Asymmetric Radical Reaction in the Coordination Sphere. 2. Asymmetric Addition of Alkane- and Arenesulfonyl Chlorides to Olefins Catalyzed by a Ruthenium(II)-Phosphine Complex with Chiral Ligands[1]

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The addition of arenesulfonyl chlorides to styrene in the presence of a catalytic amount of a ruthenium(II) complex with chiral phosphine ligands, $Ru_2Cl_4[(-)\text{-DIOP}]_3$ or $Ru_2Cl_4[(+)\text{-DIOP}]_3$, proceeds under mild conditions to give optically active 1:1 adducts, 2-chloro-2-phenylethyl aryl sulfones **3**, with 20–40% enantiomeric excess. When a chiral ligand of the ruthenium(II) complex (-)-DIOP or (+)-DIOP was used, *R*-(+)-adduct (+)-**3** or *S*-(-)-adduct (-)-**3** was obtained, respectively. A reaction mechanism involving radical redox chain mechanism was proposed, and the asymmetric induction was attributed to complexing of a sulfonyl moiety and olefin with the ruthenium species containing chiral ligands.

The organometallic compounds have played a major role in organic synthesis both in academic laboratories and industry since the discovery of Grignard reagents at the turn of the century. Today it is difficult to accomplish an efficient and selective multistep synthesis without using organometallics.[2] The activation of organohalogen compounds by transition-metal complexes is one of the most important elementary processes among a number of catalytic processes of those complexes.[3]

Recently, we reported that the reaction of alkane- and arenesulfonyl chloride with olefins catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) under mild conditions affords 1:1 adducts.[4] These reactions are considered to proceed by a radical redox transfer chain mechanism and were shown to have definite advantages (e.g., high yields of 1:1 adducts, unique selectivities, simplicity of the system, etc.) compared to usual free radical addition reactions.[5] The sulfonyl moiety formed by interaction with the ruthenium(II) complex and the carbon fragment formed by the addition of the sulfonyl moiety to olefins are considered to be complexed with the ruthenium species.

Meanwhile, extensive studies of asymmetric induction reactions such as hydrogenation, hydrosilylation, and hydroformylation catalyzed by transition-metal complexes with a chiral ligand have been reported.[6] Nozaki and Noyori also reported asymmetric additions of alkyl diazoacetates with olefins catalyzed by a copper complex with a chiral ligand which give optically active cyclopropanes.[7]

Table I. Reaction of *p*-Toluenesulfonyl Chloride with Styrene Catalyzed by Ruthenium(II) Chiral Phosphine Complex

catal.[a]	temp, °C	reacn time, h	chem yield, %	$[\alpha]_D$, deg (*c*, $CHCl_3$)
(-)-**1a**	60	6	45	+25 (2.7)
(+)-**1a**	60	6	40	-20 (6.5)
(-)-**1a**[b]	60	6	24	+22 (2.4)
(-)-**1a**	60	24	96	+23 (3.8)
(-)-**1a**	80	6	100	+19 (3.5)
(-)-**1b**	60	6	78	+1.4 (5.8)
(+)-**1b**	60	6	83	-1.6 (5.3)
(-)-**1c**	60	6	0	

[a] (-)-**1a**, $Ru_2Cl_4[(-)\text{-DIOP}]_3$; (+)-**1a**, $Ru_2Cl_4[(+)\text{-DIOP}]_3$; (-)-**1b**, $Ru_2Cl_4[(-)\text{-BINAP}]_3(NEt_3)$; (+)-**1b**; $Ru_2Cl_4[(+)\text{-BINAP}]_3(NEt_3)$; (-)-**1c**; $Ru_2Cl_2[(-)\text{-BPPM}]_3(NEt_3)$. 1 mol% of **1** was used. [b] 0.5 mol% of (-)-**1a** was used.

The reaction involves a carbenoid intermediate that differentiates the enantioface of the olefin in the addition step by the effect of the chiral ligand. These reports prompt us to apply the asymmetric addition of sulfonyl chlorides to olefins by employing a chiral phosphine ligand on the ruthenium complex with the expectation that species in the coordination sphere may also be affected by the chiral ligand resulting in asymmetric induction. We studied the reactions of alkane- and arenesulfonyl chlorides with styrenes catalyzed by a ruthenium(II) complex with chiral ligands and the results are described herein (eq 1).

$$RSO_2Cl + R'C_6H_4CH{=}CH_2 \xrightarrow{Ru^{II}L^*} R'C_6H_4\overset{*}{C}H(Cl)CH_2SO_2R \quad (1)$$

$$R = CH_3 \text{ or aryl}$$

Results and Discussion

The reactions of arenesulfonyl chlorides with styrene were carried out in benzene, in the presence of a catalytic amount of a ruthenium(II) chiral phosphine complex in degassed sealed tubes. When $Ru_2Cl_4[(-)\text{-DIOP}]_3$ ((-)-**1a**) (DIOP = 2,3-(isopropylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane[8] was used as a catalyst, the reaction of *p*-toluenesulfonyl chloride with styrene at 60 °C for 6 h gave 1:1 adduct **3a** in 45% yield. The adduct **3a** showed a specific rotation $[\alpha]_D$ +25° (*c* 2.7, chloroform).

(1) For Part 1, see: Kameyama,M.; Kamigata, N.; Kobayashi, M. *Chem. Lett.* **1986**, 527.

(2) (a) Alper, H. *Transition Metal Organometallics in Organic Synthesis*; Academic: New York, 1976. (b) Tsuji, J. *Organic Synthesis with Palladium Compounds*; Springer-Verlag: Berlin, 1980. (c) Negishi, E. *Organometallics in Organic Synthesis*; Wiley: New York, 1980. (d) Davies, S. F. *Organotransition Metal Chemistry Applications to Organic Synthesis*; Pergamon: Oxford, 1982.

(3) (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978. (b) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(4) (a) Kamigata, N.; Sawada, H.; Kobayashi, M. *J. Org. Chem.* **1983**, *48*, 3793. (b) Kamigata, N.; Sawada, H.; Suzuki, N.; Kobayashi, M. *Phosphorus Sulfur* **1984**, *19*, 199. (d) Kamigata, N.; Suzuki, N.; Kobayashi, M. *Phosphorus Sulfur* **1984**, *20*, 139. (e) Kamigata, N.; Ozaki, J.; Kobayashi, M. *J. Org. Chem.* **1985**, *50*, 5045.

