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1- AND 2-METHYLTRIGERMANE

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SUMMARY

The reaction of trigermane with iodine at −63°, followed by addition of MeMgI in ether, gives the two monomethyltrigermane isomers. The yield of the 2-methyl isomer $GeH_3GeH(CH_3)GeH_3$ is six times that of 1-methyltrigermane, $GeH_2(CH_3)$-GeH_2GeH_3. The isomers were separated by VPC and characterised by their vapour pressures and by mass, ^1H NMR and vibrational spectroscopy. The effect of reaction temperature is discussed.

INTRODUCTION

A substitution chemistry of digermane has recently been established with routes to halides[1], and organic derivatives[2,3,4], found. For trigermane only a preliminary study is reported[5], in which evidence was produced that reaction with iodine followed by deuteration led to Ge_3H_7D, with substitution probably on the central germanium atom. Halogen derivatives were far too unstable to be isolated. The early studies were restricted as trigermane was available only in very small yields from the acid hydrolysis of magnesium germanide. The development of the efficient borohydride route to monogermane[6], coupled with the silent electric discharge synthesis[7,8], has made trigermane more readily available allowing the fuller study of its reaction with iodine, which is now reported. By reacting the iodinated trigermane with MeMgI at low temperatures, the unstable iodides were converted into the stable, volatile alkyl derivatives which were readily characterised. Of the products when the iodination was carried out at −63°, 78.7% was 2-methyltrigermane, $GeH_3GeHMeGeH_3$ and 12.5% was 1-methyltrigermane, confirming the earlier[5] indication that substitution was mainly on the central germanium atom. Thus reaction[5] (1) is confirmed by step (2).

$$Ge_3H_8 + I_2 \rightarrow Ge_3H_7I + HI \qquad (1)$$

$$Ge_3H_7I + MeMgI \rightarrow Ge_3H_7Me + MgI_2 \qquad (2)$$

Traces of polysubstituted trigermane species were obtained. The characterisation of the monomethyl isomers and the effect of the reaction temperature are reported.

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The only other partly substituted trigermanes are some ethyl derivatives[3], which were side-products from the reaction of ethylene with digermane.

EXPERIMENTAL

Infrared spectra were measured on gas samples using Perkin–Elmer 521 and 457 spectrometers, Raman spectra on liquid samples in a capillary cell using a Cary 81 instrument with helium–neon laser excitation, ^{1}H NMR spectra at 100 MHz on 20% solutions in benzene with a Varian HA 100 spectrometer using internal TMS as standard and the solvent as lock signal, and the mass spectra were run on the Sheffield University M.S.9. Manipulations were carried out on a vacuum line and the products were separated by VPC on a silicone-active phase, using a modified Autoprep 705 with a cross-section detector, as described for previous work[9]. A splitting ratio of 1/10 and a column temperature of 80° were used with hydrogen as the carrier gas. Vapour pressures were measured using a spiral gauge fitted with a Teflon tap.

The trigermane was prepared from germane in a silent electric discharge and purified by VPC[8] and the iodine was twice resublimed. In a representative reaction, trigermane (276 mg, 1.22 mmole) was condensed on to iodine (312 mg, 1.23 mmole) and allowed to warm to $-63°$. Reaction took place over 2 h to leave a pale-greenish liquid. Only a trace of gas incondensible in liquid nitrogen was observed and then hydrogen iodide [134 mg, 1.05 mmole, 85.4% based on eqn. (1)] was removed at $-78°$ and shown to be free of germanes by IR. A twofold excess of MeMgI in diethyl ether was then added against a stream of dry nitrogen to the reaction mixture frozen in liquid nitrogen. After evacuation and warming to $-22°$ two layers were found which reacted completely within 2 min. All volatile products were distilled out into a septum tube and separated by VPC. Apart from the ether, the three main products were trigermane and two less volatile species with relative retention times 1.00, 1.40 and 1.66 and in relative yield 5.5, 100 and 16.4 (evaluated from peak areas). In addition, a number of less volatile products were observed on the chromatogram in trace amounts and these were estimated to total less than 8% of the reaction products. No germanium species of greater volatility than trigermane were observed and the IR spectrum of the ether fraction showed no detectable GeH absorptions. Thus cleavage of Ge–Ge bonds to give mono- or digermanes was negligible.

