We intend to investigate these systems in more detail and in particular to study the crystal structures and magnetic susceptibilities of $Na_2Cu\text{-}dl\text{-}C_4O_6H_2 \cdot 5H_2O$, $Cu\text{-}dl\text{-}C_4O_6H_4 \cdot 3H_2O$, and $Cu\text{-}meso\text{-}C_4O_6H_4 \cdot 1.75H_2O$.

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O-Trialkylstannyl Oximes

By P. G. HARRISON and J. J. ZUCKERMAN

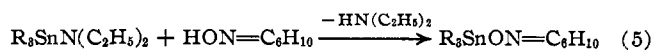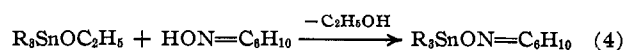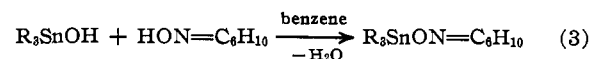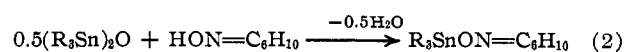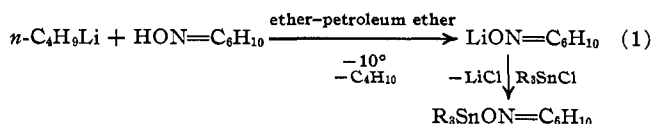Fourth-group oximes have been synthesized from (a) the organoelement chlorides and the oxime in the presence of a strong Lewis base, (b) organotin chlorides with the O-lithio oxime to split out lithium chloride, and (c) bis(organotin) oxides and organotin hydroxides, ethoxides, and diethylamines with the oxime to split out water, ethanol, and diethylamine, respectively. The products are monomeric in solution; all are liquids except O-trimethylstannylcyclohexanone oxime whose ir spectrum differs from that in solution and whose mass spectrum shows peaks above the parent mass which are revealed by high-resolution work to contain the Sn–O–Sn backbone, presumably resulting from cyclic Sn–O–Sn–O structures in the solid. Confirmation of the high-coordination solid state structure comes from Sn^{119m} Mössbauer quadrupole splitting values which are *ca.* 1 mm/sec higher for the trimethyltin derivatives. The O-trialkyltin oximes undergo metathetical reactions with water and hydrogen chloride and with other fourth group chlorides to give the silicon and germanium analogs, and insertion reactions with isocyanates, isothiocyanates, chloral, bromal, etc., to give novel adducts where reactivity is seen to be in the orders Sn > Ge ≫ Si and SnOR > SnON=C< and $X_3CCHO > C_6H_5NCO > RNCO > C_6H_5NCS$.

The O-group III derivatives of acetoxime are all dimers in benzene, with the dimethylboron compound somewhat dissociated. In the vapor the dimethylboron oxime is a monomer, while the other dimethyl derivatives retain their dimeric character. Six-membered "BONBON"-type ring structures seem likely for these compounds, although the evidence does not allow the four-membered "BOBO" structures to be ruled out.[1] The methylzinc derivative of acetoxime is a tetramer in which zinc atoms in a six-membered "ZnONZnON" achieve four-coordination by binding two such rings into a cage structure.[2]

In tin chemistry there is precedent for the four-membered SnOSnO ring structure in the stannoxanes,[3] and adducts with nitrogenous ligands are easily formed as well. Thus it seemed of interest in investigating the oxime derivatives of the fourth group to concentrate on the organotin oximes in order to take advantage of the more powerful Lewis acidity of tin and also to be able to bring to bear additional evidence from nmr, ir, and Sn^{119m} Mössbauer spectroscopies. Because Lewis acids are known to catalyze the rearrangement of oximes to amides,[4] cyclohexanone oxime was chosen to ensure that all of the group IV derivatives would have the $R_3MO\text{-}N=C<$ structure.

Discussion

The organotin cyclohexanone oxime derivatives reported here were prepared by the five routes

(1) J. R. Jennings and K. Wade, *J. Chem. Soc., A*, 1333 (1967).
(2) G. E. Coates and D. Ridley, *ibid., A*, 1064 (1966).
(3) R. Okawara and M. Wada, *Advan. Organometal. Chem.*, **5**, 151 (1967).
(4) C. R. Hauser and D. S. Hoffenberg, *J. Org. Chem.*, **20**, 1482 (1955).

$$n\text{-}C_4H_9Li + HON=C_6H_{10} \xrightarrow[\substack{-10° \\ -C_4H_{10}}]{\text{ether–petroleum ether}} LiON=C_6H_{10} \quad (1)$$

$$\xrightarrow[-LiCl]{R_3SnCl}$$

$$R_3SnON=C_6H_{10}$$

$$0.5(R_3Sn)_2O + HON=C_6H_{10} \xrightarrow{-0.5H_2O} R_3SnON=C_6H_{10} \quad (2)$$

$$R_3SnOH + HON=C_6H_{10} \xrightarrow[-H_2O]{\text{benzene}} R_3SnON=C_6H_{10} \quad (3)$$

$$R_3SnOC_2H_5 + HON=C_6H_{10} \xrightarrow{-C_2H_5OH} R_3SnON=C_6H_{10} \quad (4)$$

$$R_3SnN(C_2H_5)_2 + HON=C_6H_{10} \xrightarrow{-HN(C_2H_5)_2} R_3SnON=C_6H_{10} \quad (5)$$

Unlike the third group element and zinc alkyls which react directly with acetoxime to liberate methane and generate the oxime derivative,[1,2] tetraphenyltin pyrolyzes when heated at 190° with cyclohexanone oxime. Other fourth-group oximes were prepared in the presence of a strong Lewis base

$$R_3MCl + HON=C_6H_{10} \xrightarrow{(C_2H_5)_3N} R_3MON=C_6H_{10} +$$

$$(C_2H_5)_3NHCl \quad (6)$$
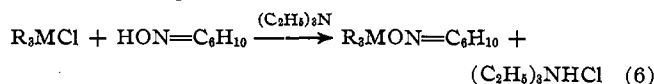
where $R = CH_3$ and M = Si, Ge.

