INFRARED SPECTRA OF ORGANOGERMANES

R. J. CROSS AND F. GLOCKLING
Department of Chemistry, The University, Durham (England)
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The infrared spectra of 80 organogermanes have been examined in the region 2500–200 cm^{-1} with the main object of assigning characteristic group-frequencies. Absorption bands due to carbon-hydrogen stretching vibrations have been ignored throughout. Bands due to the symmetric and asymmetric germanium–carbon stretch are given for methyl-, ethyl-, isopropyl-, butyl- and benzylgermanes. For compounds containing more than one type of alkyl group specific assignments are uncertain and, in these cases, all bands attributable to ν(Ge–C) are given (Tables 1, 2, 3 and 4).

Abbreviations: w, weak; m, medium; s, strong; a, broad; c, complex; sh, shoulder; b, absent or extremely weak; d, region obscured; e, range not covered.

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Methyl derivatives

Table 1 lists the useful methyl–germanium bands of which the methyl rock is the most characteristic. The germanium–carbon stretch is *generally* stronger and at higher frequency than for other alkylgermanes[1–5], with the exception of *trans*-butylgermanium compounds.

TABLE 1

CHARACTERISTIC METHYLGERMANIUM BANDS

	$\delta_{asym}(CH_3)$	$\delta_{sym}(CH_3)$	$\rho(CH_3)$	$\nu(Ge–C)$
$MeGeI_3$	b	1259 w	810 s	600 m
$MeGePh_3$	d	1235 w	788 m	586 m
$MeGe(GePh_3)_3$	d	d	787 w	559 w
$MeGe(CH_2Ph)_3$	d	d	800 s	573 m, 556 m, 542 w
$MeGe(H)Ph_2$	d	1239 w	797 s	594 m
$[MeGe(CH_2Ph)_2]_2$	d	d	801 m	576 w, 556 w
$Me_2Ge(CH_2Ph)_2$	1427 w	1227 m	802 s, 752 w	599 m, 576 m, 542 sh, w
Me_3GeCH_2Ph	1422 w	1229 m	820 s, 744 m	595 s, 563 w

Ethyl derivatives

In addition to the various carbon–hydrogen deformations and germanium–carbon stretching vibrations[4,6], ethylgermanes usually show characteristic bands (Table 2) in the regions 1020, 965, 325, and 295 cm^{-1}. Earlier work on Group IV metal alkyls[4,7,8] suggests that the two higher frequency bands which are often complex, involve a

TABLE 2

CHARACTERISTIC ETHYLGERMANIUM BANDS

	$\delta_{asym}(CH_3)$	$\delta_{asym}(CH_2)$	$\delta_{sym}(CH_3)$	$\delta_{sym}(CH_2)$				$\nu(Ge–C)$	
Ph_3GeEt	1456 w	d	d	d	d	960 w	688 m	565 m	d
$(PhCH_2)_3GeEt$	d	d	d	d	1013 m	958 m	d	558 m, 552 $^{sh}_{w}$	297 m
$(Ph_2EtGe)_2$	1450 m	d	d	1209 w	1021 m, 1019 m,	949 m	683 s	560 m	d
Ph_2GeEt_2	1460 m	d	d	1231 w	1019 $^{c}_{m}$	961 w	d	579 m, 553 m	d
$PhGeEt_3$	1462 m	d	d	1233 w	1021 $^{c}_{m}$	971 w	d	576 m, 540 w	d
Et_3GeBr	1458 s	1420 m	1377 m	1227 m	1025 s, 1010 s,	971 m	707 $^{s}_{s}$	581 s, 538 m	325 m, 298 m
$(Et_3Ge)_2O$	1451 m	1414 m	1374 w	1218 w	1016 $^{c}_{m}$	962 $^{c}_{w}$	699 s	582 s, 536 w	323 $^{s}_{m}$, 296 $^{sh}_{m}$
Et_4Ge	1460 m	1428 m	1374 m	1234 w	1029 s, 1005 m,	968 m	703 s, 673 s	570 s	325 s, 294 $^{s}_{m}$
Et_3GeBu	1462 s	1425 m	1376 m	1232 w	1017 $^{c}_{s}$	962 m	699 $^{c}_{s}$	570 s, 535 w	c
Et_3GePPh_2	1451 m	d	1372 m	1214 w	1020 s, 1009 s,	966 m	d	569 m, 532 w	313 $^{s}_{m}$
$Et_3GeOP(O)Ph_2$	1453 w	d	d	1220 w	d	d	725 s	578 s d	c
$(Et_3GePPh_2)AgI$	1449 m	d	1368 w	1217 w	1008 s	966 m	d	590 m, 533 w	c
Et_3GeCH_2Ph	1460 m	1427 w	1379 w	1220 $^{sh}_{w}$	1020 $^{c}_{m}$	971 w	730 m	573 m, 554 w, 535 w	321 m, 293 w
$Ph_2Ge(Et)Bu$	1456 $^{c}_{m}$	d	d	1224 w	1014 m	962 w	d	565 m	c
$(PhCH_2)_3GeGeEt_3$	1460 $^{sh}_{m}$	1425 w	1376 w	d	1012 m	968 w	d	d	327 m, 300 w

