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THE PREPARATION AND SPECTROSCOPIC PROPERTIES OF THE PERMETHYLCYCLOPOLYGERMANES

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SUMMARY

The preparation and characterization of the new five- and seven-membered cyclopolygermanes, decamethylcyclopentagermane and tetradecamethylcycloheptagermane, are reported. An improved preparative method is also presented for the hexamer, dodecamethylcyclohexagermane. In addition, ultraviolet, NMR, infrared, and mass spectral studies of all three compounds are described and discussed. All attempts to reduce the cyclopolygermanes to anion radicals for subsequent electron spin resonance studies were unsuccessful.

INTRODUCTION

A number of preparative and spectroscopic studies of Group IV organocyclopolymers have recently been reported[1–4]. Although dodecamethylcyclohexagermane was first prepared by Nefedov in 1962[5], only little work has been done with other permethylcyclopolygermanes.

Small amounts of a compound reported to be octamethylcyclotetragermane were found along with many other compounds when an etherate of trichlorogermane was treated with methylmagnesium bromide or methyllithium[6]. A melting point of 89–90° was given for the substance but no further characterization was reported. In 1965, the pyrolysis of dodecamethylcyclohexagermane was reported to yield a complex mixture of compounds, two of which were tentatively assigned as octamethylcyclotetragermane and decamethylcyclopentagermane[7]. The compounds were not isolated, however, and were identified only by a correlation of the logarithms of their gas chromatographic retention times.

In some of our previous work with silicon–germanium heterocyclics we noted that gas chromatographic analyses of many reaction mixtures showed the presence of compounds then tentatively identified as the permethylated cyclopentagermane and cycloheptagermane[4]. We now report the specific preparation and characterization of the compounds decamethylcyclopentagermane and tetradecamethylcycloheptagermane along with a comprehensive spectroscopic study of the permethylcyclopolygermane series $(Me_2Ge)_n$, $n=5,6,7$.

RESULTS AND DISCUSSION

Preparation by coupling

The previously reported method for the preparation of dodecamethylcyclohexagermane[5] has been found to be difficult to reproduce in our laboratories. The reaction appears to be very dependent upon temperature and time, and many other products were often obtained. Attempts in our laboratories to improve the reliability of the reaction by using naphthalene as an anion radical source* gave outstanding results in several cases, but unfortunately this preparation likewise was not consistently reproducible.

The procedure employed for most dependable results involves the rapid addition of dimethyldichlorogermane to a stirred suspension of lithium dispersion in tetrahydrofuran at room temperature. The first stage of the reaction occurs within 5–30 min and is characterized by the formation of a whitish-gray suspension, which is a mixture of lithium salts and polydimethylgermane. Gas chromatographic analysis of the mixture at this point indicates that only small amounts of soluble products are present. Upon further stirring at room temperature (2–3 h) the mixture assumes a yellow to green coloration and the amount of insoluble dimethylpolygermane polymer decreases. After stirring an additional hour, workup and sublimation yields 35–50% cyclic products, decamethylcyclopentagermane, dodecamethylcyclohexagermane, and tetradecamethylcycloheptagermane (in a ratio of about 1/18/1). Usually no polymeric material is obtained; however, if the reaction is stopped soon after the appearance of the yellow to green color, fairly large amounts of polymer can be isolated.

Recrystallization of the crystalline product from acetone yields the pure cyclohexagermane; the mother liquor is then evaporated down to give an oil containing large amounts of the cyclopentagermane and cycloheptagermane which can then be easily isolated by preparative gas chromatography.