The trialkyl fourth-group cyclohexanone oxime derivatives are sensitive to hydrolysis except for the trimethylsilyl derivative which is air stable. They are colorless, mobile liquids except the trimethyltin derivative which is a solid. All of the compounds studied are monomeric in dilute benzene (osmometry) at ambient temperatures, and this is reflected in the infrared and nmr data. The absorption assigned to $\nu(C=N)$ is at 1665 cm^{-1} in cyclohexanone oxime. In the group III series, the frequency of this band in the free oxime is lowered by *ca.* 30 cm^{-1} in the partially associated
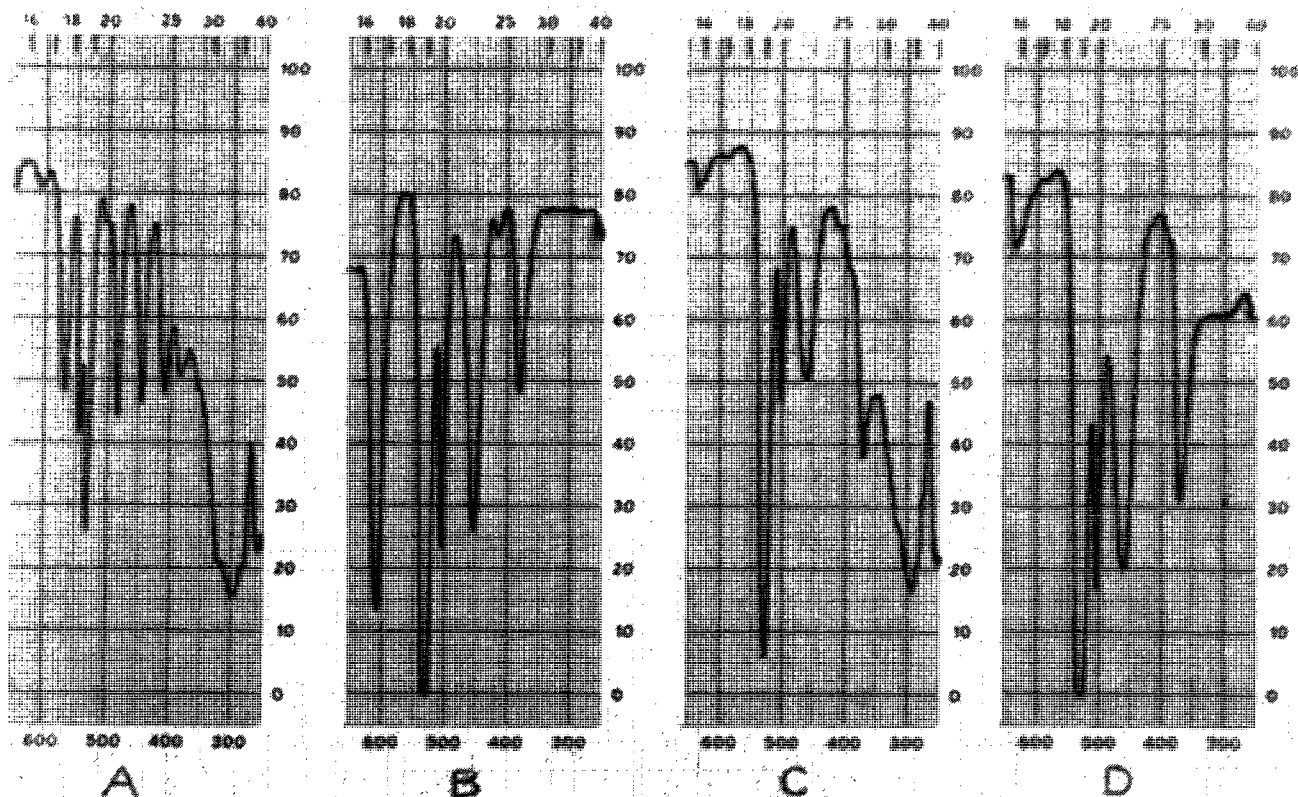
Figure 1.—Infrared spectra: (A) O-trimethylstannylcyclohexanone oxime (Nujol mull); (B) O-trimethylstannylcyclohexanone oxime (5% solution in carbon tetrachloride); (C) O-trimethylstannylacetoxime (neat liquid film); (D) O-trimethylstannylacetoxime (5% solution in carbon tetrachloride).

dimethylboron derivative, and by *ca.* 40 cm^{-1} in the dimeric dimethylaluminum derivative. We ascribe the low ν(C=N) absorption in O-lithiocyclohexanone oxime (1598 cm^{-1}) similarly to association in this intractable, infusible, polymeric material, but the fall in frequency to 1634 and 1629 cm^{-1} in the trimethylsilyl and -germyl derivatives likely arises simply from the operation of a mass effect in these vibronically coupled systems. Likewise, in the four triorganotin derivatives higher than methyl, ν(C=N) is found in the range 1625–1630 cm^{-1} for the neat liquids. However, in the trimethyltin oxime, which is a solid, the frequency falls further to 1617 cm^{-1}. Additional information is available for methyltin derivatives in the 650–300-cm^{-1} region where ν(SnC$_3$) is found, and Figure 1 shows the spectra of O-trimethylstannylcyclohexanone oxime both as the solid and as a 5% solution in carbon tetrachloride. We have synthesized for comparison the O-trimethylstannylacetoxime which is a mobile liquid, monomeric in solution and whose infrared spectra, either as the neat liquid or in dilute solution, give ν(C=N) as 1624 cm^{-1}. It may be seen from the figure that the solid cyclohexanone oxime derivative differs drastically from the acetoxime in this range but that in solution where both the oximes are monomeric the spectra are strikingly similar. We conclude that the O-trimethylstannylcyclohexanone oxime is apparently able to enjoy additional association in the condensed phase not available to either the acetoxime or higher alkyl- or aryltin derivatives and that this association is disrupted in

solution where the compound is monomeric. The nmr J(Sn^{117,119}-C-H^1) is also sensitive to association, and the values recorded for the methyltin cyclohexanone oxime in dilute solution [J(Sn^{117,119}-C-H^1) = 54.4, 57.2 cps] correspond to normal four-coordination at tin. In addition, the absorption assigned to ν(C=N) in the cyclohexanone oxime moves from 1617 cm^{-1} in the solid to a solution value of 1625 cm^{-1}, in the range of the other O-trialkylstannyl oximes (1624–1626 cm^{-1}).

Sn^{119m} Mössbauer spectroscopy can be used to corroborate these conclusions. The quadrupole splitting data gathered in Table I indicate that the value for the methyltin cyclohexanone oxime is higher by *ca.* 1.0 mm/sec than the 1.4–2.0 mm/sec range observed for the other oximes. Moreover, the ratio of the quadrupole splitting to the isomer shift (QS/IS = ρ) is *ca.* 2.1 for the methyltin cyclohexanone oxime and below 1.8 for the rest. Such data lead to the conclusion that the coordination number of the tin atoms in the solid methyltin cyclohexanone oxime derivative must be greater than 4.[5]

The Mössbauer spectra of the organotin oximes reported here are run at liquid nitrogen temperatures. Data for neat solids such as the trimethyltin cyclohexanone oxime, neat liquids, such as the trimethyltin acetoxime, or each substance in solution can be recorded at 77°K. At cryoscopic temperatures the tendency for

(5) R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, **42**, 2447 (1965). See also J. J. Zuckerman in "Mössbauer Effect Methodology" Vol. 3, I. J. Gruverman, Ed., Plenum Press, New York, N. Y., 1967, p 15; J. J. Zuckerman, *Advan. Organometal. Chem.*, in press.

