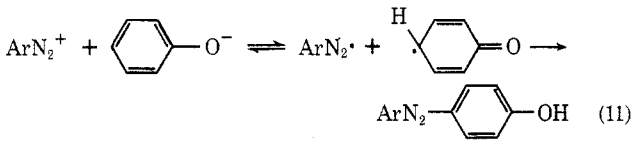
in alkaline methanolic solution in the presence of phenol (conditions which favor radical formation) a homolytic diazo coupling reaction (eq 11) may take



(11)

place.[64f] To the present author it seems probable that the precursor of the radical intermediates in (11) is a (covalent) aryl diazo ether.

^{13}C CIDNP of *p*-methoxybenzenediazonium ions in CH_3O^-–CH_3OH–CH_3CN gives a strong positive resonance at the C_1 position of the original diazonium ion which has been tentatively attributed to a polarized diazonium salt.[64e] Polarographic data[65] are consistent with the primary formation of aryldiimine radicals.

Summarizing, it is obvious that we do not completely understand the mechanism(s) of homolytic decomposition of diazonium ions and related compounds (with the probable exception of the acylarylnitrosamine reactions). The concept of nucleofugal homolytic leaving groups and correlations with inorganic electron-transfer reactions help to rationalize the understanding of the catalytic effects in these reactions.

The question of whether there is a common intermediate for homolytic and heterolytic decompositions of diazonium ions is still open. It may be related to the N_α–N_β inversion in diazonium ions observed by Lewis,[10] a problem which also applies to the fixation of N_2 molecules by transition metal complexes (end-on and edge-on complexes).[11a,c]

As more elaborate quantum-chemical methods to consider solvation effects are not likely to be developed in the near future, we hopefully expect that the combined results from spectroscopy (esr and CIDNP) and from chain reaction kinetics will be instrumental in solving this and other problems in diazo chemistry.

I thank Dr. E. Haselbach (University of Basle) for stimulating discussions and Dr. J. R. Penton (ETHZ) for his help in the preparation of the English manuscript of this paper. For the support of our own work reported here, acknowledgment is made to the Swiss National Foundation for Scientific Research, Projects 2.245.69 and 2.722.72.

(65) R. M. Elofson and F. F. Gadallah, *J. Org. Chem.*, 34, 854, 3335 (1969).

The Utilization of Sulfoximines and Derivatives as Reagents for Organic Synthesis

Carl R. Johnson

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received February 2, 1973

Sulfoximine[1] chemistry began in 1950, when Whitehead and Bentley discovered that the sulfoximine of methionine is the agent responsible for the toxicity of wheat flour treated with nitrogen trichloride.[2] Such treatment had been widely practiced for many years.

Our work, which commenced in 1968, has focused on the utilization of sulfoximines and their derivatives as reagents for organic synthesis. Besides novelty, these compounds have great potential for synthetic applications; they enable things to be done easily which are difficult or impossible by other methods.

The sulfoximine functional group (Figure 1) is uncommonly versatile. It has acidic hydrogens on carbon and nitrogen, it is basic and nucleophilic at nitrogen, and it is potentially asymmetric.

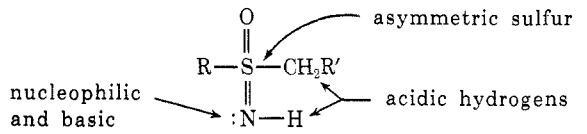


Figure 1. The sulfoximine functional group.

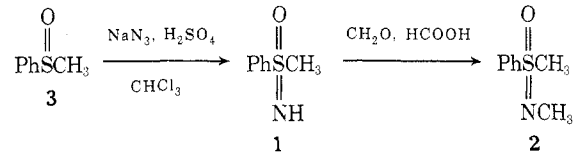
As a model system and as a starting point for much of our work we have utilized *S*-methyl-*S*-phenylsulfoximine; this Account stresses chemistry emanating from this source. The most practical method for the synthesis of **1** and its *N*-methyl derivative **2** is illustrated in Scheme I.

Several methods can be used for the high-yield oxidation of thioanisole to methyl phenyl sulfoxide (**3**).[3] We have routinely used a new laboratory meth-

Carl R. Johnson was born in Charlottesville, Va., on April 28, 1937. He received the B.S. degree in Pharmacy from the Medical College of Virginia, where he worked with Walter Hartung, and the Ph.D. degree in Organic Chemistry from the University of Illinois under the guidance of Nelson J. Leonard. In 1962 he was a research fellow at Harvard University with E. J. Corey. Later that year he joined the staff of Wayne State University where he is now Professor of Chemistry. His research has largely concerned the chemistry of organosulfur compounds, with special attention to the chemistry of sulfoxides and of compounds derived from sulfoxides.

(1) The IUPAC name is sulfoximide [(*Pure Appl. Chem.*, 11, 158 (1965)].
(2) H. R. Bentley, E. E. McDermott, J. Pace, J. K. Whitehead, and T. Moran, *Nature (London)*, 165 (1950); J. R. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952).

