Stereochemical Studies. VI. Asymmetric Selection *via* Elimination. Pyrolyses of Optically Active Sulfoxides to Optically Active Olefins[1]

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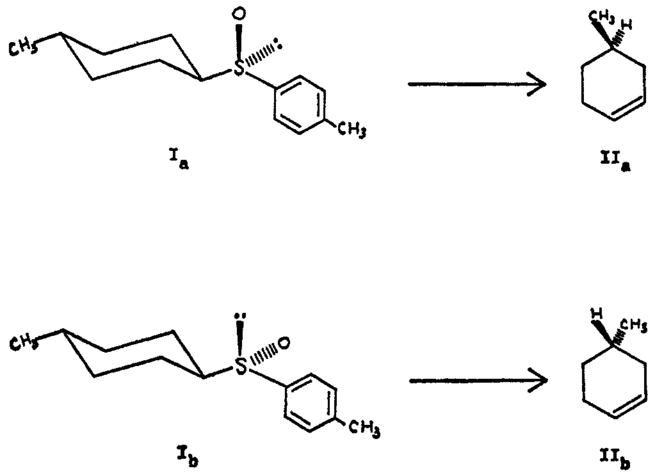
Preparation and pyrolysis of each enantiomeric sulfoxide, (+)-(*R*)- and (−)-(*S*)-*trans*-4-methylcyclohexyl *p*-tolyl sulfoxide, has been carried out to provide the predominant enantiomeric olefin, (+)-(*R*)- and (−)-(*S*)-4-methylcyclohexene, respectively, in optical yields ranging as high as 70%. A topological transition-state analysis in each case has provided an interpretation consistent with all absolute configurational details involved.

In previous papers[3-5] from this laboratory a concept of asymmetric selection centering about pyrolytic *cis* elimination was developed. Experimental verification of those ideas was initially obtained through preparation and pyrolysis of each of the four possible optically active stereoisomers of 4-methylcyclohexyl hydratropates to optically active 4-methylcyclohexene.[3,5] Preliminary results dealing with the preparation and pyrolysis of an optically active sulfoxide[4,6] also served to reinforce the generality of the concept, while formation of optically active 4-methylcyclohexene *via* pyrolytic *cis* elimination from each of the four optically active N-methyl-N-neopentyl-4-methyl-cyclohexylamine oxides[7] has provided still another example.

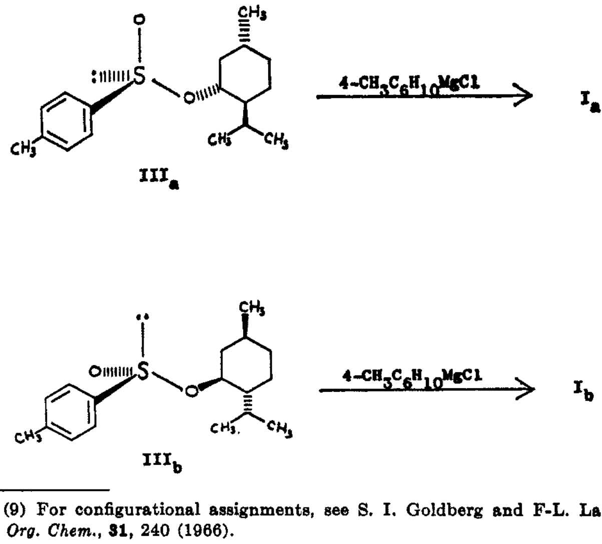
Unlike the situation present in the 4-methylcyclohexyl hydratropates[5] where the asymmetric α carbon, not being directly involved in the changes taking place during the elimination, could only influence the course of elimination to a slight degree, an asymmetric sulfur atom was expected to exert a much greater influence on the steric course of sulfoxide elimination since the sulfur atom and its configurational restrictions would be more intimately involved in the transition state of the elimination. Results of the present study have shown this to be correct. While optical yields of 4-methylcyclohexene formed *via* elimination from the hydratropate esters were less than 1%, elimination of optically active 4-methylcyclohexene from the optically active *p*-tolyl sulfoxides of the present study was shown to take place in optical yields as high as 70%. In addition, this work has provided corroboration of sulfoxide configurational generalities suggested earlier by Mislow, *et al.*[8]

