rate constant for the enzymic reaction is about 10^9 times as fast as that for the simple decarboxylation of acetoacetate ion (both constants are first order), and the data therefore suggest that the decarboxylation of the ketimine is 10^9 as fast as that for the uncatalyzed decarboxylation of acetoacetate ion.[1,4,5]

Acknowledgments. This work was supported by Grant No. GM 04712 from the Institute of General Medical Sciences of the National Institutes of Health and by the Petroleum Research Fund, administered by the American Chemical Society. One of us (K. T.) wishes to express his appreciation of a fellowship from Harvard University and the support in various forms by Teijin Limited, Japan.

Asymmetric Syntheses Using Optically Active Oxosulfonium Alkylides[1]

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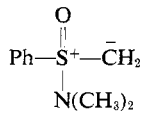
Abstract: Asymmetric inductions in the reactions of chiral (dialkylamino)aryloxosulfonium alkylides with aldehydes and ketones to give oxiranes and with electrophilic alkenes to give cyclopropanes are reported; optical yields were found to be in the range of 7–43%. The ylides were generated from optically active (dialkylamino)-alkylaryloxosulfonium fluoroborates which were prepared from resolved sulfoximines.

A convenient and stable reagent for the synthesis of oxiranes and cyclopropanes has been shown to be (dimethylamino)phenyloxosulfonium methylide (**1**).[2] The sulfur center of this ylide is chiral; if resolved into one enantiomeric form, the ylide should be capable of transferring its methylene in an asymmetric manner. Thus, optically active oxiranes and cyclopropanes would be obtained. In this paper we describe the synthesis of opically active (dialkylamino)-aryloxosulfonium alkylides and the asymmetric inductions in their reactions.[3]



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Optically active ylides derived from trialkyl- and diarylmethylsulfonium salts have been prepared, but racemize too quickly to be capable of significant asymmetric synthesis.[4] The proposed mechanism of their racemization is one of pyramidal inversion. The quaternary sulfur of the oxosulfonium ylide, *e.g.*, **1**, cannot become planar so readily and should be configurationally stable.

The preparation of optically active oxiranes by asymmetric epoxidations, and the production of optically active cyclopropanes by a variety of asymmetric syntheses is well documented.[5] Many chiral peracids have been reacted with alkenes to give optically active epoxides;[6] asymmetric induction is usually less than 2%.

A number of the chiral cyclopropane syntheses cited[5a] involve methylene or alkylidene transfer to an optically active substrate, *e.g.*, the addition of dimethyloxosulfonium methylide to (−)-menthyl cinnamates gave the enantiomer, (1*R*,2*R*)-*trans*-2-arylcyclopropanecarboxylic acids, in 3–4% excess, upon hydrolysis of the esters.[7]

For simple methylene transfer reactions, there are few asymmetric syntheses of cyclopropanes where the optical activity is introduced by the chirality of the reagent. One in which the reagent is presumed to be chiral is a Simmons–Smith reaction in the presence of (−)-menthol; for example, *trans*-methyl crotonate reacted with methylene iodide and zinc–copper couple to give *trans*-methyl 2-methylcyclopropanecarboxylate in 1.9% optical purity.[8]

An example of chiral catalyst for asymmetric methylene transfer is also known. The chelate, prepared from (−)-(*S*)-α-methylbenzylamine, salicylaldehyde, and cupric ion, has been used to effect additions of diazoalkyl compounds to alkenes in optical yields of 6–8%.[9]

Results and Discussion

Optically active (dialkylamino)alkylaryloxosulfo-

(1) Part XLV in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

(2) C. R. Johnson, M. Haake, and C. W. Schroeck, *J. Amer. Chem. Soc.*, **92**, 6594 (1970).

(3) For a preliminary report of this work, see C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968).

(4) D. Darwish and R. L. Tomilson, *ibid.*, **90**, 5938 (1968); B. M. Trost and R. F. Hammen, *ibid.*, **95**, 962 (1973).

(5) (a) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions," 1st ed, Prentice-Hall, Englewood Cliffs, N. J., 1971, pp 219–296. (b) For asymmetric epoxidations, see also the following F. Montanari, I. Moretti, and G. Torre, *Boll. Sci. Fac. Chim. Ind. Bologna*, **26**, 113 (1968); J. L. Pierre, P. Chautemps, and P. Afnaud, *Bull. Soc. Chim. Fr.*, 1317 (1969). (c) For asymmetric syntheses of cyclopropanes, see also the following R. Noyori, H. Takaya, Y. Nakanisi, and H. Nozaki, *Can. J. Chem.*, **47**, 1242 (1969); S. Inamasu, N. Horiiki, and Y. Inouye, *Bull. Chem. Soc. Jap.*, **42**, 1393 (1969); S. Sawada and Y. Inouye, *ibid.*, **42**, 2669 (1969).

(6) (a) H. B. Henbesti, *Chem. Soc., Spec. Publ.*, **No. 19**, 83 (1965); (b) R. C. Ewins, H. B. Henbest, and M. A. McKervey, *Chem. Commun.*, 1085 (1967).

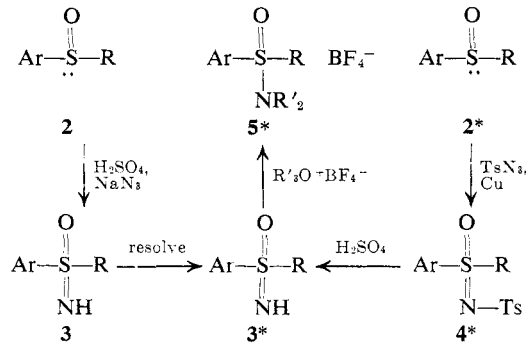
(7) H. Nozaki, H. Ito, D. Tunemato, and K. Kondo, *Tetrahedron*, **22**, 441 (1966).