Scheme I



od employing oxygen (O_2) with dinitrogen tetroxide as a catalyst in a pressure apparatus; the reaction is fast and quantitative, but must be mediated by a solvent such as methylene chloride; otherwise it can become violent.[4]

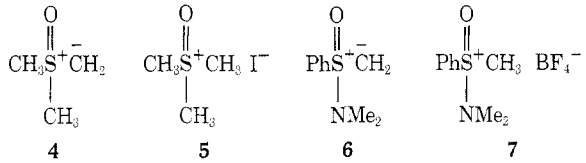
The sodium azide method[5] for the production of sulfoximines from sulfoxides is exceedingly good if both carbon substituents are either primary alkyl or aryl; otherwise heterolysis of carbon–sulfur bonds occurs in the highly acidic and polar reaction medium.

Attempts to N-alkylate **1** with typical reagents resulted in mixtures of non-, mono-, and dialkylated products. We were pleased to find the Clarke–Eschweiler conditions effective for the transformation of **1** to **2**.[6,7] At the time **2** was first prepared in our laboratory, *N*-alkyl derivatives of sulfoximines had not previously been reported.[8]

Nucleophilic Alkylidene Transfer Reagents

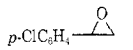
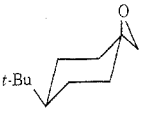
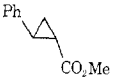
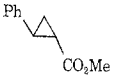
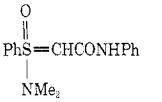
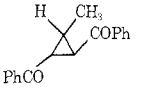
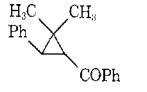
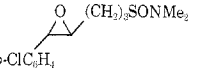
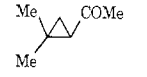
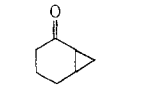
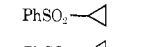
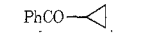
Ylides. Our interest in the production of a new type of oxosulfonium salt was fostered by the work of Corey and Chaykovsky[9] on dimethyloxosulfonium methylide (**4**), which perhaps has been the most widely used sulfur ylide in organic chemistry. This ylide is quite reactive, yet moderately stable. Furthermore, the precursor, trimethyloxosulfonium iodide (**5**), is easily available by the S-methylation of dimethyl sulfoxide. Unfortunately, S-alkylation of sulfoxides is not a general reaction and, with trivial exceptions, it is not practical to obtain other salts in the trialkyloxosulfonium series. This limits ylides in the series to the methylide.

Our investigation originated with the idea that ylides (*e.g.*, **6**) of similar desirable characteristics as those of **4** might be available by deprotonation of *N,N*-dialkyl salts of sulfoximines. Compound **7**,

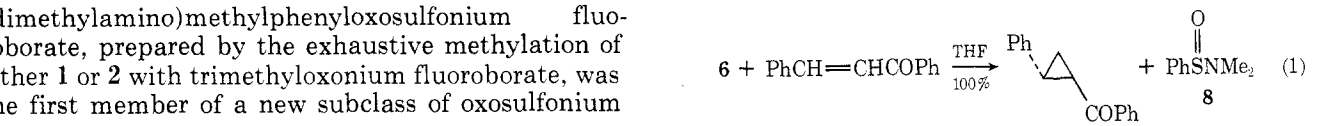


(dimethylamino)methylphenyloxosulfonium fluoroborate, prepared by the exhaustive methylation of either **1** or **2** with trimethyloxonium fluoroborate, was the first member of a new subclass of oxosulfonium salts.[10] It was apparent that such salts derived from sulfoximines could be prepared with wide structural variation.

Table I
Reactions of Ylides with Electrophilic Substrates

Ylide	Substrate	Product	Yield, %
6	*p*-Chlorobenzaldehyde		60
6	4-*tert*-Butylcyclohexanone		84
6	Methyl cinnamate		72
6	Dimethyl fumarate (or dimethyl maleate)		75
6	Phenyl isocyanate		55
9	1,4-Diphenyl-2-butene-1,4-dione		50
10	Benzalacetophenone		60
11	*p*-Chlorobenzaldehyde		66
12	Mesityl oxide		62
12	2-Cyclohexenone		60
12	Phenyl stryl sulfone		80
12	α-Bromoacetophenone		25

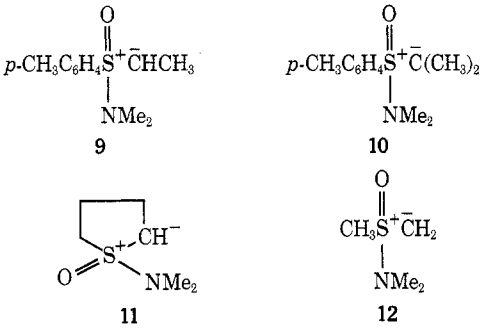
Treatment of **7** in dimethyl sulfoxide (Me_2SO) solution or as a slurry in tetrahydrofuran (THF) with sodium hydride resulted in the rapid and quantitative evolution of 1 equiv of hydrogen and the formation of a slightly yellow solution of ylide **6**; this ylide has long-term stability—in a sealed tube it remained unchanged for 2 months at 25°. The use of ylide **6** in a nucleophilic methylene transfer reaction is illustrated in eq 1. In this and other reactions, the by-



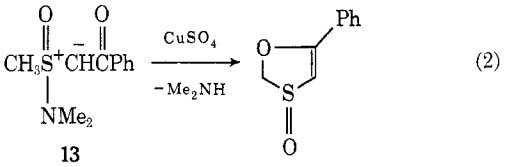
product, *N,N*-dimethylbenzenesulfinamide (**8**), could be removed by passing a benzene solution of the reaction products through a short silica gel column. Other reactions of ylide **6** with electrophilic substrates are summarized in Table I.

