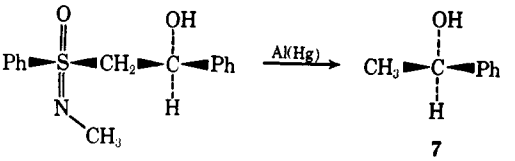
Table I. Aluminum Amalgam Reductions[a]

Reaction	Conditions	Yield, %	Starting material $[\alpha]^{25}D$ (acetone); mp, °C	Product $[\alpha]^{25}D$ (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, $[\alpha]^{25}D$ +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.

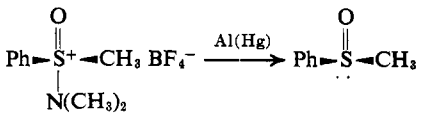
The Al(Hg) reduction of sulfoximines is a key step in a general reaction sequence under development in our laboratory to produce optically pure alcohols. For example, reduction of sulfoximine **6** produced optically pure (+)-(*R*)-1-phenylethanol (**7**). Under these mild conditions no hydrogenolysis or racemization occurred at the sensitive benzylic carbon. Analogous β-hydroxysulfones are inert to these reduction conditions. Employing slightly higher temperatures



6 **7**

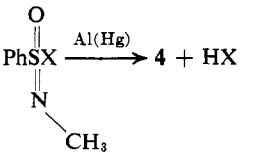
and a greater excess of the aluminum, β-hydroxy sulfoxides are quantitatively reudced to the corresponding sulfides. *N*-*p*-Toluenesulfonylsulfoximine (**3**) proved resistant to reduction under these mild conditions.

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]



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.



10, X = OPh
11, X = $N(CH_3)_2$

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

(6) (a) Prepared by methylation of resolved **2**, $[\alpha]^{25}D$ +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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Received July 6, 1971

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

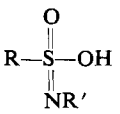
(1) Part XXXII in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

Table I. Preparation of Sulfonimidoyl Chlorides

Sulfinamide 3		Chlorination	Chloride 5[b]	Derivative
R	R′	method[a]	yield, %	mp, °C
a CH_2Cl	*p*-$CH_3C_6H_4SO_2$	A	89[i]	90–91[c]
b $CHCl_2$	*p*-$CH_3C_6H_4SO_2$	A	71	143–144[d]
c C_6H_5	CH_3	C	86	99[e]
d C_6H_5	H	B	69	73–75[f,g]
e $C_6H_5CH_2$	C_6H_5	B	100	79–80[f]
f $C_6H_5CH_2$	*p*-C_6H_4Cl	B	52	93–94[f]
g $C_6H_5CH_2$	2,4,6-$C_6H_2Cl_3$	B	77[i]	87–88[f]
h *p*-$CH_3CONHC_6H_4$	CH_3	B	~60	163–164[f]
i *p*-$CH_3CONHC_6H_4$	$Si(CH_3)_3$	C	~60	160–163[h]

[a] A = chlorine–benzene, room temperature; B = chlorine–ether, −78°; C = *N*-chlorobenzotriazole–methylene chloride, room temperature. [b] Most of the sulfonimidoyl chlorides were viscous liquids or solids and were unstable at room temperature. [c] Sulfonamide (eq 2). [d] *N*-*p*-Toluenesulfonyl trichloromethanesulfinamide. [e] Methylamide. [f] Dimethylamide. [g] Lit. mp 76–77°: E. S. Levchenko, E. S. Kozlov, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **33**, 565 (1963); *J. Gen. Chem. USSR*, **33**, 559 (1963). [h] Dimethylamide with trimethylsilyl group removed. [i] Mp 70–71°. [j] Mp 76–78°.

to derivatives of simple sulfonic acids (**2**), possess intriguing properties; the nitrogen provides an additional site for structural manipulations and renders the sulfur chiral.[3] In this communication we wish to report a new and seemingly general method for the preparation of sulfonimidoyl chlorides (**5**). Sulfonimidoyl chlorides have been previously prepared by the reaction of sulfinyl chlorides and a variety of chloroamine derivatives including chloramine-T,[4] dichloramine-T,[5] *N*,*N*-dichloromethylamine,[5] and the sodium salts of *N*-chloroamides.[6]



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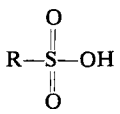

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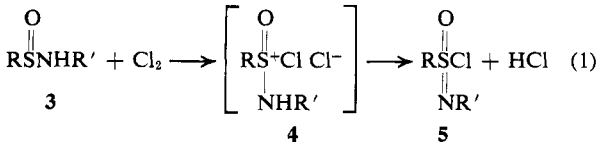
By oxidation of readily available sulfinamides (**3**) with chlorine[7a] (eq 1) or *N*-chlorobenzotriazole[7b] the



(1)

3 **4** **5**

sulfonimidoyl chlorides listed in Table I have been prepared; all except **5c**[5] are new compounds[8] and are not available by the routes previously recorded. Oxosulfonium salts (**4**) are presumed to be intermediates in these reactions. Noteworthy is the sulfonimidoyl chloride **5d** with a free NH, isolated as the hydrochloride. When **3d** was chlorinated in the presence of a hydrogen chloride acceptor, a polymeric solid was obtained.