(8) S. Sawada, J. Oda, and Y. Inouye, *J. Org. Chem.*, **33**, 2141 (1968).

(9) H. Nozaki, H. Takawa, S. Moriuti, and R. Noyori, *Tetrahedron*, **24**, 3655 (1968).

nium fluoroborates **5**, the conjugate acids of ylides **6**, were readily obtained by alkylation of optically active sulfoximines. Sulfoximines in high optical purity were obtained from optically active sulfoxides or by resolution of racemic sulfoximines, *via* (+)-10-camphorsulfonic acid[10] (Scheme I).

Scheme I[a]



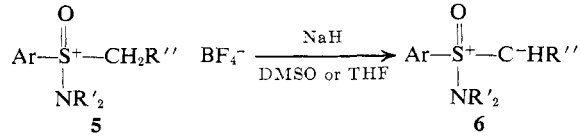
	Ar	(when shown on formula) R	R′	R″	Absolute config. (when opt. active)
a	*p*-tolyl	Me	Me	H	*R*
b	*p*-tolyl	Et	Me	Me	*R*
c	phenyl	Me	Me	H	*S*
d	2-mesityl	Me	Me	H	*R*
e	phenyl	Me	Et	H	*S*

[a] Ts = *p*-$CH_3C_6H_4SO_2$; * indicates an optically active compound.

Ylide precursor, (−)-(*R*)-(dimethylamino)methyl-*p*-tolyloxosulfonium fluoroborate (**5a**), was prepared from (+)-(*R*)-methyl *p*-tolyl sulfoxide (**2a**).[11,12] For the preparation of the *dl*-sulfoximine (**3a**), it was convenient to react the *dl*-sulfoxide **2** with hydrazoic acid (sodium azide, sulfuric acid, chloroform); it was found, however, that these conditions lead to racemization of the optically active sulfoxide (**2**) prior to conversion to sulfoximine. The problem was readily circumvented by the use of copper-catalyzed decomposition of *p*-toluenesulfonyl azide.[13,14] By an adaptation of a described procedure,[13] (−)-(*R*)-*N*-(*p*-toluenesulfonyl)-*S*-(*p*-tolyl)sulfoximine (**4a**) was prepared in high yield. Hydrolysis of **4a** in concentrated sulfuric acid gave (−)-(*R*)-*S*-methyl-*S*-(*p*-tolyl)sulfoximine (**3a**).[15] Methylation with trimethyloxonium fluoroborate yielded (−)-(*R*)-(dimethylamino)methyl-*p*-tolyloxosulfonium fluoroborate (**5a**). The overall yield for the sequence **2a** → **5a** was 71%.

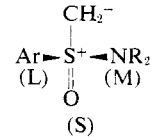
The ylide precursor fluoroborate salt **5c** was prepared beginning with racemic sulfoxide **1c**. The racemic sulfoximine (**3c**)[1] was resolved to high optical purity (presumed to be 100%) with (+)-10-camphorsulfonic acid. The dimethylation again was done with trimethyloxonium fluoroborate in the presence of anhydrous sodium carbonate. The optical purity of **5c** was shown to be at least 96% by reductive cleavage of the dimethylamino group with dissolving aluminum amalgam to give (−)-(*S*)-methyl phenyl sulfoxide.[16] It should be noted that salts **5a** and **5c** are conveniently of opposite configuration and thus, should be complementary in asymmetric syntheses.

The optically active ylides, formed by treating optically active salts **5** with sodium hydride, were generated and reacted at room temperature in dimethyl sulfoxide or THF in the same manner as that described for the racemic ylide (**1**).



Methylene Transfer Reaction with Chiral Ylides 6a and 6c. The initial asymmetric syntheses were performed using ylide **6a**.[3] In the reaction of this ylide with aldehydes and ketones, optically active oxiranes were obtained. For example, when ylide **6a** was allowed to react with benzaldehyde, the product, (+)-(*R*)-styrene oxide, was obtained in 60% yield with an optical purity of 20%.[17] Reaction of ylide **6a** with electrophilic olefins led to optically active cyclopropanes. For example, reaction with *trans*-methyl cinnamate gave a 76% yield of (+)-(1*S*,-2*S*)-*trans*-methyl 2-phenylcyclopropanecarboxylate in 30.4% optical purity. *In all cases where comparative data are available,*[5] *the optical purity obtained is the highest reported to date for a direct asymmetric synthesis.* A summary of asymmetric syntheses employing ylides **6a** and **6c** is provided in Table I.

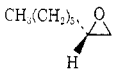
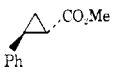
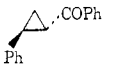
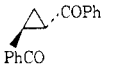
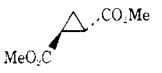
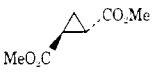
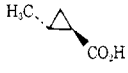
Effects of Structural Solvent and Variation. Structural variation at nitrogen was most easily achieved. Alkylation of the resolved sulfoximine (**3c**) with triethyloxonium fluoroborate gave (+)-(*S*)-(diethylamino)methylphenyloxosulfonium fluoroborate (**5e**). It was felt that the more symmetrical the structure, the less stereoselective would be its reactions. By ethylating the nitrogen, instead of methylating, the middle-sized group about sulfur, the dialkylamino group, approaches the size of the aryl group, the largest group about the sulfur. Methylide **6e** was indeed slightly less stereoselective than **6a**.



