HOMOLYTIC ADDITION REACTIONS TO SILICON-, GERMANIUM AND TIN UNSATURATED COMPOUNDS*

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Summary

In our work homolytic addition reactions of the silicon-, germanium- and tin containing unsaturated compounds were reported. Homolytic reactions of group IV alkenyl derivatives with alkanethiols, other sulfur containing compounds and halogeno derivatives were investigated in organic and organometallic synthesis. Dependence of yield on the alkyl group nature, the reagent ratio and reaction temperature was studied.

In the past decade, the use of organosilicon compounds as reagents and as intermediates in organic synthesis has become a field of considerable interest. Their wide applications are based on the characteristic properties of the silicon atom. Indeed, electrophilic attack on vinyl, allyl and alkynyl groups can often be controlled by the presence of a silyl moiety in the starting material. The silyl group usually encourages attack at that site which will generate a carbonium ion, or at least an electron deficiency, beta to silicon, and it is usually the silyl group which is lost in the second step of the reaction.

The principal regularities and mechanism of the homolytic reactions of Group IV element alkenyl derivatives is much less understood.

$$\mathrm{Et_3SnCH{=}CH_2 + CCl_3X \xrightarrow{Bz_2O_2} Et_3SnCHXCH_2Cl_3}$$

$X = \mathrm{Cl, Br}$

D. Seyferth, 1957

$$\mathrm{Et_3SnCH{=}CH_2 + HSCH_2COOC_2H_5 \xrightarrow{90\,^\circ C} Et_3SnSCH_2COOC_2H_5 + CH_2{=}CH_2}$$

D. Seyferth, 1957

$$\mathrm{Bu_3Sn(CH_2)_nCH{=}CH_2 + H_2S \xrightarrow[-70\,^\circ C]{h\nu} Bu_3Sn(CH_2)_{n+2}SH}$$

$$\mathrm{Bu_3Sn(CH_2)_nCH{=}CH_2 + CH_3COSH \xrightarrow[25\,^\circ C]{h\nu} Bu_3Sn(CH_2)_{n+2}SCOCH_3}$$

$n = 0, 1$

W. Stamm, 1963

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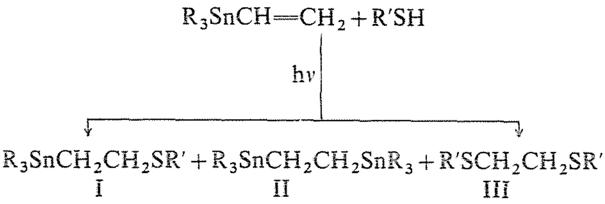
The first steps in the research of homolytic addition reactions to tin unsaturated compounds were made more than two decades ago. Polyhalomethanes add to triethylvinyltin in the presence of benzoyl peroxide at about 90–95 °C to give moderate yield of the adduct [1, 2]. Heating of equivalent quantities of triethylvinyltin and ethyl mercaptoacetate gives only the cleavage product, ethyl-S-(triethylstannyl)-mercaptoacetate.

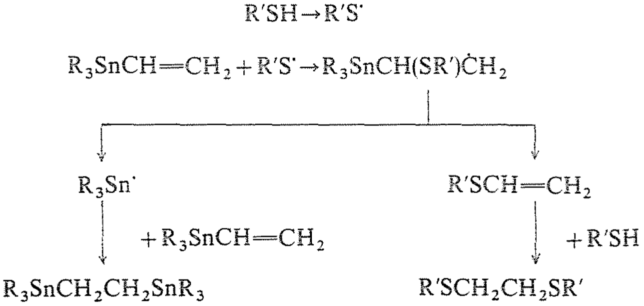
UV-catalyzed reactions of hydrogen sulfide or thiolacetic acid and tributylvinyltin proceed with formation of the corresponding adducts [3].

A similar route is observed with tributylallyltin.



R = Et, n-Bu, R' = i-Pr, n-Bu, t-Bu

We have established that the photochemical reaction of trialkylvinyltin with alkanethiols leads to three products: 1-trialkylstannyl-2-alkylthioethane (compound I), 1,2-bis(trialkylstannyl)ethane (compound II) and 1,2-bis(alkylthio)ethane (compound III) [4]. Compound I results from the attack of the thiyl radical at the beta-carbon atom of the double bond. Under the conditions employed, this adduct undergoes no disproportionation. Therefore, the formation of compounds II and III may be explained by the following scheme.



$$R_3Sn^{\cdot} + BrC_6H_5 \xrightarrow{\text{H-donor}} R_3SnBr + C_6H_6$$

This scheme suggests the addition of the thiyl radical at the alpha-carbon of the double bond followed by beta-fragmentation of the beta-carbon centered radical adduct. In order to confirm the formation of trialkylstannyl radical we have carried out the reaction in the presence of bromobenzene [5]. It is known that trialkylstannyl radicals react readily with this trap [6]. If the trialkylstannyl radical is, in fact, involved as an intermediate, the presence of bromobenzene should lead to a decrease in the yield of compound II and the appearance of trialkylbromotin and benzene in the reaction mixture. This suggestion was confirmed experimentally.

The II to III ratio is equimolar in all the cases, whereas the yield of adduct I is determined by the structure of alkanethiol and substituents at the tin atom.

