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Adamantane Structures in the Chemistry of Silicon, Germanium, and Tin

V.F.Mironov, T.K.Gar, N.S.Fedotov, and G.E.Evert

The methods of synthesis and properties of compounds with the adamantane structure containing silicon, germanium, or tin atoms in the side chain or substituting carbon atoms in the adamantane lattice are examined. The review includes studies published towards the beginning of 1979.
The bibliography comprises 177 references.

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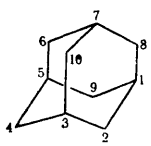
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I. INTRODUCTION

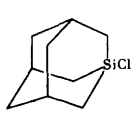
Adamantane, its analogues, and their derivatives are known to have unique physicochemical properties[1-13]. Studies designed to synthesise adamantane structures with Group IVB elements, particularly silicon, have begun to develop recently; a new field has been established in the chemistry of Group IVB elements to which more than 170 original publications have already been devoted.

Compounds of Group IVB elements having a three-dimensional skeleton comprising any atoms with the same configuration as the skeleton of carbon atoms in adamantane, which can be regarded as the unit cell of the three-dimensional carbon network in diamond, can be divided into two large classes. The first class includes compounds in which the atom of the Group IVB element is not incorporated in the adamantane skeleton. Such compounds can be called respectively silyl-, germyl-, stannyl-, and plumbyl-adamantanes. The second class includes compounds in which the atom of the Group IVB element is incorporated in the adamantane skeleton, i.e. substitutes a carbon atom. Such compounds can be called respectively sila-, germa-, stanna-, and plumba-adamantanes.

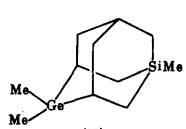
The following numbering has been adopted for the carbon skeleton of adamantane:



Regardless of the number of substituents, this skeleton is designated by the symbol Ad. If one or more carbon atoms in the adamantane skeleton have been substituted by atoms of other elements, then the principle of the "oxa-aza" nomenclature is used in naming such compounds. For example, compounds (I) and (II) are called respectively 1 chloro-1-sila-adamantane, and 1,4,4-trimethyl-1-sila-4-germa-adamantane:



(I)



(II)

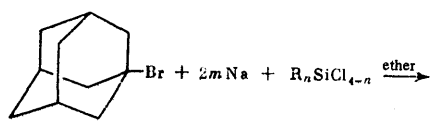
Alphabetic symbols for such structures have not as yet been proposed, since these compounds have in most cases not been synthesised or are represented by single specimens. However, for 1,3,5,7-tetrasila-adamantanes, i.e. compounds having the skeleton of the unit cell of carborundum and frequently called carborundanes, it is reasonable to introduce a designation, since this class is already represented by numerous compounds and is nowadays widely investigated. Without taking into account the substituents, the unit cell of carborundum is designated by the symbol Cb.

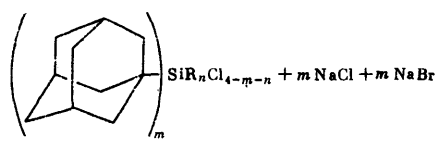
II. SILYLADAMANTANES

This class includes compounds having the structure AdSi$\lessgtr$ or AdRSi$\lessgtr$, where R can be any group of atoms or any element.

1. Methods of Synthesis

Silyladamantanes with the adamantyl group linked directly to the silicon atom have been recently obtained by the Wurtz reaction independently by several groups of investigators. No and coworkers[14-18] have studied this reaction most widely:

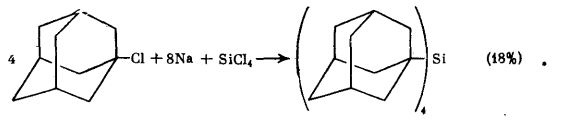




R = Et, n-Pr, n-Bu, Ph, or Me; $n = 1-3$, $m = 1-3$.

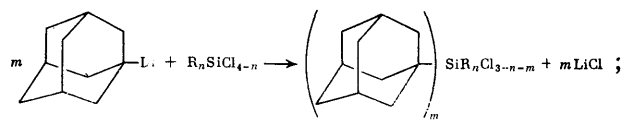
According to the authors, the reaction proceeds with high yields (50–80%) of the required products, although it is accompanied by the formation of diadamantane. The authors note that it is possible to replace only one chlorine atom in chlorosilane by the adamantyl group.

However, Roberts[19] was able to obtain tetra-adamantylsilane by the Wurtz reaction (in a low yield):



Mironov et al.[20] also investigated the synthesis of silyladamantanes using sodium and lithium, but they were able to obtain 1-trimethylsilyladamantane only in a very low yield. Roberts[19] likewise notes that trimethylsilyladamantane cannot be synthesised by the Wurtz reaction. The reported synthesis[14] of trimethylsilyladamantane by the Wurtz reaction (in 70% yield) must be regarded as erroneous. The authors of these studies claim that the melting point of their compound is 236 °C, while the true melting point of trimethylsilyladamantane proved to be ~35 °C.[21]

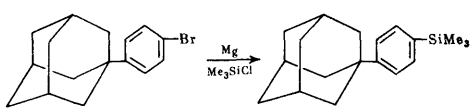
1-Adamantylalkyl(aryl)chlorosilanes can also be obtained from lithioadamantane[14]:



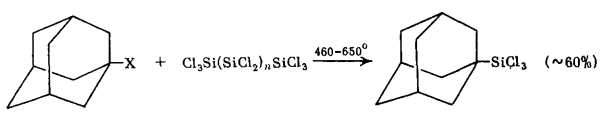
R = alkyl or aryl; $n = 1-3$, $m = 1-3$.

The reaction takes place readily; the main difficulty of the method consists in the multistage synthesis of the initial lithioadamantane, which is ultimately responsible for the very low yields of the desired adamantylalkyl(aryl)chlorosilanes.

The analogous synthesis via organomagnesium compounds has not so far been used, although the possibility of preparing a Grignard reagent from 1-bromoadamantane (in 60% yield) has been reported[22]. However, the synthesis of a compound of the type AdRHal via organomagnesium compounds has proved possible[23]:



The use of organosodium synthesis has not yet permitted the preparation of trichlorosilyladamantane. This compound has been synthesised[21,24,25] by passing adamantane or chloroadamantane mixed with hexachlorodisilane or perchloropolysilanes through a quartz tube heated to 450–650 °C.

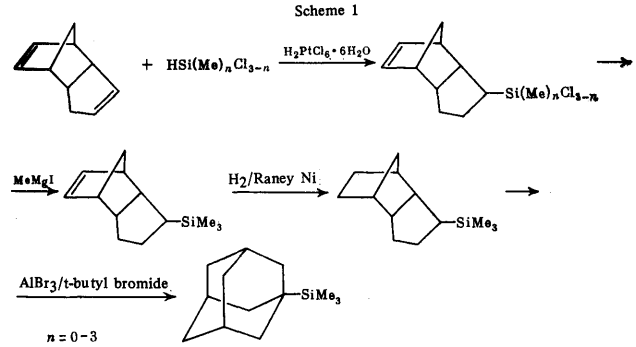


X = H or Cl; $n = 0-4$.

The reaction is carried out at atmospheric pressure and probably proceeds via a carbenoid mechanism, which involves the insertion of the $SiCl_2$ group in the C–Cl bond of chloroadamantane.

Yet another interesting method of synthesising trimethylsilyladamantane, in which the cyclopentadiene dimer and hydrochlorosilanes are used as the starting materials has been outlined recently[26] (Scheme 1).

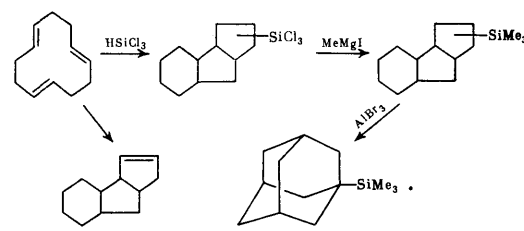
Scheme 1



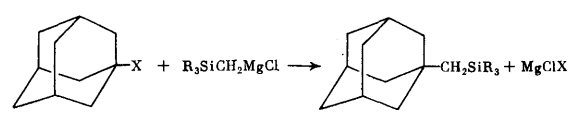
This synthesis has recently been repeated[27], but the trimethylsilyladamantane obtained had a melting point of 236 °C instead of 35 °C.

