Sulfonylation and Phosphinylation of Olefinic Compounds with Radical Species Generated by the Oxidation of Sodium Sulfinates and Diphenylphosphine Oxide

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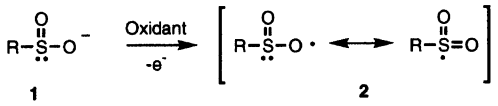
Sodium arenesulfinates are oxidized with manganese(III) 2-pyridinecarboxylate or ammonium cerium(IV) nitrates to generate sulfonyl radicals, which add to olefinic compounds to afford sulfonylated products in good yield. When 1-vinyl cyclic alcohols are used as sulfonyl radical acceptors, sulfonylation proceeds with ring-enlargement. Diphenylphosphinyl radical can also be generated by treating diphenylphosphine oxide with manganese(III) 2-pyridinecarboxylate and reacts with olefinic compounds, giving phosphinylated products.

Due to the potential utility of organosulfones in organic synthesis, sulfonylation of olefins has been widely studied for the preparation of various organosulfones.[1] Although the addition of sulfonyl radicals to olefinic compounds is a typical method for the preparation of sulfones from olefinic compounds, along with electrophilic addition reaction of sulfinic acid, the conventional radical addition reactions have some drawbacks concerning the reaction conditions. For instance, sulfonyl radicals are generated from sulfonyl halides by exposure to light,[2] by the action of a peroxide,[3] or by the reduction with metallic reagents at high temperature.[4,5] They are also formed from selenosulfonates by the homolytic scission under high temperature or by photoirradiation.[6]

Recently, we reported briefly that sulfonyl radicals are generated from sodium sulfinates and react with olefinic compounds under mild reaction conditions by the use of metallic oxidants.[7] Here, a full account of this sulfonylation method is described with the application to sulfonylation of 1-vinyl cyclic alcohols. In addition we mention a phosphinyl radical generation from a phosphine oxide and its addition reaction to olefins.

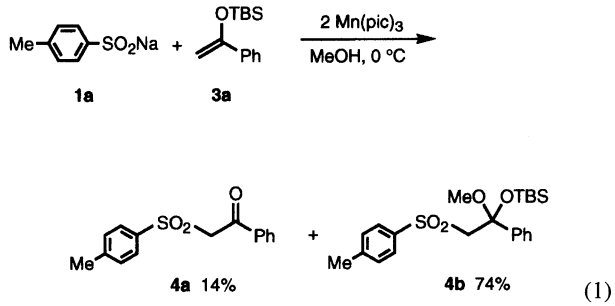
Results and Discussion

Sulfonylation of Olefinic Compounds Using $Mn(pic)_3$ (Method A). Though a sulfonyl radical can be generated from a sulfinic acid by one-electron oxidation,[8] the synthetic utility of such an oxidative method has not been demonstrated. We have reported that manganese(III) 2-pyridinecarboxylate ($Mn(pic)_3$) is utilized effectively for one-electron oxidation of β-keto carboxylic acids,[9] cyclopropanols,[10] and pentacarbonyl(1-oxidoalkylidene)-chromium(0) complexes,[11] giving the corresponding α-keto radicals, β-keto radicals, and alkyl radicals, respectively (Scheme 1). Accordingly, we attempted the oxidation of sodium sulfinates with $Mn(pic)_3$ to generate sulfonyl radicals and their addition reaction to olefinic compounds.



Scheme 1.

Sodium *p*-toluenesulfinate (**1a**) was treated with 2.2 molar amounts of $Mn(pic)_3$ in methanol in the presence of 1-(*t*-butyldimethylsiloxy)-1-phenylethene (**3a**) at 0 °C (Method A), giving a β-keto sulfone **4a** and its silyl acetal **4b** in 14 and 74% yield, respectively (Eq. 1).

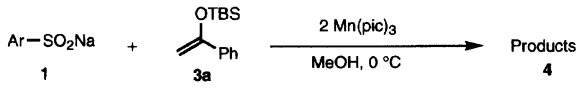


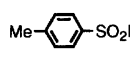
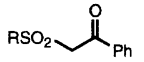
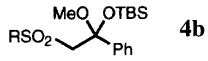
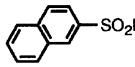
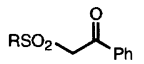
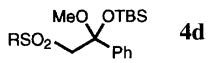
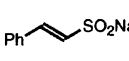
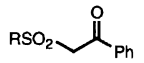
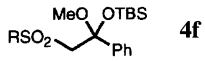
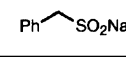
(1)

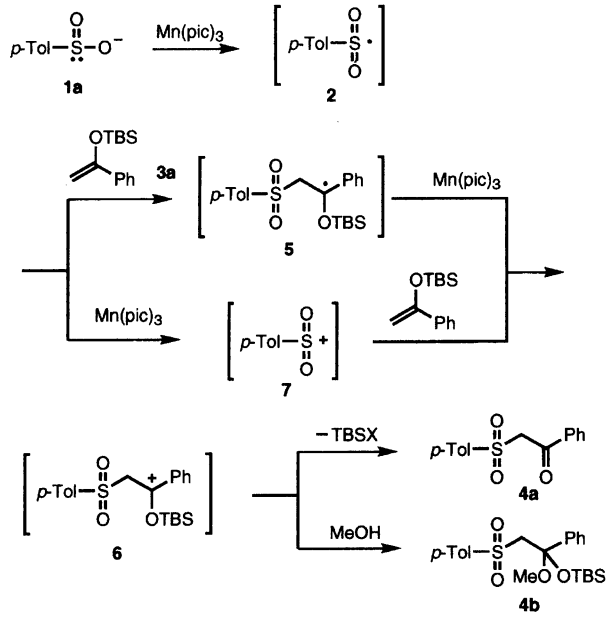
This reaction is thought to proceed as depicted in Scheme 2. A sulfonyl radical **2** is generated by oxidation of sodium *p*-toluenesulfinate (**1a**) with $Mn(pic)_3$. Two reaction pathways are possible to afford the addition products **4**. The sulfonyl radical may add to the silyl enol ether **3a** to give a radical species **5**, which is oxidized with $Mn(pic)_3$ to a cationic intermediate **6**. In an alternative pathway, the sulfonyl radical **2** initially formed is further oxidized with $Mn(pic)_3$ to a sulfonyl cation **7**, which adds to the olefin to afford **6**. Finally, the sulfonylated products **4a** and **4b** are formed from the cation **6** by an elimination of the *t*-butyldimethylsilyl (TBS) group or by a nucleophilic attack of methanol, respectively.

