independent imine hydrolysis.[50] There is no driving force for concerted proton transfer from water to the incipient hydroxide ion (to produce a new water molecule and a new hydroxide ion), and such a proton transfer would impose additional entropic requirements on the transition state.[21a,51] The alternative "concerted" mechanism for the water reaction in which water acts as a general base to remove a proton from nitrogen may be excluded on similar grounds, at least for the more basic amines. The pK_a' values for the protonated imines which are the immediate products of the elimination reaction should be about four to seven units below those of the parent amines,[50a,52,53] *i.e.*, between 0 and −3 for semicarbazide, and between 1 and 4 for hydrazine. Since the pK_a of the hydronium ion is −1.7, there is little or no thermodynamic advantage derived from proton transfer to water in the transition state and "concerted" catalysis by water is unlikely. The points for the water reactions fall far above the Brønsted lines for general base catalysis and roughly an order of magnitude above the Brønsted lines for general acid catalysis.

(50) (a) K. Koehler, W. Sandstrom, and E. H. Cordes, *J. Amer. Chem. Soc.*, **86**, 2413 (1964); (b) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N. Y., 1969, p 491.
(51) W. P. Jencks, *J. Amer. Chem. Soc.*, **94**, 4731 (1972).
(52) E. H. Cordes and W. P. Jencks, *ibid.*, **85**, 2843 (1963).
(53) R. Wolfenden and W. P. Jencks, *ibid.*, **83**, 2763 (1961).

The slope, β_N, of approximately 0.8 for the dependence of the rate of the uncatalyzed reaction on the pK_a' of the parent hydrazine (Figure 6) suggests a transition state midway between starting material and product for this reaction, since β_N for the complete transformation of carbinolamine to protonated hydrazone should be 1.4 if β_N for the equilibrium formation of neutral products is 0.4 and β_N for imine protonation is 1.0. Cordes and coworkers[40] have suggested on the basis of secondary isotope effects that the transition state for hydroxide ion attack on protonated imines derived from an aliphatic amine closely resembles the tetrahedral carbinolamine. Thus the transition state for the reverse reaction, uncatalyzed formation of Schiff bases from strongly basic carbinolamines, appears to be less far advanced toward product than the analogous hydrazone-forming elimination.

The uncatalyzed reaction is more sensitive to the nature of the amine ($\beta_N = \sim 0.8$) than the hydronium-ion catalyzed reaction ($\beta_N = \sim 0.4$, Figure 6). This is in accord with the previously described structure–reactivity considerations,[44] and is a result of the fact that the transition state for the uncatalyzed reaction is reached later than that for the hydronium ion catalyzed reaction, and hence is more sensitive to stabilization of the incipient double bond by electron donation from the amine.

Nucleophilic Alkylidene Transfer Reagents. Anions of *N*-(*p*-Tolylsulfonyl)sulfoximines[1a]

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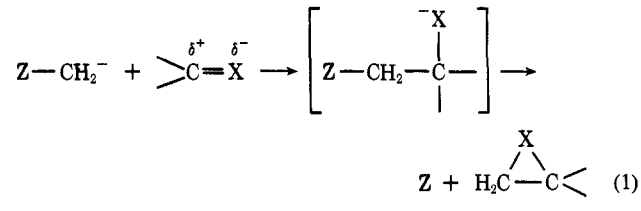
Contribution from the Department of Chemistry, Wayne State University, Detroit, Michigan 48202. *Received January 10, 1973*

Abstract: A number of symmetrical *S,S*-dialkyl- and *S*-alkyl-*S*-aryl-*N*-(*p*-tolylsulfonyl)sulfoximines have been prepared (Table I); the general method used was the copper-catalyzed reaction of *p*-toluenesulfonyl azide with sulfoxides. *S,S*-Dimethyl-*N*-(*p*-tolylsulfonyl)sulfoximine was prepared in 90% yield by the cupric ion-catalyzed reaction of Chloramine-T with DMSO. Reaction of these sulfoximines with sodium hydride or *n*-butyllithium afforded sulfonimidoyl-stabilized carbanions which act as nucleophilic alkylidene transfer reagents upon reaction with substrates containing electrophilic double bonds; ketones reacted to yield oxiranes, imines gave aziridines, and α,β-unsaturated ketones afforded cyclopropanes (Table II). Cycloalkylidene group transfer yielded spiro compounds. Examples are given showing the addition of these stabilized anions to an oxirane, a carbodiimide, and a nitrile. Reaction of the sodium or lithium salt of (−)-(*R*)-*S*-methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine with benzalacetophenone gave (1*R*,2*R*)-*trans*-1-benzoyl-2-phenylcyclopropane 49% optically pure; reaction with acetophenone gave (−)-2-methyl-2-phenyloxirane ($[\alpha]_D$ −6.9°); reaction with benzalaniline afforded (−)-1,2-diphenylaziridine ($[\alpha]_D$ −12.9°).