A typical procedure for the chlorination is illustrated by the preparation of **5c**: *N*-methylbenzenesulfinamide (**3c**) (1 g) was covered[9] with ether (25 ml) and cooled to −78°. Dry chlorine was bubbled into the mixture until a slight excess was present as denoted by the pale yellow color of the chlorine. The solution was filtered and the ether was evaporated leaving an 86% yield of **5c** as a colorless, nondistillable, moisture-sensitive oil. The other sulfonimidoyl chlorides listed in Table I were obtained in a similar or slightly modified way. When *N*-chlorobenzotriazole was used, the oxidation was carried out at room temperature in dichloromethane; the solution containing the sulfonimidoyl chloride and benzotriazole was used as such for the preparation of amides or other derivatives. Compounds **5d**, **5e**, **5f**, and **5g** are stable at −15° for several weeks but decompose fairly rapidly at room temperature.

The *N*-chlorobenzotriazole method is the procedure of choice when there are other groups in the sulfinamide likely to be chlorinated by molecular chlorine itself. With an *N*-phenyl group as in **3e**, S chlorination but no ring chlorination took place with chlorine at −78°. In this case the product crystallized from ether at −78° and could be separated from the excess chlorine by filtration. When **3e** and excess chlorine were allowed to warm to room temperature, chlorination of the *N*-phenyl occurred (sometimes violently) to produce **5f**.

Reaction of the sulfonimidoyl chlorides with water or alcohols (usually methanol) (eq 2) gave sulfonamides.[10] Reaction of the sulfonimidoyl chlorides with primary and secondary amines produced sulfonimidamides. By this method, the first sulfanilamide analogs

(2) For a review see E. S. Levchenko and A. V. Kirsanov, *Usp. Khim. Fosfororg. Seraorg. Soedin*, 175 (1969).

(3) See accompanying communication: E. U. Jonsson and C. R. Johnson, *J. Amer. Chem. Soc.*, **93**, 5308 (1971).

(4) E. S. Levchenko, N. Ya. Derkach, and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 1971 (1960); *J. Gen. Chem. USSR*, **30**, 1950 (1960).

(5) E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *Ukr. Khim. Zh.*, **33**, 337 (1967); *Zh. Org. Khim.*, **3**, 1273 (1967); *J. Org. Chem. USSR*, **3**, 1234 (1967).

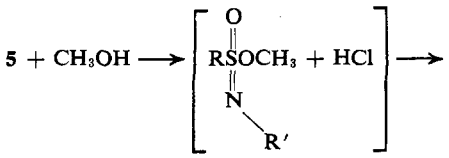
(6) E. S. Levchenko, I. N. Berzina, and A. V. Kirsanov, *Zh. Org. Khim.*, **1**, 1251 (1965); *J. Org. Chem. USSR*, **1**, 1264 (1965).

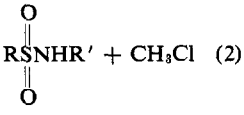
(7) (a) Sulfonimidoyl bromides have been implicated as intermediates in the conversion of sulfinamides to sulfonimidamides or sulfonimidates utilizing bromine or *N*-bromosuccinimide as oxidants in the presence of amines or phenoxides [H. Takei, I. Watanabe, and T. Mukaiyama, *Bull. Chem. Soc. Jap.*, **38**, 1989 (1965)]. (b) In these oxidations *tert*-butyl hypochlorite has also been successfully utilized (unpublished result, C. R. Johnson and A. Wamsbgans).

(8) Satisfactory spectral and/or microanalytical data have been obtained for all new compounds and/or their immediate derivatives.

(9) Depending on the particular sulfinamide, a solution or suspension may result. In the case of a suspension, the mixture typically became homogeneous during the chlorination. In a few cases the sulfonimidoyl chlorides precipitated from the ether solution.

(10) E. S. Levchenko, L. N. Markovskii, and A. V. Kirsanov, *Zh. Org. Khim.*, **3**, 1481 (1967); *J. Org. Chem. USSR*, **3**, 1439 (1967).





