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ORGANOMETALLIC OXIME AND ALLIED DERIVATIVES

II*. SYNTHESIS AND PROPERTIES OF SOME TRI-n-BUTYLGERMANIUM OXIMATES**

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SUMMARY

Tributylgermanium oximates have been prepared by reactions (*a*) of tributylgermanium chloride with (*i*) oximes in the presence of a base, (*ii*) sodium oximates, and (*iii*) organotin oximates, as well as (*b*) of tributylgermanium ethoxide and oxide with oximes.

The derivatives have been characterised by elemental analyses, molecular weight measurements and IR spectra. Their reactions have been studied in detail.

INTRODUCTION

Oximates of only a few elements, including those of Group IIIB elements[1], methylzinc[2], and of methylberyllium[3], have been studied so far, and in these derivatives, polymerisation through "MON–MON" type bonds has been presumed. Trimethyltin cyclohexanoneoximate has, on the other hand, been shown to exist as a dimer via a "SnO–SnO" type structure[4]. Furthermore, a detailed study[5] of the oximates of alkylsilanes has revealed that these compounds are all monomeric and volatile, which is to be expected on the basis of the small atomic radius of silicon; in fact the reactions of the silyl oximates appear to be very slow for this reason. Work on organogermanium derivatives have been confined[4] to the synthesis and properties of $Me_3GeON{=}\overline{C(CH_2)_4CH_2}$, and in view of this, a more detailed study of the germanium analogues seemed worthwhile.

RESULTS AND DISCUSSION

Syntheses

Tributylgermanium oximates reported here (Table 1) have been prepared by at

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[*] For Part I see ref. 5.

[**] Abstracted in part from the Ph.D. dissertation of A. Singh, University of Rajasthan, Jaipur (India), 1972.

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TABLE 1

ANALYTICAL AND PHYSICAL DATA OF SOME NEW OXIME DERIVATIVES OF GERMANIUM

Compound[a]	*Method*[b]	*Yield (%)*[c]	*B.p. (°C/mm)*	n_D^{20}	*Analyses*[d]*, found (Calcd.) (%)*			*Mol. wt.*[g] *found (calcd.)*
					C[e]	*H*[e]	*N*[f]	
$\mathrm{Bu_3GeON{=}CHMe}$	1	88	82–83/0.4	1.4570	55.53 (55.69)	10.44 (10.33)	4.58 (4.64)	309 (302)
$\mathrm{Bu_3GeON{=}CHPr}$	1	86	106–107/0.4	1.4560	58.02 (58.22)	10.62 (10.69)	4.20 (4.24)	336 (330)
$\mathrm{Bu_3GeON{=}CMe_2}$	1–6	88	106/0.6	1.4555	56.79 (57.03)	9.99 (10.52)	4.42 (4.43)	320 (316)
$\mathrm{Bu_3GeON{=}CMeEt}$	1,2,5,6	86	92–93/0.3	1.4550	58.16 (58.22)	10.59 (10.69)	4.16 (4.24)	332 (330)
$\mathrm{Bu_3GeON{=}CMe(n\text{-}C_5H_{11})}$	1	89	117–118/0.2; 123–124/0.7	1.4553	61.28 (61.34)	11.04 (11.11)	3.62 (3.77)	368 (372)
$\mathrm{Bu_3GeON{=}CMe\text{-}i\text{-}Bu}$	1	80	97–98/0.3	1.4562	59.99 (60.39)	10.80 (10.97)	3.82 (3.91)	360 (358)
$\mathrm{Bu_3GeON{=}CMePr}$	1	85	95–97/0.3	1.4568	58.96 (59.33)	10.85 (10.84)	4.10 (4.07)	346 (344)
$\mathrm{Bu_3GeON{=}CMe\text{-}i\text{-}Pr}$	1	84	110–111/0.9	1.4558	58.91 (59.33)	10.91 (10.84)	3.98 (4.07)	348 (344)
$\mathrm{Bu_3GeON{=}CEt_2}$	1	88	108/0.8	1.4556	59.28 (59.33)	10.68 (10.84)	4.00 (4.07)	346 (344)
$\mathrm{Bu_3GeON{=}CEtBu}$	1	82	104–107/0.3	1.4569	59.84 (61.34)	10.98 (11.11)	3.44 (3.77)	374 (372)
$\mathrm{Bu_3GeON{=}CHPh}$	1	84	147–149/0.5; 142/0.4	1.5090	61.97 (62.67)	9.02 (9.14)	3.82 (3.85)	362 (364)
$\mathrm{Bu_3GeON{=}CMePh}$	1	79	140/0.5	1.5053	63.94 (63.53)	9.22 (9.33)	3.56 (3.71)	380 (378)
$\mathrm{Bu_3GeON{=}\overline{C(CH_2)_3CH}_2}$	1,2,4,5,6	85	103–104/0.3	1.4725	59.52 (59.69)	10.24 (10.31)	4.10 (4.10)	350 (342)
$\mathrm{Bu_3GeON{=}\overline{C(CH_2)_4CH}_2}$	1,2,4,5,6	84	110–111/0.3	1.4755	60.45 (60.73)	10.22 (10.47)	3.90 (3.93)	360 (356)