TABLE I

PHYSICAL DATA FOR THE OXIME DERIVATIVES

Oxime	Bp, °C (P, mm); mp, °C	ν(C=N), cm⁻¹	τ(M−CH₃)	IS (±0.06), mm/sec	QS (±0.06), mm/sec
$HON=C(CH_3)_2$					
$HON=C_6H_{10}$		1665 m			
$LiON=C_6H_{10}$		1598 m			
$(CH_3)_3SiON=C_6H_{10}$	35 (0.5), 120 (8)	1634 vw	9.86		
$(CH_3)_3GeON=C_6H_{10}$	48 (0.1)	1629 vw	9.62		
$(CH_3)_3SnON=C(CH_3)_2$	58 (0.01)	1624 vw	9.66,ᵃ 9.67ᵇ	1.40	2.93
$(CH_3)_3SnON=C_6H_{10}$	58–59 (0.02); 58–59	1617 vwᶜ	9.62ᵈ	1.43, 1.37ᵉ	2.96, 3.00ᵉ
$(C_2H_5)_3SnON=C_6H_{10}$	74–76.5 (0.01)	1625 vw		1.58	1.96
$(n\text{-}C_3H_7)_3SnON=C_6H_{10}$	85 (0.02)	1626 vw		1.42	2.03
$(n\text{-}C_4H_9)_3SnON=C_6H_{10}$	120 (0.02)	1626 vw		1.48	1.76
$(C_6H_5)_3SnON=C_6H_{10}$	Oil	1630 vw		1.38	1.44

ᵃ In carbon tetrachloride; $J(Sn^{117,119}\text{-}C\text{-}H^1) = 54.5$ cps. ᵇ In benzene; $J(Sn^{117,119}\text{-}C\text{-}H^1) = 54.0, 55.8$ cps. ᶜ 1625 cm⁻¹ for a 5% solution in carbon tetrachloride. ᵈ In carbon tetrachloride; $J(Sn^{117,119}\text{-}C\text{-}H^1) = 54.4, 57.2$ cps. ᵉ 15% solution in n-butylbenzene.

additional coordination is maximized. Thus we find that both methyltin species studied exhibit high quadrupole splitting values either as neat substances or as 15% solutions in n-butylbenzene. Apparently the rate of oligomerization exceeds the increase in viscosity with falling temperature for the neat acetoxime or even for the dilute n-butylbenzene solutions as these samples become glasses when cooled to 77°K by immersion in liquid nitrogen. The optical transparency of such glasses indicates that the dimensions of the oligomers are restricted to less than the wavelength of visible light. Only the methyltin species seem so affected.

The monotin-containing, polyisotopic molecular ion (m/e 236) is the highest mass feature in the mass spectrum of the trimethyltin acetoxime derivative and corresponds to the parent peak. The remaining major peaks in the spectrum can be assigned to species resulting generally from the loss of one or more methyl groups from the parent molecular ion or from the major fission fragments such as $(CH_3)_3Sn$. Relative peak intensities and suggested assignments are listed in Table II.

The mass spectrum of O-trimethylstannylcyclohexanone oxime, on the other hand, exhibits polyisotopic ions above the calculated value for the parent (m/e 276). These fragments give rise to series of strong peaks, each corresponding to the possible mass distributions of a ditin ion,⁶ and clearly represent fragments derived from the dimer, although no peak due to the dimeric molecular ion, $[(CH_3)_3SnON=C_6H_{10}]_2$, was observed. The mass units of the eight ditin ions, along with their relative intensities, are listed in Table III. Five of these peaks are found above the mass of the monomer (m/e 276), and the eight differ from one another by 14–16 mass units based upon the $Sn^{118}\text{-}Sn^{120}$ peak, suggesting the successive loss of six methyl groups. The two most intense peaks at 329 and 299 mass units, respectively, were chosen for high-resolution work. Neither contains nitrogen. The two fragments correspond to $C_5H_{15}OSn_2$ and $C_3H_9OSn_2$, respectively, to which we assign the structures $(CH_3)_3SnOSn(CH_3)_2^+$ and $(CH_3)_2$-

TABLE II

MASS SPECTRAL DATA FOR $(CH_3)_3Sn$ OXIMES

Assignment	$(CH_3)_3Sn$-$ON=C(CH_3)_2$ Mass	Rel intens	$(CH_3)_3Sn$-$ON=C_6H_{10}$ Mass	Rel intens
$(CH_3)_3SnON=C<^+$	236	23.7	276	14.4
$(CH_3)_2SnON=C<^+$	221	59.2	261	34.4
$CH_3SnON=C<^+$	206	1.32	...	...
$SnON=C<^+$	191	17.9	231	6.2
$(CH_3)_3Sn^+$	164	100	164	100
$(CH_3)_2Sn^+$	149	12.1	149	15.2
CH_3Sn^+	134	19.7	134	30.3

TABLE III

MASS SPECTRAL DATA ON THE DITIN FRAGMENTS FROM $(CH_3)_3SnON=C_6H_{10}$

Assignment	Mass of Sn^{119}_2 peak	Rel intens
$(CH_3)_3SnOSn(CH_3)_3^+$	344	1.2
$(CH_3)_3SnOSn(CH_3)_2^+$	329ᵃ	100
$(CH_3)_2SnOSn(CH_3)_2^+$	313	1.7
$(CH_3)_2SnOSnCH_3^+$	299ᵇ	28.2
$CH_3SnOSnCH_3^+$	283	2.7
CH_3SnOSn^+	269	11.3
$SnOSn^+$	254	7.0
Sn_2^+	238	1.5

ᵃ Mass measurements: calcd, 328.916; found, 328.922.
ᵇ Mass measurements: calcd, 298.8695; found, 298.8698.

$SnOSnCH_3^+$, where the m/e 329 peak is the most intense feature in the entire spectrum. On this basis the peak at m/e 344 can be assigned to $(CH_3)_3SnOSn$-$(CH_3)_3^+$ and the one at m/e 254 to $SnOSn^+$.

From this evidence we conclude that the vapor above the solid O-trimethylstannylcyclohexanone oxime contains oligomeric units, and that barring rearrangements in the mass spectrometer, these units as dimers have the cyclic "SnOSnO" structure (A) rather than the "SnONSnON" structure (B).⁷ Further, it seems likely that these units are present in

A   B
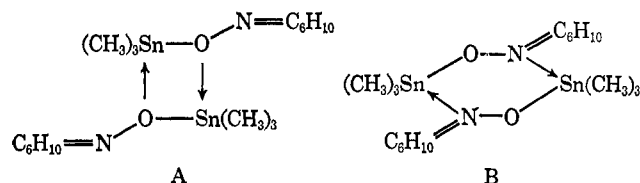
(6) D. B. Chambers, F. Glockling, and M. Weston, *J. Chem. Soc., A*, 1759 (1967).

