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Convenient Methods for the Preparation of Vinylic and Allylic Sulfones from Alkenes, Haloalkanes, and Aldehydes. Stereochemistry of the Conversion of Vinylic Sulfones to the Corresponding Allylic Sulfones

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1- or 2-*p*-Tolylsulfonyl(=tosyl)-1-alkenes, vinylic sulfones, were regioselectively prepared from 1-alkenes via iodosulfonization or sulfonylmercuration and also from 1-haloalkanes by the homologation or unhomologation methods. The vinylic sulfones thus prepared were further converted to the corresponding allylic sulfones under basic conditions. The stereochemistry of this conversion was discussed. One-carbon homologated allylic sulfones were directly obtained from aldehydes in good yields by the reaction with diethyl phenylsulfonylmethylphosphonate and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under mild conditions.

The useful synthetic procedure using vinylic and allylic sulfones as synthons have been recently developed. The importance of vinylic sulfones in synthesis is now well-established.[1-4] Allylic sulfones have been proven to be particularly useful synthetic intermediates,[1] because of the ability of the sulfonyl group to generate an adjacent carbanion[5] and to act as a leaving group in substitution reactions[6] and elimination reactions.[7]

In connection with our continued interest to extend the synthetic utility of sulfones,[8a-c] we have so far investigated the syntheses[9a-c] and reactions[10a-c] of allylic sulfones. Some of them were successfully employed for the synthesis of naturally occurring substances such as recifeiolide,[10b] squalene[10c] and coenzyme Q_{10}.[10c] We herein report facile methods for the preparation of vinylic sulfones from alkenes[11] and haloalkanes and their conversion to the corresponding allylic sulfones under mild basic conditions. On the basis of these facts, a direct preparation of one-carbon homologated allylic sulfones from aldehydes was also achieved.

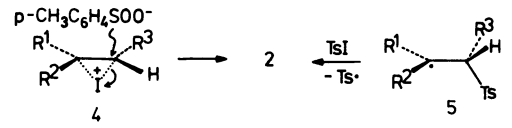
Results and Discussion

Preparation of Vinylic and Allylic Sulfones from Alkenes. Recently Kao Liu and his coworkers reported a convenient synthesis of various β-iodo sulfones,[12] which involves additions of alkane- and arenesulfonyl iodide to alkenes under the catalytic action of copper(II) chloride in aprotic solvents. Though they and others[13] established from the various evidences that tosyl iodide adds homolytically to alkenes, we thought it was possible to prepare β-iodo sulfones in an ionic fashion from iodine and sulfinate just like iodolactonization. Therefore, we tried the iodosulfonization and the subsequent elimination of hydrogen iodide with a base to yield the corresponding vinylic sulfones (**3**). It was consequently found that the iodosulfonization proceeds readily in methanol or in a two-phase system using ethyl acetate and water. The latter is favorable to avoid the formation of methyl *p*-toluenesulfinate as a by-product when an alkene is sparingly soluble in methanol (See the cases of **1d** in Table 1). The subsequent elimination was accomplished by the treatment with triethylamine in dry acetonitrile at room temperature for 15 min. The results are summarized in Table 1.

We could not exclude the possibility of the initial formation of tosyl iodide as an intermediate in the above iodosulfonization, since the reaction was retarded in the dark as in the case of the reaction of tosyl iodide with alkenes (the yield of **3a** was 75% in the reaction carried out in the dark under similar conditions).[9b] However, it was found that the addition of sodium iodide and sodium *p*-toluenesulfinate was effective to improve the yields of the addition products even for the reaction of tosyl iodide carried out in methanol.[14] These results seem to suggest that the reaction proceeds through the competitive two pathways, ionic one through the iodonium intermediate **4** and radical one for tosyl iodide produced in situ. The advantage of the present method for the preparation of vinylic sulfones from alkenes is obvious, namely it does not require the preparation of unstable tosyl iodide and the use of metal catalyst such as copper(II) chloride.

The results in Table 1 show that the iodosulfonization proceeds regiospecifically. This is considered as follows: If the reaction proceeds in an ionic fashion, *p*-toluenesulfinate ion attacks a less hindered carbon atom of the iodonium intermediate **4**, and if in a radical fashion, the more stable radical intermediate **5** is preferentially formed as shown in Scheme 1.

In contrast to the iodosulfonization, it was found that sulfonyl group is introduced on the C-2 position in sulfonylmercuration of 1-alkenes using mercury(II) chloride and sodium *p*-toluenesulfinate. The treatment of the addition product of sulfonylmercuration



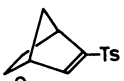
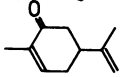
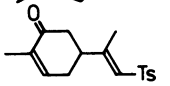
Scheme 1.

with a base afforded exclusively 2-tosyl-1-alkenes (**7a—e**) as shown in Table 2.

This fact seems to suggest that Hg(II) ion of the intermediate **8** does not exist on the central position of olefinic bond, being different from the ionic

Table 1. Preparation of Vinylic Sulfones from Alkenes via Iodosulfonization

Alkene (**1a—j**) $\xrightarrow[(A)]{p\text{-}CH_3C_6H_4SOONa\cdot 4H_2O/I_2}$ [Adduct] (**2a—j**) $\xrightarrow[\text{in } CH_3CN,\ (B)]{Et_3N}$ Vinylic Sulfone (**3a—j**)

1a—k	Alkenes	Molar Ratio of **1**/TsNa·$4H_2O$/I_2	Condition (A), (B)	Product **3a—j**	Yield/% (E/Z)
1a	$C_6H_5CH{=}CH_2$	1/1.5/1 in MeOH	(A) r.t., 15 min (B) r.t., 15 min	$C_6H_5CH{=}CHTs$	89 (100/0)
1b	$CH_3(CH_2)_2CH{=}CH_2$	1.5/1.5/1 in MeOH	(A) r.t., 1 d (B) r.t., 15 min	$CH_3(CH_2)_2CH{=}CHTs$	94 (78/22)
1c	$CH_3(CH_2)_3CH{=}CH_2$	1.5/1.5/1 in MeOH	(A) r.t., 1 d (B) r.t., 15 min	$CH_3(CH_2)_3CH{=}CHTs$	90 (78/22)
1d	$CH_3(CH_2)_7CH{=}CH_2$	1/1.5/1 in MeOH	(A)[a] r.t., 1 d (B) r.t., 15 min	$CH_3(CH_2)_7CH{=}CHTs$	77 (83/17)
1e	$(CH_3)_2C{=}CH_2$	ca. 10/1.5/1 in MeOH	(A) −70 °C/r.t., 3 h (B) r.t., 15 min	$(CH_3)_2C{=}CHTs$	quant.
1f	$(CH_3)_2C{=}CHCH_3$	1.5/1.5/1 in MeOH	(A) r.t., 16 h (B) r.t., 17 h	$(CH_3)_2C{=}C(Ts)CH_3$	80[b]
1g		1/1.5/1 in MeOH	(A) r.t., 3 d (B)[c] r.t., 15 min		76
1d	$CH_3(CH_2)_7CH{=}CH_2$	1/1.5/1 in EtOAc/H_2O	(A) r.t., 1 d (B) r.t., 15 min	$CH_3(CH_2)_7CH{=}CHTs$	96 (78/22)
1h	$(CH_3)_2CHCH{=}CHCH_3$	1/1.5/1 in EtOAc/H_2O	(A) r.t., 2 h (B)[c] r.t., 15 min	$(CH_3)_2CHCH{=}C(Ts)CH_3$	83 (76/24)
1i		1/1.5/1 in EtOAc/H_2O	(A) r.t., 2 h (B)[c] r.t., 15 min		91
1j		1/1.5/1 in EtOAc/H_2O	(A) r.t., 2 h (B) r.t., 15 min		quant. (100/0)

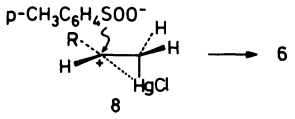
a) $MeOH/CH_2Cl_2$ (4/1) was used as solvent. b) $CH_2{=}C(CH_3)CH(Ts)CH_3$ was obtained as a by-product in 6% yield. c) DBU was used instead of Et_3N.

Table 2. Preparation of Vinylic Sulfones from Alkenes via Sulfonylmercuration

$RCH{=}CH_2$ (**1a—e**) $\xrightarrow[\text{in } MeOH/CH_2Cl_2,\ (A)]{p\text{-}CH_3C_6H_4SOONa\cdot 4H_2O/HgCl_2}$ $[RCH(Ts)CH_2HgCl]$ (**6a—e**) $\xrightarrow[\text{in THF, (B)}]{DBU}$ $RC(Ts){=}CH_2$ (**7a—e**)

Alkene **1a—e**	R	Molar Ratio of **1**/TsNa·$4H_2O$/$HgCl_2$	Condition (A), (B)	Yield/% **7a—e**
1a	C_6H_5	1/1/1	(A) r.t., 1 d (B) DBU (1.2 equiv) r.t., 10 min	61
1b	$CH_3(CH_2)_2$	1.5/1/1	(A) 0 °C, 3 d (B) DBU (1.2 equiv) r.t., 8 h	67[a]
1c	$CH_3(CH_2)_3$	1/1.5/1.2	(A) 0 °C, 3 d (B) DBU (1.7 equiv) r.t., 6 h	72
1d	$CH_3(CH_2)_7$	1/2/2	(A) r.t., 6 h (B) DBU (2.2 equiv) r.t., 12 h	77
1e	$C_6H_5(CH_2)_2$	1/2/2	(A) r.t., 18 h (B) DBU (2.2 equiv) r.t., 16 h	83

a) Based on $HgCl_2$.



Scheme 2.

intermediate **4** of the iodosulfonization mentioned above, but lies on the less hindered carbon atom. Therefore, the tosylate ion attacks the C-2 position as shown in Scheme 2.