[a] The following abbreviations are used: Me = $\mathrm{CH_3}$; Et = $\mathrm{C_2H_5}$; Pr = n-$\mathrm{C_3H_7}$; i-Pr = iso-$\mathrm{C_3H_7}$; Bu = n-$\mathrm{C_4H_9}$; i-Bu = iso-$\mathrm{C_4H_9}$; Ph = $\mathrm{C_6H_5}$. All compounds are colourless mobile liquids. [b] These numbers refer to the synthetic methods described in the experimental section. [c] Yields refer to the distilled product. [d] Calculated values in parentheses. [e] Microanalyses for C and H were performed by Macroanalytical Service, Melbourne, Australia. [f] Determined by Kjeldahl procedure. [g] Ebullioscopically in benzene.

least one of the following routes;

$$\mathrm{Bu_3GeCl + HON{=}CR^1R^2 + Et_3N \xrightarrow[\text{1h reflux}]{\text{benzene}} Bu_3GeON{=}CR^1R^2 + Et_3N \cdot HCl\downarrow} \qquad (1)$$

$\mathrm{R^1, R^2 = H, Me; H, Pr; H, Ph; Me, Me; Me, Et; Et, Et; Me, Pr;}$
$\mathrm{Me, i\text{-}Pr; Me, i\text{-}Bu; Me, n\text{-}C_5H_{11}; Me, Ph; Et, Bu; (CH_2)_4; (CH_2)_5}$

$$\mathrm{Bu_3GeCl + HON{=}CR^1R^2 + NH_3 \xrightarrow[\text{1h reflux}]{\text{benzene}} Bu_3GeON{=}CR^1R^2 + NH_4Cl\downarrow} \qquad (2)$$

$\mathrm{R^1, R^2 = Me, Me; Me, Et; (CH_2)_4; (CH_2)_5}$

$$\mathrm{Bu_3GeCl + NaON{=}CR^1R^2 \xrightarrow[\text{1h reflux}]{\text{benzene}} Bu_3GeON{=}CR^1R^2 + NaCl}\downarrow \tag{3}$$

$$\mathrm{R^1, R^2 = Me, Me}$$

$$\mathrm{Bu_3GeCl + R_3SnON{=}CR^1R^2 \xrightleftharpoons{\text{1h heating}} Bu_3GeON{=}CR^1R^2 + R_3SnCl} \tag{4}$$

$$\mathrm{R = Et, Pr, Bu;\ R^1, R^2 = (CH_2)_4;\ (CH_2)_5}$$

$$\mathrm{Bu_3GeOEt + HON{=}CR^1R^2 \xrightarrow[\textit{p}\text{-toluenesulphonic acid}]{\text{Benzene, 4h reflux}} Bu_3GeON{=}CR^1R^2 + EtOH}\uparrow \tag{5}$$

$$\mathrm{R^1, R^2 = Me, Me;\ Me, Et;\ (CH_2)_4;\ (CH_2)_5}$$

$$\mathrm{(Bu_3Ge)_2O + 2HON{=}CR^1R^2 \xrightarrow[\textit{p}\text{-toluenesulphonic acid}]{\text{Benzene, 3h reflux}} 2Bu_3GeON{=}CR^1R^2 + H_2O}\uparrow \tag{6}$$

$$\mathrm{R^1, R^2 = Me, Me;\ Me, Et;\ (CH_2)_4;\ (CH_2)_5}$$

Route (6) does not appear to give any oximate with hexamethyldisiloxane. Oximolysis (route 5) of tributylgermanium ethoxide appears to be much more facile than oximolysis of the silicon analogue; thus it has been shown[6] that the oximolysis of germanium tetraethoxide may be completed without a catalyst, whereas the corresponding reaction with silicon ethoxide is extremely slow even in the presence of a catalyst. This behaviour parallels the comparative facility with which silicon[7] and germanium alkoxides undergo alcoholysis and can be understood on the basis of (*i*) larger radius and (*ii*) lesser tendency for $(p \rightarrow d)\pi$ bond formation in the case of germanium.

Properties

All the oximates, $\mathrm{Bu_3GeON{=}CR^1R^2}$, are colourless, monomeric, mobile moisture-sensitive liquids which are soluble in common organic solvents and can readily be distilled under reduced pressure. Their boiling points increase with increase in the molecular weight of the oxime molecule, and the parent oximes are regenerated upon mild hydrolysis (*e.g.*, treatment with aqueous methanol) indicating that they have the $\mathrm{Bu_3Ge{-}O{-}N{=}C}\langle$ structure.