The following experiment suggested to us a possibility of the sulfonyl radical addition reaction. While the sulfo-

Table 1. Sulfonylation of **3a** with Sodium Sulfinates

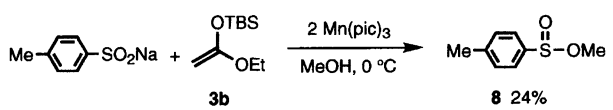


Entry	RSO_2Na		Products (Yield / %)			
1		**1a**		**4a** (14)		**4b** (74)
2		**1b**		**4c** (14)		**4d** (72)
3		**1c**		**4e** (11)		**4f** (48)
4		**1d**	No adduct			



Scheme 2.

nylation of 1-(*t*-butyldimethylsiloxy)-1-phenylethene (**3a**) proceeded in good yield by Method A, the sulfonylation of a ketene silyl acetal **3b** under the same reaction conditions afforded no sulfonylated product but methyl *p*-toluenesulfinate **8** (Eq. 2). Since a ketene silyl acetal is a good nucleophile but is not suitable for a radical acceptor,[12] this result indicates that the sulfonylation proceeds by addition of the sulfonyl radical **2** to **3a**.

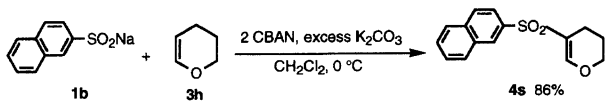


(2)

The sulfonylation of the silyl enol ether **3a** was examined by employing some sodium sulfinates. As depicted in Table 1, arylic and vinylic sulfinates, such as *p*-toluenesulfinate (**1a**), 2-naphthalenesulfinate (**1b**), and 2-phenylethenesulfinate (**1c**), reacted with **3a** to give sulfonylated products **4** (Entries 1—3). However, the reaction with sodium phenylmethanesulfinate (**1d**) did not afford the products (Entry 4). Thus, as sulfonyl radical sources, it is required to employ sulfinates which have an R group π-conjugating with the sulfonyl group.

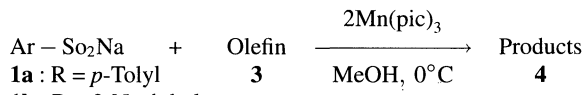
The present Method A was applied for the sulfonylation of various electron rich olefins with sodium 2-naphthalenesulfinate (**1b**) or sodium *p*-toluenesulfinate (**1a**), as shown in Table 2. α-Aryl β-non and monosubstituted silyl enol ethers reacted with the arenesulfinates (**1a** and **b**), giving sulfonylated products is good yield (Entries 1, 2, and 9), while the β,β-disubstituted one was found not to be the suitable substrate for this reaction (Entry 10). As shown in Entries 3—6, this sulfonylation method can be also applied to the sulfonylation of an aryl substituted vinyl ether **3c** and a ketene dithioacetal **3d**; however, an α-alkyl substituted silyl enol ether **3e** afforded the corresponding sulfones in poor yield (Entries 7 and 8). In the reaction of the dithioacetal **3d**, olefinic compounds **4i** and **4j**, they were supposed to be generated directly by the elimination of a proton from the cationic intermediate which corresponds to **6** in Scheme 2.

Sulfonylation of Cyclic Vinyl Ethers Using a CBAN in Dichloromethane (Method B). If one used $Mn(pic)_3$ in methanol (Method A), little 3,4-dihydro-2*H*-pyran (**3h**) was sulfonylated with sodium *p*-toluenesulfinate (Table 2, Entry 11). Since it was supposed that the dihydropyran **3h** was consumed by acid-catalyzed addition of methanol, the sulfonylation was examined in the presence of K_2CO_3; however, the reaction did not proceed. Though the reaction was also tried in DMF, the yield of the product is only 28%. Therefore, we attempted the reaction by using cerium(IV) reagents as a one-electron oxidant. When a mixture of sodium 2-naphthalenesulfinate (**1b**) and the dihydropyran **3h** was oxidized with cerium(IV) tetrabutylammonium nitrate (CBAN) in the presence of K_2CO_3 in CH_2Cl_2, 5-(2-naphthylsulfonyl)-3,4-dihydro-2*H*-pyran (**4s**) was obtained in 86% yield (Method B) (Eq. 3).



(3)

Table 2. Sulfonylation of Olefins Using $Mn(pic)_3$ (Method A)



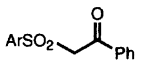
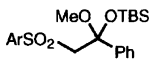
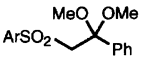
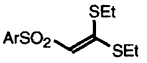
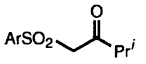
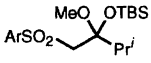
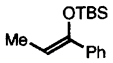
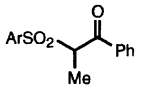
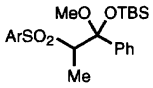
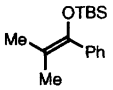
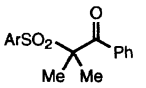
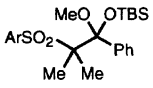
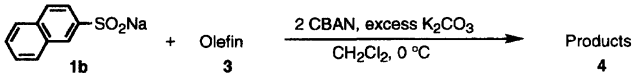
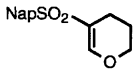
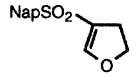
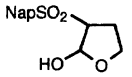
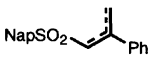
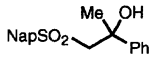
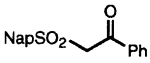
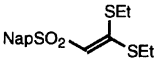
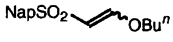
Entry	Olefin		Sulfinate	Products (Yield / %)			
1		**3a**	**1a**		**4a** (14)		**4b** (74)
2	**3a**		**1b**		**4c** (14)		**4d** (72)
3		**3c**	**1a**		**4g** (quant.)		
4	**3c**		**1b**		**4h** (89)		
5		**3d**	**1a**		**4i** (87)		
6	**3d**		**1b**		**4j** (84)		
7		**3e**	**1a**		**4k** (11)		**4l** (13)
8	**3e**		**1b**		**4m** (20)		**4n** (30)
9		**3f**	**1a**		**4o** (34)		**4p** (52)
10		**3g**	**1a**		**4q** (trace)		**4r** (trace)
11		**3h**	**1a**	No adduct			

Table 3. Sulfonylation of Olefins Using CBAN in CH_2Cl_2 (Method B)

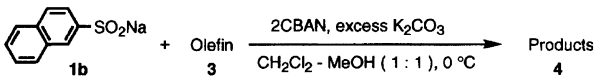


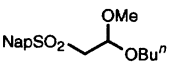
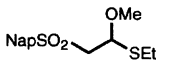
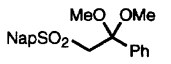
Entry	Olefin		Products (Yield / %)[a]			
1		**3h**		**4s** (86)		
2		**3i**		**4t** (20)		**4u** (42)
3		**3j**		**4v** (46)		**4w** (32)
4		**3a**		**4c** (30)		
5		**3d**		**4j** (50)		
6		**3k**		**4x** (18)		

a) Nap=2-Naphthyl.

