

unit could either spontaneously trimerize or be formed as a trimer as a result of the intermolecular elimination of $(\text{CH}_3)_2\text{Sn(SCH}_3)\text{Br}$ rather than intramolecular elimination as depicted above.

The structure in Figure 1 satisfies the requirements of the "inert gas rule" and is consistent with the infrared, magnetic, and molecular weight measurements.

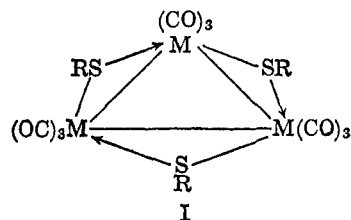


Figure 1. Proposed structure for $\text{M(CO)}_3\text{SR}$ trimers; $\text{M} = \text{Mn}$ and Re .

The formation and recognition of metal clusters⁷ is becoming increasingly interesting in inorganic chemistry, and we believe that the use of "fissionable ligands," as above, can be a powerful tool for the synthesis of a wide variety of such systems.

Acknowledgment. We are grateful to the International Tin Council for a grant in support of this work.

(7) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962); J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *ibid.*, **2**, 1166 (1963); B. H. Robinson and J. E. Fergusson, *J. Chem. Soc.*, 5683 (1964); J. Lewis, *Pure Appl. Chem.*, **10**, 11 (1965).

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Stereochemistry of Nucleophilic Substitution at Sulfur. Stereospecific Synthesis of an Optically Active Sulfilimine¹

Sir:

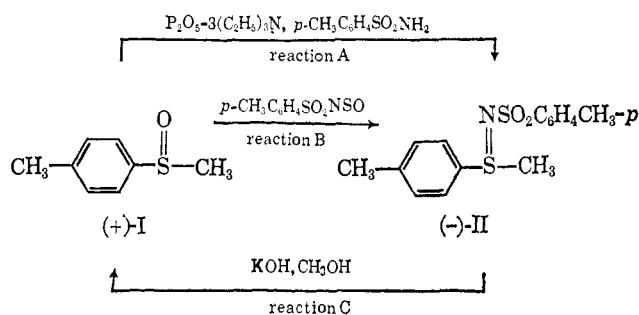
Considerable evidence has accumulated that nucleophilic substitution at silicon^{2a} or phosphorus^{2b,c} can proceed with retention or inversion of configuration or with racemization. Nucleophilic substitution at sulfur has been observed to occur only with racemization or with partial or complete inversion.³

(1) The authors wish to express their appreciation to the Public Health Service for a grant used in support of this investigation.

(2) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965; (b) R. F. Hudson and M. Green, *Angew. Chem.*, **75**, 47 (1963); (c) L. Horner, *Pure Appl. Chem.*, **9**, 225 (1964).

(3) (a) H. Phillips, *J. Chem. Soc.*, 2552 (1925); (b) C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963); (c) F. Montanari, *Tetrahedron Letters*, No. **38**, 2685 (1964); (d) K. Mislow, M. M. Green, P. Laur,

We have studied the stereochemical course of the reactions formulated. Evidence for the optical purity of I, m.p. 74.5–75.5°, $[\alpha]_D^{25} +180.5^\circ$ ($c = 1.612$, acetone), $[\alpha]_D^{25} +146^\circ$ ($c = 1.612$, acetone) has been given previously.^{3d,e} An optically impure sample of II (m.p. 121.5–123°) after five successive recrystallizations exhibited a constant melting point (125–125.5°) and rotation ($[\alpha]_D^{25} -320.0^\circ$ ($c = 1.682$, acetone)) and is presumed to be optically pure. Satisfactory n.m.r., ultraviolet, and infrared spectra, as well as carbon, hydrogen and sulfur analyses, were obtained for both I and II.



Reaction A, carried out at 0° for 11 hr. in methylene dichloride with a 1:3 molar ratio of phosphorus pentoxide and triethylamine and optically pure (+)-I, gave (-)-II (66%) which was 70% optically pure.⁴ The product was separated from the 17% of starting material remaining (26% racemized) by silica gel chromatography with acetonitrile as solvent,⁵ and rotations were taken on whole samples without recrystallization (all cases). Controls demonstrated the isolation method to be satisfactory and that (-)-II was optically stable under the conditions of its formation. Reaction B was conducted in pyridine at 0° for 3.5 hr. with optically pure (+)-I to give (-)-II (95%) which was 98% optically pure.⁶ Reaction C was conducted in methanol saturated with potassium hydroxide at 16° for 24 hr. with optically pure (-)-II to give (+)-I in 94% yield and 96% optical purity.⁷ These cyclic series of transformations unequivocally establish that compound II was at least 94% optically pure. Acidic hydrolysis of (-)-II in 12 N sulfuric acid at 100° for 3 hr., or 12 N hydrochloric acid at 25° for 40 min., or 12 N hydrochloric acid at 100° for 3 min. gave racemic I.⁸ Sulfoxides undergo racemization with hydrochloric acid under a variety of condi-