(5) Walling, C. *Free Radicals in Solution*; Wiley: New York, 1957.

(6) Morrison, J. D. *Asymmetric Synthesis*; Academic: New York, 1985, Vol. 5.

(7) Nozaki, H.; Moriuti, S.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1966**, 5239.

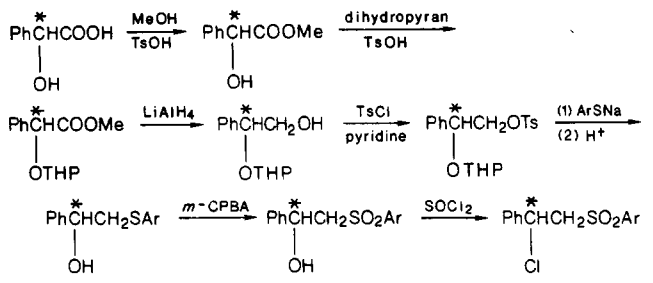
(8) James, B. R.; Wang, D. K.; Voight, R. F. *J. Chem. Soc., Chem. Commun.* **1975**, 574.

0022-3263/87/1952-3312$01.50/0

Table II. Reaction of Arenesulfonyl Chloride with Styrene Catalyzed by Ruthenium(II)-DIOP Complex 1a

2, Ar	DIOP	product	$[\alpha]_D$, deg (c, $CHCl_3$)	optical yield, % ee	abs config
p-$CH_3C_6H_4$	(−)	**3a**	+25 (2.7)	29	R
p-$CH_3C_6H_4$	(+)	**3a**	−20 (6.5)	24	S
C_6H_5	(−)	**3b**	+23 (3.8)	26	R
C_6H_5	(+)	**3b**	−22 (3.7)	27	S
p-ClC_6H_4	(−)	**3c**	+19 (2.6)	25	R
p-ClC_6H_4	(+)	**3c**	−19 (2.3)	24	S
p-$CH_3OC_6H_4$	(−)	**3d**	+20 (1.7)	40	R
p-$CH_3OC_6H_4$	(+)	**3d**	−17 (4.0)	31	S

Scheme I



3

Similarly, when $Ru_2Cl_4[(+)\text{-DIOP}]_3$ ((+)-**1a**) was used as a catalyst, the adduct **3a** was obtained in 40% yield and showed $[\alpha]_D$ −20° (c 6.5, chloroform). When the addition reaction was carried out for 24 h at 60 °C, **3a** was obtained quantitatively; however, the specific rotation indicated a similar value ($[\alpha]_D$ +23° (c 3.8, chloroform)). On raising the reaction temperature to 80 °C, the specific rotation was $[\alpha]_D$ +19° (c 3.5, chloroform). By the use of Ru_2Cl_4-

$$\underset{\mathbf{2}}{ArSO_2Cl} + PhCH{=}CH_2 \xrightarrow{Ru^{II}L^*\ (1)} \underset{\mathbf{3}}{PhCH(Cl)CH_2SO_2Ar}$$

$[(-)\text{-BINAP}]_3(NEt_3)$ ((−)-**1b**) or $Ru_2Cl_4[(+)\text{-BINAP}]_3(NEt_3)$ ((+)-**1b**) as a catalyst[9] (BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), the product (+)-**3a** or (−)-**3a** was obtained in high yield; however, the specific rotations were very low. When $Ru_2Cl_4[(-)\text{-BPPM}]_3(NEt_3)$[9] ((−)-**1c**) was used (BPPM = (2S,4S)-N-(*tert*-butoxycarbonyl)-4-(diphenylphosphino)-2-[(diphenylphosphino)methyl]-pyrrolidine), no reaction was observed, and the starting p-toluenesulfonyl chloride and styrene employed were recovered. The results are summarized in Table I. Thus, an asymmetric induction was observed in the addition of p-toluenesulfonyl chloride to styrene when ruthenium(II) chiral phosphine complex $Ru_2Cl_4[(-)\text{-DIOP}]_3$ ((−)-**1a**) or $Ru_2Cl_4[(+)\text{-DIOP}]_3$ ((+)-**1a**) was used.

The reaction of several arenesulfonyl chlorides with styrene was carried out with (−)-**1a** or (+)-**1a** as a chiral catalyst in a similar way. The results are summarized in Table II. The enantiomeric excess and absolute configuration of the products **3a–d** in the present reactions were estimated by comparison with optically pure samples of **3a–d**, which were prepared by the following procedure starting from commercially available optically pure mandelic acid (Scheme I). (R)-(+)-and (S)-(−)-**3** were formed with retention from (S)-(+)-mandelic acid and (R)-(−)-mandelic acid, respectively.

In this asymmetric addition, the optical yields were 25–40% ee. Although the optical yields are not high, an asymmetric induction was clearly observed in the addition

(9) Ikariya, T.; Ishii, Y.; Kawano, H.; Arai, T.; Saburi, M.; Yoshikawa, S.; Akutagawa, S. *J. Chem. Soc., Chem. Commun.* **1985**, 922.