Ammonium cerium(IV) nitrate (CAN), which is less soluble in organic solvent as compared with CBAN, could be also used as an oxidant in propiononitrile; however, the yield of **4a** was slightly lower than that in the reaction by using

Table 4. Sulfonylation of Olefins Using CBAN in CH_2Cl_2–MeOH (Method C)



Entry	Olefin		Products (Yield / %)[a]	
1		**3k**		**4y** (84)
2		**3l**		**4z** (68)
3		**3c**		**4h** (81)

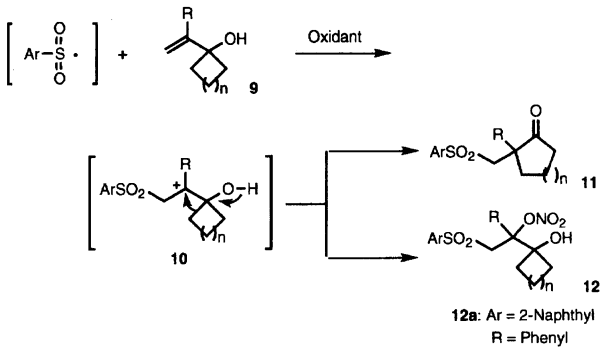
a) Nap=2-Naphthyl.

CBAN.

In contrast to the electrophilic sulfonylation of the dihydropyran **3h** with a sulfinic acid to give 6-sulfonyl-3,4-dihydro-2*H*-pyran,[13] the present method introduces a sulfonyl group at the 5 position of the dihydropyran **3h**. Thus, the electrophilic and the radical sulfonylation reactions can be employed alternatively for the regioselective sulfonylation of dihydropyran.

Though this method was also effective for sulfonylation of a 2,3-dihydrofuran (**3i**) and 1-methyl-1-phenylethene (**3j**) (Table 3, Entries 2 and 3), satisfactory results were not obtained in the sulfonylation of the silyl enol ether of acetophenone **3a** and the ketene dithioacetal **3d** (Entries 4 and 5), whose sulfonylation products were obtained in good yield by Method A. Since 1,4-diphenyl-1,4-butanedione was obtained in the reaction of **1a** and **3a**, these olefinic compounds **3a** and **3d** were thought to be oxidized by CBAN under the reaction conditions.

Sulfonylation of Vinyl Ethers and Sulfides with CBAN in Dichloromethane–Methanol (Method C). As shown in Entry 6 in Table 3, Method B is not suitable for the sulfonylation of a non-substituted vinyl ether **3k**. Since the low yield of the product **4x** was presumably due to a side reaction, such as cationic polymerization of the vinyl ether, the reaction was carried out in the presence of methanol to trap the cationic



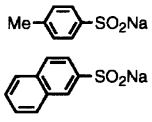
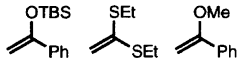
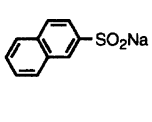
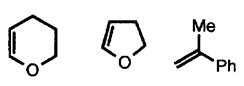
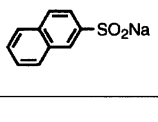
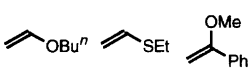
Scheme 3.

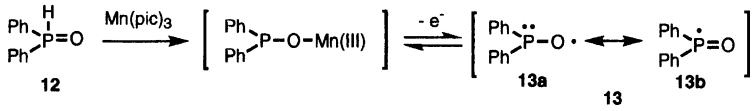
intermediate which corresponds to **6** in Scheme 2. By the reaction in a mixed solvent of dichloromethane and methanol (1 : 1), a sulfonylated product was obtained as an acetal **4y** in 84% yield (Method C) (Table 4, Entry 1). Under these conditions, the sulfonylation of a vinyl sulfide **3l** and 1-methoxy-1-phenylethene (**3c**) also proceeded in good yield (Entries 2 and 3).

For the sulfonylation of olefinic compounds with sodium sulfinates, three types of methods were developed by employing metallic oxidants. Various kinds of electron rich olefins are sulfonylated by choosing an appropriate method as depicted in Table 5. For the sulfonylation of olefinic compounds which are good radical acceptors and readily suffer from oxidation, Method A is suitable because $Mn(pic)_3$ is a mild oxidation reagent as compared to CBAN. The reaction of cyclic vinyl ethers has to be carried out in an aprotic solvent, dichloromethane, with CBAN (Method B). Non-substituted vinyl ethers and vinyl sulfides are sulfonylated in a mixed solvent of dichloromethane and methanol by using CBAN (Method C).

Sulfonylation of 1-Vinyl Cyclic Alcohols. One of the typical features of the present sulfonylation reaction is that the radical reaction is terminated by the formation of cationic intermediates. The resulting cationic intermediates are thought to be utilized for successive transformations. When a 1-vinyl cyclic alcohol **9** is employed for the sulfonylation, it would be possible to undergo a pinacol-type rearrangement via a cationic intermediate **10**, giving a ring-

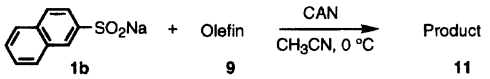
Table 5. Applicability of Method A, B, and C for the Sulfonylation of Olefins

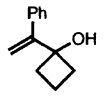
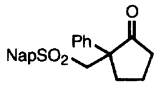
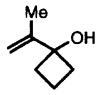
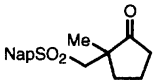
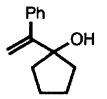
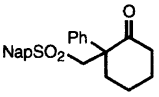
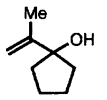
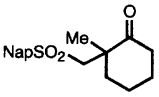
Sodium sulfinates	Reaction conditions	Applicable olefins
	$Mn(pic)_3$, MeOH, 0 °C (Method A)	
	CBAN, K_2CO_3, CH_2Cl_2, 0 °C (Method B)	
	CBAN, K_2CO_3, CH_2Cl_2–MeOH (1 : 1), 0 °C (Method C)	



Scheme 4.

Table 6. Sulfonylation of 1-Vinyl Cyclic Alcohols



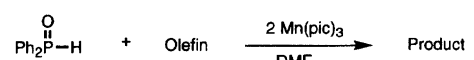
Entry	Olefin		Product (Yield / %)[a]	
1		**9a**		**11a** (70)
2		**9b**		**11b** (72)
3		**9c**		**11c** (43)
4		**9d**		**11d** (34)

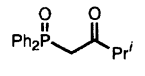
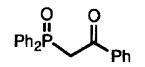
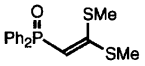
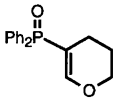
a) Nap=2-Naphthyl.

enlarged ketone **11** as depicted in Scheme 3. In fact, when a mixture of 1-(1-phenylvinyl)cyclobutanol (**9a**) and **1b** in dichloromethane was treated with CBAN, the ring-enlarged product **11a** was obtained as a mixture with an unidentified compound. The structure of the side product, however, made it seem to be a nitrate **12a** because it showed the peaks corresponded to nitrate moiety in the IR spectrum and was readily converted to the cyclopentanone **11a** by treatment with 1 M aq HCl. These results indicated that the rearrangement of **10** to **11** proceeds rather slowly and the cationic intermediate **10** is trapped with a nitrate ion. To facilitate the rearrangement, the reaction was attempted in more polar solvent, acetonitrile, by using ammonium cerium(IV) nitrate (CAN) as an oxidizing reagent to give the cyclopentanone **11a** exclusively in 70% yield.

