Asymmetric Radical Reaction in the Coordination Sphere. IV.[1] Ruthenium(II)-Catalyzed Asymmetric Addition of Sulfonyl Chloride to 1-Phenylpropene

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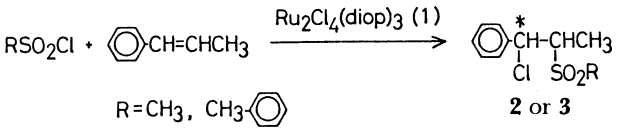
Synopsis. The asymmetric addition of methane- and *p*-toluenesulfonyl chloride to 1-phenylpropene catalyzed by $Ru_2Cl_4[(-)\text{-diop}]_3$ affords optically active 1 : 1 adducts, (+)-(1*R*,2*RS*)-1-chloro-2-methylsulfonyl-1-phenylpropane (**2**) and (+)-(1*R*,2*RS*)-1-chloro-1-phenyl-2-tosylpropane (**3**), with about 13—19%ee. Similarly, (−)-(1*S*,2*RS*)-**2** and (−)-(1*S*,2*RS*)-**3** were obtained when $Ru_2Cl_4[(+)\text{-diop}]_3$ was employed. A enantioface differentiation is considered to occur in the chlorine atom transferring step from the ruthenium(III) species to the carbon radical in the coordination sphere.

Polyhaloalkanes and sulfonyl chlorides reacted with olefins in the presence of transition metal complexes such as $RuCl_2(PPh_3)_3$ to give 1 : 1 adducts in high yields.[2,3] It is considered that these reactions proceed by a radical redox mechanism and the intermediate radicals are restricted in the coordination sphere of the metal complexes. We assume that the resulting radical complexes closely resemble carbene-metal complexes. The asymmetric addition of alkyl diazoacetates to olefins catalyzed by copper-chiral ligands complexes is known to form optically active cyclopropanes and in which reaction involves a carbenoid intermediate.[4] An asymmetric addition of bromotrichloromethane to styrene catalyzed by a rhodium complex with a chiral ligand has also been reported.[5] Thus, an asymmetric induction is expected in the reaction of sulfonyl chlorides with olefins which proceeds by a radical intermediate in the coordination sphere. We recently found that alkane- and arenesulfonyl chlorides,[6] trichloromethanesulfonyl chloride, and carbon tetrachloride[1] reacted with olefins in the presence of a catalytic amount of ruthenium(II) complex with chiral ligand, $Ru_2Cl_4[(+)\text{-diop}]_3$ ((+)-**1**) or $Ru_2Cl_4[(-)\text{-diop}]_3$ ((−)-**1**), to give optically active adducts with about 10—40% ee. However, we have only observed an asymmetric induction to a benzylic carbon bonding to a chlorine atom since terminal olefins, such as styrene, were used in these addition reactions. An asymmetric induction to the *β*-position of olefins, bonding to the sulfonyl group, may also be possible by using internal olefins. Here, we report on the asymmetric addition of methane- and *p*-toluenesulfonyl chloride to *trans*- and *cis*-1-phenylpropene catalyzed by the ruthenium(II) complex with chiral ligand **1**.

The addition of methanesulfonyl chloride with 1-phenylpropene was carried out in the presence of the ruthenium(II)-DIOP complex **1** as a catalyst. When $Ru_2Cl_4[(-)\text{-diop}]_3$ ((−)-**1**) was used as a catalyst, the reaction of methanesulfonyl chloride with *trans*-1-phenylpropene at 100 °C for 24 h in a degassed sealed tube gave a 1 : 1 adduct (**2**) in 47% yield. Adduct **2** showed a specific rotation $[\alpha]_D$ +4.7° (*c* 5.3, $CHCl_3$). In



a similar manner, the reaction of methanesulfonyl chloride with *trans*-1-phenylpropene catalyzed by $Ru_2Cl_4[(+)\text{-diop}]_3$ ((+)-**1**) was carried out; 1 : 1 adduct (**2**) was formed in 47% yield and showed $[\alpha]_D$ −4.9° (*c* 6.0, $CHCl_3$). Methanesulfonyl chloride reacted with *cis*-1-phenylpropene by using (−)-**1** as a catalyst to give adduct **2**, which showed $[\alpha]_D$ +4.2° (*c* 11, $CHCl_3$). Adduct **2** showed the same positive optical rotation as product **2**, which formed in the reaction of *trans*-1-phenylpropene.

