211. *The Chromatography of Gases and Vapours. Part IX.*[1] *The Preparation of Some Mixed Hexa-alkyldigermanes and the Elucidation of their Isomer Ratios.*

By J. A. SEMLYEN, G. R. WALKER, and C. S. G. PHILLIPS.

A number of mixed hexa-alkyldigermanes have been prepared from germanium tetrachloride by using mixed organometallic reagents. The isomer ratios of several of these compounds have been determined by gas–liquid-chromatographic methods.

TETRA-ALKYL and tetra-aryl derivatives of monogermane are most frequently prepared by the reaction of germanium tetrachloride with a Grignard reagent.[2] Rijkens [3] and Glockling and Hooton [4] have discussed how the normal course of this reaction can be affected by reductive coupling and by steric hindrance. Phenyl-,[4] vinyl-,[5] and ethyl-magnesium bromide [6] react with germanium tetrachloride to give, respectively, 69% (but only in the presence of an excess of magnesium), 25%, and 8% yields of the corresponding digermanes,

---

[1] Part VIII, J. A. Semlyen, G. R. Walker, R. E. Blofeld, and C. S. G. Phillips, *J.*, 1964, 951.
[2] D. Quane and R. S. Bottei, *Chem. Rev.*, 1963, **63**, 403.
[3] F. Rijkens, " Organogermanium Compounds," Germanium Research Committee, 1960.
[4] F. Glockling and K. A. Hooton, *J.*, 1962, 3509.
[5] D. Seyferth, *J. Amer. Chem. Soc.*, 1957, **79**, 2738.
[6] H. Gilman, M. B. Hughes, and C. W. Gerow, *J. Org. Chem.*, 1959, **24**, 352.

in addition to the tetra-substituted monogermanes. This coupling has been interpreted [4] as proceeding primarily through the formation of R_3GeMgX:

$$R_3GeX + Mg \longrightarrow R_3GeMgX$$
$$R_3GeMgX + R_3GeX \longrightarrow Ge_2R_6 + MgX_2$$

As an example of steric hindrance, we cite the unsuccessful attempt to prepare tetraisopropylgermane.[7] In the reaction of isopropylmagnesium bromide with germanium tetrachloride, tri-isopropylgermanium hydride was obtained as the main product.[8] This is thought to be produced by hydrolysis of tri-isopropylgermylmagnesium bromide. Similarly, Glockling and Hooton [4] found that hydrolysis of (o-, m-, or p-$C_6H_4Me)_3GeMgX$ gave the corresponding hydride. Alkyl-lithium reactions also give rise to polygermanes, and Gilman *et al.*[6] obtained an 8% yield of hexaethyldigermane from the reaction of germanium tetrachloride with ethyl-lithium. Disilanes have not been observed in the products of the corresponding Grignard and alkyl-lithium reactions with silicon tetrachloride, although hexaphenyldisilane is formed when chlorotriphenylsilane reacts with a Grignard reagent in tetrahydrofuran.[9]

We have prepared some mixed hexa-alkyldigermanes of general formula $Ge_2Me_xR_{6-x}$ ($R = Et, Pr^n$, or Pr^i), in 7—35% yields, by reaction of germanium tetrachloride with mixed Grignard and mixed alkyl-lithium reagents. Diethyltetramethyl- and tetramethyldi-n-propyl-digermane were isolated from the products of alkyl-lithium reactions, and their isomer ratios were found to be close to the values calculated by assuming a random distribution of alkyl groups. In contrast, isomer ratios of diethyltetramethyl-, triethyltrimethyl-, tetramethyldi-n-propyl-, and di-isopropyl-tetramethyl-digermane, formed by mixed Grignard reactions, were found to differ by factors of four to fourteen from the calculated values. There is evidence for the presence of mixed octa-alkyltrigermanes in the reaction products, and for the formation of di-isopropylmethylgermanium hydride, as well as tri-isopropylgermanium hydride, in the mixed isopropyl–methyl Grignard reaction.