The isomerisation of a three-membered cyclic compound containing a silyl substituent also yielded trimethylsilyladamantane[28] (Scheme 2):

Scheme 2

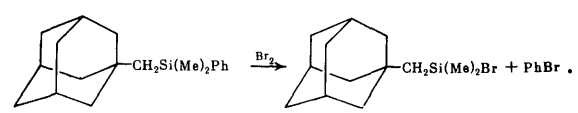


Treatment of chloro- or bromo-adamantane with Grignard reagents obtained from the corresponding α-chloromethylsilanes led to the formation of α-silylmethyladamantanes in good yields (70–80%)[29]:

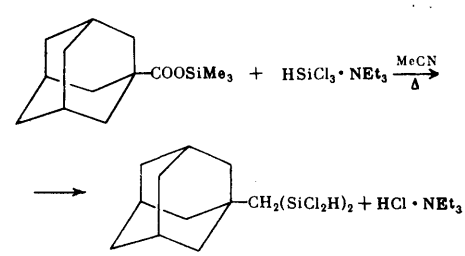


X = Cl or Br, R_3 = Me_3, $PhMe_2$, or Me_2H.

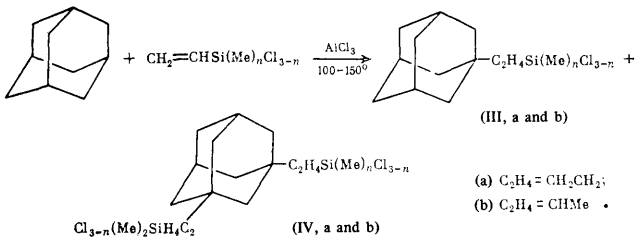
In the presence of the phenyl group at the silicon atom, there is a possibility of obtaining compounds with halogenosilyl substituents:



The Benkeser reaction has also been used to synthesise α-silylmethyladamantanes, but, after treating adamantanecarboxylic acid or its trimethylsilyl ester with the "trichlorosilane–triethylamine" complex in acetonitrile, the product is 1,1-bis(dichlorosilyl)methyladamantane instead of the postulated 1-trichlorosilylmethyladamantane:

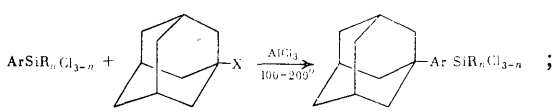


The first representatives of α- and β-silylethyladamantanes have been obtained by the Friedel–Crafts reaction[20,30–32]:



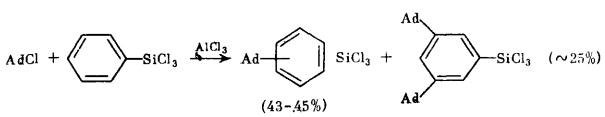
This reaction results in the formation of both 1-monosilyialkylated [compound (III)] and 1,3-bis-silylalkylated [compound (IV)] adamantanes. The ratio of compounds (III) and (IV) is determined by the nature of the unsaturated chlorosilane; for example, 70% of compound (III) and 30% of compound (IV) are obtained from vinyltrichlorosilane, while methylvinyldichlorosilane gives 60% of compound (III) and 40% of compound (IV). After methylation of the mixture of isomers (III, a and b), the isomer having the normal structure (IIIa), which is crystalline, can be readily separated from isomer (IIIb) by freezing out. The silyialkylation of adamantane and 1-chloroadamantane proceeds similarly also under γ-irradiation[13]. In the alkylation of adamantane with trimethylvinyl- and dimethylvinylchlorosilanes this method is also more suitable, because in the presence of aluminium chloride the reaction mixture contains a large amount of tar and it is almost impossible to isolate the adamantane alkylation products.

The Friedel–Craft reaction can also take place between halogenoadamantanes and a number of arylchlorosilanes, despite the fact that the view that phenylchlorosilanes cannot be used in this reaction because of the ready "elimination" of the phenyl group under the influence of Lewis acids has been firmly established in the chemistry of organosilicon compounds for a long time[23,26,33–35]:



X = H or Cl; Ar = phenyl or thienyl; Ar' = phenylene or thienylene.

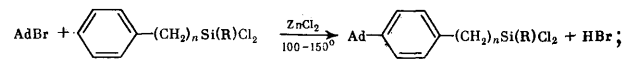
The best alkylation catalyst in the synthesis of adamantylthienylchlorosilanes proved to be tin tetrachloride. The highest yields of adamantyl(phenyl)trichlorosilanes[23,33] have been obtained on heating a mixture of 1-chloroadamantane and phenyltrichlorosilanes in the presence of $AlCl_3$ (in proportions of 4 : 13 : 1) for 3 h at 145–180 °C; under these conditions, up to 25% of *m,m*-diadamantylphenyltrichlorosilane is formed:



(43–45%)

1-Bromoadamantane is more reactive in this reaction than 1-chloroadamantane; in the presence of $AlBr_3$ it interacts with phenyltrichlorosilane even at 30 °C, giving rise to a 60% yield of *p,m*-adamantylphenyltrichlorosilanes[23,35,36]. The use of other catalysts ($ZnCl_2$, $SnCl_4$, and $FeCl_3$) did not lead to the desired results; the starting materials did not react or were converted into a tar.

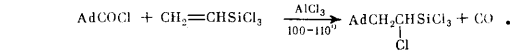
Phenylalkylchlorosilanes of the type $ArR'Si(R)_nCl_{3-n}$ (R' = alkylene) show a greater tendency towards this reaction than phenyltrichlorosilane[36]:



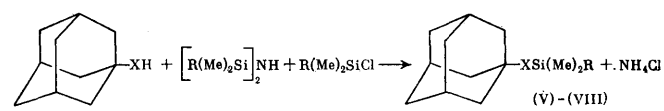
R = Cl or Me; $n = 1, 2$.

The best catalyst for the introduction of the adamantyl group into benzyltrichlorosilane is $ZnCl_2$, while the use of other catalysts ($AlCl_3$ and $FeCl_3$) leads to the formation of products with more than one adamantyl group[37].

No et al.[38] reported an unusual course of the silylalkylation of the chloride of adamantanecarboxylic acid:



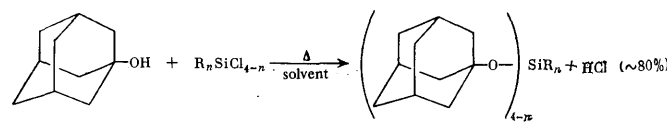
Oxygen- and nitrogen-containing silyladamantanes $AdXSiR_3$ (where X = O or N) were obtained for the first time by Mironov and Fedotov[39] by silylating 1-hydroxyadamantane and adamantanecarboxylic acid on heating them with a mixture of hexamethyldisilazane and trimethylchlorosilane:



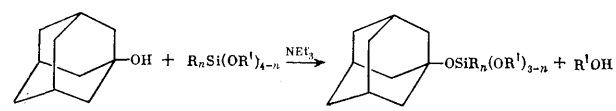
X = O or COO; R = Me[(V), (VI)] or H[(VII), (VIII)].

The authors note that hexamethyldisilazane alone does not silylate 1-hydroxyadamantane even on prolonged heating. It was found later[40–44] that 1-hydroxyadamantane is readily silylated by various chloro- and alkoxy-silanes (Scheme 3):

Scheme 3

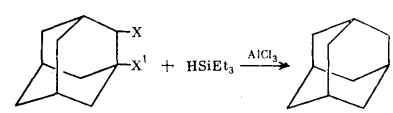


R = CH_2=CH, Ph, or MeO; n = 0–3;



R = alkyl, Ph, CH_2 = CH, or $ClCH_2$; R' = alkyl.

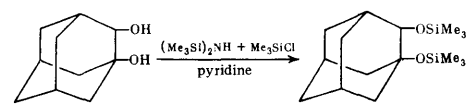
It is of interest that in the presence of Lewis acids triethylsilane reduces 1-bromoadamantane and 2-adamantanol to adamantane[45]:



X' = Br, X = H; X = Br, X' = H.

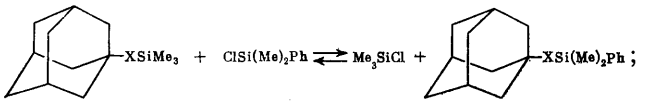
The photoinitiated oxidation of trimethylsilylketen acetal, containing the adamantyl group, to the corresponding peroxyacetate[46] and oxidation of adamantylphenylhydrosilanes with $SnCl_4$ [47] have also been described.

Exhaustive silylation of various dihydroadamantanes proceeds exclusively in pyridine:



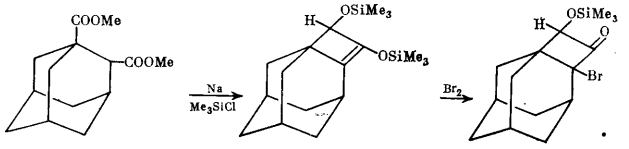
All possible isomers and conformers of bis(trimethylsiloxy)-adamantane were obtained in this way[48] and their NMR spectra were investigated. In addition, it was established that various silyl ethers of 1-hydroxyadamantane and esters of adamantanecarboxylic acid can be readily obtained by the

trans-silylation reaction[20,39]:

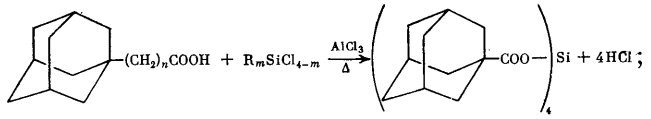


X = —O— or —COO— .