The addition of an alkylidene group across an electrophilic double bond to form a three-membered ring is usually achieved by employing diazoalkanes or sulfonium ylides. Such reactions can be illustrated in the most general terms by eq 1. The driving forces for these nucleophilic alkylidene transfer reactions are (1) the formation of a relatively stable



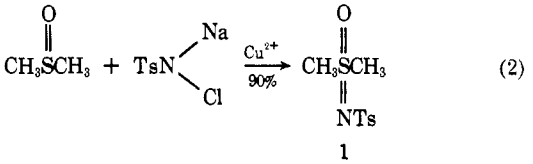
(1)

intermediate adduct and (2) the expulsion of a good leaving group by the intermediate. In the typical cases noted above, both the reagent (diazo compounds

(1) (a) Part XLII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623). (b) Research Scientist on leave from CSIRO, Canberra, Australia.

or ylides) and the leaving group (nitrogen or sulfides, etc.) are neutral molecules. In this paper we detail the preparation and utilization of a new series of nucleophilic alkylidene transfer reagents, metal salts of *N*-(*p*-tolylsulfonyl)sulfoximines.[2] These reagents differ from ylides in that the reagent, itself, and the resulting leaving group are metal salts.

Preparation of the Reagents. The simplest member of the series, dimethyl-*N*-tosylsulfoximine (**1**), is commercially available[3] or may be prepared readily by a copper-catalyzed[4] reaction of Chloramine-T and DMSO (eq 2). For high yield preparative purposes, this reaction appears to be limited to use with DMSO.

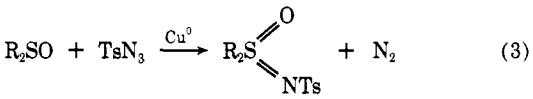


(2)

1

Ts = *p*-$CH_3C_6H_4SO_2$

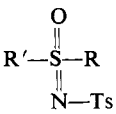
The method of choice for the preparation of *N*-tosylsulfoximines, in general, is the copper-catalyzed decomposition of *p*-toluenesulfonyl azide in the presence of a sulfoxide (eq 3). This method, discovered by Kwart



(3)

and Kahn,[5] has proven to be exceedingly general (Table I). It may be used for the preparation of

Table I. Preparation of *N*-(*p*-Tolylsulfonyl)sulfoximines by Reaction of Sulfoxides with *p*-Toluenesulfonyl Azide

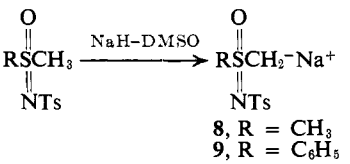


Compd	R′	R	Yield (%)	Mp, °C
1	CH_3	CH_3	94	167–169
2	CH_3CH_2	CH_3CH_2	60	89–91
3	$(CH_3)_2CH$	$(CH_3)_2CH$	57	75–77
4	C_6H_5	CH_3	90	107–109
5	C_6H_5	c-C_5H_9	58	142.5–143.5
6	C_6H_5	c-C_6H_{11}	52	145.5–146
7	C_6H_5	$C_6H_5CH_2$	73	148–149

optically active *N*-tosylsulfoximines from optically active sulfoxides without any apparent racemization.[6]

Other methods for the preparation of *N*-tosylsulfoximines include the reaction of "free" sulfoximines with *p*-toluenesulfonyl chloride[7] and the oxidation of *N*-tosylsulfilimines.[8] However, both of these methods have serious limitations. Free sulfoximines are often difficult to prepare, especially in those cases where one or more of the *S*-alkyl groups is other than aryl or primary alkyl. Sulfoximines unsubstituted on nitrogen are usually prepared under strongly acidic conditions in polar media, *e.g.*, reaction of sulfoxides with hydrazoic acid in a mixture of sulfuric acid and chloroform. Under these conditions, heterolysis of a carbon–sulfur bond usually occurs in those cases where one or more of the alkyl groups is secondary or tertiary. *N*-Tosylsulfilimines are easily prepared from sulfides and Chloramine-T, but oxidation of these materials to sulfoximines is often difficult due to the low nucleophilicity of the sulfur substituted by the highly electronegative *N*-tosyl group.

