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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR,
Moscow

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# ETHYNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

L. K. Luneva

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## I. INTRODUCTION

Many papers have been published on the synthesis and study of the properties of unsaturated organoelemental compounds of the elements of Group IV of the Mendeleev Periodic System. Practical interest in these compounds arose in connection with the need to create new types of polymers. The investigation of the structure and reactivity of such compounds is of great theoretical importance since there is a specific interaction between carbon–carbon multiple bonds and the elements, an interaction which brings about the appearance of anomalous properties.

There is special interest in the unsaturated derivatives of the elements of the carbon subgroup since it is in this very series, situated at the heart of the Periodic System, that we can expect both an analogy with the purely carbon compounds, and also a considerable difference connected with the electronic structure of the atoms of the Group IV elements. Vinyl and allyl derivatives of silicon, germanium, tin, and lead have been studied most fully. The absence of reliable methods for the preparation of the ethynyl derivatives until recently retarded investigation in this field. It was only in the nineteen-forties, with the development of the chemistry of acetylene, that the first information appeared on the synthesis of alkynylsilanes[1,2]; the more systematic investigation of the alkynylsilanes started much later[3].

The first communication on the preparation of organogermanium compounds containing an acetylenic bond was published in 1958.[4] The first organotin acetylene derivatives were obtained in 1954.[5] A large number of acetylene derivatives of silicon, germanium, and tin are now known.

The present review considers only the acetylene derivatives of silicon, germanium, tin, and lead having a triple bond in the $\alpha$ or $\beta$ positions to the atom of the element. Organoelemental compounds with a triple bond in the $\alpha$ position show most markedly the mutual influence of the $\pi$-electrons of the triple bond and the electrons of the element atoms.

The prop-2-ynyl derivatives of the Group IVb elements (C≡C in the $\beta$ position) are interesting because they allow the influence of the elements on the prop-1,2-dienyl–prop-2-ynyl isomerism to be studied. The prop-1,2-dienyl derivatives formed as a result of the isomerisation are electronic analogues of ethynyl compounds ($sp$-hybridisation) [sic (Ed. of Translation)]; the resulting intramolecular interaction with the atoms of the Group IV elements should give effects analogous to those found with ethynyl groups [sic (Ed. of Translation)]. Therefore the preparation and properties of prop-2-ynyl compounds will also be considered within the bounds of our review.

This review describes in succession the synthesis and the chemical and physical properties of the ethynyl and

prop-2-ynyl derivatives of silicon, germanium, tin, and lead from literature sources, including work up to the middle of 1966.

## II. PREPARATION OF ETHYNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

### 1. Preparation of Ethynyl Derivatives from the Alkali Metal Acetylides

This method allows compounds containing a triple bond in the $\alpha$ position to the element to be obtained:

$$(a)\quad R_{4-n}EX_n + MC{\equiv}CR' \rightarrow R_{4-n}E(C{\equiv}CR')_n,$$

where $n = 1, 2, 3,$ and 4; R = alkyl, aryl, H; X = Cl, Br; M = Na, Li.

$$(b)\quad 2R_3EX + MC{\equiv}CM \rightarrow R_3E{-}C{\equiv}C{-}ER_3.$$

Judging from the literature the method has certain limitations. Thus, with sodium acetylide in liquid ammonia alkynylsilanes and alkynylgermanes are not formed, evidently owing to ammonolysis of the alkyl- or aryl-silicon (or germanium) halides[10]. On the other hand all the organotin and organolead halogen derivatives react rapidly with NaC≡CR under these conditions[5-10] with the formation of disubstituted acetylenes ($R_3E{-}C{\equiv}C{-}ER_3$).

Quan and Cadiot[11] made a detailed investigation of the reaction of alkali metal acetylides with $Ph_3SnX$. They found that when triphenyltin iodide was used in this reaction and this was carried out rapidly, monosubstituted ethynyltriphenyltin(IV) was obtained.

The reaction of sodium acetylide with silicon and germanium halides was effected under other conditions. Thus in a patent[12] Boldebuch described the condensation of sodium acetylide with chloro(ethoxy)silanes in pyridine, with the formation of $(C_2H_5O)_{4-n}Si(C{\equiv}CH)_n$.

Beerman and Hartmann[5] obtained compounds of the type of $Ph_3E{-}C{\equiv}C{-}EPh_3$ by the reaction of monosodium acetylide with bromotriphenylsilane or triphenyltin bromide at 200°C. An analogous compound was obtained with lithium acetylide (through PhLi) in tetrahydrofuran[13].

Symmetrical organogermanium compounds with an acetylene bridge were obtained[14] by the reaction of sodium acetylide with chlorotriphenyl-and chlorotriethyl-germanium in tetrahydrofuran.

Davidson and Henry[15] prepared tetraethynylsilane, tetraethynylgermanium, diethynyldiphenylsilane, diethynyldiphenylgermanium, di-n-butyldiethynylgermanium, and ethynyltriphenylgermanium by the reaction of the corresponding germanium and silicon chlorides with sodium acetylides in tetrahydrofuran.

A patent[16] describes the preparation of ethynyl derivatives of tin, $R_{4-n}Sn(C{\equiv}CH)_n$, by the reaction of tin chlorides with alkali metal acetylides in ether, hexane, or benzene.

West and Kraihanzel[17] proposed a similar method for preparing

$$(CH_3)_3Sn(C{\equiv}CH).$$

Reaction with alkali metal acetylides has also been used for the preparation of poly-yne derivatives of tin and lead[11,18,19]. When the reaction is carried out in ether or hydrocarbons, then only the monosubstituted compounds are formed[17,18]. When the reaction is carried out in liquid ammonia the yield of mono- and di-substituted compounds depends on the ratio of the initial substances[11].

Some authors[20-27] have used the reaction of sodium and lithium acetylides of monosubstituted acetylenes with halogen derivatives of silicon, germanium, and tin for the preparation of compounds of the type $R_{4-n}E(C{\equiv}CR')_n$ and $R_3E(C{\equiv}C)_2R'$, where R = alkyl, aryl; and E = Si, Ge, or Sn.

