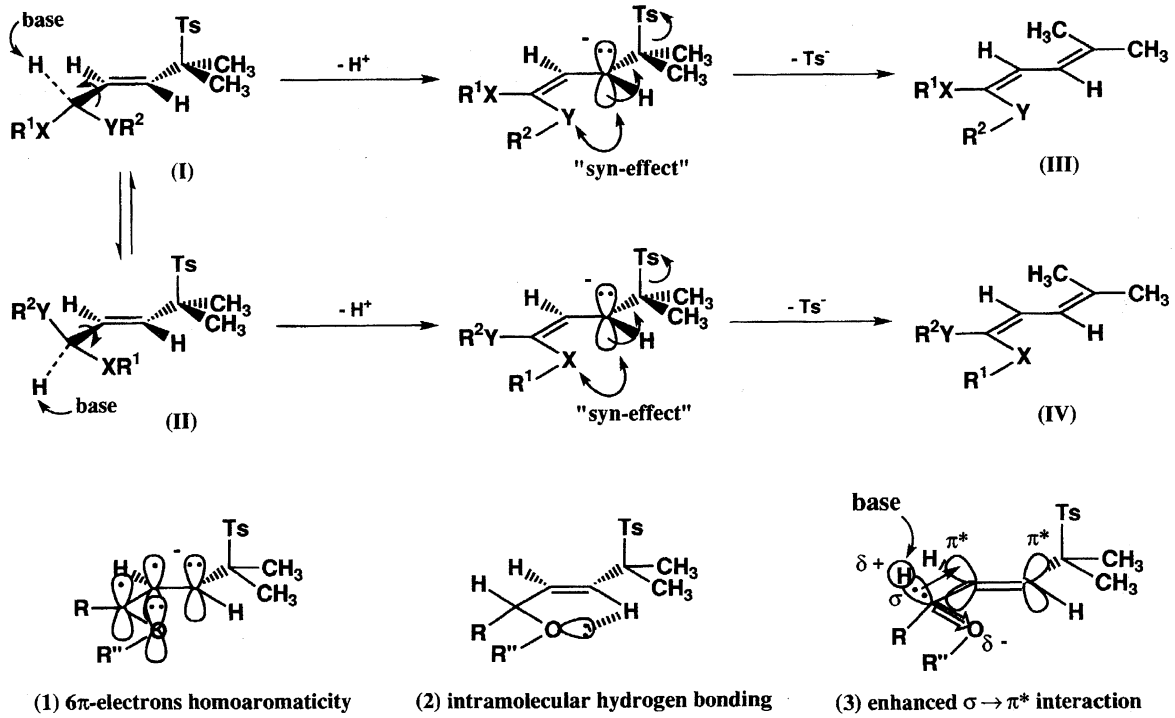
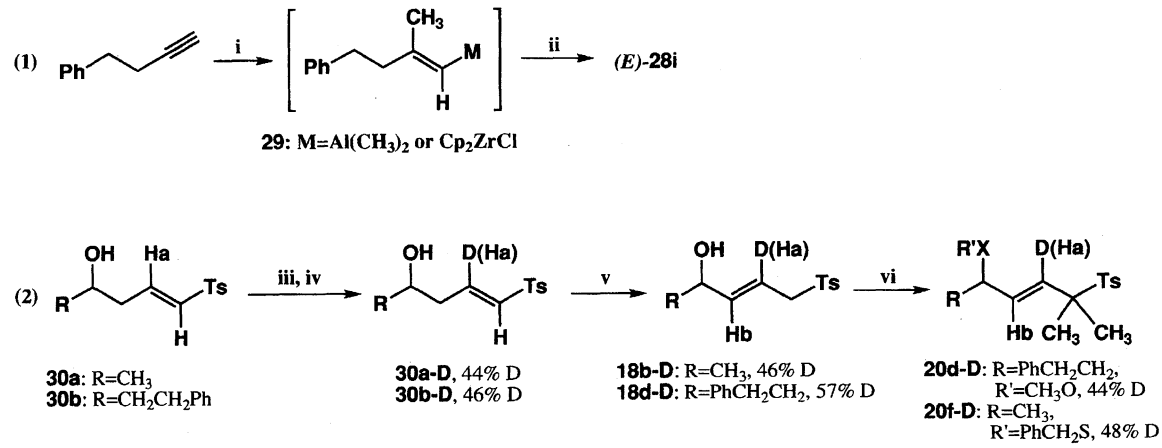


Fig. 5.



(i) $(CH_3)_3Al$ (2.0 molar amounts), Cp_2ZrCl_2 (1.0 molar amount) in $ClCH_2CH_2Cl$, 50 °C, 3 h; (ii) $ZnCl_2$ (1 molar amount), $PdCl_2(Ph_3P)_2$ (5 mol%), DIBAL-H (10 mol%), $BrCH=C(CH_3)_2$, r.t., overnight; (iii) $NaBD_4$ (2 molar amounts) in MeOH, 0 °C, quant. from **30a**, 94% from **30b**; (iv) LDA (3 molar amounts), $(PhSe)_2$ (1.1 molar amounts), then H_2O_2 in THF/AcOEt, **30a-D** (83%), **30b-D** (77%); (v) DBU (2 molar amounts) in CH_3CN, 25 °C, 5 h, **18b-D** (93%), **18d-D** (67%); (vi) see Scheme 7 (1).

Scheme 8.

orbital of olefin.

In the case of alkyl groups, intramolecular hydrogen bonding is not possible. Thus, the difference among them must arise from a difference in (i) the effectiveness of the pseudo p-orbital useful to 6π-electrons homoaromaticity, (ii) the electron-releasing effect to reduce the $\sigma \rightarrow \pi^*$ interaction by lowering the acidity of the allylic proton(s), (iii) the steric hindrance to avoid a *syn*-conformation.

Consequently, it was confirmed that the concept of the "*syn-effect*" is applicable to the present desulfonylation reaction as well as in the conversion of vinylic sulfones to allylic sulfones.[1,2]

Related studies, which utilize various kinds of substrates, are also in progress in our laboratory to reveal the exact origin of the "*syn-effect*".

Experimental

All of the melting points were determined using a micro melting apparatus (Yanagimoto Seisakusho), and were uncorrected. The ^1H NMR, IR, and MS spectra were recorded on a JEOL JNM-GX 400 (400 MHz) FT-NMR spectrometer, a JASCO IRA-1 diffraction grating infrared spectrometer, and a Hitachi M-80 mass spectrom-

eter, respectively. The chemical shifts of NMR are reported in the δ-scale relative to TMS as an internal standard. All of the solvents were distilled and stored over a drying agent. Thin-layer chromatography (TLC) and flash column chromatography were performed using Merck's silica gel 60 PF_{254} (Art. 7749) and Wakogel C-300, respectively, unless otherwise noted.

Preparation of (Z)-2-Methyl-3-tosyl-4-tridecene [(Z)-4]. To a mixed solution of (Z)-1-tosyl-2-undecene[5] (**3**, 150 mg, 0.486 mmol) and HMPA (0.170 ml, 0.972 mmol) in THF (10 ml) was added a solution of *n*-BuLi in hexane (f=0.630 ml mmol^{-1}, 0.306 ml, 0.486 mmol) at −70 °C under nitrogen, followed by the addition of 2-iodopropane (0.053 ml, 0.531 mmol) after 30 min. The reaction mixture was stirred for 30 min and then quenched by the addition of a phosphate buffer solution (pH 7). After removing the solvent under reduced pressure, the organic substances were extracted with ethyl acetate, followed by washing with brine and drying over Na_2SO_4. An alkylated product (**Z**)-**4** was isolated by preparative TLC (SiO_2, hexane/AcOEt=5/1, v/v) in 84% yield (143 mg). An oil; MS *m/z* 351 (M^++1; 7.08 %), 195 (100.00), 194 (38.02), 157 (16.40), 111 (11.17), 97 (14.67), 83 (23.37), 68 (23.94); IR (neat) 3040, 2930, 2860, 1595, 1490, 1440, 1300, 1140, 1080, 810, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.02 Hz), 0.98 (3H, d, J=6.71 Hz), 1.12 (3H, d, J=6.71 Hz), 0.96—1.39 (12H, m), 1.61 (2H, m), 2.42 (3H, s), 2.73 (1H, dh, J=6.71, 3.66 Hz), 3.70 (1H, dd, J=10.99, 3.66 Hz), 5.45 (1H, t, J=10.99 Hz), 5.66 (1H, dt, J=10.99, 7.32 Hz), 7.28 (2H, d, J=8.24 Hz), 7.71 (2H, d, J=8.24 Hz).

Similarly, (**E**)-**4** was prepared from (**E**)-isomer of **3**.

(E)-2-Methyl-3-tosyl-4-tridecene [(E)-4]. An oil; MS *m/z* 351 (M^++1; 3.23%), 195 (100.00), 194 (24.24), 157 (20.67), 125 (11.55), 111 (19.84), 97 (24.29), 83 (36.98), 68 (47.63); IR (neat) 2940, 2860, 1595, 1490, 1440, 1300, 1140, 1080, 965, 810 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.02 Hz), 0.97 (3H, d, J=6.71 Hz), 1.10 (3H, d, J=6.71 Hz), 1.12—1.31 (12H, m), 1.94 (2H, m), 2.42 (3H, s), 2.64 (1H, dh, J=6.71, 3.36 Hz), 3.25 (1H, dd, J=10.38, 3.36 Hz), 5.23 (1H, dt, J=15.25, 6.72 Hz), 5.43 (1H, dd, J=15.25, 10.38 Hz), 7.28 (2H, d, J=8.24 Hz), 7.67 (2H, d, J=8.24 Hz).

Preparation of (Z)-2-Methyl-2-tosyl-3-dodecene [(Z)-5]. Prepared in a similar manner to that described above for (**Z**)-**4** in 44% yield, using two molar amounts of *n*-BuLi and iodomethane, respectively. An oil; MS *m/z* 337 (M^++1; 0.19%), 181 (100.00), 125 (100.00), 111 (100.00), 97 (100.00), 83 (100.00), 69 (99.87), 57 (80.13), 55 (84.55); IR (neat) 2920, 2840, 1590, 1450, 1290, 1140, 1070, 800, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.31 Hz), 1.18—1.29 (12H, m), 1.54 (6H, s), 1.93 (2H, m), 2.43 (3H, s), 5.27 (1H, d, J=12.20 Hz), 5.52 (1H, dt, J=12.20, 7.31 Hz), 7.31 (2H, d, J=8.24 Hz), 7.71 (2H, d, J=8.24 Hz).

The physical and spectral data of (**E**)-**5** are shown as **11d** in the following.

Preparation of 2-(1-Pyrrolidinyl)-1-tosylpentane (8a). An aqueous solution (10 ml) of sodium *p*-toluenesulfinate tetrahydrate (*p*-$CH_3C_6H_4SO_2Na{\cdot}4H_2O$, 1.752 g, 7.0 mmol) was vigorously stirred with a solution of iodine (1.269 g, 5.0 mmol) in ethyl acetate (5 ml) under nitrogen. To this mixture was added a solution of 1-pentene (**7a**, 0.55 ml, 5.0 mmol) in ethyl acetate (5 ml) at room temperature. After stirring for 1 h 20 min, the product was extracted with ethyl acetate and washed successively with an aqueous solution of $NaHCO_3$ containing a small amount of $NaHSO_3$, brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was treated with pyrrolidine (1.25 ml, 15.0 mmol) in CH_3CN (12.5 ml) at room temperature overnight under nitrogen. After removing the solvent, the resulting residue was taken up in ethyl acetate, washed with brine, and dried over Na_2SO_4. After evaporation of the solvent, **8a** was isolated by alumina column chromatography (Merck, Aluminum oxide 90 active basic, Activity III, hexane/AcOEt=5/1, v/v) in quantitative yield (1.525 g). Mp 45.5—46.0 °C (from Hex); MS *m/z* 295 (M^+; 4.29 %), 252 (90.36), 155 (13.32), 126 (93.25), 97 (66.01), 91 (100.00), 69 (31.96), 65 (31.13), 41 (24.33); IR (KBr) 2948, 2870, 2799, 1596, 1454, 1411, 1383, 1305, 1186, 1146, 1086, 1018, 821, 774, 675 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.33 Hz), 1.30—1.42 (2H, m), 1.44—1.64 (6H, m), 2.30—2.37 (2H, m), 2.42—2.50 (2H, m), 2.45 (3H, s), 3.03 (1H, dd, J=13.73, 5.80 Hz), 3.19—3.31 (2H, m), 7.33 (2H, d, J=8.24 Hz), 7.79 (2H, d, J=8.24 Hz). Found: C, 64.84; H, 8.55; N, 4.72%. Calcd for $C_{16}H_{25}NO_2S$: C, 65.05; H, 8.53; N, 4.74%.