EXPERIMENTAL

Mixed Grignard Reactions.—Six mol. of each Grignard reagent were used per mol. of germanium tetrachloride in the ethyl–methyl and methyl–n-propyl reactions. Two mol. of methylmagnesium iodide and six mol. of isopropylmagnesium bromide were used in the isopropyl–methyl reaction. The mixed alkyl halides, in diethyl ether, were added dropwise, with 10 ml. of germanium tetrachloride, to an excess [4] of magnesium in diethyl ether, under dry nitrogen, with stirring. When addition was complete, the mixture was refluxed for 1 hr. on a water-bath. Dilute hydrochloric acid was then slowly run into the ice-cooled flask. The ether layer was separated and dried (Na_2SO_4), and then distilled at 1 atm. or under reduced pressure. Yields of the mixed germanium compounds were in the range 40—73%. Tetramethylgermane distilled over in the ether fraction and was not recovered.

Mixed Alkyl-lithium Reactions.—Two mol. of methyl-lithium and 4 mol. of either ethyl-lithium or n-propyl-lithium were prepared together in diethyl ether. This solution was slowly added, with stirring, to 10 ml. of germanium tetrachloride (1 mol.) in diethyl ether, under dry nitrogen, at $-10°$. After the addition was complete, the solution was refluxed for $1\frac{1}{2}$ hr., and was then run into an excess of water, cooled in an ice-bath. The ether layer was separated and dried. Distillation gave 30—40% yields of mixed alkyl-mono-, -di-, and -tri-germanes; some polymeric material remained.

Cleavage Reactions of Di- and Tri-germanes.—The germanium–germanium bonds of the liquid di- and tri-germanes were cleaved by means of bromine, which was added dropwise. The reactions proceeded with a sharp crack. The bromine was added until one drop retained its colour. The resulting bromogermanes were analysed by gas chromatography. For isomer determinations, dry diethyl ether was then added and the bromogermanes were converted to

---

[7] H. H. Anderson, *J. Amer. Chem. Soc.*, 1953, **75**, 814.
[8] P. Mazerolles, *Bull. Soc. chim. France*, 1961, 1911.
[9] T. G. Selin and R. West, *Tetrahedron*, 1959, **5**, 97.

tetra-alkylgermanes by the addition of an excess of Grignard reagent. After hydrolysis, drying, and concentrating the ethereal layer, the mixture was analysed by gas chromatography.

Gas-chromatographic Apparatus.—The apparatus is described in Part VIII.[1] Samples were analysed on 3% squalane and 3% Silicone 702 columns at 100°, with Embacel treated with hexamethyldisilazane as the solid support. Retention data were calculated relative to mesitylene ($\log t_R = 2$). The preparative column was 13·5% squalane on treated Embacel at 100°. Compounds were prepared on the 10—100-mg. scale, and their purity was established by gas chromatography.

Infrared Spectra.—Infrared spectra of the tetra-alkylmonogermanes, hexa-alkyldigermanes, octa-alkyltrigermanes, and trialkylgermanium hydrides, separated on the preparative column, were recorded on a Perkin-Elmer 221 infrared spectrophotometer between 2 and 12 μ.

RESULTS AND DISCUSSION

The Mixed Reactions.—A modified Kraus–Flood reaction may be used to prepare mixed tetra-alkylgermanes in 60—70% yields.[1] When a large excess of mixed Grignard reagents, prepared *in situ*, is reacted with germanium tetrachloride in diethyl ether, yields of tetra-alkylgermanes are lower, but those of mixed hexa-alkyldigermanes and octa-alkyltrigermanes are higher. In the methyl–isopropyl reaction there is evidence for the formation of di-isopropylmethyl- and tri-isopropyl-germanium hydrides, with retention times similar to those of hexamethyl- and isopropylpentamethyl-digermane. Glockling and Hooton [4] have isolated corresponding triarylgermanium hydrides. A chromatogram of one of the reaction-product fractions is shown in Fig. 1; there is no trace of a peak corresponding to tetraisopropylgermane.

