(5 mL) was treated with dihydropyran (110 mg, 1.32 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (33 mg, 0.13 mmol) at room temperature for 16 h. The reaction mixture was diluted with Et_2O (25 mL), washed with half-saturated brine (2 × 10 mL), and dried. Removal of solvent followed by flash chromatography (10% EtOAc in hexane) afforded **12x** (185 mg, 99.6%); ^1H NMR δ 1.48–1.93 (8 H), 2.59 (2 H, t, J = 7.6 Hz), 3.36–3.57 (2 H), 3.68–3.98 (2 H), 3.76 (6 H, s), 4.56 (H, t, J = 3.8 Hz), 6.39 (H, dd, J = 9.6 and 2.4 Hz), 6.41 (H, s), 7.01 (H, d, J = 7.9 Hz); mass spectrum, m/z obsd 280.1674 (M^+, calcd for $C_{16}H_{24}O_4$, 280.1675).

3-(3-Hydroxy-2,4-dimethoxyphenyl)propanol (15m). To an ice-cold solution of **12x** (140 mg, 0.5 mmol) in Et_2O (4 mL) containing TMEDA (226.4 μL, 1.5 mmol), was added *n*-BuLi (745 μL, 2.02 M in hexane, 1.5 mmol) dropwise with stirring under argon. After complete addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for 16 h followed by boiling under reflux for 16 h during which the color turned from yellow to brown. The reaction mixture was cooled to −10 °C and to it was added a solution of $B(OMe)_3$ (171.5 mg, 1.65 mmol) in THF (1 mL) with vigorous stirring upon which a white sludge appeared. After stirring for an additional 15 min, cold HOAc (129 μL, 2.24 mmol) was added all at once followed by addition of a solution of H_2O_2 (168 μL, 30%) in H_2O (168 μL). The cooling bath was then removed. The reaction mixture was allowed to warm to room temperature, then transferred into a separatory funnel with Et_2O (5 mL), and washed with a saturated aqueous solution of $(NH_4)_2SO_4$ containing $Fe(NH_3)_2(SO_4)_2$ until no more brown precipitate was formed. The organic layer was then washed with water (3 × 3 mL) and dried. Removal of solvent by rotary evaporation afforded the starting material (89 mg). The alkaline aqueous layer was acidified (cold concentrated HCl) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were dried. Removal of EtOAc afforded the phenolic product (65 mg, 0.224 mmol) which, without further purification, was treated in EtOH (2 mL) solution with PPTS (5.5 mg, 0.022 mmol) at 55 °C for 2 h. Removal of EtOH followed by purification of the residue by preparative TLC (75% EtOAc–hexane) afforded **15m** [24.4 mg, 62% based on consumed **12x**]: ^1H NMR δ 1.78 (2 H, quin), 2.14 (H, br s), 2.64 (2 H, t, J = 7.4 Hz), 3.55 (2 H, t, J = 6.2 Hz), 3.82 (3 H, s), 3.84 (3 H, s), 5.75 (H, br s), 6.55 (H, d, J = 8.4 Hz), 6.61 (H, d, J = 8.4 Hz).

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Simple and Stereocontrolled Preparation of Optically Pure (*E*)- and (*Z*)-1-Alkenyl *p*-Tolyl Sulfoxides via 1-Alkynyl *p*-Tolyl Sulfoxides

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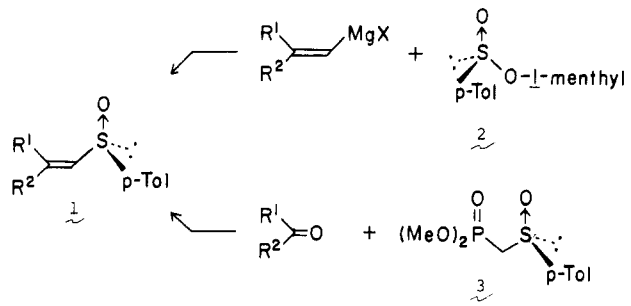
1-Alkynylmagnesium bromides react cleanly and stereospecifically with (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate (**2**) in toluene to produce chiral 1-alkynyl *p*-tolyl (+)-(*S*)-sulfoxides **5a–d** in high yields. Reduction of **5a–d** with lithium aluminum hydride in THF at −90 °C proceeds stereospecifically to give (*E*)-1-alkenyl *p*-tolyl (+)-(*R*)-sulfoxides (*E*)-**7** in excellent yields, while catalytic hydrogenation of **5a–d** using Wilkinson catalyst, $RhCl(PPh_3)_3$, in benzene affords quantitatively (−)-(*R*)-*Z* isomers (*Z*)-**7**. Conjugate addition of organocopper reagents to **5** also proceeds stereoselectively.

