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N. G. DZHURINSKAYA, V. F. MIRONOV

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Abstract

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N. G. DZHURINSKAYA, V. F. MIRONOV
and Corresponding Member of the Academy of Sciences of the USSR
A. D. PETROV

ADDITION OF GERMANIUM HYDRIDES TO UNSATURATED COMPOUNDS

In previous papers (^{1,2}) we established for the first time that $HGeCl_3$ readily adds, without any activation and without catalysts, to practically any unsaturated compounds

$$Cl_3GeH + \;\; >C=C< \quad Cl_3GeC-CH.$$

We therefore came to the conclusion that $HGeCl_3$ is more reactive in this reaction than $HSiCl_3$, whose addition takes place only in the presence of catalysts and under more severe conditions.

In the present investigation we carried out the addition of $HGeCl_3$ to a number of further unsaturated compounds (see Table 1). The preparation by this method, for example, of n-$C_3H_7GeCl_3$, is considerably more convenient than the "direct" or organomagnesium syntheses of this compound (^{3}). Trichlorogermane adds vigorously to cyclopentadiene, whereas we were unable to carry out the addition of trichlorosilane to the latter even in the presence of H_2PtCl_6 and on boiling.

Table 1*

Starting compound	Compound obtained*	b.p., °C	p, mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %
$CH_2=CHCH_3$	$Cl_3GeCH_2CH_2CH_3$	163.5	756	1.4749	1.5146	41.27	40.17	85
$CH_2=CHOOCCH_3$	$Cl_3GeCH_2CH_2OOCCH_3$	97	15	1.4868	1.5923	48.02	46.57	57
$Cl_3GeCH_2CH=CH_2$	$Cl_3GeCH_2CH_2CH_2GeCl_3$	123.5	5	1.5314^{25}	solid, m.p. 25.5°	–	–	65
$CH_2=CHCH=CH_2$	$Cl_3GeCH_2CH=CHCH_3$	177	759	1.5080	1.5127	46.12	44.34	61
$C_6H_5C\equiv CH$	$Cl_3GeCH=CHC_6H_5$	146–148	16	1.5833	1.5328	61.53	59.45	43.5
cyclopentadiene	$Cl_3GeC_5H_7$	87	11	1.5270	1.5327	49.35	46.94	58
$Cl_2C=CH_2$	$Cl_3GeCH_2-CHCl_2^{**}$	74	10	1.5176	1.8166	46.14	45.30	62

Starting compound	Compound obtained*	b.p., °C	p, mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, %
$CH_3CH_2CH=CH_2$	$Cl_3GeCH_2CH_2CH_2CH_3$	182	737	1.4780	1.4520	46.03	44.82	75
$C_6H_5CH=CH_2$	$Cl_3GeCH_2CH_2C_6H_5$	132	10	1.5550	1.4816	61.55	61.60	30

* All the compounds listed show, on titration (²), the theoretical amount of chlorine.
** Titrates four chlorine atoms.

To assess the relative reactivity of hydrides other than Cl_3MH, we obtained $(C_2H_5)_3MH$ (^{4,5}) (where $M = \mathrm{Si, Ge,}$ and Sn) by reducing the corresponding $(C_2H_5)_3MHal$ with $LiAlH_4$.

An attempt to synthesize $(C_2H_5)_3GeH$ by the action of C_2H_5MgBr on Cl_3GeH was unsuccessful; mainly $(C_2H_5)_4Ge$ was formed, whereas $(C_2H_5)_3SiH$ is obtained by an analogous route in high yield.