O'Connor and Lyness have reported that the equilibrium between 1-methylsulfonyl-1-hexene (**9**) and 1-methylsulfonyl-2-hexene (**10**) under basic conditions (*t*-BuOK in *t*-BuOH at room temperature) almost completely shifts to **10**.[15] We therefore tried the conversion of **3b—d** to the corresponding allylic sulfones (**11b—d**) with DBU as a base in acetonitrile as shown in Scheme 3. In each case, the proton rearrangement products (**11b—d**) were obtained in excellent yields.

On the other hand, it was found that the 2-tosyl-1-alkenes (**7b—d**), prepared above from 1-alkenes via sulfonylmercuration, were also converted to the corresponding allylic sulfones (**11b—d**) by the treatment with *p*-toluenesulfinic acid and DBU in refluxing dioxane (Table 3). This reaction appears to proceed through the addition of *p*-toluenesulfinate anion to give **12**, elimination (**12** to **3**) reaction of *p*-toluenesulfinic acid and the subsequent isomerization as shown in the scheme of Table 3. The intermediate **12** was actually isolated by decreasing the amount of DBU from 4 to 1.5 equiv.

Consequently, the present reactions provide a convenient method for the preparation of allylic sulfones from alkenes via vinylic sulfones.

Table 3. Conversion of 2-Tosyl-1-alkenes to Allylic Sulfones

$$R'CH_2C(Ts)=CH_2 \xrightarrow[\text{dioxane, reflux}]{p\text{-}CH_3C_6H_4SOOH\cdot xH_2O/DBU} \underset{\textbf{7b—d}}{}$$

$$[R'CH_2CH(Ts)CH_2Ts] \xrightarrow[-p\text{-}CH_3C_6H_4SOOH]{} \underset{\textbf{12b—d}}{}$$

$$[\textbf{3b—d}] \xrightarrow{DBU} R'CH=CHCH_2Ts \quad (\textbf{11b—d})$$

Substrates 7b—d	R′	Reaction time[a] h	Yield of 11b—d/% (E/Z)
7b	CH_3CH_2	5	95 (81/19)
7c	$CH_3(CH_2)_2$	4.5	94 (81/19)
7d	$CH_3(CH_2)_6$	4	94 (79/21)

a) ca. 2 equiv of p-$CH_3C_6H_4SOOH\cdot xH_2O$ ($x<1$) and 4 equiv of DBU were used.

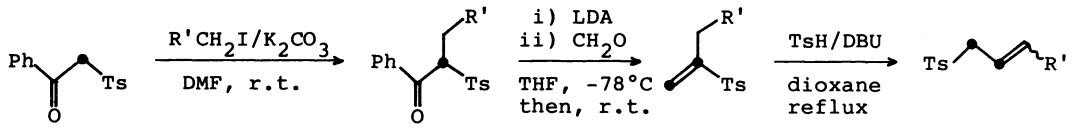
Preparation of Vinylic and Allylic Sulfones from 1-Haloalkanes. In the previous papers,[9c,10d] we have reported the convenient methods for the preparation of two- or three-carbons homologated allylic sulfones from 1-haloalkanes using 2-(1-pyrrolidinyl)ethyl sulfone[9c] or allyl *p*-tolyl sulfone[10d] as a starting material, respectively. We herein report facile and new methods for the preparation of two- or one-carbon(s) homologated and unhomologated vinylic and allylic sulfones from 1-haloalkanes.

It was previously found that the anions of β-keto sulfones react with formaldehyde to give the corresponding vinylic sulfones via deacylation.[8b] The application of this reaction enabled the preparation of two-carbons homologated vinylic (**15**) and allylic (**16**) sulfones starting from 1-haloalkanes as shown in Scheme 4.

$$R'CH_2CH=CHTs \xrightarrow[\text{in } CH_3CN,\ r.t.,\ overnight]{DBU\ (2\ equiv)} R'CH=CHCH_2Ts$$

3b, R′=CH_3CH_2, E/Z=78/22 — **11b**, 91%, E/Z=84/16
3c, R′=$CH_3(CH_2)_2$, E/Z=78/22 — **11c**, 89%, E/Z=52/48
3d, R′=$CH_3(CH_2)_6$, E/Z=83/17 — **11d**, 97%, E/Z=65/35

Scheme 3. Conversion of 1-tosyl-1-alkenes to allylic sulfones.



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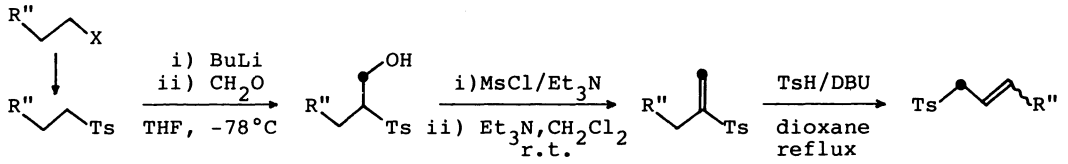
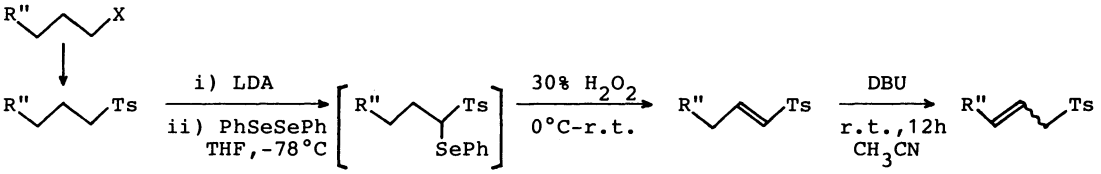
14a, R′=CH_3, 79% — **15a**, 95% — **16a**, 95%, E/Z=72/28
14b, R′=CH_2CH_3, 74% — **15b**, 93% — **16b**, 95%, E/Z=81/19
14c, R′=$(CH_2)_4CH_3$, 64% — **15c**, 93% — **16c**, 100%, E/Z=79/21

Scheme 4. Preparation of two-carbons homologated vinylic and allylic sulfones from 1-haloalkanes.



17a, R″=$(CH_2)_5CH_3$ **18a**, 68% **19a**, 93% **20a**, 96%, E/Z=80/20
17b, R″=$(CH_2)_7CH_3$ **18b**, 66% **19b**, 88% **20b**, 100%, E/Z=78/22
17c, R″=$(CH_2)_8CH_3$ **18c**, 62% **19c**, 95% **20c**, 97%, E/Z=77/23

Scheme 5. Preparation of one-carbon homologated vinylic and allylic sulfones from 1-haloalkanes.



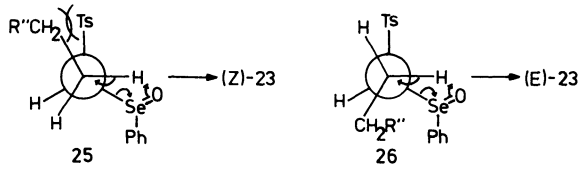
21a, R″=CH_3 **22a—d** **23a**, 86% (E) **24a**, 97%, E/Z=19/81
21b, R″=$(CH_2)_4CH_3$ **23b**, 95% (E) **24b**, 96%, E/Z=31/69
21c, R″=$(CH_2)_6CH_3$ **23c**, 91% (E) **24c**, 97%, E/Z=31/69
21d, R″=$(CH_2)_7CH_3$ **23d**, 87% (E) **24d**, 97%, E/Z=30/70

Scheme 6. Preparation of unhomologated vinylic and allylic sulfones from 1-haloalkanes.

The synthesis of one-carbon homologated vinylic (**19**) and allylic (**20**) sulfones from 1-haloalkanes was accomplished according to Scheme 5. Haloalkanes were initially transformed to the corresponding *p*-tolyl sulfones (**17**) by a general method using sodium *p*-toluenesulfinate.[8e]

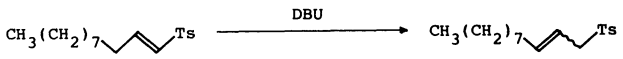
Unhomologated vinylic (**23**) and allylic (**24**) sulfones were prepared from 1-haloalkanes in a similar manner used in the preparation of 1-cyano-1-alkenes[16] according to Scheme 6.

In contrast to the case of cyanoalkane,[16] this reaction was found to afford only (E)-isomer of **23** from the observation of its 400 MHz ^{1}H NMR spectrum. This may be due to the bulkiness of tosyl group, namely cis-elimination of benzeneselenenic acid might proceed preferentially via the conformation illustrated in the structure **26** in which the unfavorable steric interaction between alkyl and tosyl groups, represented in the structure **25**, does not exist.



The final transformation of (*E*)-vinylic sulfones (**23**) to the corresponding allylic sulfones (**24**) was performed with DBU in acetonitrile at room temperature. It is noteworthy that Z-isomers of **24** were predominantly formed in contrast to the results of similar reaction using E/Z-mixture of vinylic sulfones (**3b—d** to **11b—d** in Scheme 3).

Table 4. Conversion of (*E*)-Vinylic Sulfone (**23d**) to Allylic Sulfone (**24d**) Using DBU as a Base under Various Conditions[a]



23d **24d**

Entry No.	Condition	Product ratio[b] **23d** : **24d** (E/Z)
1	CH_3CN, r.t., 12 h	3 : 97 (30/70)
2	DMF, r.t., 12 h	5 : 95 (27/73)
3	THF, r.t., 12 h	29 : 71 (18/82)
4	CH_2Cl_2, r.t., 12 h	36 : 64 (22/78)
5	Dioxane, r.t., 12 h	54 : 46 (21/79)
6	Benzene, r.t., 12 h	68 : 32 (10/90)
7	$CHCl_3$, r.t., 12 h	94 : 6 (20/80)
8	CH_3CN, −20 °C, 48 h	77 : 23 (3/97)
9	CH_3CN, 0 °C, 30 h	4 : 96 (22/78)
10	THF, 0 °C, 48 h	28 : 72 (19/81)
11	CH_3CN, reflux, 1.5 h	2 : 98 (78/22)
12	Dioxane, reflux, 1.5 h	4 : 96 (66/34)

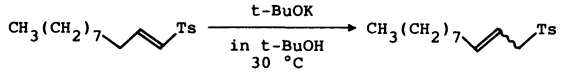
a) 2 equiv of DBU (0.26 mmol) was used toward **23d** (0.13 mmol) in each solvent (1 ml). b) Determined by 400 MHz ^{1}H NMR spectra.