(3) C. R. Johnson and J. E. Keiser, *Org. Syn.*, **46**, 78 (1967).
(4) R. A. Kirchhoff and C. R. Johnson, unpublished results.
(5) J. R. Whitehead and H. R. Bentley, *J. Chem. Soc.*, 1572 (1952).
(6) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, in press; C. W. Schroeck, Ph.D. Dissertation, Wayne State University, 1971.
(7) T. R. Williams, R. E. Booms, and D. J. Cram, *J. Amer. Chem. Soc.*, **93**, 7338 (1971); H. Schmidbauer and G. Kammer, *Chem. Ber.*, **104**, 3234 (1971).
(8) C. R. Johnson, J. J. Rigau, M. Haake, D. McCants, Jr., J. E. Keiser, and A. Gertseema, *Tetrahedron Lett.*, 3719 (1968).
(9) E. J. Corey and M. J. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965).
(10) C. R. Johnson, E. R. Janiga, and M. Haake, *J. Amer. Chem. Soc.*, **90**, 3890 (1968); C. R. Johnson, M. Haake, and C. W. Schroeck, *ibid.*, **92**, 6594 (1970).

The fluoroborate salts which were precursors to ylides **9** and **10** were prepared beginning with the appropriate sulfide *via* the sulfoxide–hydrazoic acid route. The yield of isopropyl-*p*-tolylsulfoximine was poor because of carbon–sulfur bond heterolysis. Ylide **10** was prepared also by the alkylation of **9** with methyl iodide followed by treatment of the reaction mixture with 1 equiv of base, but small amounts of **9** remained.[11] Table I includes examples of reaction of ylides **9**, **10**,[10] **11**,[12] and **12**.[13] The stabilized ylide **13**,



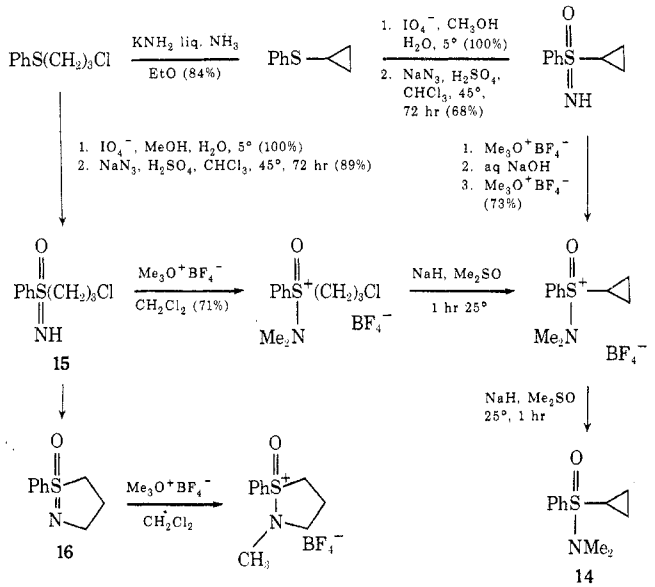
produced by reaction of **12** with benzoic anhydride, undergoes a curious cyclization catalyzed by copper sulfate (eq 2).[13]



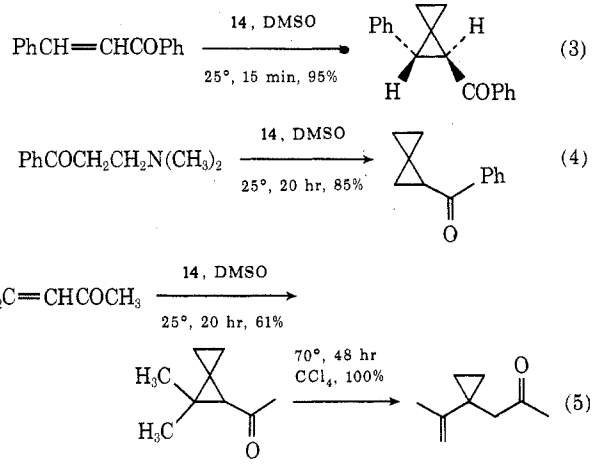
(2)

The production and utilization of cyclopropylide **14** has provided a remarkably facile synthesis of spiropentane derivatives.[14] Scheme II outlines alternate

Scheme II

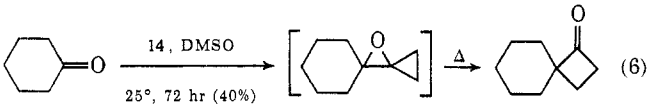


routes for the preparation of **14**. For large-scale preparation, the route involving cyclopropyl phenyl sulfide is preferable. The spontaneous cyclization of **15** to **16**[14] provided an interesting sidelight in that, at the time, **16** was the only known example of a sulfoximine with the sulfur and nitrogen contained within a ring.[15] Some typical reactions of **14** with electrophilic olefins are shown in eq 3, 4, and 5.



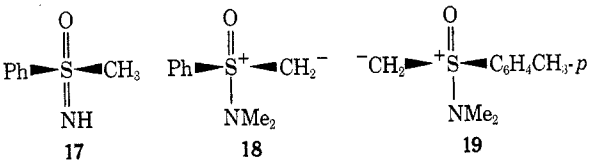
(3) (4) (5)

Reaction of ylide **14** with cyclohexanone produced the unstable dispiroepoxide which rearranged during isolation to give a cyclobutanone (eq 6).