For the preparation of $Pb(C{\equiv}CR)_4$ through the corresponding lithium acetylide rubidium hexachloroplumbate(IV) was used as the initial organolead compound[20] [sic (Ed. of Translation)].

### 2. Preparation of Ethynyl Compounds of Silicon, Germanium, Tin, and Lead Through Magnesium Bromide Derivatives of Acetylenes

$$R_{4-n}EX_n + XMgC{\equiv}CR' \rightarrow R_{4-n}E(C{\equiv}CR')_n,$$
$$R_3EX + XMgC{\equiv}C{-}R'{-}C{\equiv}CMgX \rightarrow R_3E{-}C{\equiv}C{-}R'{-}C{\equiv}C{-}ER_3.$$

Vol'nov and Reutt[1] first obtained alkynylsilanes by organomagnesium synthesis; as a result of the reaction of tetraethoxysilane with phenylethynylmagnesium bromide they obtained triethoxy(phenylethynyl)silane and diethoxybis(phenylethynyl)silane, and by reaction of ethynylmagnesium bromide with silicon tetrachloride, hexaethynyldisiloxane. At that time the use of polar solvents for the preparation of ethynylmagnesium bromide was unknown and the reaction was effected in boiling xylene; consequently, the yields of the products were insignificant.

After Jones[28] had developed the method of making ethynylmagnesium bromide in tetrahydrofuran, many investigators used this reagent for the preparation of ethynyl derivatives of silicon, germanium, and tin. Petrov and coworkers[23,29,30] synthesised alkynylsilanes of the type $R_3SiC{\equiv}CH$ and $R_2Si(C{\equiv}CH)_2$ from ethynylmagnesium bromide in tetrahydrofuran. Sladkov and Luneva[31] obtained diethynylmethylphenylsilane, diethynyldiphenylsilane, ethyldiethynylphenylgermanium, diethynyldiphenylgermanium, and *p*-bis(ethynyldimethylsilyl)benzene by the reaction of the corresponding germanium and silicon chlorides with ethynylmagnesium bromide in tetrahydrofuran. This method was also used to prepare monoethynyl derivatives of germanium[32] ($R_3GeC{\equiv}CH$) and tin[11,14]; to obtain the tin derivatives a method of precipitating the products from the reaction medium was used.

Mazerolles and coworkers[33] obtained tetraethynylgermanium by the reaction of germanium tetrachloride with ethynylmagnesium bromide.

Organomagnesium derivatives of monosubstituted acetylenes were used to make organoelemental ethynyl derivatives of the $R_{4-n}E(C{\equiv}CR')_n$ type[26,32-41], where E = Si, Ge, Sn; R = alkyl, aryl, vinyl.

Petrov and Shchukovskaya[3] found that symmetrical Iotsich reagent reacts with chlorotrialkylsilanes to form the corresponding symmetrical acetylene derivatives of silicon $R_3Si{-}C{\equiv}C{-}SiR_3$. At the same time Frisch and Young[42] condensed ethynylenedimagnesium dibromide with dichlorodimethylsilane in the presence of CuCl and as a result isolated

$$Cl(CH_3)_2Si{-}C{\equiv}C{-}Si(CH_3)_2Cl.$$

This reaction was used by many investigators[5,6,11,16,40] to prepare $R_3E—C\equiv C—ER_3$, where R = alkyl, aryl; E = Si, Ge, Sn.

Shikhiev and coworkers[43] carried out a similar reaction with butadiynylenedimagnesium dibromide:

$$BrMg—C\equiv C—C\equiv CMgBr + 2\,R_3SiCl \rightarrow R_3Si(C\equiv C)_2SiR_3.$$

Recently Shostakovskii and coworkers[44-46] reported the preparation of organotin acetylene compounds by the reaction of stannanols [hydroxo(trialkyl)tin(IV) complexes (Ed. of Translation)] and dialkyltin oxides [oxodialkyltin(IV) complexes (Ed. of Translation)] with an excess of magnesium bromide derivatives of monosubstituted acetylenes:

$$R_3SnOH + BrMgC\equiv CR' \rightarrow R_3Sn—C\equiv CR',$$

where R′ = vinyl, alkyl, aryl.

$$(R_2SnO)_n + 2n\,BrMgC\equiv CR' \rightarrow n\,R_2Sn(C\equiv CR')_2.$$

Alkynyl silanols are formed in the reaction of poly(diorganosiloxanes) with derivatives of ethynylmagnesium bromide[47-49]:

$$(R'R''SiO)_n + BrMgC\equiv CR \rightarrow R'R''(R—C\equiv C)SiOH.$$

### 3. Other Methods of Obtaining Ethynyl Organoelemental Compounds

a. Preparation through alkali metal derivatives of a triaryl- or trialkyl-tin. This preparation is based on the reaction of the sodium derivatives of tin with halogen derivatives of acetylene in liquid ammonia. Nothing has been published on the preparation of acetylene derivatives of silicon and germanium by this method and evidently this method is inapplicable for these compounds because the initial products may react with ammonia.

The reaction of sodium triphenylstannate(IV) or a sodium trialkylstannate(IV) with di-iodoacetylene produces the compound[5,10]: $R_3Sn—C\equiv C—SnR_3$.

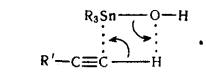
Compounds of similar structure can be obtained by the reaction of sodium triarylstannates(IV) or trialkylstannates(IV) with iodo- or bromo-acetylene[50]; in the first stage the sodium derivative of tin reacts with the labile hydrogen at the acetylenic carbon with the formation of $R_3SnC\equiv CBr$, which subsequently reacts again with the sodium derivative to form a disubstituted acetylene:

$$R_3SnNa + BrC\equiv CH \rightarrow R_3SnC\equiv CBr \xrightarrow{R_3SnNa} R_3SnC\equiv CSnR_3.$$

Reactions with halides of monosubstituted alkynes proceed analogously, with formation of $R_3Sn—C\equiv CR$.[19,51,52] $R_3Pb(C\equiv CR)$ were obtained in the same way[52].

b. Reaction of organic oxygen and amino-derivatives of tin with acetylene. Investigations showed that hydroxotrialkyltin(IV) complexes react with acetylene compounds containing labile hydrogen at the carbon with the triple bond, to form ethynyl derivatives of tin[53-57]. As a result of the reaction, trialkylstannyl derivatives of acetylene, vinylacetylene, and alkyl- and aryl-substituted acetylenes were obtained. The reaction with acetylene requires the use of pressure (15-20 atg) and elevated temperature (100-120°C)[57]. With vinylacetylene and phenylacetylene the reactions take place at room temperature and ordinary pressure[56,57]; this is explained by the increase in acidity of the acetylenic hydrogen.

