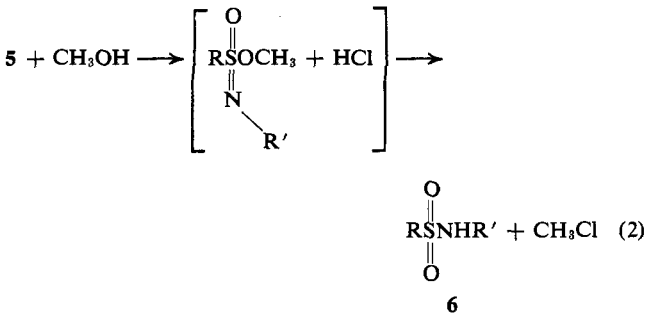
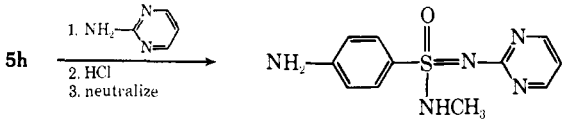


with structural variation involving the sulfonyl group have been prepared, *e.g.*, **7**.



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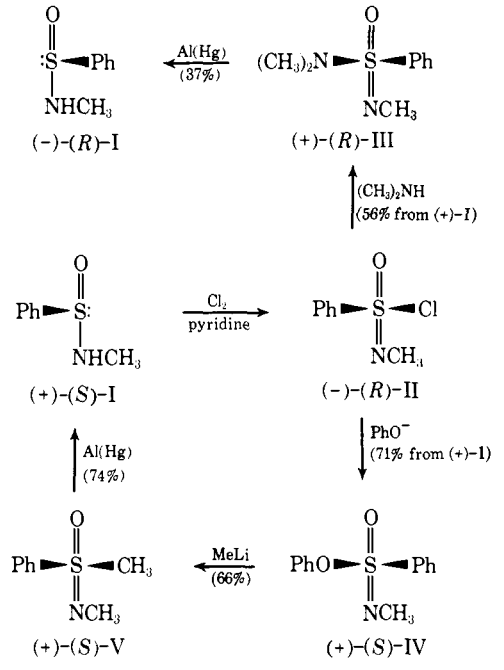
The Stereochemistry of Substitution at Tetracoordinate Hexavalent Sulfur. Nucleophilic Reactions at Sulfur in Sulfonimidoyl Compounds[1]

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

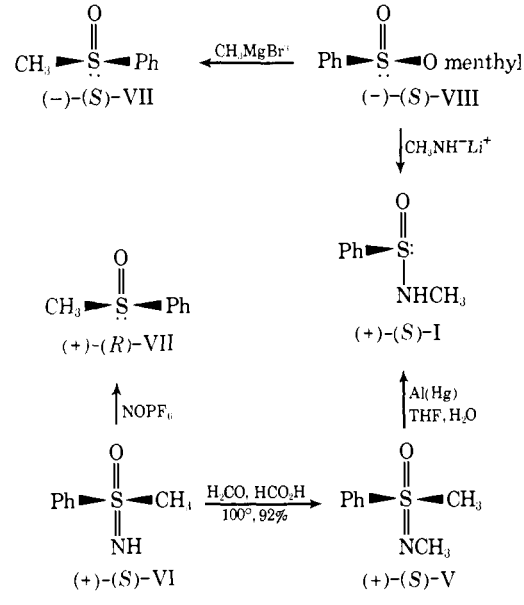
Chart I



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).

tion at sulfur,[5,6] and it is known that optically active sulfinamides are easily racemized by amide ion.[6] The absolute configuration of (+)-VI has already been correlated with (−)-(*S*)-VII by use of nitrosyl hexafluorophosphate.[7,8] In our hands by treating (+)-VI, $[\alpha]^{25}D$ +34.7 (*c* 1.26, acetone) (95% optically pure), with nitrosylhexafluorophosphate in nitromethane at 0°, (−)-(*S*)-VII, $[\alpha]^{25}D$ −130.0 (*c* 1.6, ethanol) (86% optically pure), was obtained. Formaldehyde and formic acid at steam bath temperatures quantitatively N-methylated VI.[10] The methylation of (+)-(*S*)-VI to (+)-V does not involve substitution at sulfur and therefore, the configuration is preserved and is *S*. Optically pure (+)-(*S*)-I, $[\alpha]^{25}D$ +174° (*c* 1.1, acetone), was obtained from optically pure (+)-(*S*)-V, $[\alpha]^{25}D$ +183° (*c* 1.2, acetone),[11] by reduction with aluminum amalgam,[9] a reaction which proceeds with retention of configuration at the sulfur.