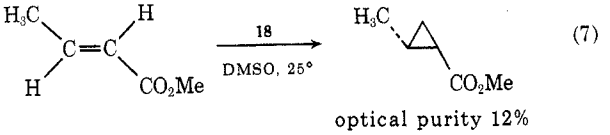
(6)

As noted above, an unsymmetrically substituted sulfoximine contains a chiral sulfur; our model system, methylphenylsulfoximine, is such a compound. Resolution of **1** has been found to be facile.[16] We have been able to obtain a high yield of the optically pure *S* enantiomer[17] after one recrystallization of diastereomeric salts formed from racemic **1** and (+)-10-camphorsulfonic acid.[6] Exhaustive methylation of **17** followed by treatment with base resulted in the generation of chiral ylide **18**. The (*R*)-ylide **19** was produced by a scheme based on the Anderson synthesis of optically pure sulfoxides.[17]



We have found that optically active methylides **18** and **19** are capable of transferring methylene in a symmetric manner to suitably substituted electrophilic double bonds, *e.g.*, eq 7, 8, and 9.[6,18]

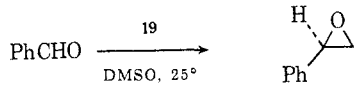
The complementary behavior of dimethyloxosul-



(7)

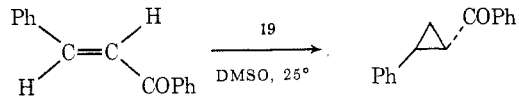
optical purity 12%

(11) E. R. Janiga, Ph.D. Dissertation, Wayne State University, 1972.
(12) C. R. Johnson and L. J. Pepoy, *J. Org. Chem.*, **37**, 671 (1972).
(13) C. R. Johnson and P. E. Rogers, *J. Org. Chem.*, **38**, 1793, 1798 (1973).
(14) C. R. Johnson, G. F. Katekar, R. F. Huxol, and E. R. Janiga, *J. Amer. Chem. Soc.*, **93**, 3771 (1971).
(15) For other examples see P. Stoss and G. Satlzinger, *Angew. Chem., Int. Ed. Engl.*, **10**, 79 (1971), and T. R. Williams and D. J. Cram, *J. Org. Chem.*, **38**, 20 (1973).
(16) R. Fusco and F. Tericoni, *Chem. Ind. (Milan)*, **47**, 61 (1965).
(17) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962).
(18) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **90**, 6852 (1968).



(8)

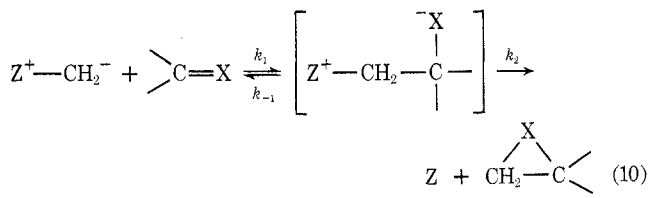
optical purity 20%



(9)

optical purity 35%

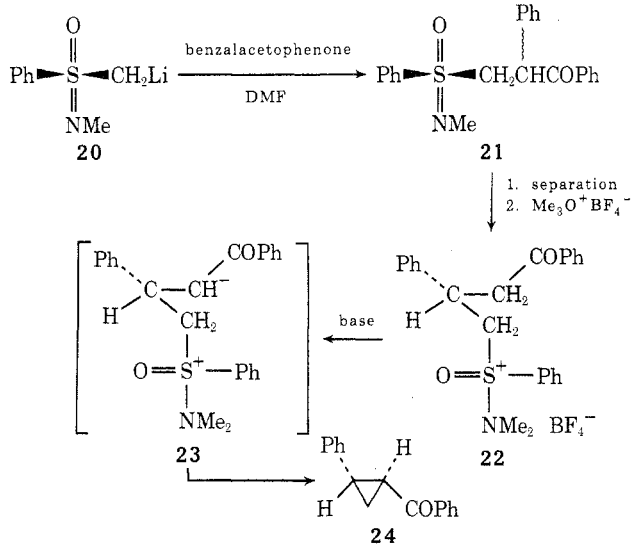
fonium methylide (4) and the simpler dimethylsulfonium methylide in their stereo- and regioselectivity is an intriguing phenomenon.[9] The reaction of 4 with 4-*tert*-butylcyclohexanone gives the (*Z*)-oxirane, whereas dimethylsulfonium methylide yields principally the (*E*)-oxirane; α,β-unsaturated ketones react with 4 to give cyclopropyl ketones but with dimethylsulfonium methylide to give vinyloxiranes. We have now gained considerable knowledge bearing on this selectivity by studies involving the independent generation[19] of the zwitterionic structures that long had been accepted as intermediates in these alkylidene transfer reactions (eq 10).