The preparation of the *N*-(*p*-tolylsulfonyl)sulfonimidoyl-stabilized carbanions was accomplished by reaction of the *N*-tosylsulfoximines in DMSO with sodium hydride or *n*-butyllithium and in THF by treatment with *n*-butyllithium (*e.g.*, eq 4). The most frequently used system was the sodium hydride–DMSO system; hydrogen evolution began immediately and it was usually complete in from 2 to 4 hr at room temperature. Such anions are generally quite

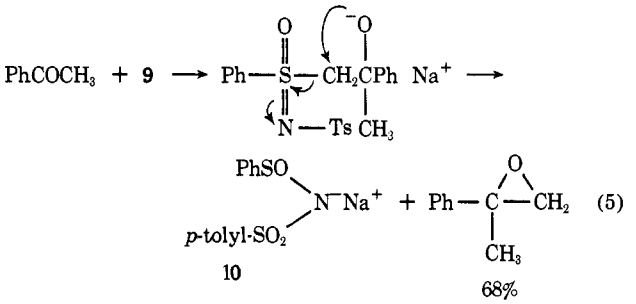


(4)

8, R = CH_3
9, R = C_6H_5

stable at room or slightly elevated temperatures. Thus, **4** was quantitatively recovered by acidification of a dimethyl sulfoxide solution of **9** after standing for 24 hr at 27°; after 25 hr at 70° only 45% of **4** was recovered.

Reactions of *N*-(*p*-Tolylsulfonyl)sulfonimidoyl-Stabilized Carbanions. A summary of the reactions of these reagents with a variety of electrophilic substrates is presented in Table II. The reaction of **9** with a typical substrate containing an electrophilic double bond is illustrated in eq 5. The products were usually ob-



(5)

10

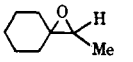
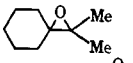
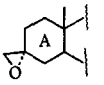
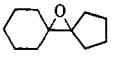
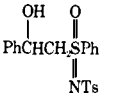
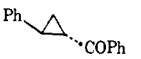
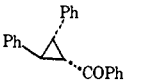
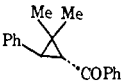
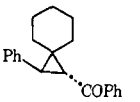
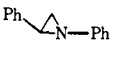
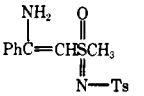
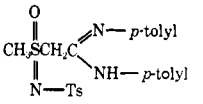
68%

tained by quenching the reaction mixture with water and extraction with an appropriate solvent. The sodium salt of *N*-phenylsulfinyl-*p*-toluenesulfonamide (**10**) (or related salts) as well as the usual reaction solvent (DMSO) remained in the aqueous layers. Acidification of the aqueous phase from reaction (eq 5) and extraction provided the relatively unstable *N*-phenylsulfinyl-*p*-toluenesulfonamide.

Our experience in working with these and a variety of sulfonium ylide reagents leads us to believe that for simplicity of preparation and manipulation these new reagents are competitive with or superior to any others previously described for the preparation of substituted oxiranes from ketones. The utility of these reagents for such transformations is well demonstrated by the reactions of the anions derived from dimethyl-, diethyl-,

(2) For a preliminary report, see C. R. Johnson and G. F. Katekar, *J. Amer. Chem. Soc.*, **92**, 5753 (1970); C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *ibid.*, **93**, 3771 (1971).
(3) Columbia Organic Chemicals Co., Inc., Columbia, S. C.
(4) D. Carr, T. P. Seden, and R. W. Turner, *Tetrahedron Lett.*, 477 (1969), employed copper powder as catalyst. We have found soluble cupric salts to be convenient catalysts for this reaction.
(5) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).
(6) C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968).
(7) H. R. Bentley and J. K. Whitehead, *J. Chem. Soc.*, 2081 (1950); C. R. Johnson and J. J. Rigau, *J. Org. Chem.*, **33**, 4340 (1968).
(8) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 2721 (1968).