Reactions

In view of the reactivity of germanium–oxygen bonds in alkoxides[8,9], the nature of the germanium–oxygen bond in oximates, $\mathrm{Bu_3Ge{-}O{-}N{=}CR^1R^2}$, has been investigated:

(*i*). Treatment of $\mathrm{Bu_3GeON{=}CR^1R^2}$ with compounds containing highly reactive carbon–chlorine bonds, such as acid chlorides, RCOCl, (R = Me or Ph) resulted in the formation of tributylgermanium chloride and oxime esters, $\mathrm{R^1R^2C{=}NOCOR}$, separated by fractional distillation:

$$\mathrm{Bu_3GeON{=}CR^1R^2 + MeCOCl \xrightarrow[\text{1h reflux}]{\text{benzene}} Bu_3GeCl + R^1R^2C{=}NOCOMe}$$

$$\mathrm{(R^1, R^2 = Me, Me;\ Me, Et)}$$

$$\mathrm{Bu_3GeON{=}CMe_2 + PhCOCl \xrightarrow{140^\circ} Bu_3GeCl + Me_2C{=}NOCOPh}$$

(*ii*). Treatment of $Bu_3GeON{=}CMe_2$ (4 moles) with germanium tetrachloride (1 mole) in benzene followed by mild refluxing for 1 h, resulted in replacement of chlorine by the oximate group:

$$4\,Bu_3GeON{=}CMe_2 + GeCl_4 \xrightarrow[\text{1h mild reflux}]{\text{benzene}} Ge(ON{=}CMe_2)_4 + 4\,Bu_3GeCl$$

(*iii*). Tributylgermanium oximates could be expected to undergo reversible reactions with alcohols:

$$Bu_3Ge{-}O{-}N{=}CR^1R^2 + ROH \rightleftarrows Bu_3GeOR + R^1R^2C{=}NOH$$

$$R^1, R^2 = Me, Me;\ Me, i\text{-}Pr$$

With higher alcohols (n-octanol), the reaction can be driven to completion by employing excess of alcohol and distilling off the oximes at about 200°; however in case of lower alcohols (*e.g.*, methanol or ethanol), fractional distillation of the reaction mixture even under reduced pressure regenerates the parent oximate quantitatively. The reaction between tri-n-butylgermanium acetoneoximate (b.p. acetoneoxime 136.3°) and n-pentanol (b.p. 138.1°) in the mole ratio of 1/1 has been found to yield a 1.6/1 mole ratio mixture of $Bu_3GeON{=}CMe_2$ and $Bu_3GeOC_5H_{11}$, indicating that the equilibrium constant of the reaction

$$Bu_3GeON{=}CMe_2 + C_5H_{11}OH \rightleftarrows Bu_3GeOC_5H_{11} + HON{=}CMe_2$$

is about 0.3–0.4.

(*iv*). Tributylgermanium oximates appear to undergo hydrolysis readily regenerating the parent oxime quantitatively:

$$Bu_3GeON{=}CR^1R^2 + H_2O \rightarrow Bu_3GeOH + R^1R^2C{=}NOH \rightarrow$$
$$\rightarrow \tfrac{1}{2}(Bu_3Ge)_2O + \tfrac{1}{2}H_2O$$

$$R^1R^2 = Me;\ Me;\ (CH_2)_4;\ (CH_2)_5$$

However, this reaction, similar to the alcoholyses, appears to be slightly reversible and the IR spectrum of the hydrolysis product showed it to be a mixture of tributylgermanium oxide and parent oxime, together with traces of the original oximate.

(*v*). Similar to alcoholyses[10–12] of lower alkoxides, the oximolyses of lower tributylgermanium oximates with higher oximes can be driven to completion, if the resulting lower oximes are continuously removed by fractionation

$$Bu_3GeON{=}CR^1R^2 + Me(n\text{-}C_5H_{11})C{=}NOH \xrightarrow[\text{4h}]{200^\circ}$$
$$Bu_3GeON{=}CMe(n\text{-}C_5H_{11}) + R^1R^2C{=}NOH$$

$$R^1, R^2 = Me, Me;\ Me, i\text{-}Pr$$

(*vi*). Bubbling anhydrous hydrogen chloride gas through a solution of oxime derivatives, $Bu_3GeON{=}CR^1R^2$, in anhydrous diethyl ether at 0° resulted in the cleavage of germanium–oxygen bond and formation of Bu_3GeCl; the corresponding oxime hydrochlorides are precipitated from solution:

$$Bu_3GeON{=}CR^1R^2 + HCl(gas) \xrightarrow[\text{0°C}]{Et_2O} Bu_3GeCl + R^1R^2C{=}NOH\cdot HCl\downarrow$$

$$R^1, R^2 = Me, Me;\ (CH_2)_5$$

(*vii*). Treatment of $Bu_3GeON{=}CR^1R^2$ with an equimolar quantity of acetic anhydride, followed by heating at 140° for 2 h gave a mixture of $Bu_3GeOCOMe$ and *O*-acyl oxime esters which can be separated by fractional distillation:

$$Bu_3GeON{=}CR^1R^2+(MeCO)_2O \xrightarrow[2h]{140^\circ} Bu_3GeOCOMe+R^1R^2C{=}NOCOMe$$

$$R^1, R^2 = Me, Me;\ Me, Et$$

Infrared spectra

The infrared spectra of the new oximates $Bu_3GeON{=}CR^1R^2$ have absorption bands (Table 2) in the expected regions. The structurally significant bands [*e.g.*, $\delta(CH_2Ge)$, $\nu(C{=}N)$, $\nu(Ge{-}Bu)$, $\nu(N{-}O)$, $\nu(Ge{-}O)$, $\rho(CH_2Ge)$, and $\nu(Ge{-}C)$ (*trans* and *gauche*)] have been assigned from infrared data published previously for oximes[13-15] and organogermanium compounds[16-18].