The weight recovered of the major product (t_R 1.40) was 172 mg which is 58.5% of the yield of monomethyltrigermane calculated on the basis of complete conversion of the trigermane. When the proportional yield of the minor product of t_R 1.66 (also a monomethyltrigermane, see below) is added, the recovery is 68.1% which compares well with the 85.4% of HI when allowance is made for the 10% loss in the detector, and the contribution of the less volatile materials.

In a separate experiment, trigermane was treated directly with an excess of MeMgI at 0°. After 2 h contact, only trigermane and a trace of the product with t_R 1.40 were recorded. Thus direct attack of the Grignard reagent on Ge–H bonds is negligible under the reaction conditions used. It was reported earlier[4] that Ge_2H_5I, isolated by distillation, gave only small yields of dimethyldigermanes when treated with MeMgI under similar conditions.

Thus the yield of trigermane products matches the yield of hydrogen iodide indicating that eqns. (1) and (2) hold but with a minor amount of polysubstitution.

RESULTS

Mass spectra

The major product with t_R 1.40 showed a parent ion with *m/e* 250 corresponding to $^{12}C_1{}^1H_{10}{}^{76}Ge_3^+$. The compound is thus $MeGe_3H_7$. Because there are five germanium isotopes and hydrogen may be lost stepwise, fragment ions fall into overlapping envelopes which cannot readily be analysed to give monoisotopic spectra. Such envelopes were observed for ions $CH_xGe_3^+$ (*m/e* 250 ~ 225, where $x=3$) $H_xGe_3^+$ *m/e* ~ 225 to 210), $CH_xGe_2^+$ and $H_xGe_2^+$ (*m/e* 172 to 140), CH_xGe^+ (*m/e* 94 to 82) and H_xGe^+ (*m/e* 79 to 70). The second product with t_R 1.66 has a very similar mass spectrum with a parent ion at *m/e* 250, again corresponding to a compound $MeGe_3H_7$. Fragment ions were observed as for the major product. The spectra therefore contain the ions expected from compounds of the formula $CH_3Ge_3H_7$, and the envelopes of peaks assigned to the groups of ions $(H_xGe_3)^+$ indicates the presence, in both compounds, of a GeGeGe skeleton.

In addition, the spectrum of the less volatile compound (t_R 1.66) showed extremely weak peaks in the *m/e* ranges 264–250, 186–172 and 108–94, which indicates the presence of about 5% of a compound $C_2H_{12}Ge_3$ of similar retention time. The 2,2-dimethyltrigermane isomer has an almost identical retention time to this monomethyl species[10].

^1H NMR spectra

These two monomethyltrigermanes were identified by their proton NMR spectra shown in Table 1. The signals are approximately first-order with only the GeH_3GeH_2 part of the $MeGeH_2GeH_2GeH_3$ overlapping. The integrated intensities confirm the indicated assignments. The chemical shifts fall in very similar regions to those observed for methyldigermanes[2,4], and for trigermanes[8,3] As $J(HCGeH) \approx J(HGeGeH)$ multiplet signals, like those of the central GeH in $2\text{-}MeGe_3H_7$, are close to a binomial distribution of intensities. The ^1H NMR spectra show that the more volatile isomer, t_R 1.40, is 2-methyltrigermane while the less volatile species, t_R 1.60, is the 1-methyl isomer. The retention time is least for the branched-chain isomer, as for the polymethyldigermanes[4] and for the ethyl analogues[3].

