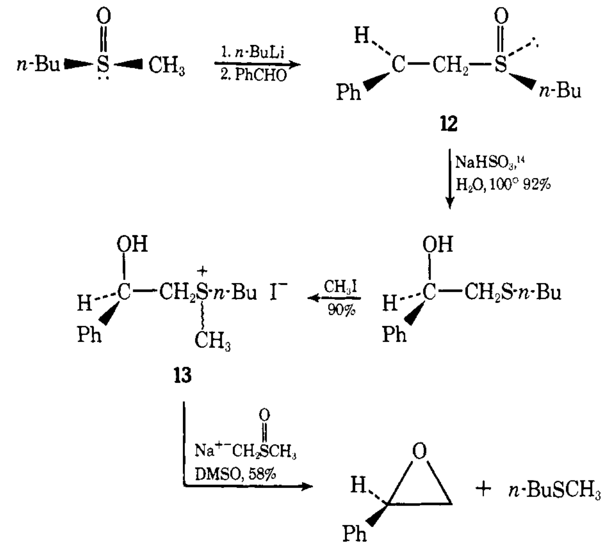
sium *tert*-butoxide-*tert*-butyl alcohol gave (−)-(*S*)-styrene oxide (71%), $[\alpha]^{25}\mathrm{D}$ −1.46° (*c* 4.7, acetone), of 22% optical purity.[11] This lowered value of optical purity is the same order of magnitude that would be expected from the direct reaction of optically pure ylide **3** and benzaldehyde,[11] which suggests that the betaine from **10** is in equilibrium with **3** and benzaldehyde. This suspicion was confirmed by generating the betaine (NaH, DMSO) in the presence of 1 equiv of a more reactive ylide substrate, *trans*-benzalacetophenone; an 80% yield of cyclopropane **9** was observed by vpc analysis of the reaction mixture. The ylide **3** was also trapped by protonation; the betaine conjugate acid **10**, when dissolved in aqueous sodium carbonate, was quantitatively converted to benzaldehyde and (dimethylamino)methylphenyloxosulfonium fluoroborate.[12]

Beginning with (+)-(*S*)-*n*-butyl methyl sulfoxide, $[\alpha]^{25}\mathrm{D}$ +112° (*c* 1.02, isooctane, 94% optically pure),[13] the reactions summarized in Scheme I were completed.

Scheme I



Diastereomer **12**, mp 113.5–114.5°, was obtained pure by fractional recrystallization. Iodide **13** was produced and used as a mixture of diastereomers, mp 95.5–97.5°. By fractional distillation to separate *n*-butyl methyl sulfide, a 58% yield of styrene oxide, $[\alpha]^{25}\mathrm{D}$ +32° (*c* 0.96, *dl*-styrene oxide, 90.3% optically pure)[11] was obtained.

The data cited in the foregoing three paragraphs clearly implicate betaine intermediates in nucleophilic methylene transfer reactions of sulfur ylides. Furthermore, it can be concluded that the initial attack of an oxosulfonium ylide at a carbonyl site is "reversible" (eq 1, $k_{-1} \geq k_2$), whereas attack by a simple sulfonium ylide is "irreversible" ($k_{-1} \ll k_2$). Since oxosulfonium ylides (*e.g.*, **1**) are known to be more stable than simple sulfonium ylides (*e.g.*, **2**), it is not surprising that the oxosulfonium ylides are better "leaving groups."[3b] The high optical purity of cyclopropane **9** and its enantiomer indicates that for collapse of their betaine precursors $k_2 \gg k_{-1}$. All comparative results in this 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.

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(11) Optical data for an authentic sample assumed to be optically pure; $[\alpha]\mathrm{D}$ +6.64° (*c* 4.9, acetone), +35.2° (neat). Highest reported value, $[\alpha]\mathrm{D}$ +34.2° (neat) [D. J. Pasto, C. C. Cumbo, and J. Fraser, *J. Amer. Chem. Soc.*, **88**, 2194 (1966)]. The 5% optical purity of styrene oxide reported [C. R. Johnson and C. W. Schroeck, *ibid.*, **90**, 6852 (1968)] from an optically active ylide and benzaldehyde should read "23% optically pure."

(12) A similar sequence of reactions has been accomplished employing heptaldehyde rather than benzaldehyde.

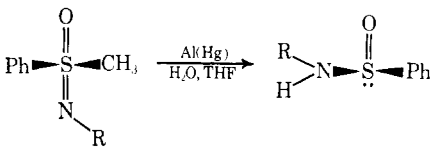
(13) The synthesis of this substance will be reported in a future paper.

(14) C. R. Johnson, C. C. Bacon, and J. J. Rigau, to be published.