The 3160 to 2820 cm^{-1} region is characterised by the phenyl C–H, the methyl C–H, and the methylene C–H stretching vibrations. Absorption of weak to medium intensity in the 1690–1580 cm^{-1} region is assignable to C=N stretching mode, in view of the fact that in parent oximes, $\nu(C{=}N)$ absorbs in the region 1690–1620 cm^{-1}. A weak band at ~1588 cm^{-1} is attributed to the phenyl "C=C" and oxime C=N vibrations. Another phenyl "C=C" absorption band is found near 1490–1470 cm^{-1}. The two absorption bands characteristic of the phenyl C–H out-of-plane deformation occur at 753±2 and 703±1 cm^{-1}. In the oximates for which an alicyclic grouping[19] is known to be present there is a strong band near 998 cm^{-1}. The intense bands in the 1415–1390 and 690–680 cm^{-1} regions are assigned to the $(CH_2)Ge$ deformation and rocking vibrations respectively by analogy with the assignment of Marchand *et al.*[17]. The very intense band between 930–910 cm^{-1} in $Bu_3GeON{=}CR^1R^2$ compounds probably corresponds to an N–O stretching frequency; this vibration occurs near 930 cm^{-1} in oximes $(R^1R^2C{=}NOH)$[13-15]. The maximum intensity band in the 895–867 cm^{-1} region may be assigned to the Ge–Bu grouping; similar values are quoted[16,17] for various other butylgermanium compounds. The band of variable intensity between 850–840 cm^{-1} might be due to the Ge–O stretch which occurs at 845±5 cm^{-1} in butylgermanium alkoxides[18]. The infrared spectra of n-butylgermanes provide evidence[16] for *trans* and *gauche* forms in the 648–635 and 568–556 cm^{-1} regions respectively and in view of this, similar assignments are made for the bands at 670–650 cm^{-1} [ν(Ge–C *trans*)] and at 580–550 cm^{-1} [ν(Ge–C *gauche*)] in tributylgermanium oximates.

A comparative study (Table 2) of C=N stretching vibrations in tri-n-butylgermanium oximates reveals the following facts:

(*i*). Aromatic and acyclic oxime derivatives exhibit a frequency lowering and intensity increase in the $\nu(C{=}N)$ region as compared to other oximates, which appears to be due to conjugation[20,21] in the former case and ring strain[22] in the latter,

(*ii*). Oximates Bu_3GeL, where LH = acetaldoxime, butylraldoxime, and acetoneoxime, invariably show two weak absorptions in the 1690–1600 cm^{-1} region, attributable to C=N stretch, while in all the other cases only one band assignable to $\nu(C{=}N)$ is observed. The infrared spectra of $Bu_3GeON{=}CHMe$, $Bu_3GeON{=}CHPr$, and $Bu_3GeON{=}CMe_2$ in 5% CCl_4 exhibit only the higher absorption band.

(*continued on p.* 308)