A methylide with increased bulk on the aryl group was also studied; this decrease in the symmetry of the ylide was expected to increase its stereoselectivity. By methylation of sulfoximine (**3d**), (−)-(*R*)-dimethylamino)-2-mesitylmethyloxosulfonium fluoroborate (**5d**) was prepared. The corresponding methylide (**6d**) was found, however, to be less stereoselective in some cases and slightly more stereoselective in others than the *p*-tolyl ylide (**6a**). More surprisingly, **6d** gave products of opposite chirality to those obtained from the *p*-tolyl reagent.

(10) R. Fusco and F. Tericoni, *Chem. Ind. (Milan)*, **47**, 61 (1965); *Chem. Abstr.*, **62**, 10357*h* (1965).
(11) K. K. Anderson, *Tetrahedron Lett.*, 93 (1962).
(12) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **87**, 1958 (1965).
(13) H. Kwart and A. A. Kahn, *ibid.*, **89**, 1950 (1967).
(14) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *ibid.*, **90**, 2721 (1968); D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, and D. J. Duchamp, *ibid.*, **92**, 7369 (1970).
(15) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950).
(16) J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).
(17) In the preliminary communication (ref 3) this optical purity was erroneously reported to be 5%.

Table I. Reactions of Optically Active Methylides **6a** and **6c**[a]

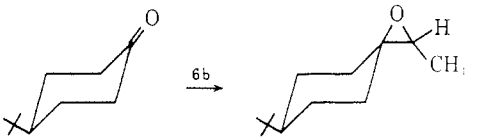
Substrate	Ylide	Product[b]	Mol % excess ylide	Time, hr	Yield, %	$[\alpha]_D$, deg (acetone)	Optical purity, %	Absolute config.[c]
Benzaldehyde	**6a**		20	25	60[d]	+1.56	20[e]	*R*
p-Chlorobenzaldehyde	**6a**		20	12	74[d]	+0.60		(*R*)
Acetophenone	**6a**		20	120	38[d]	+1.90		(*R*)
n-Heptaldehyde	**6c**		50	2[f]	39[d]	−0.77		(*S*)
trans-Methyl cinnamate	**6a**		50	72	76[d]	+95.0	30.4[g]	1*S*,2*S*
trans-Benzalacetophenone	**6a**		20	12	94[d]	+137.7	35.3[h]	(1*S*,2*S*)
trans-1,4-Diphenyl-2-butene-1,4-dione	**6a**		20	12	76[d]	+46.9		(1*S*,2*S*)
Dimethyl fumarate	**6a**		20	12	60[d]	+30.4	15.2[i]	1*S*,2*S*
Dimethyl maleate	**6a**		20	12	56[d]	+35.7	17.8[i]	1*S*,2*S*
trans-Methyl crotonate	**6c**		20	16	54[j]	−9.9[k]	11.9[k]	1*R*,2*R*

[a] All of the reactions were run in dimethyl sulfoxide at 25°. [b] All of the products were liquids except that from *trans*-benzalacetophenone. [c] Absolute configuration shown in parentheses are tentative assignments based solely on analogy to the established configurations of related products produced by reaction of ylide **6a**. [d] Compared with an authentic racemic sample. [e] The rotation was measured at a concentration of 9.0%. This optical purity is based on an $[\alpha]_D$ +7.94° (*c* 9.78, acetone) of an authentic sample assumed to be pure; $[\alpha]_D$ +35.17° (neat). (The maximum rotation is reported to be $[\alpha]_D$ +34.2° (neat).) [f] The aldehyde was added to the ylide over the 45 min of this reaction time to minimize condensation. [g] Based on $[\alpha]_D$ (max) +311° [Y. Inouye, T. Sugita, and H. M. Walborsky, *Tetrahedron*, **20**, 1965 (1964)]. [h] Based on $[\alpha]_D$ (max) +390.5° (obtained by fractional crystallization, mp 70–71°). [i] Based on $[\alpha]_D$ (max) +200° (ethanol) [S. Sawada, K. Takehana, and Y. Inouye, *J. Org. Chem.*, **33**, 1767 (1968)]. A control sample obtained later showed the same $[\alpha]_D$ in acetone or ethanol. [j] Isolated as the acid after basic hydrolysis of the ester. *Anal.* Calcd for $C_5H_8O_2$: C, 59.98; H, 8.05. Found: C, 60.15; H, 8.31. [k] This optical rotation was obtained in chloroform. The optical purity is based on a literature value corrected to 100% of $[\alpha]_D$ +83.6° for the enantiomer in chloroform: T. Sugita and Y. Inouye, *Bull. Chem. Soc. Jap.*, **39**, 1075 (1966).

Another striking difference between the *p*-tolyl and mesityl ylides (**6a** and **6d**) was the effect of solvent. Ylide **6a** was more stereoselective in dimethyl sulfoxide than in tetrahydrofuran. The opposite effect, though less pronounced, was observed with ylide **6d**. Data summarizing the effects of structural variation and solvent are shown in Table II.