The reaction with sodium 2-naphthalenesulfinate **1b** and some 1-vinyl cyclic alcohols was examined with CAN as an oxidant in acetonitrile (Table 6). The reaction of 1-vinylcyclobutanol derivatives **9a** and **9b**, which have a phenyl or methyl group at the 1-position of the vinyl group, afforded ring-enlarged cyclopentanones **11a** and **11b** in good yield (Entries 1 and 2). Furthermore, 1-vinylcyclopentanols were also transformed to the corresponding cyclohexanone derivatives (Entries 3 and 4), though the yield was not sufficiently high. 1-Vinyl cyclic alcohols are easily prepared from cyclic ketones by the action of vinyl Grignard reagents. Accordingly, the above reaction enables the transformation of simple cyclic ketones to one-carbon enlarged cyclic ketones which have a sulfonylmethyl substituent in their α-position.

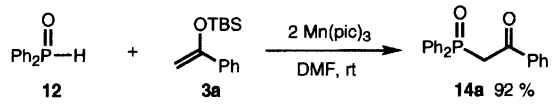
Table 7. Phosphinylation of Olefins



Entry	Olefin		Product (Yield / %)	
1		**3e**		**14b** (77)
2		**3c**		**14a** (80)
3		**3m**		**14c** (70)
4		**3h**		**14d** (37)

Phosphinylation of Olefins. Oxidative generation of a phosphinyl radical and the addition reaction to olefins were examined by employing diphenylphosphine oxide (**12**). Metallic salts of **12** are known to have an oxygen–metal bond,[14] and it seemed to be possible that the oxygen-centered radical **13a** initially formed by oxidation would conjugate to the phosphorous radical **13b** as the previously mentioned sulfonyl radical does (Scheme 4).

When **12** was treated with $Mn(pic)_3$ in the presence of the silyl enol ether **3a** in dimethylformamide (DMF), a phosphinylated product **14a** was obtained in 92% yield as expected (Eq. 4).



(4)

Some electron-rich olefins were employed for the phosphinylation, as shown in Table 7. Like the α-alkyl substituted silyl enol ethers **3e**, 1-methoxy-1-phenylethene (**3c**) and ketene dithioacetal **3m** were phosphinylated in good yield (Entries 1—3). The addition reaction to the dihydropyram **3h** also proceeded, affording a 5-phosphinyl derivative **14d** in 37% yield (Entry 4). Some phosphinyl radical addition reactions have been reported in which phosphinyl radicals were generated by the action of a peroxide or by the photo irradiation at high temperature,[15] while the present reaction proceeds under very mild conditions.

Experimental

General. IR spectra were measured with a Horiba FT 300-S spectrometer. ^{1}H NMR spectra (500 MHz) were recorded on a Bruker AM 500 spectrometer with $CHCl_3$ (δ=7.24) used as an internal standard. High-resolution mass spectra were recorded on a JEOL JMS-SX102A mass spectrometer operating at 70 eV. All

melting points were uncorrected.

Methanol was distilled from magnesium methoxide, then dried over Molecular Sieve 3A (MS 3A). Acetonitrile and dichloromethane were distilled from P_2O_5, then from CaH_2, and dried over Molecular Sieve 4A (MS 4A). DMF was dried over P_2O_5, then distilled from CaH_2, and stored under argon atmosphere over MS 4A. $Mn(pic)_3$ was prepared according to a literature method.[16] CAN (Kanto Chemical Co., Inc., guaranteed grade) and K_2CO_3 (Kanto Chemical Co., Inc., guaranteed grade) were dried under a vacuum at 80 °C before use. CBAN was prepared by a known method.[17] Silyl enol ethers **3a**, **3b**, **3e**, **3f**, and **3g** were prepared by a literature method.[18] 1-Methoxy-1-phenylethene (**3c**),[19] ketene dithioacetals **3d** and **3m**,[20] and ethyl vinyl sulfide (**3l**)[21] were prepared according to the literature methods. 3,4-Dihydro-2*H*-pyran (**3h**), 2,3-dihydrofuran (**3i**), 1-methyl-1-phenylethene (**3j**), butyl vinyl ether (**3k**) were purified by distillation. Sodium *p*-toluenesulfinate (**1a**) (Tokyo Kasei Kogyo Co., Ltd.) was used without purification. Other sodium sulfinates (**1b—d**) were synthesized by a literature method.[22] Diphenylphosphine oxide (**12**) (Aldrich) was used without purification.

Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art. 7734. Preparative TLC was performed on a silica-gel (Wakogel B-5F). All reactions were carried out under an argon atmosphere.

Typical Procedure for the Sulfonylation of Olefinic Compounds by Using $Mn(pic)_3$ (Method A). A solution of sodium *p*-toluenesulfinate (**1a**, 182 mg, 1.0 mmol) and 1-(*t*-butyldimethylsiloxy)-1-phenylethene (**3a**, 520 mg, 2.2 mmol) in methanol (15 ml) is added to a suspension of $Mn(pic)_3$ (931 mg, 2.2 mmol) in methanol (5 ml) at 0 °C. After the mixture was stirred overnight, a pH 7 buffer solution was added to the reaction mixture, and the resulting precipitates were filtered off through Celite. The filtrate was extracted with ethyl acetate and dried over Na_2SO_4. The crude product was purified by silica-gel column chromatography to afford the β-keto sulfone **4a** (40 mg, 14%) and the silylacetal **4b** (315 mg, 74%).

Spectral data and physical properties of the new compounds are as follows.

1-Phenyl-2-(*p*-tolylsulfonyl)ethanone (4a):[23] IR (CH_2Cl_2) 1681, 1326, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.34 (3H, s), 4.70 (2H, s), 7.32—7.33 (2H, m), 7.44—7.48 (2H, m), 7.58—7.62 (1H, m), 7.72—7.75 (2H, m), 7.93—7.95 (2H, m).

1-Phenyl-2-(*p*-tolylsulfonyl)ethanone *t*-Butyldimethylsilyl Methyl Acetal (4b): Mp 100—103 °C (ether); IR (CH_2Cl_2) 1321, 1161, 1084, 1043 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.22 (3H, s), 0.17 (3H, s), 0.92 (9H, s), 2.32 (3H, s), 3.17 (3H, s), 3.80 (2H, d, *J*=15.3 Hz), 3.96 (2H, d, *J*=15.3 Hz), 7.02 (2H, d, *J*=8.1 Hz), 7.10—7.13 (2H, m), 7.15—7.18 (1H, m), 7.28—7.32 (4H, m). Found: C, 62.69; H, 7.55; S, 7.70%. Calcd for $C_{22}H_{32}O_4SSi$: C, 62.82; H, 7.67; S, 7.62%.

