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Ethynylisopropylgermanes and Their Trimethylsilyl Derivatives

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Abstract — The reaction of ethynylmagnesium bromide with chloroisopropylgermanes ($i\text{-Pr}_{4-n}\text{GeCl}_n$, n = 1–3) was used to prepare previously unknown ethynylisopropylgermanes $i\text{-Pr}_{4-n}\text{Ge(C}\equiv\text{CH)}_n$ (n = 1–3). The reaction of $\text{Me}_3\text{SiC}\equiv\text{CMgBr}$ with $i\text{-PrGeCl}_3$ afforded $i\text{-Pr(Me}_3\text{SiC}\equiv\text{C)}_{3-n}\text{GeCl}_n$ (n = 1, 2). The reaction of the monochloride with $\text{BrMdC}\equiv\text{CH}$ gave $i\text{-Pr(HC}\equiv\text{C)}_2\text{GeC}\equiv\text{CSiMe}_3$, while with the dichloride, $i\text{-Pr(HC}\equiv\text{C)}\cdot\text{Ge(C}\equiv\text{SiMe}_3)_2$ formed. The latter compounds were obtained by independent synthesis from $i\text{-PrGe(C}\equiv\text{CH)}_3$, EtMgBr, and ClSiMe_3. The reaction of (bromomagnesioethynyl)triisopropylgermane with Me_3SiCl gave $i\text{-Pr}_3\text{GeC}\equiv\text{SiMe}_3$.

Organogermanium compounds containing an ethynyl group on the germanium atom are poorly explored. The only known compounds are $\text{R}_{4-n}\cdot\text{Ge(C}\equiv\text{CH)}_n$ (R = Me, n = 1–4 [1, 2]; R = Et, n = 1, 2 [3, 4]; R = H, n = 1 [5]; R = n-Bu, n = 1, 2 [4, 6]; R = Cl, n = 1 [3]).

Continuing research into acetylenic germanium compounds [7], we turned to the reaction of isopropylgermanes $i\text{-Pr}_{4-n}\text{GeCl}_n$ (n = 1–3) with ethynylmagnesium bromide in THF with the purpose of preparing ethynylisopropylgermanes. It was expected that the sterically congested isopropyl groups at the germanium atom would specifically affect the reactivity of the starting compounds and the final products. Therewith, we prepared formerly unknown ethynylgermanes of the above series with R = i-Pr.

$$i\text{-Pr}_{4-n}\text{GeCl}_n + n\text{BrMgC}\equiv\text{CH} \longrightarrow \underset{\textbf{I–III}}{i\text{-Pr}_{4-n}\text{Ge(C}\equiv\text{CH)}_n}, \quad (1)$$

$$n = 3\ (\textbf{I}),\ 2\ (\textbf{II}),\ 1\ (\textbf{III}).$$

The starting chloroisopropylgermanes were prepared by the reactions of isopropylmagnesium bromide with GeCl_4 at 2 : 1 and 2.5 : 1 molar ratios, respectively. In the first case, $i\text{-PrGeCl}_3$, $i\text{-Pr}_2\text{GeCl}_2$, and $i\text{-Pr}_3\text{GeCl}$ were formed in a 9 : 5 : 3 ratio, and in the second, in a 1 : 1 : 1 ratio. Up to now these compounds have been prepared by a multistage procedure in low yields [8–10].

The reaction of trichloroisopropylgermane with trimethylsilylethinylmagnesium bromide (1 : 1 molar ratio) occurs in a similar way and involves substitution of one or two chlorine atoms by trimethylsilylethynyl groups.

$$i\text{-PrGeCl}_3 + \text{BrMgC}\equiv\text{CSiMe}_3$$
$$\longrightarrow \underset{\textbf{IV}}{i\text{-Pr(Me}_3\text{SiC}\equiv\text{C)GeCl}_2} + \underset{\textbf{V}}{i\text{-Pr(Me}_3\text{SiC}\equiv\text{C)}_2\text{GeCl}}. \quad (2)$$

The reactions of compounds **IV** and **V** with ethynylmagnesium bromide lead to the corresponding ethynyl derivatives.

$$\textbf{IV} + 2\text{BrMgC}\equiv\text{CH} \longrightarrow \underset{\textbf{VI}}{i\text{-Pr(HC}\equiv\text{C)}_2\text{GeC}\equiv\text{CSiMe}_3}, \quad (3)$$

$$\textbf{V} + \text{BrMgC}\equiv\text{CH} \longrightarrow \underset{\textbf{VII}}{i\text{-Pr(HC}\equiv\text{C)Ge(C}\equiv\text{CSiMe}_3)_2}. \quad (4)$$

Compounds **VI** and **VII** were also obtained by independent synthesis from triethynylisopropylgermane, ethylmagnesium bromide, and chlorotrimethylsilane.

$$i\text{-PrGe(C}\equiv\text{CH)}_3 + \text{EtMgBr} + \text{ClSiMe}_3 \longrightarrow \textbf{VI} + \textbf{VII}. \quad (5)$$

Triisopropylgermane under these conditions forms triisopropyl(trimethylsilylethynyl)germane.

$$i\text{-PrGeC}\equiv\text{CH} + \text{EtMgB} + \text{ClSiMe}_3$$
$$\longrightarrow \underset{\textbf{VIII}}{i\text{-Pr}_3\text{GeC}\equiv\text{CSiMe}_3}. \quad (6)$$

The resulting data show that even three isopropyl groups on the germanium atom only slightly affect the reactivity of the Ge–Cl bond.