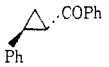
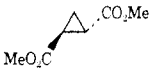
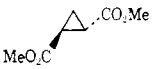
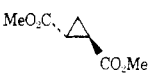
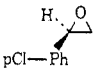
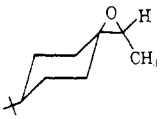
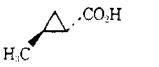
Alkylidene Transfer Reactions. Substitution on the carbanionic site of a chiral ylide introduced a somewhat different type of asymmetric synthesis. In the reaction of a methylide with a symmetrical ketone or a terminal methylene compound, a chiral product would not be obtained. With a substituted methylide, however, chiral products would result. In previous syntheses, a carbon of the electrophile became an asymmetric center upon attack by a methylide. In the reaction of an alkylide with a symmetrical ketone or terminal methylene compound, it is the nucleophilic carbon of the ylide which becomes the asymmetric center (see examples below with an ethylide).

The precursor of a chiral ethylide, (+)-(*R*)-(dimethylamino)ethyl-*p*-tolyloxosulfonium fluoroborate (**5b**), was readily synthesized starting with the optically active sulfoxide (**1b**). The ethylide (**6b**) was reacted with the symmetrical ketone, 4-*tert*-butylcyclohexanone to give only the (*Z*)-oxirane in 64% yield $[\alpha]_D$ +3.2° (*c* 1.0, acetone).



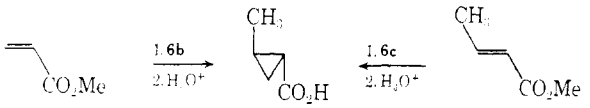
It should be noted that in an asymmetric synthesis with this monosubstituted methylide, the asymmetric atoms of the betaine intermediates are adjacent to one another. With a methylide, the two asymmetric centers are separated by a methylene. Thus, products of higher optical purity might be expected from asymmetric synthesis with the former. When the ethylide (**6b**) was reacted with methyl acrylate, the product after hydrolysis, (+)-(1*S*,2*S*)-*trans*-2-methylcyclopropane-

Table II. Effects of Solvent and Structural Variation on the Stereoselectivity of the Chiral Ylides (**6**)[a]

Substrate	Ylide	Product	Solvent	[α]D, deg (acetone)	Optical[b] purity, %	Yield, %
trans-Benzalacetophenone	**6a**		DMSO	+137.7	35.3	94
	6c		THF[c]	−27.4	7.0	84
	6d		DMSO	−83.2	21.3	55
	6d		THF[c]	−142.8	36.5	78
	6e		DMSO	−112.0	28.7	75
Dimethyl maleate	**6a**		DMSO	+35.7	17.8	60
	6a		THF[c]	+16.2	8.1	
Dimethyl fumarate	**6a**		DMSO	+30.4	15.2	60
	6d		DMSO	−38.1	19.0	55
p-Chlorobenzaldehyde	**6a**		DMSO	+0.60		74
	6d		DMSO	0.00		51
4-*tert*-Butylcyclohexanone	**6b**		DMSO	+3.24		64[d]
Methyl acrylate	**6b**		DMSO	+29.8 +36.1[e]	43.2	74[f]

[a] All of the reactions were run at 25° with a 10–20% mole excess of the ylide. [b] See Table I for [α] (max) values and literature references. [c] These reactions were complete after a standard "overnight"-reaction time. It was observed with the less reactive substrate, *trans*-methyl cinnamate, that the reaction proceeded more slowly in tetrahydrofuran than in dimethyl sulfoxide. [d] This reaction was run with a 50% mole excess of ylide for 72 hr. The oxirane was compared with an analyzed sample produced by reaction with the racemic ethylide **6b**. [e] This measurement was made in chloroform. [f] This material was compared with an analyzed sample prepared by the reaction of the methylide **6c** with methyl crotonate (Table I).

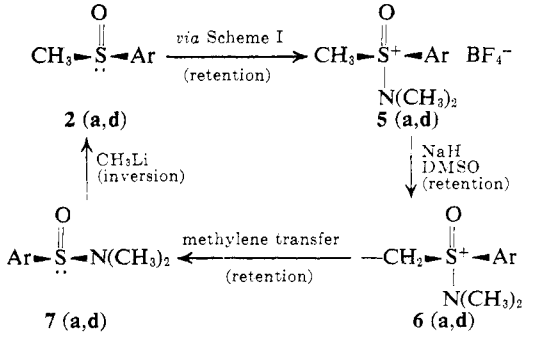
carboxylic acid, was obtained in 74% yield with an optical purity of 43%. The enantiomer resulted from the reaction of methylide **6c** with methyl crotonate, but with a much lower optical purity of 12%. See Table II for the details of these ethylide examples.



Attempts were made to synthesize the benzylide precursor, (dimethylamino)benzylphenyloxosulfonium fluoroborate. Hydrazoic acid–sulfuric acid led to destruction of the benzyl methyl sulfoxide. The racemic sulfoxide did react cleanly in a copper-catalyzed reaction with *p*-toluenesulfonyl azide to give a 73% yield of *N*-(*p*-toluenesulfonyl)-*S*-benzyl-*S*-phenylsulfoximine. This material decomposed in an attempt to hydrolyze it with concentrated sulfuric acid. Numerous attempts with milder conditions or reductive methods also failed to yield the desired free NH sulfoximine.