TABLE 2

INFRARED DATA[a] (CM^{-1}) FOR THE NEW $Bu_3GeON{=}CR^1R^2$ DERIVATIVES

Compound[b]	ν(C=N)	ν(N–O)	ν(Ge–O)	ν(Ge–Bu)	$(CH_2)Ge$ *deform* *rock*	ν(Ge–C) *trans* *gauche*	*Other bands*
$Bu_3GeON{=}CHMe$	1668 w 1614 w	923 s	845 m	892 vs 880 vs	1410 s 685 s	660 s 560 m	3419–3219 w, br; 2995 vs; 2969 vs; 1451 vs, 1369 s; 1360 m; 1329 m; 1293 m; 1270 w; 1260 w; 1195 m; 1183 m; 1171 m; 1120 m; 1082 s; 1045 m; 1022 m; 998 m; 980 vs; 960 s; 815 m; 770 m; 745 w; 720 vs; 580 w; 531 s; 452 m
$Bu_3GeON{=}CHPr$	1678 w 1605 w	928 vs	844 m	893 vs 878 vs	1405 s 683 s	654 s 554 m	3410–3260 w; br; 2960 vs; 2927 vs; 2860 vs; 1451 vs; 1365 s; 1329 m; 1296 m; 1268 m; 1258 m; 1195 m; 1181 m; 1170 m; 1120 m; 1046 m; 1013 m; 998 m; 983 m; 958 m; 778 m; 742 m; 718 s; 703 s; 538 m; 478 w; 450 w
$Bu_3GeON{=}CMe_2$	1648 w 1617 w	918 vs	844 w	880 s 868 m	1415 s 684 s	654 m 558 w	3367–3242 w, br; 2960 vs; 2924 vs; 2867 vs; 2855 vs; 1444 s; 1392 m; 1356 s; 1342 s; 1315 m; 1293 w; 1263 m; 1194 w; 1180 w; 1170 m; 1081 s; 1061 s; 1023 m; 998 m; 958 s; 820 w; 768 w; 728 vs; 582 w; 488 m; 458 w
$Bu_3GeON{=}CMeEt$	1619 w	913 vs	844 w	882 vs 869 s	1405 s 684 s	654 s 555m	3410–3260 w, br; 2962 vs; 2929 vs; 2874 vs; 2855 vs; 1451 vs; 1365 vs; 1351 s; 1328 m; 1293 m; 1269 w; 1259 w; 1241 w; 1222 m; 1195 m; 1183 m; 1173 m; 1083 s; 1049 m; 1024 m; 999 s; 971 s; 963 vs; 809 w; 779 w; 765 m; 743 m; 714 vs; 577 w; 542 m; 514 w; 477 w
$Bu_3GeON{=}CEt_2$	1601 w	915 vs	845 w	882 s 870 s	1396 m 687 s	656 m 560 w	3400–3250 w; br; 2966 vs; 2928 vs; 2874 vs; 2859 vs; 1451 vs; 1364 s; 1328 m; 1294 m; 1270 w; 1260 w; 1196 m; 1182 m; 1172 m; 1100 m; 1082 s; 1046 m; 1030 m; 998 m; 960 m; 948 s; 815 w; 780 w; 767 w; 744 w; 712 vs; 580 w; 500 w; 453 w
$Bu_3GeON{=}CMePr$	1619 w	930 vs	846 m	880 vs	1410 s 685 vs	655 s 555 m	3419–3269 w, br; 2964 vs; 2924 vs; 2869 vs; 1455 vs; 1369 vs; 1355 s; 1332 s; 1294 m; 1270 m; 1255 m; 1215 m; 1196 m; 1182 m; 1172 s; 1100 s; 1082 vs; 1045 m; 1024 m; 998 s; 960 s; 823 m; 782 s; 766 m; 745 s; 715 s; 702 vs; 578 m; 480 m; 450 w
$Bu_3GeON{=}CMe\text{-}i\text{-}Bu$	1619 w	926 vs 918 vs	846 m	881 s 868 vs	1410 m 683 s	655 m 563 s	3419–3169 w; br; 2960 vs; 2928 vs; 2873 vs; 2860 vs; 1455 s; 1369 s; 1356 s; 1333 m; 1293 m; 1258 w; 1214 w; 1194 m; 1182 m; 1166 m; 1118 m; 1110 s; 1080 s; 1046 m; 1008 s; 998 s; 958 vs; 948 s; 823 w; 807 w; 767 w; 742 vs; 712 s: 486 w: 453 w

$Bu_3GeON{=}CEtBu$	1605 w	938 vs 908 vs	846 m	882 vs 870 vs	1405 s 688 vs	658 s 558 m	3450–3205 w, br; 2955 vs; 2855 vs; 1455 vs; 1368 vs; 1328 s; 1295 m; 1270 m; 1260 m; 1224 w; 1196 m; 1184 m; 1173 m; 1107 s; 1082 vs; 1043 m; 1023 m; 998 s; 960 s; 813 w; 787 m; 768 m; 743 s; 716 vs; 578 w; 513 w; 453 w
$Bu_3GeON{=}CHPh$	1588 w	939 vs 914 w	844 w	881 s	1397 m 689 vs	664 m 575 m	3450–3200 w, br; 3051 w; 3015 w; 2958 vs; 2924 vs; 2869 s; 2951 s; 1474 w; 1444 s; 1433 s; 1368 m; 1315 m; 1295 w; 1209 w; 1172 w; 1083 m; 1073 m; 1025 w; 999 w; 951 vs; 769 w; 751 s; 704 vs; 589 w; 506 m; 451 m
$Bu_3GeON{=}CMePh$	1588 w	922 vs 908 s	847 w	880 m 867 m	1406 m 687 vs	666 m 569 m	3156 w; 2957 vs; 2931 vs; 2856 s; 2824 s; 1488 m; 1456 s; 1438 s; 1369 m; 1356 m; 1328 w; 1297 w; 1197 w; 1177 w; 1081 m; 1027 m; 993 vs; 960 w; 799 m; 755 vs; 702 vs; 548 m
$Bu_3GeON{=}\overline{C(CH_2)_3CH_2}$	1634 w	925 vs 912 vs	845 m	880 vs 868 s	1418 vs 685 vs	656 s 562 m	3344 w, br; 2956–2856 vs, br; 1458 vs; 1428 s; 1370 vs; 1333 s; 1293 m; 1268 m; 1258 m; 1210 s; 1196 m; 1184 m; 1172 m; 1148 m; 1130 w; 1082 s; 1045 m; 1022 m; 1015 m; 998 s; 955 vs; 832 s; 778 m; 742 m; 715 vs; 592 vs; 450 w
$Bu_3GeON{=}\overline{C(CH_2)_4CH_2}$	1610 w	933 vs 917 vs	848 m	896 vs 881 vs	1390 m 684 s	657 m 559 w	3335 w, br; 2960 vs; 2896 vs; 2860 vs; 1451 vs; 1442 vs; 1362 s; 1328 m; 1293 w; 1265 w; 1251 w; 1217 m; 1194 w; 1182 m; 1171 m; 1134 w; 1102 m; 1081 s; 1045 w; 1019 w; 999 m; 986 s; 960 m; 834 s; 783 w; 771 w; 741 w; 719 vs; 627 s; 597 w; 469 m
$Bu_3GeON{=}CMe$- $(n$-$C_5H_{11})$	1601 w	918 vs	840 m	878 s	1400 m 688 vs	658 s 560 m	3350 w; br; 2959 vs; 2928 vs; 2859 vs; 1445 s; 1359 m; 1348 m; 1327 w; 1293 m; 1250 w; 1198 w; 1176 w; 1103 m; 1080 s; 1018–998 m, br; 960 m; 783 w; 768 w; 733 s; 703 s; 482 w, br