In recent years, 1-alkenyl *p*-tolyl sulfoxides **1** with the optically active center at the sulfur atom have been used successfully in various asymmetric syntheses: the Michael reaction,[1] the Diels–Alder reaction,[2] the additive Pummerer rearrangement,[3] the sequential prototropic shift and [2,3] sigmatropic rearrangement,[4] the 1,3-dipolar cycloaddition,[5] and the reaction as the vinylic carbanion species.[3b,6] The *R* enantiomers of **1** are usually prepared by the Andersen synthesis using (−)-menthyl (−)-(*S*)-*p*-toluenesulfinate **2** and vinylic Grignard reagents[7] or by the Horner–Wittig procedure using carbonyl compounds and the anion of dimethyl ((*R*)-*p*-tolylsulfinyl)methanephosphonate **3**[8] (Scheme I). However, applicability of the former method depends on the availability of stereochemically pure 1-alkenyl halides for preparing Grignard reagents, and the latter usually leads to a mixture of (*E*)- and (*Z*)-vinylic sulfoxides. Pursuing our interest in the asymmetric synthesis of acyclic compounds using chiral

Scheme I



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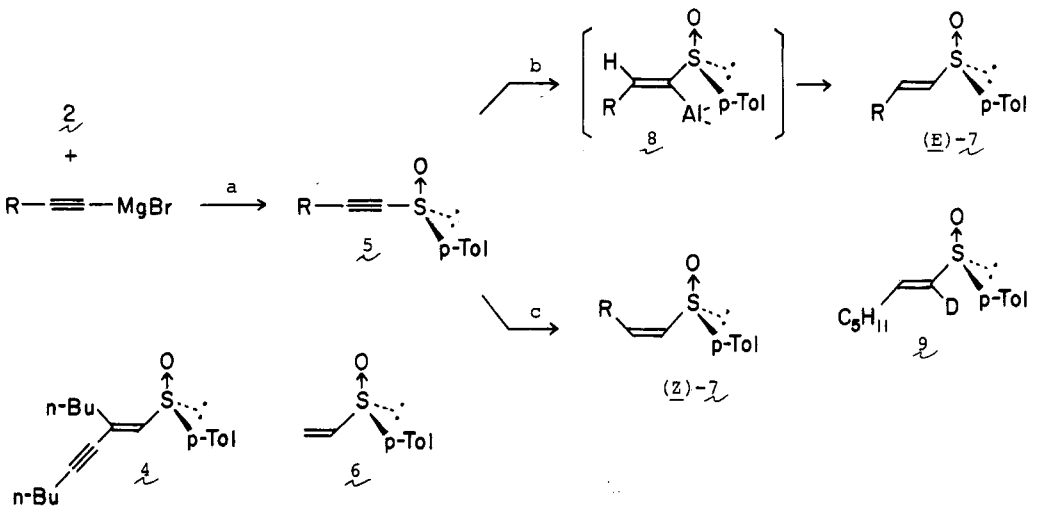
Scheme II[a]



[a] (a) Et_2O/toluene, −20 °C, 1 h; (b) DIBAH, THF or toluene, −90 to −95 °C, 15 min or LAH, THF, −90 °C, 30 min; (c) H_2, $RhCl(PPh_3)_3$, benzene, room temperature.

sulfoxides,[3c,4b,9] we needed a variety of chiral α,β-unsaturated sulfoxides with high optical and stereoisomeric purities and have sought a new stereocontrolled method for preparing them. We report here the results of this investigation, which has resulted in the successful development of a simple and stereocontrolled method for preparing either chiral (*E*)-1-alkenyl or (*Z*)-1-alkenyl *p*-tolyl sulfoxides **7** via 1-alkynyl *p*-tolyl sulfoxides **5** (Scheme II).[10]

The Andersen procedure has been widely used for the preparation of chiral diaryl, alkyl aryl, and alkenyl aryl sulfoxides of high optical purity,[7,11] but there has been little information about the preparation, absolute configuration, and chemical reactivity of chiral 1-alkynyl sulfoxides.[12] Thus, we examined first the reaction of the chiral sulfinate ester **2** with hexynyllithium or hexynylmagnesium bromide (R = n-C_4H_9) under a variety of conditions. In the case of hexynyllithium, 2:1 adduct **4** was always obtained as the major product. The reaction of **2** with hexynylmagnesium bromide in ether,[13] THF, or benzene, which are commonly used as solvents for the Andersen procedure,[7,11] was found to be also unsatisfactory, giving the desired 1-hexynyl *p*-tolyl sulfoxide (**5b**) in only 20% yield along with the recovery (60%) of **2**. However, when the Grignard reagent in ether was treated with a solution of **2** in toluene, not only it was found that the reaction proceeded cleanly and stereospecifically even at low temperature but also a superior yield (80%) of the dextrorotatory 1-hexynyl sulfoxide **5b** was achieved. In the same manner, the reaction of **2** with other acetylenic Grignard reagents also gave the corresponding (+)-1-alkynyl sulfoxides **5** in high yield, and the results are summarized in Table I. In the case of the reaction with [(trimethylsilyl)ethynyl]magnesium bromide, the initial product **5** (R = Me_3Si) was hydrolyzed during chromatographic purification to produce ethynyl *p*-tolyl sulfoxide (**5e**, R = H) in 80% yield. The absolute configuration of these acetylenic sulfoxides **5** was assigned on the basis of the fact that Grignard reaction with chiral sulfinate esters proceeds stereospecifically with inversion of configuration at the sulfur atom;[7,11] this and the optical purity (100%) were finally confirmed by the conversion of **5** into the corresponding (*E*)-1-alkenyl *p*-tolyl (+)-(*R*)-sulfoxides (*E*)-**7** as discussed below. The effectiveness of toluene as a cosolvent was also observed in the reaction of **2** with vinylmagnesium bromide; *p*-tolyl vinyl sulfoxide (**6**) was obtained in better chemical and optical yields than the reported ones[14] (see Experimental Section).

