

Organometallic Oxime & Allied Derivatives: Part VI—Preparation, Reactions & Spectral Data of Some Bis(iminoxy)dimethylgermanes

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The synthesis and characterization by elemental analyses, molecular weights, and spectra (IR and NMR) of the title compounds are described. Reactions of these derivatives with Me_2SiCl_2 , SiCl_4 , GeCl_4 and CH_3COCl lead to a facile germanium-oxygen bond fission.

WE recently described the preparation and characterization of some new tris(iminoxy)-organosilanes¹. The work reported here is part of a continuing programme on the synthesis, chemical reactions and spectral studies of oxime and allied derivatives containing organometallic moieties.

Materials and Methods

Oximes², diethoxydimethylgermane³, and *n*-butyllithium⁴ were prepared according to published procedures.

The reactions were carried out under rigorous anhydrous conditions. Commercial sample of triethylamine was dried over potassium hydroxide pellets for 48 hr, heated under reflux, and fractionally distilled. Solvents and liquid reagents were dried and purified by standard methods.

Infrared spectra (as liquid films) in the range 4000-400 cm^{-1} were recorded on a Perkin-Elmer 337 spectrophotometer. PMR spectra were recorded in CCl_4 (or benzene) on Varian Associates A-60 and Perkin-Elmer R12B instruments; chemical shifts are in τ -scale with respect to TMS as internal reference. Molecular weights were determined ebullioscopically in benzene and refractive indices with an Abbe refractometer.

Nitrogen was estimated by the Kjeldahl method. Ethanol was analysed oxidimetrically⁵. The microanalyses were performed by the Australian Micro-analytical Service, Melbourne. Germanium in $\text{Ge}(\text{ON} = \text{CMe}_2)_4$ was determined as GeO_2 .

Bis(iminoxy)dimethylgermanes: *Method (A)*—All the compounds reported in Table 1 were prepared by the following general method: Triethylamine and the appropriate oxime were dissolved in anhydrous benzene (20 ml); to the resulting solution stoichiometric amount of dimethyldichlorogermane was added dropwise. For all preparations the mole ratios chlorogermane: oxime: triethylamine were 1:2:2. The resulting reaction mixture was refluxed at 100° for 1 hr. The white precipitates of $\text{Et}_3\text{N}\cdot\text{HCl}$ obtained were filtered and washed with benzene. Benzene was removed from the filtrate under

reduced pressure (30°/1 mm Hg). Distillation of the residual liquid under reduced pressure afforded the desired product.

Method (B)—In the presence of a catalytic amount of *p*-toluene-sulphonic acid, a benzene (100 ml) solution of diethoxydimethylgermane (1.82 g, 0.009 mole) and acetoxime (1.38 g, 0.019 mole) was refluxed under an efficient fractionating column provided with a total-condensation variable take-off stillhead. Ethanol formed in the reaction was removed as an azeotrope with benzene, the analysis of which indicated completion of the reaction in about 6 hr. Ethanol liberated (0.84 g); calc. for two moles (0.87 g). The catalyst was neutralized with a few drops of Et_3N and benzene removed at 30°/1 mm Hg. Distillation of the resulting liquid gave $\text{Me}_2\text{Ge}(\text{ON} = \text{CMe}_2)_2$ as a colourless liquid (2.12 g, 91%), b.p. 60°/0.6 mm, n_D^{20} 1.4625 (Found: C, 38.64; H, 7.30; N, 11.32; mol. wt 251. $\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2\text{Ge}$ requires C, 38.94; H, 7.35; N, 11.35%; mol. wt, 247).

Using the above procedure $\text{Me}_2\text{Ge}(\text{ON} = \text{CHMe}_2)_2$ (90%), b.p. 60-62°/0.8 mm, n_D^{20} 1.4620 (Found: C, 32.98; H, 6.36; N, 12.52; mol. wt 216. $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2\text{Ge}$ requires C, 32.94; H, 6.45; N, 12.80%; mol. wt, 219) was also prepared.

Method (C)—An ether solution of dimethyldichlorogermane (1.36 g, 0.0078 mole) was added dropwise to an ether suspension of $\text{LiON} = \text{CMe}_2$ (1.24 g, 0.015 mole) [prepared by adding *n*-BuLi (1.01 g, 0.019 mole) in hexane to an ether solution of acetoxime (1.15 g, 0.016 mole)]. The reaction mixture was stirred for 4 hr and then filtered. The solvent was removed under reduced pressure, and distillation of the residual liquid afforded $\text{Me}_2\text{Ge}(\text{ON}:\text{CMe}_2)_2$ (1.74 g, 90%), b.p. 59°/0.6 mm, n_D^{20} 1.4625 (Found: C, 38.84; H, 7.30; N, 11.20; mol. wt, 248. $\text{C}_8\text{H}_{18}\text{O}_2\text{N}_2\text{Ge}$ requires C, 38.94; H, 7.35; N, 11.35%; mol. wt, 247).

