

## ORGANOMETALLIC ACETYLENE CHEMISTRY

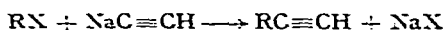
## I. TETRAETHYNYLSILANE, TETRAETHYNYLGERMANE AND SOME SUBSTITUTED ETHYNYL ORGANOGERMANES

WENZEL DAVIDSOHN AND MALCOLM C. HENRY

*U.S. Army Natick Laboratories, Natick, Mass. (U.S.A.)*

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One of the preferred methods of synthesizing monosubstituted acetylenic compounds is the reaction of sodium acetylide with alkyl halides.



Although this reaction is usually restricted to primary halo compounds and is usually carried out in liquid ammonia, recent published results by Rutledge<sup>1</sup>, Jenkner<sup>2</sup> and others<sup>3,4</sup> have shown both that a variety of solvents may be used in this reaction and further, that both the silicon- and tin-acetylenic linkages are relatively stable. We were interested in ascertaining the extent to which a variety of group IVB-acetylenic compounds could be prepared.

Of the Group IVB tetraethynyl compounds only the tetraethynylstannane has been isolated and characterized<sup>2</sup>. Tetraethynylsilane is the subject of a patent claim, with no evidence presented for its existence or for its having actually been obtained. The carbon, germanium and lead analogues have not been prepared or characterized.

## PROCEDURE AND DISCUSSION

For the preparation of Group IVB organometallic acetylenes sodium acetylide was allowed to react with selected organometallic halides using anhydrous tetrahydrofuran as a solvent. We have prepared and identified the corresponding ethynyl compounds (Table 1) by treating silicon tetrachloride, germanium tetrachloride, diphenyldichlorosilane, diphenyldichlorogermane, di-*n*-butyldichlorogermane and triphenylchlorogermane with sodium acetylide. Also identified were several interesting organometallic acetylenic byproducts (Table 2).

The mass spectral patterns of tetraethynylsilane and tetraethynylgermane are shown in Figs. 1 and 2 respectively. Both spectra are very simple and show the molecular ions  $N(m/e\ 128$  and  $m/e\ 172)$  and the stepwise loss of  $-C\equiv CH$  fragments at  $m/e\ 103; 78; 53$  for the silicon compound and  $m/e\ 147; 122; 97; 72$  for the germanium compounds. The peaks with the highest relative intensity in the latter case are  $m/e\ 174$  (molecular ion) and  $149; 124; 99; 74$  which is in agreement with the natural distribution of the germanium isotopes <sup>74</sup>Ge being the one with the highest percentage (37.1%). In the spectrum of the silicon compound no peak was observed at  $m/e\ 28-30$ .

TABLE 1

DATA AND ANALYSES OF ORGANOMETALLIC ACETYLIDES

Reaction No.	Product	M.p./b.p.	Mol. wt. calcd. (found)	Analyses calcd. (found)			Yield <sup>d</sup>
				C	H	Ge	
1	Si(C≡CH) <sub>4</sub> <sup>a</sup>	88-89°	—	—	—	—	50 mg
2	Ge(C≡CH) <sub>4</sub>	91-92°	172.72 (175 dioxane)	55.63 (55.56)	2.33 (2.31)	42.03 (42.20)	34%
3	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Si(C≡CH) <sub>2</sub> <sup>b</sup>	43°	232 (243 benzene)	82.71 (82.89)	5.20 (5.22)	—	37%
4	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> Ge(C≡CH) <sub>2</sub>	49°	267.87 (276 benzene)	69.42 (69.61)	4.37 (4.40)	26.22 (26.29)	56%
5	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> Ge(C≡CH) <sub>2</sub>	46°/0.5 mm	236.89 (239 benzene)	60.80 (60.70)	8.51 (8.35)	—	57%
6	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC≡CH <sup>c</sup>	150°/0.5 mm	329 (323 benzene)	73.02 (72.80)	4.90 (4.98)	22.07 (21.95)	13.7%

<sup>a</sup> Claimed in patent literature but not identified. <sup>b</sup> Described by Korshak *et al.*, *Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk.*, (1962) 2251; prepared by (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SiCl<sub>2</sub> + HC≡CMgBr → (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(C≡CH)<sub>2</sub>, m.p. 44-45°. <sup>c</sup> Molecular distillation. <sup>d</sup> No attempts have been made to obtain optimal yields; values should be taken as indicative rather than exact.