The silyl ethers of complex alcohols derived from adamantane have been obtained by a modified Ruhlman scheme[49]:



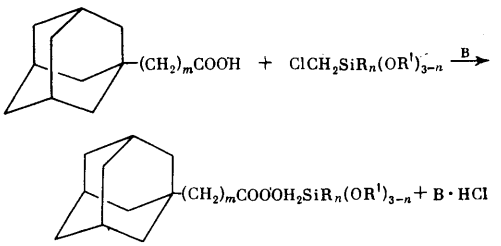
The silyl esters of adamantanecarboxylic acid are readily formed when they interact with chlorosilanes[50,51]:



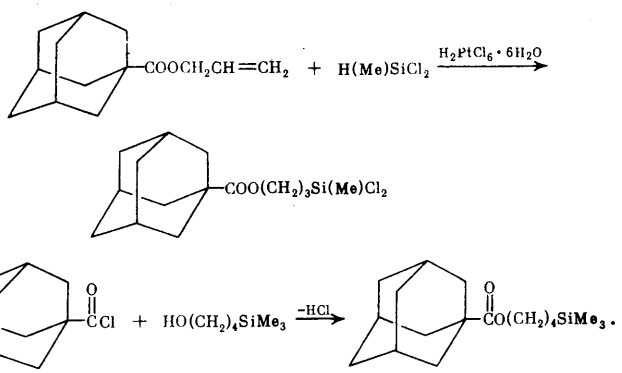
R = $ClCH_2$, CH_2=CH or Ph; n = 0, 1; m = 0, 1 .

The methods of synthesis of esters of adamantanecarboxylic acids and organosilicon alcohols are illustrated in Scheme 4 below[39,50-53]:

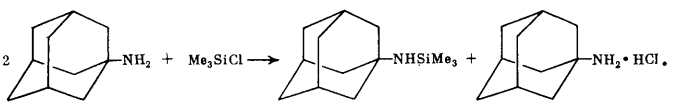
Scheme 4



R = Me; R^1 = Me; n = 0, 1; m = 0, 1; B = tertiary base (for example, NEt_3);

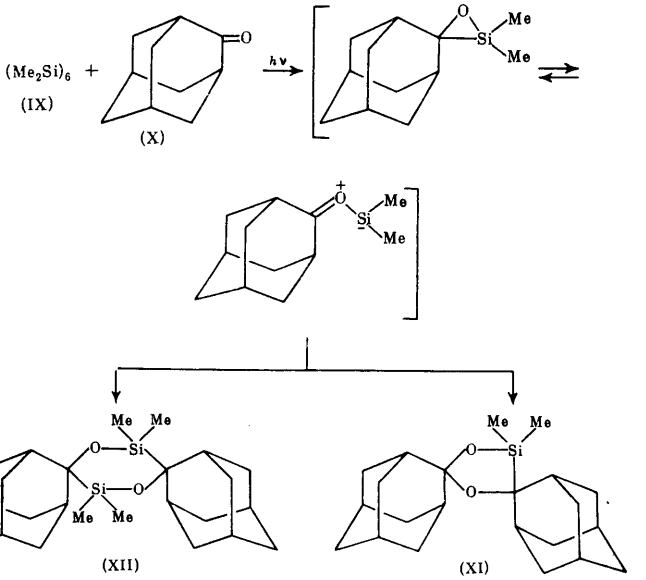


Like the usual primary amines, 1-aminoadamantane is also readily silylated by trimethylchlorosilane[39]:



Japanese investigators[54] obtained dioxasilacyclopentanes with adamantyl groups by the reaction of dodecamethylcyclohexasilane and adamantanone in an ethereal medium under irradiation (Scheme 5).

Scheme 5

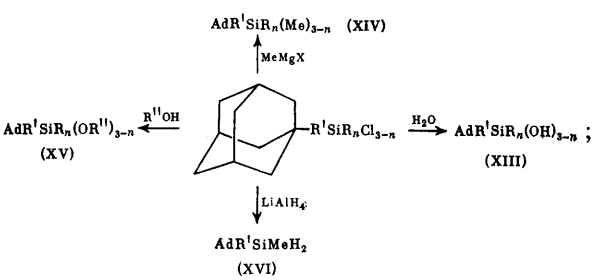


They found[54] that the interaction of compounds (IX) and (X) in the presence of alcohol lead to the formation of $EtOSiMe_2H$ (XI) and 2-ethoxydimethylsilyl-2-adamantanol.

2. Chemical Properties

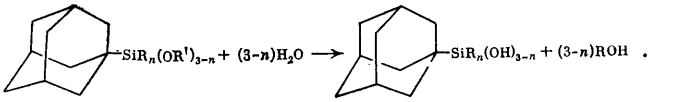
1-Adamantylalkyl(aryl)halogenosilanes are hydrolysed by water and react with alcohols, phenols, and other reagents more slowly than the usual alkyl(aryl)chlorosilanes and form compounds (XIII)[14,15,41,55,56,58], (XIV)[21,23,32,36,58], (XV)[14-16,18,36,37,55-59,61], and (XVI)[29,32,36,58] (Scheme 6).

Scheme 6

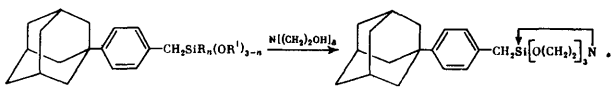


R = alkyl or aryl; R' = alkylene or arylene; n = 0, 1, 2.

1-Adamantyl(aryl)alkoxysilanes are comparatively resistant to hydrolysis by atmospheric moisture but are readily hydrolysed on heating with dilute alkali in diethyl ether[62]:



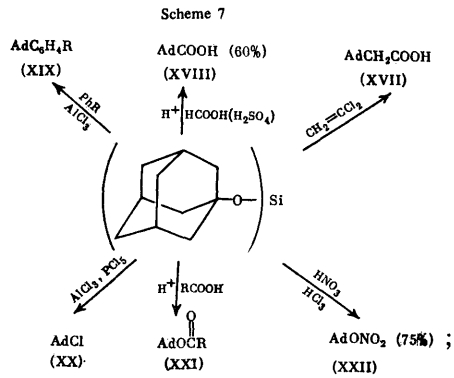
It has been shown[37] that they are readily converted into the corresponding silatranes:



Trimethylsiloxyadamantane is resistant to hydrolysis by cold water but is readily hydrolysed by hot water[39].

The reactions of compounds containing the Ad–O–Si ≡ linkage, particularly tetra-adamantyloxysilane, are illustrated in Scheme 7. A series of adamantane derivatives have been obtained as a result: (XVII)[67], (XVIII)[66–68], (XIX)[40,41,69], (XX)[40,63–65], (XXI)[67], and (XXII)[66]:

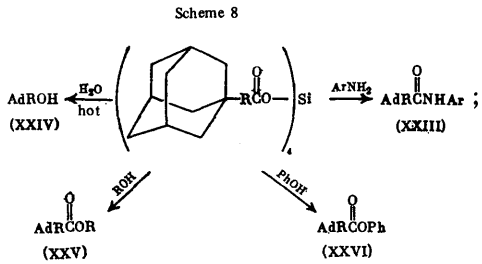
Scheme 7



R = Me, Et, $(Me)_2CH$, or MeO.

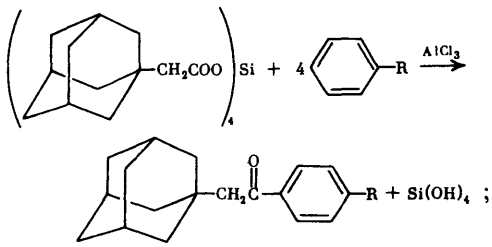
Tetra(1-adamantylcarboxy)silane and tetra(1-adamantylacetoxy)silane have also been investigated in various chemical reactions leading to the corresponding adamantane derivatives: (XXIII)[38,50,51,72], (XXIV)[70,71], (XXV)[70,73], and (XXVI)[73] (Scheme 8):

Scheme 8



Ar = Ph, *o,m*-MeC_6H_4, or $MeOC_6H_4$;
R = Me, Et, n-C_3H_7, n-C_4H_9, iso-C_4H_9, or n-C_5H_{11};
R' = OMe .