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[a] Spectra were measured as thin liquid film on a Perkin–Elmer Model 337 with grating optics and were calibrated against polystyrene; the following abbreviations are used: s, strong; m, medium; w, weak; v, very; br, broad. [b] For abbreviations see footnote *a* Table 1.

On the basis of the above findings some speculative suggestions for the existence of two C=N stretching frequencies may be made in few cases:

(*i*). Lower oximates exist in the pure liquid state in a dimer (association through nitrogen) $\rightleftharpoons$ monomer equilibrium, whereas depolymerisation appears to occur in solution.

(*ii*). The existence of *syn–anti* isomerism in oximes.

(*iii*). Conformational factors and slight hydrolysis of the compounds may be contributing factors.

No doubt (*i*) described above seems probable in view of, (*a*) the larger size of germanium atom, (*b*) lesser steric factors involved with lower oximes (*e.g.*, acetaldoxime, butyraldoxime, and acetoneoxime), and (*c*) in solution (5% CCl_4) spectra the existence of only one peak of the higher side in case of $Bu_3GeON{=}CHMe$, $Bu_3GeON{=}CHPr$, and n-$Bu_3GeON{=}CMe_2$ and unaltered position of $\nu(C{=}N)$ in case of all the other oximates. However, the possibility of reasons (*ii*) and (*iii*) cannot be ruled out.

A decrease of 48 ± 9 cm^{-1} in $\nu(C{=}N)$ relative to the parent oxime in oximates reported here might be due to a mass effect in these vibronically coupled systems. As $\nu(C{=}N)$ stretching vibrations appear to be sensitive[23] to resonance effects, to changes in the force constants of the attached bonds, to changes of phase, and also to inductive forces, no clear-cut decision can be made about factors responsible for such lowering.

Finally, the marked similarity of the infrared (except the three compounds $Bu_3GeON{=}CR^1R^2$, where $R^1, R^2 = H, Me; H, Pr; Me, Me$) spectra in the neat liquid as well as in solution, indicates that these oximate derivatives are not associated even in the liquid phase. This is in agreement with the observed molecular weights (ebullioscopically) in benzene, in which all the oximates are monomeric. The only observable solvent effect is that ν(Ge–O and $\nu(C{=}N)$ seem to be stronger in pure liquid state.

EXPERIMENTAL

Details of apparatus and chemicals,. common physical measurements, estimations, and preparation of Bu_3GeOEt have been described previously[24].

Syntheses

The following typical examples illustrate the methods used to prepare the new oxime derivatives $Bu_3GeON{=}CR^1R^2$ listed in Table 1.

Method 1. To an equimolar mixture of appropriate oxime and triethylamine ($\approx$10% excess) in benzene (25 ml) was added dropwise the calculated quantity of Bu_3GeCl in the same solvent (5 ml). After boiling the reaction mixture under reflux for an hour, the resulting dense white precipitate ($Et_3N \cdot HCl$) was removed by filtration. Excess benzene and triethylamine were removed, and distillation of the residual liquid under reduced pressure gave the corresponding oximate $Bu_3GeON{=}CR^1R^2$ (see Table 1 for properties and analysis).

Method 2. Anhydrous ammonia gas was bubbled through a benzene (30 ml) solution containing stoichiometric quantities of Bu_3GeCl and $R^1R^2C{=}NOH$ [$R^1, R^2 = Me, Me; Me, Et; (CH_2)_4; (CH_2)_5$] until the reaction mixture had cooled to room temperature. The mixture was then boiled under reflux for 2 h to remove excess of ammonia. After removal of excess benzene, distillation under reduced pressure gave a colourless liquid (80% yield). The identity of compounds synthesised by this procedure was established by elemental analyses, refractive index, molecular weight, and infrared determinations, which showed excellent agreement with products prepared by Method 1 and listed in Table 1.

Method 3. Bu_3GeCl (1.32 g, 4.73 mmole) in benzene (5 ml) was added dropwise to a suspension of $NaON{=}CMe_2$ (0.47 g, 4.73 mmole) in the same solvent (20 ml). The mixture was refluxed for 1 h, then sodium chloride was removed by filtration and, following removal of solvent, distillation gave $Bu_3GeON{=}CMe_2$ (1.045 g, 70%), b.p. 84–86°/0.2 mm, n_D^{20} 1.4552. (Found: C, 56.82; H, 10.12; N, 4.32%; mol.wt., 318. $C_{15}H_{33}GeNO$ calcd.: C, 57.03; H, 10.52; N, 4.43%; mol..wt., 316.)