2-(2-Naphthylsulfonyl)-1-phenylethanone (4c): Mp 130—131 °C (ether); IR (KBr) 1670, 1315, 1277, 1153, 762, 742 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.80 (2H, s), 7.42—7.45 (2H, m), 7.56—7.61 (2H, m), 7.64—7.67 (1H, m), 7.84—7.86 (1H, m), 7.89—7.98 (5H, m), 8.44 (1H, s). Found: C, 69.74; H, 4.66; S, 10.73%. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55; S, 10.33%.

2-(2-Naphthylsulfonyl)-1-phenylethanone *t*-Butyldimethylsilyl Methyl Acetal (4d): IR (CH_2Cl_2) 1323, 1163, 1045, 781 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.21 (3H, s), 0.20 (3H, s), 0.94 (9H, s), 3.17 (3H, s), 3.89 (1H, d, *J*=15.5 Hz), 4.06 (1H, d, *J*=15.5 Hz), 6.85—6.87 (1H, m), 6.90—6.93 (2H, m), 7.26—7.28 (2H, m), 7.46—7.48 (1H, m), 7.51—7.54 (1H, m), 7.57—7.60 (1H, m), 7.71—7.72 (2H, m), 7.79—7.81 (2H, m). HRMS Found: *m/z* 425.1609. Calcd for $C_{25}H_{32}O_4SSi-OCH_3$: M, 425.1607.

1-Phenyl-2-styrylsulfonylethanone (4e): IR (neat) 1614, 1448, 1309, 1279, 1128, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.71 (2H, s), 7.06 (1H, d, *J*=15.6 Hz), 7.38—7.43 (3H, m), 7.51—7.57 (4H, m), 7.59 (1H, d, *J*=15.6 Hz), 7.61—7.63 (1H, m), 7.97—7.99 (2H, m). HRMS Found: *m/z* 286.0652. Calcd for $C_{16}H_{14}O_3S$: M, 286.0664.

1-Phenyl-2-styrylsulfonylethanone *t*-Butyldimethylsilyl Methyl Acetal (4f): IR (CH_2Cl_2) 1317, 1153, 1105 cm^{-1}; ^1H NMR ($CDCl_3$) δ=−0.10 (3H, s), 0.23 (3H, s), 2.44 (3H, s), 0.95 (9H, s), 3.27 (3H, s), 3.72 (1H, d, *J*=15.3 Hz), 3.87 (1H, d, *J*=15.3 Hz), 5.72 (1H, d, *J*=15.6 Hz), 7.06 (1H, d, *J*=15.6 Hz), 7.10—7.12 (2H, m), 7.16—7.19 (1H, m), 7.27—7.35 (5H, m), 7.54—7.56 (2H, m). HRMS Found: *m/z* 401.1599. Calcd for $C_{23}H_{32}O_4SSi-OCH_3$: M, 401.1607.

1-Phenyl-2-(*p*-tolylsulfonyl)ethanone Dimethyl Acetal (4g): Mp 101—102 °C (ether); IR (CH_2Cl_2) 1599, 1450, 1326, 1153, 968 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.33 (3H, s), 3.08 (6H, s), 3.82 (2H, s), 7.06 (2H, d, *J*=8.1 Hz), 7.16—7.18 (3H, m), 7.24—7.31 (2H, m), 7.40 (2H, d, *J*=8.1 Hz). Found: C, 63.59: H, 6.08%. Calcd for $C_{17}H_{20}O_4S$: C, 63.73; H, 6.29%.

2-(2-Naphthylsulfonyl)-1-phenylethanone Dimethyl Acetal (4h): Mp 135—136 °C (ether); IR (KBr) 1317, 1165, 1147, 1103, 1072 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.10 (6H, s), 3.92 (2H, s), 6.89—6.91 (1H, m), 6.95—6.98 (2H, m), 7.71—7.73 (1H, m), 7.77—7.82 (2H, m), 8.01 (1H, s). Found: C, 67.30; H, 5.61; S, 9.04%. Calcd for $C_{20}H_{20}O_4S$: C, 67.39; H, 5.66; S, 8.99%.

2,2-Bis(ethylthio)vinyl *p*-Tolyl Sulfone (4i): IR (CH_2Cl_2) 1301, 1147 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.13 (3H, t, *J*=7.4 Hz), 1.27 (3H, t, *J*=7.4 Hz), 2.39 (3H, s), 2.80 (2H, q, *J*=7.4 Hz), 2.89 (2H, q, *J*=7.4 Hz), 6.16 (1H, s), 7.27 (2H, d, *J*=8.4 Hz), 7.85 (2H, d, *J*=8.4 Hz). HRMS Found: *m/z* 302.0466. Calcd for $C_{13}H_{18}O_2S_3$: M, 302.0469.

2,2-Bis(ethylthio)vinyl 2-Naphthyl Sulfone (4j): IR (CH_2Cl_2) 1309, 1142, 1122 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (3H, t, *J*=7.4 Hz), 1.28 (3H, t, *J*=7.4 Hz), 2.82 (2H, q, *J*=7.4 Hz), 2.88 (2H, q, *J*=7.4 Hz), 6.23 (1H, s), 7.56—7.63 (2H, m), 7.87—7.89 (1H, m), 7.91—7.94 (2H, m), 7.96—7.98 (1H, m), 8.58 (1H, s). Found: C, 56.56; H, 5.24; S, 28.56%. Calcd for $C_{16}H_{18}O_2S_3$: C, 56.77; H, 5.36; S, 28.41%.

3-Methyl-1-(*p*-tolylsulfonyl)-2-butanone (4k): IR (CH_2Cl_2) 1716, 1324, 1157 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (6H, d, *J*=6.9 Hz), 2.43 (3H, s), 2.90 (1H, sept., *J*=6.9 Hz), 4.18 (2H, s), 7.34 (2H, d, *J*=8.2 Hz), 7.74 (2H, d, *J*=8.2 Hz). HRMS Found: *m/z* 240.0828. Calcd for $C_{12}H_{16}O_3S$: M, 240.0820.

3-Methyl-1-(*p*-tolylsulfonyl)-2-butanone *t*-Butyldimethylsilyl Methyl Acetal (4l): IR (CH_2Cl_2) 1321, 1151 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.13 (3H, s), 0.14 (3H, s), 0.87 (9H, s), 0.91 (3H, d, *J*=6.8 Hz), 0.94 (3H, d, *J*=6.8 Hz), 2.33—2.39 (1H, m), 2.42 (3H, s), 3.08 (3H, s), 3.43 (2H, s), 7.31 (2H, d, *J*=8.3 Hz), 7.74 (2H, d, *J*=8.3 Hz). HRMS Found: *m/z* 355.1755. Calcd for $C_{19}H_{34}O_4SSi-OCH_3$: M, 355.1763.