Reactions of bis(iminoxy)dimethylgermanes: (a) *With dimethyldichlorosilane*—When $\text{Me}_2\text{Ge}(\text{ON} = \text{CEt}_2)_2$ (1.48 g, 0.0049 mole) and Me_2SiCl_2 (0.63 g, 0.0049 mole) were mixed together, an exothermic reaction occurred. Subsequent distillation of the resulting liquid after heating at 100° for 2 hr afforded Me_2GeCl_2 (0.75 g, 88%), IR (cm^{-1}): 1405 *m* (δ_{asym} GeCH_3); 1248 *s* (δ_{sym} GeCH_3); 850 *vs*, 828 *vs*, 773 *s* (ρGeCH_3);

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641 *vs* ($\nu_{\text{asym}} \text{GeC}_2$); 598 *vs* ($\nu_{\text{asym}} \text{GeC}_2$) and $\text{Me}_2\text{Si}(\text{ON}=\text{C}(\text{Et})_2)_2$ (1.12 g, 90%), b.p. 85-86°/3 mm (lit.⁶, 97°/4 mm), n_D^{20} 1.4285 (lit.⁶, n_D^{20} 1.4284), IR: 1630 *m* ($\nu\text{C}=\text{N}$), 1253 *s* ($\delta_{\text{sym}} \text{SiCH}_3$), 918 *s* ($\nu\text{N}-\text{O}$), 818 *s* ($\rho_{\text{asym}} \text{SiCH}_3$), 803 *s* ($\rho_{\text{sym}} \text{SiCH}_3$), 665 *s* ($\nu_{\text{asym}} \text{SiC}_2$); PMR spectrum: 9.73 (S, Me Si).

(b) *With SiCl₄*—Silicon tetrachloride (0.47 g, 0.0028 mole) was slowly added to $\text{Me}_2\text{Ge}(\text{ON}=\text{CMe}_2)_2$ (1.36 g, 0.0055 mole) at 0°. The reaction mixture was heated at 100° for 2 hr. Fractional distillation gave dimethyldichlorogermane (0.82 g, 85%), b.p. 119-23° (authentic IR spectrum) and $\text{Si}(\text{ON}=\text{CMe}_2)_4$ (0.70 g, 80%), b.p. 126-28°/0.5 mm (lit.⁶, 128°/0.5 mm) (Found: Si, 8.70; N, 17.52; mol. wt, 314. Calc. for $\text{C}_{12}\text{H}_{24}\text{O}_4\text{N}_4\text{Si}$: Si, 8.85; N, 17.70%; mol. wt, 316) as a white solid.

(c) *With GeCl₄*— $\text{Me}_2\text{Ge}(\text{ON}=\text{CMe}_2)_2$ (1.12 g, 0.0045 mole) and GeCl_4 (0.49 g, 0.0023 mole) were heated at 100° together for 4 hr. Distillation gave Me_2GeCl_2 (0.69 g, 87%), b.p. 119-23° (identified by its IR spectrum) and $\text{Ge}(\text{ON}=\text{CMe}_2)_4$ (0.60 g, 73%), b.p. 152°/0.5 mm (lit.⁷, 153-54°/0.7 mm) (Found: Ge, 20.02; N, 15.38; mol. wt, 358. Calc. for $\text{C}_{12}\text{H}_{24}\text{O}_4\text{N}_4\text{Ge}$: Ge, 20.10; N, 15.52%; mol. wt, 361).

(d) *With acetyl chloride*—Acetyl chloride (1.25 g, 0.016 mole) was added slowly to $\text{Me}_2\text{Ge}(\text{ON}=\text{CMeEt})_2$ (2.12 g, 0.0077 mole) at 0°C. A vigorous reaction took place. The reaction mixture after heating at 100° for 1 hr was fractionally distilled to give Me_2GeCl_2 (1.22 g, 91%) (characterized by its b.p., and IR spectrum) and *O*-acyloxime ester $\text{MeEtC}=\text{NOCOCH}_3$ (1.72 g, 87%), b.p. 72-74°/10 mm (lit.⁸, 76-77°/11 mm) (Found: N, 10.62; mol. wt, 128. $\text{C}_6\text{H}_{11}\text{O}_2\text{N}$ requires N, 10.85%; mol. wt, 129); IR: 1751 *vs* ($\nu\text{C}=\text{O}$), 1647 *s* ($\nu\text{C}=\text{N}$), and 934 *vs* ($\nu\text{N}-\text{O}$).