carbon–carbon stretch and carbon–hydrogen deformations, whilst the two low frequency bands, possibly Ge–C–C deformations, are broad and frequently masked in the presence of phenylgermanium groups. The band near 700 cm^{-1} is probably a methylene rock.

n-Butyl derivatives

In addition to the normal methyl and methylene deformations, two weak bands near 880 and 870 cm^{-1} are characteristic of *n*-butylgermanium compounds. Most of the *n*-butylgermanes examined (Table 3) were liquids, and comparison with the spectra of *n*-propyl and *n*-butyltin compounds[8,9] provides evidence for *trans* and *gauche* forms, having ν(Ge–C) near 645 and 550 cm^{-1} respectively. Triphenylbutylgermane is a crystalline solid, and as such it shows the stretching mode of the *trans*-form only. However, in solution or as a melt, it shows both *trans* and *gauche* forms. Absorption bands in the far infrared which are not attributable to phenyl, benzyl or ethyl groups are also given in Table 3.

TABLE 3

CHARACTERISTIC *n*-BUTYLGERMANIUM BANDS

		ν(Ge–Bu) *trans*	ν(Ge–C) [*including* ν(Ge–Bu) *gauche*]	
$(PhCH_2)_3GeBu$	882 sh, w, 872 w	643 w	556 sh, w, 549 w, 543 sh, w	408 w
$Ph_2Ge(Et)Bu$	877 w, 867 w	645 w	Table 2	e
$Ph_2Ge(H)Bu$	881 c, w d	635 m	568 w	b
Ph_2GeBu_2	880 w, 870 w	647 w	565 m	e
$(PhCH_2)_2GeBu_2$	881 m, 872 sh, m	645 w	549 w	405 w, 369 sh, w, 288 a, w
$PhCH_2GeBu_3$	882 m, 870 sh, m	645 w	550 w	415 w, 400 sh, w, 374 w, 290 a, m
Bu_4Ge	881 s d	641 m	556 m	415 m, 400 m, 375 s, 294 a, m
Et_3GeBu	917 w, 907 w	641 w	Table 2	e
Ph_3GeBu	888 w, 873 m	648 m	565 w (liquid only)	b

Isopropyl derivatives

The spectra available show a close similarity to isopropyl bromide for which assignments have been made[10] (1466 s, 1385 w, 1370 w, 1160 w, 1082 w, 1006^{c}_{m}, 918 w, 878 m). Two strong bands near 420 and 310 cm^{-1} are probably C–C–C and Ge–C–C deformations (Table 4).