Stereochemistry of the Conversion of Vinylic Sulfones to the Corresponding Allylic Sulfones. In order to rationalize the above peculiar phenomenon, the conversion of (*E*)-vinylic sulfone (**23d**) to the corresponding allylic sulfone (**24d**) was investigated using DBU as a base under various conditions as shown in Table 4. The polar solvent such as

acetonitrile (Entry 1) or *N,N*-dimethylformamide (DMF, Entry 2) seemed to be preferable to the less polar ones (Entries 3—7) for the conversion. It is noteworthy that (Z)-isomer of **24d** was preferentially formed at room temperature or at lower temperature in any solvent examined (Entries 1—10), while (E)-isomer was predominant in the reaction carried out at higher temperature (Entries 11 and 12). These results suggest that (Z)-isomer of **24d** is the kinetically-controlled product and the more stable (E)-isomer is the thermodynamically-controlled one.

The results of the similar reaction of **23d** with *t*-BuOK in *t*-BuOH made this point clearer, though the selectivity was not so high as that in the case of DBU. (Z)-Isomer of **24d** was initially formed predominantly and it gradually changed to the (E)-isomer (Table 5).

Table 5. Conversion of (*E*)-Vinylic Sulfone (**23d**) to Allylic Sulfone (**24d**) with *t*-BuOK[a)]

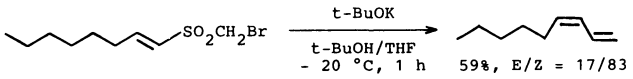


23d **24d**

Reaction time/h	Product ratio[b)]	
	23d :	**24d** (E/Z)
0.5	5	95 (41/59)
1	5	95 (51/49)
2	3	97 (63/37)
4	2	98 (75/25)
15	<1	>99 (86/14)

a) 2 equiv of *t*-BuOK (0.26 mmol) was used toward **23d** (0.13 mmol) in *t*-BuOH (6 ml). b) Determined by 400 MHz ^{1}H NMR spectra.

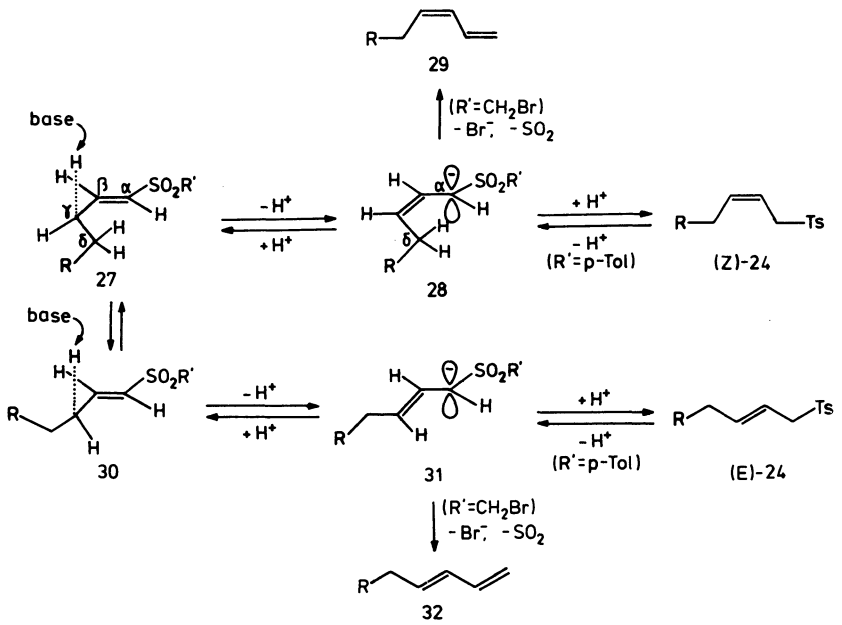
The question arised from the above experimental results is why (*E*)-**23** afford predominantly (*Z*)-**24** as a kinetically-controlled product. During the preparation of this manuscript, Block and his coworkers reported independently the similar results for the vinylogous Ramberg-Bäcklund reactions as shown in the following.[17)]



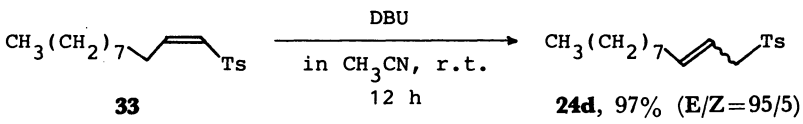
They attributed the stereoselectivity of the reaction to a stabilizing, attractive interaction between the developing negative charge at the α-position and the CH_2 group at the δ-position (a "*syn effect*"[18)]) favoring transition state **27** over **30** for deprotonation (Scheme 7).

Namely, these experimental results including ours suggest that the acidity of the protons at γ-position of vinylic sulfones varies remarkably in each conformation. We would like to propose to call such acidity of a proton chracteristic to each conformation "*Conformational Acidity.*" However, it should be noted that the anionic intermediate **31** is more stable than its (Z)-isomer **28** as can be seen in the above results, while it could not be observed in the Ramberg-Bäcklund reactions since the subsequent desulfonylation proceeded readily at low temperature.

On the other hand, (*Z*)-vinylic sulfone (**33**) and α-alkylated vinylic sulfones (**34a—c**) gave exclusively the corresponding (*E*)-allylic sulfones (**24d** and **35a—c**), respectively, as shown in Scheme 8 and Table 6. It may be due to the steric congestion which precludes



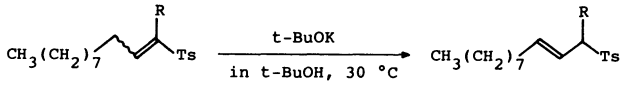
Scheme 7. A probable course of the conversion of (*E*)-vinylic sulfones (**23**=**27**, **30**) to the corresponding allylic sulfones (**24**).



33 **24d**, 97% (E/Z=95/5)

Scheme 8. Conversion of (*Z*)-vinylic sulfone (**33**) to allylic sulfone (**24d**) with DBU.

Table 6. Conversion of α-Alkylated Vinylic Sulfones to Allylic Sulfones

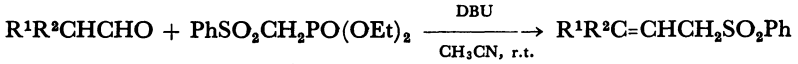


34a—c **35a—c**

Substrate R (E/Z)	Time h	Product ratio[a] 34 : 35	Substrate R (E/Z)	Time h	Product ratio[a] 34 : 35
34a, CH_3 (100/0)	1	58 : 42	**34a**, CH_3 (0/100)	1	32[b] : 68
	3	27 : 73		3	13 : 87
	10	23 : 77		10	14 : 86
	24	22 : 78		24	16 : 84
34b, $CH_3(CH_2)_2$ (100/0)	1	64 : 36	**34b**, $CH_3(CH_2)_2$ (0/100)	1	9[b] : 91
	3	32 : 68		3	10 : 90
	10	13 : 87		10	11 : 89
	24	11 : 89		24	11 : 89
34c, CH_3CH_2 (45/55)	1	24[c] : 76			
	3	12 : 88			
	10	10 : 90			
	24	9 : 91			

a) Determined by 400 MHz ^{1}H NMR spectra. Products consisted of only (*E*)-isomers (**34**, **35**) except the case noted in b). b) (*Z*)-isomer. c) (*E*)-isomer.

Table 7. Direct Preparation of Allylic Sulfones from Aldehydes



36a—e **37** **38a—e**

36a—e	Aldehyde R[1]	R[2]	Time h	Yield/% (E/Z) 38a—e
36a	$C_6H_5CH_2$	H	4.5	79 (37/63)
36a	$C_6H_5CH_2$	H	67.5	72 (86/14)
36b	$CH_3(CH_2)_6$	H	18	73 (40/60)
36c	$CH_3(CH_2)_7$	H	10.5	87 (46/54)
36d	$(CH_3)_2C=CH(CH_2)_2CH(CH_3)$	H	19.5	81 (50/50)
36e	CH_3	CH_3	12	88

the possibility of a stabilizing syn interaction between the α- and δ-position as being pointed out by Block et al.[17]

It is noteworthy that the Z-ratio of **24a** (R″=CH_3) is higher in the conversion of **23a** (R″=CH_3) than other cases (**23b—d** to **24b—d**) in Scheme 6. This may suggest that the syn interaction between the α- and δ-position is more effective when R″ is methyl group. Further, the reverse conversion of **24a** to **23a** may be retarded by the stabilization of the allylic structure owing to the hyperconjugation of methyl group with the double bond,[19] therefore, the initially formed (Z)-isomer may be retained better when R″ is methyl group than other cases.

Preparation of Allylic Sulfones from Aldehydes. The direct preparation of allylic sulfones from aldehyde was next investigated.

Posner and Brunelle reported the conversion of carbonyl substrates to vinylic sulfones using sulfonylmethylphosphonate carbanions.[20] They gen-

erated the carbanions with butyllithium in THF at −78 °C. On the other hand, we have established above the conversion of the vinylic sulfones to the corresponding allylic sulfones using DBU as a base catalyst. Therefore, the direct preparation of allylic sulfones from aldehydes seemed to be possible if the carbanion of sulfonylmethylphosphonate was generated with DBU itself. Actually, this reaction proceeded well with diethyl phenylsulfonylmethylphosphonate (**37**) and 2 or 3 equiv of DBU in acetonitrile at room temperature as shown in Table 7. The predominant formation of (*Z*)-allylic sulfones (**38a—e**) was observed when the reaction was quenched within a relatively short time (See the cases of **38a**). These results agree with the discussion on the stereochemistry described above since it is known that the present Horner-Wittig type reaction initially affords (*E*)-vinylic sulfones.[20] Similar reaction with ketones afforded neither vinylic sulfones nor allylic sulfones, but a small amount of reduced product, methyl phenyl sulfone, was obtained (3—4%) along with recovery of sulfonylmethylphosphonate (60—70%).