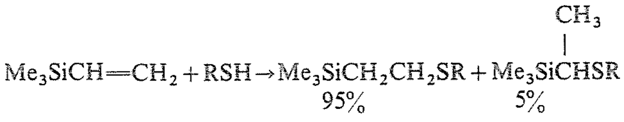
Table I

Dependence of the yield of $R_3SnCH_2CH_2SR'$ on the R and R' nature

R	R'		
	i-Pr	n-Bu	t-Bu
Et	64	60	67
n-Bu	94	—	—

So, the thiylation of trialkylvinyltin proceeds in a non-regioselective fashion. This is in contrast to the highly regioselective behaviour of isostructural carbon compounds.

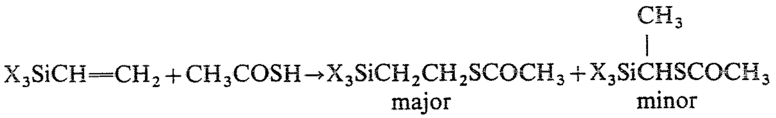
Therefore, we decided to examine the factors governing the regioselectivity of homolytic thiylation of compounds of the type $R_3MCH{=}CH_2$ with M = Si, Ge, Sn.



$$Me_3SiCH{=}CH_2 + RSH \rightarrow \underset{95\%}{Me_3SiCH_2CH_2SR} + \underset{5\%}{Me_3Si\overset{\overset{\displaystyle CH_3}{|}}{C}HSR}$$

$R = Ph, PhCH_2, CH_2COOH, CH_2CH_2COOH$

K. Wetterling, 1964

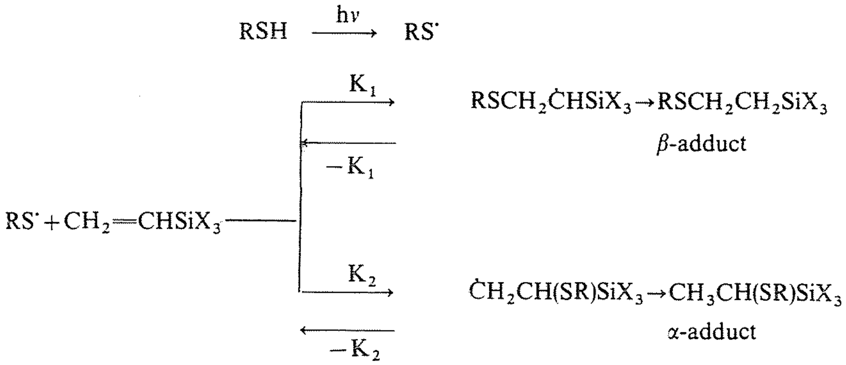


$$X_3SiCH{=}CH_2 + CH_3COSH \rightarrow \underset{\text{major}}{X_3SiCH_2CH_2SCOCH_3} + \underset{\text{minor}}{X_3Si\overset{\overset{\displaystyle CH_3}{|}}{C}HSCOCH_3}$$

$X = Me, MeO, EtO, Cl$, etc.

G. A. Gornowicz, 1968

As early as two decades ago it was found that the free-radical reactions of triorganylvinylsilanes with thiols led to two isomeric adducts [7, 8].



R = Me, i-Pr, n-Bu, t-Bu
X = Me, Et, MeO

We have shown that the regioselectivity of the homolytic reaction of triorganylvinylsilanes with alkanethiols is determined by initial compound ratio, reaction temperature and the nature of alkanethiol and substituents at silicon [9].

As seen from this slide an increase in the reaction temperature and a decrease in the alkanethiol concentration lead to a slight decrease in the alpha-adduct yield and an increase of the regioselectivity. This may be explained in terms of different degree of reversibility at the primary steps of the reaction [10].

Next slide shows the data concerning the effect of the alkanethiol structure and the substituent at the silicon atom on the regioselectivity of homolytic thiylation of triorganylvinylsilanes. It is seen that greater steric hindrance, i.e. more bulky substituents at the silicon atom and branching of the thiyl radical, enhances the regioselectivity of the reaction.

Table II

Dependence of the regioselectivity of homolytic addition of n-BuSH (I) to $Me_3SiCH{=}CH_2$ (II) on the reagent ratio and reaction temperature

I:II	Reaction temperature	Yield of α-adduct, %	β:α
1:2	45	6.0	15.7
1:1	45	6.6	14.2
2:1	45	7.6	12.2
1:1	15	8.6	10.6
1:1	30	7.7	12.0
1:1	60	6.0	15.7

Table III

Effect of the structure of RSH and $X_3SiCH{=}CH_2$ on the yield of α- and β-adducts

R	X_3	Yield of α-adduct, %	β:α
Me	Me_3	12.0	7.3
n-Bu	Me_3	7.0	13.3
i-Pr	Me_3	6.0	15.7
t-Bu	Me_3	3.0	32.3
Me	Et_3	6.0	15.7
n-Bu	Et_3	5.0	19.0
i-Pr	Et_3	4.0	24.0
t-Bu	Et_3	1.8	53.5
Me	Me_2MeO	11.0	8.1
Me	$Me(MeO)_2$	9.8	9.0
Me	$(MeO)_3$	4.0	24.0

The regioselectivity also increases when electronegative substituents are attached to the silicon atom. In the addition of methylmercaptane the lowest alpha-adduct yield is observed with vinyltrimethoxysilane. This is due to the fact that the methoxy groups favour delocalization of the unpaired electron into the adjacent vacant d-orbitals of silicon and stabilization of the alpha-carbon centered radical formed.