It is interesting to note that treatment of $(C_2H_5)_3MH$ with a one-normal alcoholic solution of KOH at 20° in a Zerevitinov apparatus led to quantitative evolution of hydrogen only with the silicon and tin hydrides (the latter evolved H_2 more rapidly). Triethylgermane did not evolve hydrogen at all, even when the temperature was raised to 80°. At the same time, there are data (^{6}) that SnH_4 and GeH_4, in contrast to SiH_4, do not react with wat-

alkali. All three hydrides $(C_2H_5)_3MH$ add to propargyl alcohol and to acrolein. Triethylstannane adds to these compounds extremely vigorously, and we were unable to isolate any individual substances: only polymers are formed. Triethylgermane, on the contrary, adds to propargyl alcohol only with a catalyst (H_2PtCl_6), i.e., in the same way as $(C_2H_5)_3SiH$ (^{7}):

$$(C_2H_5)_3GeH + HC \equiv CH_2OH \to (C_2H_5)_3GeCH = CHCH_2OH.$$

A difference between $(C_2H_5)_3GeH$ and $(C_2H_5)_3SiH$ could be established only in their reaction with allyl alcohol. Whereas triethylsilane forms exclusively allyloxytriethylsilane (^{8}):

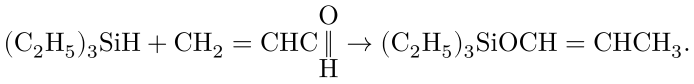
$$CH_2 = CHCH_2OH + (C_2H_5)_3SiH \to CH_2 = CHCH_2OSi(C_2H_5)_3 + H_2,$$

$$(C_2H_5)_3GeH$$

adds already at the multiple bond:

$$CH_2 = CHCH_2OH + (C_2H_5)_3GeH \to (C_2H_5)_3GeCH_2CH_2CH_2OH.$$

The addition of these two hydrides to acrolein also proceeds at different reaction centers. Triethylsilane, as is known (^{9}), adds in the 1,4-position:



$$\mathrm{(C_2H_5)_3SiH + CH_2 = CHC\overset{O}{\underset{H}{\|}} \rightarrow (C_2H_5)_3SiOCH = CHCH_3}.$$

We repeated the experiment of Lesbre and Satgé (^{10}) and found that triethylgermane adds to acrolein with considerable difficulty, indeed apparently forming the corresponding aldehyde (poor analysis, but the IR spectra indicate the presence of an aldehyde group).

We carried out the synthesis of other organogermanium carbo-substituted alcohols according to the following schemes:

$$\mathrm{CH_2 = CH(CH_2)_{\mathit{n}}O_2CCH_3 \xrightarrow{HGeCl_3} Cl_3GeCH_2CH_2(CH_2)_{\mathit{n}}O_2CCH_3 \xrightarrow{CH_3MgCl}}$$

$$\mathrm{\rightarrow (CH_3)_3Ge(CH_2)_{\mathit{n}}CH_2CH_2OH} \qquad (\text{where } n = 0, 1);$$

$$\mathrm{CH \equiv CCH_2OH \xrightarrow{RMgX} XMgC \equiv CCH_2OMgX \xrightarrow[H_2O]{(C_2H_5)_3GeBr} (C_2H_5)_3GeC \equiv CCH_2OH}.$$

And, finally, starting from allyltrimethylgermane, we obtained the first representative of organogermanium mercaptans, which, as it turned out, is readily cyanoethylated.

$$\mathrm{(CH_3)_3GeCH_2CH = CH_2 \xrightarrow{HSOCCH_3} (CH_3)_3GeCH_2CH_2CH_2SOCCH_3 \xrightarrow{NaOH}}$$

$$\mathrm{\rightarrow (CH_3)_3GeCH_2CH_2CH_2SH \xrightarrow{CH_2{=}CHCN} (CH_3)_3GeCH_2CH_2CH_2SCH_2CH_2CN}.$$

The properties of the compounds obtained are presented in Table 2.
The Raman spectra (k. r. s.) were recorded by L. A. Leites.

Experimental part

Propyltrichlorogermane $n\text{-}C_3H_7GeCl_3$. A stream of propylene was passed for 4 h through 116 g of trichlorogermane (with ~ 30% $GeCl_4$) (1). Self-heating to ~ 50° was observed. After cooling, the contents of the flask were heated on a hot plate at ~ 90° for 2 h under a continuous stream of propylene. Distillation on a column gave 38 g of $GeCl_4$, b.p. 83°, and 81 g of propyltrichlorogermane, b.p. 163.5°. Yield 85% based on pure trichlorogermane.