Table II. Reactions of Anions of *N*-Tosylsulfoximines

Reaction no.	*N*-Tosyl-sulfoximine	Solvent-base[a]	Substrate	Product	Reaction time, hr[b]	Yield, %
1	**1**	A	Cyclohexanone		12	78
2	**2**	A	Cyclohexanone		20	62
3	**3**	A	Cyclohexanone		16	63
4	**1**	A	4-*tert*-Butyl cyclohexanone		24	84
5	**1**	A	Androstane-3,17-dione		24	49
6	**5**	A	Cyclohexanone		20	34
7	**6**	A	Cyclopentanone		20	22
8	**1**	A	Acetophenone		12	68
9	**4**	A	Acetophenone		12	68
10	**4**	A	Benzaldehyde		0.25	43
11	**4**	C	Styrene oxide		1	66
12	**1**	A	Benzalaceto-phenone		16	88
13	**4**	A			16	86
14	**4**	B			3	86
15	**7**	A			1	77
16	**3**	A			12	86
17	**6**	A			2	39
18	**4**	A	Benzalaniline		1	86
19	**1**	C	Benzonitrile		24	67
20	**1**	B	Di-*p*-tolyl-carbodiimide		3	47

[a] A = NaH-DMSO; B = *n*-BuLi-THF; C = *n*-BuLi-DMSO. [b] In many cases the reactions were not monitored and excess reaction times were used for convenience.

and diisopropyl-*N*-tosylsulfoximines with cyclohexanone to give the corresponding spiro epoxides (Table II, reactions 1, 2, and 3). The production of the oxirane in reaction 3 utilizing the sulfoximine derived reagent, in our hands, was found to be far superior than the route involving the synthesis and manipulation of diphenylsulfonium isopropylide.[9]

When the product is an epoxide which is readily subject to ring opening by nucleophiles, somewhat reduced yields of the epoxides are obtained; *e.g.*, when benzaldehyde was reacted with **9** the yield of styrene oxide was only 43%. In a subsequent experiment it was found that styrene oxide reacted rapidly with the reagent to produce an adduct (Table II, reaction 11).

These reagents exhibit both regio- and stereoselectivity. Reaction of **8** with 4-*tert*-butylcyclohexanone resulted in the production of the (Z)-orirane exclusively. Reaction of **8** with a steroid containing both a five- and six-membered ketonic ring resulted in reaction at the sterically more accessible 3 position (reaction 5). These reagents react with α,β-unsaturated ketones to produce cyclopropyl ketones resulting from conjugate addition of the reagent. In contrast to sulfonium ylides, use of these carbanionic reagents for

(9) E. J. Corey, M. Jaulelat, and W. Oppolzer, *Tetrahedron Lett.*, 2325 (1967).

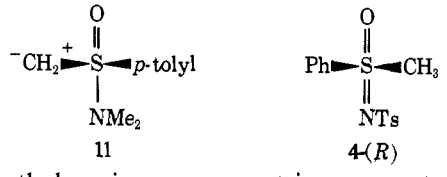
the production of cyclopropanes is restricted to α,β-unsaturated ketones; esters apparently acylate the reagent, although the reaction is not a good one for the synthesis of acyl derivatives.

Cycloalkylidine groups may be added across electrophilic double bonds utilizing these new reagents; note reactions 6, 7, and 17 in Table II. Yields in these cases are not high, but the compounds are difficult to make otherwise even using multistep methods.

These reagents also react with substrates containing electrophilic carbon–nitrogen multiple bonds. Reaction of **9** with benzalaniline gave 1,2-diphenylaziridine in 86% yield; this yield is comparable to that obtained by reaction of the same substrate with dimethylsulfonium methylide[10] but is a considerable improvement of that obtained by reaction with oxosulfonium methylides.[10,11] Reaction of the lithium salt of **1** with di-*p*-tolylcarbodiimide gave an adduct (reaction 20), while reaction with benzonitrile gave an enamine (reaction 19) which could be quantitatively hydrolyzed to the corresponding β-ketosulfoximine. The chemistry of these β-carbonyl derivatives of *N*-tosylsulfoximines will be the subject of a future paper.

As expected from mechanistic considerations, these reagents fail to react with nonelectrophilic olefins; *trans*-stilbene was quantitatively recovered after treatment with reagent **9** in DMSO for 72 hr at 65°.

Reactions of Chiral Reagents. In an earlier study, we observed that optically active *N,N*-dialkylaminooxosulfonium methylides (*e.g.*, **11**) are capable of trans-



11 4-(*R*)

fer of methylene in an asymmetric manner to suitably substituted electrophilic double bonds.[6] It seemed to us that chiral salts prepared from optically active *N*-tosylsulfoximines should also be capable of direct asymmetric syntheses of oxiranes, azidirines, and cyclopropanes.