The mechanism of the reaction is explained by the donor-acceptor interaction of the unpaired electrons of oxygen of the hydroxyl group with the labile acetylenic hydrogen and by the $d\pi$-interaction between the tin atom and the triple bond[56,57]:



The use of trialkyltin halides in this reaction seemed possible[58]. The method consists in the successive reaction of the tin compound with powdered alkali (NaOH or KOH) and the acetylenic compound:

$$R_3SnX \xrightarrow{NaOH} [R_3SnOH] \xrightarrow{HC\equiv CR'} R_3SnC\equiv CR'.$$

A new method was developed[53,55,59] for the preparation of acetylenic derivatives of tin, consisting in the direct reaction of monosubstituted acetylenes with bis(trialkyltin) oxides:

$$(R_3Sn)_2O + 2\,HC\equiv CR' \rightarrow 2\,R_3SnC\equiv CR'.$$

The reaction mechanism is evidently the same as for the stannols and proceeds in two stages:

$$R_3SnOSnR_3 + HC\equiv CR' \rightarrow R_3SnC\equiv CR' + R_3SnOH,$$
$$R_3SnOH + HC\equiv CR' \rightarrow R_3SnC\equiv CR' + H_2O.$$

Lutsenko and Ponamarev[60] described the preparation of trialkyl(phenylethynyl)tin complexes from trialkyl(methoxy)tin complexes and phenylacetylene. This reaction is more difficult than that with the hydroxotrialkyltin compounds and requires heating to 100-110°C.

Several other interesting preparations of acetylenic organotin compounds have been proposed.

Luijten and van der Kerk[61] observed the formation of organotin compounds in the thermal decarboxylation of triaryltin(IV) cyanoacetates:

$$(C_6H_5)_3SnOCOCH_2CN \xrightarrow{-CO_2} (C_6H_5)_3SnCH_2CN.$$

This method was next extended to the tin derivatives of phenylpropiolic and but-2-yndioic acids[61]:

$$R_3SnOCOC\equiv C—C_6H_5 \xrightarrow{-CO_2} R_3SnC\equiv CC_6H_5,$$
$$R_3SnOCO—C\equiv C—OCO—SnR_3 \xrightarrow{-2CO_2} R_3SnC\equiv CSnR_3.$$

In studying the reactions of nucleophilic substitution in organotin derivatives of dimethylamine it was found[62,63] that the N-Sn bond is readily split by compounds which contain a labile hydrogen, for example, phenylacetylene and hex-1-yne; acetylenic derivatives of tin are formed:

$$R_3Sn—N(CH_3)_2 + HC\equiv CR' \longrightarrow R_3Sn(C\equiv CR').$$

## III. PREPARATION OF PROP-2-YNYL DERIVATIVES OF SILICON, GERMANIUM, TIN, AND LEAD

Le Quan and Cadiot[64] first reported the preparation of monoprop-2-ynyl derivatives of silicon and tin by the reaction of prop-2-ynylmagnesium bromide with trialkylhalogenosilanes and stannanes. This method became general for the preparation of most of the prop-2-ynyl derivatives of silicon, germanium, tin, and lead[18,31,40,65-67]:

$$R_{4-n}EX_n + BrMgCH_2—C\equiv CH \longrightarrow R_{4-n}E(CH_2—C\equiv CH)_n,$$

where $n$ = 1, 2; R = alkyl, aryl; E = Si, Ge, Sn, Pb.

The reaction of lithium triphenylstannate with 1-bromoprop-2-yne was also used for the preparation of triphenylprop-2-ynyltin[67]. Note that here the prop-2-ynyl derivative is not formed, but exclusively its allene isomer with 30% yield. At the same time, chlorotriphenyltin and prop-2-ynylmagnesium bromide form only 10% of the allene isomer with a total yield of reaction products of 80%.[67]

## IV. CHEMICAL PROPERTIES OF ETHYNYL ORGANOELEMENTAL COMPOUNDS

There has been little investigation of the chemical properties of the organoelemental compounds of acetylene described above. The reactions of these compounds, both nucleophilic and electrophilic, depend strongly on the nature of the element (Si, Ge, Sn, Pb) linked with ethynyl or prop-2-ynyl groups.

The reactions are considered below in the following order: (a) reactions with splitting of the E–C bond; (b) additions at the triple bond; (c) replacement of the acetylenic hydrogen; (d) isomerisation.

a. Reactions with splitting of the E–C bond. Many investigators have found that the Si–C≡ bond in alkynylsilanes is hydrolytically stable towards dilute acids and alkalis[5,40,68,69]. Concentrated solutions of alkalis break the silicon–carbon bond[5,68,69].

On changing alkyl groups at the silicon atom the higher homologues of the alkynylsilanes are less stable to the action of acids than the lower[68].

Bis(triphenylsilyl)acetylene is stable to cold water but is hydrolysed by alkalis[5]. Ethynyltriphenylsilane differs from the trialkylethynylsilanes in being hydrolysed in the cold[23].

The hydrolytic stability of the E–C≡ bond decreases in the order Si > Ge > Sn > Pb with increase in the polarity of the E–C≡ bond.

The disubstituted acetylenes $R_3E-C\equiv C-ER_3$, where R = aryl and E = Ge or Sn are fairly stable to atmospheric moisture but are split under the action of dilute alkali[10,16], unlike their silicon analogues. On replacing a phenyl radical by alkyls the sensitivity to moisture decreases[5,10]. Monophenylethynyl derivatives of germanium are fairly stable to atmospheric moisture but are hydrolysed by aqueous alkalis[21]. Strong organic acids[13] break the Ge–C≡ bond. Corresponding tin compounds are less stable and the hydrolytic stability decreases on replacing the triphenylstannyl radical by trialkylstannyl radicals[11,14]. Similarly, in trialkylstannylacetylene the Sn–C≡ bond is less stable than in triarylstannylacetylenes[11].