Method 4. An exothermic reaction ensued when Bu_3GeCl (1.78 g, 6.41 mmole) was added to $Bu_3SnON{=}\overline{C(CH_2)_3CH_2}$ (2.49 g, 6.42 mmole). After heating the mixture for 1 h, distillation gave Bu_3SnCl (b.p. 150–152°/10 mm; 1.18 g, 72%) (identified by its IR spectrum) and $Bu_3GeON{=}\overline{C(CH_2)_3CH_2}$ (b.p. 103–104°/0.3 mm; 1.54 g, 70%). (Found: C, 59.12; H, 10.18; N, 4.02%; mol.wt., 340. $C_{17}H_{35}GeNO$ calcd.: C, 59.69; H, 10.31; N, 4.10%; mol.wt., 342.)

$Bu_3GeON{=}CR^1R^2$ compounds [R^1, R^2 = Me, Me; $(CH_2)_5$] were similarly prepared; their analytical data, refractive index, molecular weight, and infrared spectra were in agreeement with authentic samples (prepared by Method 1).

Method 5. A benzene solution of Bu_3GeOEt (3.46 g, 11.98 mmole) and cyclohexanoneoxime $\overline{CH_2(CH_2)_4C}{=}NOH$ (1.36 g, 12.01 mmole) was refluxed for 4h and the benzene/ethanol azeotrope was collected. On analysis, the azeotrope was found to contain only 0.067 g (1.45 mmole) of ethanol. The reaction mixture was again refluxed with a catalytic quantity (0.002 g) of *p*-toluenesulphonic acid for about 2 h with continuous removal of ethanol azeotropically; 0.47 g (10.20 mmole) ethanol being present in the azeotrope. After completion of the reaction, the solution was neutralised with a few drops of triethylamine. Excess of benzene was removed under reduced pressure at room temperature (20°/1.5 mm), and distillation gave the product $Bu_3GeON{=}\overline{C(CH_2)_4CH_2}$ in 98% yield, b.p. 132–134°/0.5 mm, n_D^{20} 1.4755. (Found: C, 60.60; H, 10.32; N, 3.78%; mol.wt., 354. $C_{18}H_{37}GeNO$ calcd.: C, 60.73; H, 10.47; N, 3.93%; mol.wt., 356.) The total ethanol liberated was 0.54 g (11.71 mmole) as against 0.55 g (11.93 mmole).

The oxime derivatives $Bu_3GeON{=}CR^1R^2$ [R^1, R^2 = Me, Me; Me, Et; $(CH_2)_4$] have also been synthesised by this procedure their analytical data agreed well with the theoretical values and their infrared spectra were similar with authentic samples.

Method 6. A mixture of $(Bu_3Ge)_2O$ (1.59 g, 3.16 mmole) and cyclopentanone oxime $\overline{CH_2(CH_2)_3C}{=}NOH$ (0.65 g, 6.55 mmole) in benzene (50 ml) was refluxed for 3 h with a catalytic quantity (0.002 g) of *p*-toluenesulphonic acid, during which time water produced was removed by azeotropic fractionation. The reaction was checked for completion by following the disappearance of the broad strong band at 841 cm^{-1} characteristic of Ge–O–Ge asymmetric stretch[17]. After the reaction was completed the solution was neutralised with a few drops of triethylamine. Excess of benzene was removed and distillation of the residual liquid afforded a colourless product (1.88 g, 87% yield), b.p. 120–122°/0.65 mm, n_D^{20} 1.4724. (Found: C, 59.32; H, 10.21; N, 3.96%; mol.wt., 340. $C_{17}H_{35}GeNO$ calcd.: C, 59.69; H, 10.31; N, 4.10%; mol.wt., 342.)

Reactions of tri-n-butylgermanium oximates

(1). (*a*). *Acetyl chloride.* Acetyl chloride (0.79 g, 10.07 mmole) in benzene (5 ml) was added dropwise to $Bu_3GeON{=}CMe_2$ (3.12 g, 9.97 mmole) in the same solvent (10 ml) at 0°, and the mixture was gently refluxed for 1 h. Solvent was removed (30°/1.5 mm), and distillation gave $Me_2C{=}NOCOMe$ (yield 78%), b.p. 72–73°/15 mm, n_D^{30} 1.4362 (Found: N, 12.08%; mol.wt., 120. $C_5H_9NO_2$ calcd.: N, 12.20%; mol.wt., 115.) and Bu_3GeCl (yield 80%), b.p. 133°/9 mm. (Found: Cl, 13.10%. $C_{12}H_{27}ClGe$ calcd.: Cl, 12.72%.)

(*b*). In an experiment similar to (1*a*) above, known molar ratios of $Bu_3GeON{=}CMeEt$ and MeCOCl gave $MeEtC{=}NOCOMe$ (yield 80%), b.p. 75–76°/10 mm (Found: N, 10.70%; mol.wt., 130. $C_6H_{11}NO_2$ calcd.: N, 10.85%; mol.wt., 129), and Bu_3GeCl (identified by its IR spectrum).

