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Abstract

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ALKYLGERMANIUM HYDRIDES AND ALKYLGERMANIUM DEUTERIDES

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Since the discovery of germanium by Winkler in 1886, and also since his synthesis of the first germanium hydride $HGeCl_3$ (1), up to the present time a comparatively small number of inorganic and organic germanium hydrides has been obtained.* As for germanium deuterides, the first representatives of this class of compounds** were obtained only in 1954; however, among them there is not a single organic germanium deuteride.

At the same time, germanium hydrides and deuterides are of considerable interest from the standpoint of developing new methods for preparing organogermanium compounds and studying the chemical and physical characteristics of the Ge—H and Ge—D bonds (in comparison with C—H and C—D, Si—H and Si—D bonds, as well as M—H and M—D bonds in hydrides of various elements).

From the chemical standpoint, it seemed of interest to study the possibility of broad use of lithium hydride and deuteride for the synthesis of the indicated organogermanium compounds,*** which had not been studied prior to our work.

From the standpoint of the physical properties of the Ge—H and Ge—D bonds, we were interested in the change in the vibrational frequencies of these bonds as they accumulate at the germanium atom.

In addition to the above, it was necessary to determine, at least with a certain approximation, the refractions of the Ge—H and Ge—D bonds, data on which are absent in the literature.

The present work describes the preparation and properties of the following organic germanium hydrides and deuterides:

1. $CH_3GeH_3 \rightarrow (CH_3)_2GeH_2 \rightarrow (CH_3)_3GeH$.
2. $CH_3GeD_3 \rightarrow (CH_3)_2GeD_2 \rightarrow (CH_3)_3GeD$.
3. $C_2H_5GeH_3 \rightarrow (C_2H_5)_2GeH_2 \rightarrow (CH_3)_2(C_2H_5)GeH$.
4. $C_2H_5GeD_3 \rightarrow (C_2H_5)_2GeD_2 \rightarrow (CH_3)_2(C_2H_5)GeD$.

All of them were obtained in fairly good yield under conditions analogous to those for obtaining alkylsilane hydrides and deuterides (6), from the corresponding alkylgermanium chlorides (bromides), LiH and LiD. The physical properties of the compounds obtained are presented in Table 1. From the data of Table 1 it follows that the refraction of the Ge–H bond should be taken as, on average, about 3.38 ml/mole, and the refraction of the Ge–D bond as 3.34 ml/mole.

In preparing the starting $(CH_3)_2(C_2H_5)GeCl$ and $(C_2H_5)_2GeCl_2$ by the organomagnesium method using C_2H_5MgBr, we, as in the case of $(CH_3)_2GeCl_2$ and CH_3MgBr (8), observed the reaction of exchange of chlorine for bromine. The yield of bromides under these conditions was sufficiently high. All these facts

Table 1

Compound no.	Formula	B.p., °C/mm Hg	d_4^{20}	n_D^{20}	*MR* found	Refraction of GeH and GeD bonds
I	CH_3GeH_3	−23.5/745	–	–	–	–
II	CH_3GeD_3	−23.5/752	–	–	–	–
III	$(CH_3)_2GeH_2$	6.5/744	–	–	–	–
IV	$(CH_3)_2GeD_2$	6.5/745	–	–	–	–
V	$(CH_3)_3GeH$	26/755.5	1.0128	1.3890	27.72	3.36
VI	$(CH_3)_3GeD$	26/758.5	1.0207	1.3893	27.76	3.40
VII	$C_2H_5GeH_3$	11.5/743.5	–	–	–	–
VIII	$C_2H_5GeD_3$	11.3/748.5	–	–	–	–
IX	$(C_2H_5)_2GeH_2$	72.5/740.5	1.0378	1.4208	32.42	3.46
X	$(C_2H_5)_2GeD_2$	71.5/743.5	1.0525	1.4200	32.39	3.45
XI	$(CH_3)_2(C_2H_5)GeH$	62/755.5	1.0158	1.4090	32.31	3.32
XII	$(CH_3)_2(C_2H_5)GeD$	60/737.4	1.0262	1.4083	32.17	3.18

make it possible to conclude that chlorine atoms at Ge have an enhanced ability (as compared with analogous silicon compounds) to be exchanged for bromine atoms under the conditions of the Grignard reaction.