With increase in the number of acetylene radicals the sensitivity of the compound to hydrolysis increases[39]. All acetylene derivatives are extremely sensitive to water[5,9,20] and rapidly decompose in moist air. On the basis of a study of the hydrolytic splitting of the Sn–C≡ bond in triphenylstannylacetylenes it has been shown[11] that the ethynyl group is weakly bound to the tin atom and in the empirical series found by Seyferth[70] it should occupy a place before the aryl radical as regards ease of removal: ethynyl > aryl > vinyl > alkyl[11].

The increase in polarity of the E–C≡ bond in ethynyl organoelemental derivatives that results from the increase in the electronegativity of the carbon atom at the triple bond should therefore facilitate both electrophilic attack at the carbon atom and also nucleophilic attack at the atom of element E.

Copper and silver ions break the E–C≡ bond. Thus, $R_3Ge-C\equiv CH$ is split by silver nitrate in alcoholic solution and by an ammoniacal solution of CuCl, with the formation of silver and copper acetylides[32]:

$$R_3GeC\equiv CH \xrightarrow[NH_4OH]{Cu+} Cu-C\equiv C-Cu.$$

Under analogous conditions the ethynyl derivatives of tin and lead are decomposed with the formation of the same acetylides[5,9,11].

Breaking of Sn–C and Pb–C bonds is also observed under the action of Grignard reagents[5,11,45]:

$$R_3SnC\equiv C-R' + RMgBr \rightarrow R_4Sn + R'-C\equiv CMgBr.$$

The rate at which the C–E bond is broken by halogens also increases from Si to Pb. The Sn–C and Pb–C bonds in $R_3Sn-C\equiv CH$ and $R_3Pb-C\equiv CH$ are readily broken even under the action of iodine at room temperature with the formation of di-iodoacetylene and the corresponding organoelemental compound[5,11]. Even at room temperature bromine breaks the E–C bond in the ethynyl derivatives of germanium, tin, and lead[5,32,36,41].

In the organoelemental acetylene compounds containing a triple bond in the β-position to a silicon, germanium, tin, or lead atom the prop-2-ynyl radicals are much less strongly bound to the element atom than acetylene radicals would be. They are much less resistant to moisture, alkalis, acids[32,40,65]. Just like allyl and benzyl derivatives, the unsaturated radical in prop-2-ynyl compounds also exhibits electron-acceptor properties. Therefore the $E-CH_2$ bond breaks down and becomes more labile, which is explained by the σπ-conjugation of the 1–2 and 3–4 bonds associated with the electromeric effect.

b. Additions. Little has been published about additions at the triple bonds of ethynyl derivatives of the Group IVb elements. Compounds of the type $R_3EC\equiv CER_3$ and $R_3EC\equiv CR'$, where R' = H, alkyl, aryl, react differently with halogens. Alkynylsilanes do not react with iodine[5] and add only two atoms of bromine even on boiling in $CCl_4$.[30,35,39] It has been reported[71] that four bromine atoms add to $R_3Si-C\equiv C-CH_3$ but then HBr is lost and $R_3Si-CBr_2-CBr=CH_2$ is formed. At −80°C bromine adds to the triple bond of $R_3Ge-C\equiv CH$ but breaks the Ge–C bond in $R_3Ge-CH_2-C\equiv CH$.[32]

Davidson and Henry[15] brominated tetraethylgermanium with bromine at room temperature and isolated $Ge(CBr=CHBr)_4$ from the products.

Disilyl-substituted acetylenes do not add hydrogen under ordinary conditions for the catalytic hydrogenation of the C≡C bond; under severe hydrogenation conditions cracking of the molecule occurs[43,72,73].

$R_3Si(C\equiv CR')$ compounds are catalytically hydrogenated, two or four hydrogen atoms being added[39,43,72,73]. The monoethynyl derivatives of germanium $R_3GeC\equiv CH$, $R_3GeC\equiv CR'$, and $R_3GeCH_2-C\equiv CH$ readily add hydrogen at 20°C in the presence of Raney nickel, with the formation of saturated compounds[32,34].

Silicon and germanium hydrides are added quantitatively to alkynylsilanes and alkynylgermanes in the presence of hydrogen hexachloroplatinate(IV)[74,75]:

$$R_3Si-C\equiv CH + R_3Si-H \rightarrow R_3Si-CH=CH-SiR_3$$
$$R_3Ge-C\equiv CH + R_3Ge-H \rightarrow R_3Ge-CH=CH-GeR_3.$$

Diazomethane adds to diethynyldiphenylgermanium(IV) to form diphenyldipyrazolylgermanium(IV)[15].

Some recent papers describe investigations of the chemical reactions of enyne and diyne organoelemental compounds of silicon, germanium, and tin. Alkylvinylacetylenes are known to add bromine almost exclusively at the double bond[76]. Trialkyl(but-3-en-1-ynyl)silanes add bromine mainly in the 1 : 4 position:

$$R_3Si{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow[-10^\circ]{Br_2} R_3Si{-}CBr{=}C{=}CH{-}CH_2Br.$$

When heated, such dibromo-compounds isomerise to form the dibromo-1,3-diene.

Triphenyl(but-3-en-1-ynyl)silane exhibits low reactivity towards electrophilic reagents, as the triphenylsilyl group is a strongly electrophilic substituent and by drawing off electrons from the enyne system it makes the latter inactive towards bromination. Different substituents in the but-3-en-1-ynyl group at the double bond also effect the direction of bromination. Thus the introduction of a methyl group into but-3-en-1-ynyl(trimethyl)silane leads to a change in the direction of bromination, facilitating the addition of bromine at the double-bond[77-79]:

$$(CH_3)_3Si{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}CH_2 \xrightarrow{Br_2} (CH_3)_3Si{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}Br{-}CH_2Br.$$

In vinyl- and allyl-dimethyl(but-3-en-1-ynyl)silanes bromination proceeds perferentially at the vinyl and allyl groups[79].

