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Synthesis of tri- and tetraalkynylgermanes

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A straightforward synthesis of tetra- and trialkynylgermanes by reactions of compounds containing Ge—N or Ge—Cl bonds with alk-1-ynes was proposed. Reactions of appropriate amino- or halogermanes with alk-1-ynes were effective only in the presence of an equivalent amount of zinc dihalide.

Key words: alk-1-ynes, zinc dihalides, alkynylgermanes, aminogermanes, organogermanium compounds, germanium tetrachloride, chlorogermanes.

Acetylene derivatives of germanium, in which the Ge atom is bound to sp-hybridized C atoms, are well known and are conventionally synthesized by reactions of alkali metal or magnesium alkynides with halogermanes.[1,2]

However, direct replacement of the acid H atom in alk-1-ynes by germanium has been reported for only a few cases,[3,4] in contrast to similar reactions of alk-1-ynes with compounds containing Sn—Cl,[5] Sn—O,[6] Sn—N,[7] and Pb—O bonds.[8] Earlier,[9] we have shown that dialkylaminosilanes react with alk-1-ynes in the presence of zinc dihalides to give silylalkynes in high yields.

Here we found that reactions of tetrakis(dialkylamino)germanes **1** and tris(dialkylamino)phenylgermanes **2** with alk-1-ynes **3** in dioxane or THF at 70—100 °C in the presence of zinc dihalides afford alkynylgermanes in high yields (Scheme 1; Tables 1, 2).

Scheme 1

$$\underset{\textbf{1a,b; 2a,b}}{R^1_nGe(NR^2_2)_{4-n}} + \underset{\textbf{3a—g}}{4-n\ HC{\equiv}CR^3} + 4-n\ ZnHal_2 \longrightarrow$$

$$\longrightarrow \underset{\textbf{4a—g; 5a—g}}{R^1_nGe(C{\equiv}CR^3)_{4-n}} + 4-n\ R^2_2NH \cdot ZnHal_2$$

$n = 0$; $NR^2_2 = NEt_2$ (**1a**), $N(CH_2)_5$ (**1b**);
R^3 = Bu (**3a**, **4a**), Me_3Si (**3b**, **4b**), Ph (**3c**, **4c**), CH_2OAc (**3d**, **4d**), C_6H_{13} (**3e**, **4e**), 4-BrC_6H_4 (**3f**, **4f**); 1-$C_{10}H_7$ (**3g**, **4g**);

$n = 1$; R^1 = Ph; $NR^2_2 = NEt_2$ (**2a**), $N(CH_2)_5$ (**2b**);
R^3 = Bu (**3a**, **5a**), Me_3Si (**3b**, **5b**), Ph (**3c**, **5c**);
Hal = Cl, Br

With an excess of the acetylene component, three or four amino groups were exhaustively replaced in the reactions with tris(dialkylamino)phenylgermanes **2** or tetrakis(dialkylamino)germanes **1**, respectively. In the absence of zinc dihalides, the reaction did not occur even at elevated temperatures. This distinguishes tri- and tetraaminogermanes from trialkyl(amino)germanes, which react with alk-1-ynes at 150—180 °C for a long time.[3,4]

The starting tris- and tetrakis(dialkylamino)germanes are easily accessible *via* reactions of secondary amines with appropriate halogermanes.[14] When used in excess, these amines serve as a reaction medium and provide virtually quantitative yields of aminogermanes **1** and **2**.

We also found that germanium tetrachloride and trichloro(phenyl)germane in the presence of zinc dihalides react with alk-1-ynes differently from what has been reported earlier.[15] The presence of zinc dihalide increases the alkynylation degree and allows one to obtain tetraalkynylgermanes from germanium tetrachloride and trialkynyl(phenyl)germane from trichloro(phenyl)germane (Scheme 2).