(7) Although we have not ruled out the compositions $C_5H_9ONSn_2$ and CH_3ONSn_2 for the weak features at 313 and 283 mass units, respectively.

TABLE IV

REACTIONS OF $R_3SnON{=}C_6H_{10}$ WITH ISOCYANATES

| Isocyanate	R	Adduct	$\nu(C{=}O)$, cm^{-1}
C_6H_5NCO	C_2H_5	$R_3Sn\overset{\displaystyle O}{\overset{\|}{N}}CON{=}C_6H_{10}$ $\|$ C_6H_5	1710 m, 1680 vs, 1650 s
	$n\text{-}C_3H_7$		1685 vs
	$n\text{-}C_4H_9$		1705 vs, br
CH_3NCO	$CH_3{}^{a,b}$	$R_3Sn\overset{\displaystyle O}{\overset{\|}{N}}CON{=}C_6H_{10}$ $\|$ CH_3	1660 vs, br
	$n\text{-}C_3H_7{}^b$		1680 vs, br
	$n\text{-}C_4H_9{}^c$		1685 vs, 1710 vs, sh
C_2H_5NCO	$n\text{-}C_4H_9{}^d$	$R_3Sn\overset{\displaystyle O}{\overset{\|}{N}}CON{=}C_6H_{10}$ $\|$ C_2H_5	1700 vs, br

[a] $\tau(SnCH_3)$ 9.62; $J(Sn^{117,119}{-}C{-}H^1) = 54.0, 56.7$ cps.   [b] $\tau(NCH_3)$ 7.34.   [c] $\tau(NCH_3)$ 7.32.   [d] $\tau(NCH_2CH_3)$ 6.97 (quartet center); $J(H^1{-}H^1) = 7.0$ cps.

the solid trimethyltin cyclohexanone oxime derivative, although structural work is necessary to clarify this point, as well as to supply an explanation for the greater solid-state stability of the cyclohexanone oxime compared with the acetoxime analog, despite the apparently greater spatial requirements of the former.

The O-trialkylstannyl oximes react with water and other acidic reagents such as hydrogen chloride to cleave the tin–oxygen bond and regenerate quantitatively the parent oxime

$$R_3MON{=}C_6H_{10} + HE \rightleftharpoons R_3ME + HON{=}C_6H_{10} \quad (7)$$
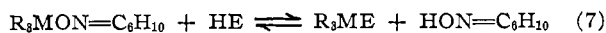
where $E = OH, Cl$. Of more interest are the reactions whereby cleavage of the tin–oxygen bond results in the transformation of the tin oxime into its other fourth-group analogs

$$R_3SnON{=}C_6H_{10} + (CH_3)_3MCl \rightleftharpoons$$
$$R_3SnCl + (CH_3)_3MON{=}C_6H_{10} \quad (8)$$
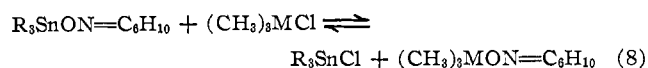
where $R = n\text{-}C_4H_9$ and $M = Si, Ge$. Investigations in this laboratory have demonstrated that a wide variety of transformation reactions of the general type

$$M{-}E + Q{-}X \rightleftharpoons M{-}X + Q{-}E \quad (9)$$
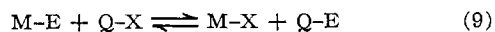
where M and Q are metals or metalloids, X is a halogen, and E– is an organic grouping such as RO–, R_2N–, etc., are possible.[8] In the case described by eq 9 where M = Sn, Q = Si or Ge, and X = Cl, the transformations are exothermic. Barring a large heat of mixing, a large enthalpy change in such a reaction can only arise if the decrease in bond energy in going from Si–Cl and Ge–Cl to Sn–Cl is more than offset by the increase in bond energy expected in transforming Sn–O into Si–O or Ge–O. We are able to distinguish no differences in exothermicity between the silicon and germanium reactions. For the chlorides, the bond energies are given as 91, 81, and 76

kcal/mol for Si, Ge, and Sn, respectively; for the oxygen bonds the data are 185, 157, and 132 kcal/mol, respectively.[9]

Apart from these metathetical reactions, the O-stannyl oximes undergo reactions involving additions to multiple bonds of the type well known in organotin systems[10]

$$R_3MON{=}C_6H_{10} + A{=}B \rightleftharpoons R_3MABON{=}C_6H_{10}$$
$$\text{or} \qquad\qquad (10)$$
$$R_3MBAON{=}C_6H_{10}$$
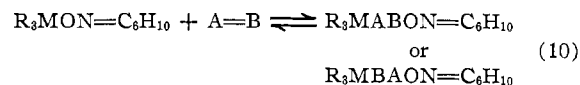
Alkyl and aryl isocyanates and isothiocyanates have been used along with chloral and bromal to give adducts. The data for these reactions are gathered in Tables IV and V. The adducts are viscous oils rapidly hydrolyzed by atomspheric moisture.

We can record our observations on these reactions in general summary form. (a) The stannyl oximes are less reactive toward multiply bonded reagents than are the analogous stannyl alkoxides; i.e., they react within reasonable times with the stronger acceptor reagents such as the isocyanates and trihaloacetaldehydes but only slowly with phenyl isothiocyanate, a reagent which reacts immediately and exothermally with tri-n-butyltin methoxide.[11] (b) Reactivity decreases sharply ascending the fourth group in the order Sn > Ge ≫ Si. The trimethylsilyl oxime did not undergo reaction with any A=B reagent used. (c) On the basis of the inert nature of the silyl derivative stated in (b), it can be assumed that in the other reactions studied no addition occurs across the oxygen–nitrogen bond, and hence all of the products can be considered to result from the expected M–O addition. (d) The normal sequence of acceptor

(8) C. H. Yoder and J. J. Zuckerman, *J. Am. Chem. Soc.*, **88**, 2170 (1966).

(9) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth and Co. Ltd., London, 1958.

(10) M. F. Lappert, *Organometal. Chem. Rev.*, **1**, 67 (1966).

(11) A. J. Bloodworth, A. G. Davies, and S. C. Vasishtha, *J. Chem. Soc.*, C, 1309 (1967).