In going from triorganylvinylsilanes germanium compounds the regioselectivity of homolytic thiylation drops and the yield of the alpha-adduct in the reaction of triethylvinylgermane with n-butanethiol reaches 12%.

Let us consider the factors reducing the regioselectivity of homolytic thiylation of vinyl derivatives of IV B group elements in going from carbon to tin. It is known that the rate and direction of the homolytic addition are determined by stability of the radical adduct formed, steric availability of the carbon atom being attacked, electrophilicity or nucleophilicity of the radical and distribution of electron density in the alkenyl moiety. The alkenyl derivaties studied are characterized by decreased steric screening of the alpha-carbon atom of the double bond in the series carbon < silicon < germanium < tin, which is due to an increase in the element-carbon bond length and the bulk of the element atom. This should reduce the regioselectivity of homolytic addition in the above series. Other two factors work in the same direction. These are relatively higher charge of the alpha-carbon atom of the double bond as compared to carbon analogs and the electrophilicity of thiyl radicals. And, finally, the R_3M group with M=Si, Ge and Sn is able to stabilize the beta-carbon centered radical which favours the formation of the alpha-isomer [11–13]. Thus, the low selectivity of homolytic thiylation of triorganylvinylstannanes becomes quite understandable. The formation of 1,2-bis(triorganylstannyl)ethane (compound II) and 1,2-bis(alkylthio)-ethane (compound III) instead of the corresponding alpha-adduct results from the low energy of the tin-carbon bond. Since the alkanethiols are good chain transfer agents the beta-carbon centered radical formed with M=Si and Ge abstract readily the hydrogen atom from the thiol to give the alpha-adduct. With M=Sn, the low energy of the Sn—C bond leads predominantly to the "beta-fragmentation" of the intermediate radical. The possibility of such processes with M=Ge and Si is not excluded, however, when reactants less capable for chain transfer than the alkanethiols studied are used.

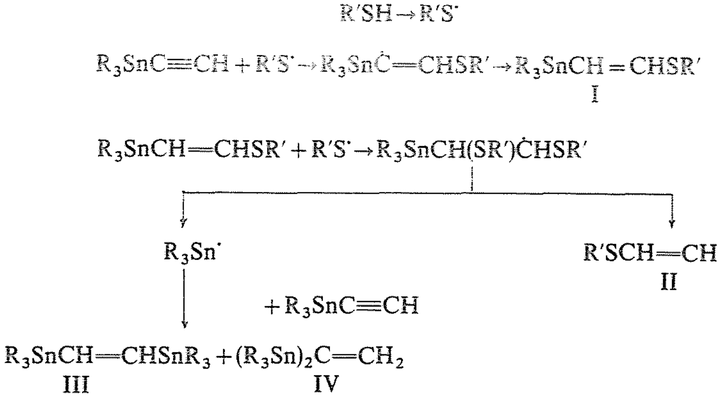
Further on the regioselectivity of homolytic thiylation of trialkylethynylstannanes have been studied.

$$\begin{gathered} Et_3SnC{\equiv}CH + RSH \\ \downarrow h\nu \\ Et_3SnCH{=}CHSR + Et_3SnCH_2CH(SR)_2 + Et_3SnSR \end{gathered}$$

N. V. Komarov et al., 1974

As it has been established previously, alkanethiols and thiophenol react with triethylethynylstannanes in the presence of radical initiators to form 1-(triethylstannyl)-2-organylthioethylene, 1-(triethylstannyl)-2,2-bis(organylthio)ethane and triethyl(organylthio)stannane [14]. The yield of the monoadduct is within 4–50%. Triethyl(organylthio)stannane was supposed to be formed by homolytic cleavage of the tin-acetylenic bond.

It has been shown, however, that the formation of triethyl(n-butylthio)stannane is completely excluded when the reaction is carried out upon UV-irradiation at 25 °C in the presence of azobisisobutyronitrile using freshly distilled starting reagents. Triethyl(n-butylthio)stannane was the only reaction product when the reaction mixture contained hydroquinone. These data indicate that triethyl(n-butylthio)stannane results from an ionic reaction.



$$R'SH \rightarrow R'S^{\cdot}$$

$$R_3SnC{\equiv}CH + R'S^{\cdot} \rightarrow R_3Sn\dot{C}{=}CHSR' \rightarrow \underset{I}{R_3SnCH{=}CHSR'}$$

$$R_3SnCH{=}CHSR' + R'S^{\cdot} \rightarrow R_3SnCH(SR')\dot{C}HSR'$$

$$R_3SnCH(SR')\dot{C}HSR' \rightarrow R_3Sn^{\cdot} + \underset{II}{R'SCH{=}CHSR'}$$

$$R_3Sn^{\cdot} \xrightarrow{+R_3SnC\equiv CH} \underset{III}{R_3SnCH{=}CHSnR_3} + \underset{IV}{(R_3Sn)_2C{=}CH_2}$$

$R = Et$, n-Bu; $R' =$ n-Bu, i-Pr

UV-irradiation of triethylethynylstannane and butanethiol affords a complex mixture of products separated by preparative GLC [15, 16]. The structure of the compounds was confirmed by NMR spectroscopy.