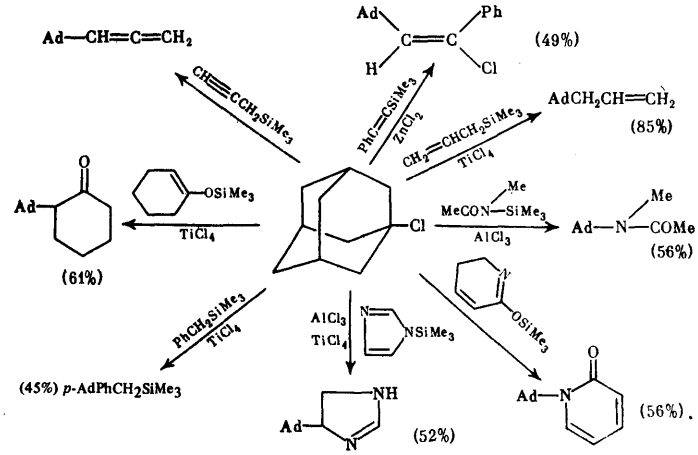
It has been established[42] that tetra(1-adamantylacetoxy)silane is less reactive in reactions with alcohols, 1-adamantanol, and phenol than tetra(1-adamantylcarboxy)silane, but is more reactive in reactions with aromatic amines. Tetra(1-adamantylacetoxy)silane undergoes the Friedel–Crafts reaction with benzene and alkylated aromatic compounds, forming the corresponding 1-adamantyl methyl ketones[42,50]:



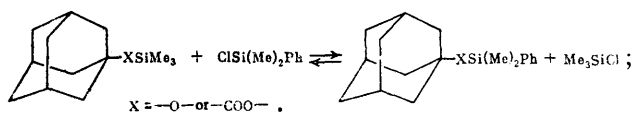
R = Me, Et or $(Me)_2CH$.

Sasaki et al.[74] achieved the interaction of various organic compounds containing trimethylsilyl groups with chloroadamantane in the presence of Lewis acid catalysts. In this way they obtained a number of organic derivatives of adamantane and in only one case a silicon-containing adamantane derivative—*p*-adamantylbenzyltrimethylsilane (Scheme 9):

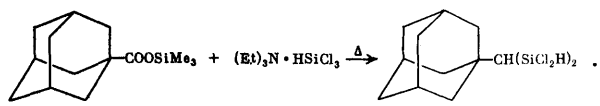
Scheme 9



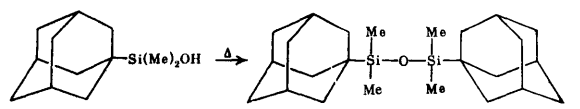
It has been found[39] that, like trimethylsilyl ethers and esters[75], the trimethylsilyl ethers of 1-hydroxyadamantane and the corresponding esters of adamantanecarboxylic acid are capable of undergoing the reversible *trans*-silylation reaction:



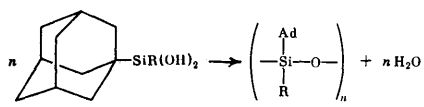
Trimethylsilyl adamantanecarboxylate enters into the Benkeser reaction[24,29]:



The study of the properties of 1-adamantylalkyl(aryl)silanols, obtained by the hydrolysis of the corresponding chloro-, alkoxy-, and acetoxy-derivatives, showed[14] that they are not appreciably dehydrated up to 80–100 °C and are fully dehydrated only at 150–200 °C after 10–15 h. Thus the thermal dehydration of 1-adamantyldimethylsilanol yields the corresponding disiloxane:



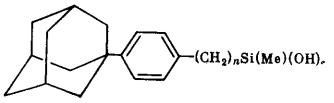
while 1-adamantylalkyl(aryl)silanediols give rise to polymers with the adamantyl group at the silicon atoms, whose molecular weights are in the range 5500–9000:



R = alkyl or aryl.

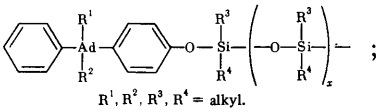
These polysiloxane polymers are resistant to the action of dilute acids and concentrated alkalies at 80–90 °C for 15–20 h.

Novikov et al.[76] obtained monomers of the type



where $n = 1$ or 2, which have been used to synthesise polymers with an increased thermal stability.

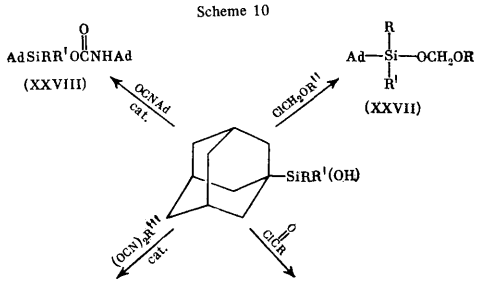
Polysiloxanes containing adamantyl groups of another type have been obtained recently[77]:



R^1, R^2, R^3, R^4 = alkyl.

Adamantylsilanols are fairly reactive and react with various reagents, forming the corresponding derivatives: (XXVII)[14,78,79], (XXVIII)[80,81], (XXIX)[82], and (XXX)[83] (Scheme 10):

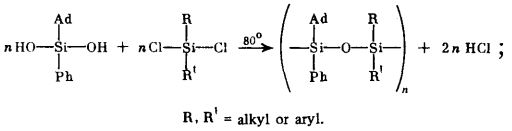
Scheme 10



R = R' = Me or Et, $R'' = MeC_6H_4$;

R'' = Me or C_6H_{11}; cat. = $Bu_2Sn(OCOC_{11}H_{23})_2$

1-Adamantyl(alkyl)arylsilanols can also undergo the polycondensation reaction with various alkyl(aryl)dichlorosilanes[14,18]:

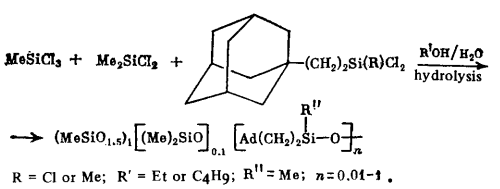


R, R' = alkyl or aryl.

The molecular weights of the polymers thus obtained are 4500–5600, which corresponds to 10–14 elementary units in the chain of the macromolecule.

Cohydrolysis of adamantylalkylhalogenosilanes with the corresponding alkyl(aryl)chlorosilanes made it possible to obtain liquid polysiloxanes—resins with the adamantyl(alkyl)-aryl groups at the silicon atom[84,85] (see, for example, Scheme 11):

Scheme 11



R = Cl or Me; R' = Et or C_4H_9; R'' = Me; $n = 0.01$–1.

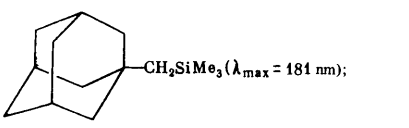
If there are aryl substituents[29] or hydrogen[47,60] in the silyl group of adamantylsilanes, they can be readily substituted by a halogen.

3. Physical Properties

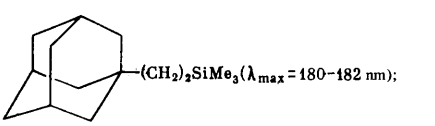
Silyl- and silylalkyl(aryl)adamantanes are as a rule crystalline substances or viscous high-boiling liquids, soluble in the majority of organic solvents. The frequencies of their absorption bands in the infrared spectra are characteristic of both the adamantane structure[86] and of the silyl and siloxane atomic groups linked to it. For example[13], β-(trimethylsilyl)ethyladamantane has a group of bands characteristic of the adamantane structure (970 and 950 cm^{-1}) and also the absorption bands of the Si–H (2120 cm^{-1}) and Si–Me (1800 cm^{-1}) groups.

There are no literature data for the NMR spectra of silyladamantanes, but it is clear that the proton spectra must contain signals due to protons of both the adamantane nucleus and the organosilicon substituents. The ^{13}C NMR spectra, in which it is possible to observe the individual signals of all types of carbon atoms in the molecule, as shown in relation to germyladamantanes[87], contain a particularly large amount of information about the structure. With the aid of ^{13}C NMR, it is possible to determine the position of the silicon-containing substituent in the adamantane skeleton. A satisfactory correlation between the chemical shifts of the ^{13}C NMR signal of the carbon atoms in the adamantane system and the inductive constants of the substituents has been established for substituted adamantanes[88]. The study of ^{29}Si and ^{13}C NMR spectra of mono- and bis-(trimethylsilyl)adamantanols[45] established that the chemical shifts of the ^{29}Si signals of 1- and 2-adamantyl derivatives occur in different regions, the position of the chemical shift being sensitive to steric interactions. This makes it possible to employ the ^{29}Si and ^{13}C NMR methods to establish the structure of any adamantyl derivative after first converting it into the corresponding trimethylsilyl derivative.