It has been shown that germanium-enynes also add bromine in the 1–4 and (partly) 3–4 positions[30,80]. When heated, the dibromides obtained are isomerised into dibromodienes. The direction of bromination in substituted germanium-enynes is less dependent on the substituent at the double bond than in the silicon-enynes, since the $R_3Ge$ group compensates to a greater extent the influence of the alkyl groups at the double bond[77], because the $R_3Ge$ radicals are less electrophilic than the $R_3Si$ radicals. It is assumed[77-79] that the increase (in comparison with alkylvinylacetylenes) in the ability to add bromine in the 1, 4 position possessed by the silicon- and germanium-enynes is apparently due to an additional positive charge on the first carbon atom owing to electron displacement due to interaction of the *d*-orbitals of silicon and germanium with the $\pi$-electrons of the triple bond:

$$R_3E \longrightarrow C{\equiv}C{-}C{=}C.$$

Bromine breaks the Sn–C bond in tin-enynes[26,37]. The triple bond is more active in the catalytic hydrogenation of vinylacetylene hydrocarbons[81]. Trialkyl(but-3-en-1-ynyl)silanes[78,79] ($R_3Si{-}C{\equiv}C{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}CH_2$) add hydrogen preferentially at the double bond in the presence of $Pd/CaCO_3$ forming two addition products:

$$R_3Si{-}C{\equiv}C{-}\underset{\displaystyle R'}{\underset{|}{CH}}{-}CH_3 \text{ and } R_3Si{-}CH{=}C{=}\underset{\displaystyle R'}{\underset{|}{C}}{-}CH_3.$$

The ratio of the acetylene and allene isomers depends on the radical R′: the more bulky the radical the more allene isomer is formed[82].

Under these conditions germanium-enynes[74] are hydrogenated much more slowly than the corresponding silicon-enynes. The main direction of the reaction is the addition of hydrogen at the double bond but a certain amount of a diene derivative is formed. The existence of all three possible isomers has been found with the aid of infrared spectra[74]:

$$R_3Ge{-}C{\equiv}C{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CH_3$$
$$R_3Ge{-}CH{=}C{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CH_3$$
$$R_3Ge{-}CH{=}CH{-}\underset{\displaystyle R}{\underset{|}{C}}{=}CH_2.$$

Under these conditions tin-enynes are not hydrogenated[79].

The difference in the direction of the catalytic hydrogenation of silicon and germanium-enynes of hydrocarbons is explained[74,82] by the steric factors under the conditions of heterogeneous catalysis (the presence of the bulky $R_3E$ groups).

It is known[83,84] that alkylbut-3-en-1-ynes add alkyllithium complexes in the 1,4-position, with the formation of lithium derivatives of allene hydrocarbons. Under these conditions silicon-enynes and germanium-enynes form mixtures of isomeric allene and acetylene silicon hydrocarbons, the ratio of which depends on the structure of the enyne groupings and the nature of the radical in the alkyllithium[85-87].

Alkyl-lithium complexes break the Sn–C≡ bond in tin-enynes, with formation of tetra-alkyltin(IV) complexes[52,79,88].

From the above it is clear that nucleophilic (alkyl-lithium) and electrophilic (bromine, etc.) reagents break the Sn–C≡ bond. Zavgorodnii and Petrov[88] studied the stability of this bond in radical processes. It seemed that the triphenylmethyl radical adds to but-3-en-1-ynyltriethyltin(IV) mainly in the 3,4-position but to triethyl(3-methylbut-3-en-1-ynyl)tin(IV) in the 1,4-position, owing to steric factors[88] due to the presence of the methyl group. The same investigators also succeeded[88,90] in adding diazomethane to the above tin-enynes. The addition of diazomethane takes place at the double bond of the vinylacetylene residue, with formation of ethynylpyrazoline derivatives, from which cyclopropane compounds are subsequently formed:

$$(C_2H_5)_3Sn{-}C{\equiv}C{-}\underset{\displaystyle \underset{\displaystyle N}{\underset{\|}{}}}{\underset{|}{C}}{-}CH_2 \rightarrow (C_2H_5)_3Sn{-}C{\equiv}C{-}\underset{\displaystyle CH_2}{\underset{\diagdown\diagup}{CH}}{-}CH_2 + N_2.$$
$$\underset{\displaystyle NH}{\underset{\diagdown\diagup}{CH_2}}$$

Petrov and coworkers also investigated electrophilic and nucleophilic additions to trialkylsilylalkadiynes[91,92]. It was shown[93] that with 1,3-diene silicon-hydrocarbons the first molecule of bromine adds to the triple bond in the $\alpha$-position to the silicon atom; when heated, the resulting dibromo-compound isomerises into 1,3- and 3,4-dibromo-compounds. This was shown by infrared and NMR spectra. An investigation of the addition of lithium alkyl-lithium complexes to 1,3-diyne silicon-hydrocarbons showed[92] that, irrespective of the nature of the radical in the LiR, the addition proceeds at the 3,4-position with fixation of the alkyl radical at the quaternary carbon atom. The results of the bromination and addition of LiR to silicon-diynes, carried out by the author, agree with the following scheme for the direction of polarisation of silicon-diynes, due to the $d\pi$-conjugation effect:

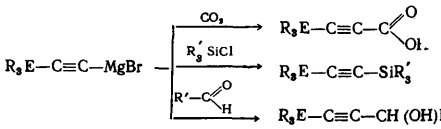
$$R_3Si{-}\overset{\delta-}{C}{\equiv}\overset{2}{C}{-}\overset{3}{C}{\equiv}\overset{\delta+}{\overset{4}{C}}{-}R.$$

c. Substitutions. The hydrogen atom at the H–C≡ bond retains its activity in silicon and germanium-substituted acetylenes. The ethynyl derivatives of silicon

and germanium readily form organomagnesium derivatives[23,30,32,94]:

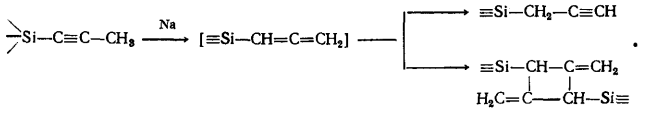
$$R_3E-C\equiv CH + R'MgX \rightarrow R_3E-C\equiv C-MgX + R'H.$$

These compounds can be used for the preparation of various germanium- and silicon-acetylene derivatives[30,32,95]:

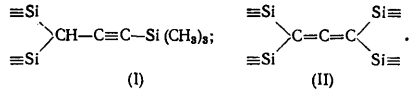


d. Isomerisation of acetylenic organoelemental compounds. Favorskii[96] investigated the isomerisation of acetylenic hydrocarbons; it has been discussed repeatedly[97,98].