Scheme II

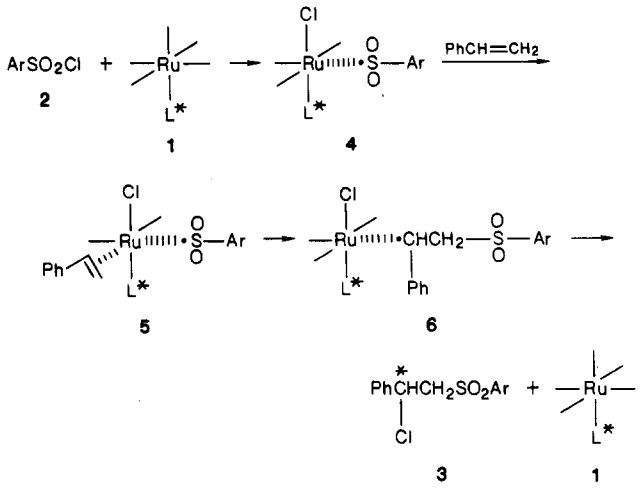


Table III. Reaction of Methanesulfonyl Chloride with Styrene Derivatives

9, R′	DIOP	product	$[\alpha]_D$, deg (c, $CHCl_3$)	chem yield, %	optical[a] yield, % ee	abs config
H	(−)	**10a**	+6.5 (8.8)	99	15 (9)	R
H	(+)	**10a**	−6.2 (5.4)	82	13 (8)	S
p-CH_3	(−)	**10b**	+5.0 (5.6)	95	9	R
p-CH_3	(+)	**10b**	−5.2 (5.5)	80	10	S
p-Cl	(−)	**10c**	+5.6 (5.6)	84	12	R
p-Cl	(+)	**10c**	−5.2 (6.7)	94	10	S
m-NO_2	(−)	**10d**	+10.3 (1.8)[b]	40	c	R
m-NO_2	(+)	**10d**	−6.9 (1.7)[b]	37	c	S

[a] Optical yields were estimated by ^1H NMR with $Eu(hfc)_3$, and optically pure sample yields are in parentheses. [b] Ethyl acetate was used as a solvent. [c] Optical yields could not estimated by ^1H NMR with $Eu(hfc)_3$ since the product **10d** was insoluble in $CDCl_3$.

of arenesulfonyl chlorides to styrene catalyzed by the ruthenium(II) complex with a chiral ligand such as (−)-**1a** or (+)-**1a**.

The reaction can be explained by the following mechanism which involves a radical redox transfer chain process in the coordination sphere of ruthenium(II) complexes (Scheme II). In Scheme II, the ruthenium(II) catalyst **1** at first abstracts a chlorine atom from arenesulfonyl chloride **2** to give an arenesulfonyl radical and a ruthenium(III) species in which the sulfonyl moiety is complexed with the ruthenium(III) species **4**. Then, the π-complex **5** forms between the ruthenium(III) species and styrene, and the coordinated styrene reacts with the confined sulfonyl moiety to give 2-(arylsulfonyl)-1-phenylethyl radical confined to the ruthenium(III) species **6**. The carbon radical in **6** abstracts the chlorine atom from the ruthenium(III) species with chiral ligand to give the adduct **3** and regenerates the ruthenium(II) catalyst **1**. A direct reaction of **4** with styrene to give **6** without forming the intermediate **5** may be also probable. As shown in Scheme II, the arenesulfonyl and 2-(arylsulfonyl)-1-phenylethyl radicals are considered to be confined in the coordination sphere of the ruthenium complexes with a chiral ligand. An enantioface differentiating reaction may be occurring in the last step in Scheme II (abstraction of the chlorine atom from ruthenium(III) species by the carbon radical). The chlorine atom abstraction from the ruthenium(III) species is considered to be more facile from one enantioface than the other face. In other words, the asymmetric induction found in the ruthenium-catalyzed reaction supports our assumption that the sulfonyl and carbon radicals are complexed to the ruthenium species and have different features from those of the usual sulfonyl and carbon free

radicals. It is reported that β-(phenylsulfonyl)-*sec*-butyl free radical, generated by bromine atom abstraction from 2-bromo-3-(phenylsulfonyl)butane with tributyltin radical, rotates about the C_2–C_3 bond.[10]

The reactions of methanesulfonyl chloride (**8**) with several styrene derivatives (**9**) catalyzed by (−)-**1a** or (+)-**1a** were carried out by heating the reaction mixture of **8** and **9** at 100 °C for 6 h in the presence of the ruthenium complex to give 1:1 adducts **10a–d** quantitatively. The results

$$\underset{\mathbf{8}}{CH_3SO_2Cl} + \underset{\mathbf{9}}{R'C_6H_4CH{=}CH_2} \xrightarrow{\mathbf{1a}} R'C_6H_4\overset{*}{C}H(Cl)CH_2SO_2CH_3 \quad \mathbf{10}$$

are summarized in Table III. The enantiomeric excess and absolute configuration of **10a** were estimated by comparison with an optically pure sample **10a**, which was prepared in a similar way to that of **3**. The optically pure sample (*R*)-(+)-**10a** was prepared from (*S*)-(+)-mandelic acid and showed $[\alpha]_D$ +76° (*c* 0.76, chloroform). The optical yield of the adduct **10a** showed $[\alpha]_D$ +6.5° (*c* 8.8, chloroform), corresponding to 9% ee of *R* isomer. The optical yield was also determined by ^1H NMR using a chiral shift reagent. When tris[3-((heptafluoropropyl)-hydroxymethylene)-*d*-camphorato]europium(III) derivative ($Eu(hfc)_3$, Aldrich Chemicals) was used, the enantiomeric excess of the adduct (*R*)-(+)-**10a** was estimated to be 15% ee. The optical yield determined by two different methods was roughly consistent. The optical yields in Table III were estimated by ^1H NMR method. However, the ^1H NMR method could not apply to determine the ee value in the reaction products **3a–d** since they did not show any difference in ^1H NMR spectrum by using shift reagents.

In summary, asymmetric induction was clearly observed in the additions of sulfonyl chlorides to olefins catalyzed by the ruthenium(II) complex with a chiral ligand such as (−)-DIOP or (+)-DOIP. The sulfonyl radicals generated from sulfonyl chlorides and ruthenium(II) complexes are considered to be complexed to the metal species.

Experimental Section

Measurement. Melting points and boiling points were uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer with samples as either neat liquids or KBr disks. 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 $CDCl_3$. The optical rotations were measured with a JASCO DIP-140 polarimeter. The ultraviolet absorption spectra were determined on a Hitachi 220 A spectropolarimeter. The circular dichroism spectra were recorded with a JASCO J40 A spectropolarimeter equipped with a JASCO J-DPY data processor. Mass spectra were determined with a JEOL JMX-DX 300 mass spectrometer with JEOL JMA 5000 mass data system at an ionizing voltage of 20–70 eV.

