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THE REACTION OF ETHYLENE WITH DIGERMANE: ETHYLPOLYGERMANES

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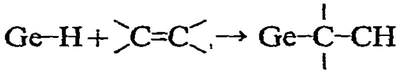
SUMMARY

Ethylene reacts directly with digermane at 120–160° and 5–10 atm pressure to yield not only digermanes, $Et_nGe_2H_{6-n}$, but also monogermanes and trigermanes.

Ethyldigermane and the new compounds 1,1- and 1,2-diethyldigermane, 1,1,2-triethyldigermane and 1- and 2-ethyltrigermane were produced, and identified by infrared and mass spectra.

INTRODUCTION

Although a substantial number of hydrogermation reactions are known[1], the



$$\mathrm{Ge{-}H} + {>}\mathrm{C{=}C}{<} \rightarrow \mathrm{Ge{-}\overset{|}{\underset{|}{C}}{-}CH}$$

majority involve R_3GeH or Cl_3GeH as the germane. No reaction of the parent germanium hydrides has been reported and only a very limited number of reactions with the parent silanes[1,2]. Polygermanes and polysilanes have scarcely been investigated.

In preliminary studies, we found that no reaction took place directly between monogermane, GeH_4, and ethylene under relatively mild conditions of temperature and pressure. Reaction does occur readily at room temperature in the presence of aluminium halides and similar catalysts[3]. We then investigated the uncatalysed reaction between digermane, Ge_2H_6, and ethylene to see whether the Ge–H or the Ge–Ge bond would add across the double bond and seek a route to organodigermanes which retained a number of GeH bonds**. This work follows some preliminary observations by Roebuck[5].

The reaction produces ethylgermanes as well as ethyldigermanes. These were identified using the results of earlier studies on the proton magnetic resonance spectra[6] and infrared spectra[6,7] of ethylgermanes and on the characterisation of ethyldigermane[8].

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** For a preliminary account see ref. 4.

EXPERIMENTAL

Digermane was freed from traces of trigermane by VPC. Commercial ethylene was used after repeated trap to trap distillation: no impurity was detected in the infrared spectrum.

Reaction conditions

Reactions were carried out in sealed Pyrex tubes of 40 ml capacity charged with 1.5 mmole Ge_2H_6 and 4.5 mmole C_2H_4. Batches of six tubes were used in larger scale studies. The oven temperature was constant to $\pm 2°$. After heating, the tubes were opened; very volatile fractions were separated on the vacuum line, and digermane and less volatile products were separated by VPC. Samples were injected as liquids in an inert atmosphere and separated on silicone oil (10% on silica) using hydrogen carrier gas and a cross-section detector with a splitting ratio of 1–10. Fractions were collected in U-traps fitted with Teflon taps. As the detector signal is approximately proportional to the number of electrons in the compound, the relative yields of identified compounds could be calculated from peak areas.

Preliminary runs showed no reaction after 64 h at 107° or 16 h at 110°. Traces of ethylgermanium species were detected after 60 h at 115°. Extensive decomposition to hydrogen and brown solids occurred at 180° but a sample heated for 60 h at 120° yielded ethyldigermane, $EtGe_2H_5$, identical with a sample prepared from Ge_2H_5I[8]. Thus, the useful temperature range was defined as 120–160°.

IR spectra were measured on a Perkin–Elmer 521 spectrometer, PMR spectra in benzene with internal TMS at 60 MHz on a Perkin–Elmer R10 spectrometer and mass spectra on an Atlas CH4 instrument with gas sampling.

RESULTS

The widest range of products was isolated from the reaction of 7.81 mmole Ge_2H_6 and 18.9 mmole C_2H_4 for 65 h at 154° (run 1). When the tubes were opened, only a trace of incondensible gas was present. The fraction volatile at $-95°$ contained GeH_4 and unreacted ethylene ($77 \pm 8\%$ of original). All other products volatile up to 50° at 0.001 mm Hg were chromatographed (Table 1). Relative yields could be calculated on the basis of the identifications discussed below. The known germanes[9] and ethylmonogermanes were identified as indicated in the Table. Recovered Ge_2H_6 was $28 \pm 4\%$ of the original, making the reaction ratio of Ge_2H_6/C_2H_4 approximately 1/1.

Peaks

Peak F. As the parent ethylated digermane, the identification of this compound is important. The mass spectrum showed a parent ion at $m/e = 210$ ($^{76}Ge_2C_4H_{10}^+$) and an identical fragment ion pattern to ethyldigermane[8]. In addition, the retention time, infrared and PMR spectra were identical proving F to be ethyldigermane, $EtGe_2H_5$ (Tables 2 and 3). The yield of F was 0.164 g corresponding to $\sim 16\%$ of the Ge_2H_6 reacted.