All three cyclopolygermanes are white crystalline compounds. The hexamer is a very stable compound; the pentamer, however, undergoes air oxidation easily as does the silicon analog. The heptamer appears to be stable like the hexamer but

TABLE 1

PROPERTIES OF THE PERMETHYLCYCLOPOLYGERMANES

Compound	M.p. (°C)	Analysis (%)[a]		Mol. wt.[b] (calcd.)
		C	H	
$Me_{10}Ge_5$	170–173	23.13	6.00	513.0
$Me_{12}Ge_6$	229–233	23.34	5.97	615.6
$Me_{14}Ge_7$	208–213	23.57	5.67	718.2

[a] Calcd. for $(C_2H_6Ge)_n$ = C, 23.41; H, 5.85%. [b] Since several isotopes exist in appreciable amounts for germanium, molecular weight determination by mass spectroscopy is difficult due to the complex groups of peaks observed in the parent peak regions. Nonetheless, the theoretical intensities of these peaks were calculated, and the results were found to be in excellent agreement with the observed intensities (Table 6).

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* Use of naphthalene as an anion radical source in the analogous silicon reaction produced dodecamethylcyclohexasilane in yields consistently above 90%[2].

pyrolyzes at temperatures above 250° to form pentamer and hexamer. Some properties of the permethylcyclopolygermanes are summarized in Table 1.

Preparation by polymer redistribution

In some of our coupling-type reactions a white polymeric powder was isolated. The material is insoluble in most solvents. The IR spectrum shows the presence only of dimethylgermylene groups, and therefore the structure is believed to be linear, $(Me_2Ge)_x$, similar in nature to the polymer found in the analogous polysilane preparations.

The polymer was found to undergo redistribution to cyclic compounds when added to a small amount of naphthalene radical anion in tetrahydrofuran and stirred for about 2 h. Workup showed a 60% conversion to $Me_{10}Ge_5$, $Me_{12}Ge_6$, and $Me_{14}Ge_7$ in a ratio of about 2/20/1. These results are similar to those obtained with the analogous silicon polymer[2].

Preparation by photolysis reactions

Recently Kumada and Ishikawa reported[8] that the photolysis of a cyclohexane solution of dodecamethylcyclohexasilane produced a mixture of octamethylcyclotetrasilane and decamethylcyclopentasilane in a ratio of about 1/5. These compounds would result from the splitting out of silylene species from the hexameric starting compound. In addition, there was obtained both polymer and a small amount of oxidation product from the air sensitive tetrasilane.

We now report that dodecamethylcyclohexagermane undergoes a similar photolysis reaction to produce the cyclopentagermane in about 65% yield. A small amount of polydimethylgermane polymer is also formed. Attempts were made to detect the presence of the tetramer. However, gas chromatographic analysis of a number of such reaction mixtures showed that photolysis of only very dilute solutions would produce such a compound. Unfortunately the extremely dilute solutions required and the apparent unstable nature of the compound made isolation of the pure compound impossible.

Spectroscopic studies

The three cyclopermethylpolygermanes, like the corresponding polysilane series, give almost identical IR spectra in the region from 4000 to 500 cm^{-1} (Table 2). Only the cyclopentagermane shows a band in the region below 500 cm^{-1}. It is likely that this absorption represents a type of Ge–Ge vibration.

As expected, the PMR spectrum of each of the three cyclic compounds is a singlet at room temperature at nearly the same chemical shift, about 0.33 ppm downfield from tetramethylsilane. Unlike the analogous silicon compounds, however, the chemical shift does not decrease in a regular way with increasing ring size (Table 3).

The UV spectra of the cyclic permethylpolygermanes, like those of their silicon analogs, show absorptions above 200 nm. The spectra, however, are less featured than those of the silicon compounds. Data for the germanium compounds are summarized in Table 4. For $Me_{12}Ge_6$, data agreeing well with ours already appear in the literature[9]. As in the cyclopolysilane series, the long-wavelength band is found to undergo a hypsochromic shift with increasing catenation. The nature of the transitions involved in compounds of this type is not fully understood, but it is clear

TABLE 2

IR SPECTRA (cm^{-1}) OF THE PERMETHYLCYCLOPOLYGERMANES

$Me_{10}Ge_5$	$Me_{12}Ge_6$	$Me_{14}Ge_7$	Assignment
2965 s	2965 s	2965 s	C–H asym. stretch
2895 s	2895 s	2895 s	C–H sym. stretch
2800 w	2800 w	2800 w	
2425 vw	2430 vw	2425 vw	
2335 vw			
1412 m	1412 m	1410 m	C–H deformation
1230 m	1232 m	1230 m	Ge–Me deformation
	1223 w	1220 w	Ge–Me deformation
830 s	828 s	830 m	Ge–Me rock
796 vs	790 vs	790 vs	Ge–Me rock
580 s	575 s	576 s	Ge–C asym. stretch
555 s	552 s	554 s	Ge–C sym. stretch
367 m			Ge–Ge stretch