Materials. Optically active ligands such as DIOP (Tokyo Kasei Chemicals), BINAP, and BPPM (Fluka Chemicals) were used without further purification. The ruthenium complexes such as $Ru_2Cl_4[(-)\text{-DIOP}]_3$ ((−)-**1a**), $Ru_2Cl_4[(+)\text{-DIOP}]_3$ ((+)-**1a**), $Ru_2Cl_4[(-)\text{-BINAP}]_3(NEt_3)$ ((−)-**1b**), $Ru_2Cl_4[(+)\text{-BINAP}]_3(NEt_3)$ ((+)-**1b**), and $Ru_2Cl_4[(-)\text{-BPPM}]_3(NEt_3)$ ((−)-**1c**) were prepared by the methods described in the literature.[8,9] *p*-Toluenesulfonyl chloride (Tokyo Kasei Chemicals), *p*-chlorobenzenesulfonyl chloride (Wako Chemicals), and *p*-methoxybenzenesulfonyl chloride (Aldrich Chemicals) were recrystallized prior to use. Benzenesulfonyl chloride, methanesulfonyl chloride, styrene, *p*-methylstyrene, *p*-chlorostyrene (Tokyo Kasei Chemicals), and *m*-nitrostyrene (Aldrich Chemicals) were purified by distillation under nitrogen prior to use.

General Procedure for the Reaction of Sulfonyl Chlorides with Olefins. A solution containing 1.0 mmol of arenesulfonyl chloride, 1.5 mmol of olefin, and 0.01 mmol of ruthenium complex 1 in 2.0 mL of benzene was degassed and heated in a sealed tube at 60 °C for 6 h. The reaction mixture was chromatographed on silica gel by using benzene as an eluent. Similarly, the reaction of methanesulfonyl chloride with olefin was carried out at 100 °C for 6 h. The products were identified by their melting points, infrared absorption spectra, proton magnetic resonance spectra, mass spectra, and analytical data. The physical and spectral data of the compounds **3** and **10** are as follows.

(*R*)-(+)-2-Chloro-2-phenylethyl *p*-tolyl sulfone (3a): mp 77–78 °C; IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (3 H, s), 3.77–3.90 (2 H, m), 5.29 (1 H, t, *J* = 7.2 Hz), 7.20 (7 H, s), and 7.58 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 294 and 296 (M^+). Anal. Calcd for $C_{15}H_{15}O_2SCl$: C, 61.11; H, 5.13. Found: C, 61.24; H, 5.00.

(*S*)-(−)-2-Chloro-2-phenylethyl *p*-tolyl sulfone (3a): mp 76–77 °C; IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.35 (3 H, s), 3.77–3.90 (2 H, m), 5.28 (1 H, t, *J* = 7.2 Hz), 7.17 (7 H, s), and 7.57 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 294 and 296 (M^+). Anal. Calcd for $C_{15}H_{15}O_2SCl$: C, 61.11; H, 5.13. Found: C, 61.23; H, 5.04.

(*R*)-(+)-2-Chloro-2-phenylethyl phenyl sulfone (3b): mp 84–85 °C; IR (KBr) 1325, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80–3.92 (2 H, m), 5.30 (1 H, t, *J* = 7.2 Hz), 7.18 (5 H, s), and 7.30–7.78 (5 H, m); MS, *m/z* 280 and 282 (M^+). Anal. Calcd for $C_{14}H_{13}O_2SCl$: C, 59.89; H, 4.67. Found: C, 60.07; H, 4.66.

(*S*)-(−)-2-Chloro-2-phenylethyl phenyl sulfone (3b): mp 84–85 °C; IR (KBr) 1325, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80–3.94 (2 H, m), 5.32 (1 H, t, *J* = 7.2 Hz), 7.18 (5 H, s), and 7.30–7.75 (5 H, m); MS, *m/z* 280 and 282 (M^+). Anal. Calcd for $C_{14}H_{13}O_2SCl$: C, 59.89; H, 4.67. Found: C, 60.06; H, 4.62.

(*R*)-(+)-2-Chloro-2-phenylethyl *p*-chlorophenyl sulfone (3c): mp 80–81 °C; IR (KBr) 1325 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80–3.93 (2 H, m), 5.29 (1 H, t, *J* = 7.2 Hz), 7.19 (5 H, s), 7.30 (2 H, d, *J* = 9.0 Hz), and 7.61 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 314 and 316 (M^+). Anal. Calcd for $C_{14}H_{12}O_2SCl_2$: C, 53.34; H, 3.83. Found: C, 53.55; H, 3.78.

(*S*)-(−)-2-Chloro-2-phenylethyl *p*-chlorophenyl sulfone (3c): mp 78–79 °C; IR (KBr) 1325 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80–3.95 (2 H, m), 5.30 (1 H, t, *J* = 7.2 Hz), 7.18 (5 H, s), 7.30 (2 H, d, *J* = 9.0 Hz), and 7.63 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 314 and 316 (M^+). Anal. Calcd for $C_{14}H_{12}O_2SCl_2$: C, 53.34; H, 3.83. Found: C, 53.46; H, 3.78.

(*R*)-(+)-2-Chloro-2-phenylethyl *p*-methoxyphenyl sulfone (3d): mp 78–79 °C; IR (KBr) 1325, 1310, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 3.80–3.89 (2 H, m), 5.28 (1 H, t, *J* = 7.2 Hz), 6.81 (2 H, d, *J* = 9.0 Hz), 7.19 (5 H, s), and 7.60 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 310 and 312 (M^+). Anal. Calcd for $C_{15}H_{15}O_3SCl$: C, 57.97; H, 4.86. Found: C, 57.93; H, 4.92.

(*S*)-(−)-2-Chloro-2-phenylethyl *p*-methoxyphenyl sulfone (3d): mp 76–77 °C; IR (KBr) 1325, 1310, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (3 H, s), 3.80–3.90 (2 H, m), 5.30 (1 H, t, *J* = 7.2 Hz), 6.83 (2 H, d, *J* = 9.0 Hz), 7.22 (5 H, s), and 7.63 (2 H, d, *J* = 9.0 Hz); MS, *m/z* 310 and 312 (M^+). Anal. Calcd for $C_{15}H_{15}O_3SCl$: C, 57.97; H, 4.86. Found: C, 58.06; H, 4.76.