Tosyl chloride was reacted with (−)-(*R*)-*S*-methyl-*S*-phenylsulfoximine (optical purity 84%) to give the *N*-tosylsulfoximine **4**-(*R*) (assumed to have a minimum optical purity of 84%). Reaction of the sodium anion of **4**-(*R*) in DMSO with acetophenone produced (−)-(*S*)-2-methyl-2-phenyloxirane, $[\alpha]D$ −6.9°; the same reagent reacted with benzalaniline to give (−)-1,2-diphenylaziridine, $[\alpha]D$ −12.9°. Reaction of the lithium salt of **4**-(*R*) in THF with *trans*-benzalacetophenone gave (1*R*,2*R*)-1-benzoyl-2-phenylcyclopropane, $[\alpha]D$ −190° (optical purity 49%). Reaction of optically pure **11** in DMSO with acetophenone gave (+)-(*R*)-2-methyl-2-phenyloxirane with $[\alpha]D$ +1.90°; with benzalacetophenone (1*S*,2*S*)-1-benzoyl-2-phenylcyclopropane was obtained with an optical purity of 35%.[6]

Experimental Section[12]

***S,S*-Dimethyl-*N*-(*p*-tolylsulfonyl)sulfoximine (1).** To 78 ml of DMSO containing 2 g of cupric chloride, Chloramine-T·$3H_2O$ (28.2 g, 0.1 mol) was added in portions. The reaction mixture assumed an orange color and the temperature rose to 60°. When the addition was about half completed, the mixture had turned green and a solid had precipitated. After the addition was completed, the reaction mixture was heated on the steam bath for 1 hr. The mixture was poured into 500 ml of water and 80 ml of saturated Na_2EDTA. A white precipitate and a blue solution were produced. The solid was collected by filtration and recrystallized[13] from ethanol to give the product (21 g, 90%), mp 167–169° (lit.[4] 170°).

***S,S*-Diethyl-*N*-(*p*-tolylsulfonyl)sulfoximine (2).** Diethyl sulfoxide (10.6 g, 0.1 mol) and *p*-toluenesulfonyl azide (29.4 g, 0.15 mol) were dissolved in 50 ml of methanol, and *ca.* 4 g of Raney copper active powder was added. The mixture was stirred and refluxed for 12 hr. The methanol was removed on an evaporator and 50 ml of saturated aqueous Na_2EDTA solution was added to the residue. The mixture was stirred. Methylene chloride (75 ml) was added with a small amount of activated charcoal. The mixture was stirred and then filtered through Celite. The filtrate was washed with water and dried over $MgSO_4$. The methylene chloride was removed. The crude material was recrystallized from ethanol to give a white solid (16 g, 60%), mp 89–91°.

***S,S*-Diisopropyl-*N*-(*p*-tolylsulfonyl)sulfoximine (3).** Diisopropyl sulfoxide (4.1 g, 0.03 mol), tosyl azide (9.9 g, 0.05 mol), methanol (35 ml), and Raney copper active powder (1.5 g) were mixed and refluxed for 6 hr. An additional 1.5 g of the Raney copper powder was added and the solution continued to reflux for 18 hr. Work-up, as described above for the diethyl compound, gave a white solid (5.2 g, 57%), mp 75–77°.

***S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (4).** Methylphenylsulfoximine[11] (70 g, 0.45 mol) was dissolved in 300 ml of pyridine and tosyl chloride (86 g, 0.45 mol) was added in portions; the mixture was allowed to stir overnight. The precipitated pyridine hydrochloride was separated by filtration. To the filtrate was added 1200 ml of water; a white solid separated. The mixture was extracted with 800 ml of methylene chloride. The organic layer was separated and washed twice with 200-ml portions of 10% hydrochloric acid and once with water. After drying over $MgSO_4$ and recrystallization from ethanol, the product was obtained as white needles (117 g, 83%), mp 197–109°.

***S*-Cyclohexyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (6)** was prepared by reaction of tosyl azide–Raney copper with crude cyclohexyl phenyl sulfoxide. (The sulfoxide, mp 62–63°, was prepared by sodium metaperiodate oxidation of cyclohexyl phenyl sulfide, bp 90–91° (0.07 mm).) The mixture was refluxed for 65 hr. The decomposition of the tosyl azide was monitored by observing the 2130-cm^{-1} band in the infrared spectrum. The crude product was recrystallized from methanol to yield 52% of a white solid, mp 145.5–146°.