J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **87**, 1958 (1965); (e) K. K. Andersen, W. Gaffield, N. Papanikolaou, J. W. Foley, and R. I. Perkins, *ibid.*, **86**, 5637 (1964); (f) K. Mislow, A. L. Ternay, Jr., and J. T. Melillo, *ibid.*, **85**, 2329 (1963); (g) K. K. Andersen, *Tetrahedron Letters*, No. **3**, 93 (1962).

(4) D. S. Tarbell and C. Weaver [*J. Am. Chem. Soc.*, **63**, 2939 (1941)] and N. Newman [Ph.D. Dissertation, University of Minnesota, 1964] have prepared sulfilimines with phosphorus pentoxide and *p*-toluenesulfonamide (no triethylamine).

(5) C. D. Ritchie and A. L. Pratt, *J. Am. Chem. Soc.*, **86**, 1571 (1964), found that acetonitrile complexes with sulfoxides.

(6) G. Schulz and G. Kresze, *Angew. Chem.*, **75**, 1022 (1963), first used *N*-sulfinylsulfonamides to convert optically inactive sulfoxides to the corresponding sulfilimines.

(7) R. Appel and W. Büchner [*Ber.*, **95**, 855 (1962)] reported that simple sulfilimines (e.g., dimethylsulfilimine, which is unstable at room temperature) quickly undergo hydrolysis in the presence of base.

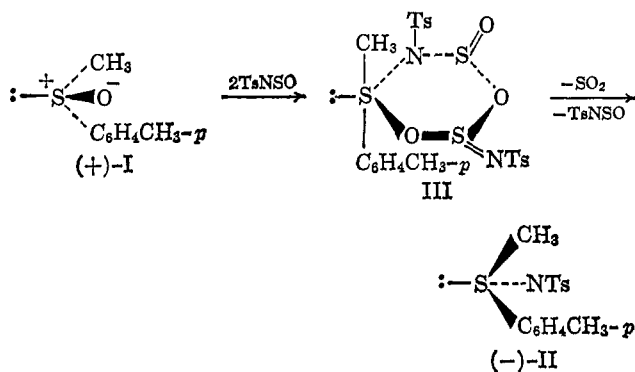
(8) G. Kresze and B. Wustrow, *ibid.*, **95**, 2652 (1962), reported that optically active *S*-methyl-*S*-(3-carboxyphenyl)-*N*-*p*-toluenesulfonylsulfilimine [first prepared by S. G. Clarke, J. Kenyon, and H. Phillips, *J. Chem. Soc.*, 188 (1927)] underwent hydrolysis stereospecifically with 12 N hydrochloric acid at 100°.

tions.⁹ Optically pure (+)-I became completely racemic when dissolved in polyphosphoric acid at 25° and recovered.

The relative configurations of (+)-I and (-)-II were determined from the opposite signs of the Cotton effects in their optical rotatory dispersion curves (absolute ethanol, Cary Model 60 spectropolarimeter). The curves have very similar shapes except that the center of the Cotton effect in the spectrum of (-)-II lies at shorter wave length than that in the spectrum of (+)-I, possibly due to a greater positive charge on asymmetric sulfur in the sulfilimine. In the curve of (-)-II, principal maxima occur at 243 ($[\phi] -45,500^\circ$) and 225 $m\mu$ ($[\phi] +35,500^\circ$), and $[\phi]$ is 0° at 234 $m\mu$ and 213 $m\mu$. In the curve of (+)-I, principal maxima occur at 256 ($[\phi] +21,000^\circ$) and 226 $m\mu$ ($[\phi] = -112,000^\circ$), and $[\phi]$ is 0° at 246 and 214 $m\mu$.