With the chiral 1-alkynyl sulfoxides **5** successfully prepared, we next attempted reduction of **5a–d** to 1-alkenyl sulfoxides. We first examined hydroalumination with

Table I. Preparation of Optically Active 1-Alkynyl *p*-Tolyl Sulfoxides 5

RC≡C-MgBr, R	product	yield,[a] %	$[\alpha]_D$, deg (*c*)[b]	config[c]
n-C_3H_7	**5a**	83	+88.6 (1.009)	*S*
n-C_4H_9	**5b**	80	+77.6 (1.195)[d]	*S*
n-C_5H_{11}	**5c**	86	+73.8 (0.469)	*S*
n-C_6H_{13}	**5d**	82	+70.0 (1.087)	*S*
Me_3Si	**5e** (R = H)[e]	80	+154.0 (0.182)	*R*

[a] Yields are for the isolated pure products. [b] Measured for solutions in $CHCl_3$ at 20 °C. [c] Determined by conversion into (*R*)-(*E*)-**7**. [d] Lit.[12] $[\alpha]^{20}_D$ +91° (*c* 1.0, acetone). [e] See the text.

Table II. Reduction of 1-Alkynyl *p*-Tolyl Sulfoxides 5 to (*E*)-1-Alkenyl *p*-Tolyl Sulfoxides (*E*)-7

			reducing agent and yield,[a] %		
no.	substr	product	DIBAH[b]	LAH[b]	$[\alpha]_D$, deg (*c*)[c]
1	**5a**	(*E*)-**7a**	84	87	+177.9 (1.003)
2	**5b**	(*E*)-**7b**	87	94	+158.2 (0.500)
3	**5c**	(*E*)-**7c**	88	95	+148.2 (0.517)
4	**5d**	(*E*)-**7d**	81	94	+138.2 (0.503)[d]

[a] Yields are for the isolated pure products. [b] Carried out for solutions in THF at −90 to −95 °C. [c] Measured for solutions in acetone at 20 °C. [d] Lit.[7b] +104° (*c* 0.05, acetone), prepared in 60% yield by the reaction of **2** with (*E*)-1-octenylmagnesium bromide in THF.

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(13) Cozzi et al. (ref 12) prepared 1-hexynyl sulfoxide **5b** in 70% yield from the reaction of **2** with hexynylmagnesium bromide in ether, but we could not obtain **5b** in such a good yield.

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Table III. Catalytic Hydrogenation of 1-Alkynyl *p*-Tolyl Sulfoxides 5 to (*Z*)-1-Alkenyl *p*-Tolyl Sulfoxides (*Z*)-7

		reaction conditions[a]					
no.	substr	catalyst	solvent	time, h	product	yield,[b] %	$[\alpha]_D$, deg (*c*)[c]
1	**5d**	Pd–$BaCO_3$	MeOH–EtOAc	24	(*Z*)-**7d**[d]	65	
2	**5d**	Pd–C	MeOH–EtOAc	60	(*Z*)-**7d**[d]	59	
3	**5d**	$RhCl(PPh_3)_3$	benzene	24	(*Z*)-**7d**	98	−279.6 (0.193)
4	**5a**				(*Z*)-**7a**	99	−322.3 (0.554)
5	**5b**				(*Z*)-**7b**	90	−298.1 (0.505)
6	**5c**				(*Z*)-**7c**	97	−304.7 (0.597)

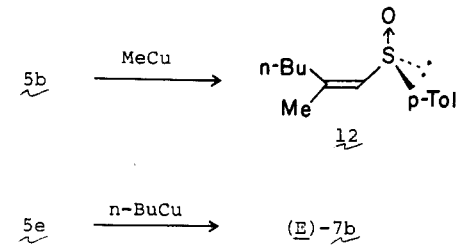
[a] Carried out at room temperature under an atmospheric pressure. [b] Yields are for the isolated pure products. [c] Measured for solutions in acetone at 20 °C. [d] Byproducts were also produced.