TABLE 2

COMPOUNDS IDENTIFIED AS BY-PRODUCTS

Reaction No	Product	M.p./b.p.	Mol. wt. calcd. (found)	Analyses calcd. (found)			Yield
				C	H	Ge	
2	(HC≡C) <sub>2</sub> Ge-C≡C-Ge(C≡CH) <sub>3</sub> 143° $\begin{array}{c} n\text{-C}_4\text{H}_9 \quad n\text{-C}_4\text{H}_9 \\   \quad   \\ \text{HC}\equiv\text{C}-\text{Ge}-\text{C}\equiv\text{C}-\text{Ge}-\text{C}\equiv\text{CH} \\   \quad   \\ n\text{-C}_4\text{H}_9 \quad n\text{-C}_4\text{H}_9 \end{array}$		319 (325 benzene)				100 mg
5	HC≡C-Ge-C≡C-Ge-C≡CH $\begin{array}{c} n\text{-C}_4\text{H}_9 \quad n\text{-C}_4\text{H}_9 \\   \quad   \\ \text{HC}\equiv\text{C}-\text{Ge}-\text{C}\equiv\text{C}-\text{Ge}-\text{C}\equiv\text{CH} \\   \quad   \\ n\text{-C}_4\text{H}_9 \quad n\text{-C}_4\text{H}_9 \end{array}$	130°/0.5 mm	448 (436 benzene)	59.02 (59.32)	8.56 (8.80)	32.41 (32.77)	5.3%
6	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> GeC≡CGe(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub>	148-149°	632 (653 benzene)	72.24 (72.25)	4.79 (4.84)	22.96 (22.80)	55.5%

TABLE 3

INFRARED ABSORPTIONS

	Si(C≡CH) <sub>4</sub> in CCl <sub>4</sub> (cm <sup>-1</sup> )	Ge(C≡CH) <sub>4</sub> in CCl <sub>4</sub> (cm <sup>-1</sup> )
≡C-H stretch	3306 m	3303 m
C≡C stretch	2062 m-s	2059 m-s
Overtone C-H wag	1370 w	1361 w
≡C-H wag	712 vs	694 vs

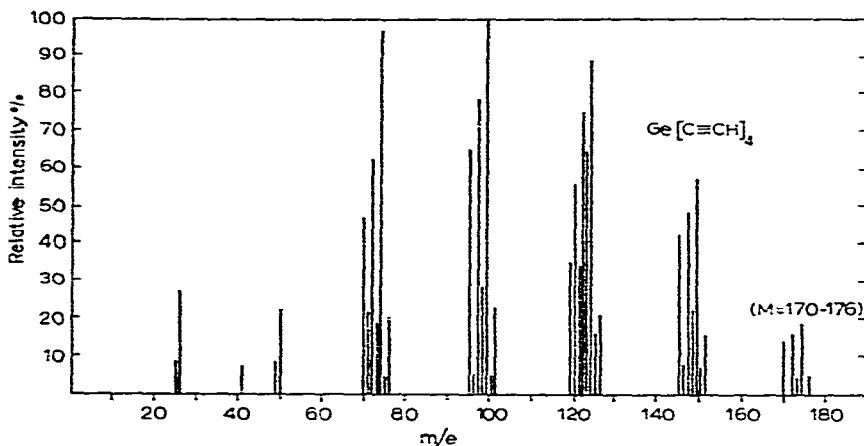


Fig. 1.

The essential important absorptions from the infrared spectra of tetraethynylsilane and tetraethynylgermane are shown in Table 3.

The typical fundamental vibrations of the acetylenic groups were observed at the following frequencies ( $\text{cm}^{-1}$ ):  $\text{H}-\text{C}\equiv\text{C}$  stretch 3300  $m$ ;  $\text{C}\equiv\text{C}$  stretch 2055–2045  $m$ -s;  $\text{H}-\text{C}\equiv$  wag 712–676  $vs$ . The overtone  $\text{C}-\text{H}$  wag was also observed at 1375–1345  $\text{cm}^{-1}$ . Bis(triphenylgermyl)acetylene (Table 2, Reaction No. 6) did not show any acetylenic absorption in the mid-infrared region (2–16 micron) due to the symmetry of the molecule. It did, however, show a Raman band at 2095  $\text{cm}^{-1}$  which is the assigned frequency for an acetylenic stretch. This spectrum was obtained from a Cary-81 Raman spectrophotometer. The absorptions of the butyl and phenyl groups were found in the expected frequency range.

