

monohaloamidine is preceded.^{10,11} After the second halogenation step the mechanism appears to be closely related to the Neber reaction.¹² The ring closure to the proposed intermediate, N-halodiazirine, might involve the nitrene as pictured or be a direct displacement of halide by the N-halo anion.¹³ The same question arises in considering the mechanistic details of the Neber reaction.^{14,15} Whether the N-halodiazirine dissociates as shown to the diazirinium ion followed by competitive reaction of the carbonium ion with nucleophiles present or reacts by an SN2' process with the nucleophiles is a moot question. The former alternative is interesting because the stability of the diazirinium ion would derive from its aromatic character according to Hückel's $4n + 2$ rule.¹⁶ This heterocyclic ion is isoelectronic with the well-characterized cyclopropenecarbonium ion derivatives.¹⁷ The prominence of the fragments of m/e corresponding to the diazirinium ions in the mass spectra suggests that their formation under solvolytic conditions is not unreasonable.

Most of the halodiazirines prepared were comparable in stability to diazirines reported previously.² However, methoxychlorodiazirine decomposed spontaneously at room temperature to give 1,4-dimethoxy-1,4-dichloro-2,3-diaza-1,3-butadiene.¹⁸ Phenylchlorodiazirine decomposed at room temperature over a period of several days to give 1,4-diphenyl-1,4-dichloro-2,3-diaza-1,3-butadiene.

The chemistry unique to the 3-halodiazirines remains to be investigated. However, like other diazirines, they appear to decompose thermally to produce carbene intermediates.^{19,20} Thus, methylchlorodiazirine yields vinyl chloride and nitrogen upon thermal decomposition; decomposition of phenylchlorodiazirine in refluxing cyclohexene gave a mixture believed to be *exo*- and *endo*-7-chloronorcaradiene.²¹

This synthesis provides ready access to a large number of diazirine derivatives of potential biological activity.²² Also the synthesis affords a wide variety of diazirine precursors to carbene intermediates which are not now readily available.

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Trimeric Alkylthiotricarbonyls of Manganese and Rhenium

Sir:

During recent studies of the properties of organotin-sulfur compounds, we have noted two general reactions. Firstly, the sulfur in these compounds can behave simply as a donor atom and replace carbon monoxide in metal carbonyls; secondly, these tin-sulfur compounds react with metal and metalloid halides causing fission of the Sn-S bond, with subsequent formation of a mercapto derivative of the metal or metalloid and an organotin halide as a by-product.¹

We now wish to report the formation of novel metal carbonyl derivatives from the reaction of organotin-sulfur compounds with metal carbonyl halides—a system in which both substitution and fission reactions could occur.

Bromopentacarbonylmanganese reacts with bis(methylthio)dimethyltin² in diethylene glycol dimethyl ether above 70° to give the diamagnetic, trimeric methylthiotricarbonylmanganese, obtained as orange crystals in 69% yield. *Anal.* Calcd. for C₁₂H₉Mn₃O₉S₃: C, 25.8; H, 1.6; O, 25.8; S, 17.2; mol. wt., 558. Found: C, 26.0; H, 1.6; O, 26.0; S, 17.2; mol. wt.,³ 548. Infrared C-O stretching modes are observed at 2021 (vs), 2014(w), and 1950(s) cm.⁻¹. Chloropentacarbonylrhenium reacts similarly above 120° to give pale yellow crystals of methylthiotricarbonylrhenium in 59% yield. *Anal.* Calcd. for C₁₂H₉Re₃O₉S₃: C, 15.1; H, 1.0; O, 15.1; mol. wt., 952. Found: C, 15.4; H, 1.1; O, 15.2; mol. wt.,³ 971. In addition to these two compounds a number of alkyl and aryl analogs of both of these compounds have been similarly prepared. In addition to the well-known dimeric alkylthiotetracarbonyls⁴ of manganese and rhenium, mention has been made in the patent literature⁵ of "hydrocarbylthio-manganese tricarbonyls, existing as trimers and dimers under varying conditions."

The formation of the methylthiotricarbonylmanganese unit and its trimerization in this reaction can be rationalized as follows. Reaction of a bidentate sulfur ligand with bromopentacarbonylmanganese has been previously shown⁶ to replace two carbon monoxide groups to produce LMn(CO)₃Br. Regarding (CH₃)₂Sn(SCH₃)₂ as a bidentate ligand, one would expect (CH₃)₂Sn(SCH₃)₂Mn(CO)₃Br to be formed, but subsequent fission of the Sn-S bond owing to presence of halogen causes the reaction shown. The Mn(CO)₃SCH₃

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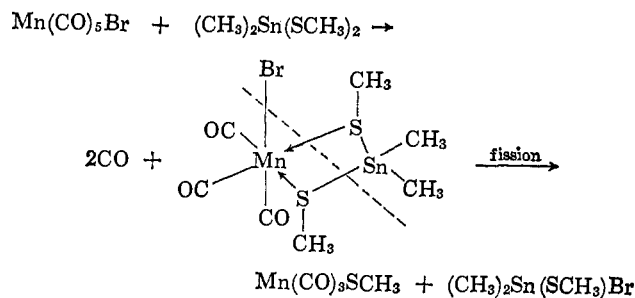
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(20) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 758 (1965).

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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.

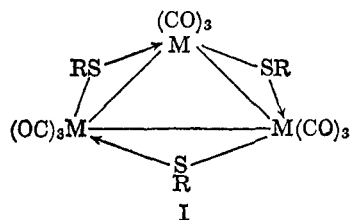


Figure 1. Proposed structure for $\text{M(CO)}_3\text{SR}$ trimers; $\text{M} = \text{Mn}$ and Re .

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.

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

Sir:

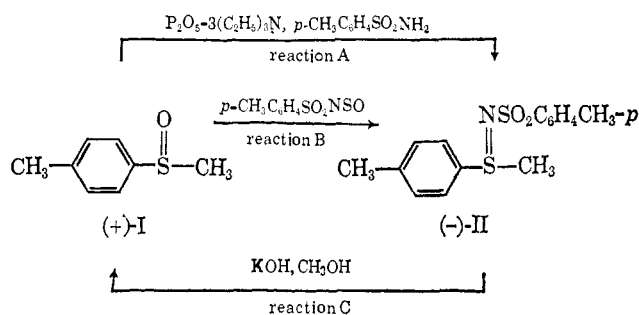
Considerable evidence has accumulated that nucleophilic substitution at silicon^{2a} or phosphorus^{2b,c} can proceed with retention or inversion of configuration or with racemization. Nucleophilic substitution at sulfur has been observed to occur only with racemization or with partial or complete inversion.³

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

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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-

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