SCHEME I



The optically active sulfoxides prepared and pyrolyzed during the present study were enantiomers of the 4-methylcyclohexyl *p*-tolyl sulfoxide system which were shown to be (+)-(*R*)-*trans*- and (−)-(*S*)-*trans* Ia and Ib, respectively. Separate pyrolysis of each enantiomer gave optically active 4-methylcyclohexene: Ia produced (+)-(*R*)-4-methylcyclohexene[9] (IIa) and Ib gave the (−)-(*S*) olefin[9] as predominant enantiomers (Scheme I). Each sulfoxide was directly obtained by treatment of enantiomeric menthyl *p*-toluenesulfinates[8,10] with 4-methylcyclohexylmagnesium chloride. Thus, the levorotatory sulfinate (IIIa) with sulfur possessing the (*S*) configuration[8] gave Ia. The dextrorotatory sulfinate (IIIb) was obtained as the predominant diastereomer from the reaction of *rac-p*-toluenesulfinyl chloride[11] and (+)-menthol.[12] Upon treatment with 4-methylcyclohexylmagnesium chloride, Ib was produced (Scheme II). Both IIIa and IIIb

SCHEME II



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[1] For paper V in this series, see S. I. Goldberg and I. S. Ragade, *J. Org. Chem.*, **32**, 1046 (1967).

[2] Taken in part from the doctoral dissertation submitted in Jan 1966 by M. S. S. to the Graduate School, University of South Carolina, in partial fulfillment of the requirements for the Ph.D. degree.

[3] S. I. Goldberg and F-L. Lam, *Tetrahedron Letters*, 1893 (1964).

[4] S. I. Goldberg and M. S. Sahli, *ibid.*, 4441 (1965).

[5] S. I. Goldberg and F-L. Lam, *J. Org. Chem.*, **31**, 2336 (1966).

[6] The observation of stereospecificity during pyrolysis of a steroidal sulfoxide by D. M. Jones and M. A. Saeed [*Proc. Chem. Soc.*, 81 (1964)] was probably another example of the general concept.

[7] S. I. Goldberg and F-L. Lam, unpublished work. G. Berti and G. Bellucci [*Tetrahedron Letters*, 3853 (1964)] have also shown that optically active N-methyl-N-(4-methylcyclohexyl)-N-phenylamine oxide gives optically active 4-methylcyclohexene.

[8] K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965).

[9] For configurational assignments, see S. I. Goldberg and F-L. Lam, *J. Org. Chem.*, **31**, 240 (1966).

[10] H. F. Herbrandson, R. T. Dickerson, Jr., and J. Weinstein, *J. Am. Chem. Soc.*, **78**, 2576 (1956).

[11] I. B. Douglas and B. S. Farah, *Org. Syn.*, **40**, 62 (1960).

[12] A. W. Ingersoll, *Org. Reactions*, **2**, 376 (1944).