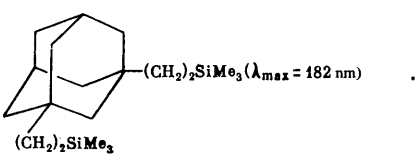
Interesting results have been obtained[89] in the study of the adsorption spectra of both adamantane itself and of silylalkyl(aryl)adamantanes in the far ultraviolet (175–200 nm). It has been established that adamantane has an intense absorption band at 180 nm. Silicon-containing substituents exert a definite influence on the main absorption band: the introduction of trimethylsilylalkylene groups causes a slight shift of the absorption band in the spectra of both mono- and di-substituted adamantanes:



CH_2SiMe_3 (λ_{max} = 181 nm);



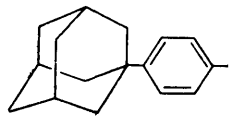
$(CH_2)_2SiMe_3$ (λ_{max} = 180–182 nm);

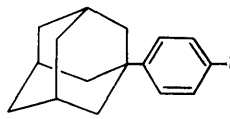


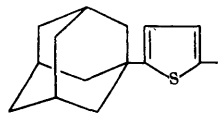
$(CH_2)_2SiMe_3$ (λ_{max} = 182 nm)

$(CH_2)_2SiMe_3$

The introduction of trimethylsilylarylene groups is accompanied by a bathochromic shift.







A mass-spectrometric study[32], carried out in order to determine the isomeric composition of the products of the silylalkylation of adamantane by alkenylchlorosilanes, showed that there is virtually no peak of the $(M-HR)^+$ ion in the mass spectra of all the compounds investigated, while the intensity of the peak of the $(M-R)^+$ ion is high. It is known that 1-substituted adamantanes (Ad–R) typically lose the substituent R in the form of a free radical[90,91], while 2-substituted adamantanes eliminate the MR molecule from the molecular ion[92]. Thus the substituents in all the compounds investigated were either in the 1-position or in the 1- and 3-positions. The spectra of all the mono-substituted adamantanes show the peak of the molecular ion, whose relative intensity increases with increase of the number of methyl groups attached to the silicon atom. The loss of the second substituent from the $(M-R)^+$ ion with migration of the hydrogen atom to the charged fragment, which leads to the formation of the adamantyl cation with *m/e* 135, is characteristic of all substituted adamantanes[32].

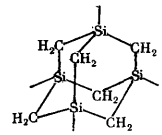
4. The Applications of Silyl- and Silylalkyl(Aryl)-Adamantanes

Silyl- and silylalkyl(aryl)-adamantanes have been synthesised quite recently. The study of their properties as well as the properties of polymers obtained on their bases has been initiated. Nevertheless, in view of the specificity of the properties which polysiloxane polymers acquire after the introduction of adamantyl or adamantylalkyl(aryl)groups, they are already of definite interest as substances with effective stabilities in relation to heat, light, and radiation[84,93].

III. SILA-ADAMANTANES

1. Carborundanes

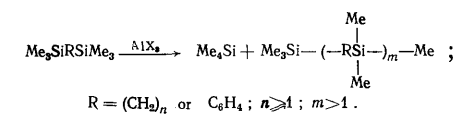
Carborundanes or 1,3,5,7-tetrasila-adamantanes constitute a new class of organosilicon compounds, which have been relatively little investigated and which have extremely unusual physical and chemical properties. The molecular skeleton of tetrasila-adamantane can be regarded as the unit cell of silicon carbide–carborundum (hence the name carborundane), the rigid crystal lattice of which is free from angular and conformational strains, like the diamond lattice:



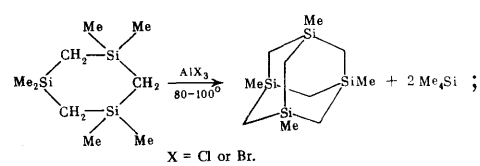
Like diamond, carborundum has exceptional chemical, thermal, and mechanical stabilities. The new class of carborundanes could not therefore fail to interest chemists working in the field of the chemistry of Group IV elements. It might have been expected, in particular, that tetrasila-adamantanes would prove to be extremely promising for the modification of siloxane polymers and for the creation of new thermally and chemically stable materials. At the beginning of 1970 there were only six papers in the literature on the synthesis and properties of carborundanes, while at the beginning of 1980 there were already about 70 original publications and six reviews[11,12,94–97]. However, one should note that the review of Frye and Klosowski[96] is very short and incomplete (the bibliography contains only 11 references), while other reviews are devoted to broader topics—heteroadamantanes[11,12,97] and carbosilanes[94,95], while the information about carborundanes is scanty and non-systematic.

(a) Methods of Synthesis of Carborundanes

There are two methods of synthesising carborundanes. They both consist in a far-reaching degradation of various methylsilanes and silcarbanes (i.e. compounds containing the $\rangle SiCH_2Si\langle$ fragment) under the influence of aluminium halides or on thermolysis. The first method is in fact a development of the reaction of Vdovin[98–100], who discovered the following new reaction in a study of the action of aluminium halides on a wide variety of bridged compounds†:



However, the amounts of aluminium halides used in the reaction was so small that it stopped at the stage involving the formation of the silmethylene oligomer[100]. Later Frye and Weyenberg[103] achieved a more far-reaching transformation of various silmethylene compounds into sila-adamantanes under the influence of increased amounts to aluminium halides (20–200% of the weight of the initial compound), for example:



† This reaction was found subsequently to be fairly general and to occur even when R is oxygen or nitrogen[101]. Furthermore, the reaction is fully characteristic also of the series of analogous organogermanium compounds[102].

Under the reaction conditions, some of the methyl groups at the silicon atom are substituted by the halogen X under the influence of AlX_3, so that Me_3CbX and Me_2CbX_2 are formed together with Me_4Cb. The overall yield of sila-adamantanes for X = Br was 27%.[103] Apart from the six-membered ring, $(Me_2SiCH_2)_n$, where n varies from 2 to 50, $(Me_2XSi)_2CH_2$ (X = Cl or Br), and $Me_3SiCH_2SiMe_3$ have been proposed for the synthesis of carborundanes[104]. The syntheses of sila-adamantanes from $(Me_2SiCH_2)_3$ and $AlBr_3$ (yield 27%), $(Me_2.SiCH_2)_2$ and $AlCl_3$, $Me_3SiCH_2SiMe_3$ and $AlCl_3$, and $(Me_2.SiCH_2)_n$ and $AlBr_3$ ($n = 4-50$) have been described as specific examples[104]. Furthermore, a mixture of $CbCl_4$ and $MeCbCl_3$ has been obtained from $(Me_2ClSi)_2CH_2$ and $AlCl_3$. The above communications[103,104] contain no data on the properties of the individual sila-adamantanes obtained (yields, melting points, etc.). Frye and Weyenberg apparently did not isolate and purify the substances synthesised. They merely state that the mixtures of sila-adamantanes can be separated by fractional sublimation or adsorption chromatography[104].

Frye's method was developed by other investigators. Thus Fritz and Kreilein[105] showed that, when the heterocycle $(Me_2.SiCH_2)_3$ is heated with $AlBr_3$ at 80 °C for 24 h, 18% of Me_4Cb and 1.5% of Me_3CbBr is formed, but, on increasing the reaction time to 72 h and the temperature to 100 °C, the overall yield of desired products falls to 9.5%. Vdovin and coworkers[106] studied the rearrangement of tetramethyldisilacyclobutane under the influence of aluminium halides in greater detail than in Frye's study. They note that Me_4Cb is not formed on treatment with an equimolar amount of $AlCl_3$ at 20 °C; this requires more severe conditions ($AlBr_3$, 70 °C):

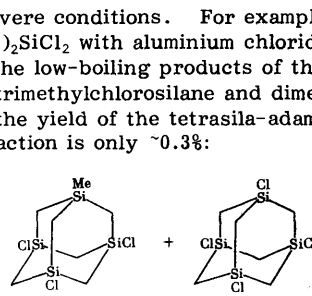
$$(Me_2SiCH_2)_2 \xrightarrow{AlBr_3} Me_4Cb + Me_3SiCH_2SiMe_3 + Me_4Si + \text{oligomers}.$$

The yield of Me_4Cb is ~5% on the basis of data quoted by Vdovin and coworkers[106].

The catalytic rearrangements of disilylmethylene compounds $(Me_2SiCH_2)_n$ ($n = 2-11$) have also been studied by Mironov et al.[107]. They established that tetrasila-adamantanes can be obtained from a mixture of oligomers ($n \cong 11$) in a yield not exceeding 4%. The mixture of oligomers is readily formed when $ClCH_2SiMe_2Cl$ is treated with sodium[108] or magnesium[109].