3-Methyl-1-(2-naphthylsulfonyl)-2-butanone (4m): Mp 104—105 °C (ether); IR (CH_2Cl_2) 1716, 1323, 1153, 1130, 1035 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.08 (6H, d, *J*=6.9 Hz), 2.91 (1H, sept., *J*=6.9 Hz), 4.29 (2H, s), 7.60—7.66 (2H, m), 7.83—7.85 (1H, m), 7.90—7.92 (1H, m), 7.97—7.99 (2H, m), 8.46 (1H, s). Found: C, 64.98; H, 5.82; S, 12.76%. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84; S, 11.60%.

3-Methyl-1-(2-naphthylsulfonyl)-2-butanone *t*-Butyldimethylsilyl Methyl Acetal (4n): IR (CH_2Cl_2) 1319, 1155, 1126, 1039

cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.15 (3H, s), 0.16 (3H, s), 0.87 (9H, s), 0.93 (3H, d, J=6.8 Hz), 0.97 (3H, d, J=6.8 Hz), 2.38—2.44 (1H, m), 3.09 (3H, s), 3.53 (2H, s), 7.59—7.67 (2H, m), 7.87—7.92 (2H, m), 7.96—7.99 (2H, m), 8.48 (1H, s). Found: C, 62.45; H, 8.04; S, 8.11%. Calcd for $C_{22}H_{34}O_4SSi$: C, 62.52; H, 8.11; S, 7.59%.

1-Phenyl-2-(*p*-tolylsulfonyl)-1-propanone (4o): IR (CH_2Cl_2) 1684, 1425, 1327, 1149, 1139 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.54 (3H, d, J=6.9 Hz), 2.41 (3H, s), 5.13 (1H, q, J=6.9 Hz), 7.24—7.30 (2H, m), 7.45—7.48 (2H, m), 7.58—7.61 (1H, m), 7.63 (2H, d, J=7.9 Hz), 7.96 (2H, d, J=7.9 Hz). HRMS Found: *m/z* 288.0835. Calcd for $C_{16}H_{16}O_3S$: M, 288.0820.

1-Phenyl-2-(*p*-tolylsulfonyl)-1-propanone *t*-Butyldimethylsilyl Methyl Acetal (4p): IR (CH_2Cl_2) 1315, 1298, 1151, 1134, 1082, 1047 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=−0.43 (3H, s), 0.11 (3H, s), 0.93 (9H, s), 1.23 (3H, d, J=7.1 Hz), 2.41 (3H, s), 2.99 (3H, s), 3.73 (1H, q, J=7.1 Hz), 7.25 (2H, d, J=8.2 Hz), 7.28—7.34 (3H, m), 7.60—7.62 (2H, m), 7.68 (2H, d, J=8.2 Hz). HRMS Found: *m/z* 403.1743. Calcd for $C_{23}H_{34}O_4SSi-OCH_3$: M, 403.1763.

Typical Procedure for the Sulfonylation of Olefinic Compounds by Using CBAN in CH_2Cl_2 (Method B). To a dichloromethane (30 ml) suspension of CBAN (9.4 g, 9.4 mmol) and K_2CO_3 (3.0 g, 22 mmol) was added a dichloromethane (30 ml) solution of 3,4-dihydro-2*H*-pyran (**3h**, 840 mg, 9.9 mmol) and then a dichloromethane (30 ml) suspension of sodium 2-naphthalenesulfinate (**1b**, 930 mg, 4.3 mmol) at 0 °C under an argon atmosphere. After the mixture was stirred overnight, pH 7 buffer solution was added to the reaction mixture, and the mixture was filtered through Celite. After being extracted with ethyl acetate, the extract was dried over Na_2SO_4. The crude product was purified by silica-gel column chromatography to afford the vinylsulfone **4s** (1.00 g, 86%).

Spectral data and physical properties of the new compounds are as follows.

5-(2-Naphthylsulfonyl)-3,4-dihydro-2*H*-pyran (4s): Mp 114—115 °C (ether); IR (KBr) 1624, 1298, 1227, 1149, 1011, 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.80—1.85 (2H, m), 2.18 (2H, t, J=6.3 Hz), 4.00 (2H, t, J=5.2 Hz), 7.58—6.45 (2H, m), 7.68 (1H, s), 7.77—7.79 (1H, m), 7.88—7.90 (1H, m), 7.93—7.97 (2H, m), 8.43 (1H, s). Found: C, 65.53; H, 5.15; S, 12.03%. Calcd for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14; S, 11.69%.

4-(2-Naphthylsulfonyl)-2,3-dihydrofuran (4t): IR (KBr) 1603, 1309, 1142, 1130, 1105, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.80 (2H, dt, J_d=1.6 Hz, J_t=9.8 Hz), 4.58 (2H, t, J=9.8 Hz), 7.27 (1H, t, J=1.6 Hz), 7.60—7.76 (2H, m), 7.83—7.84 (1H, m), 7.90—7.91 (1H, m), 7.96—7.97 (2H, m), 8.46 (1H, s). HRMS Found: *m/z* 260.0520. Calcd for $C_{14}H_{12}O_3S$: M, 260.0507.

3-(2-Naphthylsulfonyl)tetrahydrofuran-2-ol (4u): IR (KBr) 3360 (broad), 1302, 1146, 1124, 1022, 916 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.28—2.35 (1H, m), 2.40—2.46 (1H, m), 2.8—3.0 (1H, br), 3.80 (1H, ddd, J=1.7, 6.2, 8.9 Hz), 4.05 (2H, dd, J=5.6, 8.2 Hz), 5.85 (1H, d, J=1.7 Hz), 7.62—7.70 (2H, m), 7.85—7.87 (1H, m), 7.92—7.94 (1H, m), 7.98—8.02 (2H, m), 8.49 (1H, s). HRMS Found: *m/z* 278.0624. Calcd for $C_{14}H_{14}O_4S$: M, 278.0613.

2-Naphthyl 2-Phenyl-2-propenyl Sulfone (4v-1-Isomer): This compound was obtained as a mixture with 2-naphthyl 2-phenyl-1-propenyl sulfone at 8 : 1 ratio. IR (KBr) 1304, 1122, 704 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=4.33 (2H, s), 5.20 (1H, s), 5.55 (1H, s), 7.09—7.14 (3H, m), 7.22—7.24 (2H, m), 7.56—7.59 (1H, m), 7.61—7.65 (1H, m), 7.74—7.76 (1H, m), 7.84—7.88 (3H, m), 8.31 (1H, d, J=1.3 Hz). HRMS Found: *m/z* 308.0864. Calcd for $C_{19}H_{16}O_2S$: M, 308.0871.

2-Naphthyl 2-Phenyl-1-propenyl Sulfone (4v-2-Isomer): ^{1}H NMR ($CDCl_3$) δ=2.55 (3H, s), 6.66 (1H, s), 7.33—7.38 (5H, m), 7.59—7.65 (3H, m), 7.91—8.00 (3H, m), 8.55 (1H, s). HRMS Found: *m/z* 308.0860. Calcd for $C_{19}H_{16}O_2S$: M, 308.0871.