Anal. Calcd for $C_{19}H_{23}NO_3S_2$: C, 60.45; H, 6.14. Found: C, 60.26; H, 6.21.

***S*-Cyclopentyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (5)** was prepared from crude cyclopentyl phenyl sulfoxide using tosyl azide–Raney copper in refluxing methanol for 50 hr. The product, mp 142.5–143.5°, was obtained in 58% yield.

Anal. Calcd for $C_{18}H_{21}NO_3S_2$: C, 59.47; H, 5.82. Found: C, 59.61; H, 6.10.

***S*-Benzyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (7).** This material was prepared from benzyl phenyl sulfoxide and tosyl azide in the presence of Raney copper powder. The product was recrystallized from ethanol to give white crystals (64–73%): mp 148–149°; ir (Nujol) 690, 753, 815, 1050, 1145, 1220, and 1290 cm^{-1}; nmr ($CDCl_3$) δ 6.9–8.1 (m, 14), 4.83 (s, 2), 2.38 (s, 3).

Anal. Calcd for $C_{20}H_{19}NO_3S$: C, 62.31; H, 4.97. Found: C, 62.26; H, 4.85.

***N*-(*p*-Tolylsulfonyl)sulfonimidoyl Carbanions. General Methods of Preparation of Metal Salts of Sulfoximines. A.** Sodium hydride (0.12 g, 5 mmol) as a 57% dispersion in mineral oil was placed in a round-bottomed flask equipped with a gas inlet tube and a magnetic stirrer and fitted with a serum stopper. The flask was flushed with dry nitrogen, and the sodium hydride dispersion was washed three times with pentane before being dried in a stream of nitrogen. Dry dimethyl sulfoxide (15–20 ml) was added *via* syringe, and the *N*-tosylsulfoximine (5 mmol) was added to the

(10) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).

(11) C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

(12) Microanalyses performed by Midwest Microlab, Inc., Indianapolis, Ind. Melting points are uncorrected.

(13) We have found that, in general, the unrecrystallized product and the commercially available material (ref 3) are suitable for use in methylene transfer reactions.

stirring mixture. Hydrogen evolution began immediately and was usually complete in 2–4 hr at room temperature.

B. The sulfoximine (5 mmol) was dissolved in 25 ml of THF, and the solution was cooled in a Dry Ice–acetone bath. The solution was stirred and 5 mmol of *n*-butyllithium in hexane was added all at once. After a few minutes the yellow solution was removed from the bath and allowed to attain room temperature.

C. A stirring solution of the sulfoximine (5 mmol) in 15–25 ml of dry dimethyl sulfoxide was treated with *n*-butyllithium (5 mmol) (as a 1.66 *M* solution in hexane) by dropwise addition from a syringe. Stirring was continued until a clear solution was obtained.

Alkylidene Transfer Reactions. General Method. To a solution of the carbanion in DMSO or THF was added 1 equiv of the electrophilic substrate contained in a small amount of the same solvent. The reactions were allowed to stir at room temperature for an appropriate time (see Table II). When DMSO was used, the reactions were poured into water and the mixture was extracted with pentane (or other suitable solvent). The extract was washed with water and dried over $MgSO_4$ and the solvent was evaporated. The resulting products were distilled, recrystallized, or chromatographed on a short column of silica gel. When THF was used as the solvent, at the end of the reaction time the THF was evaporated on the rotary evaporator, and the residue was partitioned between water and ether. The work-up was continued in a manner similar to that for DMSO. Several specific examples of experimental details are given below.

6-Oxaspiro[5.2]octane (Methylenecyclohexene Oxide). Sodium *N*-(*p*-tolylsulfonyl)methylsulfonimidoylmethide (**8**) prepared from dimethyl-*N*-tosylsulfoximine (11 mmol) and sodium hydride (11 mmol) in 25 ml of DMSO was treated with cyclohexanone (0.98 g, 10 mmol) in 5 ml of DMSO. The reaction was stirred at room temperature overnight, poured into water, and extracted with pentane. The pentane extracts were washed with water, dried, and distilled. The fraction boiling at 56–62° (20 mm) was collected and found to be the desired product (0.88 g, 78%). Vpc showed only one peak which corresponded with that of an authentic sample.