In a similar manner, **8b—d** were prepared in quantitative yields. Their physical and spectral data are given in the following:

2-(1-Pyrrolidinyl)-1-tosylhexane (8b). Mp 46 °C (from Hex); IR (KBr) 2910, 2795, 1587, 1395, 1275, 1138, 1079, 1008, 905, 803, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, t, J=7.02 Hz), 1.24—1.35 (4H, m), 1.50—1.68 (6H, m), 2.44 (3H, s), 2.35—2.55 (4H, m), 3.06 (1H, dd, J=14.04, 6.10 Hz), 3.21—3.26 (1H, m), 3.31 (1H, dd, J=14.04, 4.58 Hz), 7.33 (2H, d, J=8.24 Hz), 7.79 (2H, d, J=8.24 Hz). Found: C, 65.82; H, 9.01; N, 4.32%. Calcd for $C_{17}H_{27}NO_2S$: C, 65.98; H, 8.79; N, 4.53%.

2-(1-Pyrrolidinyl)-1-tosylundecane (8c). An oil; MS *m/z* 379 (M^+; 1.97%), 252 (100.00), 210 (65.92), 112 (14.45), 97 (20.75); IR (neat) 2955, 2925, 2854, 2802, 1598, 1459, 1314, 1301, 1146, 1088, 816, 768, 674 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.02 Hz), 1.18—1.38 (14H, m), 1.43—1.66 (6H, m), 2.30—2.37 (2H, m), 2.40—2.50 (2H, m), 2.44 (3H, s), 3.04 (1H, dd, J=14.04, 6.11 Hz), 3.15—3.23 (1H, m), 3.28 (1H, dd, J=14.04, 4.89 Hz), 7.33 (2H, d, J=8.24 Hz), 7.78 (2H, d, J=8.24 Hz).

2-(1-Pyrrolidinyl)-1-tosyldodecane (8d). An oil; MS *m/z* 393 (M^+; 2.25%), 252 (100.00), 225 (10.85), 224 (58.03), 112 (17.48), 110 (11.85), 97 (32.96), 91 (8.40), 84 (12.47), 70 (13.07), 69 (10.68), 43 (12.80), 41 (12.97); IR (neat) 2920, 2840, 2780, 1585, 1450, 1290, 1140, 1080, 800, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7.02 Hz), 1.10—1.43 (16H, m), 1.44—1.60 (6H, m), 2.30—2.47 (4H, m), 2.44 (3H, s), 3.03 (1H, dd, J=14.34, 6.10 Hz), 3.17—3.22 (1H, m), 3.28 (1H, dd, J=14.34, 4.58 Hz), 7.33 (2H, d, J=8.24 Hz), 7.78 (2H, d, J=8.24 Hz).

Preparation of 4-Tosyl-4-octene (9a). To a solution of **8a** (940 mg, 3.18 mmol) and HMPA (0.83 ml, 4.77 mmol) in THF (22.3 ml) was added *n*-BuLi (f=0.610 ml mmol^{-1}, 2.04 ml, 3.34 mmol) at −70 °C under nitrogen, followed by the addition of 1-iodopropane (0.34 ml, 3.50 mmol) after 30 min. Methanol was added after stirring for 2.5 h at −70 °C. The crude product, obtained by the usual work-up, was treated with *m*-chloroperbenzoic acid (*m*-CPBA, ca. 70% pure, 1.096 g, 4.45 mmol) in the presence of Na_2CO_3 (674 mg, 6.36 mmol) in CH_2Cl_2 (30.8 ml) at room temperature overnight. After the usual work-up, **9a** (*E*/*Z*-mixture) was isolated by preparative TLC (SiO_2, hexane/AcOEt=10/1, v/v) in 61% yield (520 mg) as an oil; MS *m/z* 266 (M^+; 49.91%), 157 (70.61), 139 (52.74), 119 (67.90), 81 (44.81), 71 (34.05), 69 (100.00), 55 (68.70), 41 (51.36); IR (neat) 2960, 2880, 1630, 1590, 1460, 1300, 1130, 1080, 800, 700, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=0.83 (3H, t, J=7.63 Hz), 0.95 (3H, t, J=7.63 Hz), 1.36 (2H, sx, J=7.63 Hz), 1.52 (2H, sx, J=7.63 Hz), 2.13—2.22 (4H, m), 2.43 (3H, s), 6.88 (1H, t, J=7.63 Hz), 7.31 (2H, d, J=8.24 Hz), 7.73 (2H, d, J=8.24 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=0.88 (3H, t, J=7.63 Hz), 0.90 (3H, t, J=7.63 Hz), 1.41 (2H, sx, J=7.63 Hz), 1.51 (2H, sx, J=7.63 Hz), 2.26 (2H, dt, J=7.63, 1.22 Hz), 2.43 (3H, s), 2.61 (2H, q, J=7.63 Hz), 5.96 (1H, tt, J=7.63, 1.22 Hz), 7.31 (2H, d, J=8.24 Hz), 7.76 (2H, d, J=8.24 Hz). *E*/*Z*=53/47.

In a similar manner, **9b—e** were prepared in 52, 81, 93, and 70% yields, respectively. Their physical and spectral data are given in the following:

4-Tosyl-4-nonene (9b). An oil; MS *m/z* 280 (M^+; 63.67%), 157 (81.28), 139 (50.21), 119 (60.12), 95 (54.72), 83 (55.62), 69 (100.00), 55 (78.83), 41 (37.30); IR (neat) 2920, 2880, 1630, 1590, 1460, 1300, 1130, 1080, 800, 700, 680 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.83 (3H, t, *J*=7.32 Hz), 0.92 (3H, t, *J*=7.32 Hz), 1.22—1.58 (6H, m), 2.15—2.21 (4H, m), 2.43 (3H, s), 6.88 (1H, t, *J*=7.32 Hz), 7.30 (2H, d, *J*=8.24 Hz), 7.73 (2H, d, *J*=8.24 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.88 (6H, t, *J*=7.32 Hz), 1.22—1.58 (6H, m), 2.26 (2H, dt, *J*=7.63, 0.91 Hz), 2.43 (3H, s), 2.61 (2H, dt, *J*=7.63, 7.02 Hz), 5.96 (1H, tt, *J*=7.63, 0.91 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.76 (2H, d, *J*=8.24 Hz). *E*/*Z*=47/53.

4-Tosyl-4-tetradecene (9c). An oil; MS *m/z* 350 (M^+; 43.90%), 251 (19.64), 157 (100.00), 139 (34.43), 96 (39.24), 82 (44.02), 69 (39.76), 67 (38.93), 55 (49.46); IR (neat) 2950, 2910, 2840, 1620, 1587, 1450, 1305, 1130, 1075, 803, 703 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.83 (3H, t, *J*=7.32 Hz), 0.89 (3H, t, *J*=7.02 Hz), 1.21—1.53 (16H, m), 2.14—2.22 (4H, m), 2.43 (3H, s), 6.88 (1H, t, *J*=7.32 Hz), 7.30 (2H, d, *J*=8.24 Hz), 7.72 (2H, d, *J*=8.24 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.85—0.92 (6H, m), 1.20—1.39 (14H, m), 1.51 (2H, sx, *J*=7.63 Hz), 2.27 (2H, dt, *J*=7.63, 0.91 Hz), 2.43 (3H, s), 2.60 (2H, q, *J*=7.63 Hz), 5.96 (1H, tt, *J*=7.63, 0.91 Hz), 7.31 (2H, d, *J*=8.55 Hz), 7.76 (2H, d, *J*=8.55 Hz). *E*/*Z*=45/55.

2-Tosyl-2-dodecene (9d). An oil; MS *m/z* 322 (M^+; 24.50%), 223 (26.07), 197 (28.40), 166 (64.66), 157 (100.00), 139 (55.53), 69 (43.70), 68 (45.53), 55 (66.67); IR (neat) 2920, 2850, 1635, 1590, 1490, 1460, 1310, 1135, 1075, 805 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.88 (3H, t, *J*=7.02 Hz), 1.21—1.35 (12H, m), 1.42—1.52 (2H, m), 1.81 (3H, s), 2.16 (2H, q, *J*=7.63 Hz), 2.43 (3H, s), 6.87 (1H, t, *J*=7.63 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.73 (2H, d, *J*=8.24 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.89 (3H, t, *J*=7.02 Hz), 1.21—1.43 (14H, m), 1.96 (3H, s), 2.44 (3H, s), 2.64 (2H, q, *J*=7.63 Hz), 5.97 (1H, t, *J*=7.63 Hz), 7.32 (2H, d, *J*=8.24 Hz), 7.76 (2H, d, *J*=8.24 Hz). *E*/*Z*=53/47.

2-Tosyl-2-tridecene (9e). An oil; MS *m/z* 336 (M^+; 57.95%), 180 (67.21), 157 (100.00), 139 (53.72), 55 (38.78); IR (neat) 2920, 2830, 1620, 1580, 1475, 1440, 1280, 1125, 1060, 790, 690, 660 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.88 (3H, t, *J*=7.02 Hz), 1.26—1.45 (16H, m), 1.81 (3H, s), 2.16 (2H, q, *J*=7.02 Hz), 2.43 (3H, s), 6.87 (1H, t, *J*=7.02 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.72 (2H, d, *J*=8.24 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.88 (3H, t, *J*=7.02 Hz), 1.26—1.45 (16H, m), 1.97 (3H, d, *J*=1.52 Hz), 2.43 (3H, s), 2.64 (2H, q, *J*=7.02 Hz), 5.98 (1H, tq, *J*=7.02, 1.52 Hz), 7.32 (2H, d, *J*=8.24 Hz), 7.76 (2H, d, *J*=8.24 Hz). *E*/*Z*=53/47.

Preparation of (*E*)-5-Tosyl-3-octene (10a). To a solution of *t*-BuOK (405 mg, 3.61 mmol) in *t*-BuOH (13 ml) was added a solution of **9a** (481 mg, 1.81 mmol) in *t*-BuOH (6 ml) at 30 °C under nitrogen. After stirring for 24 h, a saturated ammonium chloride solution was added. The residue obtained by evaporating the solvent was extracted with ethyl acetate. The extract was successively washed with water and brine, and dried over sodium sulfate. After evaporating the solvent, the residue was separated by preparative TLC (SiO_2, hexane/AcOEt=20/1, v/v, developed five times) to afford **10a** in 83% yield (399 mg) as an oil; MS *m/z* 267 (M^++1; 0.56%), 157 (15.03), 112 (22.35), 111 (100.00), 110 (40.05), 91 (41.27), 69 (98.66), 65 (22.21), 55 (80.44), 41 (59.13); IR (neat) 2940, 2880, 1650, 1585, 1450, 1305, 1130, 1070, 960, 800, 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, *J*=7.33 Hz), 0.90 (3H, t, *J*=7.33 Hz), 1.16—1.30 (1H, m), 1.36—1.50 (1H, m), 1.54—1.67 (1H, m), 1.94—2.10 (3H, m), 2.44 (3H, s), 3.38—3.45 (1H, m), 5.18 (1H, ddt, *J*=15.26, 9.46, 1.53 Hz), 5.43 (1H, dt, *J*=15.26, 6.41 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.69 (2H, d, *J*=8.24 Hz).