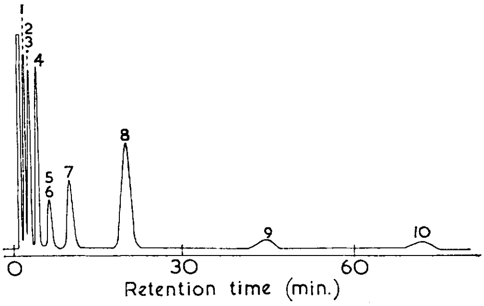

FIG. 1. Chromatogram of an isopropyl–methyl Grignard reaction-product fraction on Silicone 702 at 100°, using a flame-ionisation detector.

1, GeMe$_3$Pr^i; 2 and 3, Ge$_2$Me$_6$ and GeMePr$^i_2$; 4, GeMe$_2$Pr$^i_2$; 5 and 6, Ge$_2$Me$_5$Pr^i and GePr$^i_3$H; 7, GeMePr$^i_3$; 8, Ge$_2$Me$_4$Pr$^i_2$; 9, Ge$_3$Me$_7$Pr^i; 10, Ge$_2$Me$_3$Pr$^i_3$.

Average yields in the Grignard reactions are shown in Fig. 1. Di-isopropyltetramethyldigermane forms well over half the digermane yield in the isopropyl–methyl reaction; in the ethyl–methyl and methyl–n-propyl reactions, relatively more of the other digermanes are produced.

Table 1 also shows the yields in the alkyl-lithium reactions. Larger quantities of catenated products were obtained than in the Grignard reactions; yields of octa-alkyl-

TABLE 1.

Average yields in the mixed reactions.

	Yields of products (mole %)			
Grignard reactions	GeR$_4$	Ge$_2$R$_6$	Ge$_3$R$_8$	GeR$_3$H
Ethyl–methyl	40	7	2	Nil
Methyl–n-propyl	35	10	1	Nil
Isopropyl–methyl	30	35	4	4
Alkyl-lithium reactions				
Ethyl–methyl	18	9	8	Nil
Isopropyl–methyl	20	8	5	Nil

trigermanes were greater and more solid polymeric material remained after distillation. In these reactions, only 2 mol. of methyl-lithium were used per mol. of germanium tetrachloride, for when 4 mol. of methyl-lithium and 4 mol. of ethyl-lithium reacted with 1 mol. of germanium tetrachloride, over 60% of the product consisted of hexamethyldigermane, octamethyltrigermane, and a compound assigned to decamethyltetragermane on the basis of gas-chromatographic evidence. Ethylheptamethyltrigermane was the only other catenated product formed in appreciable quantities.

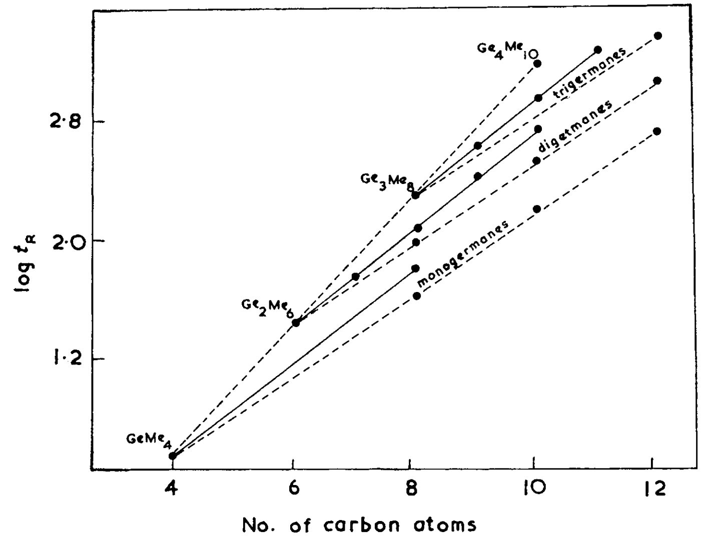

FIG. 2. Retention data for alkyl-mono-, -di-, and -tri-germanes on 3% Silicone 702 at 100°.