Peaks I, J, and K. Of the new compounds, the three most volatile have similar retention times. J and K overlapped on the chromatogram and were collected and

TABLE 1

VAPOUR PHASE CHROMATOGRAM OF PRODUCTS FROM ETHYLENE AND DIGERMANE

Run 1: 65 h at 154°; run 2: 80 h at 160°.

Peak	Relative yield		Relative retention time	Compound	Identification[a]
	Run 1	Run 2			
A	—	—	0.31	N_2	
B	—	—	0.40	$GeH_4+C_2H_4$[b]	IR
C	160	—	0.86	$EtGeH_3$	IR[7], NMR[6]
D	—	—	1.00	Ge_2H_6	IR
E	100	100	2.74	Et_2GeH_2	IR, NMR[6]
F	110	50	3.55	$EtGeH_2GeH_3$	IR, NMR, M[8]
G	25	2.5	4.35	Ge_3H_8	IR[9]
H	10	20	8.56	Et_3GeH	IR[6]
I	15	14	10.71	New compound	IR, M
J	25	33	12.47	New compounds[c]	IR, M, NMR
K	~5		12.78		
L	~0.2	< 0.1	14.3	Iso-Ge_4H_{10}	
M	10	3	15.27	New compound	IR
N	2	1.5	18.65	n-Ge_4H_{10}	IR[9]
O	< 0.1	< 0.1	30.30	Et_4Ge	
P	< 0.1	0.1	33.40		
Q	23	21	38.10	New compound	IR, M
R	7	2	45.00	[c]	IR
S			46.40		
T	< 1	< 0.1	54.50		
U	< 0.1	?	101.80		
V	< 1		109.80		

[a] All known compounds identified by their retention time and by methods shown: IR = infrared spectrum, NMR = proton magnetic resonance spectrum, M = mass spectrum. [b] Traces left in solution after distillation at −95°. [c] Overlapping peaks.

studied together. By comparison with the retention times of Et_nGeH_{4-n} and of $EtGe_2H_5$ these peaks will include the diethyldigermanes.

In each case, the infrared spectrum (Table 2) shows the presence of ethyl groups, and of GeH and GeC bonds. For I, the very low value of 2018 cm^{-1} for one of the GeH stretches is reminiscent of the value 2016 cm^{-1} found for Et_3GeH[6] and is in the region typical of germanes with a single GeH bond[10]. The two components of the GeC stretch and the positions and intensities of the GeH_x deformations for peak I are similar to the spectrum of 1,1-dimethyldigermane[11] while the stronger bands in the spectrum of J plus K resemble those of 1,2-dimethyldigermane[11]. This suggests that I is 1,1-diethyldigermane and J (the major compound of the J+K mixture) is 1,2-diethyldigermane. On a silicone column, branched chain isomers have shorter retention times than straight chain ones for hydrocarbons, silanes[12], and germanes[13] so it is reasonable to find the branched 1,1-isomer more volatile than 1,2-diethyldigermane.

In the mass spectra I shows a maximum value of $m/e = 215$ which fits for $^{76}Ge_2C_4H_{14}^+$ containing one ^2H (or ^{13}C) atom. The spectrum shows the remaining pattern of peaks expected for the $Ge_2C_4H_n^+$ species and major fragment ions Ge_2-