1-(2-Naphthylsulfonyl)-2-phenyl-2-propanol (4w): IR (CH_2Cl_2) 3508 (broad), 1309, 1273, 1155, 1124, 1115 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.68 (3H, s), 3.67 (1H, d, J=14.8 Hz), 3.80 (1H, d, J=14.8 Hz), 4.66 (1H, br), 6.93—6.94 (1H, m), 7.01—7.04 (2H, m), 7.23—7.25 (2H, m), 7.55—7.64 (3H, m), 7.78—7.79 (1H, m), 7.82—7.85 (2H, m), 8.03 (1H, s). HRMS Found: *m/z* 326.0981. Calcd for $C_{19}H_{18}O_3S$: M, 326.0977.

Butyl (*E*)-2-(2-Naphthylsulfonyl)vinyl Ether (4x): IR (CH_2Cl_2) 1628, 1606, 1309, 1219, 1146, 1124, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, t, J=7.4 Hz), 1.35—1.39 (2H, m), 1.63—1.68 (2H, m), 3.82 (2H, t, J=6.5 Hz), 5.72 (1H, d, J=12.2 Hz), 7.64 (1H, d, J=12.2 Hz), 7.57—7.64 (2H, m), 7.79—7.82 (1H, m), 7.88—7.89 (1H, m), 7.94—7.96 (2H, m), 8.45 (1H, s). HRMS Found: *m/z* 290.0952. Calcd for $C_{16}H_{18}O_3S$: M, 290.0977.

Butyl (*Z*)-2-(2-Naphthylsulfonyl)vinyl Ether (4x): IR (CH_2Cl_2) 1624, 1309, 1143, 1126, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.72 (3H, t, J=7.4 Hz), 1.10—1.14 (2H, m), 1.44—1.50 (2H, m), 3.91 (2H, t, J=6.4 Hz), 5.59 (1H, d, J=6.4 Hz), 6.48 (1H, d, J=6.4 Hz), 7.56—7.63 (2H, m), 7.88—7.91 (1H, m), 7.93—7.96 (3H, m), 8.54 (1H, s). HRMS Found: *m/z* 290.1007. Calcd for $C_{16}H_{18}O_3S$: M, 290.0977.

Typical Procedure for the Sulfonylation of Olefinic Compounds by Using CBAN in a Mixed Solvent of CH_2Cl_2 and MeOH (Method C). To a dichloromethane (2 ml) suspension of CBAN (324.2 mg, 0.325 mmol) and K_2CO_3 (107.7 mg, 0.779 mmol) was added a methanol (2 ml) solution of sodium 2-naphthalenesulfinate (**1b**, 30.4 mg, 0.142 mmol) and butyl vinyl ether (**3k**, 33.9 mg, 0.338 mmol) at 0 °C under an argon atmosphere. After the mixture was stirred overnight, pH 7 buffer solution was added to the reaction mixture, and the mixture was filtered through Celite. After being extracted with ethyl acetate, the extract was dried over Na_2SO_4. The crude product was purified by silica-gel column chromatography to afford the product **4y** (38.4 mg, 84%).

Spectral data and physical properties of the new compounds are as follows.

2-Buthoxy-2-methoxyethyl 2-Naphthyl Sulfone (4y): IR (CH_2Cl_2) 1313, 1149, 1114, 1072 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.76 (3H, t, J=7.4 Hz), 1.09—1.16 (2H, m), 1.27—1.31 (2H, m), 3.19 (3H, s), 3.32 (1H, dt, J_t=6.6 Hz, J_d=9.1 Hz), 3.43 (1H, dt, J_t=6.8 Hz, J_d=9.1 Hz), 3.50 (2H, d, J=5.3 Hz), 4.95 (1H, d, J=5.3 Hz), 7.60—7.67 (2H, m), 7.84—7.86 (1H, m), 7.91—7.92 (1H, m), 7.97—8.00 (2H, m), 8.46 (1H, s). HRMS Found: *m/z* 322.1224. Calcd for $C_{17}H_{22}O_4S$: M, 322.1239.

2-Ethylthio-2-methoxyethyl 2-Naphthyl Sulfone (4z): IR (CH_2Cl_2) 1311, 1141, 1126, 1107, 1072, 976 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.18 (3H, t, J=7.5 Hz), 2.46—2.53 (2H, m), 3.20 (3H, s), 3.57 (1H, dd, J=2.4, 14.6 Hz), 3.82 (1H, dd, J=10.0, 14.6 Hz), 4.91 (1H, dd, J=2.4, 10.0 Hz), 7.59—7.66 (2H, m), 7.84—7.86 (1H, m), 7.90—7.92 (1H, m), 7.96—7.98 (2H, m), 8.46 (1H, s). HRMS Found: *m/z* 310.0702. Calcd for $C_{15}H_{18}O_3S_2$: M, 310.0697.

Preparation of Cyclic Vinyl Alcohol. 1-(1-Phenylvinyl)cyclobutanol (**9a**), 1-(1-methylvinyl)cyclobutanol (**9b**),[24] 1-(1-phenylvinyl)cyclopentanol (**9c**), and 1-(1-methylvinyl)cyclopentanol (**9d**)[25] were prepared from the reaction between 1-phenylvinylmagnesium bromide or 1-methylvinylmagnesium bromide and cyclobutanone or cyclopentanone.

1-(1-Phenylvinyl)cyclobutanol (9a): IR (neat) 3400 (broad), 1495, 1249, 906, 777, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.60—1.64 (1H, m), 1.94—2.01 (2H, m), 2.20—2.26 (2H, m), 2.44—2.49 (2H,

m), 5.34 (1H, s), 5.36 (1H, s), 7.27—7.33 (3H, m), 7.46—7.48 (2H, m). HRMS Found: *m/z* 174.1048. Calcd for $C_{12}H_{14}O$: M, 174.1045.

1-(1-Phenylvinyl)cyclopentanol (9c): IR (neat) 3400 (broad), 1493, 1441, 1194, 997, 912, 775, 702 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50—1.60 (1H, broad), 1.66—1.69 (2H, m), 1.75—1.81 (2H, m), 1.83—1.90 (4H, m), 5.06 (1H, d, J=1.1 Hz), 5.42 (1H, d, J=1.1 Hz), 7.27—7.32 (3H, m), 7.36—7.38 (2H, m). HRMS Found: *m/z* 188.1192. Calcd for $C_{13}H_{16}O$: M, 188.1201.