The optically active sulfonimidoyl chloride (−)-II was prepared from sulfinamide (−)-I by oxidation with chlorine (Chart I).[12] Pyridine was added to prevent racemization of the starting sulfinamide and the acid chloride by the HCl formed during the reaction. Pyridine (10% excess) and (+)-I in ether were cooled to −78° and dry chlorine was added to a slight excess (pale yellow color). The cold ether solution was used without filtering in the subsequent steps because (−)-II racemizes within minutes at higher temperature. When a cold ether solution of (−)-II was added to excess dimethylamine in ether at −78°, (+)-III, $[\alpha]^{25}D$ +50.9° (*c* 1.22, acetone), mp 75–76°, was obtained in 56% yield. The precipitate of dimethylamine hydrochloride was filtered at room temperature, the ether was evaporated, and the product was recrystallized from ethanol–water. The third reaction in the series was accomplished by reduction of (+)-III, $[\alpha]^{25}D$ +47.8° (*c* 1.47, acetone) (94% optical purity), with aluminum amalgam in 10% aqueous tetrahydrofuran. After chromatography on silica gel (ether) a 37% yield of (−)-(*R*)-I, $[\alpha]^{25}D$ −157.5° (*c* 1.34, acetone), 91% optically pure, was obtained. In this series of transformations (+)-I → (−)-II → (+)-III → (−)-I, one step must occur with inversion of configuration and two steps with retention or all three must go with inversion. The reduction of (+)-III to (−)-I with aluminum amalgam is analogous to transformation (+)-V → (+)-I and others[9] which have been shown to occur with retention at sulfur and, therefore, it can be concluded that compound (+)-III has the *R* configuration.[13] This conclusion is compatible with the stereochemical course of reaction (+)-I → (−)-II which is expected to proceed with retention since this reaction can be considered as an electrophilic substitution occurring on sulfur without perturbation of the tetrahedral structure. Thus, the nucleophilic displacement reaction at tetracoordinate hexavalent sulfur (−)-II → (+)-III must proceed with inversion of configuration.

A third cycle (Chart I) of transformation was completed by the sequence I → II → IV → V → I. Starting from (+)-(*S*)-I of 98% optical purity, (+)-IV was obtained by adding a cold ether solution of (−)-II to an excess of sodium phenoxide in dimethylformamide at 0° and stirring for 0.5 hr. After extraction with ether, the crude ester was recrystallized twice from methanol–pentane, $[\alpha]^{25}D$ +81.1° (*c* 1.71, acetone), mp 106–107°, yield 40%. A sample of crude ester was chromatographed on silica gel (pentane–ether) and found to have $[\alpha]^{25}D$ +62.8° (*c* 1.82, acetone), mp 96–99°. Recrystallization (four times) of this sample of (+)-IV to constant specific rotation and melting point gave the following values: $[\alpha]^{25}D$ +81.7° (*c* 1.51, acetone), mp 106–107°. The loss of optical purity during the two-step reaction sequence is probably caused by racemization of the acid chloride II prior to reaction with phenoxide.

To (+)-IV ($[\alpha]^{25}D$ +81.1°) in ether at 0° was added a severalfold excess of methyllithium; the reaction mixture was stirred at room temperature for 0.5 hr. After adding water, the product was extracted with dichloromethane, chromatographed on silica gel (ether), and sublimed. A 66% yield (not maximized) of sulfoximine VI, $[\alpha]^{25}D$ +174.8° (*c* 1.15, acetone) (96% optically pure), was obtained. This reaction which proceeded with at least 97% stereospecificity exemplifies a new synthetic route to N-substituted sulfoximines. In this cycle, transformations (+)-I → (−)-II and (+)-V → (+)-I occur with retention (above) and therefore (−)-II → (+)-IV and (+)-IV → (+)-V both must have the same stereochemistry. The conversion of (−)-II to (+)-IV very likely proceeds with the same stereochemical course as for the similar conversion (−)-II → (+)-III, and thus, both occur with inversion.[14,15]

(5) S. Colonna, R. Giovini, and F. Montanari, *Chem. Commun.*, 865 (1968).

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

(7) D. Cram, J. Day, D. Rayner, D. von Schriltz, D. Duchamp, and D. Garwood, *ibid.*, 92, 7369 (1970).

(8) For an alternative method of relating the configuration of (+)-VI and (−)-VII see ref 9.

(9) C. W. Schroeck and C. R. Johnson, *ibid.*, 93, 5305 (1971).

(10) This reaction, which represents a new and convenient method for the N-methylation of sulfoximines, was developed by C. W. Schroeck in our laboratory (Ph.D. Dissertation, Wayne State University, 1971).

(11) C. W. Schroeck, private communication.

(12) E. U. Jonsson, C. C. Bacon, and C. R. Johnson, *J. Amer. Chem. Soc.*, 93, 5306 (1971).

(13) In the configurational designation of (+)-III as *R* we follow the same considerations as customary for sulfinate esters; see footnote 10 in K. Mislow, M. Green, P. Laur, J. Milillo, T. Simmons, and A. Ternay, Jr., *ibid.*, 87, 1958 (1965).

(14) Appropriate analytical and/or spectral data are on hand to confirm structures and purity of new compounds.

(15) A referee has suggested that we classify our stereochemical reaction cycles employing the system of D. C. Garwood and D. J. Cram [*J. Amer. Chem. Soc.*, 92, 4575 (1970)]. Accordingly, we note that in Chart I the cycle (+)-I → (−)-II → (+)-III → (−)-I is a diligiostatic antipodal three-reaction stereochemical cycle involving one inversion, the cycle (+)-I → (+)-V → (+)-IV → (−)-II → (+)-III → (−)-I is a diligiostatic antipodal five-reaction stereochemical cycle involving three inversions, and the cycle (+)-I → (−)-II → (+)-IV → (+)-V → (+)-I is a diligiostatic podal four-reaction stereochemical cycle involving two inversions. In Chart II, the sequence (−)-VII to (+)-VII is a diligiostatic antipodal five-reaction stereochemical cycle involving two inversions and one ligand metathesis.

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A Mild Procedure for Transforming Nitro Groups into Carbonyls. Application to the Synthesis of *cis*-Jasmone

Sir:

1,4-Diketones are valuable intermediates for further elaboration into either furan or cyclopentenone systems,