The nature of the transition responsible for these Cotton effects is not certain, but a sulfur $n \rightarrow \pi^*$ transition is thought to be involved with alkyl aryl sulfoxides,^{3d} and the close similarity of the two curves indicates the transition of the sulfilimine to be of the same type. Since (+)-I possesses an *R* configuration,^{3d} we may assign the *S* configuration to (-)-II and conclude that reactions A, B, and C have proceeded with inversion of configuration.¹⁰

In reaction B sulfur dioxide is formed, and thus the entering and leaving nucleophile must be coupled in a ring system, formally similar to the Wittig reaction.¹¹ This fact, together with the observed inversion, provides strong evidence for a mechanism involving a trigonal bipyramidal intermediate or transition state such as III in which the entering and leaving groups both occupy radial positions in the trigonal bipyramid,¹² whose formation and decay involve similar bond movements. In the formulation of this mechanism, two moles of *N*-sulfinylsulfonamide is implicated, a postulate subject to kinetic verification. Preliminary results indicate the reaction is second order in *N*-sulfinyl-*p*-toluenesulfonamide. The molecular weight (Signer) of *N*-sulfinyl-*p*-toluenesulfonamide in dichloromethane was found to be 223 (monomer mol. wt. 217). The same steric result is predicted whether the methyl, *p*-tolyl, or electron pair of III occupy the radial posi-



(9) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Am. Chem. Soc.*, **86**, 1452 (1964).

(10) Kresze and Wustrow (ref. 8) based their assignment of an inversion process for hydrolysis of their sulfilimine on the inadequate evidence that starting material and product possessed opposite signs of rotation in the visible region.

(11) Schulz and Kresze (ref. 6) noted this similarity. However, the Wittig reaction occurs with retention of configuration at phosphorus [W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, **86**, 2378 (1964), and quoted references].

(12) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

tion. Similar cyclic or noncyclic mechanisms can be formulated for reactions A and C in which the entering and leaving groups both occupy radial positions.

The classical inversion mechanism in which the leaving and entering groups occupy the axial positions of a trigonal bipyramid clearly cannot apply when these groups are in the same ring system (normal size). If the entering and leaving groups are identical in character but different from the other substituents, both entering and leaving groups are more likely to occupy the same kind of position on the trigonal bipyramid (both in radial or both in axial positions). Formation and decay of the trigonal bipyramid should be essentially the microscopic reverse of one another, and inversion of configuration must result. If the entering and leaving groups are sufficiently dissimilar, then one might occupy an axial and the other a radial position of the trigonal bipyramid, with retention of configuration as the stereochemical result. In this case, formation and decay of the trigonal bipyramid would not be the microscopic reverse of one another. Possibly many of the inversion mechanisms observed at second row elements^{2,3} involve the incoming and leaving groups at radial positions of a trigonal bipyramid.

Structural analogies for III are found in the structures of sulfur tetrafluoride^{13a} and the γ form of solid sulfur trioxide.^{13b}

(13) (a) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963); (b) R. Westrik and C. H. MacGillivray, *Rec. trav. chim.*, **60**, 794 (1941).

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Biosynthesis of Nicotine in *Nicotiana glutinosa* from Carbon-14 Dioxide. Labeling Pattern in the Pyrrolidine Ring¹

Sir:

Since the small fraction of nicotine activity at C-2' found on short term exposure of *Nicotiana glutinosa* to ¹⁴CO₂² was not readily reconcilable with the generally accepted³ symmetrical intermediate formed via the tricarboxylic acid cycle,⁴ nicotine obtained from ¹⁴CO₂ biosynthesis was further degraded.⁵ Within the limits of the degradation used, results were consistent with the symmetry postulate in that C-2' and C-5' were equally labeled, but a new pathway to glutamic acid from CO₂ was required. However, the symmetrical intermediate hypothesis could not be fully evaluated until a ¹⁴CO₂ biosynthesis was performed from which C-3' or C-4', or both, were determined along with C-2' and C-5'. We now wish to report the results of such experiments.

(1) Sponsored in part by the U. S. Atomic Energy Commission.

(2) W. L. Alworth, R. C. DeSelms, and H. Rapoport, *J. Am. Chem. Soc.*, **86**, 1608 (1964).

(3) A. R. Battersby, *Quart. Rev. (London)*, **15**, 259 (1961); K. Mothes and H. R. Schutte, *Angew. Chem.*, **75**, 265 (1963); E. Ramstad and S. Agurell, *Ann. Rev. Plant Physiol.*, **15**, 143 (1964).

(4) E. Leete, *J. Am. Chem. Soc.*, **78**, 3520 (1956); **80**, 2162 (1958); E. Leete, E. G. Gros, and T. J. Gilbertson, *Tetrahedron Letters*, 587 (1964); E. Leete, *Science*, **147**, 1000 (1965).

(5) W. L. Alworth, A. A. Liebman, and H. Rapoport, *J. Am. Chem. Soc.*, **86**, 3375 (1964).