Results and Discussion

The bis(iminoxy)dimethylgermanes were prepared in 90% yields by the interaction of dimethyldichlorogermane and the appropriate oxime in the presence of triethylamine (method A) giving $\text{Me}_2\text{Ge}(\text{ON}=\text{CRR}')_2$ and triethylamine hydrochloride (R, R' = H, Me; H, Et; H, Prⁿ; H, Prⁱ; Me, Me; Me, Et; Me, Prⁿ; Et, Et).

The reactions of diethoxydimethylgermane with oximes (acetoxime and acetaldoxime) were slow, but could be pushed to completion by continuous removal of ethanol azeotropically with benzene (which was used as a solvent) in the presence of *p*-toluenesulphonic acid as a catalyst. The yields by this synthetic route (method B) were quantitative. By this method compounds of the type $\text{Me}_2\text{Ge}(\text{ON}=\text{CRR}')_2$ where RR' = H, Me; Me, Me, were obtained.

In method C, an ether solution of acetoxime was treated with *n*-butyllithium in *n*-hexane followed by Me_2GeCl_2 in the required molar ratios, when the compound $\text{Me}_2\text{Ge}(\text{ON}=\text{CMe}_2)_2$ was isolated in 90% yield. Lithium chloride and *n*-butane gas were the other products.

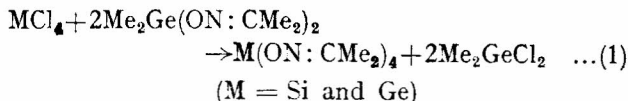
These new compounds are all colourless, monomeric, and moisture-sensitive liquids. The germanium-oxygen bond in these compounds could

be readily cleaved with a variety of reagents, e.g. Me_2SiCl_2 , SiCl_4 , GeCl_4 , and CH_3COCl .

Interaction of $\text{Me}_2\text{Ge}(\text{ON}=\text{C}(\text{Et})_2)_2$ and dimethyldichlorosilane (Me_2SiCl_2) results in an exothermic reaction. The mixture on heating at 100° for 2 hr and subsequent distillation affords Me_2GeCl_2 (88%) and $\text{Me}_2\text{Si}(\text{ON}=\text{C}(\text{Et})_2)_2$ (90%), which were identified by their b.p.s., IR and NMR spectra.

The above exothermic exchange reaction appears to obey the general rule that the harder moiety prefers to be attached to silicon, so that reaction to give Si-O bonds are essentially almost quantitative. The driving force for this reaction may be due to the fact that decrease in bond energy in going from Si-Cl to Ge-Cl is more than compensated by the increase in bond energy expected for the Ge-O to Si-O transformation. The enthalpy, ΔH , of formation of one mole $\text{Me}_2\text{Si}(\text{ON}=\text{C}(\text{Et})_2)_2$ from one mole each of $\text{Me}_2\text{Ge}(\text{ON}=\text{C}(\text{Et})_2)_2$ and Me_2SiCl_2 has been calculated and found to be $\sim 10\text{-}20$ kcal mole⁻¹.

The reaction of bis(dimethyliminoxy)dimethylgermane with covalent tetrachlorides of Group IVb elements in the mole ratio 2:1, afforded on distillation



the corresponding tetraoximate and dimethyldichlorogermane (Eq. 1). The analytical results for the products showed good agreement with those of the authentic samples.

Acetyl chloride readily cleaves the germanium-oxygen bond of the compound $\text{Me}_2\text{Ge}(\text{ON}=\text{CMeEt})_2$, forming dimethyldichlorogermane and *o*-acyl oxime ester $\text{MeEtC}=\text{NOCOCH}_3$, which were separated by fractional distillation.