In order to examine an asymmetric induction to a *β*-carbon of 1-phenylpropene bonding to the methanesulfonyl group, the adduct (+)-**2** ($[\alpha]_D$ +4.7° (*c* 5.3, $CHCl_3$)) was reduced by lithium aluminum hydride to afford 2-methylsulfonyl-1-phenylpropane, which was an optically inactive compound.[7] This means that an asymmetric induction did not occur in the *β*-position. In other words, the methanesulfonyl radical, generated by an interaction of the ruthenium(II)-DIOP complex **1**, was not interacted with effectively by the chiral ligands in the addition step to the olefin.

The reaction of *p*-toluenesulfonyl chloride with *trans*- and *cis*-1-phenylpropene was also carried out with (+)-**1** or (−)-**1** as a chiral catalyst, in a similar way, to give 1 : 1 adducts (**3**). The results are summarized in Table 1.

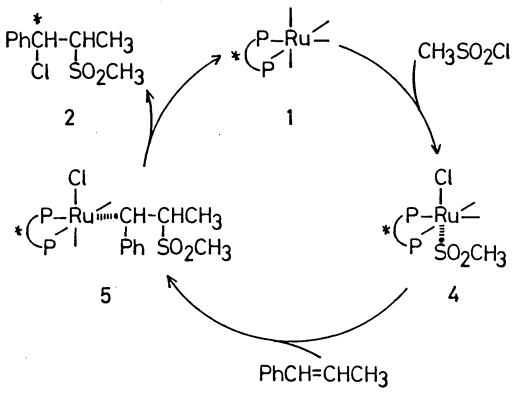
The enantiomeric excess and absolute configuration of products **2** and **3** in the present reactions were estimated by making comparison with optically pure compounds, which were prepared by a similar procedure to that mentioned in our previous report.[5] Starting from commercially available, optically pure (+)-(*S*)- and (−)-(*R*)-mandelic acid, (+)-(*R*)-**2** or (+)-(*R*)-**3** and (−)-(*S*)-**2** or (−)-(*S*)-**3** were synthesized with retention, respectively.

The ruthenium(II)-catalyzed asymmetric addition can be explained by the following process involving a radical redox mechanism in the coordination sphere of the ruthenium(II) complexes[8] (Scheme 1). Methanesulfonyl chloride is activated by the ruthenium(II) complex **1** to give a methanesulfonyl radical confined in the coordination sphere of the ruthenium(III) complex (**4**). Then, the confined sulfonyl radical intermediate **4** reacts with 1-phenylpropene without any effect of the chiral ligands to form a 1-phenyl-2-(methylsulfonyl)propyl radical confined in the ruthenium(III) species (**5**). The carbon radical in **5** abstracts the chlo-

Table 1. Reaction of Sulfonyl Chloride with 1-Phenylpropene

R	$PhCH=CHCH_3$	DIOP	Product	Chemical yield/%	$[\alpha]_D$/° (*c*, in $CHCl_3$)	Optical yield/%ee[a)]	Absolute configuration
CH_3	Trans	(−)	**2**	47	+4.7 (5.3)	15 (12)	R
CH_3	Trans	(+)	**2**	47	−4.9 (6.0)	14 (12)	S
CH_3	Cis	(−)	**2**	29	+4.2 (11)	14 (11)	R
CH_3	Cis	(+)	**2**	30	−4.5 (11)	13 (11)	S
p-$CH_3C_6H_4$	Trans	(−)	**3**	91	+9.0 (13)	19	R
p-$CH_3C_6H_4$	Trans	(+)	**3**	85	−8.0 (10)	16	S
p-$CH_3C_6H_4$	Cis	(−)	**3**	89	+7.8 (11)	16	R
p-$CH_3C_6H_4$	Trans	(+)	**3**	83	−9.3 (11)	19	S

a) Optical yields were estimated by optically pure compounds and ^1H NMR with E(hfc)$_3$ in parentheses.