As seen from this slide, mono-adduct, 1-(triethylstannyl)-2-(alkylthio)-ethylene forms at the first stage. The addition of the thiyl radical at the alpha-carbon of this monoadduct leads to a beta-carbon centered which, similarly to the case of homolytic thiylation of alkylvinylstannanes, undergoes "beta-fragmentation" to yield 1,2-bis(alkylthio)ethylene (compound II) and triethylstannyl radical. The latter reacts with the triethylethynylstannane in the presence of the hydrogen donor (alkanethiol) to form a mixture of trans-1,2- and 1,1-bis(triethylstannyl)ethylene (compound III and IV, respectively).

The formation of triethylstannyl radicals in this reaction was proved by "bromobenzene trap". The addition of bromobenzene results in nearly complete disappearance of bis(triethylstannyl)ethylene isomers from the reaction mixture. Instead, considerable amounts of benzene and triethylbromostannane appear.

$$R_3MC{\equiv}CH + HSR' \rightarrow R_3MCH{=}CHSR' + R_3MCH(SR')CH_2SR' + R_3MCH_2CH(SR')_2$$

$M = C, Si, Ge$

$R = Me, Et; R' = n\text{-}Bu, i\text{-}Pr, t\text{-}Bu$

Table IV

Effect of the structure of alkanethiol and triorganylethynylsilane on the ratio of $X_3SiCH(SR)CH_2SR$ (I) and $X_3SiCH_2CH(SR)_2$ (II)

X_3	R	I:II
Me_3	n-Bu	19:1
Me_3	i-Pr	19:1
Me_3	t-Bu	3:1
Et_3	n-Bu	3:2
Et_3	i-Pr	1:2
Et_3	t-Bu	0:1
Me_2MeO	i-Pr	1:2
$Me(MeO)_2$	n-Bu	1:1
$Me(MeO)_2$	i-Pr	0:1
$Me(MeO)_2$	t-Bu	0:1

In order to establish general rules of free-radical reactions of this type the homolytic thiylation of germanium and silicon ethynyl derivatives and their isostructural carbon analog, tert-butylacetylene, occurring according to the scheme, shown on the slide [17, 18] have been studied.

The addition of the first molecule of alkanethiol is regiospecific leading to mono-adduct as a mixture of cis- and trans-isomers the latter being predominant. The yield of the mono- and di-adducts depends on the starting reagent ratio, the M atom nature, the alkane thiol structure and substituent at the M atom. The portion of the diadducts decreases in going from carbon to silicon and germanium. The relative yield of diadduct increases with increasing the concentration of alkanethiol and with decreasing the length and branching of alkanethiol and the bulk of substituent at M.

The addition of the second molecule of alkanethiol is more complex. If tert-butylacetylene is the case, the alkanethiol adds regiospecifically to the monoadduct to form only the alpha, beta-diadduct. The only exclusion is the reaction of tert-butylacetylene with tert-butanethiol, which stops at the stage of the monoadduct formation seemingly due to strong steric hindrance disfavouring the addition of the second alkanethiol molecule.

With M=Ge, the addition of the second alkanethiol molecule also leads predominantly to the alpha, beta-diadduct. The yield of the beta, beta-diadduct does not exceed 1–2%.

The addition of two molecules of alkanethiol to triorganyl-ethynylsilanes gives, on the contrary, a mixture of the isomeric diadducts in a ratio depending on the structure of alkanethiol and substituents at the silicon atom.

As seen from this slide, the formation of a considerable amount of the beta,beta-diadduct is observed only with triorganylethynylsilanes. This shows that the silicon atom stabilizes the alpha-carbon centered radical more effectively than carbon and germanium do. This is in agreement with the data on the regioselectivity of homolytical thiylation of triorganylvinylsilanes.

In going from trimethyl—to triethylethynylsilane the relative content of the beta,beta-isomer increases due to steric factors.

The ratio of the isomeric diadducts is greatly influenced by the structure of alkanethiol.

The yield of beta,beta-diadduct increases in going from methylthiol to n-propylthiol to iso-propylthiol and to tert-butylthiol. This order cannot be explained in terms of steric factors only, since an increase in the bulk of thiyl radical should have hindered the addition at both the alpha- and beta-carbon atom of the monoadduct. From the ^{13}C NMR data, an increase in the bulk of the alkyl radical at the sulfur atom decreases the electron density at alpha-carbon of the double bond of the monoadduct [19]. This is caused by lower conjugation between the sulfur atom and the double bond due to disorder in p-pi coplanarity. In view of the electrophilicity of the thiyl radicals, this should increase the relative yield of the beta,beta-diadducts with increasing the size of alkanethiol observed experimentally.

$$\begin{tikzcd}
\mathrm{Me_3SiCH{=}CHSBu + t\text{-}BuS^{\cdot}} \arrow[r, shift left] & \mathrm{Me_3Si\dot{C}HCH(SBu)(SBu\text{-}t)} \arrow[l, shift left] \arrow[r, "\text{H-donor}"] \arrow[d, shift right] & \mathrm{Me_3SiCH_2{-}CHSBu(SBu\text{-}t)} \\
 & \mathrm{Me_3SiCH{=}CHSBu\text{-}t + BuS^{\cdot}} \arrow[u, shift right] &
\end{tikzcd}$$

This slide illustrates that the homolytic addition of alkanethiols to 1-(triorganylsilyl)-2-(alkylthio)ethylenes is a reversible reaction. Thus, 1-(trimethylsilyl)-2-(tert-butylthio)ethylene was identified as one of the reaction products after UV-irradiation of a mixture of 1-(trimethylsilyl)-2-(n-butylthio)ethylene with tert-butanethiol [20].