TABLE 4

CHARACTERISTIC ISOPROPYLGERMANIUM BANDS

	$\delta(Me_2C{-}H)$	ν_{asym}(Ge–C)	ν_{sym}(Ge–C)	
iso-Pr_3GeH	1211 w	565 m	556 sh, m	420 s, 313 a, s
iso-Pr_3GeD	1224 w	564 s	542 s	420 s, 311 a, s
iso-Pr_3GeCl	1224 m	562 s	521 w	421 m, 323m
(iso-$Pr_2GeO)_n$	1215 w	578 m	545 w	e

Benzyl derivatives

The spectra are highly complex [the $(PhCH_2)_3Ge$ bands in $(PhCH_2)_3GeCl$ occur at: 1949 w, 1869 w, 1805 w, 1745 w, 1595 s, 1577 w, 1488 s, 1447 s, 1404 w, 1333 w, 1314 w, 1282 w, 1250 w, 1218 w, 1203 m, 1181 w, 1155 w, 1145 w, 1055 m, 1026 w, 996 w, 980 w, 967 w, 901 m, 848 w, 813 w, 800 m, 781 m, 763 s, 694 s, 617 w, 557 w, 541 w, 461 m, 448 m, 337 w, 251 m cm^{-1}], but a number of bands are strikingly characteristic of benzyl-germanium groups, and may be used for characterisation purposes. Three bands, near 815, 805 and 775 cm^{-1}, which probably include a CH_2 rocking mode, give a very characteristic pattern. The germanium–carbon stretch occurs near 550 cm^{-1}, and is generally weaker than in the methyl-, ethyl- and butylgermanes; two bands are usually observed in compounds having more than one benzyl group and these probably correspond to the asymmetric and symmetric stretching vibrations. For compounds of the type $(benzyl)_nGe(alkyl)_{4-n}$ it is not possible to distinguish the different types of Ge–C stretch with any certainty and reference is made to the earlier tables, where all the possible bands are included.

The far infrared spectra also show bands characteristic of the benzylgermanium group; of these the medium intensity band at 245 ± 15 cm^{-1} is the most useful. Both this and the weak band near 335 cm^{-1} are present in benzyl bromide and are absent from methylene bromide.

TABLE 5

CHARACTERISTIC BENZYLGERMANIUM BANDS

	ν(Ge–C)	
$(PhCH_2)_3GeCl$	559 w, 540 w	337 w, 251 m
$(PhCH_2)_3GeBr$	557 w, 541 w	343 w, 256 s
$(PhCH_2)_3GeMe$	Table 1	340 w, 245 s
$(PhCH_2)_3GeEt$	Table 2	334 w, 251 w
$(PhCH_2)_3GeBu$	Table 3	333 w, 247 c, m
$(PhCH_2)_4Ge$	563 w, 550 m	336 w, 257 m, 237 m
$(PhCH_2)_6Ge_2$	556 w, 539 w	342 w, 238 m
$[(PhCH_2)_3Ge]_2O$	559 m, 544 w	b 260 s
$(PhCH_2)_3GeH$	541 w	334 c, w, 239 m
$(PhCH_2)_3GeD$	563 m, 541 w	334 c, w, 238 m
$(PhCH_2)_3Ge–SiMe_3$	554 w	335 w, 261 m
$(PhCH_2)_3Ge–GeEt_3$	d	d 267 m or 234 a, m
$(PhCH_2)_2GeMe_2$	Table 1	345 w, 249 m
$(PhCH_2)_2GeBu_2$	Table 3	334 w, 238 a, w
$(PhCH_2)_2GeH_2$	556 w, 532 w	e
$(PhCH_2)_2GeD_2$	564 w	e
$[(PhCH_2)_2MeGe]_2$	Table 1	334 w, 245 m
$PhCH_2GeBu_3$	Table 3	b b
$PhCH_2GeEt_3$	Table 2	d b
$PhCH_2GeMe_3$	Table 1	b b
$PhCH_2GePh_3$	562 w	d 245 w