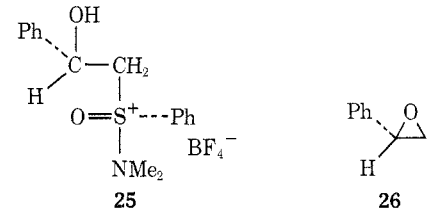
(10)

In earlier studies[10] we found that ylide 6 was similar in stability, reactivity, and selectivity to methylide 4. We considered that it would be more feasible to synthesize independently oxosulfonium betaine intermediates derived from 6 than those derived from 4. Lithium (*S*)-*N*-methylphenylsulfonimidoylmethide (**20**), prepared by treating (+)-**2** with *n*-butyllithium, added in the conjugate manner to benzalacetophenone to give a mixture of diastereomers **21**. After separation on a silica gel column, the diastereomeric adducts were methylated to give **22** and its epimer. Betaine **23**, generated by treatment of **22** with base, collapsed to give optically pure cyclopropane **24** (Scheme III). The epimer of **22** led to the enantiomer of **24**.

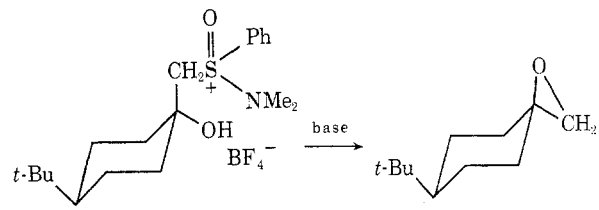
Scheme III



The reaction of **20** with benzaldehyde gave a mixture of diastereomers from which one was obtained pure by recrystallization. Methylation of the pure diastereomer gave **25**, which upon treatment with base gave (−)-styrene oxide (**26**) of 22% optical purity.



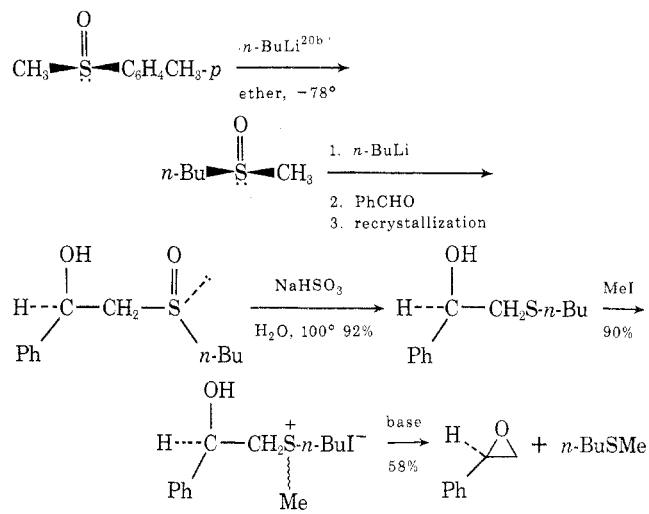
This optical purity is of the same order of magnitude as that obtained from the direct reaction of benzaldehyde with optically pure ylide **19**,[18] which suggested that betaine from **25** is in equilibrium with **18** and benzaldehyde. This was confirmed by appropriate trapping experiments.[19] The result[20a] shown in eq 11 also indicates reversible addition of the oxosulfonium ylide.



(11)

Scheme IV illustrates the independent synthesis of

Scheme IV

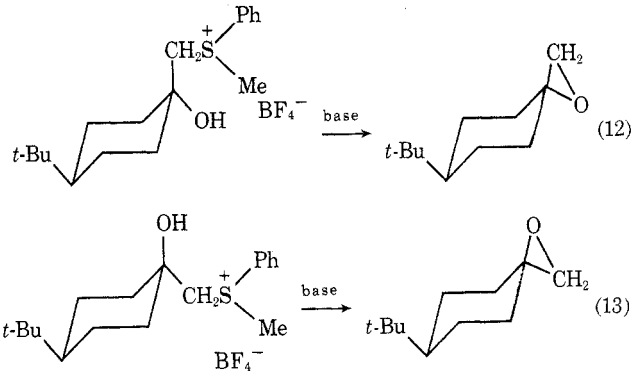


the type of betaine that would be derived from the addition of a simple sulfonium methylide to a carbonyl. The first step of Scheme IV shows that optically active *n*-butyl methyl sulfoxide is produced by reaction of *n*-butyllithium with resolved methyl *p*-tolyl sulfoxide; the reaction illustrates a new and general method for the preparation of optically active dialkyl sulfoxides.[20b] The styrene oxide obtained by this scheme was better than 90% optically pure,

(19) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, 93, 5303 (1971).

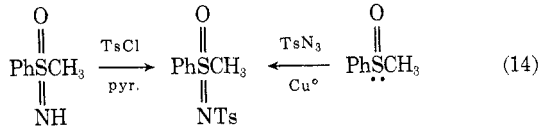
(20) (a) C. R. Johnson and J. R. Shanklin, unpublished results; (b) C. R. Johnson, J. P. Lockard, and C. W. Schroeck, *Synthesis*, 485 (1973).

which suggests that in such cases collapse of the betaine to product is much faster than reversion to ylide and carbonyl compound (see also eq 12 and 13).[20a]