Research of the homolytic thiylation of carbon, silicon and germanium acetylenic derivatives has shown that the addition of the second molecule of alkanethiol gives mainly the corresponding alpha,beta-diadducts, in yield increasing in going from carbon to germanium.

$$\mathrm{RC{\equiv}CH + HSMR'_3} \xrightarrow{h\nu} \mathrm{RCH{=}CHSMR'_3}$$

$\mathrm{M = Ge, Si;\ R = t\text{-}Bu, Ph, Me_3Si, Et_3Ge}$

Heteroatomic thiols, such as trialkylgermane- and trialkylsilanethiols can be readily involved in the homolytic thiylation of monosubstituted acetylenes [21, 22].

The yield of monoadducts is nearly quantitative. These monoadducts are a mixture of cis- and trans-isomers, the latter being predominant. As established by NMR, the above monoadducts within the 20–200 °C temperature range do not undergo metallotropic rearrangements common to their oxygen analogs [23].

$$\begin{tikzcd}
 & \mathrm{R_3SnC(SR'')\!=\!CHR'} \\
\mathrm{R_3SnC{\equiv}CR' + HSR''} \arrow[ur] \arrow[dr] & \\
 & \mathrm{R_3SnSR'' + R'C{\equiv}CH}
\end{tikzcd}$$

$\mathrm{R = Me, Et;\ R' = Ph, SBu, n\text{-}Bu}$

The homolytic reaction of 1-(trialkylstannyl)-2-organylacetylenes with alkanethiols is much slower than that with the corresponding trialkylethynylstannanes. The former is accompanied by heterolytic cleavage of the tin-acetylenic bond. It was possible to obtain the adducts only with phenyl and butylthio derivatives, whereas with 1-trialkylstannyl-2-n-butylacetylene the formation of only cleavage product is observed. In the case of bis(trialkylstannyl)acetylene only one trialkylstannyl moiety is abstracted, the yield of trialkylethynylstannane amounting to 65%. This reaction may be recommended as a convenient preparative method of the synthesis of trialkylethynylstannanes [24].

$$R_3MC{\equiv}CPh + n\text{-}BuSH \xrightarrow{h\nu} R_3MC(SBu\text{-}n){=}CHPh$$

$M = Ge, Si$

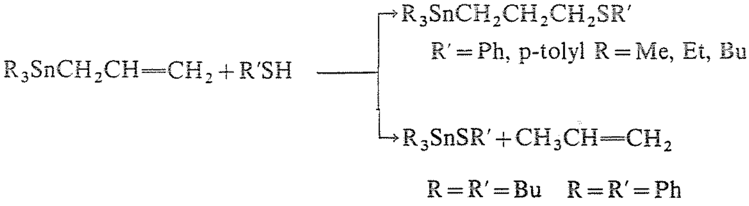
Analogous reactions of 1-trialkylgermyl- and 1-trialkylsilyl derivatives of 2-substituted acetylene have been studied. Bis(trialkylsilyl)- and bis-(trialkylgermyl)acetylenes are inert towards alkanethiols. 1-Trialkylsilyl- and 1-trialkylgermyl-2-phenylacetylenes react with alkanethiols very slowly to form adducts. The yield of the adducts after UV-exposure for 30 hours at 60 °C is 39 and 66% for silicon and germanium derivatives, respectively. This seems to reflect the difference in the triple bond steric availability.

$$R_3MCH{=}CH_2 + R_{Hal}X \rightarrow R_3MCXHCH_2R_{Hal}$$

$$R_3MC{\equiv}CH + R_{Hal}X \rightarrow R_3MCX{=}CHR_{Hal}$$

For comparison with the homolytic thiylation of trialkylvinyl and ethynyl tin, germanium and silicon derivatives the other free-radical reactions of these compounds have been studied in particular, the addition of polyhalomethanes. [25, 26] The reaction proceeds in all cases regioselectively to give the polyhaloalkyl terminal adduct.

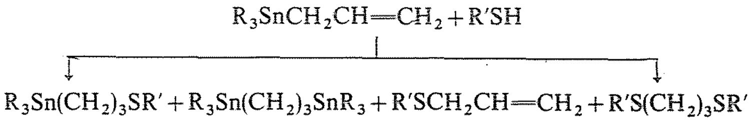
The investigation of the homolytic addition to vinyl and ethynyl derivatives of tin, germanium and silicon shows that the reactions which seem to involve the formation of beta-carbon centered radical with respect to the heteroatom are most interesting from the synthetic point of view. This is related first of all, to the addition reaction to allyl, propargyl, vinyloxy-, vinylthio- and some other unsaturated derivatives of tin, and, to a less extent, germanium and silicon.



$$R_3SnCH_2CH{=}CH_2 + R'SH \rightarrow R_3SnCH_2CH_2CH_2SR' \quad R' = Ph,\ p\text{-tolyl}\ R = Me, Et, Bu$$

$$R_3SnCH_2CH{=}CH_2 + R'SH \rightarrow R_3SnSR' + CH_3CH{=}CH_2 \quad R = R' = Bu \quad R = R' = Ph$$