TABLE V
REACTIONS OF $R_3M^{IV}ON=C_6H_{10}$ WITH TRIHALOACETALDEHYDES

Trihaloacetaldehyde	R₃M	Adduct	$\nu(C=N)$, cm⁻¹	$\tau(O—CH—)$
$\underset{\displaystyle Cl_3CCH}{\overset{\displaystyle O}{\parallel}}$	(CH₃)₃Si	...	...	...
	(CH₃)₃Ge	$\underset{\displaystyle CCl_3}{\overset{\displaystyle \mid}{R_3MOCHON=C_6H_{10}}}$	1643 w	4.71ᵃ
	(CH₃)₃Sn		1643 wᵇ	4.47ᶜ
	(n-C₄H₉)₃Sn		1640 w	4.68ᵈ
$\underset{\displaystyle Br_3CCH}{\overset{\displaystyle O}{\parallel}}$	(C₂H₅)₃Sn	$\underset{\displaystyle CBr_3}{\overset{\displaystyle \mid}{R_3MOCHON=C_6H_{10}}}$	1641 w	4.88
	(n-C₃H₇)₃Sn		1648 wᵉ	4.88ᶠ

ᵃ $\tau(GeCH_3)$ 9.52.   ᵇ Benzene solution.   ᶜ $\tau(SnCH_3)$ 9.64; $J(Sn^{117,119}-C-H^1) = 52.1, 56.1$ cps.   ᵈ $J(Sn-O-C-H^1) = 14.5$ cps.   ᵉ Carbon tetrachloride solution.   ᶠ $J(Sn-O-C-H^1) = 12.2$ cps.

strengths of multiply bonded reagents was in evidence: $X_3CCHO > C_6H_5NCO > RNCO > C_6H_5NCS$. (e) Nmr $J(Sn^{117,119}-O-C-H^1)$ spin–spin coupling is detected in some of the adducts of the tin oximes with trihaloacetaldehydes as satellites on the aldehyde proton signal ($J = 12.2–14.5$ cps). Such couplings have been previously observed in the chloral adduct of tri-n-butyltin methoxide ($J = 20.4$ cps),[12] and their detection serves in our case to rule out exchange processes involving breakage of the Sn–O bond with rates greatly in excess of $2\pi \times 12$ sec⁻¹, *i.e.*, approximately 72 sec⁻¹. No coupling is apparent in tri-butyltin methoxide at 33°, presumably because of rapid exchange as ellucidated for the organotin amines, where temperature-induced spectral changes have been studied for several systems.[13]
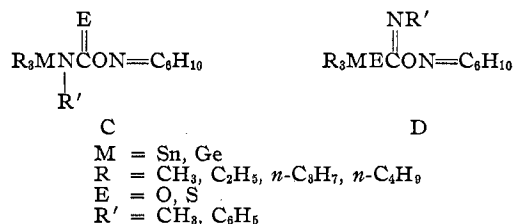
The structures of the adducts deserve separate comment. In conformity with earlier workers,[12] we formulate the product from the reactions with the trihaloacetaldehydes as

$$\underset{\displaystyle CX_3}{\overset{\displaystyle \mid}{R_3MOCHON=C_6H_{10}}}$$
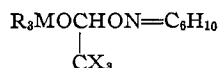
rather than as a donor–acceptor complex of tin with the carbonyl group of the aldehyde. This view is corroborated by the values of the nmr $J(Sn^{117,119}-C-H^1)$ for the trimethyltin oxime adduct with trichloroacetaldehyde which are in the range expected for four- and not five-coordination (52.1 and 56.0 cps for Sn¹¹⁷ and Sn¹¹⁹, respectively). In all of these cases in the Sn¹¹⁹ᵐ Mössbauer spectra the ratio of QS to IS (ρ) is less than 1.8, denoting four-coordination.[5] The observation of tin satellites on the aldehyde proton discussed above can be taken as corroboratory.

The structures of the adducts with the isocyanates are less easy to decide. Again, in conformity with earlier workers[14] we can formulate the products as having structure C, although structure D is certainly

possible. Where $E = O$, the conclusions from infrared evidence are ambiguous, since the absorptions

$$\overset{\displaystyle E}{\underset{\displaystyle \mid}{\underset{\displaystyle R'}{R_3MNCON=C_6H_{10}}}} \qquad \overset{\displaystyle NR'}{R_3MECON=C_6H_{10}}$$

<div align="center">

C   D

M = Sn, Ge
R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉
E = O, S
R' = CH₃, C₆H₅

</div>

appearing in the region usually associated with the carbonyl stretching frequency may in fact arise from $\nu(>C=N-)$.[15] While the structure of the hydrolysis product might constitute strong corroboratory evidence, by itself it is ambiguous since there are easy routes available for the isomerization of the adducts during hydrolysis or other chemical reactions.[14] The problem is somewhat less difficult for $E = S$ since $\nu(C=N)$ and $\nu(C=S)$ may be more readily distinguished, and also because what is known concerning the reactivities toward hydrolysis of organotin–nitrogen and –sulfur bonds may allow them to be distinguished on the basis of the rate of the reaction.

The phenyl isothiocyanate adduct of tri-n-butylstannylcyclohexanone oxime is a viscous oil with a strong absorption at 1590 cm⁻¹. The adduct hydrolyzes quickly in air to give an absorption at 3230 cm⁻¹. Assuming that ready hydrolysis is characteristic of the tin–nitrogen bond, then we can assign the absorptions mentioned above to $\nu(C=S)$ and $\nu(N—H)$, respectively, and discuss the compound in terms of structure C. On the other hand the closely analogous

$$-O-\overset{\displaystyle S}{\underset{}{\overset{\parallel}{C}}}-O-$$
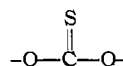
grouping is said to give rise to absorptions in the 1370–1230-cm⁻¹ range,[16] far outside that observed, which argues for the assignment of structure D. In addition, while the instability of $(n-C_4H_9)_3SnSC(=NC_6-$

(12) A. G. Davies and W. R. Symes, *J. Chem. Soc., C*, 1009 (1967).
(13) E. W. Randall, C. H. Yoder, and J. J. Zuckerman, *J. Am. Chem. Soc.*, **89**, 3438 (1967).
(14) A. J. Bloodworth and A. G. Davies, *J. Chem. Soc.*, 5238 (1965).

(15) Typical absorptions for the tin(IV) adducts fall in the range 1725–1595 cm⁻¹.
(16) N. Sheppard, *Trans. Faraday Soc.*, **46**, 429 (1950); R. Mecke and A. Lüttringhaus, *Z. Naturforsch.*, **10b**, 367 (1955).

$H_5)OCH_3$ toward hydrolysis has been noted,[11] it is also true that $(n\text{-}C_4H_9)_2Sn[SC(=NC_6H_5)OCH_3]_2$ hydrolyzes quickly.[17] It seems that rapid hydrolysis may be a result of the ability of tin–sulfur bonded adducts to coordinate internally through the oxime nitrogen in our case, and this view with the infrared evidence would favor structure D.