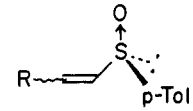
diisobutylaluminum hydride (DIBAH). Treatment of **5** with DIBAH in toluene or THF followed by hydrolysis of the resulting adducts **8** with water afforded (*E*)-1-alkenyl *p*-tolyl (+)-(*R*)-sulfoxides (*E*)-**7** in high yield.[10] The results are summarized in Table II. It is noted that the known (*E*)-1-octenyl derivative (*E*)-**7d** was obtained with much higher optical purity by the present method (entry 4) than that prepared by the direct Andersen procedure.[7b] The *E* geometry of the double bond in other products was unambiguously confirmed by the same coupling patterns of the olefinic proton signals as those of (*E*)-**7d**, at approximately δ 6.1 (d, J = 15.5 Hz, H_α) and 6.4 ppm (dt, J = 15.5 and 6 Hz, H_β),[7b] in their ^1H NMR spectra. It should be noted that, in contrast to a usual hydroalumination of simple unactivated acetylenes with DIBAH,[15] the hydroalumination of these acetylenic sulfoxides **5** proceeded smoothly even at low temperature (−90 to −95 °C) and formally in a trans addition manner. Orientation and configuration of the addition of DIBAH to the triple bond in **5** (formation of **8**) was proved by hydrolysis of the adduct **8c** with deuterium oxide to give 1-deuteriated heptenyl derivative **9** [δ 6.43 (br t, J = 6 Hz, H_β)]. The formation of trans adducts **8**, that is, (*E*)-**7**, may be accounted for by the configurational instability of the α-metallated *Z* isomers in such a 1-alkenyl sulfoxide system.[16] The optical purity (100% ee) of these alkenyl sulfoxides (*E*)-**7** was estimated by high-pressure liquid chromatographic (HPLC) analysis on a chiral stationary phase (Chiralcel OB column); the racemates of (*E*)-**7** were completely resolved on this column. From the same HPLC behaviors and the same positive signs in the specific rotations as those of known sulfoxide (*R*)-(*E*)-**7d**, the new chiral alkenyl sulfoxides (*E*)-**7a–c** would have *R* absolute configuration. Thus, from the above results, alkynyl sulfoxides **5** prepared by the present method are optically pure and have the absolute configurations, *S* for **5a–d** and *R* for **5e**, respectively, as shown in Scheme II and Table I.

Furthermore, it was found that lithium aluminum hydride (LAH) was superior to DIBAH as a reducing agent. Thus, alkynyl sulfoxides **5** were reduced cleanly with LAH at low temperature without reduction of the sulfoxide function to furnish (*E*)-1-alkenyl sulfoxides (*E*)-**7** in excellent yields as shown in Table II.

Then, we extended our study to conversion of alkynyl sulfoxides **5** to (*Z*)-1-alkenyl sulfoxides by catalytic hydrogenation. The octynyl derivative **5d** was chosen as a model substrate and hydrogenated by using a variety of catalyst–solvent systems, and the typical results are shown in Table III (entries 1–3). The best result was achieved when catalytic hydrogenation of **5d** was carried out by the use of Wilkinson catalyst, chlorotris(triphenylphosphine)rhodium(I), in benzene (entry 3). Thus, the desired (*Z*)-1-octenyl sulfoxide (*Z*)-**7d** was obtained quantitatively. With palladium catalysts in various solvent systems the product (*Z*)-**7d** was produced in only 50–60% yields along with a few byproducts (entries 1 and 2), and palladium on barium sulfate or platinum oxide was found to be ineffective. In the same manner, other alkynyl sulfoxides **5a–c** also afforded the corresponding (*Z*)-1-alkenyl sulfoxides (*Z*)-**7a–c** in excellent yields. In the ^1H NMR spectra of these compounds, the two olefinic proton signals appear as a multiplet around δ 5.9–6.4 ($J_{H_\alpha H_\beta}$ = 9.0 Hz, observable in benzene-d_6), indicating *Z* configuration of the double bond. From the fact that the starting alkynyl sulfoxides **5** are optically pure as described above, sulfoxides (*Z*)-**7** thus obtained would be also optically pure. As seen from Tables II and III, (*E*)-**7** isomers are dextrorotatory, whereas (*Z*)-**7** isomers are levorotatory and have the considerably larger rotation values than those of *E* isomers. The same trends in the specific rotations have been observed in styryl (**10**)[8b] and propenyl[7a] *p*-tolyl (*R*)-sulfoxides (**11**).

Scheme III





10: R = Ph { E: $[\alpha]_D$ +160° ($CHCl_3$); Z: $[\alpha]_D$ −736° ($CHCl_3$)

11: R = Me Z: $[\alpha]_D$ −306° (EtOH)

Since terminal acetylenes are more readily available than stereochemically pure 1-alkenyl halides (for the direct Andersen synthesis), the present procedure through alkynyl sulfoxides provides a convenient and efficient method for preparing a variety of stereochemically and optically pure 1-alkenyl *p*-tolyl sulfoxides.

Finally, the additional usefulness of an alkynyl sulfoxide for preparing a chiral β,β-disubstituted alkenyl sulfoxide is shown in Scheme III. It has been reported[17] that achiral α,β-acetylenic sulfoxides undergo smooth conjugate addition with organocopper reagents, giving β-alkylated $\alpha,$-

(15) Mole, T.; Jeffery, E. A. In *Organoaluminium Compounds*; Elsevier: Amsterdam, 1972; p 263.