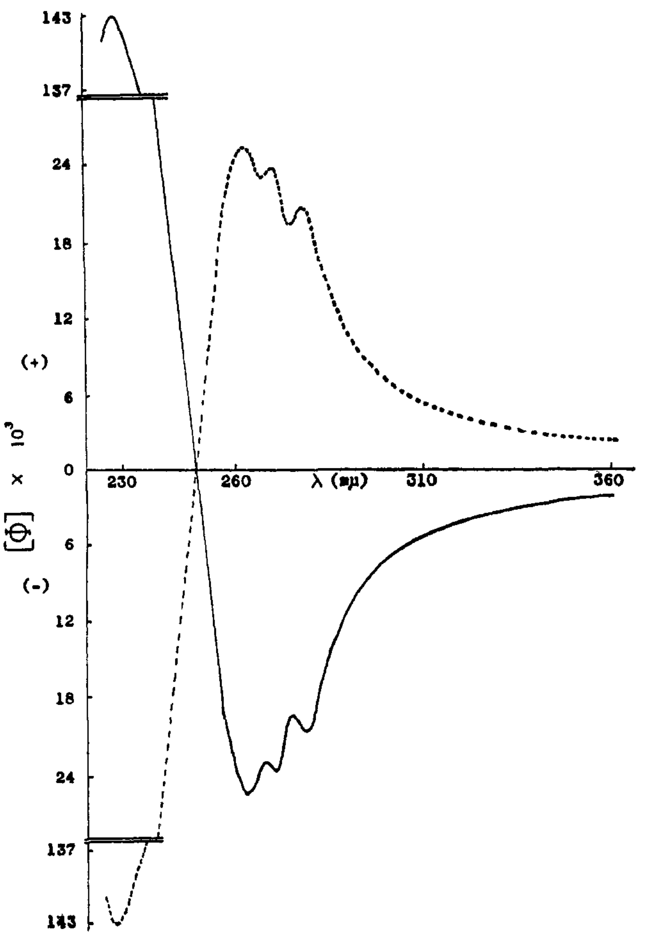

Figure 1.—ORD curves in methanol: - - - -, Ia; ———, Ib.

and Ia and Ib were clearly indicated as being enantiomeric pairs, first by the sodium D line specific rotations, −199.6 and +197.8° for IIIa and IIIb, respectively, and +165.5 and −173.8° for Ia and Ib, respectively. The enantiomorphic connections were more definitively shown by the object mirror image relationship of the ORD curves (Figure 1) determined from the individual substances of each pair.

The 4-methylcyclohexyl group in Ia and Ib was assigned the *trans* configuration. This assignment was indicated from the experience of previous workers in which the stereochemistry of the formation of Grignard reagent from reaction of alkyl halide and magnesium, governed by thermodynamic control, led to the more stable isomer. Thus, Goering and McCarron[13] showed that individual treatment of *cis*- and *trans*-3-methyl-1-chlorocyclohexane, prepared from reaction of phosphorus pentachloride with *trans*- and *cis*-3-methylcyclohexanol, respectively, with magnesium in dry ether, followed by carbonation, gave rise to the same product mixture in each case: *cis*-3-methylcyclohexane-1-carboxylic acid (74%) and *trans*-3-methylcyclohexane-1-carboxylic acid (26%). While the earlier work of Darling, Macbeth, and Mills[14] may not be exactly applicable, those investigators did observe apparent exclusive formation of *trans*-4-methylcyclohexane-1-carboxylic acid (VI) by treatment of a mixture of isomeric 3-methylcyclohexanols with hydrochloric acid, followed by carbonation of the Grignard reagent prepared from the intermediate chlorides.

In the present investigation, it was shown that individual treatment of *cis*- and *trans*-4-methyl-1-chlorocyclohexane (IV and V, respectively), prepared from reaction of phosphorus pentachloride with *trans*- and *cis*-4-methylcyclohexanol,[5] respectively, with magnesium in dry ether, followed by carbonation, gave rise, in each case, to the same acid *trans*-4-methylcyclohexane-1-carboxylic acid (VI) as the only product (Scheme III). It appeared, therefore, a reasonable assumption to extrapolate these results to the similar reactions of the Grignard reagents (prepared from IV and V) with the enantiomeric sulfinates (IIIa and IIIb), and to assign the *trans* configuration to the 4-methylcyclohexyl group present in the resulting sulfoxides (Ia and Ib). The correctness of this assignment may be seen from the consistent picture of configurational analysis which follows.

The analysis may be developed using one of the two enantiomeric sulfoxides—Ia. Since Ia was shown to give rise to (+)-(*R*)-4-methylcyclohexene (IIa) as the predominant enantiomeric olefin, then the transition-state possibilities (with the *trans*-4-methylcyclohexyl group) leading to IIa may be represented by VIIa and VIIb. Of the two, VIIa with the (*R*) configuration at sulfur is clearly the more favored since the *p*-tolyl group is relatively free of serious nonbonded interactions with cyclohexyl protons, while VIIb possessing the (*S*) configuration at sulfur has its *p*-tolyl group involved in close nonbonded interactions with cyclohexyl protons. Therefore, with the 4-methylcyclohexyl group *trans*, the dextrorotatory sulfoxide should possess the (*R*) configuration at sulfur.