Experimental Section

Compounds containing tin–oxygen or germanium–oxygen bonds were handled in a dry nitrogen atmosphere. Infrared spectra were recorded as liquid films, as Nujol mulls, or as dilute solutions on a Beckman IR-8 or IR-10 instrument. Nmr spectra were recorded on a Varian A-60A instrument as carbon tetrachloride solutions using tetramethylsilane as an internal standard. Molecular weight determinations were carried out in benzene using a Mechrolab vapor pressure osmometer. Mass spectra were recorded on an AEI MS-9 instrument. Sn^{119m} Mössbauer spectra were obtained at liquid nitrogen temperatures on our cam-drive, constant-acceleration spectrometer by procedures already described[18] using $BaSn^{119m}O_3$ (New England Nuclear Corp.) as the source at ambient temperatures. Microanalytical data were determined by Galbraith Laboratories, Inc. Tin was determined gravimetrically as the oxide.

Preparations of the Oximes.[19] **O-Lithiocyclohexanone Oxime.**—*n*-Butyllithium (6.25 ml 1.6 *M* in hexane, 10 mmol) was added slowly to cyclohexanone oxime (1.13 g, 10 mmol) in ether (50 ml) at −10°. The lithium derivative precipitated immediately as a white solid. After stirring for 2 hr following the addition of the butyllithium, the solid was filtered under nitrogen, washed with ether, and dried by suction, mp (sealed tube) 250° dec (1.19 g, 100%). *Anal.* Calcd for $C_6H_{10}LiON$: C, 37.9; H, 5.3; N, 7.4; Li, 3.7. Found: C, 38.0; H, 5.4; N, 7.5; Li, 3.8. The infrared spectrum exhibited a weak band at 1598 cm^{-1} [$\nu(C=N)$].

O-Trimethylstannylcyclohexanone Oxime.—(a) Butyllithium (1.6 *M* in hexane; 31.3 ml, 50.0 mmol) was added to cyclohexanone oxime (5.7 g, 50.0 mmol) in ether–petroleum ether (1:1 mixture, 100 ml) at −10° to precipitate the lithium oxime. The stirred mixture was allowed to reach room temperature, and trimethyltin chloride (9.8 g, 50.0 mmol) in ether (50 ml) was added. The mixture was refluxed for 2 hr and then filtered under nitrogen. The solvent was removed from the filtrate under reduced pressure, and the residue was distilled [bp 58–59° (0.02 mm), bath temperature 110–120°] to yield a white, crystalline (needles) solid, mp (sealed tube) 58–59° (8.4 g, 62%). *Anal.* Calcd for $C_9H_{19}NOSn$: C, 39.2; H, 6.9; N, 5.1; Sn, 42.9; mol wt, 276. Found: C, 38.86; H, 6.93; N, 4.92; Sn, 42.6; mol wt, 289. The infrared spectrum showed prominent absorptions at 1617 (vw) [$\nu(C=N)$], 1252 (w), 1248 (w) (doublet), 1218 (w), 1190 (w), 1140 (w), 1102 (m), 990 (m), 928 (m), 916 (m), 885 (s), 839 (m), 780 (vs) (broad) (Sn–CH$_3$ rock), and 665 (w) cm^{-1}. On exposure of the ir plates to air for 10 min the spectrum exhibited peaks consistent with the formation of the parent oxime and trimethyltin hydroxide. Nmr: τ

9.86 (Sn–CH_3); $J(Sn^{117,119}\text{–C–H}^1) = 54.4$, 57.2 cps. Integrated nmr: Sn–CH_3:cyclohexyl protons ratio: calcd, 9:10; found, 9:10.2. Sn^{119m} Mössbauer spectrum: IS = 1.43 ± 0.06 mm/sec; QS = 2.96 ± 0.06 mm/sec.

(b) The identical compound was obtained when trimethyltin hydroxide (9.0 g, 0.05 mol) and cyclohexanone oxime (5.6 g, 0.05 mmol) were refluxed in benzene (50 ml), the apparatus being equipped with a Dean and Stark water separator. Water (0.9 ml) distilled immediately, and when the reaction appeared complete, the mixture was allowed to cool. The solvent was removed under reduced pressure, leaving the stannyl oxime as a white solid (13.8 g, 100%). Distillation [bp 58–60° (0.02 mm)] gave the pure product as a hard solid (mp 58–59°). The ir of the compound (Nujol mull) in the region 650–350 cm^{-1} exhibited seven absorptions: 388 (m), 415 (m), 451 (m), 488 (m), 537 (s), 548 (m) (doublet), 573 (m) cm^{-1}, with $\nu(C=N)$ at 1617 (vw) cm^{-1}. The ir in solution (5% CCl$_4$, in 0.5-mm KBr cells) in the same range exhibited five peaks in a drastically changed spectrum: 388 (m), 460 (s), 511 (s), 539 (vs) (doublet), 617 (s) cm^{-1} with the $\nu(C=N)$ now at 1626 cm^{-1} [*cf.* (CH$_3$)$_3$-SnON=C(CH$_3$)$_2$].

O-Trimethylstannylacetoxime.—(a) Trimethyltin hydroxide (9.0 g, 0.05 mol) and acetoxime (3.65 g, 0.05 mol) were brought to reflux in benzene (50 ml) in an apparatus fitted with a Dean and Stark water separator. Water (0.9 ml) distilled immediately, and, when the reaction had finished, the mixture was allowed to cool. Removal of the solvent under reduced pressure gave a mobile, colorless oil [bp 58° (0.01 mm), bath temperature 70°] in 79% yield (9.4 g). *Anal.* Calcd for $C_6H_{15}NOSn$: C, 30.5; H, 6.4; N, 5.9; Sn, 50.2; mol wt, 236. Found: C, 30.6; H, 6.4; N, 5.9; Sn, 50.6; mol wt, 236. The infrared spectrum of the neat liquid exhibited prominent absorptions in the 1300–350-cm^{-1} range at 1624 (vw) [$\nu(C=N)$], 1262 (m), 1189 (w), 1061 (s), 954 (m), 913 (vs), 770 (vs) (broad) (Sn–CH$_3$ rock), 691 (s), 511 (m), 470 (m), and 380 (m) cm^{-1}. No change was observed in the spectrum in 5% CCl$_4$ solution.

(b) O-Trimethylstannylacetoxime was also obtained in an exothermic reaction when acetoxime (0.73 g, 10.0 mmol) was added to trimethylstannyldiethylamine (2.36 g, 10.0 mmol). Diethylamine was removed under reduced pressure, and the residue was distilled [bp 58° (0.01 mm)] yielding the stannyl oxime as a colorless mobile liquid, identified by comparison of its infrared spectrum with that of an authentic sample.