(16) The complete isomerization of (*Z*)-1-alkenyl sulfoxides to the *E* isomers through α-deprotonation by lithium diisopropylamide has been reported. Posner, G. H.; Tang, P.-W.; Mallamo, J. P. *Tetrahedron Lett.* **1978**, 3995.

(17) Truce, W. E.; Lusch, M. *J. Org. Chem.* **1978**, *43*, 2252.

β-ethylenic sulfoxides by a cis addition to the triple bond exclusively. This reaction would be applicable to the present chiral acetylenic sulfoxides. Reaction of the hexynyl sulfoxide **5b** with methylcopper in THF proceeded well to give a single product, (Z)-2-methyl-1-hexenyl p-tolyl (−)-(R)-sulfoxide (**12**), $[\alpha]_D$ −261.1° (c 0.50, acetone),[18] in 77% yield; the stereoisomer could not be detected from the analysis of the ^1H and ^{13}C NMR spectra. The Z stereochemistry is assigned on the basis of the results obtained in the reaction of achiral sulfoxides[17] and by a separate experiment using ethynyl sulfoxide **5e** and n-butylcopper, affording in 80% yield (E)-hexenyl sulfoxide (E)-**7b**, $[\alpha]_D$ +154° (c 1.02, acetone).

We are currently studying the utility of these alkynyl and alkenyl sulfoxides as chiral synthons for asymmetric syntheses.

Experimental Section

Infrared spectra were obtained for solutions in $CHCl_3$ with a JASCO A-3 spectrophotometer and are reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on a JEOL PMX-60 (60 MHz) or PS-100 (100 MHz) instrument with Me_4Si as internal standard. Optical rotations were measured on a JASCO DIP-4S polarimeter. Analytical HPLC was carried out on a Waters ALC/GPC 244 instrument. Merck 60 GF-254 silica gel was used for preparative TLC (PTLC). Elemental analyses were performed by the microanalytical laboratory of this institute.

l-Menthyl (−)-(S)-p-toluenesulfinate (**2**) was prepared according to the literature:[19] $[\alpha]^{18}_D$ −202° (c 0.569, acetone) (100% ee).

General Procedure for the Synthesis of 1-Alkynyl p-Tolyl Sulfoxides 5. An excess 1-alkyne was added to an ethereal solution of ethylmagnesium bromide (EtMgBr) (2.17 M solution) at 0 °C, and the mixture was heated under reflux for 1 h under nitrogen. To the cooled solution was added a solution of l-menthyl (−)-(S)-p-toluenesulfinate (**2**) in toluene (ca. 70 mL for ca. 20 mmol of **2**) dropwise at −20 °C, and the reaction mixture was stirred at −20 °C for 1 h. The reaction was quenched with saturated aqueous NH_4Cl, and the product was thoroughly extracted with a mixed solvent (ether/EtOAc/CH_2Cl_2, 2:2:1). The extracts were washed with saturated brine. Removal of the solvent under reduced pressure followed by chromatography of the residue on silica gel (hexane/EtOAc, 20:1) gave the pure sulfoxide **5**.

1-Pentynyl p-Tolyl (+)-(S)-Sulfoxide (5a). The reaction using 1-pentyne (1.63 g, 24 mmol), EtMgBr (14.4 mmol), and **2** (3.53 g, 12 mmol) gave **5a** (2.05 g, 83%): IR 2890, 2190, 1600, 1495, 1090, 1055, 1020; ^1H NMR δ (CCl_4) 1.00 (t, J = 7 Hz, 3 H), 1.60 (6 peaks, J = 7 Hz, 2 H), 2.40 (t, J = 7 Hz, 2 H), 2.42 (s, 3 H), 7.43 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.88; H, 6.84. Found: C, 69.82; H, 6.86.

1-Hexynyl p-Tolyl (+)-(S)-Sulfoxide (5b). The reaction using 1-hexyne (3.3 g, 40 mmol), EtMgBr (24 mmol), and **2** (5.88 g, 20 mmol) gave **5b** (3.52 g, 80%): IR 2890, 2190, 1600, 1495, 1090, 1055, 1020; ^1H NMR δ (CCl_4) 0.80–1.16 (t, J = 6 Hz, 3 H), 1.16–1.85 (m, 4 H), 2.40 (t, J = 6 Hz, 2 H), 2.43 (s, 3 H), 7.40 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.89; H, 7.32. Found: C, 70.83; H, 7.29.

1-Heptynyl p-Tolyl (+)-(S)-Sulfoxide (5c). The reaction using 1-heptyne (2.6 g, 27 mmol), EtMgBr (18 mmol), and **2** (4.3 g, 15 mmol) gave **5c** (2.94 g, 86%): IR 2980, 2190, 1600, 1495, 1090, 1055, 1020; ^1H NMR δ (CCl_4) 0.90 (br t, J = 6 Hz, 3 H), 1.16–1.85 (m, 6 H), 2.40 (t, J = 6 Hz, 2 H), 2.43 (s, 3 H), 7.42 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.77; H, 7.74. Found: C, 71.58; H, 7.73.