———, Ethylmethylgermanes. — — —, Methyl-n-propyl-germanes.

Retention Data for Di- and Tri-germanes.—The values of log t_R for some di- and trigermanes produced in the reactions are listed in Table 2.

Those compounds with isomers showed only single peaks on squalane and on Silicone 702. As with tetra-alkylgermanes, there is an approximately constant increment of log t_R for adjacent members of each homologous series; for both ethylmethyl-digermanes and -trigermanes, it is about 0·33.

The evidence for the nature of the octa-alkyltrigermanes is largely derived from gas chromatography. Fig. 2 shows a plot of log t_R against the number of carbon atoms for some ethylmethyl- and isopropylmethyl-mono-, -di-, and -tri-germanes, and shows the similarity in the retention behaviour of the three series. Decamethyltetragermane is thought to be formed in the alkyl-lithium reactions, and its log t_R value lies on a straight line joining those of tetramethylgermane (found by extrapolation from GeR_4, GeR_3Me, GeR_2Me_2, and $GeRMe_3$), hexamethyldigermane, and octamethyltrigermane.

TABLE 2.

Log t_R values in 3% Silicone 702 at 100°.

Compound	log t_R	Compound	log t_R	Compound	log t_R	Compound	log t_R
Ge_2Me_6	1·43	Ge_2MeEt_5	3·07	$Ge_2Me_2Pr^n{}_4$	3·58	Ge_3Me_7Et	2·63
Ge_2Me_5Et	1·75	Ge_2Et_6	3·45	$Ge_2Me_5Pr^i$	2·00	$Ge_3Me_6Et_2$	2·96
$Ge_2Me_4Et_2$	2·08	$Ge_2Me_5Pr^n$	1·99	$Ge_2Me_4Pr^i{}_2$	2·57	$Ge_3Me_5Et_3$	3·29
$Ge_2Me_3Et_3$	2·42	$Ge_2Me_4Pr^n{}_2$	2·55	$Ge_2Me_3Pr^i{}_3$	3·15		
$Ge_2Me_2Et_4$	2·75	$Ge_2Me_3Pr^n{}_3$	3·08	Ge_3Me_8	2·30		

Confirmation of the Nature of the Products.—Elemental analysis. A number of mono- and di-germanes, separated from the product samples by preparative gas chromatography, were analysed (see Table 3).

TABLE 3.

	Found (%)		Calc. (%)			Found (%)		Calc. (%)	
Formula	C	H	C	H	Formula	C	H	C	H
$GeMe_2Et_2$	44·9	10·0	44·8	10·0	$GeMe_2Pr^n{}_2$	51·2	10·9	51·0	10·6
$GeMeEt_3$	48·3	10·4	48·1	10·4	$GeMePr^n{}_3$	54·9	11·2	55·3	11·2
$GeEt_4$	50·9	10·8	50·6	10·7	$GeMe_3Pr^i$	45·1	9·9	44·9	10·0
Ge_2Me_5Et	33·3	8·0	33·7	8·1	$GeMe_2Pr^i{}_2$	51·1	10·5	51·0	10·7
$Ge_2Me_4Et_2$	36·8	8·3	36·5	8·4	$Ge_2Me_4Pr^i{}_2$	41·0	9·1	41·2	9·0
$Ge_2Me_3Et_3$	39·6	8·8	39·0	8·7					