G. Ayrey et al., 1972



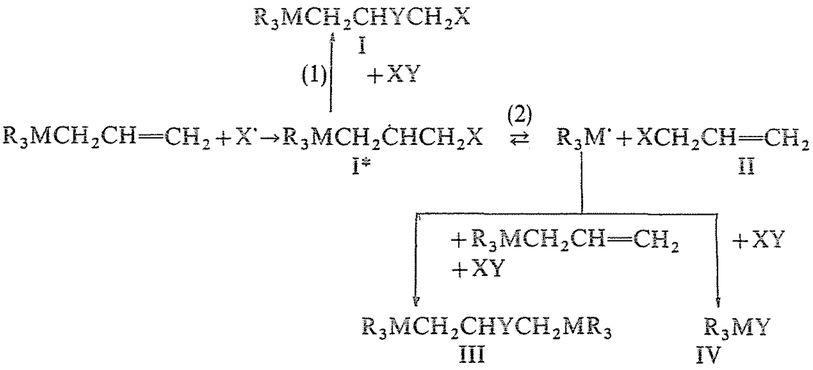
$$R_3SnCH_2CH{=}CH_2 + R'SH \rightarrow R_3Sn(CH_2)_3SR' + R_3Sn(CH_2)_3SnR_3 + R'SCH_2CH{=}CH_2 + R'S(CH_2)_3SR'$$

M. G. Voronkov et al., 1980

As it has been shown by Ayrey et al., [27] the homolytic addition of arenethiols to trialkylallylstannanes leads to 1-(trialkylstannyl)-3-alkylthiopropanes. Preferential cleavage of the allyl group occurs in the case of butanethiol.

This reaction has been studied in detail and found to proceed in a more complicated way [28].

$$X-Y \rightarrow X^{\cdot}-Y^{\cdot}$$



This reaction is a particular case of the general homolytic addition of X−Y species to Group IVB trialkylallyl derivatives involving the "beta-fragmentation" of intermediate radical and may be represented as shown on this slide.

According to this scheme, the yield of compounds I–IV is determined by chain transfer rate of the step 1 and reversibility at step 2. Other conditions being equal, the chain transfer rate accelerates with increasing of XY concentration.

Table V

Dependence of the yield of products of the homolytic reaction of Me_3SH (A) with $Et_3SnCH_2CH{=}CH_2$ (B) on the reagent ratio

Product	Yield, %			
	A:B 1:2	1:1	2:1	3:1
$Et_3SnCH_2CH_2CH_2SMe$	50.5	60.0	70.5	78.0
$Et_3SnCH_2CH_2CH_2SnEt_3$	37.0	30.0	20.0	14.0
$CH_2{=}CHCH_2SMe$	12.0	7.5	2.7	0.3
Et_3SnSMe	0	2.0	6.0	7.0

The data of this table show that an increase in the concentration of alkanethiol in the reaction with triethylallylstannane enhances the yield of normal adduct and diminishes the yield of anomalous product. When the reaction is carried out in the presence of bromobenzene, the reaction mixture contains benzene and triethylbromotin, the yield of adduct I decreasing with an increase in the bromobenzene concentration.

The reversibility at step 2 should be greatly affected by thermodynamic factors. In fact, with an increase in the M – C bond strength the reaction is shifted to the left. In the case of the addition of ethanethiol to triethylallylgermane, for example, the terminal adduct is formed only.

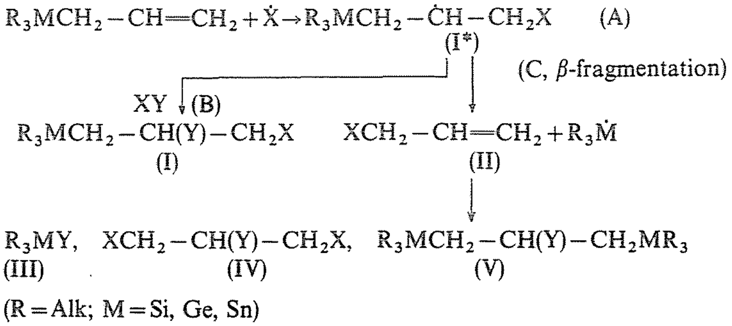
Table VI

Effect of the addend structure on the homolytic reactions of triethylallylstannane

Product	Yield, %		
	EtSD	EtSH	EtSeH
$Et_3SnCH_2CHYCH_2X$	33	43	100
$Et_3SnCH_2CHYCH_2SnEt_3$	55	47	0
$Et_3SnY + XCH_2CH{=}CH_2$	12	10	0

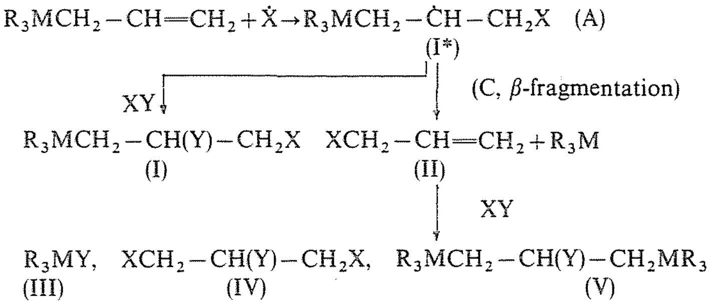
This table illustrates the effect of the addend structure on the radical addition to triethylallylstannane. In this reaction the yield of the terminal adduct drops in going from ethylselenol to ethylthiol and its deutero analog. The ability of these reagents for chain transfer changes in the same order.