There have been a few investigations[36,99,100] concerning the isomeric changes of acetylenic silicon hydrocarbons. Petrov and coworkers[36] obtained interesting results in an attempt to isomerise triethyl(prop-1-ynyl) silane into the allene isomer by the Favorskii reaction. Spectroscopic analysis of the products showed the presence of a cyclodimer and a little triethyl(prop-2-ynyl)silane:



West and coworkers[100] described the reaction of prop-1-ynyl-lithium with chlorotrimethylsilane, which led to the formation of a mixture of tri- and tetra-silyl derivatives:



(I) (II)

Thermolysis and photolysis of (I) leads to disproportionation and formation of an allene derivative.

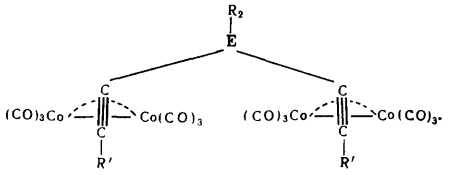
Investigators[20,31,38,40,62-64,101,102] who have been engaged in the preparation of prop-2-ynyl derivatives of organo-silicon, -germanium, -tin, and -lead compounds have noted that a mixture of allene, prop-2-ynyl, and prop-1-ynyl isomers is formed in the reaction:

$$R_3E-CH_2-C\equiv CH; \quad R_3E-CH=C=CH_2; \quad R_3EC\equiv C-CH_3$$

where E = Si, Ge, Sn, Pb; R = alkyl, phenyl.

The structure of the isomers obtained was studied by molecular and radio-frequency spectroscopy, and by analytical gas chromatography[20,63,101,102]. The amounts of the isomers obtained depend on the temperature, the basicity of the solvent, the order in which the initial compounds are added, and their structure[38]. With increase in the atomic weight of the element the proportion of allene isomers increases (Si < Ge < Sn < Pb)[63]. For example, in the preparation of triphenyl(prop-2-ynyl)-lead, 90% triphenyl(prop-1,2-dienyl)-lead(IV) is formed[20]. Prop-2-ynyl derivatives are especially readily isomerised into allene ones on heating in electron-donating solvents[67]. Thus when triphenylprop-2-ynyltin was boiled in 95% ethanol for 12 min it was completely converted into the allene isomer[67].

e. Other reactions. Hübel and Hoogzand[103] reported that trialkylethynylsilanes undergo cyclic trimerisation. Thus trimethylsilylacetylene forms 1,2,4-tris(trimethylsilyl)benzene at 100°C in the presence of tetracarbonylcobalt(IV)[103]. Possibly this reaction takes place through a stage of formation of an intermediate complex. This was confirmed recently by information published about the production of stable complexes from dialkynyl derivatives of silicon and germanium with tetracarbonylcobalt at room temperature in petroleum ether[104]:



## V. PHYSICAL PROPERTIES

$R_3EC\equiv CR'$ and $R_3EC\equiv CER_3$, where E = Si, Ge, Sn, are liquids which can be distilled when R = alkyl and solids when R = aryl. The boiling point rises from the derivatives of silicon to those of tin. All the compounds are readily soluble in most organic solvents. Most of the liquid acetylene derivatives of silicon, germanium, and tin are thermally stable; they can be readily distilled. Solid acetylene derivatives of silicon and germanium usually melt without decomposition as distinct from the tin and lead derivatives, which usually melt with decomposition.

The dipole moments of the silicon- and tin-enynes were measured[105,106]. The tin-enynes have a greater dipole moment than hydrocarbons and silicon-hydrocarbons of analogous structure. The dipole moments are always directed from the tin or silicon towards the acetylene grouping[106]. Stadnichuk and Petrov[80] calculated the dipole moment of triethylvinylacetylenegermane [but-3-en-1-ynyltriethylgermanium(IV)], which had a greater dipole moment than the silicon-enyne of analogous structure[80].

Many papers on the spectra of ethynyl compounds of Group IVb elements have been published recently. Usually the infrared spectra of the compounds obtained are used to identify the structure. The most complete information on the vibrational spectra of ethynyl organoelemental derivatives is given in Chumaevskii's review[107] and in the papers of Petrov, Shostakovskii, and their coworkers[37,44], Cadiot[11,40], Hartmann[5,10], and others[108,109].

Of the special spectroscopic studies, that of Shigorin and coworkers[110] deserves mention.

The greatest interest is in the position and intensity of the characteristic frequencies of the C≡C and ≡C–H stretching vibrations.

Study of the infrared spectra of acetylene derivatives of silicon, germanium, tin, and lead showed the shift and change in intensity of the absorption bands characteristic of the acetylene bond[13,108,109,111-116]. For example, the stretching vibration of the acetylene bond in the t-butylacetylene spectrum corresponds to a frequency of 2110 $cm^{-1}$, that for ethynyltrimethylsilane 2040 $cm^{-1}$, and for triethylethynylsilane[112] the analogous vibration appears at $\nu_{C\equiv C}$ = 2008 $cm^{-1}$. The intensity of the absorption bands of the acetylenic bond in these compounds increases on going from carbon to tin[113,114].

It is known[115,116] that in unsymmetrical disubstituted alkynes the frequency of the stretching vibrations of the C≡C bond is in the 2200–2260 $cm^{-1}$ region. Replacement of the carbon atom in the α position to the triple bond by a silicon atom[117] shows a drop in the frequency of the C≡C vibration of 75 $cm^{-1}$, and replacement of silicon by tin[115,116] leads to a further drop in frequency of 20 $cm^{-1}$.

Stadnichuk and Petrov investigated the infrared spectra of germanium-enynes[80] and showed that the triple bond in these compounds corresponds to an absorption band of 2147 $cm^{-1}$, that is, the same as in the silicon-enyne[116].