TABLE 3

PROTON NMR DATA FOR THE PERMETHYLCYCLOPOLYGERMANES

Compound	Chemical shifts[a]		^{13}C–H coupling const. (Hz)
	ppm (δ)	Hz	
$Me_{10}Ge_5$	−0.330	−19.9	126
$Me_{12}Ge_6$	−0.340	−20.4	126
$Me_{14}Ge_7$	−0.328	−19.6	126

[a] All shifts are downfield from TMS.

TABLE 4

UV DATA FOR THE PERMETHYLCYCLOPOLYGERMANES

Compound	λ_{max} (nm)	ε[a]
$Me_{10}Ge_5$	270	2000
	250	4000
$Me_{12}Ge_6$	255	4000
	235	13000
$Me_{14}Ge_7$	240	12000

[a] All absorptions occur as poorly defined shoulders; therefore band positions and extinction coefficient values are only approximate.

that σ electrons must be involved[10].

Many attempts were made to reduce the cyclopolygermanes to anion radicals for subsequent study by electron spin resonance spectroscopy. These experiments appeared to be especially interesting because the analogous silicon compounds were found to undergo such reduction at low temperatures*. However, all attempts to reduce the cyclopolygermanes, both chemically and electrolytically, using a variety of solvent systems at various temperatures from −80° to −125°, were without success.

Studies of both the ESR spectra and electronic spectra of the anion radicals of the cyclopolysilane series indicate that it is reasonable to assume that the ease of reduction is directly proportional to the effectiveness of the overlap of the π-type orbitals on adjacent ring atoms[3]. Thus, if one assumes that $Me_{10}Ge_5$ and $Me_{10}Si_5$ are both nearly planar, then one can conclude that poorer overlap of the orbitals on germanium and thus wider spacing of the molecular energy levels is responsible for the failure of $Me_{10}Ge_5$ and the other cyclopolygermanes to reduce easily. This may be due to the considerably greater radius of germanium as well as the increased diffuseness of the *d* orbitals on germanium.