On the other hand, if the 4-methylcyclohexyl group is assumed to be *cis*, then transition-state possibilities, VIIc and VIId, leading to IIa may be represented (Scheme IV). By means of the same evaluation presented above for the *trans* case, transition state VIIc with the (*S*) configuration at sulfur would be favored. The choice then is clear-cut: the (*R*) sulfur configuration means the *trans* configuration for the 4-methylcyclohexyl group, while the (*S*) configuration at sulfur means the 4-methylcyclohexyl group is *cis*.

Of the two possibilities, only VIIa with the (*R*) sulfur configuration is consistent with the established stereochemical course of the reaction of sulfinate ester with Grignard reagent to give sulfoxide.

While there is strong evidence[15] for inversion of sulfur configuration during reaction of sulfinate ester with nucleophile in general, specific evidence consistent with inversion of sulfur configuration during reaction of sulfinate ester with Grignard reagent has recently been obtained.[8,16,17] Since the dextrorotatory sulfoxide under discussion was prepared *via* Grignard reagent displacement on (−)-menthyl *p*-toluenesulfinate which is known to possess the (*S*) configuration at sulfur[8] (as shown in IIIa), then the resultant sulfoxide must possess the (*R*) configuration; and, therefore, by the

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(13) H. L. Goering and F. H. McCarron, *J. Am. Chem. Soc.*, **80**, 2287 (1958).

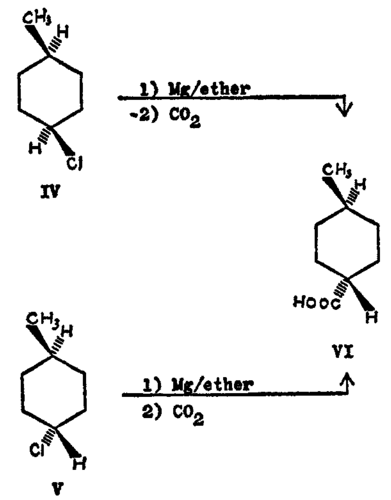
(14) L. H. Darling, A. K. Macbeth, and J. A. Mills, *J. Chem. Soc.*, 1364 (1953).

(15) H. Phillips, *ibid.*, **127**, 2552 (1925); J. Day and D. J. Cram, *J. Am. Chem. Soc.*, **87**, 4398 (1965); C. R. Johnson D. and McCants, Jr., *ibid.*, **87**, 5404 (1965).

(16) M. Kobayashi and M. Terao, *Bull. Chem. Soc. Japan*, **39**, 1343 (1966).

(17) P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, *J. Am. Chem. Soc.*, **89**, 697 (1967).

SCHEME III



SCHEME IV

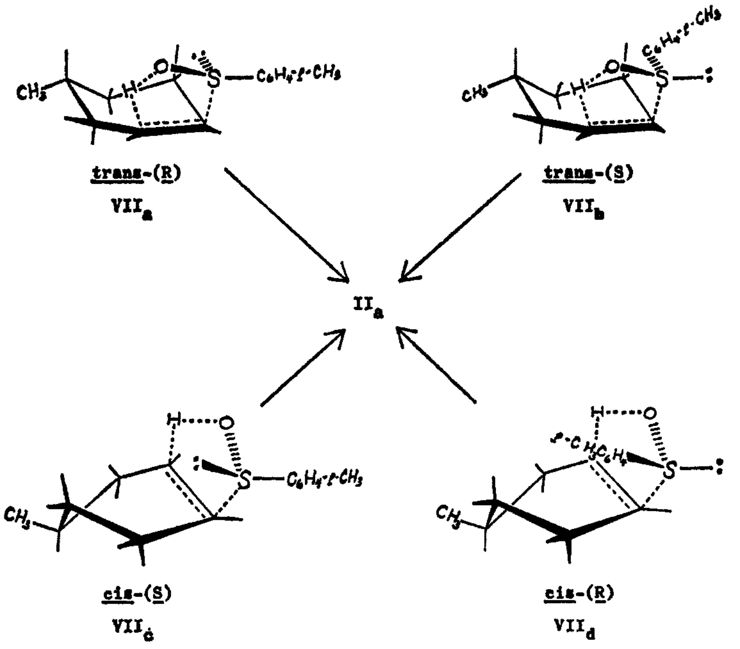


TABLE I

SUMMARY OF PYROLYSIS RESULTS

Sulfoxide		Olefin		
Enantiomer	Pyrolysis temp, °C	Enantiomer	Convn, %	Optical yield, %[a]
(+)-(*R*)-*trans* Ia	200	(+)-(*R*) IIa	15	70
(+)-(*R*)-*trans* Ia	226	(+)-(*R*) IIa	33	51
(+)-(*R*)-*trans* Ia	250	(+)-(*R*) IIa	40	42
(−)-(*S*)-*trans* Ib	250	(−)-(*S*) IIb	29	47