Attempts to prepare the allylic sulfones from aldehydes by Peterson olefination using phenyl trimethylsilylmethyl sulfone and DBU were unsuccessful.[21] Desilylated sulfone was obtained as a main product.

Experimental

All the melting points were determined with a micro melting apparatus (Yanagimoto-Seisakusho) and were uncorrected. The ^{1}H NMR and IR spectra were recorded on JEOL JNM-GX 400 (400 MHz) FT-NMR spectrometer and JASCO IRA-1 diffraction grating infrared spectrometer, respectively. The chemical shifts of NMR are reported in the δ scale relative to TMS as an internal standard.

Materials. All the solvents were distilled and stored over a drying agent. Thin-layer chromatography (TLC) was performed on Merck's silica gel 60 PF_{254} (Art. 7749).

Preparation of 1-Tosyl-2-phenylethene (3a) via Iodosulfonization in methanol. To a mixed solution of styrene (**1a**, 104 mg, 1 mmol) and sodium *p*-toluenesulfinate tetrahydrate (375 mg, 1.5 mmol) in methanol (2 ml) was added iodine (254 mg, 1.0 mmol) at room temperature with stirring. A lot of yellowish solid[22] precipitated immediately. The solvent was replaced by ethyl acetate after stirring for 15 min, and the solution was successively washed with water, aqueous $NaHCO_3$ containing a small amount of $NaHSO_3$, and brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was treated with Et_3N (202 mg, 2 mmol) in dry acetonitrile (2 ml) at room temperature for 15 min. The residue after removal of solvent was taken up in ethyl acetate and successively washed with 1 mol dm^{-3} HCl, aqueous $NaHCO_3$, and brine, and dried over Na_2SO_4. The solvent was evaporated in vacuo and the resulting residue was subjected to preparative TLC (solvent; hexane-AcOEt=5:2, v/v) to afford 229 mg of **3a** (89% yield) as a solid. Mp 120—121 °C (from ethanol, lit,[12] 120—121 °C). IR (KBr) 3032, 1602, 1586, 1442, 1296, 1134, 1076, 964, 800, 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.43 (s, 3H), 6.85 (d, 1H, *J*=15 Hz), 7.30—7.52 (m, 7H), 7.65 (d, 1H, *J*=15 Hz), 7.83 (d, 2H, *J*=8 Hz). Found: C, 69.80; H, 5.35%. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

Other vinylic sulfones (**3b—g**) were prepared in a similar manner.

3b: An oil; MS *m/z* 224 (M^+, 71%), 139 (100), 91, 41; IR (neat) 3016, 2908, 2848, 1606, 1580, 1436, 1302, 1130, 1072, 954, 798 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.92 (t, 3H of E and Z, *J*=7.5 Hz), 1.41—1.55 (m, 2H of E and Z), 2.16—2.24 (m, 2H of E), 2.43 (s, 3H of E and Z), 2.60—2.68 (m, 2H of Z), 6.19—6.35 (m, 2H of Z, 1H of E), 6.95 (dt, 1H of E, *J*=7, 15 Hz), 7.33 (d, 2H of E and Z, *J*=8 Hz), 7.76 (d, 2H of E, *J*=8 Hz), 7.80 (d, 2H of Z, *J*=8 Hz); E/Z=78/22.

3c: An oil; MS *m/z* 238 (M^+, 23%), 139 (100), 91, 41; IR (neat) 3024, 2908, 2842, 1606, 1582, 1440, 1304, 1136, 1076, 962, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.89 (t, 3H of E and Z, *J*=7 Hz), 1.27—1.48 (m, 4H of E and Z), 2.19—2.26 (m, 2H of E), 2.43 (s, 3H of E and Z), 2.61—2.68 (m, 2H of Z), 6.18—6.35 (m, 2H of Z, 1H of E), 6.95 (dt, 1H of E, *J*=7, 15 Hz), 7.32 (d, 2H of E and Z, *J*=8 Hz), 7.75 (d, 2H of E, *J*=8 Hz), 7.79 (d, 2H of Z, *J*=8 Hz); E/Z=78/22.

3d: An oil; MS *m/z* 294 (M^+, 13%), 209, 157 (100), 139, 138, 96, 55; IR (neat) 3032, 2916, 2840, 1608, 1582, 1454, 1312, 1139, 1076, 960, 801 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.84—0.92 (m, 3H of E and Z), 1.25 (m, 12H of E and Z), 1.35—1.50 (m, 2H of E and Z), 2.17—2.26 (m, 2H of E), 2.43 (s, 3H of E and Z), 2.61—2.67 (m, 2H of Z), 6.18—6.35 (m, 2H of Z, 1H of E), 6.95 (dt, 1H of E, *J*=7, 15 Hz), 7.32 (d, 2H of E and Z, *J*=8 Hz), 7.75 (d, 2H of E, *J*=8 Hz), 7.79 (d, 2H of Z, *J*=8 Hz); E/Z=83/17.

3e: Mp 62—63 °C (from cyclohexane); IR (KBr) 3020, 1614, 1584, 1430, 1276, 1132, 1076, 800 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.87 (d, 3H, *J*=1 Hz), 2.14 (d, 3H, *J*=1 Hz), 2.43 (s, 3H), 6.17 (m, 1H, *J*=1 Hz), 7.33 (d, 2H, *J*=8 Hz), 7.78 (d, 2H, *J*=8 Hz). Found: C, 62.75; H, 6.72%. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71%.

3f: Mp 65 °C (from cyclohxane, lit,[12] 66—67 °C); IR (KBr) 1610, 1582, 1428, 1286, 1136, 1062, 794 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.86 (s, 3H), 1.99 (s, 3H), 2.21 (s, 3H), 2.43 (s, 3H), 7.31 (d, 2H, *J*=8 Hz), 7.74 (d, 2H, *J*=8 Hz).

3g: Mp 81—82 °C (from ethanol, lit,[12] 81—82 °C); IR (KBr) 3018, 2906, 2842, 1624, 1580, 1434, 1270, 1128, 1082, 802 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.52—1.69 (m, 4H), 2.12—2.21 (m, 2H), 2.21—2.30 (m, 2H), 2.43 (s, 3H), 7.01—7.06 (m, 1H), 7.32 (d, 2H, *J*=8 Hz), 7.73 (d, 2H, *J*=8 Hz).

Preparation of 1-Tosyl-1-decene (3d) via Iodosulfonization in Ethyl Acetate and Water. To a heterogeneous mixture of *p*-$CH_3C_6H_4SOONa \cdot 4H_2O$ (375 mg, 1.5 mmol) in water (1 ml) and ethyl acetate (2 ml) were added 1-decene (**1d**, 140 mg, 1 mmol) and iodine (254 mg, 1 mmol) at room temperature with stirring. The dark brown color of the mixture diminished gradually. After stirring for 24 h, 20 ml of ethyl acetate was added. The organic phase was separated and washed successively with aqueous $NaHCO_3$ containing a small amount of $NaHSO_3$ and brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was treated with Et_3N to give **3d**, in a similar manner described for **3a**. Spectral data of **3d** is given above.

Other vinylic sulfones (**3h—j**) were prepared in a similar way.

3h: (E)- and (Z)-isomers were separated on preparative

TLC (solvent; hexane–AcOEt–Et_2O=10:1:1, v/v) and characterized based on the known deshielding of alkyl groups syn to the sulfonyl group in vinylic sulfones.[23] (*E*)-**3h**: Yield 63%. Mp 71—72 °C (from ethanol); IR (KBr) 2940, 2844, 1626, 1580, 1454, 1298, 1128, 1079, 804 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05 (d, 6H, J=7 Hz), 1.82 (s, 3H), 2.43 (s, 3H), 2.49—2.61 (m, 1H), 6.70 (d, 1H, J=10 Hz), 7.32 (d, 2H, J=8 Hz), 7.72 (d, 2H, J=8 Hz). Found: C, 65.30; H, 7.76%. Calcd for $C_{13}H_{18}O_2S$: C, 65.51; H, 7.61%. (*Z*)-**3h**: Yield 20%. An oil; MS *m/z* 238 (M^+, 52%), 140, 139, 83, 82, 67 (100), 55; IR (neat) 2948, 2852, 1626, 1586, 1456, 1278, 1134, 1081, 804 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (d, 6H, J=7 Hz), 1.94 (s, 3H), 2.44 (s, 3H), 3.61—3.74 (m, 1H), 5.74 (d, 1H, J=11 Hz), 7.33 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz).

3i: Mp 89—90 °C (from ethanol); IR (KBr) 3028, 2932, 2852, 1581, 1564, 1434, 1278, 1134, 1081, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.94—1.02 (m, 1H), 1.07—1.15 (m, 1H), 1.21—1.28 (m, 1H), 1.49—1.56 (m, 1H), 1.62—1.71 (m, 1H), 1.71—1.83 (m, 1H), 2.44 (s, 3H), 3.05—3.12 (m, 1H), 3.12—3.17 (m, 1H), 6.90 (d, 1H, J=3 Hz), 7.32 (d, 2H, J=8 Hz), 7.77 (d, 2H, J=8 Hz). Found: C, 67.60; H, 6.56%. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49%.

3j: An oil; MS *m/z* 304 (M^+, 18%), 165, 149 (100), 148, 133, 123, 108, 107 (100), 105, 91, 82 (100), 54; IR (neat) 3012, 2912, 1658, 1612, 1584, 1438, 1290, 1136, 1078, 806 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.77 (s, 3H), 2.16 (s, 3H), 2.33—2.56 (m, 4H), 2.45 (s, 3H), 2.69—2.81 (m, 1H), 6.21 (s, 1H), 6.68—6.76 (m, 1H), 7.35 (d, 2H, J=8 Hz), 7.78 (d, 2H, J=8 Hz).