Absolute Configurations of the Reagents. The absolute configuration of salt **5c** was established by reductive cleavage of the dimethylamino group with dissolving aluminum amalgam to give (−)-(*S*)-methyl phenyl sulfoxide. Such reductive cleavage reactions are known to proceed with retention of configuration.[18] The absolute configuration of **5e** follows directly from that of **5c** since the two were made from the same precursor. The absolute configurations of salts **5a** and **5b** can be assumed from their syntheses from sulfoxides of known absolute configuration. The absolute configuration of **5a** was confirmed and that of **5d** established by analysis of the stereochemical reaction cycle depicted in Scheme II.

Scheme II



From methylene transfer reactions the by-products, *N*,*N*-dimethyl arenesulfinamides (**7a** and **7d**), were isolated and treated with methyllithium in ether at −78°.[19,20] This reaction, which proceeds by inversion of configuration, gave the corresponding sulfoxides (+)-**2a** and (+)-**2d**; both known to be of *R* absolute configuration.[21] In Scheme II, the steps **2** → **5**, **5** → **6**, and **6** → **7** all involve retention of configuration at

(18) C. W. Schroeck and C. R. Johnson, *J. Amer. Chem. Soc.*, **93**, 5305 (1971).

(19) S. Colonna, R. Giovine, and F. Montanari, *Chem. Commun.*, 865 (1968).

(20) J. Jacobus and K. Mislow, *ibid.*, 253 (1968).

(21) J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).

the chiral sulfur atom. The reaction cycle can be classified by the Cram designations[22] as a diligiostatic (the Ar and oxygen ligands remain static) podal (the cycle starts and ends on the same enantiomer) stereochemical cycle involving one inversion and one ligand metathesis (the electron pair and the methyl interchange their bonding sites on the chiral sulfur tetrahedron).

Considering that the *p*-tolylsulfonium salt (**5a**) was synthesized from the optically active sulfoxide (+)-**2a**, it is interesting to note that the reaction of methyllithium with sulfinamide **7a** returned the sulfoxide (+)-**2a** ([α]D +125.1°, optical purity 81%). This, in theory, could eliminate the need for a new resolution step with each asymmetric synthesis.

Experimental Section

General. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a 1-dm cell. Infrared spectra were obtained on a Perkin-Elmer 137 Infracord. Nuclear magnetic resonance (nmr) spectra were obtained on either a Varian A-60 or a T-60 spectrometer. Microanalyses were performed by Midwest Microlab Inc., Indianapolis, Ind. 46226.

(−)-(*R*)-*N*-(*p*-Toluenesulfonyl)-*S*-methyl-*S*-(*p*-tolyl)sulfoximine (4a).[13,14] To a solution of 10 g (0.065 mol) of (+)-(*R*)-methyl *p*-tolyl sulfoxide (**2a**), [α]D +149.9° (*c* 1.2, acetone), and 25.6 g (0.130 mol) of *p*-toluenesulfonyl azide in 50 ml of absolute methanol was added Raney copper (*ca.* 3 g) wet from a methanol suspension. The mixture was gently refluxed and the decomposition of the azide was monitored by observing the 2130-cm^{-1} band in the infrared spectrum. After 24 hr, more copper (*ca.* 1 g) was added, and the mixture was refluxed for an additional 24 hr. The mixture was then transferred to a 1-l. erlenmeyer flask, using 300 ml of methylene chloride and 200 ml of a saturated Na_2EDTA solution. After 30 min of vigorous stirring, the mixture was filtered through Celite; the residue was washed with several portions of water and methylene chloride. The organic layer was separated, and the aqueous layer was further extracted with methylene chloride. The combined organic extracts were then washed with 5% sodium hydroxide solution in order to remove any *p*-toluenesulfonamide. The solution was then dried over magnesium sulfate and evaporated. The residue was recrystallized from methylene chloride–ether yielding 18.4 g (90.3%) of a white solid: mp 158–161°; [α]D −144° (*c* 1.15, acetone) [lit.[14] mp 160–162°; [α]D −142° (*c* 1.060, acetone)].

(−)-(*R*)-*S*-Methyl-*S*-(*p*-tolyl)sulfoximine (3a).[14,15] A solution of 17.7 g (0.0568 mol) of (−)-(*R*)-*N*-(*p*-toluenesulfonyl)-*S*-methyl-*S*-(*p*-tolyl)sulfoximine (**4a**), [α]D −144° (*c* 1.15, acetone), in 27 ml of concentrated sulfuric acid was heated on a steam bath for 15 min. The mixture was then carefully poured into 100 ml of water. Upon cooling, crystals began to form, but they were not filtered. The mixture was made slightly alkaline with 20% sodium hydroxide solution and extracted with methylene chloride. The solution was dried over magnesium sulfate and evaporated giving 8.2 g (85%) of a light brown oil. The material crystallized upon standing, mp 58–62°; [α]D −33.8° (*c* 1.13, acetone) [lit.[14] mp 59–61°; [α]D −32.4° (*c* 0.885, acetone)].