Scheme 2

$$R^1_nGeCl_{4-n} + \underset{\textbf{3a—d}}{4-n\ HC{\equiv}CR^2} + 4-n\ Et_3N + 4-n\ ZnCl_2 \longrightarrow$$

$$\longrightarrow \underset{\textbf{4b—d; 5a—c}}{R^1_nGe(C{\equiv}CR^2)_{4-n}} + 4-n\ Et_3NH^+ \cdot ZnCl_3^-$$

$n = 0$; $R^2 = Me_3Si$ (**3b**, **4b**), Ph (**3c**, **4c**), CH_2OAc (**3d**, **4d**);
$n = 1$; R^1 = Ph; R^2 = Bu (**3a**, **5a**), Me_3Si (**3b**, **5b**), Ph (**3c**, **5c**)

The yields of tetraalkynylgermanes **4** and trialkynyl(phenyl)germanes **5** were up to 85 and 75%, respectively. We found this method to be inapplicable to trialkylchlorogermanes and dialkyl(dichloro)germanes: they did not react with alk-1-ynes in the presence of

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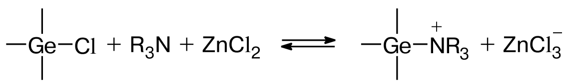
Table 1. Yields and physicochemical characteristics of tetra- and trialkynylgermanes **4a—g** and **5a—c**

Compound	Yield (%) (method)	M.p./°C	n_D^{20}	d_4^{20}	Found/Calculated (%) C	H	Ge	IR, ν(C≡C)/cm^{-1}	Reference
4a	78 (*A*)	—	1.4909	0.9970	72.37 72.60	8.98 9.14	17.83 18.28	2185	—
4b	85 (*C*)	160	—	—	51.82 52.06	7.61 7.86	15.29 15.73	2180	10
4c	86 (*C*)	187—188	—	—	80.37 80.59	4.01 4.23	14.78 15.22	2180	11
4d	81(*C*)	57	—	—	48.86 49.12	3.92 4.12	14.45 14.84	2195	—
4e	79 (*A*)	—	1.4840	0.9745	75.24 75.46	10.08 10.30	13.83 14.25	2185	—
4f	81 (*A*)	255—266	—	—	48.25 48.49	1.84 2.03	8.69 9.16	2190	12
4g	80 (*A*)	—	1.6357	1.0017	84.88 85.12	3.90 4.12	10.29 10.72	2190	—
5a	83 (*B*)	—	1.5198	0.9961	75.01 75.24	8.19 8.42	18.41 18.95	2185	—
5b	87 (*C*)	121	—	—	56.96 57.15	7.04 7.31	16.06 16.45	2180	—
5c	85 (*C*)	108—109	—	—	79.30 79.53	4.22 4.45	15.67 16.02	2180	13

equimolar amounts of $ZnCl_2$ and triethylamine. This fact casts doubt on the possible formation of intermediate zinc alkynides in the reactions under study, although this assumption has been made earlier.[16,17] Apparently, the germylation of an alkyne follows an analogous electrophilic mechanism proposed earlier for direct silylation of alk-1-ynes and confirmed experimentally.[9] In this case, coordination of zinc dihalide to aminogermane through its N atom makes the Ge atom more electrophilic and simultaneously forms an effective leaving group. The formation of a similar germylating system from a tertiary amine and germanium halides is also possible in the reactions shown in Scheme 2. In this case, zinc dihalide seems to bind the chloride anion and shift the reaction equilibrium to the right (Scheme 3).

Scheme 3



$$-\overset{|}{\underset{|}{Ge}}-Cl + R_3N + ZnCl_2 \rightleftarrows -\overset{|}{\underset{|}{Ge}}-\overset{+}{N}R_3 + ZnCl_3^-$$

The reactions outlined in Schemes 1 and 2 can be used to obtain not easily accessible tri- and tetraalkynylgermanes. The method we propose has undoubted advantages over conventional ones involving metallated terminal alkynes. It is essential that our method is applicable to functionalized acetylene derivatives. The resulting alkynylgermanes are undistillable oils or crystalline solids that are stable up to their melting points. They can find use in the synthesis of scarcely accessible organogermanium compounds and polymeric materials.

Experimental

IR spectra were recorded on an Infra-LUM FT-02 spectrometer in the 4500—350 cm^{-1} range (experimental error ±0.5 cm^{-1}). ^{1}H NMR spectra were recorded on a Tesla BS 587 instrument (80 MHz) in $CDCl_3$ with HMDS as the internal standard.