(*R*)-(+)-2-Chloro-2-phenylethyl methyl sulfone (10a): mp 96–97 °C; IR (KBr) 1310, 1280, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (3 H, s), 3.67 (1 H, d, *J* = 7.2 Hz), 3.75 (1 H, d, *J* = 7.2 Hz), 5.38 (1 H, t, *J* = 7.2 Hz), 7.40 (5 H, s); MS, *m/z* 218 and 220 (M^+). Anal. Calcd for $C_9H_{11}O_2SCl$: C, 49.42; H, 5.07. Found: C, 49.60; H, 4.93.

(*S*)-(−)-2-Chloro-2-phenylethyl methyl sulfone (10a): mp 95–96 °C; IR (KBr) 1310, 1280, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (3 H, s), 3.69 (1 H, d, *J* = 7.2 Hz), 3.76 (1 H, d, *J* = 7.2 Hz), 5.37 (1 H, t, *J* = 7.2 Hz), and 7.37 (5 H, s); MS, *m/z* 218 and 220 (M^+). Anal. Calcd for $C_9H_{11}O_2SCl$: C, 49.42; H, 5.07. Found: C, 49.40; H, 5.03.

(*R*)-(+)-2-Chloro-2-*p*-tolylethyl methyl sulfone (10b): mp 106–107 °C; IR (KBr) 1300 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s), 2.72 (3 H, s), 3.68 (1 H, d, *J* = 7.2 Hz), 3.74 (1 H, d, *J* = 7.2 Hz), 5.32 (1 H, t, *J* = 7.2 Hz), and 7.05–7.35 (4 H, m); MS, *m/z* 232 and 234 (M^+). Anal. Calcd for $C_{10}H_{13}O_2SCl$: C,

(10) Boothe, T. E.; Greene, J. L., Jr.; Shevlin, P. B. *J. Org. Chem.* **1980**, *45*, 794.

51.61; H, 5.63. Found: C, 52.07; H, 5.56.

(*S*)-(-)-2-Chloro-2-*p*-tolylethyl methyl sulfone (10b): mp 106–107 °C; IR (KBr) 1300 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.38 (3 H, s), 2.74 (3 H, s), 3.70 (1 H, d, J = 7.2 Hz), 3.76 (1 H, d, J = 7.2 Hz), 5.36 (1 H, t, J = 7.2 Hz), and 7.08–7.40 (4 H, m); MS, m/z 232 and 234 (M^+). Anal. Calcd for $C_{10}H_{13}O_2SCl$: C, 51.61; H, 5.63. Found: C, 51.94; H, 5.55.

(*R*)-(+)-2-Chloro-2-(*p*-chlorophenyl)ethyl methyl sulfone (10c): mp 83–84 °C; IR (KBr) 1310 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (3 H, s), 3.64 (1 H, d, J = 7.2 Hz), 3.72 (1 H, d, J = 7.2 Hz), 5.33 (1 H, t, J = 7.2 Hz), and 7.30 (4 H, s); MS, m/z 252 and 254 (M^+). Anal. Calcd for $C_9H_{10}O_2SCl_2$: C, 42.70; H, 3.98. Found: C, 43.01; H, 3.80.

(*S*)-(-)-2-Chloro-2-(*p*-chlorophenyl)ethyl methyl sulfone (10c): mp 83–84 °C; IR (KBr) 1310 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.82 (3 H, s), 3.64 (1 H, d, J = 7.2 Hz), 3.73 (1 H, d, J = 7.2 Hz), 5.33 (1 H, t, J = 7.2 Hz), and 7.30 (4 H, s); MS, m/z 252 and 254 (M^+). Anal. Calcd for $C_9H_{10}O_2SCl_2$: C, 42.70; H, 3.98. Found: C, 43.15; H, 3.97.

(*R*)-(+)-2-Chloro-2-(*m*-nitrophenyl)ethyl methyl sulfone (10d): mp 136–139 °C; IR (KBr) 1540, 1360, 1300, and 1140 cm^{-1}; ^1H NMR ($(CD_3)_2C{=}O$) δ 2.98 (3 H, s), 4.00 (1 H, d, J = 7.2 Hz), 4.06 (1 H, d, J = 7.2 Hz), 5.61 (1 H, t, J = 7.2 Hz), and 7.48–8.34 (4 H, m); MS, m/z 264 and 266 (M^+); HRMS, m/z 263.0087 ($C_9H_{10}O_4SNCl$ requires 263.0019). Anal. Calcd for $C_9H_{10}O_4SNCl$: C, 40.99; H, 3.82; N, 5.31. Found: C, 42.04; H, 3.69; N, 5.40.[11]

(*S*)-(-)-2-Chloro-2-(*m*-nitrophenyl)ethyl methyl sulfone (10d): mp 137–140 °C; IR (KBr) 1540, 1360, 1300, and 1140 cm^{-1}; ^1H NMR ($(CD_3)_2C{=}O$) δ 2.95 (3 H, s), 4.05 (1 H, d, J = 7.2 Hz), 4.10 (1 H, d, J = 7.2 Hz), 5.68 (1 H, t, J = 7.2 Hz), and 7.53–8.40 (4 H, m); MS, m/z 264 and 266 (M^+); HRMS, m/z 263.0020 ($C_9H_{10}O_4SNCl$ requires 263.0019). Anal. Calcd for $C_9H_{10}O_4SNCl$: C, 40.99; H, 3.82; N, 5.31. Found: C, 42.12; H, 3.81; N, 5.43.[11]

Preparation of Optically Pure 2-Chloro-2-phenylethyl Methyl and Aryl Sulfones. A solution containing 3.0 g (20.0 mmol) of (*S*)-(+)-mandelic acid ($[\alpha]^{24}_D$ +154° (c 2.8, water), 100% optically pure), 100 mL of dry methanol, and 0.03 g (0.2 mmol) of *p*-toluenesulfonic acid monohydrate in 160 mL of dichloromethane was refluxed for 24 h. To the mixture was added 150 mL of water, the organic layer was separated and dried over magnesium sulfate, and the solvent was evaporated to give 3.3 g (96%) of (*S*)-(+)-methyl mandelate: mp 55–56 °C; $[\alpha]^{27}_D$ +144° (c 1.1, methanol); IR (KBr) 3450 and 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.58 (3 H, s), 3.95 (1 H, s), 5.12 (1 H, s), and 7.27 (5 H, s).