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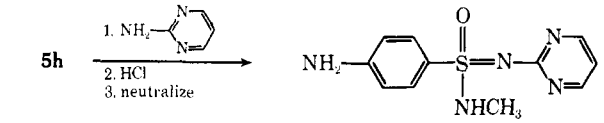
with structural variation involving the sulfonyl group have been prepared, *e.g.*, 7.



7[11]

The synthesis of analogs of sulfonyl-containing biologically active compounds and optically active polymers and the utility of sulfonimidates (and derivatives) as highly reactive leaving groups are among a number of applications of sulfonimidoyl chlorides currently under investigation in our laboratories.

(11) Nmr evidence indicates that the tautomeric form shown is the preferred structure.

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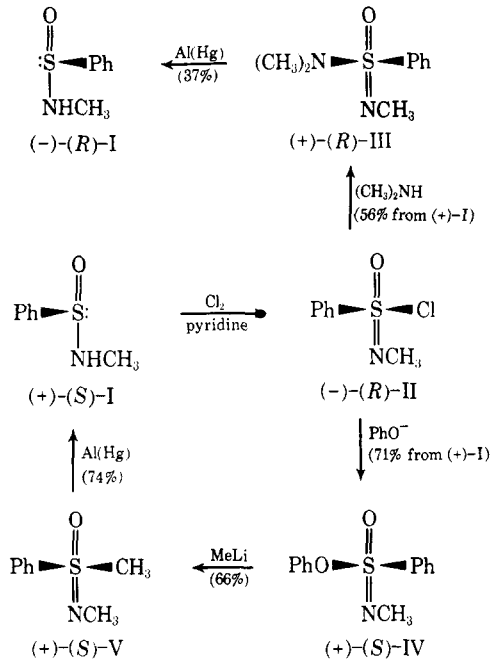
The Stereochemistry of Substitution at Tetracoordinate Hexavalent Sulfur. Nucleophilic Reactions at Sulfur in Sulfonimidoyl Compounds[1]

Sir:

Our general interest in the stereochemistry of substitution at sulfur led us to examine the course of nucleophilic substitutions at tetracoordinate hexavalent sulfur. In the singular report of a study of this type Sabol and Andersen[2] examined the reaction of an optically active, ^{18}O-labeled sulfonate ester with a Grignard reagent which produced an optically active sulfone with chirality due to isotopic label. Their results implicated an inversion mechanism, but because of extraordinarily low rotations, the interpretation relied on the complete removal of all interfering optically active impurities. In this communication definitive evidence confirming an inversion mechanism is given.

Chart I summarizes the transformations which complete new cycles of reactions at asymmetric sulfur. These reactions go with high stereospecificity and are

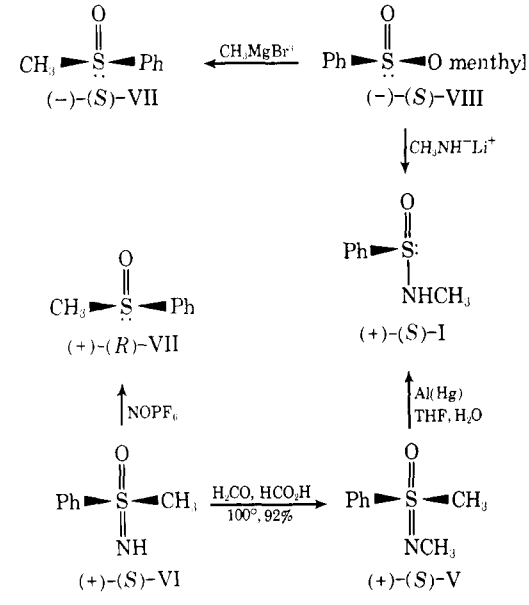
Chart I



useful in establishing configurational relationships and for the preparation of optically active sulfur compounds.

The absolute configurations of I and V were determined by a series of reactions with known stereochemical course starting from (−)-menthyl (*S*)-benzenesulfinate (VIII) (Chart II).[3,4] By adding the lithium

Chart II



salt of methylamine at 0° to an excess of (−)-(*S*)-VIII, $[\alpha]^{25}D$ −202.8° (acetone, 99% optically pure), (+)-(*S*)-I, $[\alpha]^{25}D$ +41.8° (*c* 1.74, acetone), with 24% optical purity was obtained. Similar substitution reactions have been shown to occur with inversion of configura-

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

(2) M. Sabol and K. Andersen, *J. Amer. Chem. Soc.*, **91**, 3603 (1969).

(3) J. Jacobus and K. Mislow, *ibid.*, **89**, 5228 (1967).

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