If silmethylene compounds with Si–Cl bonds are used for the synthesis, the reaction with aluminium chloride must be carried out under more severe conditions. For example, the interaction of $(ClMe_2SiCH_2)_2SiCl_2$ with aluminium chloride begins only at 200 °C. The low-boiling products of the rearrangement consist of trimethylchlorosilane and dimethyldichlorosilane (1:2), but the yield of the tetrasila-adamantanes isolated after the reaction is only ~0.3%:

$$(ClMe_2SiCH_2)_2SiCl_2 \xrightarrow[200-215^\circ]{AlCl_3}$$



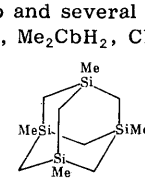
Analogous results are obtained also when the above reaction is carried out in a flow system in the gas phase. The initial chloride together with hydrogen chloride was passed over aluminium filings at 500–600 °C. The yield of sila-adamantanes was ~1% relative to the chloromethylsilane consumed[107]. It was shown experimentally that one of the causes of the low yield of products is the decomposition of the molecular skeleton of methylchlorosila-adamantanes under the influence of aluminium chloride under severe conditions.

Lower methylchlorosilanes can also be used as starting materials for the synthesis of chlorocarborundanes. It is known, for example, that the first representative of the class of 1,3,5,7-tetrasila-adamantanes was obtained by Smith and Clark in 1961 [110] as a result of an accidental overheating to 500 °C of an autoclave containing a mixture of trimethylchlorosilane, silicon tetrachloride, and aluminium chloride. Together with six- and eight-membered silmethylene rings, tetrachlorocarborundane ($CbCl_4$) was isolated in 0.1% yield. The substance was not obtained in an analytically pure form, but it was readily characterised with the aid of infrared and ^1H NMR spectra and by determining the molecular weight.

Much later Klosowski and Barry[111] took out a patent for a method of synthesis of sila-adamantanes which is extremely similar to that of Smith and Clark. These compounds are obtained from methylhalogenosilanes Me_nSiX_{4-n} (X = Cl or Br; $n = 1-4$) at 350–450 °C and a pressure of 70–176 atm. The catalyst consists of a mixture of aluminium halide (2.5–15%), silicon, and (or) aluminium (2.5–50% of the weight of the reagents) in order to bind the acid (probably HCl). In the examples described a mixture of Me_2CbCl_2 and $MeCbCl_3$ was obtained from Me_3SiCl, while Me_2SiCl_2 gave mainly $CbCl_4$. The overall yields (according to our calculations based on the data in the patent) are ~13–18%.

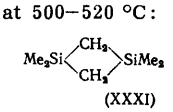
Thus Frye's method gives the best results for low-molecular-weight fully methylated silmethylene compounds, which happen to be the least available silcarbanes. Silmethylene compounds with $SiCl_2$ or $SiCl_3$ groups, which are readily obtained by direct synthesis from chloromethylsilanes $ClCH_2.SiRR'R''$, are apparently relatively unsuitable for the synthesis of sila-adamantanes. On the other hand, the lowest methylchlorosilanes are converted into carborundanes only under very severe conditions and with low yields.

There is also another method of synthesis of tetrasila-adamantanes—the pyrolytic method. Thus the tetramethyl derivative Me_4Cb was first detected[112] in the products of the pyrolysis of tetramethylsilane at 700 °C. In subsequent years Fritz and coworkers carried out a laborious and troublesome separation of the very complex mixtures formed in the pyrolysis of Me_4Si,[113-115] $MeSiCl_3$,[116] and Me_3SiCl.[117] The authors published several large monographs and three reviews which describe in detail the methods used to separate and identify the pyrolysis products[94,95,118-121]. It is stated that the most suitable method of fractionating sila-adamantane mixtures is adsorption chromatography[104,113]. The study of the pyrolysis of tetramethylsilane led to the following results: the low-molecular-weight fraction of the reaction mixture consisted of 39 substances containing from one to three silicon atoms in the molecule and also of 12% of Me_4Cb relative to the pyrolysis reaction mixture, which corresponds to a yield of 3%.[115] In the high-molecular-weight fraction (Si_4-Si_8) it was possible to identify[118] ~60% of the compounds, among which Me_4Cb and several of its analogues are again present, i.e. Me_3CbH, Me_2CbH_2, $CbCH_2SiMe_2H$, $CbCH_2SiMe_3$, $CbCH=CH_2$, and

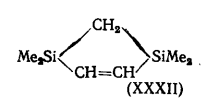


The remaining compounds are complex polycyclic systems of the sila-adamantane types which are described below.

Fritz and Götz[115] established that Me_4Cb is formed in the pyrolysis not only of tetramethylsilane but also of other compounds, for example the heterocycles (XXXI) at 480 °C and (XXXII) at 500–520 °C:



(XXXI)

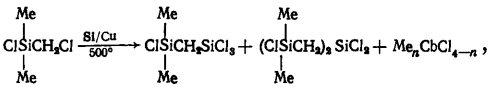


(XXXII)

According to the authors, Me_4Cb is formed via a multistage radical mechanism[115].

The pyrolysis of trimethylchlorosilane leads to a mixture of all four possible chlorosila-adamantanes: $CbCl_4$, $MeCbCl_3$, Me_2CbCl_2, and Me_3CbCl in the proportions 170 : 16 : 3 : 1.[117] The substances were characterised with the aid of ^1H NMR and mass spectrometry.

Finally yet another method of synthesising sila-adamantanes has been discovered recently. In the course of direct syntheses of silcarbanes from α-chloromethylsilanes, for example (chloromethyl)dimethylchlorosilane[122]



it was established that higher-boiling compounds as well as a non-distillable polymeric residue are always formed together with the products indicated. If the initial silane is passed over a mixture of silicon and copper powders at 500 °C, a crystalline deposit, consisting of Me_3CbCl, Me_2CbCl_2, and $MeCbCl_3$, with the dichloride predominating, is precipitated from the still residues. The overall yield of sila-adamantane is ~0.3% relative to the chloromethylsilane passed over the catalyst[107].

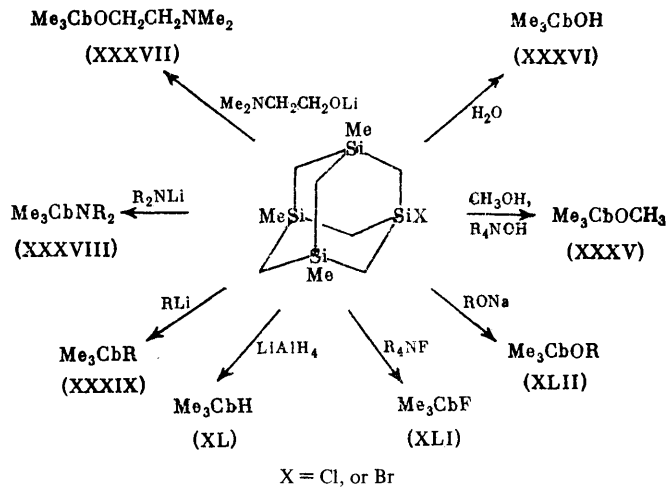
(b) Chemical Properties of Carborundanes

1,3,5,7-Tetrasila-adamantanes have continuously attracted the attention of investigators concerned with problems of the stereochemistry and mechanisms of the reactions involving the silicon atom as the reaction centre. The carborundane molecules incorporate four silicon atoms located in bridgehead positions. The system is rigid and free from angular and conformational strains. According to Sommer[123], such structures should be extremely inert in nucleophilic substitution reactions, because the mechanism involving an inversion of configuration cannot occur and that with retention of configuration is hindered by the rigidity of the cyclic system.

The first results of the study of the reactivity of carborundanes seemingly confirmed this hypothesis. Smith and Clark[110] noted the unusual resistance of $CbCl_4$ to the action of water and methylmagnesium chloride. The monohalides Me_3CbX also proved to be resistant to hydrolysis[124]. The reaction of Me_3CbBr with aqueous acetone takes place over a period of 9 days and the monochloride Me_3CbCl is hydrolysed only by alkali. The bromide is reduced with difficulty by lithium tetrahydroaluminate and the analogous reaction with the chloride takes place to an extent of only 10%.[124] It was found that $MeCbCl_3$ and $CbCl_4$ are only partially reduced by the $LiH–LiAlH_4$ mixture[117], while the mono-and di-chlorides do not react at all. However, it has been established that Me_3CbCl reacts with lithium derivatives of dialkylamines and dimethylaminoethanol. One should note particularly the fact that the derivatives obtained, containing the Si–N or Si–O bond in their molecule, which are usually hydrolytically unstable, in the present case were not hydrolysed even with hydrochloric acid[124].

The publication of the above studies was soon followed by the appearance of the paper of Homer and Sommer[125], who claimed that their results are in sharp conflict with the established view that the reactivity of the sila-adamantane system in relation to nucleophiles is reduced. Indeed, they obtained Me_3CbOMe and Me_3CbF in high yields (86–90%) (see Scheme 12).