Scheme 1.

rine atom from the ruthenium(III) species containing chiral ligands to give adduct **2** and regenerates the ruthenium(II) complex, **1**. Since 1-phenylpropene is not coordinated as strongly as the sulfonyl radical coordinated to the ruthenium(III) complex (such as **4**), an asymmetric induction does not occur in the intermolecular addition of **4** to the olefin. However, an asymmetric induction occurs in the chlorine atom abstracting step by a carbon radical effected by the chiral ligand, since the carbon radical is coordinated with the ruthenium complex as **5**. The same products were formed in both reactions of *trans*- and *cis*-1-phenylpropene. This means that the sulfonyl radical, generated by a homolytic cleavage of sulfonyl chloride with the ruthenium complex, added to the olefin and a free rotation took place around the carbon-carbon bond in intermediate **5**.

Experimental

Measurement. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer with samples as neat liquids. The proton magnetic resonance spectra were recorded at 60 MHz by using a JNM-PMX 60 SI spectrometer with Me_4Si as an internal standard in $CDCl_3$. Optical rotations were measured with a JASCO DIP-140 polarimeter. The gel-permeation liquid chromatography was performed by using a JAI LC-08 liquid chromatograph with a JAIGEL-1H column (20ϕ×600 mm×2, chloroform as an eluent). Mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with JEOL JMX 5000 Mass Data System at ionizing voltages of 20—70 eV.

Materials. The ruthenium(II) complexes, such as Ru_2Cl_4-[(−)-diop]$_3$ ((−)-**1**) and Ru_2Cl_4[(+)-diop]$_3$ ((+)-**1**), were prepared by methods described in the literature.[9] Methanesulfonyl chloride, *trans*-1-phenylpropene (Wako Chemicals), and *cis*-1-phenylpropene (ICN Pharmaceuticals) were purified by distillation under nitrogen prior to use. *p*-Toluenesulfonyl chloride (Nacalai Tesque) was purified by recrystallization from hexane prior to use.

General Procedure for the Reaction of Sulfonyl Chloride with Olefin. A solution containing 1.0 mmol of sulfonyl chloride, 1.5 mmol of 1-phenylpropene, and 0.01mmol of **1** in 2.0 cm^3 of benzene was degassed and heated in a sealed tube at 100 °C for 24 h. The reaction mixture was chromatographed on Florisil (4:1 (v/v) hexane-ethyl acetate as an eluent) to remove any ruthenium complexes. Purification by gel-permeation liquid chromatography using chloroform as an eluent gave 1:1 adducts (**2** and **3**). The products were identified by their infrared absorption spectra, proton magnetic resonance spectra, mass spectra, and high-resolution mass spectra. The physical and spectral data of the compounds (**2** and **3**) are as follows.

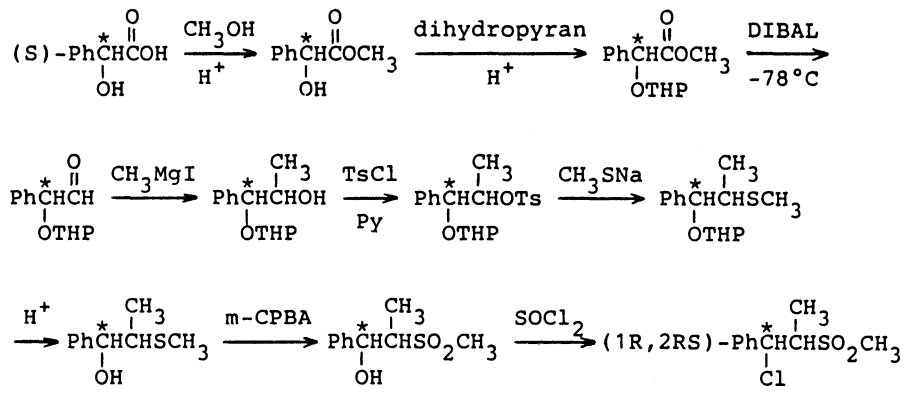
(+)-(1*R*,2*RS*)-1-Chloro-2-methylsulfonyl-1-phenylpropane (2): $[\alpha]_D$ +4.8° (*c* 7.7, $CHCl_3$); IR (neat) 1300, 1145, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.45 (3H, d, *J*=7.0 Hz), 2.60 (3H, s), 3.00—3.70 (1H, m), 5.51 (1H, d, *J*=3.0 Hz), and 7.23 (5H, s); MS *m/z* (rel intensity) 232 (M^+; 3), 197 (9), 196 (18), 156 (13), 155 (100); HRMS, Found: *m/z* 232.0343. Calcd for $C_{10}H_{13}O_2SCl$: M, 232.0325.