TABLE 5

MASS SPECTRAL DATA (70 eV) FOR THE PERMETHYLCYCLOPOLYGERMANES

$Me_{10}Ge_5$		$Me_{12}Ge_6$		$Me_{14}Ge_7$	
Ion	% of total	Ion	% of total	Ion	% of total
$Me_{10}Ge_5^+$	12.4	$Me_{12}Ge_6^+$	17.9	$Me_{14}Ge_7^+$	9.5
$Me_9Ge_5^+$	5.5	$Me_{11}Ge_6^+$	10.7	$Me_{13}Ge_7^+$	4.4
$Me_9Ge_4^+$	0.4	$Me_{10}Ge_5^+$	0.8	$Me_{11}Ge_6^+$	10.1
$Me_8Ge_4^+$	2.4	$Me_9Ge_5^+$	11.6	$Me_9CH_2Ge_6^+$	1.4
$Me_7Ge_4^+$	5.2	$Me_7CH_2Ge_5^+$	2.5	$Me_9Ge_5^+$	6.5
$Me_5CH_2Ge_4^+$	3.7	$Me_7Ge_5^+$	0.5	$Me_7CH_2Ge_5^+$	2.9
$Me_5Ge_4^+$	1.1	$Me_7Ge_4^+$	3.0	$Me_7Ge_5^+$	1.0
$Me_3Ge_4^+$	0.4	$Me_5CH_2Ge_4^+$	3.4	$Me_8Ge_4^+$	1.2
$Me_7Ge_3^+$	1.2	$Me_5Ge_4^+$	1.5	$Me_7Ge_4^+$	2.5
$Me_6Ge_3^+$	2.7	$Me_3CH_2Ge_4^+$	1.2	$Me_5CH_2Ge_4^+$	3.0
$Me_5Ge_3^+$	2.0	$Me_3Ge_4^+$	0.9	$Me_5Ge_4^+$	1.6
$Me_3CH_2Ge_3^+$	1.2	$Me_7Ge_3^+$	0.5	$Me_3CH_2Ge_4^+$	1.9
$Me_3Ge_3^+$	1.6	$Me_5CH_2Ge_3^+$	1.4	$Me_3Ge_4^+$	1.3
$MeCH_2Ge_3^+$	1.3	$Me_5Ge_3^+$	2.3	$Me_7Ge_3^+$	0.8
$MeGe_3^+$	0.8	$Me_3CH_2Ge_3^+$	4.4	$Me_5CH_2Ge_3^+$	1.3
$Me_5Ge_2^+$	2.5	$Me_3Ge_3^+$	1.9	Me_5Ge_3	1.9
$Me_4Ge_2H^+$	1.3	$MeCH_2Ge_3^+$	1.7	$Me_3CH_2Ge_3^+$	4.1
$Me_3Ge_2^+$	3.2	$MeGe_3^+$	1.0	$Me_3Ge_3^+$	1.8
$MeGe_2^+$	1.1	$Me_5Ge_2^+$	2.6	$MeCH_2Ge_3^+$	1.8
Me_3Ge^+	45.1	$Me_4HGe_2^+$	1.0	$MeGe_3^+$	1.2
Me_2GeH^+	0.9	$Me_3Ge_2^+$	2.7	$Me_5Ge_2^+$	3.7
Me_2Ge^+	0.4	$MeGe_2^+$	0.9	$Me_4Ge_2H^+$	1.0
$MeGe^+$	3.5	Me_3Ge^+	21.2	$Me_3Ge_2^+$	2.5
		Me_2GeH^+	0.9	$MeGe_2^+$	0.7
		Me_2Ge^+	0.4	Me_3Ge^+	27.6
		$MeGe^+$	3.1	Me_2GeH^+	1.0
				Me_2Ge^+	0.4
				$MeGe^+$	2.6

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* The ESR spectra of the anion radicals of both $Me_{10}Si_5$ and $Me_{12}Si_6$ show that the unpaired electron contacts equally all of the methyl protons and so is delocalized equally over all the silicon atoms in the ring in each case[3].

The 70 eV mass spectral data for $(Me_2Ge)_n$, $n = 5–7$, are shown in Table 5 with the intensities of each germanium-containing ion expressed as a percent of total ion current for all ions. The intensity of each ion includes contributions for all isotope combinations, and each ion has *m/e* values extending over a large number of units. For example, ions containing two germanium atoms are visible over 13 mass units, whereas those with six germanium atoms extend over 25 units. It is thus quite common to observe overlap of ions. The ion intensities were therefore obtained by utilizing selected peaks and normalizing by use of the proportion of the total ion given by the peak selected. For example, the ion $Me_9Ge_5^+$ has total intensity equal to the intensity of the peak at 499 (most intense of the ion) multiplied by 7.7. Any errors introduced by this procedure should be small.

The relative intensities of the peaks constituting the three parent ions were obtained by recording P^+ at 6 eV, to eliminate overlap with $(P-Me)^+$, not produced at this low electron energy, and showed good agreement with the calculated values. For the heptagermane, the resolution at $m/e \sim 700$ permitted only observation of the higher intensity peak of each pair, *i.e.*, 706, 708, etc. The results obtained are shown in Table 6.