Scheme 12



$Me_3CbCl \xrightarrow{LiH/LiAlH_4}$ does not react (Ref.117),

$Me_2CbCl_2 \xrightarrow{LiH/LiAlH_4}$ does not react (Ref.117),

$MeCbCl_3 \xrightarrow{LiH/LiAlH_4} MeCbCl_2H + MeCbH_3$[117],

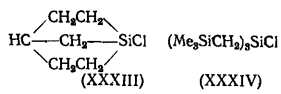
$CbCl_4 \xrightarrow{LiH/LiAlH_4} CbCl_3H + CbH_4$[117],

$Me_3CbOCH_3 + (iso\text{-}C_4H_9)_2AlH \longrightarrow Me_3CbH$[125, 127],

$Me_2CbCl_2 + CH_3ONa \longrightarrow Me_2Cb(OCH_3)_2$[127],

$CbBr_4 + Me_3SiCH_2Li \longrightarrow (Me_3SiCH_2)_4Cb$[105].

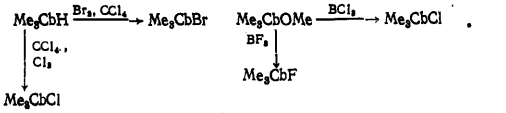
The alkylation of Me_3CbX with phenyl- and methyl-lithium was also found to be possible, although in the latter case the presence of tetramethylethylenediamine, which activates methyl-lithium, was necessary. Furthermore, Me_3CbOMe is readily reduced by di-isobutylaluminium hydride in ether, while its acyclic analogue $(Me_3SiCH_2)_3–SiOMe$ reacted 100 times more slowly[125]. It is noteworthy that all these reactions with nucleophiles has been studied earlier by Sommer and coworkers in relation to acyclic optically active silicon compounds. The results of the study of the stereochemistry and mechanisms of these reactions are surveyed in a book[123] and in a review[126]. The use of data accumulated in this field enabled Homer and Sommer[125] to put forward certain hypotheses concerning the mechanism of the interaction of sila-adamantanes with nucleophiles. Subsequently these reactions were studied more thoroughly by the authors; the reactivity of the sila-adamantane system was compared with those of two model compounds (XXXIII) and (XXXIV)[127]:



The authors concluded that their results are best explained by the interaction of Me_3CbX with the nucleophiles investigated in terms of the S_N2–Si mechanism, which postulates a considerable involvement of the *d* orbitals of silicon and operates with retention of configuration. On the other hand, the reduction of Me_3CbOCH_3 by di-isobutylaluminium hydride probably proceeds via the S_Ni–Si mechanism involving a four-centre transition state[127]. All the reactions involving the nucleophilic substitution of tetrasila-adamantanes known

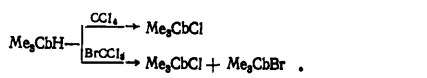
at present are surveyed in Scheme 12: (XXXVI), (XXXVII),[124] (XXXVIII),[124,128] (XXXV),[125,127] (XXXIX),[105,125,127] (XL),[124,127] and (XLI)–(XLII).[125,127]

Homer and Sommer established[129] that tetrasila-adamantanes react fairly vigorously also with certain electrophiles. For example, the halogenation of Me_3CbH takes place rapidly in the cold in scattered light, while the interaction of the methoxy-derivative with BCl_3 takes place instantaneously:

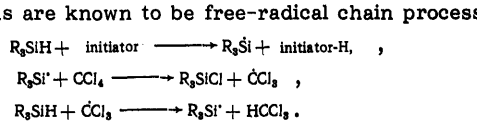


It had been shown earlier[123] that the analogous reactions with acyclic organosilicon compounds take place with retention of configuration. Evidently this type of process is not interfered with by the specific geometry of the sila-adamantane system. The interaction of Me_3CbOMe with BF_3, which goes to completion in six days, contrasts sharply with the halogenation of this sila-adamantane by boron trichloride[129]. According to Sommer's data[123], the analogous reaction of acyclic alkoxysilanes is accompanied by the inversion of configuration. This mechanism is impossible for the sila-adamantane system, so that the reaction with BF_3 proceeds, according to the hypothesis of Homer and Sommer[129], via some other pathway, least favourable as regards the nature of the reagent.

Homer and Sommer established[130] that the rigid geometry of sila-adamantanes does not hinder the formation and reactions of radicals produced from Me_3CbH under the influence of benzoyl peroxide:

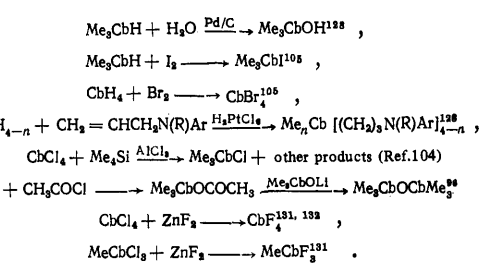


Such reactions are known to be free-radical chain processes:



It has been found[130] that the compound $(Me_3SiCH_2)_3SiH$, which is an acyclic analogue of Me_3CbH, reacts much more slowly with CCl_4; consequently the radical $Me_3Cb^{\cdot}$ is formed faster than $(Me_3SiCH_2)_3Si^{\cdot}$. The selectivity of the radical $Me_3Cb^{\cdot}$ in the elimination of a halogen atom from $BrCCl_3$ proved to be approximately the same as that of other silyl radicals (this has been inferred in relation to the Me_3CbCl and Me_3CbBr formed)[130].

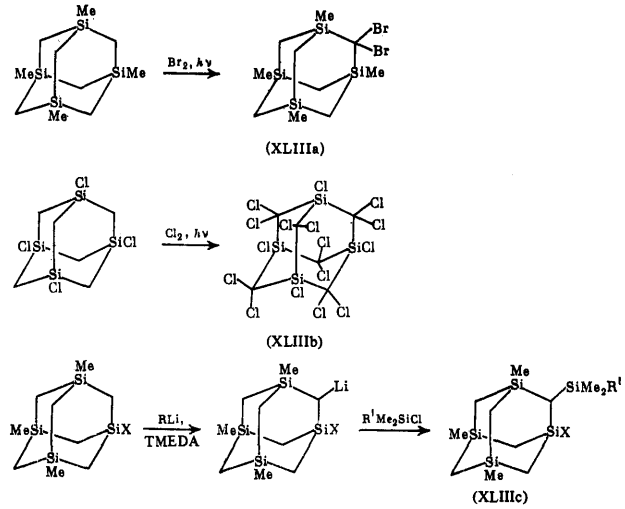
In conclusion certain other reactions of carborundanes may be mentioned:



In contrast to the fluorination of Me_3CbX by quaternary ammonium salts (Scheme 12), the reactions with ZnF_2 have been carried out under more severe conditions (in the absence of solvents at 100–160 °C).

Recently Fritz and coworkers[105,131] discovered a new property of carborundanes—the ability to be halogenated and metallated at the ring carbon atom [Scheme 13; (XLIIIa),[105] (XLIIIb),[131] (XLIIIc)[105]].

Scheme 13



X = Me or halogen; R = n-C_4H_9 or CH_2SiMe_3; R′ = Me or Ph; TMEDA = $Me_2NCH_2CH_2NMe_2$.

A further two trimethylsilyl groups were introduced in succession into the last compound (XLIIIb, R′ = Me) with the aid of butyl-lithium[105].

Thus the geometry of the relatively rigid ground state of the tetrasila-adamantane system does not prevent the reactions with radical reagents and the majority of nucleophiles and electrophiles and permits the synthesis of various derivatives of tetrasila-adamantanes. The chemical properties of sila-adamantanes are discussed by Frye's review[96], which summarises mainly the results of his own studies and those of his coworkers. However, attention is concentrated[96] on the mechanism of the rearrangement of silmethylene compounds to tetrasila-adamantanes under the influence of AlX_3 and also on the problem of "oxasila-adamantane" (see below).

(c) Physical Properties of Carborundanes

1,3,5,7-Tetramethyl-1,3,5,7-tetrasila-adamantane and its halogeno-derivatives Me_nCbX_{4-n} are colourless crystalline readily sublimed compounds with a sharp smell. Despite their high molecular weights and frequently very high melting points, the majority of sila-adamantanes can be analysed by gas–liquid chromatography. Fritz[121] also notes the high thermal stability of Me_4Cb: at 520–540 °C this substance remains unaltered for 37 h.

Various physicochemical methods have been used to investigate the catalytic characteristics of the structure of sila-adamantanes. It has been shown by X-ray diffraction of Me_4Cb [133] that the average length of the Si–C bond in the $Si-CH_3$ and $Si-CH_2$ groups is respectively 1.889 and 1.866 Å, which is within the usual limits for the silicon–carbon bond in organic compounds of silicon. An analogous study of Me_3CbBr [134,135] led to the following results: the Si–C bond lengths are 1.84–1.90 ± 0.02 Å and the Si–Br bond length is 2.15 ± 0.01 Å. A quantum-chemical calculation of the geometrical parameters of the Me_4Cb molecule has been carried out[136].