On the basis of the results obtained the authors conclude that the displacement of the triple bond vibrational band in the ethynyl derivatives of silicon, iron [germanium? (Ed. of Translation)], and tin is connected with a change in the bond polarity, which in turn can be explained by the intramolecular interaction of the $\pi$-electrons of the acetylenic bond with the vacant $d$-orbitals of silicon, germanium, and tin. By calculating the relative force constants of the triple bond in the acetylene derivatives of silicon and tin, the authors[116] were able to show that the displacement of the band of the triple bond of these compounds in the infrared spectra is not connected solely with the increase in mass of the atom on going from carbon to tin.

The peculiar light absorption of the $\alpha$-ethynyl compounds of the Group IVb elements has also been associated with $d\pi$-conjugation[118,119].

To explain the shortening of the Si–O and Si–X interatomic distances in comparison with the sum of the covalent radii of the elements forming the bond, Pauling[120] postulated in the 1940's the possibility of the participation of the $d$-orbitals of silicon in the formation of bonds. Carbon has only $s$- and $p$-orbitals in its outer shells, whereas the other elements of Group IVb have the closer $d$-orbitals, which can in principle participate in the formation of a chemical bond. When the molecule of an organoelemental compound contains multiple bonds in the $\alpha$ position to the element, it is possible for intramolecular interaction to occur, with displacement of the $\pi$-electrons and use of the vacant $d$-orbital of the element. The possibility of the participation of the $d$-orbitals in the formation of chemical bonds was given a theoretical basis by Craig and coworkers[121], Eaborn[122], and others[123].

Stone and Seyferth[123] and Webster[124] also concluded that $d\pi$-conjugation is possible.

Husk and West[125] observed that in the ion-radical of dodecamethylcyclohexasilane the electron is delocalised over the entire molecule, which also confirms the participation of the $d$-orbitals of silicon in conjugation. The hypothesis of $d\pi$-conjugation has become widely accepted. At the same time, the problem of $d\pi$-conjugation forms the subject of discussion since as yet there is no method which would allow this effect to be evaluated directly and all the evidence in support of this phenomenon is based on indirect proofs.

From the vibrational spectra of vinyl derivatives of the Group IV elements, Leites and coworkers[126] concluded that the frequency of the C=C group in carbon and organotin compounds is connected solely with a change in the inductive effect of the element. Note also that Bochvar and Gambaryan[127] made quantum-mechanical calculations of the contribution of the $d$-orbitals of silicon and germanium to the bond formation in the vinyl compounds of these elements and found that it was very small and comparable in magnitude with the energy contribution of the $p$-orbitals of the carbon atom in compounds of analogous structure.

However, most research chemists still maintain the view that there is $d\pi$-conjugation between the vacant $d$-orbitals of the silicon, germanium, and tin atoms and the $\pi$-electrons of the unsaturated bonds situated in the $\alpha$ position to the hetero-atoms. There is still no single opinion as to the relative value of the $d\pi$-interaction in the derivatives of Si, Ge, Sn, and Pb. Some authors think that the $d\pi$-conjugation diminishes in the order Si > Ge > Sn[128], others, that is it independent of the element[129].

Gastilovich and coworkers[110] carried out an interesting investigation of the infrared spectra of the compounds

$$(CH_3)_3—CH_2—C\equiv CH \quad (I)$$
$$(CH_3)_3SiC\equiv CH \quad (II)$$
$$(C_2H_5)_3Sn(C\equiv CH) \quad (III)$$

in the region of the stretching vibrations of the C≡C and ≡C–H groups and calculated the effect of the mass of the element (from C to Sn), the rigidity of the E–C bond (E = Si, Sn), and of the intermolecular interaction on anomalies in the spectra and showed that these factors are insufficient to explain the displacement and change in intensity of the frequencies of the C≡C stretching vibrations, which is observed in compounds (II) and (III). On the basis of these results conclusions were drawn about the intramolecular interaction of the $\pi$-electrons of the triple bond with the $d$-orbitals of the Si and Sn atoms, which also determines the frequency change.

Another approach to evaluation of the $d\pi$-interaction in ethynyl derivatives of Si, Ge, Sn, and Pb from their infrared spectra has been made by Cadiot[11]. The author started from Kross's results[130] on the electronegativities of the Group IVb elements calculated from the frequencies of the infrared vibrations of the phenyl nuclei connected with the element and found a linear dependence of electronegativity on the C≡C bond frequency in $(C_6H_5)_3E(C\equiv CR)$. In appeared that the change in $\nu_{C\equiv C}$ in the order Si > Ge > Sn > Pb is connected with the decrease in electronegativity from Si to Pb which had been proposed by other authors[80,115], Cadiot[11] showed that on the basis of the Bykov equation[131], which relates the wave number of bands in the infrared spectrum with the electronic charge of the C≡C bond ($\nu^{2\alpha}_{C\equiv C} = KA_{C\equiv C}$), it can be concluded that the decrease in frequency for the C≡C bond in $\gtrless E-C\equiv C$ in the series from C to Pb is connected with the decrease in the charge on this bond; this is a consequence of the partial overlap of the $\pi$-electron cloud and the $d$-orbitals of the element.

The ultraviolet spectra of the ethynyl derivatives of silicon, germanium, and tin have also been investigated[11,18,108,109]. A bathochromic shift and increase in intensity of the bands has been observed in comparison with the acetylene hydrocarbons of analogous structure.

Comparatively recently there have been papers on the proton magnetic resonance spectra of the ethynyl compounds of the Group IVb elements[11,18,26,80,101,102,132,133]. For example, Egorochkin and coworkers[134] investigated the NMR spectra of ethynyltrimethylsilane and ethynyltrimethylgermanium(IV). The proton chemical shifts for the carbon atom of the ethynyl group are displaced to weaker fields compared with the proton shifts in saturated radicals, which the authors explain by the intramolecular interaction of the C≡C bond with the element atom. The large shift of the $\pi$-electrons towards the silicon atom compared with the germanium analogue leads to a more significant decrease in the electron density at the protons at the triple bond of the ethynylsilicon compounds. This is due to a stronger displacement of the chemical shift for ≡C–H to weaker fields in ethynyltrimethylsilane.