TABLE 2

INFRARED SPECTRA OF ETHYLPOLYGERMANES

$EtGeH_2GeH_3$	I	J+K	M	Q	Assignment
2962 s	2960 s	2960 vs	2960 mw	2960 ms	CH stretches
2920 m	2935 sh	2938 sh	2941 w	2940 sh	
	2915 m	2918 m	2920 w	2917 m	
2885 2879 m	2879 m	2881 m	2880 w	2880 m	
2840 w	2830 w	2832 w		2830 w	2 × CH deformations
2745 vw	2740 vw	2742 vw		2740 vw	
2119 sh	2102 mw	2115 mw	2123 w		
2075 2063 vs	2058 vs 2018 vs	2055 sh 2040 vs	2076 vs 2052 vs	2036 s 2010 s	GeH stretches
2055 sh					
1462 w	1465 mw	1466 mw	1460 vw	1464 w	CH_3 asym. deformations
1425 vw	1430 w	1430 w		1425 w	CH_2 scissors
1308 vw	1386 w	1385 w	1390 vw	1385 w	CH_3 sym. deformation
1220 w	1224 w	1225 mw	1224 vw	1222 w	CH_2 wag
1021 m	1021 m	1023 m	1024 w	1020 mw	"C–C stretch"
970 m	971 m	969 m	971 w	968 mw	CH_3 rock
910 w, sh	901 mw, br			865 m	GeH_3 asym. def.
870 s	870 mw, br	862 w	857 m, br		GeH_2 scissors[a]
	835 w				GeH def.
800 795 s	800 vs	807 m	799 vs		GeH_3 sym. def.
		783 vs	785 sh	770 sh	GeH_2 deformations ?
734 s	740 sh 727 m	735 s	747 mw	745 m, br	CH_2 rock
702 696 s	697 mw	684 s, br	715 w	700 s, br	GeH_2 and other GeH deformations
673 s	670 m		638 s	650 w, br	
640 m, sh	647 mw	645 vs	613 s		
566 m	568 mw 550 sh	553 ms	558 mw	557 m 544 m	Ge–C stretch
455 m	442 w	455 w	460 w		GeH_3 rock
346 w		410 vw			GeH_3 rock

[a] As appropriate.

$C_2H_n^+$, $Ge_2H_n^+$, $GeC_4H_n^+$, $GeC_2H_n^+$ and GeH_n^+. The intensities of the GeC_4 and GeC_2 fragment ions are similar. The mass spectrum of J+K shows a family of peaks between $m/e = 262$ and 238 which correspond to $Ge_3C_2H_n^+$ ions and a ten times more intense group between $m/e = 214$ and 198 corresponding to $Ge_2C_4H_n^+$ ions. It thus seems likely that the larger peak of J on the chromatogram is $Et_2Ge_2H_4$ and the smaller peak K is $EtGe_3H_7$. Among the fragment ions for the mixture, the peaks due to $GeC_4H_n^+$ ions are extremely weak while the $GeC_2H_n^+$ fragment ions are the most intense in the spectrum. Thus I gives equal amounts of GeC_4 and GeC_2 fragments while J gives mainly GeC_2 fragments. While rearrangements during fragmentation are possible, it seems reasonable to conclude that I is $Et_2GeHGeH_3$ giving rise to $EtGe_2$, Ge_2, Et_2Ge and EtGe fragments, while J is $EtGeH_2GeH_2Et$ giving rise to $EtGe_2$, Ge_2 and EtGe fragments but not significantly to Et_2Ge species.

This identification is further supported by the PMR spectra of the J+K sample (available only as a very dilute solution). As K is only about 10% of the total fraction the spectrum is essentially that of J and is shown in Table 3 together with that of ethylgermane[8]. The peak areas are in the ratio GeH/CH = 19/50 which supports the formulation $Et_2Ge_2H_4$ and the position of the GeH resonance indicates an $RGeH_2Ge$ grouping [$\tau(GeH_2) = 6.42$ for methyldigermane[8]]. A very weak signal (intensity relative to above ~4) was observed at τ 6.8 and attributed to K.

TABLE 3

PROTON RESONANCE SPECTRUM OF PEAK J ($1,2\text{-}Et_2Ge_2H_4$)

	$\tau(CH_3)$	$\tau(CH_2)$	$\tau(GeH_2)$	$\tau(GeH_3)$
$C_2H_5Ge_2H_5$	9.03	9.14	6.38	6.85
Peak J	8.93	9.03	6.33	

Peak M. This compound was lost before its mass spectrum could be measured. The infrared spectrum (Table 2) showed ethyl and GeH vibrations and the CH modes were noticeably weaker relative to the GeH modes than for I. The less volatile peak M is therefore tentatively identified as 1-ethyltrigermane and peak K as the branched skeleton isomer 2-ethyltrigermane. This identification is supported by comparing the spectrum of M with the spectra of the 1- and 2-methyltrigermanes which result from a Grignard reaction on the iodination products of trigermane[14]. The spectrum of M resembles that of $1\text{-}MeGe_3H_7$, particularly in showing two strong bands between 650 and 600 cm^{-1} and only one rocking mode between 400 and 500 cm^{-1}. The $2\text{-}MeGe_3H_7$ isomer shows a strong and a weak band between 650 and 600 cm^{-1} and two rocking modes.

Peak Q. The mass spectrum contains the parent ion at $m/e = 242$ ($^{76}Ge_2C_6H_{18}$) showing that Q is a triethyldigermane and there is no indication of fragment ions $(C_2)_3GeH_n^+$. The infrared spectrum does not show the strong absorption near 800 cm^{-1} assigned as a GeH_3 deformation, nor does it show a rock about 450 cm^{-1} which is also characteristic of the presence of a GeH_3 group. Peak Q is therefore tentatively indentified as 1,1,2-triethyldigermane, $Et_2GeHGeH_2Et$.