Preparation of 1-Phenyl-1-tosylethene (7a) via Sulfonylmercuration. To a solution of styrene (**1a**, 104 mg, 1 mmol) in methanol (1.5 ml) and dichloromethane (0.7 ml) were added $HgCl_2$ (272 mg, 1 mmol) and sodium *p*-toluenesulfinate tetrahydrate (250 mg, 1 mmol) at room temperatute. After stirring for 1 d, the reaction mixture was diluted with ethyl acetate (ca. 15 ml) and the insoluble substances were filtered off through a Celite bed. The residue obtained by evaporation of solvent was treated with DBU (0.18 ml, 1.2 mmol) in dry THF (4 ml) at room temperature for 10 min. After replacing the solvent by ethyl acetate, the solution was successively washed with water and brine, and dried over Na_2SO_4, followed by evaporation of the solvent. The residue was subjected to preparative TLC (solvent; hexane–ethyl acetate=8:1, v/v) to afford 157 mg of **7a** (61% yield) as a colorless oil. MS *m/z* 258 (M^+, 13%), 139, 103 (100), 77; IR (neat) 3040, 2902, 1583, 1302, 1138, 1058, 800 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.36 (s, 3H), 5.92 (s, 1H), 6.60 (s, 1H), 7.16—7.37 (m, 7H), 7.56 (d, 2H, J=8 Hz).

Other 2-tosyl-1-alkene were prepared in a similar manner.

7b: An oil, MS *m/z* 224 (M^+, 61%), 157 (100), 139, 119, 92, 91 (100), 69, 68, 65, 41; IR (neat) 2946, 1582, 1439, 1300, 1161, 1128, 1073, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=7 Hz), 1.42—1.55 (m, 2H), 2.20 (t, 2H, J=8 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.34 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz).

7c: An oil, MS *m/z* 238 (M^+, 100%), 197, 157 (100), 139 (100), 133 (100), 92 (100), 91 (100), 67, 55 (100), 41; IR (neat) 2951, 2863, 1587, 1448, 1305, 1130, 1075, 804 cm^{-1}, ^1H NMR ($CDCl_3$) δ=0.84 (t, 3H, J=7 Hz), 1.21—1.33 (m, 2H), 1.38—1.49 (m, 2H), 2.22 (t, 2H, J=7.5 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.33 (s, 1H), 7.33 (d, 2H, J=8.5 Hz), 7.75 (d, 2H, J=8 Hz).

7d: An oil, MS *m/z* 294 (M^+, 1%), 197, 157 (100), 139, 138, 92, 55, 41; IR (neat) 2918, 2847, 1586, 1458, 1305, 1160, 1133, 1075, 803 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=7 Hz), 1.12—1.33 (m, 10H), 1.38—1.50 (m, 2H), 2.22 (t, 2H, J=8 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.33 (s, 1H), 7.32 (d, 2H, J=8.5 Hz), 7.75 (d, 2H, J=8 Hz).

7e: An oil, Ms *m/z* 286 (M^+, 78%), 181, 131 (100), 130 (100), 129 (100), 115, 92, 91 (100), 65; IR (neat) 3006, 2900, 1582, 1300, 1137, 1072, 802 cm^{-1}; ^1H NMR δ=2.44 (s, 3H), 2.54 (dd, 2H, J=7, 8 Hz), 2.77 (dd, 2H, J=7, 8 Hz), 5.65 (s, 1H), 6.35 (s, 1H), 7.03—7.39 (m, 7H), 7.75 (d, 2H, J=8 Hz).

Conversion of 1-Tosyl-1-pentene (3b) to 1-Tosyl-2-pentene (11b). To a solution of **3b** (138 mg, 0.62 mmol) in acetonitrile (2 ml) was added DBU (184 µl, 1.23 mmol) at room temperature. After being allowed to stand overnight, the solvent was replaced by ethyl acetate. The resulting solution was successively washed with 1 mol dm^{-3} HCl, aqueous $NaHCO_3$ and brine, followed by being dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; hexane–ethyl acetate–ether=10:1:1, v/v) to afford 127 mg of **11b** as an oil. 400 MHz ^1H NMR spectrum showed that it was a mixture of (E)- and (Z)-isomers (E/Z=84/16) of **11b** contaminated with a small amount of **3b** (ca. 1%). Yield 91% (unseparable **3b** was reduced in the calculation of the yield). MS *m/z* 224 (M^+, 1%), 157, 69 (100), 68, 41; IR (neat) 3012, 2952, 1584, 1440, 1294, 1132, 1076, 958, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76 (t, 3H of Z, J=8 Hz), 0.91 (t, 3H of E, J=7.5 Hz), 1.73—1.83 (m, 2H of Z), 1.97—2.07 (m, 2H of E), 2.45 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.32—5.45 (m, 1H of E and Z), 5.55 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=8, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=84/16.

3c and **3d** were also converted to **11c** and **11d**, respectively, in a similar manner.

11c: An oil; MS *m/z* 238 (M^+, 4%), 157 (100), 139, 92 (100), 91 (100), 83, 82 (100), 67 (100), 65, 55, 41 (100); IR (neat) 3012, 2944, 2912, 2852, 1584, 1444, 1306, 1134, 1076, 959, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.75 (t, 3H of Z, J=7 Hz), 0.82 (t, 3H of E, J=7 Hz), 1.10—1.21 (m, 2H of Z), 1.25—1.36 (m, 2H of E), 1.69—1.77 (m, 2H of Z), 1.94—2.02 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.34—5.45 (m, 1H of E and Z), 5.51 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=8, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=52/48. Recovery of **3c**: 2%.

11d: An oil, MS *m/z* 294 (M^+, 0.1%), 209, 157, 138, 97, 83 (100), 69, 55; IR (neat) 3012, 2908, 2836, 1584, 1448, 1310, 1132, 1078, 958, 804 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.82—0.93 (m, 3H of E and Z), 1.05—1.34 (m, 10H of E and Z), 1.69—1.78 (m, 2H of Z), 1.94—2.03 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.34—5.44 (m, 1H of E and Z), 5.51 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=8, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.72 (d, 2H of E, J=8 Hz), 7.75 (d, 2H of Z, J=8.5 Hz); E/Z=65/35. Recovery of **3d**: 3%.

Conversion of 2-Tosyl-1-pentene (7b) to 1-Tosyl-2-pentene (11b). To a solution of **7b** (84 mg, 0.38 mmol) in dioxane (2.5 ml) were added *p*-toluenesulfinic acid hydrate (*p*-$CH_3C_6H_4SOOH \cdot xH_2O$, 133 mg, ca. 0.76 mmol) and DBU (230 µl, 1.52 mmol) at room temperature. After refluxing for 5 h, the solvent was replaced by ethyl acetate.

The solution was successively washed with 1 mol dm^{-3} HCl, aqueous $NaHCO_3$, and brine, followed by being dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; hexane–ethyl acetate=8:1, v/v) to afford **11b** as an oil. It was found to be a mixture of (E)- and (Z)-isomers (E/Z=81/19) from its ^1H NMR spectrum. Physical data of **11b—d** are given above.

Alkylation of 2-Tosyl-1-phenylethanone (13). A solution of **13** (685 mg, 2.5 mmol, mp 109—110 °C (from ethanol), prepared by the reaction of 2-bromo-1-phenylethanone and p-$CH_3C_6H_4SOONa \cdot 4H_2O$ in refluxing ethanol according to a general method[8e]) in DMF (8 ml) was added into a flask containing finely powdered dry K_2CO_3 (518 mg, 3.75 mmol) under nitrogen. After stirring for 1 h at room temperature, a solution of iodoethane (468 mg, 3.0 mmol) in DMF (2 ml) was added dropwise. The reaction mixture was quenched, after stirring for 9 h, by the addition of a buffer solution (pH 7) followed by evaporation of the solvent under reduced pressure. The residue was taken up in ethyl acetate and the resulting solution was washed with brine twice and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; hexane–ethyl acetate=5:1) to afford 119 mg of 2-tosyl-1-phenyl-1-butanone (**14a**, 79% yield) as a solid. Mp 72.0—72.5 °C (from hexane–ethanol); IR (KBr) 3048, 2970, 1668, 1585, 1440, 1344, 1310, 1296, 1284, 1262, 1139, 1078, 970, 805, 746, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.5 Hz), 1.98—2.22 (m, 2H), 2.43 (s, 3H), 4.99 (dd, 1H, J=4, 11 Hz), 7.31 (d, 2H, J=8 Hz), 7.48 (dd, 2H, J=7, 8 Hz), 7.60 (t, 1H, J=7 Hz), 7.64 (d, 2H, J=8 Hz), 7.97 (d, 2H, J=8 Hz). Found: C, 67.23; H, 6.15%. Calcd for $C_{17}H_{18}O_3S$: C, 67.52; H, 6.00%.

In a similar manner, **14b** and **14c** were prepared.

14b: Mp 89—90 °C (from hexane/ethanol); IR (KBr) 3048, 2950, 1665, 1585, 1440, 1340, 1310, 1290, 1245, 1140, 1075, 950, 804, 742, 675 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7.5 Hz), 1.26 (m, 2H), 1.96—2.13 (m, 2H), 2.44 (s, 3H), 5.07 (dd, 1H, J=4, 11 Hz), 7.31 (d, 2H, J=8 Hz), 7.48 (dd, 2H, J=7, 8 Hz), 7.60 (t, 1H, J=7 Hz), 7.64 (d, 2H, J=8 Hz), 7.98 (d, 2H, J=8 Hz). Found: C, 68.24; H, 6.39%. Calcd for $C_{18}H_{20}SO_3$: C, 68.33; H, 6.37%.

14c: Mp 78.5—79.5 °C (from hexane/ethanol); IR (KBr) 3044, 2952, 2920, 1665, 1584, 1438, 1336, 1302, 1295, 1138, 1074, 940, 800, 742, 678 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.81 (t, 3H, J=7 Hz), 1.08—1.31 (m, 8H), 1.96—2.14 (m, 2H), 2.43 (s, 3H), 5.05 (dd, 1H, J=4, 11 Hz), 7.31 (d, 2H, J=8 Hz), 7.48 (dd, 2H, J=7, 8 Hz), 7.61 (t, 1H, J=7 Hz), 7.64 (d, 2H, J=8 Hz), 7.96 (d, 2H, J=8 Hz). Found: C, 70.37; H, 7.43%. Calcd for $C_{21}H_{26}O_3S$: C, 70.36; H, 7.31%.