In a similar manner, **10b—e** were prepared in 83, 77, 62, and 61% yields, respectively. Their physical and spectral data are given in the following:

(*E*)-6-Tosyl-4-nonene (10b). An oil; MS *m/z* 281 (M^++1; 0.44%), 125 (90.59), 91 (20.54), 83 (86.68), 69 (100.00), 55 (45.05), 41 (26.37); IR (neat) 2960, 2870, 1650, 1585, 1450, 1305, 1290, 1275, 1130, 1075, 960, 800, 720, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.80 (3H, t, *J*=7.32 Hz), 0.90 (3H, t, *J*=7.32 Hz), 1.19—1.49 (4H, m), 1.56—1.67 (1H, m), 1.95 (2H, q, *J*=7.02 Hz), 1.98—2.08 (1H, m), 2.44 (3H, s), 3.38—3.46 (1H, m), 5.18 (1H, ddt, *J*=15.56, 9.15, 1.22 Hz), 5.40 (1H, dt, *J*=15.56, 7.02 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.69 (2H, d, *J*=8.24 Hz).

(*E*)-4-Tosyl-5-tetradecene (10c). An oil; MS *m/z* 350 (M^+; 0.10%), 195 (37.82), 125 (26.23), 111 (52.93), 97 (78.11), 83 (100.00), 69 (75.10), 57 (38.28), 55 (54.67); IR (neat) 2975, 2940, 2865, 1590, 1490, 1460, 1310, 1295, 1280, 1140, 1080, 965, 805, 705, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—0.96 (6H, m), 1.13—1.36 (13H, m), 1.36—1.53 (1H, m), 1.55—1.70 (1H, m), 1.92—2.10 (3H, m), 2.44 (3H, s), 3.36—3.46 (1H, m), 5.17 (1H, ddt, *J*=15.56, 9.15, 1.22 Hz), 5.39 (1H, dt, *J*=15.26, 7.02 Hz), 7.30 (2H, d, *J*=8.24 Hz), 7.68 (2H, d, *J*=8.24 Hz).

(*E*)-2-Tosyl-3-dodecene (10d). An oil; MS *m/z* 167 (M^+—Ts; 7.96%), 155 (48.16), 139 (11.63), 92 (41.34), 91 (100.00), 65 (61.56), 55 (60.35), 43 (42.64), 41 (54.48); IR (neat) 2920, 2850, 1650, 1590, 1450, 1310, 1140, 1085, 965, 807, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, *J*=7.02 Hz), 1.24—1.30 (12H, m), 1.41 (3H, d, *J*=7.02 Hz), 1.97 (2H, q, *J*=6.41 Hz), 2.44 (3H, s), 3.62 (1H, p, *J*=7.01 Hz), 5.36 (1H, dd, *J*=15.57, 7.01 Hz), 5.45 (1H, dt, *J*=15.57, 6.41 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.70 (2H, d, *J*=8.24 Hz).

(*E*)-2-Tosyl-3-tridecene (10e). An oil; MS *m/z* 337 (M^++1; 0.35%), 181 (35.88), 111 (68.59), 97 (100.00), 83 (81.24), 69 (72.58), 57 (32.77), 55 (58.49); IR (neat) 2915, 2840, 1650, 1590, 1450, 1305, 1140, 1080, 1010, 960, 800, 710, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, *J*=7.02 Hz), 1.25—1.30 (14H, m), 1.41 (3H, d, *J*=7.02 Hz), 1.97 (2H, q, *J*=6.41 Hz), 2.44 (3H, s), 3.62 (1H, p, *J*=7.02 Hz), 5.37 (1H, dd, *J*=15.56, 7.02 Hz), 5.45 (1H, dt, *J*=15.56, 6.41 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.70 (2H, d, *J*=8.24 Hz).

Preparation of (*E*)-5-Propyl-5-tosyl-3-octene (11a). To a solution of **10a** (170 mg, 0.638 mmol) in THF (6.4 ml) was added *n*-BuLi (f=0.610 ml $mmol^{-1}$, 0.41 ml, 0.670 mmol) at −40 °C under nitrogen, followed by the addition of 1-iodopropane (0.07 ml, 0.766 mmol) after 30 min. After stirring for 10 min, the reaction mixture was worked up in the usual manner. Product **11a** was isolated by preparative TLC (SiO_2, hexane/AcOEt=10/1, v/v) in 96% yield (189 mg) as an oil; MS *m/z* 309 (M^++1; 0.16%), 154 (56.41), 153 (100.00), 111 (99.79), 97 (100.00), 91 (55.95), 83 (99.94), 69 (98.49), 55 (99.85), 41 (56.43); IR (neat) 2980, 2880, 1590, 1460, 1280, 1140, 1115, 1070, 970, 805, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (6H, t, *J*=7.32 Hz), 0.94 (3H, t, *J*=7.32 Hz), 1.22—1.38 (2H, m), 1.50—1.70 (4H, m), 1.88—1.98 (2H, m), 2.04 (2H, dq, *J*=7.32, 5.19 Hz), 2.43 (3H, s), 5.31 (1H, d, *J*=15.87 Hz), 5.37 (1H, dt, *J*=15.87, 5.19 Hz), 7.27 (2H, d, *J*=8.24 Hz), 7.62 (2H, d, *J*=8.24 Hz).

In a similar manner, **11b—e** were prepared in 93, 94, 99, and 99% yields, respectively. Their physical and spectral data are given in the following:

(*E*)-6-Propyl-6-tosyl-4-nonene (11b). An oil; MS *m/z* 322 (M^+; 0.53%), 168 (39.37), 167 (100.00), 111 (36.85), 97 (37.73),

91 (49.49), 83 (67.02), 69 (99.32), 55 (72.74), 41 (46.39); IR (neat) 2980, 2880, 1590, 1460, 1275, 1135, 1115, 1070, 965, 800, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7.33 Hz), 0.92 (6H, t, J=7.33 Hz), 1.24—1.40 (4H, m), 1.48—1.68 (4H, m), 1.86—1.96 (2H, m), 1.97—2.03 (2H, m), 2.44 (3H, s), 5.30—5.36 (2H, m), 7.27 (2H, d, J=8.24 Hz), 7.62 (2H, d, J=8.24 Hz). ^1H NMR (C_6D_6) δ=0.78 (3H, t, J=7.32 Hz), 0.83 (6H, t, J=7.02 Hz), 1.20 (2H, sx, J=7.32 Hz), 1.30—1.40 (2H, m), 1.60—1.78 (4H, m), 1.83 (2H, q, J=7.32 Hz), 1.88 (3H, s), 2.02—2.26 (2H, m), 5.23 (1H, dt, J=15.87, 7.02 Hz), 5.47 (1H, dt, J=15.87, 1.22 Hz), 6.78 (2H, d, J=8.24 Hz), 7.77 (2H, d, J=8.24 Hz).

(*E*)-4-Propyl-4-tosyl-5-tetradecene (11c). An oil; MS *m/z* 392 (M^+; 0.53%), 237 (100.00), 125 (41.80), 111 (38.81), 97 (51.92), 83 (77.63), 69 (73.82), 57 (30.31); IR (neat) 3040, 2930, 2870, 1740, 1590, 1485, 1450, 1280, 1140, 1075, 970, 800, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, J=7.02 Hz), 0.92 (6H, t, J=7.02 Hz), 1.24—1.32 (14H, m), 1.55—1.67 (4H, m), 1.87—1.94 (2H, m), 2.01 (2H, m), 2.43 (3H, s), 5.32—5.34 (2H, m), 7.27 (2H, d, J=8.24 Hz), 7.67 (2H, d, J=8.24 Hz).

(*E*)-2-Methyl-2-tosyl-3-dodecene [11d≡(*E*)-5]. An oil; MS *m/z* 337 (M^++1; 3.13%), 181 (100.00), 125 (9.97), 111 (19.91), 97 (19.37), 83 (19.91), 69 (2.78); IR (neat) 2940, 2870, 1590, 1460, 1300, 1155, 1120, 1075, 970, 810, 705, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (3H, t, J=7.02 Hz), 1.26—1.32 (12H, m), 1.41 (6H, s), 2.01 (2H, m), 2.44 (3H, s), 5.43 (1H, dt, J=15.57, 6.71 Hz), 5.61 (1H, d, J=15.57 Hz), 7.28 (2H, d, J=8.24 Hz), 7.67 (2H, d, J=8.24 Hz).

(*E*)-2-Methyl-2-tosyl-3-tridecene (11e). An oil; MS *m/z* 351 (M^++1; 14.19%), 195 (100.00), 125 (39.67), 111 (75.60), 97 (99.97), 83 (100.00), 69 (99.94), 57 (58.46), 55 (42.28); IR (neat) 2900, 2830, 1580, 1440, 1280, 1140, 1110, 1060, 955, 795, 695, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=6.71 Hz), 1.26—1.38 (14H, m), 1.41 (6H, s), 2.01 (2H, q, J=6.71 Hz), 2.44 (3H, s), 5.43 (1H, dt, J=15.57, 6.71 Hz), 5.58 (1H, d, J=15.57 Hz), 7.28 (2H, d, J=8.24 Hz), 7.67 (2H, d, J=8.24 Hz).

Preparation of (*E*)-5-Methyl-1-tosyl-2-hexene (14a). To a solution of **12a** (538 mg, 4.71 mmol) in ether (9.0 ml) was added triethylamine (1.31 ml, 9.42 mmol) and mesyl chloride (0.73 ml, 9.42 mmol) at 0 °C under nitrogen. After stirring for 50 min, the reaction mixture was worked up in the usual manner to obtain a crude mesylated product. To a THF (2 ml) solution of the product was added a lithium *p*-toluenethiolate solution prepared from *p*-toluenethiol (550 mg, 4.43 mmol) and *n*-BuLi (f=0.620 ml $mmol^{-1}$, 2.77 ml, 4.47 mmol) in THF (7 ml) at 0 °C; the mixture was stirred overnight at room temperature to afford the sulfide (**13a**). An aqueous solution (15 ml) of OXONE (5.447 g, 8.86 mmol) was added to a methanol solution (18 ml) of the crude **13a**; the mixture was then stirred overnight. After the decomposition of excess amounts of OXONE with $NaHSO_3$ and subsequent filtration through Celite, a residue obtained by evaporation of the solvent was partitioned between ethyl acetate and water. The organic layer was washed with brine, and dried over Na_2SO_4. After evaporating the solvent, **14a** was isolated by preparative TLC (SiO_2, hexane/AcOEt=7/1, v/v) in 42% yield (465 mg) as an oil; MS *m/z* 253 (M^++1; 0.25%), 157 (30.16), 97 (88.24), 96 (100.00), 92 (27.01), 91 (28.67), 81 (22.31), 55 (100.00); IR (neat) 2970, 2880, 1655, 1590, 1490, 1460, 1400, 1360, 1310, 1295, 1140, 1080, 960, 810, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.79 (6H, d, J=6.71 Hz), 1.54 (1H, m), 1.89 (2H, t, J=7.02 Hz), 2.44 (3H, s), 3.74 (2H, d, J=7.02 Hz), 5.37 (1H, dt, J=15.26, 7.02 Hz), 5.51 (1H, dt, J=15.26, 7.02 Hz), 7.33 (2H, d, J=8.24 Hz), 7.73 (2H, d, J=8.24 Hz).

In a similar manner, **14b** was prepared in 52% yield from **12b**.