TABLE 1

THE ^1H NMR SPECTRA OF $1\text{-}MeGe_3H_7$ AND $2\text{-}MeGe_3H_7$

Germane	Chemical shifts[a], τ (ppm)				Coupling constants (Hz)	
	CH_3	GeH_3	GeH_xMe	GeH_2	HCGeH	HGeGeH
$GeH_3GeHMeGeH_3$	9.66 d	6.70 d	6.43 m		4.2	3.9
$GeH_3GeH_2GeH_2Me$	9.78 t	6.75 t	6.40 m	6.87 m	4.3	3.3[b]
Ge_3H_8[8]		6.68 t		6.88 m		4.0
$MeGe_2H_5$[2]	9.79 t	6.79 t	6.42 m		4.3	3.9

[a] Measurements in 20% benzene solutions with internal TMS; d = doublet, t = triplet, m = multiplet.
[b] $J(H_2GeGeH_3)$ 3.3 Hz, $J(H_2GeGeH_2) \approx 4$ Hz.

The ^1H NMR spectrum of $1\text{-}MeGe_3H_7$ shows a weak singlet at 9.60 assigned to the methyl resonance of 2,2-$Me_2Ge_3H_6$. The relative intensity indicates about 6% of this impurity, corresponding to the weak signals in the mass spectrum.

Vapour pressures

A limited range of vapour pressures were measured up to room temperature and these fitted the equations:

for 2-methyltrigermane: $\log p\ (\text{mm}) = 6.45 - 1538/T$

for 1-methyltrigermane: $\log p\ (\text{mm}) = 5.69 - 1329/T$

Room temperature values were 15.56 mm at 19.5° for the 2-methyl isomer and 14.32 mm at 20.4° for 1-methyltrigermane. Long extrapolations gave approximate boiling points of 158° and 201° respectively. These compare with the boiling point of 110.8° for trigermane.

Vibrational spectra

The vibrational spectra of the two major products, listed in Table 2, show the characteristic absorptions of methyl groups, together with GeH and GeC stretches.

TABLE 2

VIBRATIONAL SPECTRA OF 1- AND 2-METHYLTRIGERMANE

1-$MeGe_3H_7$		2-$MeGe_3H_7$		Assignment
Infrared (gas)	Raman (liquid)	Infrared (gas)	Raman (liquid)	
2998 w	2985 w	3005 w	2987 w	$\nu_{as}(CH_3)$
2929 w	2920 w	2931 w	2918 w	$\nu_s(CH_3)$
2122 m		2125 m		νGeH
2062 vs	2056 vs (pol.)	2075 vs	2052 vs (pol.)	
		2043 m	2030 m	
1414 w		1423 w		$\delta_{as}(CH_3)$
1390 w		1417 w		
1241 w	1240 w	1243 w	1239 w	$\delta_s(CH_3)$
920–1000 b, m, sh		920–1000 b, m, sh		$\delta(GeH_x)$ and CH_3 rocks
875 s	873 w	879 m	870 m	
	862 w	870 m	860 m	
834 s				
829 s				
800 vs		805 s		
795 sh		798 s	798 w	
760 m		770 vs	776 w	
696 w		716 w		
653 vs, sh				$\delta(GeH_x)$
645 vs		645 vs	643 w	
617 m				
584 s	584 s (pol.)	585 m	586 s (pol.)	ν(GeC)
465 w		462 m		GeH_3 rocks
		410 w		
	286 s		287 s	ν(GeGe) anti
	243 vs (pol.)		241 vs (pol.)	$\nu_s(GeGe)$
	139 s		134 s	Ge_2C bend
	67 s		73 s	Ge_3 bend

The two GeGe stretching frequencies required for a GeGeGe skeleton, and the absence of absorptions corresponding to CH_2 groups, further indicate both compounds are methyltrigermanes.

The modes involving hydrogen are similar to those observed for the various methyldigermanes[2,4], particularly in showing the very strong bending absorption at 800 cm^{-1} characteristic of a GeH_3 group.

The skeletal modes may ke assigned fairly definitely on the basis of Raman polarisation. The GeC stretches compare with the frequency of 588 cm^{-1} found[2] for $MeGe_2H_5$ while the two GeGe stretches are in almost identical positions to those in trigermane[8]. The band near 70 cm^{-1} corresponds to that at 74 cm^{-1} in trigermane and is assigned as the Ge_3 bend leaving the 135 cm^{-1} band to cover the bending modes of the CGeGe angles.