***trans*-1-Benzoyl-2-phenylcyclopropane.** To a reagent solution prepared from dimethyl-*N*-tosylsulfoximine (5 mmol) and sodium hydride (6 mmol) in 10 ml of DMSO was added 1.05 g (5 mmol) of benzalacetophenone in 5 ml of DMSO. The solution was allowed to stir overnight and then poured into cold water. The mixture was extracted with ether, the ether extracts were washed with water and dried over $MgSO_4$, and the ether was evaporated. Chromatography of the resultant pale yellow oil on a *short* column of silica gel afforded the product (0.98 g, 88%), mp 45–48° (lit.[13] 45–48°).

1,2-Diphenylaziridine. A reagent solution was prepared from sodium hydride and methylphenyl-*N*-tosylsulfoximine (5 mmol) in DMSO. Benzalaniline (0.9 g, 5 mmol) was added to the solution with stirring; the mixture became dark immediately. After 1 hr, water was added and the mixture was extracted with pentane. After the mixture was dried and the solvent removed, the pale yellow oil which remained was distilled; the fraction boiling at 128–130° (1 mm) was collected (0.84 g, 86%) and found to be identical with an authentic sample of 1,2-diphenylaziridine.

***r*-1-Benzoyl-*t*-2,*c*-3-diphenylcyclopropane.** The sodium salt of **7** (5 mmol) was prepared in 10 ml of DMSO; the solution became red after 1 hr. Benzalacetophenone (5 mmol) in 5 ml of DMSO was added. After 1 hr the mixture was worked up. The resulting solid was recrystallized from chloroform–ethanol to yield colorless plates (77%), mp 146°. A second recrystallization raised the mp to 148–149°.

Anal. Calcd for $C_{12}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.54; H, 6.20.

12-Oxadispiro[4.0.5.1]dodecane was prepared in 34% yield by reaction of the sodium salt of *S*-cyclopentyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (**5**) with cyclohexanone. Distillation at reduced pressure was used to purify the product: bp 90° (9 mm); ir (neat) 2900, 1440, 1230, 1160, 1025, 960, and 930 cm^{-1}.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.71; H, 10.99.

The same product was also obtained (22%) by reaction of **6** with cyclopentanone.

***trans*-1-Benzoyl-2-phenylspiro[2.5]octane** was prepared by reaction of the sodium salt of **6** (1 mmol) and benzalacetophenone (1 mmol) in 15 ml of DMSO. Chromatography on 20 g of silica gel with chloroform–hexane (1:1) elution and recrystallization from pentane gave the product (39%): mp 95.97°; ir ($CHCl_3$) 1660 cm^{-1}; nmr ($CDCl_3$) δ 1.4 and 1.7 (complex multiplets, 10), 3.1 (AB quartet, J = 6 Hz, 2), 7.2 to 8.2 (m, 10).

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.79; H, 7.75.

***S*-Phenyl-*S*-(3-hydroxy-3-phenylpropyl)-*N*-(*p*-tolylsulfonyl)sulfoximine.** The lithium salt of **4** in DMSO was reacted with styrene oxide. The main fraction was eluted from a silica gel column with chloroform and recrystallized from chloroform–hexane to yield 66% of the adduct as a mixture of diastereomers, mp 132–136°.

Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 61.53; H, 5.40. Found: C, 62.19; H, 5.39.

Spiro-3α-oxiranyl-5α-androstan-17-one. The diketone, 5α-androstane-3,17-dione, dissolved in a mixture of THF and DMSO was added to 1 equiv of the sodium salt of **1** in DMSO. The crude product was chromatographed on silica gel from which chloroform eluted the epoxide (49%): mp 141–143°; ir ($CHCl_3$) 1730 cm^{-1}; nmr ($CDCl_3$) 156 Hz (sharp singlet, 2); *m/e* 302; $[\alpha]^{20}D$ +71.3° (EtOH).

Anal. Calcd for $C_{20}H_{30}O_2$; C, 79.42; H, 9.99. Found: C, 78.53; H, 10.07.

***S*-Methyl-*S*-(2-amino-2-phenylvinyl)-*N*-(*p*-tolylsulfonyl)sulfoximine.** The lithium salt of dimethyl-*N*-tosylsulfoximine (1) (10 mmol) in 20 ml of DMSO was condensed with benzonitrile (10.5 mmol). The product was recrystallized from chloroform as colorless plates (67%): mp 119–120°; ir ($CHCl_3$) 3350, 3450, 1620, 1290, 1150, 1070 cm^{-1}.