Other peaks. The remaining compounds were present in too small amounts to be characterised. Peak P may be 1,1,1-triethyldigermane from its retention time: R plus S showed GeH and ethyl vibrations. It is likely that, as none of the retention times correspond to Ge_5H_{12} isomers, most of the peaks from R to V are more highly ethylated digermanes and trigermanes.

Yields

With such small amounts of product, errors in measuring yields are considerable. On the basis of the measured yield of ethyldigermane (16%) and the relative yields in Table 1, the total yield of ethyldigermanes, based on the digermane used is about 28% and a further 40% of the germanium used was recovered as ethylgermanes or as trigermane species. The monogermane removed with the ethylene was estimated from the average molecular weight of the sample to correspond to 13% of the germanium used. The remaining 20% of the digermane used is accounted for by involatile products, and handling losses.

A similar run under slightly more vigorous conditions—160° for 80 h—gave the same compounds A to U. The relative yields are indicated in Table 1, column 2. The proportion of ethyldigermane and of the trigermanes is markedly diminished while 1,1-diethyldigermane and triethylgermane increases. The overall recovery of volatiles was reduced to about 30% and brown solid deposits were found in the tubes. In control reactions run under identical conditions to run 1, $EtGeD_3$ did not react with ethylene nor did GeH_4. Thus Et_2GeH_2 and Et_3GeH do not result from reaction of monogermanes formed by decomposition. Digermane (with argon added to maintain the total pressure) decomposes to a much greater extent in the absence of ethylene, and both GeH_4 and Ge_3H_8 were found among the volatile products. When the digermane and ethylene reaction was run in a tube fitted with glass wool, the products were essentially the same as in run 1 but the total of involatile products rose slightly to 23%.

DISCUSSION

If these identifications are accepted, the results of run 1 may be summarised as in Table 4. ($EtGeH_3 = 100$)

TABLE 4

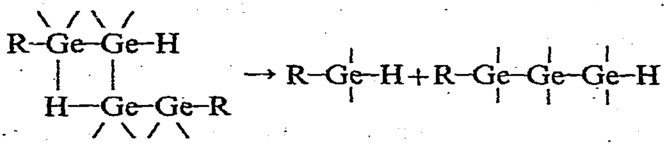
AMOUNTS OF ETHYLGERMANES FORMED IN THE REACTION BETWEEN DIGERMANE AND ETHYLENE

	No Et	Et	Et_2	Et_3	Et_4
Monogermanes		100	40	4	< 1
Digermanes		44	6 (1,1-) 10 (1,2-)	0.1 (1,1,1-) 9 (1,1,2-)	< 1
Trigermanes	10	4 (1-) 2 (2-)	< 1		
Tetragermane	1				

Use of lower temperatures enhances the proportion of ethyldigermane but at the cost of greatly reduced conversion of Ge_2H_6. Use of higher temperatures leads to more decomposition but also appears to enhance the proportion of more highly substituted species. As expected, the proportion of trigermanes drops markedly at higher temperature (run 2).

The control reactions exclude a surface reaction on glass as an important mechanism and show that the ethylmonogermane must arise from digermanes, not by reaction with GeH_4. We may speculate upon possibilities for reaction mechanisms such as radical or bimolecular schemes. Reactions at higher temperatures of silanes and germanes are known to involve radicals (and formation of brown solids) and a radical mechanism can clearly explain all the products. However, very little H_2 was formed at the temperature of run 1.

A bimolecular four-centre intermediate formed between C=C and Ge–H would provide a mechanism for addition. A further such intermediate (or variants of this) would give monogermanes and trigermanes from digermanes (R = Et or H).



While radical reactions almost certainly occur at 180°, we favour the bimolecular path at lower temperatures. Emeléus and Jellinek[15] found that the decomposition of digermane was first order and proceeded by formation of $GeH_3^{\cdot}$ radicals in the range 195–220°. When carried out in the presence of propylene, polymerisation of the latter was induced and propane was formed. At 210–220° about 40% of the germanium appeared as brown solid of composition $GeH_{0.3}$. As we find no solid, no ethane and no polymerisation products of ethylene (at least, no volatile ones) under the conditions of run 1, this is further evidence against a radical mechanism. The appearance of solids in run 2, and in the runs at 180°, suggests that radical mechanisms start to appear at these temperatures under pressure and after extended heating times.

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