(−)-(*R*)-(Dimethylamino)methyl-*p*-tolyloxosulfonium Fluoroborate (5a). To a solution of 7.5 g (0.044 mmol) of (−)-(*R*)-*S*-methyl-*S*-(*p*-tolyl)sulfoximine, [α]D −33.8° (*c* 1.13, acetone), in 80 ml of methylene chloride was added 7.6 g (0.050 mol) of trimethyloxonium fluoroborate all at once. This mildly exothermic reaction was cooled initially in a water bath (15–20°). After 1 hr, 24 g (0.220 mol) of anhydrous sodium carbonate was added, and the mixture was allowed to stir for 3 hr. Then another 7.6 g (0.050 mol) of trimethyloxonium fluoroborate was added and the stirring continued for an additional 3 hr. Finally, another 0.5 equiv (3.8 g) of the fluoroborate was added and the mixture stirred for 1 more hr. The inorganic salts were then filtered and were washed with methylene chloride and hot ethanol. After evaporation of the solvent and recrystallization from ethanol, 9.1 g (73%) of a white solid was obtained, mp 65–67°; [α]D −4.6° (*c* 2.0, acetone). The liquor was concentrated and found to contain mainly mono-N-methylated sulfoximine, so this material was treated as above with more methylating agent (*ca.* 2 g) using sodium carbonate in methylene chloride. A similar work-up yielded 2.5 g (20%) of salt **5a**, identical with the first crop; the combined yield was 93%. The spectral properties of this material were identical with those of a racemic sample, mp 85–86°, which analyzed as follows.

Anal. Calcd for $C_{10}H_{16}BF_4NOS$: C, 42.13; H, 5.66. Found: C, 42.40; H, 5.73.

(+)-(*R*)-Ethyl *p*-tolyl sulfoxide (2b) was prepared from resolved (−)-menthyl *p*-toluenesulfinate[23] and ethylmagnesium bromide.[11] The product was concentrated under high vacuum to give 7.1 g (85%) of a light amber oil: [α]D +201.7° (*c* 1.4, acetone) [lit.[12] [α]D +187.5° (acetone)]; ir (neat) 780, 810, 1010, 1045, 1085 cm^{-1}, identical with that of an authentic racemic sample.

(−)-(*R*)-*N*-(*p*-Toluenesulfonyl)-*S*-ethyl-*S*-(*p*-tolyl)sulfoximine (4b) was prepared from sulfoxide **1b** by the same procedure which was previously described for the synthesis of (−)-(*R*)-*N*-(*p*-toluenesulfonyl)methyl-*p*-tolylsulfoximine (**4a**). After concentrating the product under high vacuum, a 92% yield of viscous liquid was obtained: [α]D −121.5° (*c* 1.0, acetone); ir (neat) 750, 815, 1040, 1065, 1080, 1210, 1300 cm^{-1}.

(−)-(*R*)-*S*-Ethyl-*S*-(*p*-tolyl)sulfoximine (3b) was obtained by hydrolysis of the *N*-(*p*-toluenesulfonyl)sulfoximine (**4b**). The procedure was the same as that used for the hydrolysis of **4a** in the synthesis of (−)-(*R*)-*S*-methyl-*S*-(*p*-tolyl)sulfoximine (**3a**) (described above). A light brown oil was obtained in 54% yield: [α]D −23.5° (*c* 1.3, acetone); ir (neat) 685, 713, 773, 815, 965, 1090, 1205, 3290 cm^{-1}, identical with that of an authentic racemic sample.

(+)-(*R*)-(Dimethylamino)ethyl-*p*-tolyloxosulfonium fluoroborate (5b) was prepared by dimethylation of the sulfoximine (**3b**) with trimethyloxonium fluoroborate and sodium carbonate by the same procedure used for the synthesis of (dimethylamino)methylphenyloxosulfonium fluoroborate (**5c**).[2] A 77% yield of a white solid was obtained after recrystallization from isopropyl alcohol: mp 87–89°; [α]D +7.9° (*c* 2.0, acetone); ir (Nujol) 720, 745, 825, 950, 1050 (s), 1220, 1265 cm^{-1}, identical with that of an authentic racemic sample.

(+)-(*S*)-*S*-Methyl-*S*-phenylsulfoximine (3c).[10] A boiling solution of 62 g (0.265 mol) of (+)-10-camphorsulfonic acid in 400 ml of dry acetone was carefully added to a boiling solution of 40 g (0.258 mol) of racemic *S*-methyl-*S*-phenylsulfoximine (**3c**) in 800 ml of acetone. (Due to the slight exothermicity, this mixing should be done after removing the heat.) After mixing, the solution was concentrated to a volume of 1100 ml and allowed to cool slowly to room temperature. Crystals began to form while the mixture was boiling. After 24 hr at 25°, the crystals were filtered and washed with acetone and then ether. The off-white crystals (*ca.* 40 g), mp 180–182°, were dissolved in water and the solution was made slightly alkaline with 20% sodium hydroxide. The sulfoximine was extracted from the aqueous solution with methylene chloride. After drying over magnesium sulfate, removal of the solvent yielded 16 g (80%) of **3c** as a colorless oil, [α]D +36.5° (*c* 1.2, acetone). Upon cooling to −20°, the material crystallized, mp 31–33°.

Repetition of the above procedure with a small sample of the resolved sulfoximine failed to give a material with a higher optical rotation. The sulfoximine was, therefore, assumed to be 100% optically pure from the first crystallization. The levorotatory isomer can be obtained in fair optical purity (*ca.* 85%) from the mother liquor.

(+)-(*S*)-(Dimethylamino)methylphenyloxosulfonium fluoroborate (5c) was prepared from sulfoximine **3c**, [α]D +36.5° (*c* 1.2, acetone), by the alkylation procedure described for the preparation of the racemic salt.[2] Recrystallization from ethanol gave a white solid, mp 128–130°; [α]D +12.6° (*c* 2.05 acetone); spectral properties were identical with those of the racemic salt.