[a] Based on highest reported specific rotation (107°) for 4-methylcyclohexene: J. Zelikow, *Chem. Ber.*, **37**, 1374 (1904).

transition-state analysis presented above, the 4-methylcyclohexyl group must possess the *trans* configuration.

It should be noted, however, that this conclusion necessarily depends on the validity of the five-center transition state for the pyrolytic, *cis* sulfoxide elimination reaction.[18] Indeed, a rigorous, independent proof of the *trans* configuration of the enantiomeric sulfoxides may be used under the same argument in corroboration of the five-center transition-state mechanism.

The large amplitudes of the Cotton effects present in the ORD curves determined from Ia and from Ib (Figure 1) provide another example in support of the generalization suggested by Mislow and co-workers;[8] *i.e.*, sulfoxides that give rise to strong positive Cotton effects in their ORD curves possess the (*R*) configuration, while the (*S*) configuration is indicated for those sulfoxides that exhibit strong negative Cotton effects.

While the absolute configurational details of each sulfoxide may be correlated with that of each predominant enantiomeric olefin obtained through the topological transition-state interpretation already presented, another aspect of this work is the high degree of asymmetric selectivity observed. For nonenzymatic processes to give rise to optical yields ranging up to 70% (see Table I) is indeed remarkable. These results, therefore, indicate a relatively large $\Delta\Delta G$ for the two diastereomeric transition states leading to the enantiomeric olefins in each pyrolysis. The transition-state models, VIIa and VIIb, which depict a large difference in nonbonded interactions present in each, do reflect the significant energy difference indicated by the high optical yields observed in this work.

Experimental Section

General.—All temperature measurements were uncorrected. Infrared spectra were determined with a Perkin-Elmer, Model 337, grating spectrophotometer. Nmr spectra were obtained with a Varian Associates, Model A-60, nmr spectrometer near 30° from chloroform-*d* solutions containing tetramethylsilane (TMS) as internal standard. Chemical shifts were measured under the δ convention in parts per million (ppm) relative to TMS (δ = 0 ppm). Sodium D line polarimeter measurements were made with a Rudolph, Model 80, high-precision instrument, using 1-dm cells. Optical rotatory dispersion curves were determined with a Cary, Model 60, recording spectropolarimeter.[19]

(−)-Menthyl *p*-Toluenesulfinate (IIIa).—To a solution of (−)-menthol (3.8 g, 0.025 mole) in 30 ml of anhydrous ether, cooled to −78°, a solution of *rac-p*-toluenesulfinyl chloride[11] (5 g, 0.03 mole) in 30 ml of anhydrous ether was added dropwise. After the addition was complete and the reaction mixture was allowed to warm to room temperature and remain overnight, it was washed successively with distilled water, 10% aqueous hydrochloric acid, 10% aqueous sodium carbonate solution, and, finally, distilled water. The ethereal residue was dried and evaporated to a crystalline solid which was purified by successive recrystallizations from 15% aqueous acetone solution. Material (1.31 g, 34.2% yield) obtained from the sixth, seventh, and eighth was found to melt identically: mp 106–107° (lit.[10] mp 106–107°); $[\alpha]^{26}\text{D}$ −199.6 ± 0.6° (*c* 1.35, acetone) (lit.[10] $[\alpha]^{25}\text{D}$ −199.2°); infrared $\nu_{\max}^{\text{CCl}_4}$ 1600 (phenyl),[20] 850 (*para*-disubstituted phenyl),[20] and 1135 cm^{-1} (sulfinate ester);[20] nmr δ^{CDCl_3} 7.75–7.20 (4 H, complex multiplet, phenyl protons),[21] 2.40 (3 H singlet, CH_3-phenyl),[21] 1.02–0.70 (19 H, complex array, menthyl group); ORD in methanol (*c* 0.071) at 25–26°, $[\phi]_{262}$ −17,000° (trough with fine structure), $[\phi]_{248}$ 0°, $[\phi]_{235}$ +52,000° (peak) [lit.[8] ORD in absolute ethanol (*c* 0.130–0.0259) $[\phi]_{262}$ −15,400° (trough with fine structure), $[\phi]_{251}$ 0°, $[\phi]_{236}$ +46,100° (peak)].