Anal. Calcd for $C_{16}H_{18}N_2O_3S$: C, 54.86; H, 5.18; S, 18.27. Found: C, 54.57; H, 5.25; S, 18.55.

***S*-Benzoylmethyl-*S*-methyl-*N*-(*p*-tolylsulfonyl)sulfoximine.** The above enamine (2.0 g) was dissolved in 50 ml of ethanol and 50 ml of 2 *N* hydrochloric acid was added. The mixture was refluxed for 2 hr. The ethanol was removed at reduced pressure, and the product was recrystallized from methanol to give a 100% yield of colorless plates: mp 83–84°; ir ($CHCl_3$) 1680, 1290, 1150, 1070 cm^{-1}; nmr ($CDCl_3$) δ 2.3 (s, 3) 3.4 (s, 3) 5.2 (AB quartet, J = 15 Hz, 2), 7.6 (m, 9).

Anal. Calcd for $C_{16}H_{17}NO_4S_2$: C, 54.69; H, 4.88; S, 18.22. Found: C, 54.39; H, 4.58, S, 18.15.

***N,N'*-Di-*p*-tolyl-*N*-(*p*-tolylsulfonylmethylsulfonimidoyl)acetamidine.** Di-*p*-tolylcarbodiimide (5 mmol) was added to a solution of the lithium salt of **1** (10 mmol) in DMSO. Water work-up, pentane extraction, and recrystallization (twice) from ethanol gave the addition product (47%): mp 147–148°; nmr ($CDCl_3$) δ 2.32 (s, 6), 2.34 (s, 3), 3.17 (s, 3), 4.57 (AB quartet, J = 15 Hz, 2), 7.4 (m, 12).

Anal. Calcd for $C_{24}H_{27}N_3O_3S_2$: C, 61.40; H, 5.76. Found: C, 61.25; H, 6.09.

(−)-(*R*)-*S*-Methyl-*S*-phenyl-*N*-(*p*-tolylsulfonyl)sulfoximine (4-(*R*)). To an ice-cooled solution of (−)-*S*-methyl-*S*-phenylsulfoximine, $[\alpha]^{25}D$ −30.8° (*c* 1.00, acetone) (optical purity 84%)[14] (5.8 g, 38 mmol), in 25 ml of pyridine was added 7.25 g (38 mmol) of *p*-toluenesulfonyl chloride. The reaction mixture was stirred overnight at room temperature. The precipitated pyridine hydrochloride was removed by vacuum filtration, the filtrate was poured into water, and the mixture was extracted twice with methylene chloride. The crude solid obtained after work-up was completed was recrystallized from absolute ethanol to afford 9.3 g (84%) of the *N*-tosylsulfoximine: mp 97–98°; $[\alpha]^{25}D$ −122.4° (*c* 1.0, acetone).

(−)-(1*R*,2*R*)-*trans*-1-Benzoyl-2-phenylcyclopropane. At −78° a solution of **4**-(*R*) (0.773 g, 2.5 mmol) in 40 ml of dry THF was treated with 1.6 ml of 1.6 *M* *n*-butyllithium. After 10 min, 0.50 g (2.4 mmol) of *trans*-benzalacetophenone in 1 ml of THF was added *via* syringe. The reaction was stirred for 12 hr at room temperature. After work-up the pentane extract was dried over $MgSO_4$ and concentrated to leave 0.400 g (75%) of the expected cyclopropane, $[\alpha]^{25}D$ −190° (*c* 0.5, acetone, 49% optically pure) (lit.[6] for enantiomer +390.5°).

(−)-1,2-Diphenylaziridine. Using the chiral anion derived from **4**-(*R*) and a procedure similar to that described above for the racemic material, the product was obtained in 67% yield and had $[\alpha]^{25}D$ −12.9° (*c* 0.45, acetone).

(−)-(*S*)-2-Methyl-2-phenyloxirane,[15] $[\alpha]^{25}D$ −6.9° (*c* 0.36, acetone), was prepared in 40% yield from the sodium salt of **4**-(*R*) and acetophenone in DMSO overnight.

(14) This material was obtained from the mother liquors remaining from the after precipitation of the (−)-10-camphorsulfonic acid salt of the *S* enantiomer. The optically pure *S* enantiomer has $[\alpha]D$ +36.5° (*c* 1.2, acetone): C. W. Schroeck, Ph.D. dissertation, Wayne State University, 1971.

(15) The absolute configuration assignment is tentative.[6]