The data cited clearly implicate betaine intermediates in nucleophilic alkylidene transfer reactions of sulfonium ylides and lead to the conclusion that the initial attack of an oxosulfonium ylide at a carbonyl site is "reversible" (eq 10, $k_{-1} \geq k_2$); whereas attack by a simple sulfonium ylide is "irreversible" ($k_{-1} \ll k_2$).[21] Since oxosulfonium ylides are known to be more stable than the simple sulfonium ylides, it is not surprising that the oxosulfonium ylides are better "leaving groups." The high optical purity of cyclopropane **24** and its enantiomer indicates that for collapse of their betaine precursors $k_2 \gg k_{-1}$. All comparative results in our work and earlier studies seem to be consistent with the hypothesis that simple sulfonium ylides result in products dictated by kinetic control of betaine formation, whereas oxosulfonium ylides result in products predicted by thermodynamic considerations.[19]

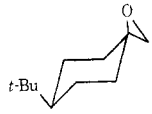
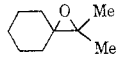
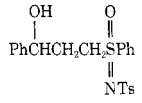
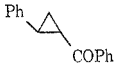
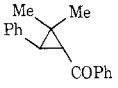
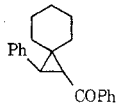
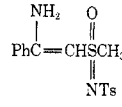
Anions of *N*-*p*-Tolylsulfonylsulfoximines.[22] The reaction of **1** with *p*-toluenesulfonyl chloride gave **27**, which could also be prepared by the copper-catalyzed reaction of *p*-toluenesulfonyl azide with methyl phenyl sulfoxide (eq 14). The latter reaction, discov-



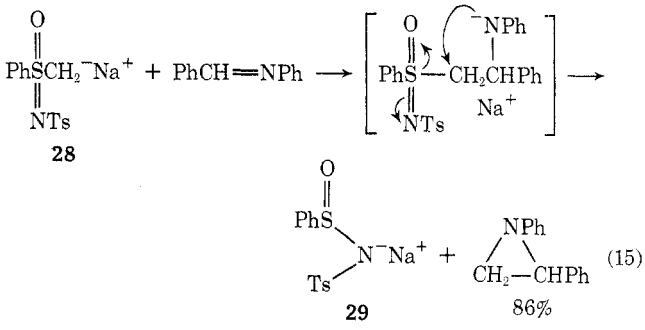
1 27

ered by Kwart and Kahn,[23] represents a very general, high-yield method for the production of *N*-*p*-tolylsulfonylsulfoximines from sulfoxides. The preparation of *N*-*p*-tolylsulfonylsulfonimidoyl-stabilized carbanions (*e.g.*, **28**) was accomplished by reaction of the *N*-tosylsulfoximines in Me_2SO with sodium hydride or *n*-butyllithium and in THF by treatment with *n*-butyllithium. Such anions, which are quite stable at room or slightly elevated temperatures, form another class of nucleophilic alkylidene transfer

Table II
Reactions of Anions of *N*-Tosylsulfoximines

N-Tosylsulfoximine	Substrate	Product	Yield, %
30	4-*tert*-Butylcyclohexanone		78
31	Cyclohexanone		63
27	Acetophenone		68
27	Styrene oxide		66
30	Benzalacetophenone		88
31	Benzalacetophenone		86
32	Benzalacetophenone		39
30	Benzonitrile		67

reagents derived from sulfoximines. The mechanism is similar to that of ylide reactions, but in these cases the leaving groups are water-soluble anions (*e.g.*, **29**) rather than neutral molecules. The reaction of **28** with a typical substrate containing an electrophilic double bond is illustrated in eq 15.



The alkylidene groups which have been transferred using reagents in this series include methylene, ethylidene, isopropylidene, benzylidene, cyclopentylidene, and cyclohexylidene.[22] Table II gives examples involving *N*-tosylsulfoximines **27**, **30**, **31**, and **32**. Reagent **30** is commercially available[24] or can be produced by the cupric ion catalyzed reaction of Chloramine-T with Me_2SO.[22] Our experience in working with these and other sulfonium ylide reagents leads us to the conclusion that, for simplicity of preparation and manipulation, these reagents are

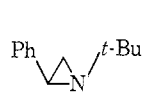
(21) For discussions of how reversibility of betaine formation might affect product stereochemistry see R. S. Bly, C. M. Dubose, and G. M. Konizer, *J. Org. Chem.*, **33**, 2188 (1968); C. E. Cook, R. E. Corley, and M. E. Wall, *Tetrahedron Lett.*, 891 (1965); and A. W. Johnson, "Ylid Chemistry," Academic Press, New York, N. Y., 1966, Chapter 9.

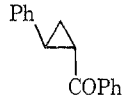
(22) C. R. Johnson and G. F. Katekar, *J. Amer. Chem. Soc.*, **92**, 5753 (1970); C. R. Johnson, R. A. Kirchhoff, R. J. Reischer, and G. F. Katekar, *J. Amer. Chem. Soc.*, **95**, 4287 (1973).

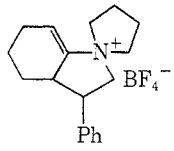
(23) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **90**, 6852 (1968).

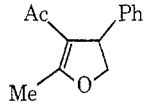
(24) Columbia Organic Chemicals Co., Inc., Columbia, S. C. 29205.