TABLE 6

PARENT PEAK REGION MASS SPECTRAL DATA (6 eV) FOR THE PERMETHYLCYCLOPOLYGERMANES

$Me_{10}Ge_5^+$			$Me_{12}Ge_6^+$			$Me_{14}Ge_7^+$		
m/e	Calc.[a]	Obs.[a]	*m/e*	Calc.[a]	Obs.[a]	*m/e*	Calc.[a,b]	Obs.[a,b]
502	0.2	0.2	604	0.2	0.3	706	0.4	0.6
504	0.9	0.9	605	0.1	0.2	708	1.2	1.5
505	0.4	0.4	606	0.8	0.9	710	2.9	3.1
506	2.5	2.4	607	0.5	0.7	712	5.8	6.1
507	1.4	1.4	608	2.1	2.1	714	9.7	9.8
508	5.3	5.4	609	1.4	1.6	716	13.6	13.3
509	3.1	3.3	610	4.3	4.4	718	16.2	15.7
510	9.0	9.0	611	2.9	3.1	720	16.4	15.8
511	5.1	5.2	612	7.2	7.1	722	13.9	13.8
512	12.1	11.8	613	4.8	5.0	724	9.9	10.1
513	6.6	6.7	614	10.0	9.6	726	5.8	5.9
514	13.0	12.8	615	6.3	6.4	728	2.8	3.0
515	6.6	6.8	616	11.4	10.9	730	1.0	1.2
516	11.1	11.0	617	6.8	7.0	732	0.3	0.3
517	5.1	5.2	618	10.7	10.4			
518	7.5	7.5	619	5.9	5.9			
519	2.9	2.9	620	8.2	8.0			
520	3.8	3.8	621	4.1	4.1			
521	1.2	1.2	622	5.1	5.0			
522	1.4	1.4	623	2.2	2.3			
523	0.3	0.2	624	2.5	2.4			
524	0.4	0.3	625	0.9	1.0			
			626	0.9	1.0			
			627	0.3	0.4			
			628	0.2	0.2			

[a] Expressed as percent of total intensity for each parent peak. [b] Odd values could not be accurately measured due to resolution of the instrument.

TABLE 7

METASTABLE-SUPPORTED FRAGMENTATIONS

Process[a]		m^*calc.	m^*obs.
$Me_{10}Ge_5^+$	$\rightarrow Me_9Ge_5^+ + CH_3$	484.4	485
$Me_{12}Ge_6^+$	$\rightarrow Me_{11}Ge_6^+ + CH_3$	586.4	587
$Me_7Ge_4^+$	$\rightarrow Me_5CH_2Ge_4^+ + CH_4$	367.5	367
$Me_7Ge_3^+$	$\rightarrow Me_5CH_2Ge_3^+ + CH_4$	291.8	291

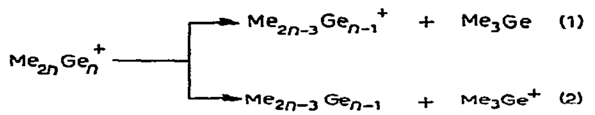
[a] There appear to be numerous other metastables coinciding with the ions themselves and it is very difficult to be completely sure that a metastable is present rather than instrumental effects.

For each germane, the most intense ion was Me_3Ge^+. It was recently suggested[11] that the formation of Ph_3Ge^+ from $(Ph_2Ge)_6$ could occur by thermal decomposition into Ph_4Ge and Ph_6Ge_2 followed by simple bond cleavage of the ions Ph_4Ge^+ and $Ph_6Ge_2^+$. In this study, the absence of the ions, Me_4Ge^+ and $Me_6Ge_2^+$ in the spectra of the polycyclogermanes eliminates this possibility. (For Me_4Ge[12], $Me_3Ge^+/Me_4Ge^+ = 58$). As an added precaution, the spectrum of $Me_{12}Ge_6$ was recorded at ionization chamber temperatures between 50° and 250°. The ratio of the intensities $Me_3Ge^+/Me_{12}Ge_6{}^+$ did not appreciably vary.

Intense ions were given for P^+, $(P-Me)^+$ and $(P-Me_3Ge)^+$. The fragmentation process

$$P^+ \rightarrow (P-CH_3)^+ + CH_3$$

was supported by a metastable peak (Table 7) for the penta- and hexagermane but not for the heptagermane, although the latter undoubtedly occurs. In all three cases, P^+ is more intense than $(P-CH_3)^+$. The $(P-Me_3Ge)^+$ ion shows a greater relative intensity for the hexa- and heptagermanes whereas Me_3Ge^+ has considerably greater intensity from pentagermane. This would indicate that if the elimination of Me_3Ge and Me_3Ge^+ can be represented as



Pathway (2) is more favored for $n = 5$ compared to $n = 6,7$, whereas (1) is more favorable for $n = 6,7$.