Aluminum Amalgam Reduction of Aryl Sulfoximines and Related Compounds[1]

Sir:

Aluminum amalgam has been employed in organic syntheses for a variety of reductive transformations,[2] including the hydrogenolysis of organosulfur compounds. This mild reagent was used for desulfurization in the structural investigation of the antibiotic gliotoxin.[3] Amalgamated aluminum foil in aqueous tetrahydrofuran has been shown to be an excellent reagent for the hydrogenolysis of β-keto sulfoxides,[4,5] sulfones,[4] and sulfonamides.[4] We wish to report new results with this reagent in the reduction of a number of tetracoordinate hexavalent sulfur compounds. Our reactions were carried out under the conditions of Corey and Chaykovsky,[4] except that in all cases the temperature was kept at 25° or below. An excess of aluminum amalgam was added to a dilute solution of the sulfur compound in 10% water–90% tetrahydrofuran. The results of these reductions are summarized in Table I; the reactions proceed with better than 95% stereospecificity.



1, R = CH$_3$
2, R = H
3, R = *p*-CH$_3$C$_6$H$_4$SO$_2$

4, R = CH$_3$
5, R = H

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

(2) For a review see L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. 1, Wiley, New York, N. Y., 1967, pp 20–22; Vol. II, 1969, p 19. See also E. J. Corey, N. H. Andersen, R. M. Carlson, J. Paust, E. Vedejs, I. Vlattas, and R. E. K. Winter, *J. Amer. Chem. Soc.*, **90**, 3245 (1968).

(3) J. D. Dutcher, J. R. Johnson, and F. W. Bruce, *ibid.*, **67**, 1736 (1945); J. R. Johnson and J. P. Buchanan, *ibid.*, **75**, 2103 (1953).

(4) E. J. Corey and M. J. Chaykovsky, *ibid.*, **86**, 1639 (1964); **87**, 1345 (1965).

(5) P. B. Gassman and G. D. Richmond, *J. Org. Chem.*, **31**, 2355 (1966).

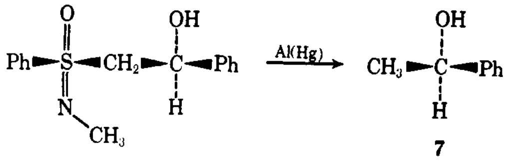
Table I. Aluminum Amalgam Reductions[a]

Reaction	Conditions	Yield, %	Starting material [α]²⁵D (acetone); mp, °C	Product [α]²⁵D (acetone); mp, °C
1 → **4**[b]	15°, 3 hr	74	+183°, liq	+173°, 49–52
2 → **5**[b]	20°, 2 hr	54	+36.5°, 31–33	+79.9°, 95–101[c]
6 → **7**	25°, 2 hr	41	+43.7°, 99–100	+46.4°,[d] liq
8 → **9**[e]	25°, 24 hr	53	+12.6°, 128–130	−142.6°,[f] liq
10 → **4**[b]	20°, 4 hr	76	Rac, 87–89	Rac, liq
11 → **4**[b]	25°, 4 hr	46	Rac, liq	Rac, liq

[a] The amalgam was prepared from commercial grade aluminum foil by immersing it into 2% aqueous mercuric chloride for 15–20 sec, followed by ethanol and ether rinses, and it was used immediately (ref 4). Generally, 10 g-atom of aluminum/mol of compound was used. The reactions were followed by tlc. All compounds have been identified and characterized by standard analytical procedures. [b] A small amount of benzenethiol was produced in these reactions by further reduction of the sulfinamide. The products were purified by chromatography on silica gel. [c] After recrystallization from ether, [α]²⁵D +82.9°, mp 102–103°. [d] Lit. +43.7° (neat) [R. L. Burwell, Jr., A. D. Shields, and H. Hart, *J. Amer. Chem. Soc.*, **76**, 908 (1954)]; authentic sample, +44.0° (neat), +47.1° (acetone). [e] In this reaction, 5 g-atom of Al/mol of **10** was used. [f] Lit. for enantiomer +149° [J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967)].