(−)-(1*S*,2*RS*)-1-Chloro-2-methylsulfonyl-1-phenylpropane (2): $[\alpha]_D$ −4.9° (*c* 6.0, $CHCl_3$); IR (neat) 1300, 1145, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.49 (3H, d, *J*=7.0 Hz), 2.70 (3H, s), 3.13—3.90 (1H, m), 5.63 (1H, d, *J*=3.0 Hz), and 7.31 (5H, s); MS *m/z* (rel intensity) 232 (M^+; 2), 197 (11), 196 (49), 156 (9), 155 (100); HRMS, Found: *m/z* 232.0342. Calcd for $C_{10}H_{13}O_2SCl$: M, 232.0325.

(+)-(1*R*,2*RS*)-1-Chloro-1-phenyl-2-tosylpropane (3): $[\alpha]_D$ +9.0° (*c* 13, $CHCl_3$); IR (neat) 1320, 1300, and 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (3H, d, *J*=7.2 Hz), 2.37 (3H, s), 3.39 and 3.45 (1H, qd, *J*=7.2 and 3.0 Hz), 5.60 (1H, d, *J*=3.0 Hz), 7.20 (5H, s), and 7.21 and 7.63 (4H, ABq, *J*=8.4 Hz); MS *m/z* (rel intensity) 308 (M^+; 1), 273 (5), 272 (11), 209 (24), 157 (100), and 155 (100); HRMS, Found: *m/z* 308.0631. Calcd for $C_{16}H_{17}O_2SCl$: M, 308.0638.

(−)-(1*S*,2*RS*)-1-Chloro-1-phenyl-2-tosylpropane (3): $[\alpha]_D$ −8.1° (*c* 7.3, $CHCl_3$); IR (neat) 1320, 1305, and 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.39 (3H, d, *J*=7.2 Hz), 2.33 (3H, s), 3.40 and 3.45 (1H, qd, *J*=7.2 and 3.0 Hz), 5.58 (1H, d, *J*=3.0 Hz), 7.13 (5H, s), and 7.14 and 7.60 (4H, ABq, *J*=8.4 Hz); MS *m/z* (rel intensity) 308 (M^+; 1). 273 (13), 272 (28), 209 (33), 157 (100), and 155 (100); HRMS, Found: *m/z* 308.0589. Calcd for $C_{16}H_{17}O_2SCl$: M, 308.0638.

Preparation of Optically Pure 1-Chloro-2-methylsulfonyl-1-phenylpropane and 1-Chloro-1-phenyl-2-tosylpropane. Starting from commercially available optically pure (+)-(*S*)-mandelic acid, (+)-(1*R*,2*RS*)-**2**, and (+)-(1*R*,2*RS*)-**3** were pre-



Scheme 2.

pared by the similar procedures described in our previous paper,[6] respectively, as shown in the following scheme. Similarly, (−)-(1*S*,2*RS*)-**2** and (−)-(1*S*,2*RS*)-**3** were prepared from (−)-(*R*)-mandelic acid.

The physical and spectral data of the authentic opically pure compounds **2** and **3** are as follows.

(+)-(1*R*,2*RS*)-1-Chloro-2-methylsulfonyl-1-phenylpropane (2): $[\alpha]_D$ +31° (*c* 1.1, $CHCl_3$); IR (neat) 1300, 1140, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.56 (3H, d, *J*=6.6 Hz), 2.80 (3H, s), 3.10—3.50 (1H, m), 5.44 (0.5H, d, *J*=6.6 Hz), 5.70 (0.5H, d, *J*=3.0 Hz), and 7.41 (5H, s); MS *m/z* (rel intensity) 232 (M^+; 3), 197 (9), 196 (18), and 155 (100); HRMS, Found: *m/z* 232.0322. Calcd for $C_{10}H_{13}O_2SCl$: M, 232.0325.