2-Mesityl Methyl Sulfoxide. Reduction of freshly prepared 2-mesitylenesulfonyl chloride with zinc dust gave 2-mesitylenethiol[24] which was alkylated with methyl iodide in basic aqueous methanol to give 2-mesityl methyl sulfide. A cold solution of 30 g (0.181 mol) of 2-mesityl methyl sulfide in 1 l. of methanol was added to a cold solution of sodium metaperiodate (40.7 g, 0.190 mol) in 400 ml of water. The mixture was allowed to stir at room temperature for 48 hr. The mixture was filtered. The solution was diluted with saturated sodium sulfate solution and extracted with methylene chloride. The extracts were dried ($MgSO_4$) and concentrated giving

(22) D. C. Garwood and D. J. Cram, *J. Amer. Chem. Soc.*, **92**, 4575 (1970).

(23) H. F. Herbrandson and R. T. Dickerson, *ibid.*, **81**, 4102 (1959).

(24) E. Bourgeois, *Recl. Trav. Chim. Pays-Bas*, **18**, 426 (1899); C. H. Wang and S. G. Cohen, *J. Amer. Chem. Soc.*, **79**, 1924 (1957).

30.9 g (94%) of a pale yellow oil. Analysis by tlc showed only one spot: ir (neat) 855, 945, 1040, 1070, 1290 (w) cm^{-1}. This material was used without further purification for the conversion to sulfoximine **3d**. A small amount of this material crystallized upon standing. Recrystallization from hexane yielded a white solid, mp 55–58° [lit.[25] mp 58–59°].

(+)-*S*-(2-Mesityl)-*S*-methylsulfoximine was prepared from the sulfoxide using hydrazoic acid by the same procedure reported for the synthesis of *S*-methyl-*S*-phenylsulfoximine.[2] A 60% yield of a light brown oil was obtained: ir (neat) 710, 853, 995, 1055, 1110, 1215, 3320 cm^{-1}.

(−)-(*R*)-*S*-(2-Mesityl)-*S*-methylsulfoximine (3d). A boiling solution of 7.3 g (0.031 mol) of (+)-10-camphorsulfonic acid in 300 ml of acetone was added to a hot solution of 6.0 g (0.031 mol) of the racemic sulfoximine (**3d**) in 300 ml of acetone. This clear brownish solution was allowed to cool very slowly to 25°. The white needles were isolated and repeatedly recrystallized from acetone until a constant rotation was obtained for the free sulfoximine. After a total of six recrystallizations, the resolved salt was dissolved in water. The solution was made slightly alkaline with 10% sodium hydroxide and extracted with methylene chloride. After drying over magnesium sulfate, the solvent was evaporated *in vacuo* giving 1.83 g (62%) of a colorless oil; $[\alpha]_D$ −39.4° (*c* 1.0, acetone). The liquor from the first crystallization was evaporated and treated in a similar manner yielding 2.47 g of light brown oil, $[\alpha]_D$ −25.3° (*c* 1.0, acetone).

(−)-(*R*)-(Dimethylamino)-2-mesitylmethyloxosulfonium Fluoroborate (5d). To 1.76 g (9.0 mmol) of (−)-(*R*)-2-mesitylmethylsulfoximine (**3d**) in 20 ml of methylene chloride was added 1.48 g (1.0 mmol) of trimethyloxonium fluoroborate all at once. After stirring for 2 hr at 25°, anhydrous ammonia[26] was bubbled into the clear solution for 10 min. The precipitated ammonium fluoroborate was filtered, and the filter cake was washed well with methylene chloride. The filtrate was evaporated to dryness to remove the dissolved ammonia and the solvent was replenished. Another equivalent (1.48 g) of trimethyloxonium fluoroborate was added, and the mixture was allowed to stir at 25°. After 2 hr, the solution was evaporated to a viscous oil which crystallized upon standing. Recrystallization from isopropyl alcohol yielded 2.25 g (78%) of white solid: mp 117–119°; $[\alpha]_D$ −17.7° (*c* 2.0, acetone); ir (neat, before recrystallization) 690, 735, 780, 860, 940, 1050 (s), 1225, 1265 cm^{-1}.

Anal. Calcd for $C_{12}H_{20}BF_4NOS$: C, 46.02; H, 6.44. Found: C, 46.23; H, 6.55.

(+)-(*S*)-(Diethylamino)methylphenyloxosulfonium Fluoroborate (5e). To a solution of 6.2 g (0.040 mol) of (+)-*S*-methyl-*S*-phenylsulfoximine (**3c**), $[\alpha]_D$ +35.4° (*c* 1.5, acetone), in 50 ml of methylene chloride in a 20° water bath was added 8.9 g (0.045 mol) of triethyloxonium fluoroborate all at once. After 30 min, 24 g (0.226 mol) of anhydrous sodium carbonate was added and the mixture was allowed to stir at 25° for 6 hr. Then another 8.9 g of triethyloxonium fluoroborate was added to the slurry. After 2 hr, the mixture was filtered and the inorganic salts were washed well with methylene chloride. Evaporation of the solvent yielded a colorless viscous liquid (96%) which crystallized upon standing at 0°. Recrystallization from absolute ethanol gave 9.7 g (81%) of a white solid: mp 71–73°; $[\alpha]_D$ +10.8° (*c* 2.5, acetone); ir (neat) 680, 750, 1050 (s), 1240 cm^{-1}; nmr (acetone-d_6) δ 8.5–7.7 (m, 5, Ph), 4.36 (s, 3, SCH_3), 3.70 (q, 4, CH_2CH_3), 1.36 (t, 6, CH_2CH_3).