Table 2. Effect of the germylation conditions on the yields of alkynylgermanes **4** and **5**

Compound	Germylation conditions: Method of the synthesis	τ*/h	Solvent	Yield (%)
4b	*A*	4	THF	81
	C	3	Dioxane	85
4c	*A*	4	THF	80
	C	3	Dioxane	86
4d	*A*	3.5	Dioxane	75
	C	2	Dioxane	81
5b	*B*	4	Dioxane	79
	C	2.5	Dioxane	87
5c	*B*	4	THF	78
	C	3.5	Dioxane	85

* The reaction duration.

Table 3. ^{1}H NMR data (80 MHz, $CDCl_3$) for selected alkynylgermanes **4** and **5**

Compound	δ	
	$C\equiv CCH_2$	Other signals
$Ge(C\equiv CBu)_4$ (**4a**)	2.27 (m, 8 H)	1.51 (m, 16 H, $\underline{CH_2CH_2}Me$); 0.92 (m, 12 H, Me)
$Ge(C\equiv CCH_2OCOMe)_4$ (**4d**)	4.75 (s, 8 H)	2.12 (s, 12 H, COMe)
$Ge(C\equiv CC_6H_{13})_4$ (**4e**)	2.21 (t, 8 H)	1.23 (m, 32 H, CH_2); 0.85 (m, 12 H, Me)
$PhGe(C\equiv CBu)_3$ (**5a**)	2.24 (m, 6 H)	7.31 (m, 5 H, Ph); 1.48 (m, 12 H, $\underline{CH_2CH_2}Me$); 0.90 (m, 9 H, Me)
$PhGe(C\equiv CSiMe_3)_3$ (**5b**)	—	7.34 (m, 5 H, Ph); 1.14 (s, 27 H, Me)

The starting reagents and solvents were thoroughly purified before use. Commercial zinc dihalides were additionally dehydrated by melting ($ZnCl_2$) or heating *in vacuo* ($ZnBr_2$).

Tetrakis(phenylethynyl)germane (4c). Procedure ***A***. A mixture of anhydrous $ZnCl_2$ (10.6 g, 77.6 mmol) and dioxane (150 mL) was heated to 85—90 °C. Phenylacetylene (7.92 g, 77.6 mmol) and tetrakis(diethylamino)germane (**1a**) (7 g, 19.4 mmol) were added. The reaction mixture was kept at 100 °C for 4 h and treated with 5% HCl. The product was extracted with chloroform and the extract was dried with $CaCl_2$. Removal of the solvent resulted in prompt crystallization of the residue. The crystals were washed with methanol and recrystallized from benzene—light petroleum, m.p. 188—189 °C (*cf.* Ref. 11: m.p. 188—189 °C). IR (CCl_4), ν/cm^{-1}: 2190 ($C\equiv C$).

Phenyltris(trimethylsilylethynyl)germane (5b). Procedure ***B***. A mixture of anhydrous $ZnCl_2$ (10.6 g, 77.6 mmol) and dioxane (150 mL) was heated to 85—90 °C. Trimethylsilylacetylene (7.92 g, 77.6 mmol) and tris(diethylamino)phenylgermane (**2a**) (7 g, 19.4 mmol) were added. The reaction mixture was kept at 100 °C for 4 h and treated with 5% HCl. The product was extracted with chloroform and the extract was dried with $CaCl_2$ and concentrated. The residue crystallized slowly; m.p. 121 °C (from hexane). IR (CCl_4), ν/cm^{-1}: 2180 ($C\equiv C$).

Tetrakis(3-acetoxypropyn-1-yl)germane (4d). Procedure ***C***. A mixture of anhydrous $ZnCl_2$ (16.32 g, 0.120 mol) and dioxane (150 mL) was heated to 85—90 °C. Triethylamine (12.2 g, 0.121 mol) and propargyl acetate (11.76 g, 0.120 mol) were added. After 10 min, $GeCl_4$ (6 g, 0.028 mol) was added. The reaction mixture was kept at 100 °C for 4 h and treated with 5% HCl. The product was extracted with chloroform and the extract was dried with $CaCl_2$ and concentrated. The resulting oil was purified by column chromatography on Merck 250 silica gel with chloroform as the eluent to give a light yellow oil that crystallized slowly, m.p. 57 °C (from hexane). IR (CCl_4), ν/cm^{-1}: 2195 ($C\equiv C$); 1750 (C=O).

All other products were obtained according to one or two procedures *A*, *B*, or *C* described above (see Tables 1, 2). The physicochemical properties and spectroscopic characteristics of the products are given in Tables 1 and 3.

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