Typical Procedure of Tandem Sulfonylation–Pinacol-Type Rearrangement Reaction. To an acetonitrile (1.0 ml) solution of CAN (172.8 mg, 0.315 mmol) was added 1-(1-phenylvinyl)cyclobutanol (**9a**, 51.9 mg, 0.297 mmol) in acetonitrile (1.0 ml) at 0 °C. Subsequently, an acetonitrile (1.0 ml) suspension of sodium 2-naphthalenesulfinate (**1b**, 32.0 mg, 0.149 mmol) was added to the solution. After stirring at 0 °C for 2 h, pH 7 buffer solution was added to the reaction mixture, and the resulting precipitates were filtered off through Celite. The organic phase was separated and the aqueous phase was extracted with ethyl acetate. The extract was dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified with preparative TLC to afford the product (**11a**, 37.8 mg, 70%).

Spectral data and physical properties of the new compounds are as follows.

2-(2-Naphthylsulfonylmethyl)-2-phenylcyclopentanone (11a): Mp 122—123 °C (hexane–ethyl acetate); IR (KBr) 1734, 1317, 1151, 1122, 1074, 764 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.72—1.82 (1H, m), 2.02—2.10 (1H, m), 2.27—2.41 (2H, m), 2.63—2.69 (1H, m), 3.09—3.13 (1H, m), 3.66 (1H, d, J=14.7 Hz), 3.84 (1H, d, J=14.7 Hz), 7.00—7.03 (1H, m), 7.09—7.12 (2H, m), 7.24—7.27 (2H, m), 7.55—7.63 (2H, m), 7.66—7.69 (1H, m), 7.84—7.86 (3H, m), 8.16 (1H, s). Found: C, 72.41; H, 5.63; S, 8.76%. Calcd for $C_{22}H_{20}O_3S$: C, 72.50; H, 5.53; S, 8.80%.

2-Methyl-2-(2-naphthylsulfonylmethyl)cyclopentanone (11b): IR (CH_2Cl_2) 1738, 1309, 1149, 1128, 762, 661 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.15 (3H, s), 1.87—1.97 (1H, m), 2.06—2.14 (2H, m), 2.32—2.41 (2H, m), 2.53—2.59 (1H, m), 3.37 (1H, d, J=14.4 Hz), 3.41 (1H, d, J=14.4 Hz), 7.59—7.67 (2H, m), 7.83—7.85 (1H, m), 7.90—7.91 (1H, m), 7.96—7.99 (2H, m), 8.44 (1H, s). HRMS Found: *m/z* 302.0981. Calcd for $C_{17}H_{18}O_3S$: M, 302.0977.

2-(2-Naphthylsulfonylmethyl)-2-phenylcyclohexanone (11c): Mp 108—109 °C (hexane–ethyl acetate); IR (KBr) 1705, 1311, 1147, 1126 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.78—1.85 (3H, m), 1.93—1.99 (1H, m), 2.20—2.34 (3H, m), 3.43—3.47 (1H, m), 3.75 (1H, d, J=15.0 Hz), 3.80 (1H, d, J=15.0 Hz), 7.01—7.03 (1H, m), 7.12—7.13 (4H, m), 7.55—7.66 (3H, m), 7.81—7.84 (2H, m), 8.09 (1H, s). Found: C, 73.01; H, 5.90; S, 8.50%. Calcd for $C_{23}H_{22}O_3S$: C, 72.99; H, 5.86; S, 8.47%.

2-Methyl-2-(2-naphthylsulfonylmethyl)cyclohexanone (11d): IR (CH_2Cl_2) 1707, 1309, 1147, 1128, 1070 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (3H, s), 1.79—1.83 (3H, m), 1.93—1.99 (1H, m), 2.21—2.23 (2H, m), 2.40—2.45 (1H, m), 2.48—2.55 (1H, s), 3.40 (1H, d, J=14.4 Hz), 3.62 (1H, d, J=14.4 Hz), 7.59—7.66 (2H, m), 7.88—7.92 (2H, m), 7.98—8.00 (2H, m), 8.46 (1H, s). HRMS Found: *m/z* 316.1120. Calcd for $C_{18}H_{20}O_3S$: M, 316.1133.

Typical Procedure of Phosphinylation of Olefinic Compounds. To a DMF (2.0 ml) suspension of $Mn(pic)_3$ (181.8 mg, 0.431 mmol) was added a DMF (1.0 ml) solution of diphenyl phosphine oxide (**12**, 41.3 mg, 0.204 mmol) and 2-(*t*-butyldimethylsiloxy)-3-methyl-1-butene (**3e**, 47.2 mg, 0.236 mmol) at 0 °C. After the mixture was stirred for 3 h, the reaction was quenched with pH 7 buffer solution, and the resulting precipitates were filtered off through Celite. Organic materials were extracted with ethyl acetate and the combined extracts were dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by preparative TLC to afford 3-methyl-1-diphenylphosphinyl-2-butanone (**14b**, 44.7 mg, 77%).

Spectral data and physical properties of the new compounds are as follows.

2-Diphenylphosphinyl-1-phenylethanone (14a):[26] IR (KBr) 1682, 1441, 1296, 1182, 744, 528, 501 cm^{-1}; ^1H NMR ($CDCl_3$) δ=4.11 (2H, d, J=15.3 Hz), 7.35—7.38 (2H, m), 7.39—7.43 (4H, m), 7.46—7.50 (3H, m), 7.75—7.79 (4H, m), 7.93—7.95 (2H, m).

1-Diphenylphosphinyl-3-methyl-2-butanone (14b): IR (CH_2Cl_2) 1707, 1439, 1201, 1120, 526 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.98 (6H, d, J=6.9 Hz), 2.82 (1H, sept., J=6.9 Hz), 3.63 (2H, d, J=15.1 Hz), 7.42—7.46 (4H, m), 7.48—7.54 (2H, m), 7.71—7.75 (4H, m). HRMS Found: *m/z* 286.1106. Calcd for $C_{17}H_{19}O_2P$: M, 286.1123.

[2,2-Bis(methylthio)vinyl]diphenylphosphine Oxide (14c): Mp 162—163 °C (ether); IR (KBr) 1510, 1437, 1180, 1118, 895 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.28 (3H, s), 2.37 (3H, s), 5.86 (1H, d, J=16.4 Hz), 7.40—7.53 (4H, m), 7.63—7.66 (2H, m), 7.73—7.77 (4H, m). Found: C, 59.79; H, 5.32; S, 19.16%. Calcd for $C_{16}H_{17}OS_2P$: C, 59.98; H, 5.35; S, 20.01%.

5-Diphenylphosphinyl-3,4-dihydro-2*H*-pyran (14d): IR (CH_2Cl_2) 1620, 1439, 1280, 1255, 1228, 1161, 1119 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.88—1.92 (2H, m), 2.14 (1H, t, J=5.7 Hz), 2.16 (1H, t, J=5.9 Hz), 4.07 (2H, t, J=5.2 Hz), 6.64 (1H, d, J=10.5 Hz), 7.42—7.46 (4H, m), 7.48—7.52 (2H, m), 7.66—7.70 (4H, m). HRMS Found: *m/z* 284.0984. Calcd for $C_{17}H_{17}O_2P$: M, 284.0966.

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