Infrared spectroscopy. The spectra of the following compounds were measured (alkyl germanes in CCl_4 solution; mixtures of alkylgermanes and alkylgermanium hydride in CCl_4 and in heptane solution). Ethyl–methyl reactions: $GeMe_3Et$; $GeMe_2Et_2$; $GeMeEt_3$; $GeEt_4$; Ge_2Me_6; Ge_2Me_5Et; $Ge_2Me_4Et_2$; $Ge_2Me_3Et_3$; Ge_3Me_8; Ge_3Me_7Et. Methyl n-propyl reactions: $GeMe_3Pr^n$; $GeMe_2Pr^n{}_2$; $GeMePr^n{}_3$; $GePr^n{}_4$; Ge_2Me_6; $Ge_2Me_5Pr^n$; $Ge_2Me_4Pr^n{}_2$; Ge_3Me_8. Isopropyl–methyl Grignard reactions: $GeMe_3Pr^i$; $GeMe_2Pr^i{}_2$; $GeMePr^i{}_3$; Ge_2Me_6 and $GeMePr^i{}_2H$; $Ge_2Me_5Pr^i$ and $GePr_3{}^iH$; $Ge_2Me_4Pr^i{}_2$.

The spectra of the compounds were in agreement with those expected for alkyl-mono-, -di-, and -tri-germanes. Spectra of ten of the compounds have been published.[10,11] Leites *et al.*[10] discussed the spectra of a number of mixed tetra-alkylgermanes; they listed bands characteristic of methyl, ethyl, and n-propyl groups in these compounds. Confirmation of the nature of the mixed di- and tri-germanes was obtained by noting the presence or absence of these characteristic bands and by comparing their relative intensities. Some of the compounds had very similar spectra (*e.g.*, diethyldimethylgermane and triethyltrimethyldigermane; hexamethyldigermane and octamethyltrigermane).

Strong Ge–H stretching bands at 2003 and 1989 cm.$^{-1}$ indicated the possible presence of di-isopropylmethyl- and tri-isopropyl-germanium hydrides in the hexamethyl- and isopropylpentamethyl-digermane samples from the methyl–isopropyl Grignard reaction product. The Ge–H stretching band of tri-isopropylgermanium hydride is known to lie at 1989 cm.$^{-1}$, while that of di-isopropylmethylgermanium hydride was estimated, from the values for tri-isopropylgermanium hydride and trimethylgermanium hydride (2031 cm.$^{-1}$),[11] as being at *ca.* 2003 cm.$^{-1}$.

Other reactions. A Grignard reaction between silicon tetrachloride, germanium tetrachloride, and methylmagnesium iodide produced a 6% yield of hexamethyldigermane: no trace of trimethyltrimethylsilylgermane was found in the product. Hexaethyldigermane was prepared from germanium tetrachloride by Grignard and alkyl-lithium reactions, in 5—15% yields. The retention times of these hexa-alkyldigermanes were in agreement with those found from mixed reaction chromatograms.

A mixed allyl–methyl Grignard reaction gave mono- and di-germanes in yields comparable with those from the corresponding methyl–n-propyl reaction. The more-volatile compounds were isolated by preparative gas chromatography, and their nature was confirmed by infrared spectroscopy. The allylmethylmonogermanes were synthesised independently from tetra-alkylgermane by the reaction of methylmagnesium iodide on the products of the two reactions:

$$Ge(C_3H_5)_4 + GeI_4 \longrightarrow Ge(C_3H_5)_xI_{4-x}$$

$$Ge(C_3H_5)_4 + I_2 \longrightarrow Ge(C_3H_5)_xI_{4-x} + C_3H_5I$$

[10] L. A. Leites, Yu. P. Egorov, G. Ya. Zueva, and V. A. Ponomarenko, *Izvest. Akad. Nauk. S.S.S.R., Otdel. khim. Nauk*, 1961, 2132.

[11] R. Mathis-Noël, F. Mathis, and J. Satgé, *Bull. soc. chim. France*, 1961, 676.

Chemical evidence. The germanium–germanium bond is quantitatively cleaved by bromine.[12] We found that mixed hexa-alkyldigermanes gave trialkylbromogermanes only. Thus, ethyl- or n-propylpentamethyldigermane gave bromotrimethylgermane and ethyl- or n-propyl-bromodimethylgermane in the approximate ratio 1 : 1. Similarly, octamethyltrigermane gave bromotrimethyl- and dibromodimethyl-germane in the ratio 2 : 1.