(*E*)-5,5-Dimethyl-1-tosyl-2-hexene (14b). Mp 48.5—48.8 °C (from Hex); MS *m/z* 266 (M^+; 1.17%), 210 (59.29), 157 (32.58), 156 (40.56), 155 (16.35), 140 (18.53), 139 (10.13), 111 (21.76), 110 (20.44), 92 (45.02), 91 (81.08), 65 (29.92), 57 (100.00), 55 (21.23), 41 (31.34); IR (KBr) 3038, 2952, 1668, 1597, 1472, 1401, 1364, 1300, 1240, 1190, 1154, 1135, 1088, 976, 876, 814, 755, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.79 (9H, s), 1.88 (2H, d, J=7.63 Hz), 2.44 (3H, s), 3.76 (2H, d, J=7.63 Hz), 5.36 (1H, dt, J=15.26, 7.63 Hz), 5.58 (1H, dt, J=15.26, 7.63 Hz), 7.33 (2H, d, J=8.24 Hz), 7.73 (2H, d, J=8.24 Hz). Found: C, 67.63; H, 8.38%. Calcd for $C_{15}H_{22}O_2S$: C, 67.63; H, 8.32%.

Preparation of (*E*)-2-Methyl-6-propyl-6-tosyl-4-nonene (11f). To a solution of **14a** (211 mg, 0.836 mmol) in THF (2.5 ml) was added *n*-BuLi (f=0.645 ml $mmol^{-1}$, 1.11 ml, 1.71 mmol) at −40 °C under nitrogen, followed by the addition of 1-iodopropane (0.204 ml, 2.09 mmol) after 50 min. After stirring for 25 min at this temperature, the reaction mixture was worked up in the usual manner. The product **11f** was isolated by preparative TLC (SiO_2, hexane/AcOEt=10/1, v/v) in 79% yield (222 mg) as an oil; MS *m/z* 181 (M^+−Ts; 100.00%), 125 (81.89), 83 (72.53), 69 (90.29), 55 (22.86); IR (neat) 2970, 2880, 1650, 1590, 1490, 1460, 1380, 1360, 1305, 1290, 1280, 1140, 1120, 1075, 970, 805, 700, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (6H, d, J=6.41 Hz), 0.92 (6H, t, J=7.02 Hz), 1.24—1.38 (1H, m), 1.47—1.71 (6H, m), 1.85—1.98 (4H, m), 2.43 (3H, s), 5.25—5.40 (2H, m), 7.27 (2H, d, J=8.24 Hz), 7.63 (2H, d, J=8.24 Hz).

In a similar manner, **11g** was prepared in 78% yield.

(*E*)-2,2-Dimethyl-6-propyl-6-tosyl-4-nonene (11g). An oil; MS *m/z* 350 (M^+; 0.25%), 195 (100.00), 179 (20.90), 139 (66.97), 125 (56.36), 97 (22.02), 95 (34.49), 91 (36.91), 83 (46.64), 69 (42.53), 67 (23.37), 57 (100.00), 55 (30.53), 41 (44.92); IR (neat) 2960, 2880, 1590, 1455, 1355, 1275, 1140, 1110, 1070, 970, 800, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (9H, s), 0.93 (6H, t, J=7.33 Hz), 1.25—1.40 (2H, m), 1.50—1.70 (4H, m), 1.87—2.00 (2H, m), 1.91 (2H, dd, J=7.33, 0.91 Hz), 2.44 (3H, s), 5.28 (1H, dt, J=15.87, 0.91 Hz), 5.42 (1H, dt, J=15.87, 7.33 Hz), 7.28 (2H, d, J=8.24 Hz), 7.63 (2H, d, J=8.24 Hz).

Preparation of 4-Tosyl-2-buten-1-ol [(*E*)-15≡18a]. An aqueous solution (20 ml) of sodium *p*-toluenesulfinate tetrahydrate (*p*-$CH_3C_6H_4SO_2Na{\cdot}4H_2O$, 3.502 g, 14.0 mmol) was vigorously stirred with a solution of iodine (2.538 g, 10.0 mmol) in ethyl acetate (10 ml) under nitrogen. To the mixture was added a solution of 3-buten-1-ol (**17a**, 0.86 ml, 10.0 mmol) in ethyl acetate (10 ml) at room temperature. After stirring for 2.5 h, the product was extracted with ethyl acetate and washed successively with an aqueous solution of $NaHCO_3$ containing a small amount of $NaHSO_3$, brine, and dried over Na_2SO_4. The residue obtained by evaporating the solvent was treated with DBU (4.50 ml, 30.0 mmol) in CH_3CN (100 ml) at room temperature under nitrogen for 2 d. After the usual work-up, **15** was isolated by preparative TLC (SiO_2, hexane/AcOEt/EtOH=1/1/0.2, v/v/v) in quantitative yield (2.400 g) as an oil (*E*/*Z*=92/8); MS *m/z* 227 (M^++1; 9.40%), 209 (43.75), 157 (49.96), 156 (73.62), 139 (65.60), 92 (100.00), 91 (70.69), 71 (19.85); IR (neat) 3520—3400, 2900, 1720, 1580, 1390, 1290, 1120, 1070, 960, 800, 710 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=1.47 (1H, t, J=5.19 Hz), 2.45 (3H, s), 3.79 (2H, d, J=7.02 Hz), 4.12 (2H, dd, J=5.19, 4.58 Hz), 5.70 (1H, dt, J=15.56, 7.02 Hz), 5.76 (1H, dt, J=15.56, 4.58 Hz), 7.35 (2H, d, J=8.24 Hz), 7.75 (2H, d, J=8.24 Hz).

Preparation of (*E*)-4-Propyl-4-tosyl-2-hepten-1-ol [(*E*)-16]. The 4-tosyl-2-buten-1-ol **15** (*E*/*Z*=92/8, 667 mg, 2.95 mmol) in THF (44 ml) was lithiated with *n*-BuLi (f=0.610 ml $mmol^{-1}$, 5.39 ml, 8.85 mmol) at −40 °C for 1 h under nitrogen, followed by the

addition of 1-iodopropane (0.58 ml, 5.90 mmol). After stirring for 40 min at this temperature, the reaction mixture was worked up in the usual way, and (*E*)-**16** was isolated by preparative TLC (SiO_2, hexane/AcOEt/EtOH=3/1/0.2, v/v/v) in 38% yield (344 mg) as an oil; MS *m/z* 155 (M^+−Ts; 40.18%), 137 (54.99), 95 (54.84), 86 (62.93), 84 (100.00), 81 (34.53), 69 (33.25); IR (neat) 3580—3400, 2980, 2880, 1585, 1450, 1270, 1130, 1105, 1070, 965, 800, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (6H, t, *J*=7.33 Hz), 1.24—1.40 (2H, m), 1.46—1.60 (2H, m), 1.61—1.71 (2H, dt, *J*=12.82, 3.96 Hz), 1.89—1.96 (3H, m), 2.43 (3H, s), 4.13 (2H, broad d, *J*=4.88 Hz), 5.52 (1H, dt, *J*=16.17, 4.88 Hz), 5.62 (1H, dt, *J*=16.17, 1.22 Hz), 7.29 (2H, d, *J*=8.24 Hz), 7.63 (2H, d, *J*=8.24 Hz).

Preparation of (*E*)-1-Phenyl-4-propyl-4-tosyl-2-heptene (11h). The alcohol (*E*)-**16** (30 mg, 0.097 mmol) obtained as mentioned above was mesylated with mesyl chloride (0.02 ml, 0.193 mmol) and triethylamine (0.03 ml, 0.193 mmol) in ether (1.0 ml) at 0 °C for 35 min. The crude product obtained by the usual work-up was reacted with Ph_2CuLi [prepared from CuI(I) (55 mg, 0.291 mmol) and PhLi (f=1.80 mmol ml^{-1}, 0.32 ml, 0.582 mmol) at −38 °C in ether for 2 h] in ether (3 ml) at −66—62 °C for 15 min to afford an α,α-dipropylated product **11h**. Isolated by preparative TLC (SiO_2, hexane/AcOEt=10/1, v/v, developed twice) in 53% yield (19 mg); Mp 86.5—87.0 °C (from MeOH); IR (KBr) 2966, 2927, 2871, 1596, 1494, 1455, 1315, 1283, 1145, 1119, 1081, 975, 819, 754, 712, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.92 (6H, t, *J*=7.02 Hz), 1.24—1.40 (2H, m), 1.48—1.70 (4H, m), 1.86—1.95 (2H, m), 2.39 (3H, s), 3.36 (2H, d, *J*=3.66 Hz), 5.45—5.49 (2H, m), 7.09 (2H, d, *J*=6.71 Hz), 7.14 (2H, d, *J*=8.24 Hz), 7.20—7.31 (3H, m), 7.55 (2H, d, *J*=8.24 Hz). ^1H NMR (C_6D_6) δ=0.80 (6H, t, *J*=7.01 Hz), 1.24—1.40 (2H, m), 1.60—1.74 (4H, m), 1.88 (3H, s), 2.00—2.08 (2H, m), 3.12 (2H, d, *J*=6.86 Hz), 5.36 (1H, dt, *J*=15.86, 6.86 Hz), 5.55 (1H, d, *J*=15.86 Hz), 6.71 (2H, d, *J*=8.24 Hz), 6.96 (2H, d, *J*=7.02 Hz), 7.04 (1H, t, *J*=7.32 Hz), 7.12 (2H, dd, *J*=7.32, 7.02 Hz), 7.70 (2H, d, *J*=8.24 Hz). Found: C, 74.55; H, 8.16%. Calcd for $C_{23}H_{30}O_2S$: C, 74.25; H, 8.37%.

Preparation of δ-Hydroxy (*E*)-Allylic Sulfones (18b—d). Iodosulfonization products of **17b—d** were treated with DBU in acetonitrile at 25 °C as described for (*E*)-**4-tosyl-2-buten-1-ol** [(*E*)-**15**≡**18a**]. Each product (**18b—d**) was isolated by preparative TLC (SiO_2, hexane/AcOEt/EtOH=1/1/0.2, v/v/v) in 92, 92, and 80% yields, respectively. The physical and spectral data of **18b—d** are given in the following:

(*E*)-5-Tosyl-3-penten-2-ol (18b). Mp 69.5—70.5 °C (from Hex/AcOEt); IR (KBr) 3400—3260, 3020, 2950, 2880, 1580, 1480, 1390, 1260, 1100, 1060, 955, 800, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.18 (3H, d, *J*=6.41 Hz), 1.66 (1H, broad s), 2.45 (3H, s), 3.75 (2H, d, *J*=6.71 Hz), 4.27 (1H, m), 5.59 (1H, dd, *J*=15.56, 4.88 Hz), 5.65 (1H, dt, *J*=15.56, 6.71 Hz), 7.35 (2H, d, *J*=8.24 Hz), 7.74 (2H, d, *J*=8.24 Hz). Found: C, 59.89; H, 6.87%. Calcd for $C_{12}H_{16}O_3S$: C, 59.97; H, 6.71%.

(*E*)-6-Tosyl-4-hexen-3-ol (18c). An oil; MS *m/z* 255 (M^++1; 5.09%), 237 (72.60), 157 (86.01), 99 (18.85), 81 (100.00); IR (neat) 3570—3440, 2980, 2940, 2880, 1590, 1485, 1450, 1400, 1310, 1140, 1080, 960, 800. 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (3H, t, *J*=7.32 Hz), 1.41—1.52 (2H, m), 1.58 (1H, s), 2.45 (3H, s), 3.78 (2H, d, *J*=6.11 Hz), 4.02 (1H, m), 5.58 (1H, dd, *J*=15.56, 5.49 Hz), 5.65 (1H, dt, *J*=15.56, 7.02 Hz), 7.35 (2H, d, *J*=8.24 Hz), 7.74 (2H, d, *J*=8.24 Hz).