Reaction temperatures

Reactions with iodine were carried out over a range of temperatures with the results shown in Table 3. In all these runs, the yield of hydrogen iodide parallels the recovery of methyltrigermanes.

TABLE 3

EFFECT OF REACTION TEMPERATURE

Temperature of iodination (°C)	Yield of HI (%)	Ratio of 2-methyl- to 1-methyltrigermane
−60 (1 run)	85.4	6.1
−45 (4 runs)	79.0, 80.5, 82.6, 77.5	4.6, 4.5, 4.9, 4.2
−30 (2 runs)	56.5, 60.5	3.1, 2.9
−22 (2 runs)	45.2, 48.1	1.55, 1.6
0 (2 runs)	5, 5	1, 1

All these reactions were carried out using equimolar amounts of iodine and trigermane and were stopped at the disappearance of the iodine colour. Apart from the runs at 0°, all followed a similar, although faster, course to that at −63°, with the reaction complete in about 30 min at −22°. The less-volatile by-products were formed in about the same ratio throughout, but, following the reactions at higher temperatures, the chromatograms showed a number of minor products identified by their retention times as monogermanes and digermanes. They did not however total more than about 6% of the products and did not increase in proportion with the drop in the HI yield. In the −22° runs, particularly, solids were formed in the iodinated layer which did not react appreciably with the Grignard reagent.

The runs at 0° were quite different. The reaction was violent and complete in about two minutes, giving a dark red-orange product mixture mainly consisting of solids. The chromatogram showed a range of mono-, di- and trigermanes but the total recovery of volatiles was very low.

Reactant ratio

In a further reaction at −45° an I_2/Ge_3H_8 ratio of 2/1 was used. The course of the reaction was very similar and yielded unreacted Ge_3H_8, 2-$MeGe_3H_7$ and 1-$MeGe_3H_7$ in the ratio 12/100/24 together with a much larger number of less-volatile compounds but still making up only about 10% of the total product.

DISCUSSION

The side experiments show that yield of methyl derivatives largely reflects the formation of iodotrigermanes in the initial reaction with iodine. At −63° the major reaction is cleavage of Ge-H on the central germanium atom accompanied by about 15% cleavage of terminal Ge–H and a minor amount of polysubstitution: cleavage of Ge–Ge bonds was insignificant. Reaction temperatures up to −22° or the use of more than one equivalent of iodine, do not change the general course of the reaction although substitution of hydrogen becomes more random and the recovery of trigermanes drops to about 50%. Less volatile products, which are probably polymethyltrigermanes, form a fairly constant proportion of the products, as does the unreacted trigermane, suggesting an equilibrium distribution of iodo derivatives. The proportion of volatile cleavage products remains low and the reduced yield of trigermanes seems to be balanced by the formation of solid products which are relatively unreactive towards the Grignard reagent.

At 0°, the reaction is quite changed in character with substantial cleavage and extensive formation of solid products. In this, the reaction resembles that between bromine and digermane at −78° where those hydride molecules attacked are completely reacted to solids, probably $GeBr_4+GeBr_2$.

The spectroscopic characteristics of these new trigermane derivatives ave very similar to those shown by trigermane[8] itself and by methyldigermane[2].

The preferred attack of I_2 on the central atom in $GeH_3GeH_2GeH_3$ is similar, but more pronounced, than the reaction[4] of I_2 with $CH_3GeH_2GeH_3$ which yielded 1,1- and 2,2-dimethyldigermane in the ratio of 2.5 to 1.

The reaction between equimolar quantities of I_2 and Ge_3H_8 at −63° or −45°, followed by addition of MeMgI at low temperatures, provides a good yield of $MeGe_3H_7$ contaminated only by small amounts of trigermane and polymethyltrigermane. The isomer $GeH_3GeHMeGeH_3$ is the major product while the 1-methyl form is never obtained in high yield since the reduced specificity of the iodine attack at higher temperatures is balanced by the reduced yield of trigermanes. The best yield of $MeGeH_2GeH_2GeH_3$ was about 12% at −45°.

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