A comparison of the ions $Me_{2n-2}Ge_{n-1}$ indicates that an increase in ring size decreases the possibility of Me_2Ge elimination from the parent. Thus the fragmentation

$$(CH_3)_{10}Ge_5^+ \rightarrow (CH_3)_8Ge_4^+ + (CH_3)_2Ge$$

is the only one occurring to any appreciable extent, although no metastable is observed.

An interesting feature is the observation of the ions $Me_9CH_2Ge_6^+$, $Me_7CH_2Ge_5^+$, $Me_5CH_2Ge_4^+$, $Me_3CH_2Ge_3^+$ which arise by elimination of CH_4 from the corresponding $Me_{2n-1}Ge_n^+$, *e.g.*:

$$\mathrm{Me_7Ge_4^+} \rightarrow \mathrm{Me_5CH_2Ge_4^+} + \mathrm{CH_4}$$

Some of these processes are supported by the observation of metastables (Table 7). A general mode of fragmentation appears to be:

$$\begin{tikzcd}
\mathrm{Me_{2n}Ge_n^+} \arrow[r, "-\mathrm{Me}"] \arrow[d, "-\mathrm{Me_3Ge}"'] & \mathrm{Me_{2n-1}Ge_n^+} \arrow[d, "-\mathrm{Me_3GeH}"] \\
\mathrm{Me_{2n-3}Ge_{n-1}^+} \arrow[r, "-\mathrm{CH_4}"] & \mathrm{Me_{2n-5}Ge_{n-1}CH_2^+}
\end{tikzcd}$$

EXPERIMENTAL

Typical preparation of permethylcyclopolygermanes by coupling

Approximately 125 ml of tetrahydrofuran was distilled under argon from lithium aluminum hydride into a 250 ml three-necked flask fitted with a reflux condenser and containing a magnetic stir bar. Lithium dispersion (0.095 g-atom, 1.32 g of 50% dispersion in cyclohexane) was introduced and to this dimethyldichlorogermane (0.043 mole, 7.53 g) was added rapidly with stirring. Heat and the formation of a light colored precipitate gave evidence of reaction. After stirring for 2.5 h the mixture began to exhibit a yellow to light green color which slowly became darker. Periodic gas chromatographic analyses of the mixture showed that the maximum amount of $\mathrm{Me_{12}Ge_6}$ was present after 4 h. The mixture was withdrawn from excess lithium with a large pipet, and several ml of methanol were added to the solution which was then evaporated down to about 30 ml under vacuum. Ether was added to bring the volume up to 100 ml and the solution was washed several times with water and saturated salt solution. The water was extracted with ether, and the combined organic solution was dried over anhydrous potassium carbonate. The solution was evaporated to dryness and sublimed under high vacuum to yield 1.7 g of cyclic products (38% yield). The product was composed of approximately 5% $\mathrm{Me_{10}Ge_5}$, 90% $\mathrm{Me_{12}Ge_6}$, and 5% $\mathrm{Me_{14}Ge_7}$. No polymeric material was obtained. Recrystallization was accomplished by dissolving in the least amount of hot acetone followed by cooling. The crystals of $\mathrm{Me_{12}Ge_6}$ were collected and the mother liquor was evaporated down under vacuum and yielded an oil containing approximately equal amounts of the three cyclic compounds. The cyclopentagermane and cycloheptagermane were then easily isolated by preparative gas chromatography. Separations were routinely carried out on a 20′ × 3/8″ column packed with 20% SE-30 silicone oil on chromosorb W. A helium flow rate of 200 ml/min and oven temperatures from 175–250° gave excellent separation.