(*E*)-1-Phenyl-6-tosyl-4-hexen-3-ol (18d). Mp 82.0—83.0 °C (from Hex/AcOEt); IR (KBr) 3550, 3020, 2920, 2860, 1720, 1655, 1590, 1485, 1440, 1395, 1275, 1120, 1070, 965, 800, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.63—1.79 (2H, m), 1.93 (1H, broad s), 2.38 (3H, s), 2.51—2.65 (2H, m), 3.76 (2H, d, *J*=6.71 Hz), 4.07—4.13 (1H, m), 5.60 (1H, dd, *J*=15.26, 5.97 Hz), 5.66 (1H, dt, *J*=15.26, 6.71 Hz), 7.13—7.20 (3H, m), 7.25—7.32 (4H, m), 7.73 (2H, d, *J*=8.24 Hz). Found: C, 69.23; H, 6.62%. Calcd for $C_{19}H_{22}O_3S$: C, 69.06; H, 6.71%.

Preparation of δ-Hydroxy-α,α-dimethyl (*E*)-Allylic Sulfones (19a-d). Dimethylation of **18a—d** was carried out according to the method described above for the preparation of (*E*)-**16** using 3 molar amounts of *n*-BuLi and 2 molar amounts of iodomethane. The physical and spectral data of **19a—d** are given in the following:

(*E*)-4-Methyl-4-tosyl-2-penten-1-ol (19a). When starting from an *E*/*Z*-mixture (=**15**) of **18a**, an *E*/*Z*-mixture of **19a** was obtained. Recrystallization from hexane/AcOEt made it possible to isolate (*E*)-**19a** in 76%. Mp 66.5—67.5 °C (from Hex/AcOEt); IR (KBr) 3520, 3050, 2980, 2850, 1585, 1445, 1395, 1260, 1110, 1060, 960, 810, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.44 (6H, s), 1.47 (1H, broad s), 2.44 (3H, s), 4.15 (2H, t, *J*=5.19 Hz), 5.66 (1H, dt, *J*=15.87, 5.19 Hz), 5.89 (1H, dt, *J*=15.87, 1.58 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.69 (2H, d, *J*=8.24 Hz). Found: C, 61.29; H, 7.26%. Calcd for $C_{13}H_{18}O_2S$: C, 61.39; H, 7.13%.

In a similar manner, **19b—d** were prepared in 98, 58, and 60% yields, respectively. Their physical and spectral data are given in the following:

(*E*)-5-Methyl-5-tosyl-3-hexen-2-ol (19b). Mp 105—106 °C (from Hex/AcOEt); IR (KBr) 3500, 2960, 2920, 2850, 1580, 1480, 1430, 1380, 1140, 1060, 960, 805, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.22 (3H, d, *J*=6.41 Hz), 1.43 (3H, s), 1.44 (3H, s), 1.64 (1H, s), 2.44 (3H, s), 4.31 (1H, m), 5.52 (1H, dd, *J*=15.87, 6.41 Hz), 5.83 (1H, dd, *J*=15.87, 1.22 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.68 (2H, d, *J*=8.24 Hz). Found: C, 62.58; H, 7.66%. Calcd for $C_{14}H_{20}O_3S$: C, 62.31; H, 7.51%.

(*E*)-6-Methyl-6-tosyl-4-hepten-3-ol (19c). An oil; MS *m/z* 283 (M^++1; 1.41%), 265 (23.39), 127 (45.10), 109 (100.00); IR (neat) 3560—3440, 3050, 2990, 2950, 2890, 1590, 1490, 1450, 1280, 1150, 1120, 1070, 970, 805, 700, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, *J*=7.33 Hz), 1.44 (6H, s), 1.45—1.57 (2H+1H, m), 2.44 (3H, s), 4.05 (1H, m), 5.51 (1H, dd, *J*=15.87, 6.11 Hz), 5.84 (1H, dd, *J*=15.87, 1.22 Hz), 7.31 (2H, d, *J*=8.24 Hz), 7.69 (2H, d, *J*=8.24 Hz).

(*E*)-6-Methyl-1-phenyl-6-tosyl-4-hepten-3-ol (19d). An oil; MS *m/z* 359 (M^++1; 0.20%), 341 (1.36), 204 (82.47), 203 (100.00), 185 (100.00), 133 (100.00), 105 (100.00), 91 (99.92); IR (neat) 3520—3420, 3010, 2965, 2910, 2840, 1720, 1580, 1480, 1440, 1270, 1140, 1110, 1060, 960, 800, 730, 700, 685, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.41 (6H, s), 1.71—1.81 (2H, m), 2.36 (3H, s), 2.54—2.71 (2H+1H, m), 4.10—4.15 (1H, m), 5.53 (1H, dd, *J*=15.56, 6.10 Hz), 5.84 (1H, dt, *J*=15.56, 1.22 Hz), 7.14—7.18 (3H, m), 7.24—7.28 (4H, m), 7.68 (2H, d, *J*=8.24 Hz).

Preparation of (*E*)-1-Benzyloxy-4-methyl-4-tosyl-2-pentene (20a). To a solution of **19a** (81 mg, 0.318 mmol) in dry DMF (1.0 ml) were added benzyl bromide (0.378 ml, 3.18 mmol) and silver(I) oxide (369 mg, 1.59 mmol) with stirring in the dark under nitrogen. After stirring for 2 d, an insoluble substance was filtered off and washed with ether. The filtrate was successively washed with water and brine, and dried over Na_2SO_4. The residue obtained by evaporating the solvent in vacuo was subjected to preparative TLC (SiO_2, benzene/AcOEt=30/1, v/v) to afford **20a** in 69% yield (75 mg) as an oil; MS *m/z* 345 (M^++1; 0.77%), 247 (55.95), 189 (100.00), 171 (100.00), 129 (97.82), 92 (100.00), 91 (100.00), 82 (57.68); IR (neat) 3010, 2960, 2900, 2835, 1580, 1480, 1440, 1270, 1140, 1110, 1060, 960, 800, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.42 (6H, s), 2.42 (3H, s), 4.63 (2H, dd, *J*=5.80, 1.53 Hz), 4.65 (2H, s),

5.55 (1H, dt, J=15.87, 5.80 Hz), 5.94 (1H, dt, J=15.87, 1.53 Hz), 7.25—7.34 (7H, m), 7.64 (2H, d, J=8.24 Hz).

In a similar manner, **20b—d** were prepared in 67, 62, and 73% yields, respectively. Their physical and spectral data are given in the following:

(*E*)-5-Benzyloxy-2-methyl-2-tosyl-3-hexene (20b). An oil; MS m/z 359 (M^++1; 4.38%), 204 (69.71), 203 (100.00), 145 (100.00), 96 (100.00), 92 (78.02), 91 (87.65); IR (neat) 3020, 2970, 2920, 2860, 1730, 1585, 1485, 1440, 1290, 1145, 1120, 1070, 965, 805, 730, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.21 (3H, d, J=6.41 Hz), 1.42 (3H, s), 1.47 (3H, s), 2.39 (3H, s), 3.95 (1H, dq, J=7.32, 6.41 Hz), 4.34 (1H, d, J=11.90 Hz), 4.41 (1H, d, J=11.90 Hz), 5.41 (1H, dd, J=15.87, 7.32 Hz), 5.84 (1H, d, J=15.87 Hz), 7.25—7.34 (7H, m), 7.68 (2H, d, J=8.24 Hz).

(*E*)-5-Benzyloxy-2-methyl-2-tosyl-3-heptene (20c). An oil; MS m/z 373 (M^++1; 0.27%), 217 (46.20), 110 (25.30), 109 (100.00), 91 (87.65); IR (neat) 3050, 3020, 2960, 2920, 2860, 1580, 1480, 1440, 1280, 1140, 1110, 1060, 960, 800, 720, 695, 660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (3H, t, J=7.33 Hz), 1.43 (3H, s), 1.46 (3H, s), 1.47—1.53 (1H, m), 1.55—1.63 (1H, m), 2.38 (3H, s), 3.69 (1H, q, J=7.02 Hz), 4.31 (1H, d, J=11.90 Hz), 4.37 (1H, d, J=11.90 Hz), 5.41 (1H, dd, J=15.87, 7.02 Hz), 5.85 (1H, d, J=15.87 Hz), 7.24—7.35 (7H, m), 7.69 (2H, d, J=8.24 Hz).

(*E*)-5-Methoxy-2-methyl-7-phenyl-2-tosyl-3-heptene (20d). An oil; MS m/z 373 (M^++1; 7.67%), 218 (98.31), 217 (100.00), 186 (100.00), 185 (100.00), 161 (100.00), 143 (39.62), 129 (65.75), 112 (54.46), 91 (99.91); IR (neat) 3010, 2960, 2910, 2810, 1725, 1585, 1480, 1440, 1285, 1145, 1110, 1065, 965, 800, 735, 700, 685, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.44 (3H, s), 1.45 (3H, s), 1.62—1.71 (1H, m), 1.77—1.86 (1H, m), 2.39 (3H, s), 2.53—2.68 (2H, m), 3.21 (3H, s), 3.52—3.57 (1H, m), 5.37 (1H, dd, J=15.57, 7.63 Hz), 5.84 (1H, dd, J=15.57, 0.92 Hz), 7.14—7.21 (3H, m), 7.25—7.30 (4H, m), 7.68 (2H, d, J=8.24 Hz).

Preparation of (*E*)-1-Benzylthio-4-methyl-4-tosyl-2-pentene (20e). An aqueous solution (60 ml) of sodium p-toluenesulfinate tetrahydrate (p-$CH_3C_6H_4SO_2Na{\cdot}4H_2O$, 11.250 g, 45 mmol) was vigorously stirred with a solution of iodine (7.614 g, 30 mmol) in ethyl acetate (60 ml) at 0 °C for 3 h in a flask equipped with a balloon containing 1,3-butadiene. After the usual work-up, **(*E*)-1-tosyl-4-iodo-2-butene (21)** was obtained as the sole product in quantitative yield (10.122 g). Mp 60.5—61.5 °C (from i-PrOH); IR (KBr) 3030, 2950, 2900, 1580, 1400, 1290, 1130, 1080, 960, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.45 (3H, s), 3.75 (2H, d, J=7.33 Hz), 3.79 (2H, d, J=7.63 Hz), 5.65 (1H, dt, J=15.06, 7.33 Hz), 5.76 (1H, dt, J=15.06, 7.63 Hz), 7.36 (2H, d, J=8.24 Hz), 7.74 (2H, d, J=8.24 Hz). Found: C, 39.60; H, 3.96%. Calcd for $C_{11}H_{13}IO_2S$: C, 39.30; H, 3.90%.

To a solution of **21** (1.008 g, 3 mmol) in THF (1.5 ml) was added 40% aqueous dimethylamine solution (9 ml, 9 mmol) at room temperature under nitrogen. After stirring for 3.5 h, the product was extracted with ether and washed successively with an aqueous $NaHSO_3$ solution, brine, and dried over Na_2SO_4. After evaporating the solvent, the resulting residue was subjected to alumina column chromatography (Et_2O/hexane=2/1, v/v) to afford 711 mg of **(*E*)-1-tosyl-4-dimethylamino-2-butene (22)** in 94% yield. An oil; MS m/z 253 (M^+; 2.77%), 98 (100.00), 97 (90.88), 91 (38.37), 82 (37.30), 58 (60.54), 55 (30.43), 44 (42.45), 42 (34.27); IR (neat) 2920, 2800, 2760, 1580, 1440, 1390, 1300, 1140, 1080, 1000, 800, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.14 (6H, s), 2.44 (3H, s), 2.89 (2H, d, J=4.58 Hz), 3.78 (2H, d, J=5.50 Hz), 5.58—5.61 (2H, m), 7.33 (2H, d, J=8.24 Hz), 7.73 (2H, d, J=8.24 Hz).