Infrared spectra—Infrared spectra of the bis(iminoxy)dimethylgermanes show absorptions in the range 1700-1600 and 930-910 cm⁻¹ characteristic of (C=N) and (N-O) groups⁹ respectively of the >C=N-O moiety of the molecule. Further, the following features can be summarized as characteristic of the Me_2Ge moiety¹⁰⁻¹⁵: (i) 1435-1420 and 1245-1238 cm⁻¹ bands are due to Ge-CH₃ asymmetric and symmetric deformation respectively; (ii) 815-800 cm⁻¹ bands can be assigned to Ge-CH₃ rocking vibration; (iii) bands at 636-630 and 596-585 cm⁻¹ are due to Ge-C asymmetric and symmetric stretch; and (iv) the band at 590-555 cm⁻¹ is probably due to the Ge-O symmetric stretch (since it is absent in the spectra of oximes⁹ and dimethyldichlorogermane¹⁰).

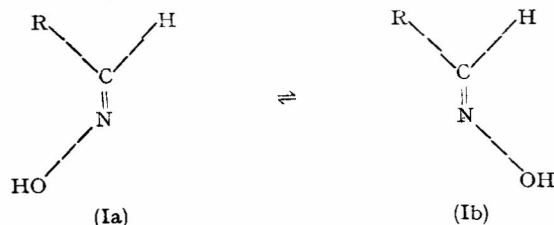
We have been unable to locate a band in the region 900-800 cm⁻¹ which could unambiguously be assigned to Ge-O asymmetric stretch in the spectra of these bis(iminoxy)dimethylgermanes, because of other absorptions in this region. Interestingly $\text{Me}_2\text{Ge}(\text{ON}=\text{CHR})_2$ (R = Me, Et, Prⁿ and Prⁱ), exhibited two absorptions in the 1700-1600 cm⁻¹ region assignable to $\nu\text{C}=\text{N}$. It is difficult to single out factors responsible for such a behaviour; however, syn-antiisomerism, tendency of association, conformational factors, and slight hydrolysis of the compound (during recording of the IR spectrum),

TABLE 1 — REACTION OF DIMETHYLDICHLORGERMANE WITH OXIMES IN THE PRESENCE OF TRIETHYLAMINE IN BENZENE

Reactants (g)			Product	b.p. (°C/mm) n_D^{20}	Found (calc.) (%)			Mol. wt found (calc.)
Me_2GeCl_2	$\text{RR}'\text{C}=\text{NHO}$ $\text{R}, \text{R}' =$	Et_3N			C	H	N	
2.07	H, Me	3.53	$\text{Me}_2\text{Ge}(\text{ON}=\text{CHMe})_2$	60-62/0.8 1.4620	33.02 (32.94)	6.43 (6.45)	12.76 (12.80)	230 (219)
1.12	H, Et	1.40	$\text{Me}_2\text{Ge}(\text{ON}=\text{CHEt})_2$	107-108/5 1.4550	38.78 (38.94)	7.20 (7.35)	11.15 (11.35)	249 (247)
2.02	H, Pr ⁿ	3.60	$\text{Me}_2\text{Ge}(\text{ON}=\text{CHPr}^n)_2$	113-115/6 1.4570	43.84 (43.68)	8.09 (8.07)	10.12 (10.19)	286 (275)
0.97	H, Pr ⁱ	1.16	$\text{Me}_2\text{Ge}(\text{ON}=\text{CHPr}^i)_2$	109-111/3.2 1.4470	43.62 (43.68)	7.98 (8.07)	9.98 (10.19)	280 (275)
2.04	Me, Me	2.75	$\text{Me}_2\text{Ge}(\text{ON}=\text{CMe}_2)_2$	60/0.6 1.4625	38.27 (38.94)	7.24 (7.35)	11.30 (11.35)	250 (247)
1.95	Me, Et	2.46	$\text{Me}_2\text{Ge}(\text{ON}=\text{CMeEt})_2$	82-84/1.5 1.4590	43.18 (43.68)	7.77 (8.07)	10.16 (10.19)	280 (275)
0.67	Me, Pr ⁿ	0.75	$\text{Me}_2\text{Ge}(\text{ON}=\text{CMePr}^n)_2$	90/0.7 1.4580	47.77 ... (47.57)	8.78 (8.65)	9.10 (9.25)	306 (303)
1.51	Et, Et	2.07	$\text{Me}_2\text{Ge}(\text{ON}=\text{CEt}_2)_2$	81-82/0.5 1.4560	46.93 (47.57)	8.35 (8.65)	9.18 (9.25)	310 (303)

may reasonably be among the contributory factors¹⁶.

NMR spectra — NMR evidence for the *syn-anti* isomerism (Ia \rightleftharpoons Ib) in aldoximes



was reported by Phillips¹⁷, who also observed that the concentration of the *syn*-isomer (Ib) increases with the bulk of the alkyl group (R). Similar evidence for isomerism in ketoximes (Ia and Ib, when H is replaced by an alkyl group) was detected by Lustig¹⁸. Further Lustig as well as Karabatsos and coworkers¹⁹ demonstrated solvent-induced chemical shift in *syn*- and *anti*-forms of oximes.