O-Triethylstannylcyclohexanone Oxime.—Cyclohexanone oxime (5.89 g, 5.21 mmol) was dissolved in bis(triethyltin) oxide (11.18 g, 2.63 mmol) giving a pale brown solution. The mixture was pumped at room temperature until no more volatile material had evolved (0.01 mm). The residue was then distilled [bp 74–76.5° (0.01 mm), bath temperature 125°] giving O-triethylstannylcyclohexanone oxime as a colorless, mobile oil (14.97 g, 90.3%). *Anal.* Calcd for $C_{12}H_{25}NOSn$: C, 45.1; H, 7.9; N, 4.4; Sn, 37.3; mol wt, 318. Found: C, 45.17; H, 7.83; N, 4.67; Sn, 37.0; mol wt, 303. The infrared spectrum exhibited prominent absorptions in the 1700–600-cm^{-1} region at 1625 (vw) [$\nu(C=N)$], 1252 (w), 1235 (w), 1220 (m), 1190 (w), 1139 (w), 1106 (m), 1015 (s), 990 (vs), 935 (vs), 919 (vs), 894 (vs), 840 (s), 780 (w), 698 (vs), 670 (vs), and 621 (vs) cm^{-1}. Sn^{119m} Mössbauer spectrum: IS = 1.58 ± 0.06 mm/sec; QS = 1.96 ± 0.06 mm/sec.

O-Tripropylstannylcyclohexanone Oxime.—The same procedure as outlined in procedure (a) for the O-trimethyltin derivative was followed using tripropyltin chloride (14.2 g, 5.0 mmol). Distillation of the residue gave an initial fraction [bp 48° (0.02 mm), bath temperature 110°] identified as tripropyltin chloride by its ir spectrum (3.5 g), followed by the main fraction [bp 85° (0.02 mm), bath temperature 140°] identified as a mobile, colorless oil (9.2 g, 51%). *Anal.* Calcd for $C_{15}H_{31}NOSn$: C, 49.9; H, 8.7; N, 3.9; Sn, 32.9; mol wt, 360. Found: C, 49.81; H, 8.52; N, 3.74; Sn, 32.5; mol wt, 331. The infrared spectrum exhibited prominent absorptions in the 1700–600-cm^{-1} region at 1626 (vw) [$\nu(C=N)$], 1278 (w), 1252 (w), 1218 (m), 1138 (w), 1105 (m), 1063 (s), 1021 (w), 990 (s), 935 (vs), 919

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(18) A. J. Bearden, H. S. Marsh, and J. J. Zuckerman, *Inorg. Chem.,* **5**, 1260 (1966).

(19) Several organosilyl oximes have been obtained by the routes shown in eq 6 [B. N. Dolgov, Z. I. Sergeeva, N. A. Zubkova, Z. M. Matveeva, and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk,* 951 (1960); B. N. Dolgov, Z. I. Sergeeva, N. A. Zubkova, and M. G. Voronkov, *Zh. Obshch. Khim.,* **30**, 3347 (1960); Z. I. Sergeeva, Z. M. Matveeva, and M. G. Voronkov, *ibid.,* 2017 (1961); F. Lukevics and M. G. Voronkov, *Khim. Geterotsikl. Soedin., Akad. Nauk Latv. SSR,* 31 (1965); *Chem. Abstr.,* **63**, 2994 (1965)] and eq 5 [F. Frainnet and F. Duboudin, *Compt. Rend.,* **262C**, 1693 (1966)] and from a complex reaction following silylation of nitromethane [J. F. Klebe, *J. Am. Chem. Soc.,* **86**, 3399 (1964)]. Organotin oximes have been claimed from the routes shown in eq 4 [G. P. Mack and E. Parker, U. S. Patent 2,727,917 (1955); *Chem. Abstr.,* **50**, 10761 (1956); Carlisle Chemical Works, German Patent 953,079 (1956); *Chem. Abstr.,* **53**, 5197 (1959)], eq 3 [G. Weissenberger, U. S. Patent 3,282,672 (1966); *Chem. Abstr.,* **66**, 28891 (1967)], eq 2 [see 3; G. Weissenberger, U. S. Patent 3,275,659 (1966); *Chem. Abstr.,* **65**, 20164 (1966)] and eq 1 [see under eq 3].

(vs), 893 (vs), 839 (m), 796 (w), 780 (w), 698 (vs), and 660 (m) cm^{-1}. On exposure of the plates to air, the compound hydrolyzes rapidly. Sn^{119m} Mössbauer spectrum: IS = 1.42 ± 0.06 mm/sec; QS = 2.03 ± 0.06 mm/sec.

O-Tri-n-butylstannylcyclohexanone Oxime. (a) From Bis-(tributyltin) Oxide.—The same method as outlined for the triethyltin derivative was followed using bis(tributyltin) oxide (7.04 g. 1.18 mmol) and cyclohexanone oxime (2.68 g, 2.37 mmol) with pumping at 0.02 mm for 2 hr. Distillation of the residue [bp 120° (0.02 mm)] gave O-tributylstannylcyclohexanone oxime as a colorless mobile oil (8.1 g, 85%). *Anal.* Calcd for C$_{18}$H$_{37}$NOSn: Sn, 29.5. Found: Sn, 29.7. The infrared spectrum exhibited prominent absorptions at 1626 (vw) [ν-(C=N)], 1297 (w), 1256 (w), 1221 (w), 1182 (vw), 1153 (vw), 1140 (vw), 1110 (w), 1078 (m), 1049 (w), 1025 (w), 991 (m), 939 (vs), 921 (vs), 896 (vs), 880 (m, sh), 870 (m, sh), 841 (m), 781 (w), 751 (vw), 700 (vs), and 671 (m) cm^{-1}. The compound is hydrolyzed rapidly when exposed to atmospheric moisture. Sn^{119m} Mössbauer spectrum: IS = 1.48 ± 0.06 mm/sec; QS = 1.76 ± 0.06 mm/sec.

(b) From Tributyltin Ethoxide.—Cyclohexanone oxime (3.14 g, 2.78 mmol) and tributyltin ethoxide (3.14 g, 2.78 mmol) were mixed and pumped under vacuum (2 hr at 0.02 mm) until no more volatile material was evolved. A pale brown mobile oil remained (12.0 g, 100%) which was distilled [bp 120° (0.02 mm)] to give the stannyl oxime, identical with that obtained above.