Redistribution of polydimethylgermane with naphthalene anion radical

A small crystal of naphthalene was dissolved in 25 ml of tetrahydrofuran distilled under nitrogen from lithium aluminium hydride. Several drops of sodium–potassium alloy (78% potassium) were added, and upon stirring with a magnetic stir bar the dark green color of naphthalene anion radical appeared. Polydimethylgermane (0.5 g) was added in small amounts from a bent tube fitted to the reaction flask. After a two-hour addition, stirring was continued for another 2 h. Filtration and evaporation yielded 0.33 g of cyclic germanium compounds (66 % yield). The crystalline product was made up of about 8 % $Me_{10}Ge_5$, 88 % $Me_{12}Ge_6$ and 4 % $Me_{14}Ge_7$. Only a very small amount (about 1 %) of polydimethylgermane was recovered.

Preparation of decamethylcyclopentagermane by photolysis

Dodecamethylcyclohexagermane (2.0 g) was dissolved in 300 ml of dry cyclohexane. Dry nitrogen was bubbled through the solution for 20 min and photolysis was carried out for 24 h with magnetic stirring. A low-pressure mercury immersion-type lamp with a principle wavelength of 2537 Å was used. Most of the solvent was then removed under vacuum, leaving a concentrated solution which was separated by preparative gas chromatography. Gas chromatographic analysis of the solution indicated a 65 % yield of $Me_{10}Ge_5$, and about 5 % of the original $Me_{12}Ge_6$ remained. A small amount of polydimethylgermane was produced during the reaction.

IR Spectra

IR spectra were examined in the region from 4000 to 250 cm^{-1} using a Perkin–Elmer Model 457 spectrometer. Cesium bromide cells were used. Both Nujol mulls and carbon tetrachloride solutions were used to confirm the peak positions in all regions.

Proton NMR spectra

The proton NMR spectra were determined on a Perkin–Elmer R-20B spectrometer using tetramethylsilane as an internal standard. The methyl proton region for each sample was run at 30 Hz sweep width. Side bands due to ^{13}C–H were determined at 300 Hz sweep width. Sweep time was 200 sec in all cases. All samples were run at 35° at about 10 % (w/v) concentration in carbon tetrachloride.

Electronic spectra

UV spectra of the compounds were determined using a Cary Model 14 recording spectrometer, scanning the region from 360 to 190 nm. Quartz cells of 1 cm width were used with solutions of various known concentrations. Data in Table 4 are for solutions in spectrograde 2,2,4-trimethylpentane.

Attempted anion radical formation

All samples were made up on a vacuum line. Solvents were distilled into sample cells containing the cyclopolygermane and then degassed several times. Electrolytic reductions were carried out in cells constructed of 4 mm Pyrex tubing with platinum wire electrodes. A glass wool frit was used to separate the electrode compartments. O-Ring flanges were used for connection of the cell to the vacuum line and for the separation of the electrode cell area. A viton needle valve allowed removal of the cell from the vacuum line for taking spectra. A 3/1 (v/v) mixture of dimethyl ether/1,2-dimethoxyethane (glyme) was used as a solvent and tetra-n-butylammonium perchlorate, 0.05 *M*, was the supporting electrolyte. Electrolysis of each sample was attempted over a wide range of currents beginning at 0.2 mA and 3.0 V.

Chemical reduction was carried out in cells consisting of 4 mm pyrex tubing joined to an O-ring vacuum fitting and bearing a side arm in which sodium–potassium alloy was placed. After the sample and solvent were added and degassed, the sodium–potassium alloy was distilled as a mirror into the midportion of the sample tube which was then sealed off under vacuum. The solution was allowed to contact the alkali metal in a methylcyclohexane slush (−126°).

The samples were studied by electron spin resonance spectroscopy on a Varian V-4502-13 spectrometer utilizing 100-Kc modulation and a Varian V-4557 variable temperature attachment.

Mass spectra

Mass spectral studies were carried out on a Perkin–Elmer Hitachi Model RMU-6E Single Focusing Spectrometer using both direct and indirect heated inlet systems. The electron energy in volts was measured with a Digitec D.C. voltmeter.

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