To a stirred solution of 3.3 g (19.2 mmol) of (*S*)-(+)-methyl mandelate and 3.3 g (39.0 mmol) of dihydropyran in 60 mL of dichloromethane at 20 °C was added 0.03 g (0.2 mmol) of *p*-toluenesulfonic acid monohydrate, and the mixture was maintained at 20 °C with cooling for 2 h. To the mixture was added 20 mL of water, the organic layer was separated and dried over magnesium sulfate, and evaporation of the solvent gave 5.1 g (101%) of (*S*)-(+)-methyl 2-phenyl-2-(tetrahydropyranyloxy)-acetate as a yellow oil: IR (neat) 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (8 H, s), 3.56 (3 H, s), 4.50 and 4.77 (1 H, s), 5.00 and 5.12 (1 H, s), and 7.18 (5 H, s).

A solution of 5.1 g (20.4 mmol) of the crude (*S*)-(+)-methyl 2-phenyl-2-(tetrahydropyranyloxy)acetate in 100 mL of dry ether was added dropwise to a stirred suspension of 2.3 g (60.0 mmol) of lithium aluminium hydride and 60 mL of dry ether at room temperature. After the addition was completed, the mixture was refluxed for additional 2 h, then cooled in an ice bath, and treated with 2.3 mL of water, 2.3 mL of 15% sodium hydroxide, and 6.9 mL of water. After being stirred for additional 30 min, the mixture was filtered with suction, and the precipitate was washed with ether. The combined ethereal solution was dried over magnesium sulfate, and the solvent was removed in vacuo to give 4.2 g (93%) of (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethanol as a yellow oil: IR (neat) 3420 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.62 (8 H, s), 3.67 (2 H, d, J = 6.0 Hz), 4.50 (1 H, s), 4.70 (1 H, t, J = 6.0 Hz), 4.90 (1 H, s), and 7.30 (5 H, s).

To a solution of 4.2 g (18.9 mmol) of the crude (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethanol in 20 mL of dry pyridine was added 5.4 g (28.4 mmol) of *p*-toluenesulfonyl chloride with cooling in an ice bath. The mixture was stirred for 24 h at 0–5 °C. Then, 20 mL of cooled water was added dropwise with stirring to give 6.9 g (97%) of (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethyl *p*-toluenesulfonate as a solid: mp 95–99 °C (from ethanol); $[\alpha]^{31}_D$ +109° (c 2.4, chloroform); IR (KBr) 1360 and 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.63 (8 H, s), 2.40 (3 H, s), 4.06–4.22 (2 H, m), 4.47 (1 H, s), 4.77–5.20 (1 H, m), 7.20 (5 H, s), 7.23 (2 H, d, J = 9.0 Hz), and 7.68 (2 H, d, J = 9.0 Hz); MS, m/z 275 (M^+ – OTHP).

To a solution of sodium *p*-toluenethiolate in dry methanol, which was prepared from 0.87 g (4.5 mmol) of 28% sodium methoxide in methanol (Tokyo Kasei Chemicals) and 0.75 g (6.0 mmol) of *p*-toluenethiol in 3.0 mL of dry methanol, was added a solution of 1.1 g (3.0 mmol) of (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethyl *p*-toluenesulfonate in 50 mL of dry dimethylformamide under nitrogen, and the mixture was heated for 12 h at 100 °C. The cooled mixture was diluted with water and extracted with benzene. The extract was washed with 2 N sodium hydroxide and with water. The organic layer was dried over magnesium sulfate, and then the solvent was evaporated to give an oil, which was found to contain a byproduct, di-*p*-tolyl disulfide, by TLC analysis. Purification by silica gel column chromatography using benzene as an eluent gave 0.83 g (84%) of (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethyl *p*-tolyl sulfide: ^1H NMR ($CDCl_3$) δ 1.63 (8 H, s), 2.27 (3 H, s), 3.13–3.35 (2 H, m), 4.43 (1 H, s), 4.73–4.95 (1 H, m), 7.00 (2 H, d, J = 8.0 Hz), 7.23 (2 H, d, J = 8.0 Hz), and 7.24 (5 H, s).

The (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethyl *p*-tolyl sulfide (0.83 g, 2.5 mmol) was heated at 45 °C with 70 mL of mixed solvent of 4:2:1 (v/v/v) acetic acid–tetrahydrofuran–water for 12 h. The mixture was cooled and poured into 30 mL of water, and the organic layer was extracted with benzene, washed with 10% sodium hydrogen carbonate and water, and dried over magnesium sulfate. The solvent was evaporated to give 0.59 g (95%) of (*R*)-(+)-2-hydroxy-2-phenylethyl *p*-tolyl sulfide: IR (neat) 3410 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32 (3 H, s), 2.99–3.19 (2 H, m), 4.53–4.75 (1 H, m), 7.06 (2 H, d, J = 8.0 Hz), 7.22 (5 H, s), and 7.28 (2 H, d, J = 8.0 Hz).

To a stirred solution of 0.59 g (2.4 mmol) of (*R*)-(+)-2-hydroxy-2-phenylethyl *p*-tolyl sulfide in 5 mL of dichloromethane was added dropwise a solution of 0.91 g (5.3 mmol) of *m*-chloroperbenzoic acid in 15 mL of dichloromethane with cooling in an ice bath. The mixture was stirred for 24 h at room temperature, and the solvent was removed in vacuo. Purification by silica gel preparative TLC using dichloromethane as an eluent gave 0.53 g (80%) of (*R*)-(+)-2-hydroxy-2-phenylethyl *p*-tolyl sulfone: IR (neat) 3500, 1300, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08 (3 H, s), 3.31–3.48 (2 H, m), 5.09–5.29 (1 H, m), 7.23 (5 H, s), 7.26 (2 H, d, J = 9.0 Hz), and 7.76 (2 H, d, J = 9.0 Hz).