The fundamental possibility of applying the Kharasch reaction to hydrogermanes was shown by Fischer, West, and Rochow (9) in 1954.

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* At the present time only 13 inorganic and 17 organic germanium hydrides are known, the majority of which are described in a review (2).

** GeD_4 (3), Ge_2D_6 (3), Ge_3D_8 (3), GeD_3H (4), GeD_3Cl (5), $GeDH_3$ (4).

*** The fundamental possibility of obtaining germanium hydrides with the aid of $LiAlH_4$ was first shown in 1947 by Finholt, Bond, Wilzbach, and Schlesinger (7).

$$Cl_3Ge-H+CH_2{=}CHCH_2CH_2CH_3 \xrightarrow[62\text{–}64°,\ 35\ h]{Bz_2O_2} Cl_3GeCH_2CH_2CH_2CH_2CH_3.$$

In the presence of benzoyl peroxide, $HGeCl_3$ and $(C_6H_5)_3GeH$ can add to a number of other unsaturated compounds as well ([10,11]).

By analogy with hydrosilanes ([12]), in the present work, using trichlorogermane* and ethylene as examples, we have shown the possibility of using chloroplatinic acid for this purpose; in its presence the reaction begins at room temperature and proceeds at a high rate.

In conclusion we shall discuss the Raman spectra of the alkylgermane hydrides and deuterides considered above.

The literature gives data on the infrared absorption spectra of compounds of the type D_nGeH_{4-n} ([13]), and also on the Raman spectra of a number of other organogermanium compounds ([14]). Both these data and earlier work by one of us ([15]), as well as the Raman spectra of light for compounds VII–XII given below, make it possible to note the following:

1. $C_2H_5GeH_3$ (VII), ν (cm^{-1}): 170 (1), 239 (0), 347 (0), 522 (6), 616 (4), 780 (0), 828 (3), 882 (4 sh), 974 (1), 1025 (1), 1220 (4), 1465 (0), 2062 (10), 2871 (6), 2917 (7 r), 2925 (2), 2950 (2).
2. $C_2H_5GeD_3$ (VIII), ν (cm^{-1}): 161 (0), 232 (1), 425 (3), 583 (7), 600 (4), 632 (3), 683 (1), 799 (0), 818 (0), 965 (1), 1024 (1), 1103 (0), 1167 (1), 1221 (2), 1460 (0), 1475 (10), 2870 (7), 2915 (6 sh), 2945 (2).
3. $(C_2H_5)_2GeH_2$ (IX), ν (cm^{-1}): 170 (1), 287 (2), 545 (5), 686 (0), 800 (0), 870 (3 sh), 966 (1), 1023 (1), 1221 (4), 1422 (0), 1460 (1), 2032 (10), 2870 (9), 2909 (10), 2928 (4), 2946 (3).
4. $(C_2H_5)_2GeD_2$ (X), ν (cm^{-1}): 172 (1), 227 (0), 278 (3), 296 (0), 459 (0), 474 (4 sh), 511 (4), 578 (8), 593 (4), 624 (3), 968 (3 sh), 1023 (3 sh), 1222 (7), 1401 (0), 1461 (10 sh), 2870 (7), 2910 (8), 2927 (4 r), 2948 (4 r).
5. $(CH_3)_2(C_2H_5)GeH$ (XI), ν (cm^{-1}): 164 (3), 185 (4), 286 (3), 554 (9), 586 (5), 624 (3), 847 (0), 969 (1), 1021 (1), 1106 (0), 1220 (3), 1240 (4), 1422 (1), 1468 (1), 2021 (5), 2871 (4), 2904 (8), 2925 (2), 2975 (3 sh).
6. $(CH_3)_2(C_2H_5)GeD$ (XII), ν (cm^{-1}): 170 (1), 198 (1), 282 (2), 493 (4 sh), 568 (10), 599 (6 sh), 704 (0), 833 (0), 968 (1), 1024 (2), 1112 (2), 1220 (3), 1242 (4), 1405 (1), 1455 (7 sh), 2870 (5), 2908 (8), 2915 (2), 2976 (3).

* $HGeCl_3$ containing an admixture of $GeCl_4$ was used in the reaction.