Synthesis of 2-Tosyl-1-butene (15a) via Deacylation. To a solution of lithium diisopropylamide (LDA, 0.74 mmol, prepared from diisopropylamine (80 mg, 0.79 mmol) and n-BuLi (hexane solution, 0.74 mmol) at −30 °C) in THF (3 ml) was added dropwise a solution of **14a** (211 mg, 0.7 mmol) in THF (7 ml) at −78 °C under nitrogen. After stirring for 30 min at −78 °C, a THF solution of excess amount of formaldehyde was added. The reaction mixture was gradually warmed up to room temperature and stirred overnight. After treatment with a buffer solution (pH 7), the insoluble substance was filtered off through a Celite bed, and the solvent was replaced by ethyl acetate. The resulting solution was washed with brine and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; hexane–ethyl acetate=5:1, v/v) to afford 139 mg of **15a** (95% yield) as a colorless solid. Mp 26—28 °C (crude); MS m/z 210 (M^+, 26%), 139 (100), 92, 55; IR (KBr) 2970, 1582, 1295, 1170, 1128, 1073, 942, 865, 800, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (t, 3H, J=7 Hz), 2.27 (dq, 2H, J=2, 7 Hz), 2.44 (s, 3H), 5.70 (t, 1H, J=2 Hz), 6.34 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

In a similar manner, **15b** and **15c** were prepared.

15b: An oil; MS m/z 224 (M^+, 61%), 157 (100), 139, 119, 92, 91 (100), 69, 68, 65, 41; IR (neat) 2956, 1584, 1442, 1302, 1162, 1130, 1080, 940, 802, 726, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7 Hz), 1.49 (m, 2H), 2.20 (m, 2H), 2.44 (s, 3H), 5.69 (t, 1H, J=2 Hz), 6.34 (s, 1H), 7.34 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz).

15c: An oil; MS m/z 266 (M^+, 10%), 197, 157 (100), 139 (100), 92 (100), 69, 55, 41; IR (neat) 2915, 2842, 1584, 1458, 1302, 1160, 1133, 1073, 940, 802, 727 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (t, 3H, J=7 Hz), 1.14—1.30 (m, 6H), 1.38—1.48 (m, 2H), 2.21 (m, 2H), 2.44 (s, 3H), 5.69 (t, 1H, J=1.5 Hz), 6.34 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

The conversion of **15a—c** to **16a—c** was carried out in a similar manner described for the conversion of **7b** to **11b**.

16a: An oil; MS m/z 210 (M^+, 22%), 156 (100), 140, 92, 91 (100), 65, 55; IR (neat) 3025, 2920, 1585, 1315, 1135, 1080, 960, 810, 718 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.37 (dd, 3H of Z, J=2, 7 Hz), 1.68 (dd, 3H of E, J=1, 6 Hz), 2.45 (s, 3H of E and Z), 3.71 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.37—5.48 (m, 1H of E and Z), 5.57 (dq, 1H of E, J=6.5, 15 Hz), 5.82 (dq, 1H of Z, J=7, 11 Hz), 7.34 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=72/28.

16b: An oil; MS m/z 224 (M^+, 1%), 157, 69 (100), 68, 41; IR (neat) 3020, 2947, 1583, 1305, 1134, 1078, 958, 802, 722 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.76 (t, 3H of Z, J=7.5 Hz), 0.91 (t, 3H of E, J=8 Hz), 1.78 (m, 2H of Z), 2.01 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7.5 Hz), 3.82 (d, 2H of Z, J=8 Hz), 5.32—5.45 (m, 1H of E and Z), 5.55 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=8, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=81/19.

16c: An oil; MS m/z 266 (M^+, 0.2%), 157, 110, 69 (100), 55, 41; IR (neat) 2915, 2842, 1587, 1458, 1310, 1135, 1080, 962, 804, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84 (t, 3H of Z, J=7 Hz), 0.87 (t, 3H of E, J=7 Hz), 1.05—1.40 (m, 6H of E and Z), 1.67—1.79 (m, 2H of Z), 1.92—2.07 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7.5 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.33—5.44 (m, 1H of E and Z), 5.50 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=8, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.75 (d, 2H of Z, J=8 Hz); E/Z=79/21.

Preparation of 2-Tosyl-1-nonanol (18a). p-Tolyl octyl sulfone (**17a**, 134 mg, 0.50 mmol) was lithiated by the reaction with n-BuLi (hexane solution, 0.55 mmol) in THF (5 ml) at −78 °C for 1 h under nitrogen, followed by the addition of a THF solution of excess amount of formaldehyde at −78 °C. After a few minute, the mixture was quenched with a phosphate buffer solution (pH 7) and the insoluble substance was filtered off through a Celite bed. The residue after removal of the solvent was taken up in ethyl acetate. The organic layer was washed with brine and dried over Na_2SO_4. The residue obtained by evaporation of

the solvent was subjected to preparative TLC (solvent; benzene–ethyl acetate=20:1, v/v) to afford 102 mg of **18a** (68% yield) as an oil. MS *m/z* 299 (M^+ +1, 1%), 280, 157, 92 (100), 83 (100), 69 (100), 55; IR (neat) 3530, 2915, 2847, 1588, 1460, 1294, 1138, 1078, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (t, 3H, J=7 Hz), 1.11—1.49 (m, 10H), 1.49—1.64 (m, 1H), 1.68—1.79 (m, 1H), 2.47 (s, 3H), 2.98 (dd, 1H of OH, J=6, 7 Hz), 3.01—3.09 (m, 1H), 3.83—3.95 (m, 2H), 7.38 (d, 2H, J=8 Hz), 7.78 (d, 2H, J=8 Hz).

18b and **18c** were prepared in a similar manner.

18b: An oil; Ms *m/z* 326 (M^+, 0.4%), 308, 157, 97, 92 (100), 83, 69, 55; IR (neat) 3515, 2958, 2842, 1588, 1458, 1294, 1136, 1078, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7 Hz), 1.08—1.48 (m, 14H), 1.48—1.62 (m, 1H), 1.68—1.79 (m, 1H), 2.47 (s, 3H), 2.99 (dd, 1H of OH, J=6, 7 Hz), 3.01—3.09 (m, 1H), 3.85—3.96 (m, 2H), 7.38 (d, 2H, J=8 Hz), 7.78 (d, 2H, J=8 Hz).

18c: Mp 49.5—50.5 °C (from hexane); MS *m/z* 340 (M^+, 1%), 322, 185, 157 (100), 111, 97, 92, 83, 69, 55; IR (KBr) 3524, 2905, 2840, 1584, 1455, 1270, 1130, 1075, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7 Hz), 1.09—1.48 (m, 16H), 1.48—1.62 (m, 1H), 1.66—1.79 (m, 1H), 2.47 (s, 3H), 2.98 (t, 1H of OH, J=7 Hz), 3.00—3.09 (m, 1H), 3.83—3.95 (m, 2H), 7.38 (d, 2H, J=8.5 Hz), 7.78 (d, 2H, J=8.5 Hz). Found: C, 66.95; H, 9.74%. Calcd for $C_{19}H_{32}O_3S$: C, 67.02; H, 9.47%.

Preparation of 2-Tosyl-1-nonene (19a). To a solution of **18a** (64 mg, 0.215 mmol) and mesyl chloride (30 mg, 0.26 mmol) in dichloromethane (1 ml) was added triethylamine (36 µl, 0.26 mmol) at room temperature. After stirring for 30 min, the reaction mixture was cooled to 0 °C and additional 60 µl (0.43 mmol) of triethylamine was added, followed by stirring for 1.5 d. The solution diluted with ethyl acetate was successively washed with 1 mol dm^{-3} aqueous $NaHCO_3$, and brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; benzene–ethyl acetate=30:1, v/v) to afford 56 mg of **19a** (93% yield) as a colorless oil. MS *m/z* 280 (M^+, 1%), 197, 157 (100), 139, 92, 69, 55, 41; IR (neat) 2920, 2850, 1588, 1308, 1162, 1077, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85 (t, 3H, J=7 Hz), 1.13—1.31 (m, 8H), 1.38—1.49 (m, 2H), 2.22 (t, 2H, J=8 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.34 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

In a similar manner, **19b** and **19c** were prepared.

19b: An oil; MS *m/z* 308 (M^+, 1%), 197, 157 (100), 152, 139, 92, 55; IR (neat) 2920, 2850, 1588, 1458, 1308, 1160, 1133, 1076, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7 Hz), 1.11—1.36 (m, 12H), 1.36—1.50 (m, 2H), 2.22 (t, 3H, J=8 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.33 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

19c: An oil; MS *m/z* 322 (M^+, 1%), 197, 166, 157 (100), 139, 92, 55; IR (neat) 2922, 2849, 1590, 1460, 1310, 1162, 1134, 1078, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7 Hz), 1.07—1.34 (m, 14H), 1.34—1.49 (m, 2H), 2.21 (t, 2H, J=8 Hz), 2.44 (s, 3H), 5.69 (s, 1H), 6.33 (s, 1H), 7.33 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

The conversion of **19a—c** to **20a—c** was carried out in a similar manner described for the conversion of **7b** to **11b**.

20a: An oil; MS *m/z* 280 (M^+, 0.2%), 157 (100), 124 (100), 83 (100), 69 (100), 55 (100), 41; IR (neat) 2918, 2845, 1588, 1458, 1314, 1138, 1082, 960, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H of Z, J=7 Hz), 0.88 (t, 3H of E, J=7 Hz), 0.98—1.36 (m, 8H of E and Z), 1.73 (m, 2H of Z), 1.99 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.33—5.44 (m, 1H of E and Z), 5.51 (dt, 1H of E, J=7, 15 Hz), 5.71 (dt, 1H of Z, J=7.5, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=80/20.