Raman spectrum, $\Delta\nu$ in cm^{-1}: 147(9sh), 173(9), 190(0), 255(5sh), 303(7), 342(2), 384(8), 419(10), 429(7sh), 589(6), 663(8), 756(0), 801(0), 877(2), 897(0), 1029(5), 1071(8), 1105(1), 1143(1sh), 1170(1), 1190(7), 1211(2), 1248(0), 1300(1d), 1343(2), 1389(1), 1410(2), 1452(6sh), 1481(1), 2875(9), 2914(9), 2937(9), 2971(7).

β-(Trichlorogermyl) ethyl acetate $Cl_3GeCH_2CH_2O_2CCH_3$. To 27 g of vinyl acetate, with stirring, 54 g of trichlorogermane (1) was added at such a rate that the temperature of the mixture did not rise above 70°. Vacuum distillation gave 32 g of $Cl_3GeCH_2CH_2O_2CCH_3$, b.p. 97-98° at 15 mm. Yield 57%.

The remaining organogermanium compounds listed in Table 1 were obtained analogously.

β-(Trimethylgermyl)ethanol $(CH_3)_3GeCH_2CH_2OH$. To CH_3MgCl, prepared from 35 g of Mg in 0.6 l of ether, 48 g of β-(trichlorogermyl)ethyl acetate was added. After boiling for one hour, the contents of the flask were decomposed with 10% HCl. The ether layer and ether extracts from the aqueous layer were dried over Na_2SO_4. Vacuum distillation gave 23 g of $(CH_3)_3GeCH_2CH_2OH$ with b.p. 48° at 10 mm.

IR spectrum, $\Delta\nu$ in cm^{-1}: 150(2 sh), 195(7 sh), 281(2 sh), 559(10), 604(8 sh), 885(3), 1051(1), 1086(0), 1242(4 sh), 1416(1 sh), 1461(2 sh), 2864(1 sh), 2915(9 sh), 2975(9 sh).

γ-(Trimethylgermyl)propanol was obtained analogously from γ-(trichlorogermyl)propyl acetate (1).

γ-(Triethylgermyl)propanol $(C_2H_5)_3GeCH_2CH_2CH_2OH$. A mixture consisting of 18 g of allyl alcohol, 20 g of $(C_2H_5)_3GeH$, and two drops of 0.1 N $H_2PtCl_6 \cdot 6H_2O$ solution in isopropyl alcohol was heated at ~90° for 4 h. Vacuum distillation gave 24 g of $(C_2H_5)_3GeCH_2CH_2CH_2OH$, b.p. 89-90° at 3 mm. Yield 73%.

γ-(Triethylgermyl)allyl alcohol $(C_2H_5)_3GeCH{=}CHCH_2OH$. Under the conditions of the preceding experiment, from 12 g of propargyl alcohol, 18 g of $(C_2H_5)_3GeH$, and 2-3 drops of catalyst, 16 g of $(C_2H_5)_3GeCH{=}CHCH_2OH$ was obtained, b.p. 112-113° at 12 mm. Yield 37%.