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Phenyl derivatives

Earlier papers on Ph_4M compounds[11] (M = Si, Ge, Sn, Pb), phenyl derivatives of tin[12] and triphenylgermyl azide[13] have established frequencies characteristic of the

TABLE 6

CHARACTERISTIC PHENYLGERMANIUM BANDS

Ph_4Ge	1091		329 s		
Ph_3GeH	1093		323 a,s	303 m	
Ph_3GeD	1093		322 a,s	303 m	
Ph_3GeCl	1092	340 sh,m	328 s	275 m	
Ph_3GeBr	1090	340 sh,m	327 s	b	
Ph_3GeI	1089		335 s	d	
Ph_3GeMe	1092		319 s	289 m	
Ph_3GeBu	1092		326 s	307 m	
Ph_3GeCH_2Ph	1092		325 s	289 m	
$(Ph_3Ge)_2$	1086		322 s	268 s	
$(Ph_3Ge)_3GeH$	1086		329 s	b	228 s
$(Ph_3Ge)_3GeMe$	1087		328 s	b	228 m
$(Ph_3Ge)_2O$	1099	340 s	328 m	284 m	
Ph_2GeH_2	1094		312 s	292 m	
Ph_2GeBr_2	1089c		314 sh,s	b	
$Ph_2Ge(H)Me$	1093		309 s	292 m	254 w
$Ph_2Ge(H)Bu$	1093		314 s	301 m	
$PhGeBr_3$	1081		317 m		

TABLE 7

ETHYLPHENYLGERMANES

Et_4Ge	b	325 s		294 a,m		
Et_3GePh	1092	327 a,s	310 m	289 a,m	254 w	
Et_2GePh_2	1092	335 s	315 s	295 m	260 w	
$[Et(Ph_2)Ge]_2$	1083	321 s		294 s	260 a,m	226 w
$EtGePh_3$	1092	341 s	322 s	297 m	260 w	

TABLE 8

GERMANIUM–PHOSPHORUS AND GERMANIUM–TRANSITION METAL COMPLEXES

Ph_3GePPh_2	1086	327 s, 273 s, 254 w, 239 w, 221 w
$Ph_2Ge(PPh_2)_2$	1079	311 s, 288 s, 272 w, 257 s, 246 m, 235 w
$Ph_3Ge-Ag(PPh_3)_3$	1094	323 w, 308 m, 296 m, 265 w
$Ph_3Ge-AuPMe_3$	1083	345 w, 316 s, 309 s
$Ph_3Ge-AuPPh_3$	1081	321 s, 307 s
$[(Ph_3Ge)_2Au]NEt_4$	1075	311 s
$(Ph_3Ge)_2Pt(PEt_3)_2$	1073	318 s, 305 s, 285 s, 242 m
$Ph_3GePt(H)(PEt_3)_2$	1074	326 s, 305 m, 292 s
$(Ph_3Ge)_2Pt(PPr_3)_2$	1076	317 s, 305 s, 287 s, 244 m

phenylgermanium grouping, which are also observed for the compounds listed in Tables 6–8. The Ph_3Ge bands in Ph_3GeCl occur at: 1965 w, 1894 w, 1826 w, 1770 w, 1653 w, 1582 w, 1484 m, 1429 s, 1381 w, 1335 w, 1305 m, 1266 w, 1183 w, 1159 w, 1092 s, 1063 w, 1026 w, 998 m, 971 w, 917 w, 855 w, 735 s, 694 s, 676 w, 615 w, 463 m, 453 m, 340 sh, 328 s, 275 m cm^{-1}. In addition to the absorption patterns characteristic of mono-substituted benzenes, the band at 1089 cm^{-1}, one of Randle and Whiffen's "X-sensitive" bands[14], is stated to be constant for phenylgermanium compounds[11,15]. We find that this strong sharp band varies from 1073 cm^{-1} in $(Ph_3Ge)_2Pt(PEt_3)_2$ to 1099 cm^{-1} in hexaphenyldigermoxane, and can overlap the positions of the equivalent band in Ph–Si and Ph–Sn compounds. The 1428 cm^{-1} band however[11,16], is constant to within 5 cm^{-1} for the range of compounds given in Tables 6–8. In contrast for the band at 450 cm^{-1}, which is reported as splitting in the less symmetrical phenyl derivatives of Group IV metals[11,17], we find the range 482–448 cm^{-1}. In compounds containing more than one phenyl group splitting does occur, but no pattern is obvious. For example, Ph_3GeCl and Ph_3GeBr both show two bands whereas Ph_3GeI shows only one; in complexes having triphenylgermyl groups bonded to platinum, three bands are observed.