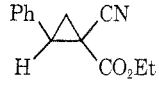
Table III
Products from the Reaction of Salt 34 with Dibasic Nucleophiles[a]

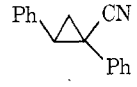

(*tert*-butylamine, THF, 86%)

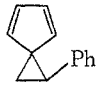

(α-dimethylaminostyrene, THF, 72%)

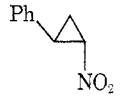

(1-pyrrolidineocyclohexene, THF, 91%)

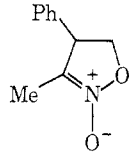

(acetylacetone NaOMe, MeOH, 85%)


(ethyl cyanoacetate, NaOEt, EtOH, 95%)


(phenylacetonitrile, *n*-BuLi, THF, 60%)

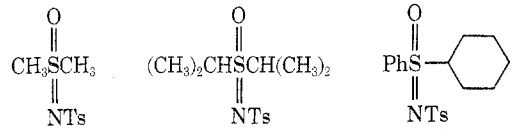

(cyclopentadienyllithium, THF, 86%)


(nitromethane, NaOMe, MeOH, 44%)


(nitroethane, NaOMe, MeOH, 77%)

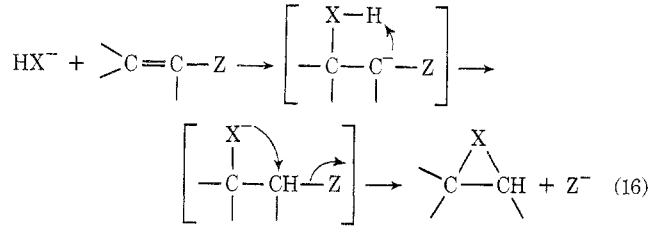
[a] All reactions were carried out at 25°. The reaction conditions, and product yields are shown in parentheses under the structures.

competitive with or superior to any others previously described for the preparation of substituted oxiranes from ketones.


30 31 32

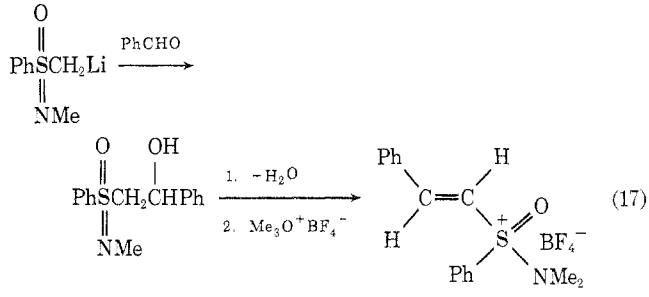
Electrophilic Ethylene Transfer to Dibasic Nucleophiles

Michael receptors in which the electronegative activator (Z) is also an excellent leaving group should be capable of ethylene transfer to dibasic nucleophiles (HX^-) (eq 16). In such reactions the intermediate,


(16)

after proton transfer, would be identical with that produced by the addition of an ylide or anion (ZCH^-) to >C=X. Prior to the work[25] described below, relatively few examples of reactions of the type described by eq 16 were known.[26]

The preparation of our model reagent, (dimethylamino)phenyl(2-phenylvinyl)oxosulfonium fluoroborate (**33**), is shown in eq 17. Dibasic nucleophiles to


(17)

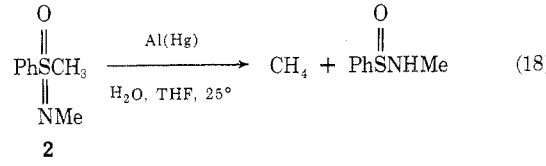
33

which ethylene transfer from salt **33** has been achieved include primary amines, enamines, and active methylene compounds. A selection of the types of compounds which have been produced is shown in Table III.[25] Note that in some instances five-membered rings are formed in preference to three-membered rings.

Optically pure (−)-(*S*)-**33** reacted with methyl cyanoacetate in methanol containing 1 equiv of sodium methoxide to give exclusively methyl (+)-(1*S*,2*R*)-1-cyano-2-phenylcylopropanecarboxylate in 81% yield with an optical purity of 25.5%. As a variant of this type of reagent we have also prepared an *S*-vinyl-*N*-tosylsulfoximine.

Aluminum Amalgam Reductions of Sulfoximines

When **2** was subjected to aluminum amalgam dissolving in aqueous THF at room temperature, carbon–sulfur hydrogenolysis occurred (eq 18).[27] This is


(18)

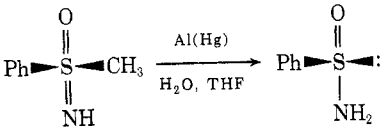
2

a curious reaction not shared by simple aryl alkyl sulfoxides or sulfones; such sulfones are inert, whereas the sulfoxides are reduced to the corresponding sulfides. Moreover, dialkylsulfoximines are also inert to these conditions. Amalgamated aluminum is known to be an excellent reagent for the hydrogenolysis of the carbon–sulfur bond in β-keto sulfides,[28] sulfoxides,[29,30] sulfones,[29] and sulfonamides.[29] In these cases, it is presumed that the resonance-stabi-

(25) C. R. Johnson and J. P. Lockard, *Tetrahedron Lett.*, 4589 (1971), and unpublished results.
(26) J. Gosselck and G. Schmidt, *Tetrahedron Lett.*, 2615 (1969); G. Schmidt and J. Gosselck, *ibid.*, 3445 (1969).
(27) C. W. Schroeck and C. R. Johnson, *J. Amer. Chem. Soc.*, **93**, 5305 (1971).
(28) J. D. Dutcher, J. R. Johnson, and F. W. Bruce, *J. Amer. Chem. Soc.*, **67**, 1736 (1945); J. R. Johnson and J. P. Buchanan, *ibid.*, **75**, 2103 (1953).
(29) E. J. Corey and M. J. Chaykovsky, *J. Amer. Chem. Soc.*, **86**, 1639 (1964); **87**, 1345 (1965).
(30) P. B. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966).

lized enol system (radical or anion) produced provides the necessary driving force for the reactions to occur.