(−)-(1*S*,2*RS*)-1-Chloro-2-methylsulfonyl-1-phenylpropane (2): $[\alpha]_D$ −34° (*c* 1.8, $CHCl_3$); IR (neat) 1300, 1140, and 1130 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.55 (3H, d, *J*=6.8 Hz), 3.09 (3H, s), 3.30—3.60 (1H, m), 5.43 (0.5H, d, *J*=6.6 Hz), 5.69 (0.5H, d, *J*=3.0 Hz), and 7.37 (5H, s); MS *m/z* (rel intensity) 232 (M^+; 1), 197 (2), 196 (2), 155 (34), and 154 (100); HRMS, Found: *m/z* 232.0318. Calcd for $C_{10}H_{13}O_2SCl$: M, 232.0325.

(+)-(1*R*,2*RS*)-1-Chloro-1-phenyl-2-tosylpropane (3): $[\alpha]_D$ +48° (*c* 4.5, $CHCl_3$); IR (neat) 1320, 1300, and 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.40 (3H, d, *J*=7.2 Hz), 2.41 (3H, s), 3.41 and 3.46 (1H, qd, *J*=7.2 and 3.0 Hz), 5.63 (1H, d, *J*=3.0 Hz), 7.20 (5H, s), and 7.22 and 7.68 (4H, ABq, *J*=8.4 Hz); MS *m/z* (rel intensity) 308 (M^+; 1), 272 (5), 271 (15), 233 (14), 209 (29), 158 (15), and 157 (100); HRMS, Found: *m/z* 308.0658. Calcd for $C_{16}H_{17}O_2SCl$: M, 308.0638.

(−)-(1*S*,2*RS*)-1-Chloro-1-phenyl-2-tosylpropane (3): $[\alpha]_D$ −50° (*c* 1.4, $CHCl_3$); IR (neat) 1320, 1300, and 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.25 (1.5H, d, *J*=7.2 Hz), 1.42 (1.5H, d, *J*=7.2 Hz), 2.44 (3H, s), 3.30—3.90 (1H, m), 5.50—7.70 (1H, m), 7.36 (5H, s), and 7.34 and 7.74 (4H, ABq, *J*=8.4 Hz); MS *m/z* (rel intensity) 308 (M^+; 1), 273 (1), 272 (4), 209 (9), 158 (14), and 157 (100); HRMS, Found: *m/z* 308.0641. Calcd for $C_{16}H_{17}O_2SCl$: M, 308.0638.

Reduction of (−)-(1*S*,2*RS*)-2 by Lithium Aluminum Hydride. To a stirred suspension of 210 mg (5.5 mmol) of lithium aluminum hydride in 5 cm^3 of dry tetrahydrofuran was added dropwise 250 mg (1.1 mmol) of (−)-(1*S*,2*RS*)-**2** in 10 cm^3 of dry tetrahydrofuran at room temperature under nitrogen. After the addition was completed, the mixture was refluxed for an additional 12 h, then cooled in an ice bath, and treated with water and then with 5% sulfuric acid. Ether was added to the mixture and the ethereal layer was separated and dried over magnesium sulfate. The solvent was evaporated to give 132 mg (61%) of 2-methylsulfonyl-1-phenylpropane; $[\alpha]_D$ 0° (*c* 6.6, $CHCl_3$); IR (neat) 1300 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.31 (3H, d, *J*=6.0 Hz), 2.76 (3H, s), 2.90—3.60 (3H, m), and 7.22 (5H, s); MS *m/z* 198 (M^+).

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7) The reduction of (+)-**2** with lithium aluminum deuteride was also carried out and quenched with deuterium oxide (99.8 atom% D) to give 2-methylsulfonyl-1-phenylpropane-1-*d*. The α-hydrogen of sulfonyl group in (+)-**2** was not found to be abstracted by lithium aluminum deuteride under the conditions since the α-hydrogen was not converted by deuterium. Thus, we confirmed that there was no racemization at C-2 during the reduction.

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