Phenylgermanium compounds show two bands in the 350–200 cm^{-1} region. The stronger, near 325 cm^{-1} is highly characteristic of the triphenylgermyl group[11] and for the analogous silicon compounds is stated to combine an in-plane ring deformation and the asymmetric M–phenyl stretch[17]. In diphenylgermyl compounds it falls at lower frequencies (314–309 cm^{-1}). The weaker band, which may involve the symmetric Ge–phenyl stretch, is more variable (303–268 cm^{-1}) and shows less splitting than has been reported for triphenylsilyl analogues[17]. The bands near 228 cm^{-1} in $(Ph_3Ge)_3GeH$ and $(Ph_3Ge)_3GeMe$[18] have been ascribed to the Ge–Ge stretch.

Phenylethylgermanes have more complex far infrared spectra; those examined (Table 7) have four bands between 350 and 200 cm^{-1}, two of which are present in tetraethylgermane. The band near 260 cm^{-1} is absent from most non-aromatic ethylgermanium compounds other than bromotriethylgermane.

Triphenylgermyl–transition metal complexes and the phosphine compounds, $Ph_3Ge–PPh_2$ and $Ph_2Ge(PPh_2)_2$, show similar complexities in this region (Table 8). Some of the additional bands are undoubtedly due to the phosphine ligands, and may also include the germanium–transition metal stretch.

A few apparently anomalous bands were found among the compounds reported in Tables 6–8. Ph_3GeH, $Ph_2Ge(Me)H$ and Ph_3GeBu show a weak band near 400 cm^{-1} which is absent or extremely weak in all the other compounds. $Ph_2Ge(Me)H$ also shows medium bands at 842, 656 and 256 cm^{-1} which are absent from related compounds.

Tolyl derivatives

Tolylgermanes (Table 9) contain two bands close to those found in phenylgermanes, near 320 and 290 cm^{-1}, which may also involve the germanium-carbon stretch. In addition their far infrared spectra contain bands which appear characteristic of *ortho*-, *meta*- and *para*-substituents.

TABLE 9

CHARACTERISTIC TOLYLGERMANIUM BANDS

$(o\text{-Tolyl})_3GeBr$	438 s	413 s	305 a,s	257 w
$(o\text{-Tolyl})_3GeH$	438 s	403 m	304 s, 291 s	245 w
$(o\text{-Tolyl})_6Ge_2$	446 s	407 m	307 m, 291 s, 286 s	253 w, 249 w
$(m\text{-Tolyl})_3GeH$	426 s	379 m	316 s, 308 s	270 w
$(m\text{-Tolyl})_4Ge$	430 s	388 m, 373 m	323 s, 303 s	261 w, 232 w
$(m\text{-Tolyl})_6Ge_2$	426 s	373 m	312 s, 304 s	259 s
$(p\text{-Tolyl})_4Ge$	437 s	373 m, 367 s	328 s, 294 m	278 m
$(p\text{-Tolyl})_6Ge_2$	484 s	362 m	316 s, 309 s	282 m, 237 m