A solution of 0.53 g (1.9 mmol) of (*R*)-(+)-2-hydroxy-2-phenylethyl *p*-tolyl sulfone in 1.0 mL of dry chloroform was heated at gentle reflux. To this vigorously stirred solution was added dropwise a solution of 0.17 mL (2.3 mmol) of thionyl chloride in 1.0 mL of dry chloroform, and the mixture was stirred for additional 3 h. The mixture was poured into 10 mL of water and extracted with ether. The ether extracts was dried over magnesium sulfate, and the solvent was evaporated to give 0.52 g (92%) of (*R*)-(+)-2-chloro-2-phenylethyl *p*-tolyl sulfone (**3a**), the overall yield from (*S*)-(+)-mandelic acid was 51%: mp 95–96 °C (from ethanol); $[\alpha]^{25}_D$ +88° (c 3.5, chloroform); $[\theta]_{222}$ +22 000 (c 9.8 × 10^{-3}, methanol); IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s), 3.77–3.92 (2 H, m), 5.32 (1 H, t, J = 7.2 Hz), 7.28 (7 H, s), and 7.63 (2 H, d, J = 9.0 Hz); MS, m/z 294 and 296 (M^+). Anal. Calcd for $C_{15}H_{15}O_2SCl$: C, 61.11; H, 5.13. Found: C, 61.25; H, 5.14.

Similarly the following authentic optically pure compounds were prepared by this procedure reacting the (*R*)-(+)-2-phenyl-2-(tetrahydropyranyloxy)ethyl *p*-toluenesulfonate with adequate sodium methylthiolate or sodium arylthiolate. The physical and spectral data of the authentic optically pure compounds **3b–d** and **10a** are as follows.

(*R*)-(+)-2-Chloro-2-phenylethyl phenyl sulfone (3b): mp 94–95 °C; $[\alpha]^{24}_D$ +90° (c 2.0, chloroform); $[\theta]_{218}$ +19 000 (c 9.9 × 10^{-3}, methanol); IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80–3.94 (2 H, m), 5.33 (1 H, t, J = 7.2 Hz), 7.22 (5

(11) Since the combusion analytical data obtained were slightly unsatisfactory, their high-resolution mass spectra were also determined.

H, s), and 7.34-7.80 (5 H, m); MS, m/z 281 and 283 ($M^+ + 1$). Anal. Calcd for $C_{14}H_{13}O_2SCl$: C, 59.89; H, 4.67. Found: C, 60.13; H, 4.72.

(*R*)-(+)-2-Chloro-2-phenylethyl *p*-chlorophenyl sulfone (3c): mp 84-85 °C; $[\alpha]^{25}_D$ +78° (c 4.4, chloroform); $[\theta]_{226}$ +19000 (c 7.1 × 10^{-3}, methanol); IR (KBr) 1325 and 1140 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.80-3.94 (2 H, m), 5.30 (1 H, t, J = 7.2 Hz), 7.17 (5 H, s), 7.30 (2 H, d, J = 9.0 Hz), and 7.60 (2 H, d, J = 9.0 Hz); MS, m/z 314 and 316 (M^+); HRMS, m/z 313.9885 ($C_{14}H_{12}O_2SCl_2$ requires 313.9935). Anal. Calcd for $C_{14}H_{12}O_2SCl_2$: C, 53.34; H, 3.84. Found: C, 54.44; H, 3.80.[11]

(*R*)-(+)-2-Chloro-2-phenylethyl *p*-methoxyphenyl sulfone (3d): mp 72-74 °C; $[\alpha]^{22}_D$ +48° (c 2.6, chloroform); $[\theta]_{226}$ +8900 (c 1.3 × 10^{-4}, methanol); IR (KBr) 1325, 1310, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77-3.90 (2 H, m), 3.80 (3 H, s), 5.29 (1 H, t, J = 7.2 Hz), 6.85 (2 H, d, J = 9.0 Hz), 7.23 (5 H, s), and 7.63 (2 H, d, J = 9.0 Hz); MS, m/z 310 and 312 (M^+). Anal. Calcd for $C_{15}H_{15}O_3SCl$: C, 57.97; H, 4.87. Found: C, 58.03; H, 4.78.

(*R*)-(+)-2-Chloro-2-phenylethyl methyl sulfone (10a): mp 119-121 °C; $[\alpha]^{23}_D$ +76° (c 0.76, chloroform); $[\theta]_{221}$ +9400 (c 1.0 × 10^{-4}, methanol); IR (KBr) 1320, 1305, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (3 H, s), 3.68 (1 H, d, J = 7.2 Hz), 3.75 (1 H, d, J = 7.2 Hz), 5.36 (1 H, t, J = 7.2 Hz), and 7.37 (5 H, s); MS, m/z 218 and 220 (M^+); HRMS, m/z 218.0111 ($C_9H_{11}O_2SCl$ requires 218.0169). Anal. Calcd for $C_9H_{11}O_2SCl$: C, 49.45; H, 5.04. Found: C, 46.69; H, 4.55.[11]

The authentic stereoisomers of compounds (-)-**3a-d** and (-)-**10a** were prepared by starting from an optically pure (*R*)-(-)-mandelic acid in a similar way.

(*S*)-(-)-2-Chloro-2-phenylethyl *p*-tolyl sulfone (3a): mp 92-93 °C; $[\alpha]^{26}_D$ -82° (c 3.4, chloroform); $[\theta]_{222}$ -24000 (c 1.1 × 10^{-4}, methanol); IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s), 3.77-3.91 (2 H, m), 5.30 (1 H, t, J = 7.2 Hz), 7.23 (7 H, s), and 7.60 (2 H, d, J = 9.0 Hz); MS, m/z 294 and 296 (M^+). Anal. Calcd for $C_{15}H_{15}O_2SCl$: C, 61.11; H, 5.13. Found: C, 61.47; H, 5.15.