To a solution of **22** (127 mg, 0.5 mmol) in THF (1 ml) was added n-BuLi (1.1 mmol) at 0 °C under nitrogen, followed by the addition of a solution of iodomethane (159 mg, 1.1 mmol) in THF (1 ml) after 30 min. After stirring for 12 h, the reaction mixture was quenched by the addition of a phosphate buffer solution (pH 7). **(*E*)-4-Methyl-1-dimethylamino-4-tosyl-2-pentene (23)** was isolated by alumina column chromatography (ether) in 76% yield (107 mg) after the usual work-up. An oil; MS m/z 281 (M^+; 0.78%), 126 (99.89), 58 (100.00); IR (neat) 2960, 2920, 2840, 2800, 2760, 1580, 1440, 1280, 1140, 1110, 1060, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.44 (6H, s), 2.16 (6H, s), 2.43 (3H, s), 2.90 (2H, dd, J=6.56, 1.35 Hz), 5.52 (1H, dt, J=15.87, 6.56 Hz), 5.80 (1H, dt, J=15.87, 1.35 Hz), 7.29 (2H, d, J=8.24 Hz), 7.67 (2H, d, J=8.24 Hz).

To a solution of **23** (28 mg, 0.1 mmol) in THF (0.15 ml) was added a solution of iodomethane (27 mg, 0.19 mmol) in THF (2 ml). After stirring for 1.5 h, the quaternary salt of **23** obtained by evaporating the solvent was used for the following reaction without purification.

To a solution of phenylmethanethiol (15 mg, 0.12 mmol) in THF (1 ml) was added n-BuLi (0.12 mmol) at 0 °C under nitrogen, followed by the addition of a solution of the crude quaternary salt of **23** in THF (2.5 ml) after 20 min. After stirring for 20 h, the reaction mixture was worked up in the usual manner. Compound **20e** was isolated in 78% (28 mg) yield by preparative TLC (SiO_2, hexane/AcOEt=4/1, v/v) as an oil; MS m/z 361 (M^+; 0.83%), 207 (16.67), 206 (44.68), 205 (100.00), 123 (16.04), 113 (60.28), 92 (48.18), 91 (100.00), 82 (27.82), 81 (100.00), 79 (21.76), 77 (15.01), 67 (30.75), 65 (53.68), 45 (24.69), 39 (22.68); IR (neat) 3020, 2960, 2910, 1580, 1440, 1280, 1110, 1060, 960, 800, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39 (6H, s), 2.42 (3H, s), 2.99 (2H, d, J=7.02 Hz), 3.60 (2H, s), 5.44 (1H, dt, J=15.57, 7.02 Hz), 5.69 (1H, d, J=15.57 Hz), 7.21—7.31 (7H, m), 7.67 (2H, d, J=8.24 Hz).

Preparation of (*E*)-5-Benzylthio-2-methyl-2-tosyl-3-hexene (20f). The hydroxyl group of **19b** (956 mg, 3.76 mmol) was brominated with phosphorous tribromide (0.356 ml, 3.76 mmol) and pyridine (0.30 ml, 3.76 mmol) in dry dichloromethane (7.5 ml) at room temperature under nitrogen. The crude bromide was then reacted with phenylmethanethiolate prepared in situ from phenylmethanethiol (0.44 ml, 3.76 mmol) and n-BuLi (f=0.620 ml $mmol^{-1}$, 2.33 ml, 3.76 mmol) in dry THF (20—30 ml) at 0 °C overnight under nitrogen. After the usual work-up, **20f** was isolated in 53% yield (746 mg) by preparative TLC (SiO_2, hexane/AcOEt=5/1, v/v) as an oil; MS m/z 374 (M^+; 0.26%), 219 (50.89), 95 (55.22), 91 (100.00); IR (neat) 3080, 3040, 2990, 2940, 2880, 1590, 1490, 1445, 1290, 1145, 1120, 1070, 960, 800, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.23 (3H, d, J=6.71 Hz), 1.38 (3H, s), 1.48 (3H, s), 2.40 (3H, s), 3.25 (1H, m), 3.60 (2H, s), 5.38 (1H, dd, J=15.57, 8.54 Hz), 5.66 (1H, d, J=15.57 Hz), 7.21—7.34 (7H, m), 7.69 (2H, d, J=8.24 Hz).

In a similar manner, **20g, h** were prepared in 70 and 75% yields, respectively. Their physical and spectral data are given in the following:

(*E*)-5-Benzylthio-2-methyl-2-tosyl-3-heptene (20g). An oil; MS m/z 389 (M^++1; 1.94%), 233 (100.00), 91 (30.96); IR (neat) 3060, 3040, 2970, 2930, 2880, 1585, 1485, 1440, 1290, 1145, 1120, 1065, 960, 800, 700, 670 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (3H, t, J=7.33 Hz), 1.45—1.62 (2H, m), 1.41 (3H, s), 1.48 (3H, s), 2.40 (3H, s), 3.03 (1H, m), 3.58 (2H, s), 5.38 (1H, dd, J=15.87, 9.15 Hz), 5.66 (1H, d, J=15.87 Hz), 7.23—7.30 (7H, m), 7.71 (2H, d, J=8.24 Hz).

(*E*)-5-Methylthio-2-methyl-7-phenyl-2-tosyl-3-heptene (20h). An oil; MS m/z 388 (M^++1; 0.78%), 233 (79.48), 185 (79.44), 149 (100.00), 95 (63.39), 91 (77.59); IR (neat) 3060, 3030, 2980, 2920,

2860, 1730, 1585, 1480, 1440, 1290, 1140, 1115, 1065, 960, 800, 740, 700, 685, 665 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.44 (3H, s), 1.47 (3H, s), 1.73—1.91 (2H, m), 1.93 (3H, s), 2.38 (3H, s), 2.59—2.64 (2H, m), 3.04—3.10 (1H, m), 5.36 (1H, dd, J=15.56, 9.15 Hz), 5.67 (1H, d, J=15.56 Hz), 7.13—7.21 (3H, m), 7.26—7.30 (4H, m), 7.68 (2H, d, J=8.24 Hz).

Preparation of (*E*)-2,5-Dimethyl-7-phenyl-2-tosyl-3-heptene (20i). Alcohol **17d** was tosylated in the usual manner to give **24** in 85% yield, which was reacted with Me_2CuLi to afford **25** in 55% yield, as described concerning the preparation of **11h**. Iodosulfonization of **25** and a subsequent treatment with DBU gave **26** (86% yield, *E*/*Z*=52/48), as described concerning the preparation of **15**. The (*E*)-Isomer of **26** was separated and dimethylated at the α-position, as described for **23**, to afford **20i** in 97% yield.

The physical and spectral data of **24—26**,**20i** are given in the following:

1-Phenethyl-3-butenyl *p*-Toluenesulfonate (24). An oil; MS *m*/*z* 331 (M^++1; 1.15%), 159 (100.00), 158 (100.00), 155 (99.87), 129 (100.00), 118 (100.00), 117 (99.85), 105 (99.93), 104 (99.93), 92 (99.89), 91 (99.50); IR (neat) 3055, 3010, 2920, 2840, 1630, 1585, 1485, 1440, 1425, 1355, 1175, 1165, 1085, 895, 740, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82—1.97 (2H, m), 2.33—2.54 (6H, m), 2.56—2.66 (1H, m), 4.58—4.66 (1H, m), 5.00—5.07 (2H, m), 5.60—5.70 (1H, m), 7.04—7.09 (2H, m), 7.15—7.20 (1H, m), 7.21—7.28 (2H, m), 7.30—7.37 (2H, m), 7.80 (2H, d, J=8.24 Hz).

4-Methyl-6-phenyl-1-hexene (25). An oil; MS *m*/*z* 174 (M^+; 15.72%), 131 (42.25), 117 (17.57), 104 (60.50), 92 (24.57), 91 (100.00); IR (neat) 3040, 3000, 2890, 1620, 1475, 1435, 1420, 1360, 975, 895, 735, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94 (3H, d, J=6.40 Hz), 1.38—1.71 (3H, m), 1.91—1.98 (1H, m), 2.08—2.14 (1H, m), 2.57 (1H, ddd, J=13.73, 10.07, 6.10 Hz), 2.66 (1H, ddd, J=13.73, 10.07, 5.80 Hz), 4.99 (1H, d, J=10.38 Hz), 5.00 (1H, d, J=17.09 Hz), 5.78 (1H, ddt, J=17.09, 10.38, 7.32 Hz), 7.13—7.30 (5H, m).

4-Methyl-6-phenyl-1-tosyl-2-hexene (26). (*E*)-form: An oil; MS *m*/*z* 328 (M^+; 0.14%), 172 (44.83), 157 (11.39), 131 (51.13), 105 (15.25), 91 (100.00), 65 (12.63); IR (neat) 3026, 2957, 2925, 1598, 1496, 1454, 1401, 1318, 1303, 1290, 1235, 1146, 1088, 973, 816, 742, 701, 667 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.93 (3H, d, J=7.02 Hz), 1.40—1.57 (2H, m), 2.08—2.20 (1H, m), 2.37 (3H, s), 2.42 (2H, t, J=7.93 Hz), 3.70—3.82 (2H, m), 5.34—5.46 (2H, m), 7.06—7.33 (7H, m), 7.73 (2H, d, J=8.24 Hz).

(*Z*)-form: Mp 87.0—88.0 °C (crude); MS *m*/*z* 328 (M^+; 0.12%), 172 (97.42), 157 (40.77), 131 (100.00), 105 (40.70), 104 (41.25), 92 (28.99), 91 (77.03), 65 (27.07), 41 (15.48); IR (KBr) 3027, 2961, 2927, 2853, 1597, 1496, 1453, 1410, 1311, 1239, 1143, 1087, 808, 769, 733, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.75 (3H, d, J=6.71 Hz), 1.27—1.40 (1H, m), 1.44—1.56 (1H, m), 2.05—2.20 (1H, m), 2.22—2.40 (5H, m), 3.77 (2H, d, J=7.63 Hz), 5.41 (1H, dt, J=10.68, 7.63 Hz), 5.52 (1H, t, J=10.68 Hz), 7.03—7.34 (7H, m), 7.73 (2H, d, J=8.24 Hz).

(*E*)-2,5-Dimethyl-7-phenyl-2-tosyl-3-heptene (20i). An oil; MS *m*/*z* 200 (M^+−TsH; 22.27%), 109 (45.76), 91 (52.44); IR (neat) 2957, 2925, 1598, 1495, 1454, 1384, 1309, 1298, 1287, 1157, 1127, 1079, 977, 816, 735, 713, 700, 685 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.97 (3H, d, J=7.02 Hz), 1.41 (3H, s), 1.45 (3H, s), 1.51—1.57 (2H, m), 2.18 (1H, m), 2.38 (3H, s), 2.48 (2H, t, J=8.24 Hz), 5.33 (1H, dd, J=15.87, 8.24 Hz), 5.60 (1H, dd, J=15.87, 0.91 Hz), 7.12—7.29 (7H, m), 7.68 (2H, d, J=8.24 Hz).