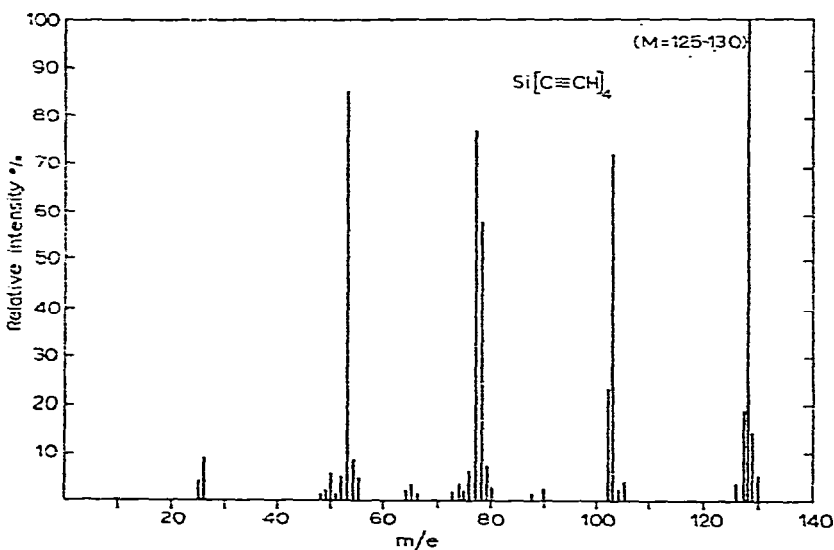
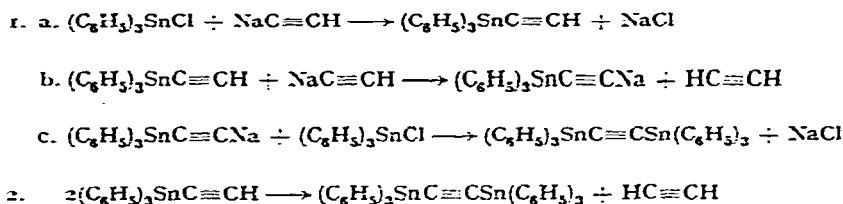


Fig. 2.

Hartmann<sup>5</sup> has reacted triphenyltin chloride and sodium acetylide in liquid ammonia. Two mechanisms were discussed to explain the formation of bis(triphenylstannyl)acetylene as the only product.



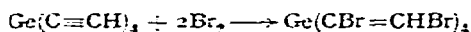
The second alternative was preferred as more likely for this reaction.

The reaction of triphenylchlorogermane with sodium acetylide in tetrahydrofuran gave two major products, triphenylethynylgermane (13.7%) and bis(triphenylgermyl)acetylene (55%). The mechanism presented by Hartmann would not seem to be applicable in this case since all of the ethynyl derivatives described in Tables 1 and 2 have considerable thermal stability even to the point of being distillable. The reaction of diphenyldichlorogermane, dibutyldichlorogermane and germanium tetrachloride with sodium acetylide in tetrahydrofuran resulted in formation of the expected ethynyl compounds in moderate to low yields, disubstituted acetylenic derivatives and red to deep brown liquid or solid residues which appear to be polymeric in nature. *The residues from the preparation of tetraethynylgermane are highly explosive and detonate violently upon contact.*

It seems likely that under the conditions of these reactions sodium acetylide disproportionates to form disodium acetylide which in turn reacts with the available organometallic halides to form the disubstituted acetylide by-products as well as polymeric acetylides.

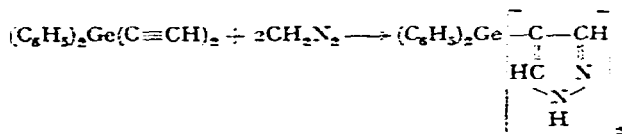
Tetraethynylsilane and -germane, although solids, have high vapor pressures and are auto-sublimable at room temperatures (thus resembling iodine in this regard). Samples left standing in closed tubes sublime onto the sides of the tubes in a very short time.

The elemental analyses of tetraethynylsilane and -germane were difficult to accomplish due to the volatile nature of these compounds and to their tendency to explode on rapid heating. The brominated derivative of tetraethynylgermane namely, tetrakis(1,2-dibromovinyl)germane, was prepared as follows:



Tetraethynylsilane was isolated in small quantities, thus a derivatization was not attempted. This compound was identified by its mass and infrared spectra only.

Diphenyldiethynylgermane was treated with diazomethane to yield diphenyldipyrzolygermane as follows:



## EXPERIMENTAL

Sodium acetylide was prepared from the reaction of sodium metal and acetylene according to the method of Rutledge<sup>6</sup>. Diphenyldichlorosilane and silicon tetrachloride were commercial samples purified by distillation. Triphenylchlorogermane, diphenyldichlorogermane and germanium tetrachloride were obtained through the auspices of the Germanium Research Committee, NYC. Tetrahydrofuran was dried over lithium aluminum hydride and distilled under argon. All reactions were carried out under argon. Molecular weights were determined with a Mechrolab Osmometer, Model 301A. Mass spectra were obtained using a 14-101 Bendix time of flight mass spectrometer. Infrared spectra of tetraethynylsilane and -germane were obtained using a Beckman Model IR-9 Spectrophotometer. The infrared spectra of all other ethynyl compounds were obtained using a Perkin-Elmer 137.