On the basis of the above reaction mechanism the yield of anomalous products in the homolytic reactions might be expected to increase in going from alkanethiols to polyhalomethanes. This is due to the fact that the latter are considerably poorer chain transfer agents.



Indeed, the reaction of various halo compounds with trialkylallylstannanes leads to only the products of tin-carbon bond cleavage, as shown on this slide [29].

The mechanistic aspects of homolytic addition to Group IV B allyl derivatives have been studied by radiofrequency probing and chemically induced dynamic nuclear polarization (CIDNP) using the reaction of triethylallylstannane with trichlorobromomethane as a model.



(R = Alk; M = Si, Ge, Sn)

The method of radiofrequency probing consists of the action of an additional radiofrequency field upon certain atoms or groups of atoms in the studied substance according to the NMR spectra detected during the reaction. [30]. As a result, the NMR signal intensity of the reaction product can be either reduced (saturation of the signal in the case of homonuclear decoupling) or increased (due to the nuclear Overhauser effect in the case of heteronuclear decoupling). Under certain conditions the radiofrequency probing of molecules allows one to trace the fate of "labelled" atoms during the reaction and to determine the reaction mechanism.

This figure shows the NMR spectra of the reaction mixture of allyltriethylstannane with bromotrichloromethane in cyclo-C_6D_{12} under

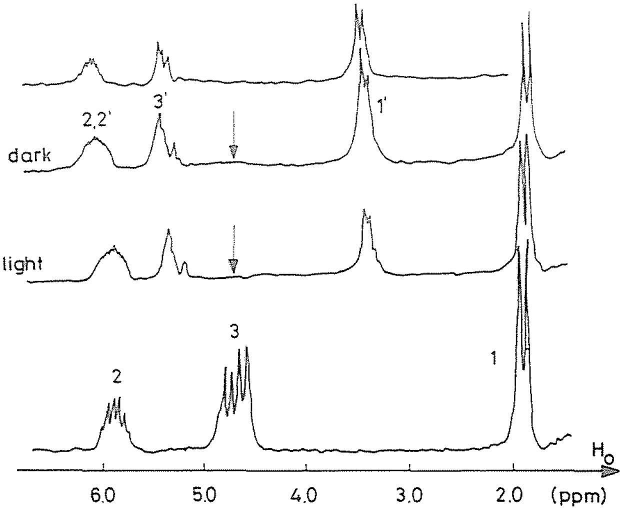


Fig. 1

successive selective saturation at homonuclear decoupling of various proton groups of the allyl fragment in triethylallylstannane molecules, under ultraviolet irradiation and in the dark. The spectra demonstrate that the saturation of the signal in position 3 of allyltriethylstannane reduces the signal intensity of protons in position 1 in the trichlorobutene molecules by 30–40%.

The saturation of the protons 1 of allyltriethylstannane reduces the signal intensity of the 3′ protons of compounds II. In this case the saturation of the protons 2 of the initial compound conveys no information, since the chemical shifts of the 2 and 2′ protons are nearly equal.

$$R_3MCH_2CH{=}CH_2 + BrCCl_3 \rightarrow R_3MCH_2CHBrCH_2CCl_3$$
$$R = Me, Et \qquad M = Si, Ge$$

The results obtained show that the initial stage in the reaction is the addition of the trichloromethyl radical to the terminal carbon atom of the allyltriethylstannane double bond, followed by cleavage of the Sn – C bond, in full accordance with this scheme. Possible alternative mechanisms (recombination of trichloromethyl and allyl radicals, or the "concerted" reaction with simultaneous breaking of carbon-bromine and tin-carbon bonds) do not fit the experimental data obtained.

The radical stages of the reaction were studied by the ^1H chemically induced dynamic nuclear polarization effects arosen during photolysis of the allyltriethylstannane and bromotrichloromethane in deuterocyclohexane or deuterobenzene in the probe of the NMR spectrometer.

Figure 2 shows the general picture of the ^1H CIDNP detected in this reaction.

$$CH_2{=}CHCH_2M(OCH_2CH_2)_3N + R_{Hal}X \xrightarrow{h\nu} XM(OCH_2CH_2)_3N$$
$$R_{Hal}X = HCCl_3,\ BrCCl_3,\ C_3F_7I$$
$$M = Si, Ge$$

Since the chemical polarization detected is mainly of an integral character, one may expect that the radical pairs showing these polarizations have noticeably different g-factor values. [31] In analysing the CIDNP effects, one can reasonably postulate that the newly generated free radicals already contain the trichloromethyl group (stage A in the scheme).

From the above reasoning it follows that the integral CIDNP of 1′ and 3′ of trichlorobutene results from the encounter of radical adduct I* and CCl_3 radical in solution.

In this case, trichlorobutene is generated by the disproportionation of the radical-adduct with separation from the radical pair formed (stage C in the scheme).

The NMR spectrum taken during the reaction showed two negatively polarized signals at δ 2.4 ppm and 3.8 ppm which are not observed in the equilibrium spectrum. The splitting pattern and the position in the spectrum make it possible to assign them to methylene protons of the normal adduct, 1-triethylstannyl-2-bromo-4,4,4-trichlorobutane.