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(18) C. A. Kingsbury and D. J. Cram, *J. Am. Chem. Soc.*, **82**, 1810 (1960).

(19) We are indebted to Dr. Herman Ziffer of the Laboratory of Physical Biology, Institute of Arthritis and Metabolic Diseases, National Institutes of Health, for the ORD data cited herein.

(20) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1959; K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962.

(21) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Inc., New York, N. Y., 1959; R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1964.

(+)-Menthyl *p*-toluenesulfinate (IIIb) was prepared in the same manner reported above for the levorotatory enantiomer; *p*-toluenesulfinyl chloride[11] (8.5 g, 0.059 mole) and (+)-menthol (5.5 g, 0.035 mole) were obtained by resolution[12] of *rac*-menthol: mp 39–40° (lit.[22] mp 42°), $[\alpha]^{20}\mathrm{D}$ +50.0 ± 0.2° (*c* 2.02, ethanol) [lit.[22] $[\alpha]^{20}\mathrm{D}$ +50.0° (*c* 2.03, ethanol)]. The dextrorotatory isomer was recrystallized five times, providing material which gave rise to an infrared spectrum superimposable upon that determined from the levorotatory enantiomer, and an ORD curve which was found to be related to that of the latter as object and mirror image: mp 101–103°, $[\alpha]^{21}\mathrm{D}$ +197.8 ± 0.5° (*c* 1.40, acetone).

(+)-(*R*)-*trans*-4-Methylcyclohexyl *p*-Tolyl Sulfoxide (Ia).—A solution of (−)-menthyl *p*-toluenesulfinate (IIIa, 8.3 g, 0.029 mole) in 100 ml of anhydrous ether was added dropwise (1 hr) to a stirred solution of 4-methylcyclohexylmagnesium chloride, prepared from 4-methyl-1-chlorocyclohexane (8 g, 0.06 mole) and magnesium turnings (1.7 g, 0.070 g-atom), in 50 ml of anhydrous ether. After the reaction was hydrolyzed by addition of saturated aqueous ammonium chloride solution, it was phase separated and the aqueous phase was extracted with ether. The ether extracts were combined with the original ethereal phase, dried, and evaporated to a crystalline residue. This material was recrystallized six times from *n*-hexane to yield constant-melting **(+)-(*R*)-*trans*-4-methylcyclohexyl *p*-tolyl sulfoxide (Ia)**: 3.5 g (51% yield); mp 126–127°; $[\alpha]^{28}\mathrm{D}$ +165.5 ± 0.6° (*c* 1.02, acetone); infrared $\nu_{\max}^{\mathrm{CCl_4}}$ 1600 (phenyl)[20] and 1048 cm^{-1} (sulfoxide);[20] nmr $\delta^{\mathrm{CDCl_3}}$ 7.7–7.2, 4 H, (multiplet, phenyl protons),[21] 2.40 (3 H, singlet, CH_3-phenyl),[22] and 1.02–0.70 (13 H, complex array, *trans*-4-methylcyclohexyl);[23] ORD in methanol (*c* 0.075) at 25–26° $[\phi]_{263}$ +28,000° (peak with fine structure), $[\phi]_{250}$ 0°, $[\phi]_{228}$ −143,000° (trough).

Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.54. Found: C, 71.48; H, 8.92.

(−)-(*S*)-*trans*-4-Methylcyclohexyl *p*-Tolyl Sulfoxide (Ib).—This material was prepared from (+)-menthyl *p*-toluenesulfinate (IIIb) (0.89 g, 0.0030 mole) and 4-methylcyclohexylmagnesium chloride (0.015 mole) in the same manner as its dextrototatory enantiomer described above. The reaction product, after six recrystallizations from *n*-hexane, gave constant-melting **(−)-(*S*)-*trans*-4-methylcyclohexyl *p*-tolyl sulfoxide (Ib)**: 0.30 g (42% yield), mp 126–127°, $[\alpha]^{24}\mathrm{D}$ −173.8 ± 1.9° (*c* 1.02, acetone). Its infrared and nmr spectra were found to be superimposable upon those obtained from the dextrorotatory enantiomer, and the ORD curves determined from the compounds were related to each other as object and mirror image.