The *O*-acyl oxime esters formed in the above two experiments were also identified by infrared spectra *e.g.*, ester products showed strong absorptions in the 1750–1700 and 1250–1200 cm^{-1} regions characteristic of an ester group[25], together with weak to medium intensity absorptions in the region 1650–1600 cm^{-1} due to C=N stretch[13–15], and strong absorptions at 930±3 cm^{-1} assignable to N–O stretch[13–15].

(*c*). *Benzoyl chloride.* Benzoyl chloride (1.20 g, 8.54 mmole) reacted exothermally with $Bu_3GeON{=}CMe_2$ (2.68 g, 8.48 mmole). After heating the reaction mixture at 140° for 1 h, distillation gave Bu_3GeCl (yield 85%), b.p. 131–133°/9 mm (identified by its IR spectrum) and $Me_2C{=}NOCOPh$ (yield 78%), b.p. 119–120°/1.5 mm (lit.[26] 120°/1.5 mm). (Found: N, 7.82%; mol.wt., 179. $C_{10}H_{11}NO_2$ calcd.: N, 7.91%; mol. wt., 177.)

(2) *Germanium tetrachloride.* A mixture of $Bu_3GeON{=}CMe_2$ (2.66 g, 8.42 mmole), germanium tetrachloride (0.45 g, 2.10 mmole), and benzene (10 ml) was refluxed for 1 h followed by removal of the solvent (30°/2 mm). Distillation under reduced pressure then gave Bu_3GeCl (2.0 g, 85% yield), b.p. 132–133°/9 mm (identified by its infrared spectrum) and $Ge(ON{=}CMe_2)_4$ (0.60 g, 80% yield), b.p. 153–154°/0.7 mm. (Found: Ge, 20.18; N, 15.42%; mol.wt., 362. $C_{12}H_{24}GeN_4O_4$ calcd.: Ge, 20.10; N, 15.52%; mol.wt., 361.)

(3). *n-Octanol.* Heating a mixture of $Bu_3GeON{=}CMe_2$ (1.62 g, 5.13 mmole) and excess of octanol at 200° for 4 h with continuous removal of displaced acetoneoxime (0.30 g, 80% yield), m.p. 58–59° (Found: N, 19.10%. C_3H_7NO calcd.: N, 19.18%.) gave $Bu_3GeOC_8H_{17}$ (1.59 g, 83% yield), b.p. 123–125°/0.3 mm, n_D^{29} 1.4485; mol.wt., 375.

(4). *n-Pentyl methyl ketoxime.* In a reaction similar to (3) above, $Bu_3GeON{=}CMe_2$ (1.82 g, 5.76 mmole) and excess of n-pentyl methyl ketoxime (4.68 g, 36.23 mmole) gave $Me_2C{=}NOH$ (0.32 g, 76% yield), m.p. 58–59° (Found: N, 19.14%. C_3H_7NO calcd.: N, 19.18%) and $Bu_3GeON{=}CMe(n\text{-}C_5H_{11})$ (1.74 g, 81% yield), b.p. 117–118°/0.2 mm, n_D^{29} 1.4555. (Found: N, 3.52%; mol. wt. 370. $C_{19}H_{41}GeNO$ calcd.: N, 3.77%; mol. wt., 372.) The products were also identified by comparison of their infrared spectra with those of authentic samples.

(5). *Acetic anhydride.* A mixture of $Bu_3GeON{=}CEtMe$ (2.65 g, 8.03 mmole) and acetic anhydride (0.82 g, 8.04 mmole) was heated at 140° for 2 h. Distillation under reduced pressure gave $MeEtC{=}NOCOMe$ (74% yield), b.p. 76°/10 mm (Found: N, 10.68%; mol.wt., 126. $C_6H_{11}NO_2$ calcd.: N, 10.85%; mol.wt., 129.) and Bu_3Ge-

OCOMe (78% yield), b.p. 78–80°/0.2 mm, n_D^{29} 1.4630 (Found: CH_3COO^-, 19.62%; mol.wt., 306. $C_{14}H_{30}GeO_2$ calcd.: CH_3COO^-, 19.47%; mol.wt., 303.) identified by its infrared spectrum which showed characteristic strong absorptions of ester group[25] at 1685 and 1278 cm^{-1}; ν(Ge–Bu) at 884 cm^{-1}, ν(Ge–C *trans*) at 604 cm^{-1}, and ν(Ge–C *gauche*) at 564 cm^{-1}.

(6). *Hydrogen chloride.* Dry hydrogen chloride gas was passed through $Bu_3GeON{=}CMe_2$ (1.33 g, 4.21 mmole) in diethyl ether (50 ml) at 0°. An immediate exothermic reaction took place and a white solid (identified as oxime hydrochloride) precipitated and was removed by filtration. Excess of ether was removed and distillation of the residue gave Bu_3GeCl, in quantitative yield, identified by its IR spectrum.

(7). *Water.* Excess of water was added to the appropriate oxime derivative and the reaction mixture was then stirred for ≈ 30 min. Distillation under reduced pressure gave three fractions: parent oxime (85% yield), unreacted oxime derivative (≈ 10%), and hexabutyldigermoxane (80% yield), identified by their infrared spectra.

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