(*S*)-(-)-2-Chloro-2-phenylethyl phenyl sulfone (3b): mp 83-84 °C; $[\alpha]^{22}_D$ -83° (c 0.62, chloroform); $[\theta]_{218}$ -17000 (c 1.1 × 10^{-4}, methanol); IR (KBr) 1320, 1305, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80-3.90 (2 H, m), 5.32 (1 H, t, J = 7.2 Hz), 7.21 (5 H, s), and 7.33-7.80 (5 H, m); MS, m/z 280 and 282 (M^+). Anal. Calcd for $C_{14}H_{13}O_2SCl$: C, 59.89; H, 4.67. Found: C, 59.83; H, 4.31.

(*S*)-(-)-2-Chloro-2-phenylethyl *p*-chlorophenyl sulfone (3c): mp 93-94 °C; $[\alpha]^{26}_D$ -80° (c 1.7, chloroform); $[\theta]_{226}$ -30000 (c 1.1 × 10^{-4}, methanol); IR (KBr) 1325 and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80-3.93 (2 H, m), 5.30 (1 H, t, J = 7.2 Hz), 7.20 (5 H, s), 7.30 (2 H, d, J = 9.0 Hz), and 7.60 (2 H, d, J = 9.0 Hz); MS, m/z 314 and 316 (M^+). Anal. Calcd for $C_{14}H_{12}O_2SCl_2$: C, 53.34; H, 3.84. Found: C, 53.63; H, 3.61.

(*S*)-(-)-2-Chloro-2-phenylethyl *p*-methoxyphenyl sulfone (3d): mp 63-66 °C; $[\alpha]^{24}_D$ -55° (c 2.0, chloroform); $[\theta]_{226}$ -22000 (c 1.2 × 10^{-4}, methanol); IR (KBr) 1325, 1310, and 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.80 (2 H, m), 3.83 (3 H, s), 5.29 (1 H, t, J = 7.2 Hz), 6.84 (2 H, d, J = 9.0 Hz), 7.20 (5 H, s), and 7.63 (2 H, d, J = 9.0 Hz); MS, m/z 310 and 312 (M^+). Anal. Calcd for $C_{15}H_{15}O_3SCl$: C, 57.97; H, 4.87. Found: C, 58.24; H, 4.88.

(*S*)-(-)-2-Chloro-2-phenylethyl methyl sulfone (10a): mp 116-118 °C; $[\alpha]^{22}_D$ -77° (c 1.7, chloroform); $[\theta]_{221}$ -11000 (c 1.3 × 10^{-4}, methanol); IR (KBr) 1320, 1305, and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.73 (3 H, s), 3.68 (1 H, d, J = 7.2 Hz), 3.75 (1 H, d, J = 7.2 Hz), 5.34 (1 H, t, J = 7.2 Hz), and 7.35 (5 H, s); MS, m/z 218 and 220 (M^+). Anal. Calcd for $C_9H_{11}O_2SCl$: C, 49.45; H, 5.04. Found: C, 49.67; H, 4.88.

Ring-Inversion Barriers for the 3- and 4-Cyclohexenyl Radicals in Solution[1]

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Ring-inversion barriers for the 3- and 4-cyclohexenyl radicals were investigated by an electron paramagnetic resonance (EPR) method and were found to be 7.0 ± 0.9 and 2.4 ± 0.5 kcal mol^{-1} in fluid solution. The inversion motions and the magnitudes of the barriers were closely related to those of the corresponding cyclohexenones and methylenecyclohexanes.

The effect of ring size on the inversion barriers for cycloalkyl radicals bears a crude relationship to the effect observed for inversions in the corresponding cycloalkanes.[2] For example, the barriers for ring inversions of the cyclopentyl,[3] cyclohexyl,[4] and cycloheptyl[2] radicals are 1.3, 4.9, and 3.4 kcal mol^{-1}, respectively, while those for the corresponding cycloalkanes are 0.6, 10, and 1-2 kcal mol^{-1}.[5] Partial unsaturation of the ring has the effect of lowering the barrier relative to that of the cycloalkane. For example, NMR studies of cyclohexene set the barrier at 5.3 kcal mol^{-1}, while infrared studies of the same system lead to the somewhat higher estimate of 7.4 kcal mol^{-1}.[6]

In cycloalkenyl radicals, the situation is somewhat more complex because the inversion barriers ought to depend upon the relative positions of the unpaired electron and the double bond. To explore this problem, we have investigated the inversion barriers for the 3- and 4-cyclohexenyl radicals.

Experimental Section

Materials. 4-Iodocyclohexene was prepared by a new method described below, which was found to be more convenient than those previously described.[7] All other materials were commercially available. Di-*tert*-butyl peroxide was washed with aqueous silver nitrate then with water. After drying over magnesium sulfate, it was finally passed through a column of activated alumina. Hexamethyldistannane was purified by vacuum distillation. Triethylsilane was used as received.

4-Iodocyclohexene. To a stirred mixture of 50 g (0.30 mol) of potassium iodide in 20 mL of 85% phosphoric acid was added dropwise 13 mL (11 g, 0.14 mol) of 1,4-cyclohexadiene. The resulting mixture was heated at 85 °C for 16 h, after which time

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(2) Burkey, T. J.; Griller, D.; Sutcliffe, R.; Harding, C. J. *J. Org. Chem.* **1985**, *50*, 1138.
(3) Lloyd, R. V.; Wood, D. E. *J. Am. Chem. Soc.* **1977**, *99*, 8269.
(4) Ogawa, S.; Fessenden, R. W. *J. Chem. Phys.* **1964**, *41*, 994. Bonnazola, L.; Leray, N.; Marx, R. *Chem. Phys. Lett.* **1974**, *24*, 88.
(5) Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. In *Conformational Analysis*; Wiley: New York, 1965. Brookeman, J. R.; Rushworth, F. A. *J. Phys. C* **1976**, *9*, 1043.
(6) Anet, F. A. L.; Haq, M. Z. *J. Am. Chem. Soc.* **1965**, *87*, 3147. Durig, J. R.; Carter, R. O.; Carreira, L. A. *J. Chem. Phys.* **1974**, *60*, 3098.
(7) Lambert, J. B.; Marko, D. E. *J. Am. Chem. Soc.* **1985**, *107*, 7978 and references cited therein.

0022-3263/87/1952-3316$01.50/0