1-Octynyl p-Tolyl (+)-(S)-Sulfoxide (5d). The reaction using 1-octyne (3.2 g, 29 mmol), EtMgBr (19 mmol), and **2** (4.5 g, 15.3 mmol) gave **5d** (3.11 g, 82%): IR 2980, 2190, 1600, 1495, 1090, 1055, 1020; ^1H NMR δ (CCl_4) 0.88 (br t, J = 6 Hz, 3 H), 1.16–1.85 (m, 8 H), 2.40 (t, J = 6 Hz, 2 H), 2.43 (s, 3 H), 7.50 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{15}H_{20}OS$: C, 72.55; H, 8.12. Found: C, 72.82; H, 8.48.

(18) The positive sign reported previously (ref 10) is incorrect.
(19) Mioskowsky, C.; Solladié, G. *Tetrahedron* **1980**, *36*, 227. Solladié, G. *Synthesis* **1981**, 185.

Ethynyl p-Tolyl (+)-(R)-Sulfoxide (5e). In this case, the ether used initially was replaced with toluene (35 mL) before addition of **2**, and the reaction with **2** was carried out at 0 °C. The reaction using (trimethylsilyl)acetylene (1.37 mL, 9.76 mmol), EtMgBr (3 mL), and **2** (2.3 g, 7.8 mmol) gave **5e** (858 mg, 80%) as colorless crystals: mp 38–40 °C; bp 70–80 °C (bath) at 0.3 mmHg; IR 3270, 2990, 2050, 1600, 1490, 1090, 1060, 1020, 650; ^1H NMR δ (CCl_4) 2.34 (s, 3 H), 3.98 (s, 1 H), 7.43 (AB q, J = 8 Hz, 4 H). Anal. Calcd for C_9H_8OS: C, 65.82; H, 4.91. Found: C, 65.98; H, 4.93.

General Procedure for the Reduction of 1-Alkynyl p-Tolyl Sulfoxides 5 to (E)-1-Alkenyl p-Tolyl Sulfoxides (E)-7. (a) With DIBAH. To a solution of the alkynyl sulfoxide **5** in THF (ca. 20 mL for ca. 6.4 mmol of **5**) was added a solution of DIBAH (1.53 M in toluene, 1.2 equiv) dropwise at −95 to −90 °C under nitrogen. The reaction was usually complete within 10 min. Thus, after 15 min the reaction was quenched with saturated aqueous NH_4Cl. A mixed solvent (ether/EtOAc/CH_2Cl_2, 2:2:1) and water were added, and the resulting mixture was passed through a column of Celite. The organic layer was washed with saturated brine. Removal of the solvent under reduced pressure, followed by chromatography of the residue on silica gel (hexane/EtOAc, 3:1) gave the (E)-1-alkenyl sulfoxide (E)-**7**.

(b) With LAH. To a slurry of LAH (1.2 equiv) in THF (ca. 50 mL for ca. 8 mmol of LAH) was added a solution of the alkynyl sulfoxide **5** in THF (ca. 30 mL for ca. 6.7 mmol of **5**) dropwise at −90 °C under nitrogen, and the reaction mixture was stirred at −90 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl (few drops) and EtOAc, and the resulting solution was passed through a short column of Celite. After removal of the solvent under reduced pressure, chromatography of the residue on silica gel (hexane/EtOAc, 5–10:1) gave (E)-**7**. These alkenyl sulfoxides (E)-**7** thus obtained were shown to be optically pure (ca. 100%) as determined by HPLC analysis on a chiral column (Chiralcel OB, hexane/2-propanol, 85:15).

(E)-1-Pentenyl p-Tolyl (+)-(R)-Sulfoxide ((R)-(E)-7a). DIBAH reduction of **5a** (2.02 g, 9.8 mmol) gave (R)-(E)-**7a** (1.71 g, 84%) and LAH reduction of **5a** (995 mg, 4.82 mmol) gave (R)-(E)-**7a** (870 mg, 87%): IR 2980, 1638, 1600, 1495, 1090, 1040, 1020, 965; ^1H NMR δ ($CDCl_3$) 0.93 (t, J = 7 Hz, 3 H), 1.50 (6 peaks, J = 7 Hz, 2 H), 2.20 (q, J = 7 Hz, 2 H), 2.40 (s, 3 H), 6.10 (d, J = 15.5 Hz, 1 H), 6.40 (dt, J = 15.5 and 6 Hz, 1 H), 7.10–7.60 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.21; H, 7.74. Found: C, 68.94; H, 7.63.