The NMR spectra of prop-2-ynyl compounds of silicon and tin have been obtained[101,102]; the chemical shifts of the protons of the methylene and acetylene groups decrease with decrease in the electronegativity of the elements and

are greatly dependent on the substituents at the elements, on the solvents, and on the concentration of the solution.

Simonnin[133] also investigated the NMR spectrum of compounds of the type $R_3E-(C\equiv C)_m-CH_3$ and $R_3E(C\equiv C)_m-H$, where E = Si, Ge, Sn and $m = 1, 2, 3$, labelled with $^{13}C$ in the $\alpha$, $\beta$, and $\gamma$ positions. The greatest difference in the chemical shifts of the ethynyl proton was observed in compounds with a $^{13}C-H$ bond (up to 39%).

Fedin and coworkers[132] found, in studying the NMR spectra of diethyldiphenyl-silane and -germane, that the silicon and germanium in these compounds are acceptors of electrons in relation to the phenyl nuclei. In diphenyldiprop-2-ynylgermane and diphenyldiprop-2-ynylsilane the signals of the ethynyl protons are shifted to stronger fields, by $0.8 \times 10^{-6}$ for silicon and by $0.5 \times 10^{-6}$ for germanium, relative to hexamethyldisiloxane.

Cadiot and coworkers[11,18] observed the proton chemical shifts in the NMR spectra of ethynyl compounds of tin. They interpreted the results from the standpoint of $d\pi$-conjugation.

To conclude this part of the review it must be emphasised that the hypothesis of $d\pi$-conjugation has been extremely fruitful and has stimulated considerably investigations in the field of the synthesis of ethynyl compounds of the Group IVb elements. This is equally true of the investigation of the physical properties of these compounds, particularly the infrared absorption spectra. Despite the fact that the interpretation of the spectral properties from the viewpoint of $d\pi$-interaction was evidently unsound, as a result of the work of many authors we have now, a large collection of spectral data, which is used successfully in chemical investigations for identification and for finding the structure of the compounds obtained.

## VI. ORGANIC POLYMERS OF SILICON, GERMANIUM, AND TIN, CONTAINING ACETYLENIC GROUPINGS

The introduction of silicon, germanium, or tin into a polymeric chain is of great interest since, being situated in the same subgroup as carbon, they should have properties analogous to those of carbon, yet having a different electronic structure they should display their own specific properties.

Since the silicon, germanium, and tin atoms exhibit acceptor properties and their $d$-orbitals can draw away the $\pi$-electrons of a multiple bond, there is particular interest in polymers in which atoms of silicon, germanium, and tin alternate with acetylenic groupings. Such polymers could be expected to show interesting electrophysical properties. The first indication that such polymers could be made came in 1962 [135,136,137].

Korshak and coworkers[136] suggested that organosilicon and organogermanium polymers with acetylenic bonds in the chain could be synthesised by polycondensation of dihalogeno-organoelemental compounds with the bis-sodium (or bromomagnesium) derivatives of alkadiynes:

$$n\,R_2ECl_2 + n\,(Na)\,BrMg-C\equiv C-R'-C\equiv C-MgBr\,(Na) \longrightarrow$$
$$\longrightarrow [ER_2-C\equiv C-R'-C\equiv C]_n + 2n\,Mg\,Br\,(Na)\,Cl$$
$$n\,R_2ECl_2 + n\,BrMgC\equiv CMgBr \longrightarrow [ER_2-C\equiv C]_n,$$

where E = Si or Ge; R = $CH_3$, $C_2H_5$, or $C_6H_5$; R′ = $-C_6H_4-$.

Later a patent[138] described the preparation of polymers of the type

$$[ER_2-C\equiv C-R'-C\equiv C]_n$$

by the reaction of dilithium derivatives of alkadiynes with halogen compounds of silicon, germanium, and tin.

Sladkov and coworkers[139] proposed the preparation of organotin polymers with acetylenic groupings by the polycondensation of dialkyldimethoxystannanes and bisacetylenes:

$$n\,CH_3O-\underset{\underset{R}{|}}{\overset{R}{|}}{Sn}-OCH_3 + n\,HC\equiv C-R'-C\equiv CH \longrightarrow \left[\underset{\underset{R}{|}}{\overset{R}{|}}{Sn}-C\equiv C-R'-C\equiv C\right]_n;$$

where R = $CH_3$, $C_4H_9$; R′ = $-C_6H_4-$, $-GeR_2-$, or $-SiR_2-$

The authors confirmed[137,139] the structure of the polymers obtained from their infrared and NMR spectra. The polymers react with bromine only at elevated temperature (70–100°C), whereupon two bromine atoms are added at each triple bond[137]:

$$[ER_2-C\equiv C]_n \xrightarrow{nBr_2} [ER_2-CBr=CBr]_n.$$

$$[ER_2-C\equiv C-R'-C\equiv C]_n \xrightarrow{2n\,Br_2} [ER_2-CBr=CBr-R'-CBr=CBr]_n.$$

Hydrogenation of the polymers (20°C, Raney nickel) leads to the preparation of polymers with completely saturated bonds.

The organosilicon and organogermanium polymers which have been obtained are thermally stable up to 450–550°C; the organotin polymers, up to 300–350°C.[137]

Investigation of the electrophysical properties of the polymers has shown that organoelemental polymers in which atoms of silicon, germanium, and or tin alternate with unsaturated bonds exhibit high electrical resistivity at room temperature ($10^{11}$–$10^{13}$ Ω cm) but it decreases with rise in temperature. The activation energy for conductivity by the polymers lies in the range 0.64–1.04 eV.[137]

A photo-e.m.f. (10 mV $mW^{-1}$) is observed with almost all the polymers that have been obtained[137,140].

It has been shown[137,141] that many of these polymers can be used as active electrographical layers.

A patent[138] has proposed the use of organoelemental polymers (where the element is silicon, germanium, tin, antimony, etc.) with acetylenic groupings for the manufacture of semiconductor materials.


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Institute of Organoelemental Compounds,
Academy of Sciences of the USSR,
Moscow

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# π-ALLYL COMPLEXES OF THE TRANSITION METALS

M. I. Lobach, B. D. Babitskii, and V. A. Kormer

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