With mixtures of polygermanes, more-accurate results were obtained by converting the mixture of bromogermanes to tetra-alkyl derivatives having known retention times; [1] n-butylmagnesium chloride was normally used, but n-propylmagnesium bromide served as a useful alternative when there was a possibility of peak overlap. Thus, in the isopropyl–methyl reaction, preparative gas chromatography gave two samples, though to be (hexamethyldigermane plus di-isopropylmethylgermanium hydride) and (isopropylpentamethyldigermane plus tri-isopropylgermanium hydride). The presence of the digermanes was demonstrated by converting them into trimethyl-n-propylgermane and (trimethyl-n-propyl- plus isopropyldimethyl-n-propylgermane), respectively, by using bromine and n-propylmagnesium bromide. Control experiments showed that the reactions with n-butylmagnesium chloride gave rise to a small quantity of a volatile by-product with a retention time close to that of n-butyltrimethylgermane. For this reason, the peak-areas of the latter compound could only be estimated approximately.

The cleavage reactions also provided evidence for the presence of tri- and possibly higher germanes. For example, a high-boiling fraction from an ethyl–methyl Grignard reaction was completely converted into GeR_3Bu^n and $GeR_2Bu_2{}^n$ by means of bromine and n-butylmagnesium chloride. The fraction contained: $Ge_2Me_4Et_2$; $Ge_2Me_3Et_3$; $Ge_2Me_2Et_4$; Ge_2MeEt_5; Ge_3Me_7Et; $Ge_3Me_6Et_2$; and $Ge_3Me_5Et_3$. The yields (mole %) of tetra-alkylgermanes produced were: $GeMe_3Bu^n$ (6%); $GeMe_2EtBu^n$ (34%); $GeMeEt_2Bu^n$ (27%); $GeEt_3Bu^n$ (4%); $GeMe_2Bu_2{}^n$ (6%); $GeMeEtBu_2{}^n$ (21%); and $GeEt_2Bu_2{}^n$ (2%). Similar results were obtained with methyl–n-propyl and isopropyl–methyl product-fractions.

Determination of Isomer Ratios of Mixed Hexa-alkyldigermanes.—Two isomeric forms can be written for each of the digermanes $Ge_2Me_4R_2$, $Ge_2Me_3R_3$, (and $Ge_2Me_2R_4$). If the compounds are formed by a random mixing of alkyl groups in the reactions, then the ratios of the isomers would be:

$$Me_2RGe{-}GeMe_2R : Me_3Ge{-}GeMeR_2 = 3 : 2; \quad Me_2RGe{-}GeMeR_2 : Me_3Ge{-}GeR_3 = 9 : 1.$$

Isomer ratios were determined for diethyl- and di-n-propyltetramethyldigermane, formed in the alkyl-lithium reactions, by bromine cleavage and reaction with n-butylmagnesium chloride, to give three tetra-alkylgermanes. The isomer ratios were close to 1·5 : 1 in each case. This is in agreement with the calculated value. The compound assigned to ethylheptamethyltrigermane was also isolated from an alkyl-lithium reaction-product, cleaved with bromine, and reacted with n-butylmagnesium chloride. Four products were obtained: $GeMe_3Bu^n$; $GeMe_2EtBu^n$; $GeMe_2Bu_2{}^n$; and $GeMeEtBu_2{}^n$; the last three were in the ratio 2·8 : 3·0 : 1. This is evidence that the compound is, in fact, ethylheptamethyltrigermane, and a ratio of about 3 : 1 is indicated for its isomers $Me_2EtGe{-}GeMe_2{-}GeMe_3$ and $Me_3Ge{-}GeMeEt{-}GeMe_3$. This is the ratio expected, assuming a random distribution of alkyl groups.

TABLE 4.

Isomer ratios of hexa-alkyldigermanes produced by mixed Grignard reactions.