(E)-1-Hexenyl p-Tolyl (+)-(R)-Sulfoxide ((R)-(E)-7b). DIBAH reduction of **5b** (1.41 g, 6.4 mmol) gave (R)-(E)-**7b** (1.23 g, 87%) and LAH reduction of **5b** (1.47 g, 6.68 mmol) gave (R)-(E)-**7b** (1.39 g, 94%): IR 2980, 1638, 1600, 1495, 1090, 1040, 1020, 965; ^1H NMR δ (CCl_4) 0.91 (br t, J = 6 Hz, 3 H), 1.10–1.70 (m, 4 H), 1.90–2.35 (m, 2 H), 2.38 (s, 3 H), 6.10 (d, J = 15.5 Hz, 1 H), 6.40 (dt, J = 15.5 and 6 Hz), 7.10–7.50 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.16. Found: C, 69.98; H, 8.29.

(E)-1-Heptenyl p-Tolyl (+)-(R)-Sulfoxide ((R)-(E)-7c). DIBAH reduction of **5c** (2.34 g, 10 mmol) gave (R)-(E)-**7c** (1.54 g, 74%) and LAH reduction of **5c** (994 mg, 4.24 mmol) gave (R)-(E)-**7c** (953 mg, 95%): IR 2980, 1635, 1600, 1495, 1090, 1040, 1020, 965; ^1H NMR δ ($CDCl_3$) 0.87 (br t, J = 6 Hz, 3 H), 1.10–1.80 (m, 6 H), 2.00–2.40 (m, 2 H), 2.40 (s, 3 H), 6.20 (d, J = 15.5 Hz, 1 H), 6.50 (dt, J = 15.5 and 6 Hz, 1 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 70.84; H, 8.23.

(E)-1-Octenyl p-Tolyl (+)-(R)-Sulfoxide ((R)-(E)-7d). DIBAH reduction of **5d** (2.05 g, 8.3 mmol) gave (R)-(E)-**7d** (1.41 g, 81%) and LAH reduction of **5d** (599 mg, 2.41 mmol) gave (R)-(E)-**7d** (565 mg, 94%): IR 2980, 1638, 1600, 1495, 1090, 1040, 1020, 965; ^1H NMR δ ($CDCl_3$) 0.89 (br t, J = 6 Hz, 3 H), 1.05–1.80 (m, 8 H), 2.05–2.40 (m, 2 H), 2.40 (s, 3 H), 6.20 (d, J = 15.5 Hz, 1 H), 6.50 (dt, J = 15.5 and 6 Hz, 1 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{15}H_{22}OS$: C, 71.97; H, 8.86. Found: C, 71.63; H, 9.22.

General Procedure for the Catalytic Hydrogenation of 1-Alkynyl p-Tolyl Sulfoxides 5 to (Z)-1-Alkenyl p-Tolyl Sulfoxides (Z)-7. A solution of the sulfoxide **5** in anhydrous benzene (ca. 15 mL for ca. 1 mmol of **5**), degassed twice by lyophilization and replacement with argon, was added to Wilkinson

catalyst [$RhCl(PPh_3)_3$] (10–15 wt %) under hydrogen. The mixture was hydrogenated overnight (24 h) at room temperature under an atmospheric pressure. The mixture was diluted with ether and passed through a short column of alumina–Celite. Removal of the solvent under reduced pressure, followed by chromatography of the residue on silica gel (hexane/EtOAc, 5:1), gave the (*Z*)-1-alkenyl sulfoxide (*Z*)-**7** in an excellent yield (see Table III).

(*Z*)-1-Pentenyl *p*-tolyl (–)-(*R*)-sulfoxide ((*R*)-(*Z*)-7a): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 1.00 (t, J = 7 Hz, 3 H), 1.53 (6 peaks, J = 7 Hz, 2 H), 2.40 (s, 3 H), 2.30–2.90 (m, 2 H), 5.90–6.40 (m, 2 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.21; H, 7.74. Found: C, 69.47; H, 7.82.

(*Z*)-1-Hexenyl *p*-tolyl (–)-(*R*)-sulfoxide ((*R*)-(*Z*)-7b): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 0.93 (br t, J = 6 Hz, 3 H), 1.10–1.70 (m, 4 H), 2.40 (s, 3 H), 2.30–2.90 (m, 2 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{13}H_{18}OS$: C, 70.24; H, 8.16. Found: C, 69.94; H, 7.90.

(*Z*)-1-Heptenyl *p*-tolyl (–)-(*R*)-sulfoxide ((*R*)-(*Z*)-7c): IR 2980, 1620, 1600, 1495, 1090, 1035; ^1H NMR δ ($CDCl_3$) 0.90 (br t, J = 6 Hz, 3 H), 1.10–1.80 (m, 6 H), 2.30–2.90 (m, 2 H), 2.40 (s, 3 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 71.38; H, 8.93.

(*Z*)-1-Octenyl *p*-Tolyl (–)-(*R*)-sulfoxide ((*R*)-(*Z*)-7d): IR 2980, 1620, 1600, 1495, 1090, 1035, 1020; ^1H NMR δ ($CDCl_3$) 0.91 (br t, J = 6 Hz, 3 H), 1.10–1.80 (m, 8 H), 2.30–2.90 (m, 2 H), 2.40 (s, 3 H), 5.95–6.40 (m, 2 H), 7.15–7.70 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{15}H_{22}OS$: C, 71.97; H, 8.86. Found: C, 72.07; H, 9.23.