O-Triphenylstannylcyclohexanone Oxime.—Triphenyltin hydroxide (4.6 g, 1.25 mmol) and cyclohexanone oxime (1.41 g, 1.25 mmol) were mixed with benzene (100 ml) in a flask equipped with a Dean and Stark water separator. The mixture was heated to reflux, when water came over immediately. After 0.5 hr of reflux, the mixture was allowed to cool, and a small amount of insoluble matter was filtered under nitrogen. Removal of the solvent under reduced pressure gave the stannyl oxime as a clear, viscous oil (5.78 g, 100%). *Anal.* Calcd for C$_{24}$H$_{25}$NOSn: Sn, 25.7. Found: Sn, 25.8. The infrared spectrum exhibited prominent absorptions at 1630 (vw) (hardly resolved) [ν(C=N)], 1080 (s), 1025 (w), 1000 (m), 990 (w), 931 (m), 916 (m), 887 (s), 839 (m), 780 (w), 732 (vs), 701 (vs), 680 (w), 665 (m), and 624 (m) cm^{-1}. On exposure of the plates to atmospheric moisture, rapid hydrolysis occurred. Sn^{119m} Mössbauer spectrum: IS = 1.38 ± 0.06 mm/sec; QS = 1.44 ± 0.06 mm/sec.

O-Trimethylsilylcyclohexanone Oxime.—Trimethylchlorosilane (5.4 g, 50.0 mmol) and cyclohexanone oxime (5.7 g, 50.0 mmol) were mixed in ether (200 ml). Triethylamine (7.2 ml, 50.0 mmol) was added slowly with vigorous stirring, and an exothermic reaction took place with triethylamine hydrochloride being precipitated. When the mixture had cooled, the amine hydrochloride was filtered, and the solvent was removed from the filtrate. Distillation of the residue [bp 35° (0.5 mm), 120° (8 mm)] gave O-trimethylsilylcyclohexanone oxime as a colorless, mobile oil (7.1 g, 76%). *Anal.* Calcd for C$_9$H$_{19}$NOSi: C, 58.1; H, 10.6; N, 7.5; Si, 15.6; mol wt, 186.5. Found: C, 59.98; H, 10.86; N, 7.63; Si, 15.0; mol wt, 196. The infrared spectrum showed prominent absorptions at 1634 (vw) [ν(C=N)], 1251 (vs), 1221 (vw), 1139 (vw), 1108 (vw), 991 (m), 934 (vs), 914 (vs), 880 (vs), 846 (vs), 800 (m), 755 (m), 731 (w), 696 (w), and 650 (m) cm^{-1}. The compound did not appear to be hydrolyzed by atmospheric moisture and could be handled without special precautions. Nmr: τ 9.86 (Si–CH$_3$).

O-Trimethylgermylcyclohexanone Oxime.—Triethylamine (5.2 ml, 50.0 mmol) was added to trimethylchlorogermane (7.7 g, 50.0 mmol) and cyclohexanone oxime (5.7 g, 50.0 mmol) in ether (50 ml). An exothermic reaction took place, and the amine hydrochloride was precipitated. After stirring for 1 hr, the mixture was filtered (yield of triethylamine hydrochloride 5.33 g, 98.8%), and the solvent was removed from the filtrate

under reduced pressure. Distillation of the residue gave O-trimethylgermylcyclohexanone oxime as a colorless, mobile oil (7.45 g, 65%) [bp 48° (0.1 mm), bath temperature 85–90°]. The infrared spectrum exhibited prominent absorptions at 1629 (vw) [ν(C=N)], 1241 (s), 1220 (m), 1139 (w), 1106 (w), 990 (s), 935 (vs), 920 (vs), 898 (vs), 824 (vs) (broad) (Ge–CH$_3$ rock), 755 (m), 730 (vs), and 619 (vs) cm^{-1}. The compound is hydrolyzed rapidly by atmospheric moisture. Nmr: τ 9.62 (Ge–CH$_3$). *Anal.* Calcd for C$_9$H$_{19}$GeNO: C, 47.1; H, 8.3; N, 6.1; Ge, 31.4; mol wt, 229. Found: C, 47.3; H, 8.1; N, 6.1; Ge, 30.6; mol wt, 241.

Reactions of the O-Stannyl Oximes.—All reactions were carried out using the usual precautions for M^{IV}–O and M^{IV}–N bonded compounds.

(a) Addition Reactions.—The O-stannyl oximes reacted immediately and exothermally at room temperature with alkyl and aryl isocyanates and with chloral and bromal to give adducts as viscous oils. The adducts were prepared by adding a slight excess of the multiply bonded reagent by syringe to the oxime derivative in a flask sealed with a rubber septum cap. After the mixture had cooled to room temperature, excess of the reagent was removed at the rotary pump. Physical properties of the adducts are listed in Tables IV and V. All of the adducts are hydrolyzed rapidly by atmospheric moisture. Phenyl isothiocyanate reacted with O-tributylstannylcycloxhexanone oxime during *ca.* 48 hr at room temperature to give an adduct.

O-Trimethylgermylcyclohexanone oxime reacted immediately and exothermally at room temperature with chloral to give an adduct as a viscous oil by the same procedure. The physical properties of the adduct are listed in Table V. The same germyl oxime, however, did not react with methyl isocyanate at room temperature. O-Trimethylsilylcyclohexanone oxime did not react with chloral at room temperature.

(b) Metathetical Reactions. (i) Hydrolysis.—The stannyl and germyl oximes were hydrolyzed rapidly and quantitatively by atomspheric moisture when capillary films of the compounds between salt plates were exposed to air. The infrared spectra of the hydrolysis products were those of a mixture of the organometallic oxide or hydroxide and the parent oxime.

(ii) Hydrogen Chloride.—Hydrogen chloride gas was passed through tri-n-butylstannylcyclohexanone oxime (1.75 g, 4.35 mmol). An immediate, exothermic reaction took place and a white solid precipitated which was filtered. Distillation of the filtrate gave tri-n-butyltin chloride [bp 87° (0.18 mm); 1.35 g, 95%], identified by its ir spectrum.

(iii) Conversion to the Silyl Derivative.—A very exothermic reaction set in when trimethylchlorosilane (1.75 g, 16.1 mmol) was added to tri-n-butylstannylcyclohexanone oxime (6.45 g, 16.07 mmol). After the mixture had cooled, distillation gave trimethylsilylcyclohexanone oxime [bp 116° (7 mm); 2.55 g, 85%] and tri-n-butyltin chloride [bp 100° (0.4 mm); 3.83 g, 73%].

(iv) Conversion to the Germyl Derivative.—In a reaction similar to (iii) above, trimethylchlorogermane (1.32 g, 8.68 mmol) reacted exothermally with tri-n-butylstannylcyclohexanone oxime (3.49 g, 8.70 mmol). Distillation gave trimethylgermylcyclohexanone oxime [bp 56° (0.2 mm); 1.31 g, 66%] and tri-n-butyltin chloride [bp 102° (0.5 mm); 1.97 g, 70%].