Desulfonylation Reaction of Allylic Sulfones to the Corresponding Alkadienes. To a solution of *t*-BuOK (10 mmol) in *t*-BuOH (10 ml) was added a solution of allylic sulfone (1 mmol) in *t*-BuOH (7.2 ml) at room temperature under nitrogen; the mixture was then refluxed. An aliquot (0.8 ml) of the reaction mixture was taken out with a syringe at arbitrary time intervals and immediately quenched by introducing it into a diluted methanolic HCl solution [or phosphate buffer solution (pH 7)]. The organic substances were extracted with either hexane or ether, followed by washing with water and brine and drying over Na_2SO_4. The ^1H NMR ($CDCl_3$) spectrum of the residue obtained by evaporating the solvent was taken to determine the ratio of the (*E*)- and (*Z*)-alkadienes and recovery of allylic sulfones. In order to determine the isolated total yield, the residue obtained from a larger portion of the reaction mixture was separated by preparative TLC (or alumina TLC, solvent; hexane). The physical and spectral data of the resulting alkadienes (**27a—h**, **28a—i**) are given in the following:

5-Propyl-2,4-octadiene (27a). An oil; MS *m*/*z* 152 (M^+; 70.33%), 123 (55.88), 109 (60.93), 95 (25.11), 81 (100.00), 57 (35.83); IR (neat) 2980, 2940, 2880, 1640, 1600, 1460, 1370, 1265, 955, 920, 710 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.90 (3H, t, J=7.33 Hz), 0.91 (3H, t, J=7.33 Hz), 1.44 (4H, m), 1.74 (3H, dd, J=7.02, 1.53 Hz), 1.99 (2H, t, J=7.63 Hz), 2.11 (2H, t, J=7.63 Hz), 5.57 (1H, dq, J=14.95, 6.71 Hz), 5.79 (1H, d, J=10.99 Hz), 6.27 (1H, ddq, J=14.95, 10.99, 1.83 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.90 (3H, t, J=7.33 Hz), 0.91 (3H, t, J=7.33 Hz), 1.44 (4H, m), 1.74 (3H, dd, J=7.02, 1.53 Hz), 2.05 (2H, t, J=7.63 Hz), 2.11 (2H, t, J=7.63 Hz), 5.40 (1H, dq, J=10.68, 7.02 Hz), 6.09 (1H, d, J=11.60 Hz), 6.22 (1H, ddq, J=11.60, 10.99, 1.83 Hz).

6-Propyl-3,5-nonadiene (27b). An oil; MS *m*/*z* 166 (M^+; 53.92%), 137 (34.06), 123 (71.03), 95 (97.27), 81 (93.10), 71 (64.44), 57 (100.00), 55 (67.89), 43 (58.97), 41 (46.49); IR (neat) 3025, 2960, 2931, 2871, 1646, 1603, 1464, 1378, 1337, 1302, 1066, 963, 888, 868, 742 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.85—0.94 (6H, m), 1.01 (3H, t, J=7.63 Hz), 1.36—1.51 (4H, m), 1.96—2.24 (6H, m), 5.60 (1H, dt, J=14.95, 7.32 Hz), 5.79 (1H, d, J=10.99 Hz), 6.25 (1H, ddt, J=14.95, 10.99, 1.52 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.85—0.94 (6H, m), 1.00 (3H, t, J=7.63 Hz), 1.36—1.51 (4H, m), 1.96—2.24 (6H, m), 5.32 (1H, dt, J=10.99, 7.32 Hz), 6.07 (1H, d, J=11.91 Hz), 6.16 (1H, tt, J=10.99, 1.53 Hz).

4-Propyl-4,6-tetradecadiene (27c). An oil; MS *m*/*z* 236 (M^+; 95.31%), 193 (37.75), 151 (50.50), 137 (22.10), 123 (49.23), 109 (86.02), 95 (100.00), 81 (58.16), 67 (51.04); IR (neat) 3040, 2960, 2930, 2880, 1630, 1595, 1460, 1370, 950 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.84—0.94 (9H, m), 1.20—1.54 (14H, m), 1.96—2.21 (6H, m), 5.56(1H, dt, J=14.96, 7.33 Hz), 5.79 (1H, d, J=10.68 Hz), 6.14—6.29 (1H, m). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.84—0.94 (9H, m), 1.20—1.54 (14H, m), 1.96—2.21 (6H, m), 5.32 (1H, dt, J=10.68, 7.33 Hz), 6.07 (1H, d, J=11.60 Hz), 6.14—6.29 (1H, m).

2-Methyl-2,4-dodecadiene (27d). An oil; MS *m*/*z* 180 (M^+; 22.55%), 97 (56.93), 82 (75.98), 69 (21.08), 67 (33.76); IR (neat) 2920, 2860, 1610, 1440, 1380, 1030, 980, 950, 850, 710 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form (**6**) δ=0.88 (3H, t, J=7.02 Hz), 1.27—1.39 (10H, m), 1.73 (3H, s), 1.80 (3H, s), 2.07 (2H, q, J=7.02 Hz), 5.55 (1H, dt, J=14.96, 7.02 Hz), 5.78 (1H, d, J=10.68 Hz), 6.21 (1H, dd, J=14.96, 10.68 Hz). ^1H NMR ($CDCl_3$) of (*Z*)-form δ=0.88 (3H, t, J=7.02 Hz), 1.27—1.39 (10H, m), 1.75 (3H, s), 1.80 (3H, s), 2.15 (2H, q, J=7.02 Hz), 5.33 (1H, dt, J=10.68, 7.02 Hz), 6.07 (1H, d, J=10.68 Hz), 6.15 (1H, t, J=10.68, 7.02 Hz).

2-Methyl-2,4-tridecadiene (27e). An oil; MS *m*/*z* 194 (M^+; 49.50%), 95 (100.00), 82 (87.88), 69 (21.97), 67 (24.76); IR (neat) 3010, 2910, 2840, 1450, 1365, 970, 950, 840, 710 cm^{-1}; ^1H NMR ($CDCl_3$) of (*E*)-form δ=0.88 (3H, t, J=6.71 Hz), 1.27—1.37 (12H, m), 1.74 (3H, s), 1.80 (3H, s), 2.07 (2H, q, J=7.32 Hz), 5.54 (1H,

dt, J=15.10, 7.32 Hz), 5.78 (1H, d, J=10.68 Hz), 6.21 (1H, dd, J=15.10, 10.68 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=0.88 (3H, t, J=6.71 Hz), 1.27—1.37 (12H, m), 1.75 (3H, s), 1.80 (3H, s), 2.15 (2H, q, J=7.33 Hz), 5.33 (1H, dt, J=10.68, 7.02 Hz), 6.06 (1H, d, J=10.68 Hz), 6.15 (1H, t, J=10.68 Hz).

2-Methyl-6-propyl-3,5-nonadiene (27f). An oil; MS *m/z* 180 (M^+; 70.69%), 165 (17.54), 151 (14.04), 137 (100.00), 123 (17.94), 109 (25.01), 95 (61.46), 81 (43.10), 67 (13.89); IR (neat) 2980, 2940, 2880, 1640, 1600, 1460, 1375, 1280, 960, 925, 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=0.85—0.94 (6H, m), 0.98 (3H, d, J=6.71 Hz), 1.01 (3H, d, J=6.41 Hz), 1.37—1.52 (4H, m), 1.97—2.15 (4H, m), 2.28—2.42 (1H, m), 5.54 (1H, dd, J=15.26, 7.02 Hz), 5.78 (1H, d, J=10.68 Hz), 6.21 (1H, ddd, J=15.26, 10.68, 1.22 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=0.85—0.94 (6H, m), 0.98 (3H, d, J=6.71 Hz), 1.01 (3H, d, J=6.41 Hz), 1.37—1.52 (4H, m), 1.97—2.15 (4H, m), 2.72—2.88 (1H, m), 5.10—5.22 (1H, m), 6.04—6.14 (2H, m).

2,2-Dimethyl-6-propyl-3,5-nonadiene (27g). An oil; MS *m/z* 194 (M^+; 15.17%), 179 (16.15), 151 (14.27), 137 (8.43), 123 (12.65), 109 (24.92), 95 (32.50), 81 (22.20), 57 (34.18), 43 (100.00); IR (neat) 2960, 2940, 2880, 1630, 1605, 1455, 1370, 1360, 1255, 1195, 960, 940, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=0.85—0.95 (6H, m), 1.04 (9H, s), 1.37—1.50 (4H, m), 1.97—2.17 (4H, m), 5.61 (1H, d, J=15.26 Hz), 5.79 (1H, d, J=10.98 Hz), 6.18 (1H, dd, J=15.26, 10.98 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=0.85—0.95 (6H, m), 1.16 (9H, s), 1.37—1.50 (4H, m), 1.97—2.17 (4H, m), 5.28 (1H, d, J=11.59 Hz), 6.02 (1H, dd, J=11.90, 11.59 Hz), 6.27 (1H, d, J=11.90 Hz).

1-Phenyl-4-propyl-1,3-heptadiene (27h). An oil; MS *m/z* 214 (M^+; 100.00%), 185 (65.98), 171 (44.15), 143 (69.95), 129 (75.08), 115 (38.02), 91 (83.51); IR (neat) 3029, 2957, 2929, 2870, 1635, 1595, 1496, 1464, 1455, 1377, 960, 746, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=0.92 (3H, t, J=7.33 Hz), 0.95 (3H, t, J=7.33 Hz), 1.48 (4H, tq, J=7.63, 7.33 Hz), 2.09 (2H, t, J=7.63 Hz), 2.23 (2H, t, J=7.63 Hz), 6.01 (1H, d, J=10.98 Hz), 6.45 (1H, d, J=15.56 Hz), 7.02 (1H, dd, J=15.56, 10.98 Hz), 7.18 (1H, t, J=7.33 Hz), 7.30 (2H, dd, J=7.63, 7.33 Hz), 7.39 (2H, d, J=7.63 Hz). ^{1}H NMR (C_6D_6) of (*E*)-form δ=0.88 (3H, t, J=7.32 Hz), 0.89 (3H, t, J=7.32 Hz), 1.43 (4H, tq, J=7.63, 7.32 Hz), 2.03 (2H, t, J=7.63 Hz), 2.17 (2H, t, J=7.63 Hz), 6.08 (1H, d, J=10.99 Hz), 6.48 (1H, d, J=15.56 Hz), 7.04 (1H, t, J=7.33 Hz), 7.11—7.18 (3H, m), 7.35 (2H, d, J=7.63 Hz). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=0.92 (3H, t, J=7.33 Hz), 0.95 (3H, t, J=7.33 Hz), 1.48 (4H, tq, J=7.63, 7.33 Hz), 2.03—2.13 (2H, m), 2.16—2.30 (2H, m), 6.31 (1H, d, J=11.29 Hz), 6.37 (1H, d, J=11.60 Hz), 6.43—6.51 (1H, m), 7.26—7.44 (5H, m). ^{1}H NMR (C_6D_6) of (*Z*)-form δ=0.88 (3H, t, J=7.32 Hz), 0.89 (3H, t, J=7.32 Hz), 1.30—1.50 (4H, m), 1.92—2.00 (2H, m), 2.10—2.18 (2H, m), 6.39 (1H, d, J=11.59 Hz), 6.53 (1H, t, J=11.59 Hz), 7.04 (1H, t, J=7.33 Hz), 7.11—7.18 (3H, m), 7.41 (2H, d, J=7.63 Hz).

(*Z*)-1-Benzyloxy-4-methyl-1,3-pentadiene (28a). An oil; MS *m/z* 188 (M^+; 44.43%), 159 (19.90), 92 (40.05), 91 (100.00), 65 (47.34), 41 (65.20), 39 (40.05); IR (neat) 3030, 2960, 2900, 2860, 1640, 1600, 1480, 1440, 1260, 1120, 1060, 845, 730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.70 (3H, d, J=1.22 Hz), 1.79 (3H, s), 4.84 (2H, s), 5.22 (1H, dd, J=11.29, 6.41 Hz), 5.98 (1H, d, J=6.41 Hz), 6.21 (1H, dq, J=11.29, 1.22 Hz), 7.28—7.38 (5H, m).