Reaction of *cis*- and *trans*-4-Methyl-1-chlorocyclohexane with Magnesium. A. *cis*- and *trans*-4-Methyl-1-chlorocyclohexanes (IV and V).—*trans*-4-Methylcyclohexanol[5] (22.8 g, 0.197 mole) and anhydrous sodium carbonate (132 g, 1.25 moles) were added to 1000 ml of pure, dry chloroform. To this stirred suspension, pure phosphorus pentachloride (208 g, 1.00 mole) was added portionwise over a period of 45 min, while the reaction mixture was cooled between −10 and −15°. After the addition was complete, the reaction mixture was allowed to warm to room temperature, and the stirring was continued for 18 hr, after which time distilled water was slowly added to the cooled mixture. The chloroform layer was separated, concentrated to 200 ml, dried, and evaporated to a residue which, upon distillation, gave **_cis_-4-methyl-1-chlorocyclohexane (IV)**: 15.8 g (59.6% yield); by 34–36° (4 mm) [lit.[24] bp 41° (10 mm)]; infrared $\nu_{\max}^{\mathrm{neat}}$ 1375 (methyl on carbon)[20] and 710 cm^{-1} (chlorine on carbon);[20] nmr $\delta^{\mathrm{CDCl_3}}$ 4.30 (1 H, multiplet, $ClCH$), 2.10–1.30 (9 H, complex array, cyclohexyl protons), and 0.92 (3 H, apparent doublet, CH_3CH).

The isomeric *trans*-chloride (V) was prepared from *cis*-4-methylcyclohexanol[5] in exactly the same manner described above for the *cis*-chloride.[25] ***trans*-4-Methyl-1-chlorocyclohexane (V)** was obtained in 28% yield, bp 37–38° (4.5 mm) [lit.[11] bp 40° (10 mm)].

B. Conversion of Each Isomeric Chloride (IV and V) to *trans*-4-Methylcyclohexane-1-carboxylic Acid (VI).—Into a solution of 4-methylcyclohexylmagnesium chloride, prepared from *trans*-4-methyl-1-chlorocyclohexane (V, 2.95 g, 0.023 mole) and magnesium turnings, in anhydrous ether, was bubbled carbon dioxide during 30 min. The reaction mixture was then hydrolyzed by addition of dilute hydrochloric acid, and then it was extracted with ether. The combined and dried ether extracts were then treated with an ethereal solution of diazomethane[27] until the yellow color of diazomethane just persisted. Evaporation of the ether gave methyl *trans*-4-methylcyclohexane-1-carboxylate (VI), 1.75 g (50.4% yield). The same, sole ester was obtained in 38.2% yield through identical treatment of *cis*-4-methyl-1-chlorocyclohexane (IV).

The two products were shown to be identical by means of their superimposable infrared spectra [$\nu_{\max}^{\mathrm{CCl_4}}$ 1740 and 1170 cm^{-1} (methyl carboxylate)[20]] and by means of identical nmr spectra [$\delta^{\mathrm{CDCl_3}}$ 3.65 (3 H, singlet, CH_3OOC) and 2.2–0.8 (13 H, complex array, pattern of which similar to that displayed by the *trans*-4-methylcyclohexyl protons in *trans*-4-methylcyclohexanol)].

Each methyl ester was examined by gas chromatography under identical conditions. Not only did each possess an identical retention time, but there was also no indication of the presence of isomeric material.

Finally, a sample of authentic *trans*-4-methylcyclohexane-1-carboxylic acid, mp 108–110 (lit.[14] mp 110–111°), was treated with diazomethane, and the resulting methyl ester was shown (infrared spectra and gas chromatographic behavior) to be identical with each of the esters obtained from the isomeric alcohols.