*Typical procedure*

A suspension of 17 g (350 mmole) freshly prepared anhydrous monosodium-acetylide in 150 ml anhydrous tetrahydrofuran was placed in a 500-ml 3-neck flask equipped with gas inlet magnetic stirrer reflux condenser with drying tube and a 50 ml dropping funnel with 40 g (155 mmole) di-*n*-butyldichlorogermane. About one-third of the dichlorogermane was added at once under rapid stirring. As soon as the mixture started to reflux (after about 15 minutes) the remaining halide was added within 20 minutes. The colorless solution turned to a red brown color and was stirred until it reached room temperature and then filtered through a coarse glass fritted funnel, and the solvent removed in vacuum. The residue was dissolved in 500 ml hexane filtered and the solvent was again removed. The remaining liquid was distilled in vacuum. After a small fraction of about 5 ml the main fraction distilled at 55°/0.5 mm and yielded 21 g of a colorless liquid, which was identified as  $(C_4H_9)_2Ge(C\equiv CH)_2$ . After increasing the temperature a second fraction was collected at 131°/0.5 mm and was identified as bis(dibutylethynylgermyl)acetylene (2 g). A thick red brown oil remained in the flask (13.5 g).

The reaction of germanium tetrachloride was carried out in a similar manner. The tetrachloride, however, was added at once and the residue obtained from the work-up solidified in the flask. In our first attempt to remove this red, crystalline mass from the flask, it exploded instantaneously. In a second experiment the solids were carefully extracted with pentane. From this pentane extract we isolated after removal of the solvent, 5 g of slightly pink crystalline material, which was purified by sublimation at room temperature and 40–50 mm pressure. The product was identified as tetraethynylgermane, m.p. 91–92°. The remaining residue was again extracted with a hexane–benzene mixture (5% benzene). From this solution 2.0 g of a red solid material was isolated and carefully transferred into a soxhlet thimble and extracted with pentane. The pentane extract yielded, after sublimation, another 1.2 g  $Ge(C\equiv CH)_4$  and a slightly pink crystalline residue of about 100 mg, m.p. 143° (dark red on melting). Mass spectrum, infrared spectrum, and molecular weight determination indicate that the compound is bis(triethynylgermyl)acetylene. A small amount of a solid, deep red residue which remained in the soxhlet thimble exploded violently when we tried to transfer it into a glass vial. The other residues from this reaction were dissolved in alcohol and discarded.

*Bromination of tetraethynylgermane*

To a solution of 1 g tetraethynylgermane (5.8 mmole) in 25 ml carbon tetrachloride a solution of 4 g bromine (25 mmole Br<sub>2</sub>) in 25 carbon tetrachloride was added dropwise under stirring within 30 minutes. The solution became hot but did not reflux. The reaction mixture was stirred for 1 h and then evaporated in vacuum. The remaining solid residue (4.9 g) was recrystallized from ligroin and yielded 3.8 g tetrakis(1,2 dibromovinyl)germane, m.p. 123°. (Found: C, 11.54; H, 0.47; Br, 80.03; mol. wt. in dioxane, 818. C<sub>8</sub>H<sub>4</sub>Br<sub>8</sub>Ge calcd.: C, 11.83; H, 0.49; Br, 78.73%; mol. wt., 812.)

*Reaction of diphenyldiethynylgermane with diazomethane*

Diazomethane (16 mmole) was generated from (*p*-toluenesulphonyl)methyl-nitrosoamid as described by Vogel<sup>7</sup> and distilled under argon into a 50 ml round bottom two-neck flask containing a stirred solution (magnetic stirrer) of 1 g diphenyldiethynylgermane (3.6 mmole) in 30 ml of ether. After the distillation was finished the solution was stirred for 2 h. A white substance precipitated during the first hour. The solvent and excess diazomethane was removed by vacuum evaporation and the remaining solid (1.3 g) was recrystallized from benzene to yield 0.9 g of diphenyldipyrzolygermane, m.p. 215°. (Found: C, 59.33; H, 4.37; Ge, 20.17; N, 15.65; mol. wt. in dioxane, 361. C<sub>18</sub>H<sub>16</sub>GeN<sub>4</sub> calcd.: C, 59.89; H, 4.47; Ge, 20.12; N, 15.52%; mol. wt., 360.9.)

## ACKNOWLEDGEMENTS

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## SUMMARY

Several new group IV organometallic acetylides have been synthesized utilizing the reaction of sodium acetylide with organometallic halides in anhydrous tetrahydrofuran. The expected mono-, di- and tetraethynyl derivatives were obtained. In addition, a number of disubstituted organometallic acetylides and polymeric residues were obtained. The nature of the reaction products leads one to the assumption that under the selected conditions monosodium acetylide disproportionates slowly into disodium acetylide. At least one of the products is highly explosive.

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