2-Benzyloxy-5-methyl-2,4-hexadiene (28b). An oil; MS *m/z* 202 (M^+; 14.10%), 159 (24.46), 111 (19.77), 91 (100.00), 43 (29.21); IR (neat) 3040, 2920, 1650, 1610, 1485, 1440, 1380, 1350, 1290, 1220, 1150, 1015, 720, 680 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.70 (3H, s), 1.79 (3H, s), 1.97 (3H, s), 4.80 (2H, s), 5.43 (1H, d, J=10.99 Hz), 5.84 (1H, d, J=10.99 Hz), 7.26—7.38 (5H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.69 (3H, s), 1.78 (3H, s), 1.94 (3H, s), 4.88 (2H, s), 5.33 (1H, d, J=10.99 Hz), 6.21 (1H, d, J=10.99 Hz), 7.28—7.37 (5H, m).

5-Benzyloxy-2-methyl-2,4-heptadiene (28c). An oil; MS *m/z* 216 (M^+; 50.85%), 159 (96.62), 125 (49.44), 91 (100.00), 57 (49.08); IR (neat) 3050, 2940, 2860, 1650, 1610, 1490, 1450, 1260, 1220, 1150, 1020, 725, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.05 (3H, t, J=7.32 Hz), 1.62 (3H, s), 1.71 (3H, s), 2.27 (2H, q, J=7.32 Hz), 4.71 (2H, s), 5.29 (1H, d, J=10.68 Hz), 5.80 (1H, broad d, J=10.68 Hz), 7.26—7.32 (5H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.03 (3H, t, J=7.32 Hz), 1.63 (3H, s), 1.70 (3H, s), 2.17 (2H, q, J=7.32 Hz), 4.74 (2H, s), 5.35 (1H, d, J=10.99 Hz), 6.14 (1H, broad d, J=10.99 Hz), 7.26—7.32 (5H, m).

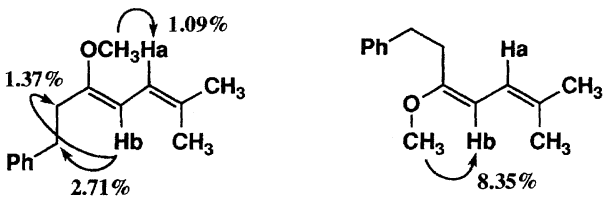
5-Methoxy-2-methyl-7-phenyl-2,4-heptadiene (28d). An oil; MS *m/z* 216 (M^+; 97.99%), 125 (100.00), 91 (61.30), 71 (27.81); IR (neat) 3060, 3030, 2920, 2860, 1640, 1600, 1485, 1440, 1360, 1290, 1130, 1060, 740, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.69 (3H, s), 1.78 (3H, s), 2.48 (2H, t, J=8.24 Hz), 2.80 (2H, t, J=8.24 Hz), 3.62 (3H, s), 5.37 (1H, d, J=10.98 Hz), 6.14 (1H, dt, J=10.98, 1.22 Hz), 7.17—7.22 (3H, m), 7.25—7.31 (2H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.71 (3H, s), 1.77 (3H, s), 2.54 (2H, t, J=8.24 Hz), 2.79 (2H, t, J=8.24 Hz), 3.61 (3H, s), 5.31 (1H, d, J=10.99 Hz), 5.81 (1H, d, J=10.99 Hz), 7.17—7.22 (3H, m), 7.26—7.30 (2H, m).

The structures of **28d** were confirmed by NOE as shown in the following (Chart 1):

1-Benzylthio-4-methyl-1,3-pentadiene (28e). An oil; MS *m/z* 204 (M^+; 10.13%), 113 (49.71), 91 (47.59), 58 (36.30), 43 (100.00); IR (neat) 3028, 2966, 2909, 2852, 1642, 1602, 1561, 1494, 1452, 1378, 1365, 1318, 1240, 1070, 1030, 935, 859, 744, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=0.70 (3H, s), 1.74 (3H, s), 3.89 (2H, s), 5.77 (1H, d, J=10.98 Hz), 6.01 (1H, d, J=14.95 Hz), 6.41 (1H, dd, J=14.95, 10.84 Hz), 7.22—7.34 (5H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.72 (3H, s), 1.80 (3H, s), 3.89 (2H, s), 5.82 (1H, d, J=9.46 Hz), 6.05 (1H, dd, J=11.29. 1.22 Hz), 6.25 (1H, dd, J=11.14, 9.61 Hz), 7.22—7.34 (5H, m).

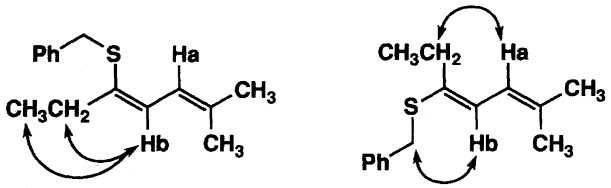
2-Benzylthio-5-methyl-2,4-hexadiene (28f). An oil; MS *m/z* 218 (M^+; 5.31%), 127 (73.25), 91 (100.00); IR (neat) 3070, 3040, 2980, 2920, 2860, 2720, 1665, 1630, 1580, 1485, 1440, 830, 700, 685 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.69 (3H, s), 1.79 (3H, s), 1.99 (3H, s), 3.96 (2H, s), 5.94 (1H, broad d, J=10.99 Hz), 6.18 (1H, d, J=10.99 Hz), 7.21—7.71 (5H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.73 (3H, s), 1.79 (3H, s), 2.06 (3H, s), 3.93 (2H, s), 6.23 (1H, d, J=12.57 Hz), 6.28 (1H, d, J=12.57 Hz), 7.21—7.71 (5H, m).

5-Benzylthio-2-methyl-2,4-heptadiene (28g). An oil; MS *m/z* 232 (M^+; 7.01%), 141 (96.62), 91 (100.00); IR (neat) 3080, 3040, 2980, 2940, 2880, 2740, 1700, 1600, 1580, 1490, 1450, 1370, 840, 760, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.11 (3H, t, J=7.33 Hz), 1.68 (3H, s), 1.78 (3H, s), 2.28 (2H, q, J=7.33 Hz),



(*Z*)-**28d** (major product) (*E*)-**28d** (minor product)

Chart 1.



(*Z*)-28g (major product) **(*E*)-28g** (minor product)

Chart 2.

3.92 (2H, s), 5.96 (1H, d, J=11.29 Hz), 6.09 (1H, d, J=11.29 Hz), 7.18—7.35 (5H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.10 (3H, t, J=7.33 Hz), 1.74 (3H, s), 1.79 (3H, s), 2.34 (2H, q, J=7.33 Hz), 3.85 (2H, s), 6.31 (1H, d, J=10.69 Hz), 6.37 (1H, d, J=10.69 Hz), 7.18—7.35 (5H, m).

The structures of **28g** were confirmed by NOESY as shown in the following (Chart 2):

7-Phenyl-5-methylthio-2-methyl-2,4-heptadiene (28h). An oil; MS *m/z* 232 (M^+; 84.87%), 217 (51.88), 141 (49.17), 105 (44.81), 93 (79.08), 91 (100.00), 77 (44.09); IR (neat) 3080, 3040, 2940, 2880, 1600, 1580, 1490, 1450, 1375, 985, 740, 690 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.75 (3H, s), 1.79 (3H, s), 2.29 (3H, s), 2.61 (2H, t, J=5.50 Hz), 2.82 (2H, t, J=5.50 Hz), 5.96 (2H, s), 7.17—7.22 (3H, m), 7.27—7.31 (2H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.71 (3H, s), 1.82 (3H, s), 2.25 (3H, s), 2.59 (2H, t, J=7.63 Hz), 2.87 (2H, t, J=7.63 Hz), 6.25 (1H, d, J=10.98 Hz), 6.30 (1H, dt, J=10.98, 1.22 Hz), 7.17—7.22 (3H, m), 7.27—7.31 (2H, m).

7-Phenyl-2,5-dimethyl-2,4-heptadiene (28i). An oil; MS *m/z* 200 (M^+; 10.71%), 199 (33.56), 131 (26.05), 112 (25.18), 111 (32.21), 105 (52.50), 91 (100.00), 85 (27.09), 43 (61.48); IR (neat) 3026, 2963, 2920, 2855, 1617, 1603, 1496, 1453, 1383, 1076, 1044, 1031, 844, 745, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) of (*E*)-form δ=1.72 (3H, s), 1.78 (3H, s), 1.80 (3H, s), 2.36 (2H, t, J=7.94 Hz), 2.74 (2H, t, J=7.94 Hz), 5.98 (1H, d, J=12.21 Hz), 6.01 (1H, d, J=12.21 Hz), 7.15—7.20 (3H, m), 7.23—7.29 (2H, m). ^{1}H NMR ($CDCl_3$) of (*Z*)-form δ=1.73 (3H, s), 1.77 (3H, s), 1.81 (3H, s), 2.44 (2H, t, J=7.94 Hz), 2.70 (2H, t, J=7.94 Hz), 5.96 (1H, d, J=12.51 Hz), 6.00 (1H, d, J=12.51 Hz), 7.16—7.20 (3H, m), 7.26—7.30 (2H, m).

References

1) a) K. Inomata, T. Hirata, H. Suhara, H. Kinoshita, H. Kotake, and H. Senda, *Chem. Lett.*, **1988**, 2009; b) T. Hirata, Y. Sasada, T. Ohtani, T. Asada, H. Kinoshita, H. Senda, and K. Inomata, *Bull. Chem. Soc. Jpn.*, **65**, 75 (1992).

2) a) K. Inomata, S. Sasaoka, T. Kobayashi, Y. Tanaka, S. Igarashi, T. Ohtani, H. Kinoshita, and H. Kotake, *Bull. Chem. Soc. Jpn.*, **60**, 1767 (1987); b) T. Kobayashi, Y. Tanaka, T. Ohtani, H. Kinoshita, K. Inomata, and H. Kotake, *Chem. Lett.*, **1987**, 1209; c) K. Inomata, *J. Synth. Org. Chem. Jpn.*, **50**, 326 (1992).

3) a) D. Cremer, *J. Am. Chem. Soc.*, **101**, 7199 (1979); b) K. N. Houk, R. W. Strozier, N. G. Rondan, R. R. Fraser, and N. Chuaqui-Offermanns, *J. Am. Chem. Soc.*, **102**, 1426 (1980), and references cited therein; c) E. Black, R. E. Penn, A. A. Bazzi, and D. Cremer, *Tetrahedron Lett.*, **22**, 29 (1981); d) E. Block, M. Aslam, V. Eswarakrishnan, K. Gebreyes, J. Hutchinson, R. Iyer, J.-A. Laffitte, and A. Wall, *J. Am. Chem. Soc.*, **108**, 4568 (1986); e) J. R. Larson, N. D. Epiotis, and F. Bernardi, *J. Am. Chem. Soc.*, **100**, 5713 (1978), and references cited therein.

4) J. Otera, H. Misawa, and K. Sugimoto, *J. Org. Chem.*, **51**, 3830 (1986).

5) N. Iwata, T. Morioka, T. Kobayashi, T. Asada, H. Kinoshita, and K. Inomata, *Bull. Chem. Soc. Jpn.*, **65**, 1379 (1992), and references cited therein.

6) Many attempts for dialkylation of **8a**—**d** were unsuccessful. The structures of **9a**—**e** were confirmed by NOE measurement and/or based on the known deshielding of alkyl group syn to tosyl group in vinylic sulfones.[8] This rule was applicable to all vinylic sulfones prepared in our laboratory without exception.

7) E. Negishi, N. Okukado, A. O. King, D. E. Van Horn, and B. I. Spiegel, *J. Am. Chem. Soc.*, **100**, 2254 (1978).

8) C. Y. Meyers and I. Sataty, *Tetrahedron Lett.*, **1972**, 4323; W. E. Truce and M. J. Lusch, *J. Org. Chem.*, **43**, 2252 (1978); M. Mikolajczyk, S. Grzejszczak, and A. Zatorski, *J. Org. Chem.*, **40**, 1979 (1975).