The physicochemical constants and elemental analyses of the obtained compounds are listed in Table 1. Their structure was proved by ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy (Table 2). Isopropylgermanes

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Table 1. Physicochemical constants and elemental analyses of compounds **I–VIII**

Comp. no.	Yield, %	bp, °C (*p*, mm)	d_4^{20}	n_D^{20}	Found, %			Formula	Calculated, %		
					C	H	Ge		C	H	Ge
I	77	70 (25)	1.0752	1.4612	56.42	5.41	38.12	$C_9H_{10}Ge$	56.66	5.28	38.05
II	90	75 (20)	1.0363	1.4615	57.20	7.99	33.50	$C_{10}H_{16}Ge$	57.51	7.72	34.76
III	85	75 (10)	0.9659	1.4620	58.52	9.73	31.97	$C_{11}H_{22}Ge$	58.23	9.77	32.00
IV	42	95 (2)	1.1870	1.4728	–	–	–	$C_8H_{16}Cl_2GeSi$	–	–	–
V	37	123 (2)	1.0894	1.4770	–	–	–	$C_{13}H_{25}ClGeSi_2$	–	–	–
VI[a]	72	89 (2)	1.0069	1.4656	54.60	6.90	27.56	$C_{12}H_{18}GeSi$	54.81	6.89	27.83
VII[b]	71	75 (10^{-3})	1.0073	1.4730	53.02	7.79	20.89	$C_{15}H_{26}GeSi_2$	53.75	7.82	21.66
VIII[c]	82	113 (2)	0.9521	1.4640	56.07	10.14	24.08	$C_{14}H_{30}GeSi$	56.22	10.11	24.27

[a] Found Si, %:10.39. Calculated Si, %: 10.68. [b] Found Si, %: 15.65. Calculated Si, %: 16.7. [c] Found Si, % 9.32. Calculated Si, %: 9.39.

Table 2. ^1H, ^{13}C, and ^{29}Si NMR data of ethynylgermanes

Comp. no.	^1H NMR spectrum, δ, ppm				^{13}C NMR spectrum, δ_C, ppm						^{29}Si NMR spectrum, δ_{Si}, ppm
	CH_3CGe	CCHGe	HC≡C	CH_3Si	*C*H_3CGe	*C*CHGe	HC≡C	GeC≡	≡CSi	CH_3Si	
I	1.21	1.57	2.45	–	19.03	17.21	94.33	80.09	–	–	–
II	1.19	1.30	2.34	–	18.57	16.30	94.40	82.56	–	–	–
III	1.16	1.38	2.24	–	19.52	14.58	93.82	86.82	–	–	–
VI	1.21	1.53	2.41	0.20	19.32	17.38	93.87	80.89, 101.89	115.88	–0.30	–17.60
VII	1.16	1.34	2.33	0.14	19.47	17.45	93.53	81.53, 102.83	115.89	–0.27	–17.79
VIII	1.17	1.25	–	0.17	18.90	16.75	–	106.23	115.14	0.11	–18.90

I–III we additionally studied by IR spectroscopy. The ethynyl group gives strong stretching absorption bands at 2020–2030 ($\nu_{C\equiv C}$) and 3280 cm^{-1} ($\nu_{\equiv CH}$). The *i*-Pr–Ge bonds give stretching vibration bands at 1360–1365 and 1460–1465 cm^{-1}. Asymmetric vibration bands of the *i*-Pr–Ge and Ge–C≡ bonds are observed at 560–570 and 490 cm^{-1}, respectively.

EXPERIMENTAL

The IR spectra were obtained on a Specord IR-75 spectrometer in thin layer. The NMR spectra were registered on a Bruker DRX-400 spectrometer for 15% solutions in $CDCl_3$ against internal TMS.

Ethynyltriisopropylgermane. To a solution of 11.1 g of trichloroisopropylgermane in 50 ml of ether, the solution of ethynylmagnesium bromide prepared from 3.65 g of Mg, 16.5 g of EtBr, and acetylene in 150 ml of THF, was added dropwise with stirring. The mixture was stirred for 1 h and then treated with water and a 5% HCl solution. After usual workup and drying over calcined $CaCl_2$, the solvents were removed in a water-jet-pump vacuum, and the residue was distilled in a vacuum to give 7.26 g (75%) of compound **I.**

Compounds **II** and **III** were prepared in a similar way, and compounds **VI** and **VII**, by reactions (3) and (4).

1-(Dichloroisopropylgermyl)-2-(trimethylsilyl)-ethyne (IV) and chloroisopropylbis(trimethylsilyl-ethynyl)germane (V). To a solution of 11.1 g of trichloroisopropylgermane in 50 ml of ether, the solution of $Me_3SiC{\equiv}CMgBr$, prepared from 1.21 g of magnesium, 5.45 g of EtBr, and 5.0 g of $Me_3SiC{\equiv}CH$ in 50 ml of THF, was added dropwise with stirring. Further treatment of the reaction mixture was carried out as described above. The yields of compounds **IV** and **V** were 6.18 g (42.2%) and 5.39 g (36.8%), respectively.

Compound **VIII** were prepared in a similar way.

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