Anal. Calcd for $C_{11}H_{18}BF_4NOS$: C, 44.17; H, 6.07. Found: C, 43.90; H, 6.27.

Isolation of *N,N*-Dimethyl-*p*-toluenesulfinamide (7a). Ylide **6a** was prepared from (−)-(dimethylamino)methyl-*p*-tolyloxosulfonium fluoroborate (**5a**), $[\alpha]_D$ −4.6° (*c* 2.0, acetone), and reacted with dimethyl fumarate by the usual method.[2] The crude product mixture was quickly chromatographed on silica gel with increasing concentrations of ether in pentane. A 0.407-g (64%) yield of the sulfinamide was obtained as a white solid: mp 65.0–66.5°; $[\alpha]_D$ −168.7° (*c* 1.0, ethanol) [lit.[19] $[\alpha]_D$ +157° (ethanol)]; ir (CCl_4) 705, 942, 1066, 1085, 1170 (w) cm^{-1}.

Reaction of *N,N*-Dimethyl-*p*-toluenesulfinamide (7a) with Methyllithium.[19,20] A solution of 0.407 g (2.1 mmol) of *N,N*-dimethyl-*p*-toluenesulfinamide (**7a**), $[\alpha]_D$ −168.7° (*c* 1.0, ethanol), in 12 ml of dry ether (distilled from sodium) was cooled to −78° under nitrogen. Then 4.5 mmol of methyllithium was added (2.35 *M* in ether, 1.92 ml) and the mixture was allowed to stir at −78° for 2.5 hr. The reaction was quenched with wet ether and poured into water. The aqueous layer was separated and extracted with more ether. The combined ethereal solutions were dried over magnesium sulfate and evaporated, giving an oil. Analysis of the infrared spectrum showed that the material was a mixture of the starting material and the expected sulfoxide. A crystalline solid was obtained upon cooling a hexane solution of the mixture. Recrystallization again from hexane gave (+)-(*R*)-methyl phenyl sulfoxide (**2a**), $[\alpha]_D$ +125.1 (*c* 1.0, acetone) [lit.[27] $[\alpha]_D$ +156° (acetone)]; its spectral properties were identical with those of an authentic sample of **2a**.

***N,N*-Dimethylbenzenesulfinamide (7c), *N,N*-Dimethylmesitylenesulfinamide (7d), and *N,N*-Diethylbenzenesulfinamide (7e).** These sulfinamides, the by-products of the methylene transfer reactions of ylides **6c, 6d,** and **6e,** respectively, were generally not isolated. Each was obtained in pure form for characterization at least once. Column chromatography on silica gel with benzene or with low concentrations (5–25%) of ether in pentane gave clean separation of the cyclic product from the amide; ether quickly eluted the sulfinamides. The physical properties of each of the title compounds are described below. Compound **7c**: liquid, ir (neat) 688, 700, 754, 923, 1056, 1086, 1170 (w) cm^{-1}; nmr ($CDCl_3$) δ 7.5 (s, 5, Ph), 2.25 (s, 6, $N(CH_3)_2$). Compound **7d**: liquid; $[\alpha]_D$ −209.3° (*c* 1.0, acetone); ir (neat) 852, 922, 1040, 1080. Compound **7e**: liquid, $[\alpha]_D$ +103.3° (*c* 1.0, ethanol); ir (neat) 680, 700, 755, 895, 1010, 1055, 1085, 1175 cm^{-1}; nmr (CCl_4) δ 7.8–7.4 (m, 5, Ph), 3.10 (q, 4, $N(CH_2CH_3)_2$), 1.10 (t, 6, $N(CH_2CH_3)_2$).

Reaction of (−)-(*R*)-*N,N*-Dimethyl-2-mesitylenesulfinamide (7d) with Methyllithium. A solution of 0.167 g (0.79 mmol) of the sulfinamide (**7d**), $[\alpha]_D$ −209.3° (*c* 1.0, acetone), in 4 ml of dry ether was treated with 2.8 mmol of methyllithium at −78°. The mixture was allowed to stir under nitrogen for 3 hr at −78°. After quenching with wet ether, the mixture was allowed to warm up and was water washed. The aqueous layer was further extracted with ether. The combined extracts were dried over magnesium sulfate and evaporated. The crude product appeared by analysis of the infrared spectrum to be a mixture of the sulfinamide starting material and the expected sulfoxide; tlc analysis (silica gel) showed two spots. Chromatography of this small amount of material on a 2 ft × 0.5 in. column of silica gel with ether gave a fair, but not complete, separation. The sulfoxide-enriched fractions were combined; the infrared spectrum of this material was identical with an authentic sample of 2-mesityl methyl sulfoxide except for the appearance of several weak bands due to traces of sulfinamide (**7d**); $[\alpha]_D$ +24.0° (*ca.* 1% acetone) [lit.[18] $[\alpha]_D$ +43.5° (*R* configuration, 30.3% optically pure)].

(25) G. M. Gasperini, G. Modena, and P. E. Tadesio, *Gazz. Chim. Ital.*, **96**, 12 (1960).

(26) An attempt to prepare this salt using anhydrous sodium carbonate by the same procedure used for the synthesis of (dimethylamino)methylphenyloxosulfonium fluoroborate (ref 2) failed; monomethylated sulfoximine was obtained.

(27) K. Mislow, M. Axelrod, D. R. Rayner, G. Gotthardt, L. M. Coyne, and G. S Hammond, *J. Amer. Chem. Soc.*, **87**, 4958 (1965).