20b: An oil; MS *m/z* 308 (M^+, 0.2%), 209, 157 (100), 152, 97, 83, 69, 55; IR (neat) 2915, 2840, 1587, 1442, 1312, 1135, 1080, 960, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H of Z, J=7 Hz), 0.89 (t, 3H of E, J=7 Hz), 1.02—1.48 (m, 12H of E and Z), 1.73 (m, 2H of Z), 1.98 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.35—5.44 (m, 1H of E and Z), 5.51 (dt, 1H of E, J=7, 15.5 Hz), 5.71 (dt, 1H of Z, J=7.5, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.73 (d, 2H of E, J=8 Hz), 7.76 (d, 2H of Z, J=8 Hz); E/Z=78/22.

20c: An oil; MS *m/z* 322 (M^+, 0.5%), 166 (100), 157 (100), 111, 97 (100), 83 (100), 69 (100), 55, 43; IR (neat) 2917, 2840, 1590, 1458, 1316, 1138, 1080, 962, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H of E and Z, J=7 Hz), 1.00—1.54 (m, 14H of E and Z), 1.72 (m, 2H of Z), 1.98 (m, 2H of E), 2.44 (s, 3H of E and Z), 3.72 (d, 2H of E, J=7 Hz), 3.83 (d, 2H of Z, J=8 Hz), 5.33—5.44 (m, 1H of E and Z), 5.51 (dt, 1H of E, J=7, 15 Hz), 5.70 (dt, 1H of Z, J=7.5, 11 Hz), 7.33 (d, 2H of E and Z, J=8 Hz), 7.72 (d, 2H of E, J=8 Hz), 7.75 (d, 2H of Z, J=8 Hz); E/Z=77/23.

Preparation of (*E*)-1-Tosyl-1-butene (23a). To a solution of LDA (2 mmol, prepared from diisopropylamine (280 µl, 2 mmol) and *n*-BuLi (hexane solution, 2 mmol) at −30 °C) in THF (7.5 ml) was added dropwise a THF (1.5 ml) solution of butyl *p*-tolyl sulfone (**21a**, 212 mg, 1 mmol) at −78 °C under nitrogen. After stirring for 1 h at −78 °C, a solution of diphenyl diselenide (343 mg, 1.1 mmol) in THF (1 ml) was added at −78 °C. The mixture was gradually warmed up to room temperature and stirred overnight. After quenching with a phosphate buffer solution (pH 7), the THF was evaporated. The product was extracted from the aqueous phase with ethyl acetate several times and the combined organic extracts were successively washed with aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The solution was condensed into ca. 6 ml followed by the addition of 3 ml of THF. To the resulting homogeneous solution was added 30% of hydrogen peroxide (0.43 ml, 5 mmol) at 0 °C. After stirring for 1 h at 0 °C and for 2 h at room temperature, the mixture was treated with aqueous $NaHCO_3$ and the product was extracted with ethyl acetate, followed by being dried over Na_2SO_4. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; benzene–ethyl acetate=50:1, v/v) to afford 181 mg of **23a** (86% yield) as a colorless oil; MS *m/z* 210 (M^+, 29%), 139 (100), 92, 91, 51; IR (neat) 3040, 2960, 1612, 1586, 1448, 1310, 1139, 1079, 958, 808 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.07 (t, 3H, J=7.5 Hz), 2.22—2.32 (m, 2H), 2.44 (s, 3H), 6.29 (d, 1H, J=15 Hz), 7.01 (dt, 1H, J=6, 15 Hz), 7.33 (d, 2H, J=8.5 Hz), 7.76 (d, 2H, J=8.5 Hz).

In a similar manner, **23b—d** were prepared.

23b: An oil; MS *m/z* 266 (M^+, 7%), 183, 157 (100), 139 (100), 111, 110 (100), 92, 91, 81 (100), 69 (100), 55, 43, 41; IR (neat) 3036, 2920, 2849, 1588, 1458, 1318, 1140, 1082, 958, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=7 Hz), 1.18—1.37 (m, 6H), 1.37—1.51 (m, 2H), 2.17—2.26 (m, 2H), 2.43 (s, 3H), 6.29 (d, 1H, 15 Hz), 6.95 (dt, 1H, J=7, 15 Hz), 7.32 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

23c: An oil; MS *m/z* 294 (M^+, 23%), 209, 183, 157 (100), 139 (100), 138 (100), 96 (100), 83 (100), 82, 55, 43, 41; IR (neat) 3042, 2918, 2851, 1588, 1460, 1315, 1140, 1080, 962, 802 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7 Hz), 1.16—1.37 (m, 10H), 1.37—1.61 (m, 2H), 2.17—2.26 (m, 2H), 2.43 (s, 3H), 6.29 (d, 2H, J=15 Hz), 6.95 (dt, 1H, J=7, 15 Hz), 7.32 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz).

23d: Mp 44 °C (from hexane); MS *m/z* 308 (M^+, 13%), 209, 157 (100), 152, 139, 96, 92, 82, 68, 55, 43; IR (KBr) 3034, 2918, 1582, 1458, 1280, 1132, 1075, 962, 797 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7 Hz), 1.24 (broad s, 12H), 1.36—1.51 (m, 2H), 2.15—2.26 (m, 2H), 2.43 (s, 3H), 6.29 (d, 2H, J=15 Hz), 6.95 (dt, 1H, J=7, 15 Hz), 7.32 (d, 2H, J=8 Hz), 7.75 (d, 2H, J=8 Hz). Found: C, 69.90; H, 9.39%. Calcd for $C_{18}H_{28}O_2S$: C, 70.08; H, 9.15%.

The conversion of **23a—d** to **24a—d** was achieved in a similar manner described for **3b** to **11b**. Their physical data were already shown above, namely, those of **24a** were similar to those of **16a, 24b** to **16c, 24c** to **11d,** and **24d** to **20b** except only the ratios of E/Z on their ^1H NMR spectra, respectively.

Conversion of (*E*)-1-Tosyl-1-undecene (23d) to 1-Tosyl-2-undecene (24d) with *t*-BuOK. To a solution of *t*-BuOK (29 mg, 0.26 mmol) in *t*-BuOH (4 ml) was added a solution of (*E*)-**23d** (40 mg, 0.13 mmol) in *t*-BuOH (2 ml) at 30 °C with stirring. One-milliliter aliquots were quenched each time shown in Table 5 with 1 mol dm^{-3} HCl followed by the addition of ethyl acetate. The organic phase was separated and washed successively with aqueous $NaHCO_3$ and brine, and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was dissolved in $CDCl_3$ and the resulting solution was passed through a small and short alumina column to dry and to remove insoluble substances. The ratios of products shown in Table 5 were determined by 400 MHz ^1H NMR spectra of the $CDCl_3$ solution thus obtained.

α-Alkylated vinylic sulfones (**34a—c**) were prepared according to the procedure described in the previous paper.[9c] In order to yield the pure (E)- and (Z)-isomers of **34a** and **34b**, their precursors, the 1-alkyl-2-(1-pyrrolidinyl)-alkyl *p*-tolyl sulfones, were separated into each diastereoisomer with preparative TLC prior to Cope elimination reaction. Physical data of **34a—c** are given below. (E)- and (Z)-isomers were characterized based on the known deshielding of alkyl group syn to the sulfonyl group in vinylic sulfones.[23] It was further confirmed by the measurement of NOE for each isomer.

(*E*)-**34a**: An oil; MS *m/z* 322 (M^+, 11%), 197, 166 (100), 157, 139, 69, 55; IR (neat) 2920, 2850, 1640, 1590, 1490, 1460, 1295, 1135, 1070, 805, 707 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7 Hz), 1.20—1.37 (m, 12H), 1.43—1.54 (m, 2H), 1.81 (s, 3H), 2.14—2.20 (m, 2H), 2.43 (s, 3H), 6.87 (t, 1H, J=7.5 Hz), 7.31 (d, 2H, J=8 Hz), 7.73 (d, 2H, J=8 Hz).

(*Z*)-**34a**: An oil; MS *m/z* 322 (M^+, 25%), 223, 197, 166, 157 (100), 139, 69, 68, 55; IR (neat) 2920, 2850, 1634, 1590, 1490, 1460, 1310, 1135, 1075, 805, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, 3H, J=7 Hz), 1.16—1.44 (m, 14H), 1.96 (s, 3H), 2.44 (s, 3H), 2.60—2.70 (m, 2H), 5.97 (t, 1H, J 7.5 Hz), 7.32 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz).

(*E*)-**34b**: An oil; MS *m/z* 350 (M^+, 12%), 194, 157 (100), 139, 119, 83, 69, 55; IR (neat) 2950, 2910, 2840, 1627, 1587, 1450, 1305, 1127, 1078, 803, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.81—0.96 (m, 6H), 1.17—1.43 (m, 14H), 1.43—1.55 (m, 2H), 2.14—2.24 (m, 4H), 2.43 (s, 3H), 6.88 (t, 1H, J=7 Hz), 7.31 (d, 2H, J=8 Hz), 7.73 (d, 2H, J=8 Hz).

(*Z*)-**34b**: An oil; MS *m/z* 350 (M^+, 44%), 251, 157 (100), 139, 96, 82, 69, 67, 55; IR (neat) 2950, 2910, 2840, 1620, 1587, 1450, 1305, 1130, 1075, 803, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—0.97 (m, 6H), 1.15—1.41 (m, 14H), 1.45—1.58 (m, 2H), 2.27 (t, 2H, J=7.5 Hz), 2.43 (s, 3H), 2.57—2.66 (m, 2H), 5.96 (t, 1H, J=7.5 Hz), 7.31 (d, 2H, J=8 Hz), 7.76 (d, 2H, J=8 Hz).