(*Z*)-2-Methyl-1-hexenyl *p*-Tolyl (–)-(*R*)-Sulfoxide (12). To a solution of methylcopper(I), prepared from methyllithium (1.25 M solution, 1.6 mL, 2 mmol) and copper(I) iodide (380 mg, 2 mmol) in THF (15 mL), was added a solution of the hexynyl sulfoxide **5b** (440 mg, 2 mmol) in THF (10 mL) dropwise at –78 °C under nitrogen, and the reaction mixture was stirred for 30 min. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with ether. The combined organic layers were washed with water and saturated brine and evaporated to dryness. PTLC of the residue (hexane/EtOAc, 5:1) gave **12** (321 mg, 68%): IR 2960, 1620, 1600, 1490, 1085, 1035, 1015; ^1H NMR δ (CCl_4) 0.97 (br t, J = 6 Hz, 3 H), 1.15–1.70 (m, 4 H), 1.80 (s, 3 H), 2.50–2.75 (m, 2 H), 5.82 (s, 1 H), 7.70–7.40 (AB q, J = 8 Hz, 4 H). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.16; H, 8.53. Found: C, 71.33; H, 8.35.

Reaction of the Ethynyl Sulfoxide 5e with Butylcopper(I). To a solution of *n*-butylcopper(I), prepared from *n*-butyllithium (1.7 M hexane solution, 0.6 mL, 1 mmol) and copper(I) iodide (190 mg, 1 mmol) in THF (5 mL), was added a solution of the ethynyl sulfoxide **5e** (142 mg, 0.86 mmol) in THF (5 mL) dropwise at –78 °C under nitrogen, and the reaction mixture was stirred for 30 min. The reaction was quenched with MeOH (10 mL) and saturated aqueous NH_4Cl, and the product was thoroughly extracted with ether. The combined extracts were washed with water and saturated brine and evaporated to dryness. PTLC of the residue (hexane/EtOAc, 5:1) gave the hexenyl sulfoxide (*R*)-(*E*)-**7b** (153 mg, 80%), identical with the sample prepared by reduction of the hexynyl sulfoxide **5b**.

***p*-Tolyl Vinyl (+)-(*R*)-Sulfoxide (6) (Improved Preparation).** To a solution of the sulfinate **2** (1.76 g, 6 mmol) in toluene (20 mL) was added a solution of vinylmagnesium bromide (1 M THF solution, 15 mL, 15 mmol) dropwise at –58 °C under nitrogen, and the reaction mixture was stirred for 10 min. The reaction was quenched with saturated aqueous NH_4Cl, and the product was extracted with a mixed solvent (ether/EtOAc/CH_2Cl_2, 2:2:1). The combined extracts were washed with saturated brine and evaporated to dryness. Chromatography of the residue on silica gel (hexane/EtOAc, 2:1) gave **6** (636 mg, 64%): $[\alpha]_D$ +413° (*c* 0.442, EtOH) [lit.[8b] $[\alpha]_D$ +386° (*c* 0.98, EtOH)]. It was reported that compound **6**, $[\alpha]_D$ +391° (*c* 1.2, acetone), was prepared in 45% yield by the reaction of **2** with vinylmagnesium bromide in ether (room temperature to reflux, 3 h).[14]

Phototransformations of Epoxyindanone Adducts. Steady-State and Laser Flash Photolysis Studies[1]

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The phototransformations of several cycloadducts of 2,3-diphenyl-2,3-epoxy-1-indanone are reported. All these substrates exhibited singlet-state-mediated transformations leading to benzoxocinones, whereas in some cases, depending on the substituents present in the alkene moiety, triplet-state-mediated reactions leading to naphthalene derivatives have also been observed. Nanosecond laser pulse excitation gave transient absorptions tentatively assigned to biradicals from Norrish type I photocleavage. In some cases, triplets acting as intermediates for di-π-methane rearrangements to naphthalene derivatives have been observed under energy-transfer sensitization.

Introduction

Phototransformations of several 1,4- and 1,2-epoxy compounds containing keto and ester substituents have already been reported.[3a-f] In a recent communication, we reported the phototransformations of few 1,4- and 1,2-epoxy compounds containing 1,2-dibenzoylalkene moieties.[3g] The photoreactions of these substrates proceed through two distinct pathways—one involving the reaction of the 1,4- or 1,2-epoxy component and the other related to the rearrangement of the 1,2-dibenzoylalkene fragment. In the present investigations we have examined the photoreactions of a few epoxyindanone adducts, **3a–e**, to study the products formed in these reactions and also to characterize the phototransients through laser flash photolysis experiments.

Results and Discussion

(1) Preparative Photochemistry and Product Identification. The starting adducts **3a–e** were prepared

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(2) (a) Indian Institute of Technology. (b) University of Notre Dame.

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