Pyrolyses of (+)-(*R*)- and (−)-(*S*)-*trans*-4-Methylcyclohexyl *p*-Tolyl Sulfoxides (Ia and Ib).—Pyrolyses were carried out by injection of a carbon tetrachloride solution of the sulfoxide into a gas chromatograph[28] with the inlet port maintained at the desired temperature. The pyrolysate was then carried in a helium stream of flow rate 100 ml/min onto a 16-ft × 0.25 in. column which was packed with 15% (w/w) Carbowax 20 M on Diatoport-W support of 60–80 mesh. The column temperature was maintained at 65°, and the pure olefinic product of each pyrolysis was collected and shown to be 4-methylcyclohexene by means of superimposable infrared spectra determined from it and from authentic 4-methylcyclohexene.

Samples of **(+)-(*R*)-*trans*-4-methylcyclohexyl *p*-tolyl sulfoxide** (Ia) (115 mg, 0.487 mmoles; 63.7 mg, 0.270 mmole; and 213 mg, 0.903 mmole) were pyrolyzed at 200, 226, and 250°, respectively, to give **(+)-(*R*)-4-methylcyclohexene (IIa)**: 6.2 mg (15% conversion), $[\alpha]^{22}\mathrm{D}$ +75 ± 1.3° (*c* 0.62, methanol), 70% optical yield;[29] 7.4 mg (33% conversion, $[\alpha]^{24}\mathrm{D}$ +55 ± 1.1° (*c* 0.74, methanol), 51% optical yield; and 30.0 mg (40% conversion), $[\alpha]^{30}\mathrm{D}$ +45.3 ± 0.5° (*c* 2.22, methanol), 42.3% optical yield,[29] respectively.

(−)-(*S*)-*trans*-4-Methylcyclohexyl *p*-tolyl sulfoxide (Ib) (103 mg, 0.436 mmole) was pyrolyzed at 250° to yield **(−)-(*S*)-4-methylcyclohexene (IIb)**: 10.7 mg (29.4% conversion), $[\alpha]^{24}\mathrm{D}$ −50.6 ± 1.1° (*c* 1.07, methanol), 47.3% optical yield.[29]

Registry No.—Ia, 13064-85-2; Ib, 13085-19-3; IIa, 5710-02-1; IIb, 5681-54-9; IIIa, 13085-18-2; IIIb, 13064-80-7; IV, 13064-81-8; V, 13064-82-9; VI, 13064-83-0.

Acknowledgment.—The authors are pleased to acknowledge their thanks to the donors of the Petroleum Research Fund of the American Chemical Society for the support provided to this work by a PRF grant.

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[22] J. Read and W. J. Grubb, *J. Soc. Chem. Ind.* (London), **51**, 329T (1932).

[23] While these alkyl proton resonances were not resolved, a clear difference in the pattern of signals was found in the spectra of *trans*- and *cis*-4-methylcyclohexanols. The pattern displayed by the methylcyclohexyl group in the sulfoxides was found to be very similar to that found in the spectrum obtained from authentic *trans*-4-methylcyclohexanol.[5] The *trans* assignment is, however, based upon more rigorous evidence which is discussed in the text of this report.

[24] M. Mousseron and R. Granger, *Compt. Rend.*, **206**, 1489 (1938).

[25] The expected configurational inversion during reaction of each isomeric alcohol with phosphorus pentachloride in chloroform solution[26] was indicated by the fact that the chlorides gave rise to infrared spectra which differed only in the region 1250–700 cm^{-1}. Also, in the nmr spectra, the pattern of signals due to the cyclohexyl protons resembled, in each case, the pattern displayed by the cyclohexyl protons of each of the corresponding isomeric alcohols.

[26] For previous examples of the use of phosphorus pentachloride in chloroform solution to effect inversion during conversion of alcohol to alkyl chloride, see R. J. Bridgewater and C. W. Shoppee, *J. Chem. Soc.*, 1709 (1953); C. W. Shoppee and G. H. R. Summers, *ibid.*, 1790 (1952); ref 13.

[27] F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons Inc., New York N. Y., 1943, p 165.

[28] F & M Scientific Corp., Model 500.

[29] Based on the highest specific rotation value (107°) reported[30] for 4-methylcyclohexene.

[30] See Zielkow, footnote *a*, Table I.