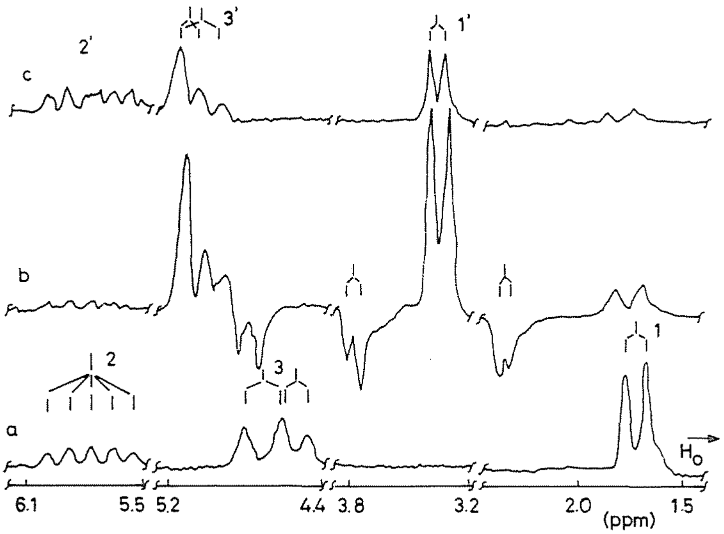


Fig. 2

The analysis shows that the CIDNP effects of compound I cannot originate in the first radical pair. Hence, it is possible to assume that they arise through the beta-decomposition of the terminal adduct. There is no evidence against the assumption that the CIDNP effects of trichlorobutene also arise in the second radical pair.

Thus, CIDNP analysis indicates two possible ways of generating the basic reaction product, trichlorobutene: beta-decomposition of normal adduct and beta-fragmentation of radical-adduct I*.

However, the experiments with radiofrequency pumping in the resonance region of the protons of normal adduct give some grounds to believe that the latter is not subjected to beta-cleavage. Thus, trichlorobutene seems to result mainly from beta-fragmentation of the radical-adduct.

The detection of CIDNP effects in normal adduct,—generated in small amounts as an intermediate—is of great importance. It is possible that the beta-decomposition of elementoorganic compounds with electron-acceptor substituents at the beta-carbon atom occurs by a radical mechanism and this assumption will be the subject of our further investigations.

It was interesting to make clear the effect of the central heteroatom and neighbouring substituents in the reaction of Group IV B allyl derivatives with polyhalomethanes.

$$Bu_3SnCH_2CH{=}CH_2 + RX \rightarrow RCH_2CH{=}CH_2 + Bu_3SnX$$

X = Cl, Br, I

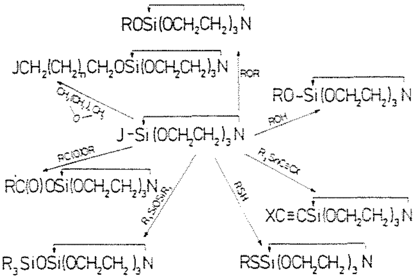
R = $HCCl_2$, CCl_3, n-Pr, All, $PhCH_2$, Cl_2CCHO, Br_2CCHO

J. Grignon, 1975

It has been observed that UV-irradiation of the equimolar mixture of trimethylallylsilane with bromotrichloromethane or heptafluoro-iodopropane gives the corresponding monoadducts. However, heating or distillation of the reaction mixture results in beta-fragmentation leading to trimethylhalosilane and the corresponding haloalkenes. The electron-withdrawing substituents at the silicon atom (methoxy group or chlorine atoms) enhance greatly the stability of the corresponding adducts, therefore no products of silicon-carbon bond cleavage are formed.

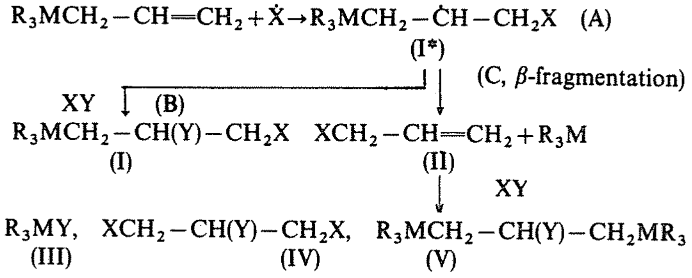
The reaction of triorganylallylgermanes with bromotrichloromethane yields a mixture of adducts and products of germanium-carbon bond cleavage, the portion of the latter decreasing with an increase in the electron-withdrawing properties of substituents attached to the germanium atom.

The radical reaction studied has served as the most convenient synthetic route to earlier hardly available 1-halometallatranes.



Thus, halogermatranes are obtained in quantitative yield when the equimolar mixture of allylgermatrane with the corresponding polyhaloalkane is exposed to UV-light for 10–15 minutes [32].

The 1-iodosilatrane obtained has proved to be a highly efficient silatranating synthon [33–35]. Next slide illustrates vast possibilities of this synthon in the preparation of new silatranes with labile substituents at the silicon atom.



(R = Alk; M = Si, Ge, Sn)

Thus, the reported data allow to draw a conclusion about a wide application of homolytic addition to tin, germanium and silicon unsaturated compounds in organic and organometallic synthesis.

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