34c (mixture of E- and Z-forms): An oil; MS *m/z* 336 (M^+, 35%), 237, 211, 180, 157 (100), 139, 82, 69, 55; IR (neat) 2910, 2840, 1625, 1587, 1480, 1450, 1303, 1125, 1075, 803, 701 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84—0.96 (m, 6H of E and 3H of Z), 1.05—1.13 (t, 3H of Z, J=7 Hz), 1.16—1.41 (m, 14H of Z and 12H of E), 1.42—1.58 (m, 2H of E), 2.15—2.30 (m, 4H of E), 2.30—2.38 (m, 2H of Z), 2.43 (s, 3H of E and Z), 2.57—2.67 (m, 2H of Z), 5.95 (t, 1H of Z, J=7 Hz), 6.86 (t, 1H of E, J=7.5 Hz), 7.30—7.35 (m, 2H of E and Z), 7.72—7.79 (m, 2H of E and Z).

(*E*)-**34c**: An oil; MS *m/z* 336 (M^+, 9%), 211, 180, 157, 139, 97, 83, 69 (100), 57, 55; IR (neat) 2910, 2840, 1625, 1587, 1480, 1455, 1367, 1307, 1145, 1075, 802, 703 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.84—0.98 (m, 6H), 1.20—1.37 (m, 12H), 1.42—1.58 (m, 2H), 2.15—2.30 (m, 4H), 2.43 (s, 3H), 6.86 (t, 1H, J=7.5 Hz), 7.31 (d, 2H, J=8 Hz), 7.73 (d, 2H, J=8 Hz).

The conversion of **34a—c** to the corresponding allylic sulfones (**35a—c**) was carried out with *t*-BuOK in *t*-BuOH in a similar manner described for the conversion of **23d** to **24d**. Physical data of **35a—c** were shown below.

(*E*)-**35a**: An oil; CIMS *m/z* 323 (M^+ +1, 12%), 199, 197, 167 (100), 158, 157 (100), 111, 97 (100), 83, 69; IR (neat) 2920, 2850, 1650, 1590, 1450, 1310, 1140, 1085, 965, 807, 710 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (t, 3H, J=7 Hz), 1.14—1.36 (m, 12H), 1.41 (d, 3H, J=7 Hz), 1.97 (q, 2H, J=7 Hz), 2.44 (s, 3H), 3.62 (quintet, 1H, J=7 Hz), 5.36 (dd, 1H, J=7, 15.5 Hz), 5.45 (dt, 1H, J=6.5, 15.5 Hz), 7.31 (d, 2H, J=8 Hz), 7.70 (d, 2H, J=8 Hz).

(*E*)-**35b**: An oil; MS *m/z* 350 (M^+, 0.1%), 195, 125, 111, 97, 83 (100), 69, 57, 55; IR (neat) 2920, 2850, 1905, 1760, 1650, 1590, 1460, 1310, 1140, 1081, 965, 807 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85—0.96 (m, 6H), 1.13—1.36 (m, 13H), 1.36—1.53 (m, 1H), 1.55—1.70 (m, 1H), 1.96 (q, 2H, J=7 Hz), 2.00—2.10 (m, 1H), 2.44 (s, 3H), 3.38—3.47 (m, 1H), 5.17 (dd, 1H, J=9, 15.5 Hz), 5.39 (dt, 1H, J=7, 15.5 Hz), 7.30 (d, 2H, J=8 Hz), 7.69 (d, 2H, J=8 Hz).

(*E*)-**35c**: An oil; CIMS *m/z* 337 (M^+ +1, 20%), 199, 197, 181 (100), 158, 157 (100), 125, 111, 97, 83, 69; IR (neat) 2920, 2840, 1720, 1590, 1450, 1308, 1140, 1080, 960, 805 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7 Hz), 0.93 (t, 3H, J=7 Hz), 1.14—1.37 (m, 12H), 1.56—1.72 (m, 1H), 1.97 (q, 2H, J=7 Hz), 2.10—2.21 (m, 1H), 2.44 (s, 3H), 3.30—3.38 (m, 1H), 5.18 (dd, 1H, J=9, 15.5 Hz), 5.42 (dt, 1H, J=7, 15.5 Hz), 7.30 (d, 2H, J=8 Hz), 7.69 (d, 2H, J=8 Hz).

Preparation of 4-Phenylsulfonyl-2-methyl-2-butene (38e) from 2-Methylpropanal (36e). To a mixed solution of diethyl phenylsulfonylmethylphosphonate (**37**, 74 mg, 0.25 mmol) and DBU (114 mg, 0.75 mmol) in acetonitrile (1.5 ml) was added 22 mg of **36e** (0.3 mmol) at room temperature with stirring. After 12 h, the reaction mixture was quenched with a phosphate buffer solution (pH 7), followed by replacing the solvent by ethyl acetate. The resulting solution was washed with brine twice and dried over

$MgSO_4$. The residue obtained by evaporation of the solvent was subjected to preparative TLC (solvent; hexane–ethyl acetate=5:1, v/v) to afford 46 mg of **38e** (88% yield) as an oil; MS *m/z* 210 (M^+, 2%), 69 (100), 41; IR (neat) 3048, 2960, 2904, 1578, 1440, 1300, 1144, 1080, 894, 774, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (s, 3H), 1.71 (s, 3H), 3.79 (d, 2H, *J*=8 Hz), 5.19 (m, 1H), 7.49—7.59 (m, 2H), 7.61—7.68 (m, 1H), 7.81—7.93 (m, 2H).

In a similar manner, **38a—d** were prepared. Their physical data are given below.

38a: An oil (contaminated with a small amount of vinylic sulfone (ca. 8%), which was reduced in the calculation of the yield of **38a**); CIMS *m/z* 272 (M^+, 100%), 142, 130 (100), 129, 91, 52; IR (neat) 3048, 3012, 2912, 1590, 1486, 1442, 1300, 1142, 1080, 965, 720, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.13 (d, 2H of Z, *J*=7 Hz), 3.32 (d, 2H of E *J*=7 Hz), 3.77 (dd, 2H of E, *J*=0.5, 7 Hz), 3.95 (d, 2H of Z, *J*=8 Hz), 5.42—5.60 (m, 1H of E and Z), 5.65 (dt, 1H of E, *J*=7, 15 Hz), 5.90 (dt, 1H of Z, *J*=7, 11 Hz), 6.93 (d, 2H of Z, *J*=7 Hz), 7.00 (d, 2H of E, *J*=7 Hz), 7.08—7.33 (m, 3H of E and Z), 7.42—7.71 (m, 3H of E and Z), 7.77—7.98 (m, 2H of E and Z).

38b: An oil; CIMS *m/z* 282 (M^+ +2, 77%), 281 (M^+ +1, 100), 183, 143 (100), 139, 138, 83, 53; IR (neat) 3052, 3012, 2920, 2844, 1580, 1440, 1314, 1140, 1080, 962, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H of Z, *J*=7 Hz), 0.88 (t, 3H of E, *J*=7 Hz), 0.96—1.36 (m, 10H of E and Z), 1.72 (m, 2H of Z), 1.99 (m, 2H of E), 3.74 (d, 2H of E, *J*=7 Hz), 3.85 (d, 2H of Z, *J*=8 Hz), 5.33—5.46 (m, 1H of E and Z), 5.50 (dt, 1H of E, *J*=7, 15 Hz), 5.71 (dt, 1H of Z, *J*=7, 11 Hz), 7.49—7.60 (m, 2H of E and Z), 7.60—7.69 (m, 2H of E and Z), 7.80—7.94 (m, 2H of E and Z).

38c: An oil; CIMS *m/z* 295 (M^+ +1, 56%), 183, 153 (100), 143 (100), 97, 83, 69, 53; IR (neat) 3048, 2912, 2840, 1576, 1438, 1310, 1138, 1080, 960, 720, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H of Z, *J*=7 Hz), 0.89 (t, 3H of E, *J*=7 Hz), 0.98—1.36 (m, 12H of E and Z), 1.72 (m, 2H of Z), 1.98 (m, 2H of E), 3.74 (d, 2H of E, *J*=7 Hz), 3.85 (d, 2H of Z, *J*=8 Hz), 5.34—5.46 (m, 1H of E and Z), 5.50 (dt, 1H of E, *J*=7, 15 Hz), 5.72 (dt, 1H of Z, *J*=7, 11 Hz), 7.49—7.59 (m, 2H of E and Z), 7.60—7.69 (m, 1H of E and Z), 7.80—7.95 (m, 2H of E and Z).

(*E*)-38d: An oil; CIMS *m/z* 293 (M^+ +1, 62%), 183, 152, 151 (100), 143, 109, 95, 81, 69, 51; IR (neat) 3052, 2952, 2900, 1578, 1440, 1312, 1140, 1080, 962, 730, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (d, 3H, *J*=7 Hz), 1.19 (m, 2H), 1.56 (s, 3H), 1.67 (s, 3H), 1.82 (q, 2H, *J*=7.5 Hz), 2.09 (m, 1H), 3.69—3.82 (m, 2H), 5.01 (m, 1H), 5.30—5.42 (m, 2H, *J* of olefinic protons=15.5 Hz), 7.50—7.58 (m, 2H), 7.60—7.67 (m, 1H), 7.81—7.92 (m, 2H).

(*Z*)-38d: An oil (contaminated with a small amount of vinylic sulfone (ca. 5%), which was reduced in the calculation of the yield of **38d**); CIMS *m/z* 293 (M^+ +1, 100%), 152 (100), 151 (100), 150 (100), 149, 143 (100), 135, 109 (100), 107, 95, 83, 82 (100), 81, 69, 67, 53, 51; IR (neat) 3052, 2952, 2912, 1580, 1440, 1312, 1140, 1080, 886, 722, 680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.66 (d, 3H, *J*=7 Hz), 0.98—1.11 (m, 1H), 1.13—1.27 (m, 1H), 1.54 (s, 3H), 1.66 (d, 3H, *J*=1 Hz), 1.73 (q, 2H, *J*=7.5 Hz), 2.02—2.16 (m, 1H), 3.71—3.82 (m, 1H), 3.85—3.95 (m, 1H), 4.95 (m, 1H), 5.31—5.41 (m, 1H), 5.47 (dd, 1H, *J*=10, 11 Hz), 7.48—7.58 (m, 2H), 7.58—7.69 (m, 1H), 7.82—7.96 (m, 2H).

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