From the work on silane hydrides and deuterides ([6,16]) it is known that accumulation of H (or D) atoms at the Si atom in compounds of the type $R_{nSiH_{4-n}}$ or $R_{nSiD_{4-n}}$ (R—aliphatic radical) causes a successive increase in the vibrational frequencies of Si—H and Si—D.

Comparison of the spectral data presented above with the data of works (^{6,16}) makes it possible to note the same character of the change in the frequencies of the stretching vibrations Ge–H and Ge–D, namely: ν(Ge—H) in the group $\equiv$ Ge—H is equal to 2020 cm^{-1}, $=$ GeH$_2$ 2030 cm^{-1}, $-$GeH$_3$ 2062 cm^{-1}, and GeH$_4$ 2110 cm^{-1} (average value between the symmetric and degenerate frequencies). For germanium deuterides these frequencies are, respectively, 1455, 1460, 1475, 1513 cm^{-1}. The difference between the frequencies ν(Ge—D) and ν(Si—D) consists in the fact that in germanium deuterides of the type $-$GeD$_3$ and $=$ GeD$_2$ only one line is observed, whereas in silane deuterides of the type $-$SiD$_3$ and $=$ SiD$_2$ there are two. This may indicate a further weakening of the interaction of the Ge–D bonds with one another. Apparently, changes in the magnitudes of the stretching-vibration frequencies Ge–H and Ge–D, as well as C–H, C–D, Si–H and Si–D, can be associated not only with mass, but also with the nature (chiefly, evidently, the magnitude of the electronegativity) of the atoms and groups attached to the central element.

From examination of the same spectra it is also possible to establish, in agreement with works (^{13,17}), the characteristic frequencies of methyl and ethyl groups bonded to Ge. For the CH$_3$ group these are the deformation frequency 1240 cm^{-1} and the stretching-vibration frequencies ν(C—H) 2904 and 2975 cm^{-1}; for the C$_2$H$_5$ group, respectively, 1220 cm^{-1}* and ν(C—C), in the ethyl chain, 965 and 1024 cm^{-1}. Deformation frequencies of the type δ(H—Ge—H) and δ(D—Ge—D) are located, according to the literature data (^{13}), in the regions 900 and 600-650 cm^{-1}, respectively. In our case, the lines 882 and 870 cm^{-1} (respectively ν (VII) and (IX)) belong to the frequencies δ(H—Ge—H), and two lines belong to the frequencies δ(D—Ge—D): 600 and 632 cm^{-1} (VIII), 593 and 624 cm^{-1} (X).

Experimental Part

The reduction of alkylgermanium chlorides (bromides) was carried out in the still pot of a rectifying column. The reaction products were withdrawn periodically and then redistilled on the same column. LiH and LiD were carefully ground before the experiment in a ball mill.

(I) was obtained in an amount of 4.5 g (50% of theory) from 34 g of CH$_3$GeBr$_3$ (b.p. 168°) and 6 g of LiH in 50 ml of dioxane.

(II) was obtained in an amount of 4.9 g (52%) from 33 g of CH$_3$GeBr$_3$ and 7 g of LiD in 45 ml of dioxane.

(III) was isolated in an amount of 11.2 g (99%) from 28 g of (CH$_3$)$_2$GeBr$_2$ (b.p. 153°) and 4 g of LiH in 50 ml of dioxane.

(IV) was obtained in an amount of 7.1 g (67%) from 26 g of (CH$_3$)$_2$GeBr$_2$ and 4 g of LiD in 50 ml of dioxane.

(V) was obtained in an amount of 6.5 g (72%) from 11 g of (CH$_3$)$_3$GeCl (b.p. 98°) and 3 g of LiH in 50 ml of dioxane.

(VI) was obtained in an amount of 4.5 g (70%) from 8 g of $(CH_3)_3GeCl$ and 3 g of LiD in 50 ml of dioxane.

(VII) was obtained in an amount of 5.6 g (54%) from 21 g of $C_2H_5GeCl_3$ (b.p. 141°) and 5 g of LiH in 50 ml of dioxane.

(VIII) was obtained in an amount of 6 g (56%) from 21 g of $C_2H_5GeCl_3$ and 7 g of LiD in 50 ml of dioxane.