PMR spectrum of the compound $\text{Me}_2\text{Ge}(\text{ON}=\text{CMe}_2)_2$ exhibited signal due to Ge-Me and $\text{Me}_2\text{C}<$ groups at 9.35 and 8.15 respectively. In an aromatic solvent (benzene), the isopropylidene methyl groups $\text{Me}_2\text{C}<$ gave two peaks (8.34 and 8.23) of about equal intensity separated by 0.11 ppm. Such a spectrum is consistent with the known geometry of the oximes, having planar skeleton with restricted rotation about the C=N bond, which causes methyl groups with attached imino carbon to be magnetically non-equivalent and leads to a small chemical shift difference between them.

In the derivatives $\text{Me}_2\text{Ge}(\text{ON}=\text{CHR})_2$ (R = Me, Et, Prⁿ, and Prⁱ) the structures of the $\alpha\text{-CH}_3$, $\beta\text{-CH}_3$, $\gamma\text{-CH}_3$, $\alpha\text{-CH}_2$, $\beta\text{-CH}_2$, azomethine and methine hydrogen resonances can be accounted for by mutual spin-spin coupling between protons of the =CH, CH₂, HC(CH₃)₂, and CH₃ groups. The PMR spectra (τ , CCl₄) of these derivatives are listed below. Integrated ratios were consistent with the structure of the compounds. $\text{Me}_2\text{Ge}(\text{ON}=\text{CHMe})_2$: 9.31 (s, Ge-Me), 8.19, (d, J = 6 Hz, N = CHMe),

3.24 (q, J = 5.85 Hz, *anti*-azomethine hydrogen), 2.60 (q, J = 6 Hz, *syn*-azomethine hydrogen, *syn/anti* ratio 0.67). NMR spectrum of this compound in benzene solution showed signals at 9.27 (s, Ge-Me), 8.52 (d, J = 6 Hz, N = CHMe *syn*), 8.34 (d, J = 6 Hz, N = CHMe *anti*), 3.26 (q, J = 5.85 Hz, *anti*-azomethine hydrogen), 2.51 (q, J = 6 Hz, *syn*-azomethine hydrogen).

$\text{Me}_2\text{Ge}(\text{ON}=\text{CHEt})_2$: 9.32 (s, Ge-Me), 8.92 (t, J = 6.67 Hz, N = C(H)CH₂CH₃), 8.02-7.36 [m, N = C(H)CH₂CH₃], 3.31 (t, J = 5.85 Hz, *anti*-azomethine hydrogen), 2.58 (t, J = 6 Hz, *syn*-azomethine hydrogen; *syn/anti* ratio 1.9).

$\text{Me}_2\text{Ge}(\text{ON}=\text{CHPr}^n)_2$: 9.34 (s, Ge-Me), 9.08 (t, J = 6.67 Hz, N = C(H)CH₂CH₂CH₃), 8.81-8.11 [m, N = C(H)CH₂CH₂CH₃], 8.07-7.45 [m, N = C(H)CH₂CH₂CH₃], 3.37 (t, J = 5.85 Hz, *anti*-azomethine hydrogen), 2.64 (t, J = 6 Hz, *syn*-azomethine hydrogen; *syn/anti* ratio 1.38).

$\text{Me}_2\text{Ge}(\text{ON}=\text{CHPr}^i)_2$: 9.27 (s, Ge-Me), 8.92-8.88 [dd, J = 6.67 Hz, N = CH(CH₃)₂], 7.85-7.10 (h, J = 6.67 Hz, *anti*-methine hydrogen), 7.08-6.32 (h, J = 6.67 Hz, *syn*-methine hydrogen), 3.46 (d, J = 6.67 Hz, *anti*-azomethine hydrogen), 2.65 (d, J = 6 Hz, *syn*-azomethine hydrogen; *syn/anti* ratio 3.80).

The above data reveal the following interesting features: (i) increase in the *syn/anti* isomer ratio (estimated from signal intensities) on germylation of the aldoximes; (ii) increase in the shielding of the Ge-CH protons in the series of aldoxime derivatives $\text{Me}_2\text{Ge}(\text{ON}=\text{CHR})_2$, when R changes from isopropyl to methyl to ethyl to *n*-propyl, and (iii) separation of the resonance lines of the imino carbon attached methyl protons in benzene solution.

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