Table 2

Compound obtained	b.p., °C	p, mm Hg	nD^{20}	d$_4$^{20}	MRD found	MRD calc.	Yield, %	Found C, %	Found H, %	Found Ge, %	Calculated C, %	Calculated H, %	Calculated Ge, %
$(C_2H_5)_3GeCH_2CH_2CH_2OH$	89-90	3	1.4695	1.0775	56.62	57.07	73	49.35	10.17	33.14	49.38	10.43	33.47
$(C_2H_5)_3GeCH=CHCH_2OH$	112-3	12	1.4808	1.0980	56.22	56.66	37	49.13	10.34	32.64	49.84	9.29	33.47
$(C_2H_5)_3GeC \equiv C-CH_2OH$	112	9	1.4822	1.1150	54.95	55.31	67	49.78	9.30	33.27	50.31	8.44	33.79
$(C_2H_5)_3GeCH_2CH_2C(=O)H$	136-8	22	1.4612	1.0280	52.77	55.90	42	49.65	9.57	32.75	49.84	9.29	33.47
$(CH_3)_3GeCH_2CH_2CH_2OH$	79-80	14	1.4513	1.1042	43.13	43.13	63	45.06	9.03	37.52	40.76	9.12	41.06
$(CH_3)_3GeCH_2CH_2OH$	48	10	1.4480	1.1344	38.42	38.55	78.5	40.03	9.14	41.85	36.89	8.67	44.60
$(CH_3)_3GeCH_2CH_2CH_2SOCCH_3$	91	7	1.4829	1.0304	59.13	58.67	94	37.19	8.88	44.90	40.90	7.72	–
$(CH_3)_3GeCH_2CH_2CH_2SH$	54-55	8	1.4749	1.0990	49.39	49.34	68	40.84	7.49	–	37.37	8.36	–
$(CH_3)_3Ge(CH_2)_3SCH_2CH_2CN$	144	8	1.4919	1.0776	63.10	63.26	45	46.06	7.59	29.85	43.96	7.79	29.52
$(C_2H_5)_3GeH$	122	769	1.4330	1.0075	41.49	41.66	89	44.29	7.56	30.36	–	–	–
$(C_2H_5)_3SnH$	146	746	1.4709	–	–	–	93	–	–	–	–	–	–

Raman spectrum, $\Delta\nu$ in cm^{-1}: 173(10), 293(3), 491(1), 526(4), 549(10 sh), 583(10 sh), 921(1), 979(5), 1024(4 sh), 1088(0), 1104(4), 1168(1), 1226(10), 1251(1), 1302(4), 1384(0), 1408(1), 1432(2), 1463(6), 1621(4), 2829(1), 2878(9), 2910(10), 2933(8), 2961(8).

γ-(Triethylgermyl)-propargyl alcohol $(C_2H_5)_3GeC \equiv CCH_2OH$. To C_2H_5MgBr, prepared in 0.3 l of ether from 25 g of Mg and 120 g of ethyl bromide, 20 g of propargyl alcohol was added, and after 5 hr, 70 g of $(C_2H_5)_3GeBr$. After boiling for 2 hr, the contents of the flask were decomposed with 10% HCl. After the usual workup, 15 g of $(C_2H_5)_4Ge$ and 42 g of $(C_2H_5)_3GeC \equiv CCH_2OH$ were isolated, b.p. 111-2° at 9 mm. Yield 67%.

γ-(Trimethylgermyl)-propyl thioacetate $(CH_3)_3GeCH_2CH_2CH_2SOCCH_3$. Addition of 20 g of thioacetic acid to 16 g of allyltrimethylgermane was accompanied by self-heating of the mixture. After heating this mixture for half an hour at 50°, vacuum distillation gave 22 g of $(CH_3)_3GeCH_2CH_2CH_2SOCCH_3$, b.p. 90-91° at 7 mm. Yield 94%.

γ-Thiolpropyltrimethylgermane $(CH_3)_3GeCH_2CH_2CH_2SH$. To a solution of 5 g of NaOH in 25 ml of water and 12 ml of alcohol, 18 g of γ-(trimethylgermyl)-propyl thioacetate was added. Vigorous stirring and boiling under a nitrogen atmosphere of the contents of the flask were continued for 3 hr. Then the organic layer was separated from the aqueous layer, and the latter was extracted with ether. After drying with Na_2SO_4, vacuum distillation gave 10 g of $(CH_3)_3GeCH_2CH_2CH_2SH$, b.p. 54–55° at 8 mm. Yield 68%.

β-(γ-(Trimethylgermyl)-propylmercapto)-propionitrile $(CH_3)_3GeCH_2CH_2CH_2SCH_2CH_2CN$. To 9 g of γ-thiolpropyltrimethylgermane, 1–2 drops of a solution of sodium methylate in methyl alcohol were added, and then 5 g of acrylonitrile was added at such a rate that the temperature did not rise above ~70°. The liquid was then washed with dilute HCl, dried with $CaCl_2$, and distilled. Obtained: 6 g of $(CH_3)_3Ge(CH_2)_3SCH_2CH_2CN$, b.p. 144–46° at 8 mm. Yield 45%.

Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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