The aluminum amalgam reduction of (+)-(*S*)-*N*,*S*-dimethyl-*S*-phenylsulfoximine (**1**)[6a] resulted in the cleavage of the sulfur–alkyl bond to give (+)-(*S*)-*N*-methylbenzenesulfinimide (**4**). The absolute configurations of **1** and **4** have been established;[7] the reduction proceeds with retention of configuration at the chiral sulfur. Sulfur–alkyl bond cleavage was also observed with (+)-(*S*)-*S*-methyl-*S*-phenylsulfoximine (**2**)[6b] which yielded (+)-(*S*)-benzenesulfinamide (**5**).[8] At first glance it may appear that a method for the transformation of a sulfoximine to a sulfinamide would offer little other than a new and useful method to correlate configurations. However, it should be noted that optically active primary sulfinamides have not been previously reported, few optically active secondary sulfinamides are known, and the synthesis of these materials in high optical purity is difficult to achieve due to racemization under the more usual reaction conditions.[9] The mild media of the aluminum amalgam reductions of the easily resolved sulfoximines allow high retention of optical activity in the production of sulfinamides.

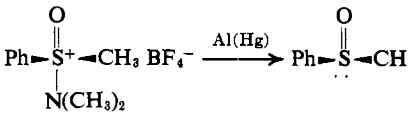
The Al(Hg) reduction of sulfoximines is a key step in a general reaction sequence under development in our laboratory to produce optically pure alcohols. For example, reduction of sulfoximine **6** produced optically pure (+)-(*R*)-1-phenylethanol (**7**). Under these mild conditions no hydrogenolysis or racemization occurred at the sensitive benzylic carbon. Analogous β-hydroxysulfones are inert to these reduction conditions. Employing slightly higher temperatures and a greater excess of the aluminum, β-hydroxy sulfoxides are quantitatively reudced to the corresponding sulfides. *N*-*p*-Toluenesulfonylsulfoximine (**3**) proved resistant to reduction under these mild conditions.



$$\mathrm{Ph{-}\overset{O}{\underset{NCH_3}{S}}{-}CH_2{-}\overset{OH}{\underset{H}{C}}{-}Ph} \xrightarrow{Al(Hg)} \mathrm{CH_3{-}\overset{OH}{\underset{H}{C}}{-}Ph}$$

6 **7**

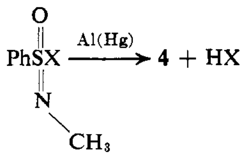
An interestingly different mode of cleavage occurs in the reduction of salts prepared by N,N-dimethylation of sulfoximines. When (+)-(*S*)-(dimethylamino)-methylphenyloxosulfonium fluoroborate (**8**) was treated with the metal amalgam, the dimethylamino group was lost with retention of configuration at sulfur to give (−)-(*S*)-methyl phenyl sulfoxide (**9**); some methyl phenyl sulfide was also isolated. This represents an alternative to the use of nitrosyl hexafluorophosphate for the removal of the nitrogen from a sulfoximine.[10]



$$\mathrm{Ph{-}\overset{O}{\underset{N(CH_3)_2}{S^+}}{-}CH_3\ BF_4^-} \xrightarrow{Al(Hg)} \mathrm{Ph{-}\overset{O}{S}{-}CH_3}$$

8 **9**

Other sulfonimidoyl compounds which were subjected to Al(Hg) reduction included phenyl *N*-methylbenzenesulfonimidate (**10**)[11] and *N*,*N*,*N*′-trimethylbenzenesulfonimidamide (**11**);[11] in each case sulfinamide **4** was produced.



$$\mathrm{Ph\overset{O}{\underset{NCH_3}{S}}X} \xrightarrow{Al(Hg)} \mathbf{4} + \mathrm{HX}$$

10, X = OPh
11, X = N(CH$_3$)$_2$

We are continuing to investigate the scope and mechanistic details of these reductions.

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(6) (a) Prepared by methylation of resolved **2**, [α]²⁵D +36.5° (*c* 1.2, acetone). (b) For the preparation of this sulfoximine see R. Fusco and F. Tericoni, *Chem. Ind. (Milan)*, **47**, 61 (1965), and C. R. Johnson, M. Haake, and C. W. Schroeck, *J. Amer. Chem. Soc.*, **92**, 6594 (1970). A forthcoming paper from our laboratory will describe an improved procedure for the resolution of this compound.

(7) E. U. Jonsson and C. R. Johnson, *ibid.*, **93**, 5308 (1971).

(8) Absolute configuration based on the correspondence of the sign of rotation with that of **4** and the assumption that the reduction proceeded with retention of configuration at sulfur.

(9) A. Nudelman and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 3869 (1968).

(10) D. J. Cram, J. Day, D. R. Rayner, D. M. von Schriltz, D. J. Duchamp, and D. C. Garwood, *ibid.*, **92**, 7369 (1970).

(11) Prepared by the methods described for the optically active compounds in ref 7.

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Preparation of Sulfonimidoyl Chlorides by Chlorination of Sulfinamides[1]

Sir:

Derivatives of "sulfonimidic acids" (**1**) are a relatively new class of compounds[2] which, in comparison

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