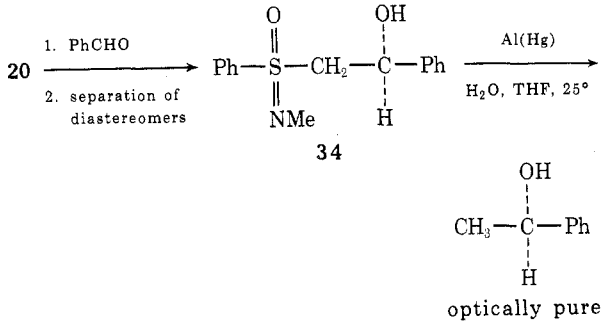
The aluminum amalgam reduction of optically active arylsulfoximines which proceeds with retention of configuration at the chiral sulfur provides a useful method for the correlation of absolute configurations.[27] More importantly, the method allows the production of arenesulfinamides of high optical purity. The synthesis of these materials in high optical purity is difficult to achieve due to racemization under the more usual reaction conditions. Optically active primary sulfinamides had not been previously prepared (eq 19).



(19)

Sulfoxides are produced by the aluminum amalgam reduction of (dialkylamino)oxosulfonium salts; this reaction allows optically active sulfoximines to be converted to optically active sulfoxides with retention of configuration at sulfur.

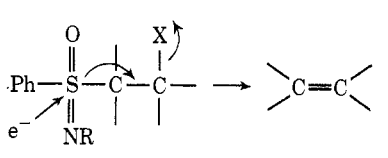
The aluminum amalgam reduction of sulfoximines is a key step in a general method under development in our laboratory for the production of optically pure alcohols. The method is illustrated by example in eq 20.[27] Reduction of the β-hydroxysulfoximine **34** pro-



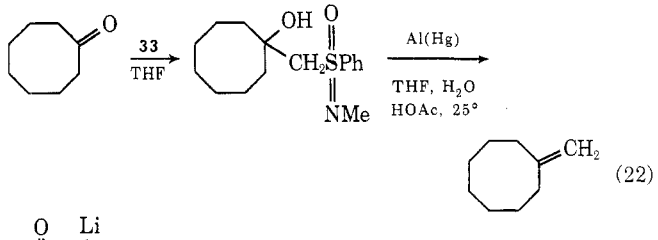
(20)

duced optically pure (+)-(*R*)-1-phenylethanol. Under these mild conditions no hydrogenolysis or racemization occurred at the benzylic carbon.

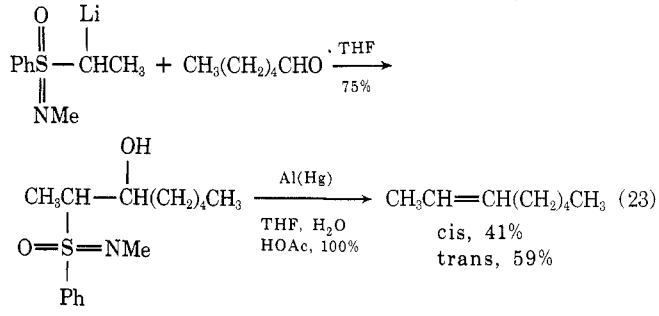
It seemed logical to us that in these reductions of sulfoximines the carbon departed the sulfur as a carbanion. If so, one should be able to generate olefins by the reduction of compounds with suitable leaving groups β to the sulfoximine (eq 21). A surprisingly simple modification of the reaction conditions noted above for the synthesis of alcohols proved effective for the production of olefins.[31] This consisted of the addition of acetic acid to the reaction medium. Although the acid may play a more complex role, its function could well be the conversion of the hydroxyl group to a better leaving group by protonation. Several examples of this olefin-forming reaction are illustrated in eq 22 and 23.



(21)



(22)



(23)

Although the method is still in the development stage the early results have been so encouraging that we expect the method may be a reasonable alternative to the Wittig reaction for the conversion of carbonyl groups to carbon–carbon double bonds.

Conclusion

Sulfur bound in organic molecules can exist in a number of stable oxidation states which provide for a wide variety or regional and stereochemical substitution patterns. This unique structural versatility allows the tailoring of sulfur molecules to perform specific functions. In this Account we have examined variations on sulfoximine chemistry and have attempted to provide a new prospect of the potentiality of organic sulfur chemistry in organic synthesis. We have shown sulfoximines and their derivatives to be useful in the synthesis of oxiranes, aziridines, cyclopropanes, alcohols, and alkenes. All except the latter class have been prepared in optically active forms using chiral sulfoximines for their synthesis.

I wish to express my sincere appreciation to my students whose efforts herein are accounted. Their names appear in the references. I am grateful to them not only for the experimental work, which is entirely theirs, but also for their stimulating discussions and many fruitful ideas. I thank the National Science Foundation for support of this program.

(31) C. R. Johnson, J. R. Shanklin, and R. A. Kirchoff, *J. Amer. Chem. Soc.*, **95**, 6462 (1973).