FUNCTIONAL GROUPS

Organogermanium hydrides and deuterides

Many organogermanium hydrides have been examined and, in addition to the Ge-H stretching frequency near 2100 cm^{-1}, various deformation modes have been identified in simpler molecules (GeH_2 bend and wag[19] near 860 and 780 cm^{-1}; GeH_3 rock[20,21] near 600 cm^{-1}). The germanium–hydrogen stretch varies from 2175 cm^{-1} in GeH_2F_2[19] to 1953 cm^{-1} in $(Ph_3Ge)_3GeH$[18], and for many organogermanes the Ge-H stretch has been related to the Taft electronegativity coefficients of the attached groups[22,23]. Table 10 gives the Ge–H and Ge–D stretching and deformation frequencies for the hydrides and deuterides examined in the present work. Germanium–deuterium deformation modes occur in uncomplicated regions of the spectrum and are easily recognised. In contrast for tribenzylgermane the germanium–hydrogen bend could not be identified, and in other cases only alternative assignments were possible. The spectrum of solid triphenylgermane showed remarkable complexities between 700 and 500 cm^{-1}, which were absent from solutions or the liquid melt, and may be con-

TABLE 10

CHARACTERISTIC GERMANIUM–HYDROGEN AND –DEUTERIUM BANDS

Hydrides			*Deuterides*		
	ν(Ge–H)	*Ge–H (deformations)*		*ν(Ge–D)*	*Ge–D (deformations)*
iso-Pr_3GeH	1989 s	710 s	iso-Pr_3GeD	1433 s	508 s
Ph_3GeH	2037 s	709 s	Ph_3GeD	1473 m	526 s
$(o\text{-Tolyl})_3GeH$	2057 m	697 s			
$(m\text{-Tolyl})_3GeH$	2034 m	719 s			
$(p\text{-Tolyl})_3GeH$	2031 m	732 s or 688 s			
$(Mesityl)_3GeH$	2033 m	707 m			
$(PhCH_2)_3GeH$	2034 m	—	$(PhCH_2)_3GeD$	1464 s	472 m
$Ph_2(Me)GeH$	2035 s	707 s			
$Ph_2(Bu)GeH$	2028 s	707 s	$Ph_2(Bu)GeD$	1465 s	525 s
$(Ph_3Ge)_2GeH$	1953 m	680 s			
Ph_2GeH_2	2051 s	866 s, (758 s or 723 s), 511 m			
$(PhCH_2)_2GeH_2$	2037 s	864 s (704 s?)	$(PhCH_2)_2GeD_2$	1466 m	615 m, 495 m
$PhGeH_3$	2062 s	870 m, 823 s, 583 a,m			

nected with the α and β crystallographic forms. Diphenyl- and dibenzylgermanes, both of which are liquids, were also complicated in this region.

Organogermanium halides

Some germanium–halogen stretching frequencies are given in Table 11. Raman spectra of several ethylgermanium chlorides[6,7] show bands at 400 and 376 cm^{-1}, ascribable to ν_{asym}(Ge–Cl) and ν_{sym}(Ge–Cl) respectively. Similarly the infrared spectrum of trichloromethylgermane[5] contains two bands at 430 and 403 cm^{-1}. The germanium–bromine stretching frequency covers a wide range and is difficult to assign in the phenylgermanes since it falls in the same region as the characteristic phenyl bands (Tables 6–8). In dibromdiphenylgermane the germanium–bromine stretch could not be resolved.

TABLE 11

GERMANIUM–HALOGEN STRETCHING FREQUENCIES

	ν(Ge–Cl)	*ν(Ge–Br)*	*ν(Ge–I)*
iso-Pr_3GeCl	369 s		
Ph_3GeCl	379 s		
$(PhCH_2)_3GeCl$	362 m		
Ph_3GeBr		313 s	
$(PhCH_2)_3GeBr$		251 s	
Et_3GeBr		269 m or 245 m	
Ph_2GeBr_2		315 sh, m	
$PhGeBr_3$		327 s, 228 w	
$GeBr_4$		330 s	
Ph_3GeI			283 s
$MeGeI_3$			256 m
GeI_4			263 s

Organogermanium oxides

The frequencies attributable to the germanium-oxygen stretch vary greatly with the structure of the molecule. Thus alkoxygermanes[24], $Ge(OR)_4$, show two bands at 1040 and 680 cm^{-1}, whilst the trimeric and tetrameric forms of diphenylgermanium oxide[25] show only one band at 850 cm^{-1}. In contrast dimethylgermanium oxide shows variations in the band position depending on the degree of polymerisation[3], as has also been found for the corresponding silicon compounds. A similar complexity is indicated for the isopropyl compound, (iso-$Pr_2GeO)_n$, in the present work.