$Ge_2Me_4Et_2$	$RMe_2Ge{-}GeMe_2R : Me_3Ge{-}GeMeR_2$	= 6 : 1
$Ge_2Me_4Pr^n{}_2$	,,	= 9 : 1
$Ge_2Me_4Pr^i{}_2$	,,	= 20 : 1
$Ge_2Me_3Et_3$	$R_2MeGe{-}GeMe_2R : Me_3Ge{-}GeR_3$	= 90 : 1

---

[12] C. A. Kraus and E. A. Flood, *J. Amer. Chem. Soc.*, 1932, **54**, 1635.

Isomer ratios were determined for diethyltetramethyl-, triethyltrimethyl-, tetramethyldi-n-propyl, and di-isopropyltetramethyl-digermane, produced by the mixed Grignard reactions. A typical isomer-ratio determination is illustrated in Fig. 3. The results are shown in Table 4. At least two determinations were carried out for each isomer, and agreement to within 10% was obtained. Different Grignard reactions carried out under the same conditions produced the same isomer distributions.

The results contrast with those obtained for digermanes formed by the alkyl-lithium reactions. The deviations from random isomer-distributions in the products of Grignard reactions may be due to steric effects, for they increase considerably from ethyl to n-propyl to isopropyl in the $Ge_2Me_4R_2$ series. Thus, the isomer with one large alkyl group on each germanium atom is preferred to that with both on the same atom. As would be expected if steric factors were operating,[4] there is relatively even less of the isomer with three ethyl groups on the same germanium atom in triethyltrimethyldigermane. The formation of di-isopropylmethylgermanium hydride as well as tri-isopropylgermanium hydride in the isopropyl–methyl reaction, although no hydrides are produced in the ethyl–methyl and methyl–n-propyl Grignard reactions, may be another indication of the much greater steric effect of the isopropyl group relative to the ethyl and n-propyl groups.

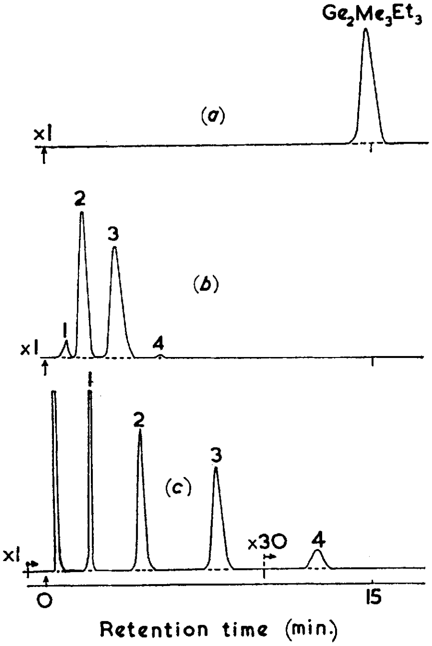

FIG. 3. Determination of the position isomers of triethyltrimethyldigermane, prepared by a mixed Grignard reaction.

(*a*) Digermane sample. (*b*) Cleavage with bromine: 1, $GeMe_3Br$; 2, $GeMe_2EtBr$; 3, $GeMeEt_2Br$; 4, $GeEt_3Br$. (*c*) Reaction with n-butyl magnesium chloride: 1, $GeMe_3Bu^n$; 2, $GeMe_2EtBu^n$; 3, $GeMeEt_2Bu^n$; 4, $GeEt_3Bu^n$.

We are indebted to the Salters' Company for a scholarship (to J. A. S.). We thank Imperial Chemical Industries Limited for the loan of a recorder, and the Germanium Center and Midland Silicones Limited for financial assistance.

INORGANIC CHEMISTRY LABORATORY, THE UNIVERSITY, OXFORD.
[Present address (J. A. S.): DEPARTMENT OF CHEMISTRY,
STANFORD UNIVERSITY, CALIFORNIA, U.S.A.]

[*Received, July* 23*rd*, 1964.]