(IX) was obtained in an amount of 7 g from 33 g of a mixture of $(C_2H_5)_2GeCl_2$ (b.p. 169°) and $(C_2H_5)_2GeBr_2$ (b.p. 201°) in 50 ml of dibutyl ether. For the reduction, a mixture of dichloride and dibromide was taken, obtained in the reaction of 104 g of $C_2H_5GeCl_3$ with C_2H_5MgBr (60 g of C_2H_5Br and 12 g of Mg) in 500 ml of ether and

* In chlorides (^{14}) 1228 cm^{-1}.

previously distilled under vacuum and on a column.

Found, %: C 36.13; 36.38; H 9.89; 9.21
$C_4H_{12}Ge$. Calculated, %: C 36.19; H 9.11

(X) was obtained in an amount of 10 g from 50 g of a mixture of $(C_2H_5)_2GeCl_2$ and $(C_2H_5)_2GeBr_2$ in 40 ml of dibutyl ether.

Found, %: C 36.35; 36.37; H + D 9.06; 9.17; Ge 53.88; 54.26
$C_4H_{10}D_2Ge$. Calculated, %: C 35.65; H + D 10.47; Ge 53.88

(XI) was obtained in an amount of 6 g from 39 g of a mixture of $(CH_3)_2Ge(Cl)(C_2H_5)$ (b.p. 125°) and $(CH_3)_2(C_2H_5)GeBr$ (b.p. 143°/755 mm, d_4^{20} 1.4952, n_D^{20} 1.4726) in 50 ml of dioxane.

Found, %: C 36.26; 36.48; H 8.19; 8.99
$C_4H_{12}Ge$. Calculated, %: C 36.19; H 9.11

Dimethylethylchloro- and bromogermanes were obtained in an amount of 16 g each by reacting 180 g of $(CH_3)_2GeCl_2$ (two experiments) with C_2H_5MgBr in 1 liter of ether. After separation of the precipitate, the ether was distilled off, and the residue was distilled under vacuum and on a column. In addition to the products indicated above, $(CH_3)_2GeBr_2$ (36 g)—b.p. 153°/755 mm—was obtained. As analysis showed, $(C_2H_5)(CH_3)_2GeCl$ contained the starting dimethyldichlorogermane. Analysis of $(C_2H_5)(CH_3)_2GeBr$ gave the following results:

Found, %: C 22.88; 22.71; H 5.15; 5.25; Br 37.43; 37.72; Ge 33.80; 33.74
$C_4H_{11}BrGeGe$. Calculated, %: C 22.70; H 5.24; Br 37.76; Ge 34.30

(XII) was obtained in an amount of 4 g from 42.9 g of a mixture of $C_2H_5(CH_3)_2GeCl$ and $C_2H_5(CH_3)_2GeBr$ and 6 g of LiD in 50 ml of dibutyl ether.

Found, %:	C 36.35;	36.45;	H + D 9.37;	9.24;	Ge 54.74
$C_4H_{11}DGe$. Calculated, %:	C 35.92;	H + D 9.80;	Ge 54.28		

$C_2H_5GeCl_3$ (XIII) was obtained as follows. 52.6 g of a mixture of $HGeCl_3$ and $GeCl_4$, obtained by the interaction of Ge with HCl at 700° and previously distilled under vacuum, and 1 ml of a 0.1 M solution of $H_2PtCl_3 \cdot 6H_2O$ in n-C_3H_7OH, were charged into an autoclave of 200 ml capacity. When ethylene (40 atm) was introduced, the reaction began immediately and was accompanied by considerable heat evolution (60—80°). In all, 35 atm of ethylene was absorbed. After distillation of the thickened reaction products under vacuum (78—80° at 110 mm Hg), and then on a column, there were isolated: 1) 5.5 g of $GeCl_4$—b.p. 82°/763.5 mm; 2) 15 g of $C_2H_5GeCl_3$—b.p. 139°/763.5 mm, d_4^{20} 1.6006, n_D^{20} 1.4730.

The considerable amount of residue (26 g) from the distillations, as well as the thickening of the reaction products, indicates possible decomposition of $HGeCl_3$ under the experimental conditions.

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