TABLE 12

GERMANIUM-OXYGEN STRETCHING FREQUENCIES

	ν(Ge–O)
$(Et_3Ge)_2O$[6]	855 a, s
$(Ph_3Ge)_2O$	858 a, s
$[(PhCH_2)_3Ge]_2O$	926 a, s
$Et_3Ge–OP(O)Ph_2$[26]	954 a, s
(iso-$Pr_2GeO)_n$	844 s, 789 s

Miscellaneous compounds

$(PhCH_2)_3Ge{-}SiMe_3$	ν(Ge—Si) probably at 351 cm^{-1}
$Et_3Ge{-}PPh_2$	ν(Ge—P) probably at 474 cm^{-1}
$(p\text{-Tolyl})_3GeCOOH$	ν(Ge—CO_2H) probably at 571 cm^{-1}

EXPERIMENTAL

Spectra were recorded on Grubb-Parsons G.S.2A, Spectromaster and D.M.2/D.B.3 Spectrometers. Except in special cases solids were examined as pressed discs in potassium bromide or potassium iodide and as nujol mulls.

Preparations of most of the phenyl[18], tolyl[27], benzyl[28], isopropyl[29] and transition metal[30,31] compounds are described elsewhere.

Butyltriphenylgermane

Triphenylgermyllithium, from hexaphenyldigermane (2.5 g) and lithium shot (0.25 g) in 1,2-dimethoxyethane (5 cc), was treated with *n*-butyl bromide (1.3 g). Hydrolysis and ether extraction gave butyltriphenylgermane (2.0 g), b.p. 160°/10^{-2} mm, m.p. 80–81° (*ex* methanol). (Found: C, 73.2; H, 6.8. $C_{22}H_{24}Ge$ calcd.: C, 73.2; H, 6.7 %.) Butyltriphenylgermane is also formed in low yield in the reaction between butyllithium and triphenylgermane contrary to earlier reports[32].

Butyldiphenylgermane and butyldiphenyldeuterogermane (with Mr. C. A. Clarke)

Diphenylgermane (6.3 g; 27.5 mmole) in ether (100 cc) was treated at —10° with *n*-butyllithium (55 mmole) in pentane (20 cc). Hydrolysis, after stirring for 4 h gave, by distillation of the ethereal extract, diphenylgermane, b.p. 80°/10^{-2} mm (22 %); butyldiphenylgermane, b.p. 120°/10^{-2} mm (2.8 g, 36 %). (Found: C, 67.5; H, 7.6; Ge, 26.4. $C_{16}H_{20}Ge$ calcd.: C, 67.4; H, 7.1; Ge, 25.5 %.) A fraction (0.9 g), b.p. 180–200°/10^{-2} mm, was shown by its NMR spectrum to consist mainly of the digermanes, $Ph_2Ge(H)Ge(H)Ph_2$ and $Ph_2Ge(H)Ge(Bu)Ph_2$, formed by reactions of the type:

$$Ph_2Ge(H)Li + Ph_2GeH_2 \longrightarrow LiH + Ph_2Ge(H)Ge(H)Ph_2$$

Butyldiphenyldeuterogermane was obtained in 30 % yield by deuterolysis of a similar reaction mixture.

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SUMMARY

Characteristic infrared frequencies are reported for a variety of organogermanes including alkyls, aryls, hydrides, deuterides, halides and oxides. Germanium–carbon

stretching frequencies for *trans* and *gauche* forms of *n*-butylgermanes have been observed.

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