The photoelectron spectra of the compounds CbX_4 (X = Me, H, F, or Cl) have been investigated[137,138] and it was found that the sila-adamantane molecules, like those of adamantane and urotropine, are not entirely free from strain, which is

due to the transannular SiC–SiC– and CH_2–CH_2-interactions. However, such interactions are 2–3 times weaker than in adamantane owing to the greater length of the Si–C bond compared with C–C. The changes in the spectra of the series of organosilicon compounds are induced by the inductive effect of the substituent. No influence of the $p\pi - d\pi$ interaction on the photoelectron spectra of sila-adamantanes has been observed.

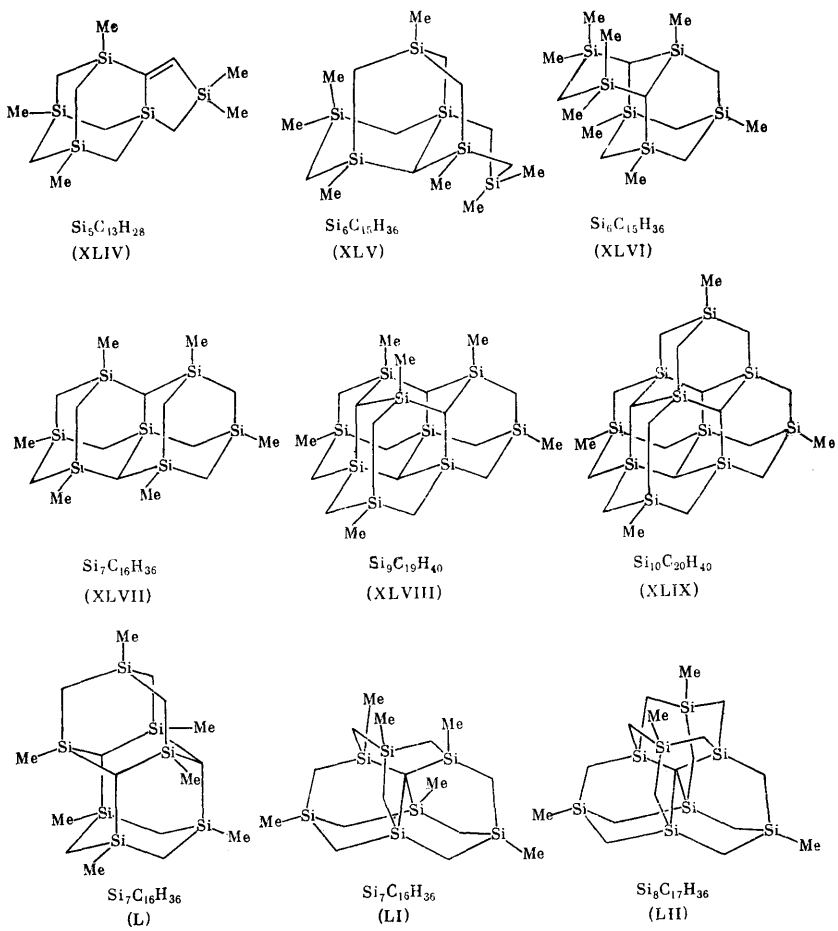
The infrared[110,124,127], ^{1}H NMR [103,105,110,115,118,124,127,131,132,139], and mass spectra[103,105,117,124,127,131] have been studied mainly in order to identify the compounds obtained. However, there has been one investigation specially devoted to the vibrational spectra of 1,3,5,7-tetramethyl-1,3,5,7-tetrasila-adamantane[140], whose author assigned the observed bands to the types of vibrations and carried out a number of calculations. The force constants obtained were compared with data for other organosilicon compounds.

The mass spectrum of $CbCl_4$, showing the presence of an intense $(M-15)^+$ peak, has been studied in greatest detail[141]. The authors noted that the appearance of this ion is probably associated with complex rearrangements of the skeleton requiring the dissociation of not less than three bonds.

Interesting results have been obtained in the determination of the basicity of Me_3CbNEt_2 in an aqueous medium and on comparing it with the basicities of other organic amines[142]. In view of the hydrolytic stability of the Si–N bond in the silylamine investigated, it was possible to achieve this for the first time. It was found that the basicity of the silylamine Me_3CbNEt_2 is much lower than those of triethyleneamine and 1-aminoadamantane. The authors[142] note that such decrease of the basicity of silylamines compared with their organic analogues is usually accounted for by the $d\pi$–$p\pi$ bonding in the ground state of the former, although one cannot rule out the possibility of the phenomenon, formulated by Pauling, as the neighbouring charge rule. It was shown in the above study that there is no appreciable 1,3-$(d-d)$ interaction in the molecules of sila-adamantanes in the excited state, the possibility of which for compounds with the Si–CH_2–Si group had been postulated earlier. This is confirmed by the results of a study of the ultraviolet spectra of $PhCbMe_3$ and Ph_2.$CbMe_2$; both phenyl groups in the latter compound proved to be electronically isolated, which indicates the absence of 1,3-$(d-d)$ interaction in this sila-adamantane nucleus[142].

(d) Applications of Carborundanes

Patents[104,111] recommend that Me_nCbX_{4-n} mixtures be used as mosquito repellents. It has been suggested that nitrogen-containing tetrasila-adamantanes be employed as emulsifying additives[128].



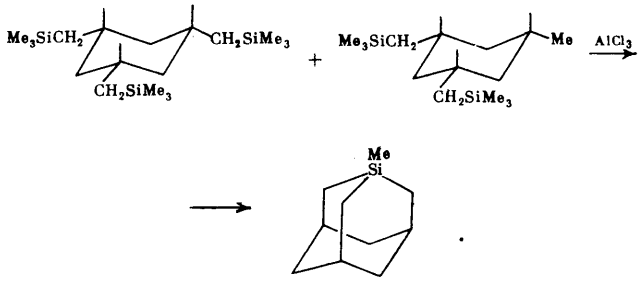
Compounds (XLIV)–(XLVII) and (L)–(LII) according to the data of Fritz and Marquardt[118] and compounds (XLVIII) and (XLIX) according to the data of Fritz et al.[113].

2. Higher Homologues of Carborundane

A number of higher homologues of Me_4Cb were obtained for the first time by Fritz from the pyrolysis products of tetramethylsilane[113,114,118]. Depending on the details of the steric structure, the authors separated these substances into two classes—"carborundanes" and "silascaphanes". Fritz used the latter name to designate polycyclic compounds belonging to a previously unknown class containing, together with the six-membered rings in the "chair" form, one or more rings in the "boat" form#[143]. Among the group of compounds (XLIV)–(XLIX) of the first type (see Figure), compound (XLVII), whose melting point and the relevant mass-spectrometric data[113,114] have been published and whose ^1H NMR [114] and photoelectron[138] spectra have been studied in detail, has been characterised most fully. The silascaphanes (L)–(LII) have been characterised in terms of the melting points, ^1H NMR data, and mass spectra[143]. Compound (LII) has been studied by X-ray diffraction[144].

3. Other Classes of Sila-Adamantanes

A compound with a single silicon atom in the adamantane nucleus has been synthesised recently[145]:

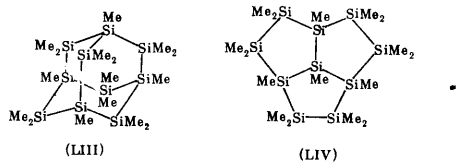


The structure of 1-methyl-1-sila-adamantane has been established by electron diffraction in the gas phase[146].

The class of sila-adamantanes includes also a group of adamantane-like compounds whose skeleton consists either of silicon atoms or of silicon and other atoms (for example, oxygen, sulphur, selenium, or phosphorus atoms). The compound $Si_{10}Me_{16}$ is of interest as a possible structural analogue of the adamantane whose skeleton consists of silicon atoms. It has been synthesised[147,148], together with other bicyclic and cellular compounds, by the reaction

$$Me_2SiCl_2 + MeSiCl_3 + Na/K \xrightarrow[C_{16}H_{34}]{THF} (MeSi)_n(Me_2Si)_m + Na(K)Cl \quad .$$

Mass-spectrometric, NMR, and infrared spectroscopic data established that the compound consists of a mixture of two postulated structural forms (LIII) and (LIV) in proportions of 3:1; the melting point of the mixture is above 360 °C.

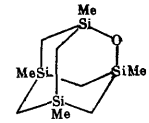


(LIII) (LIV)

According to original papers, all the rings are in the boat form in silascaphanes.

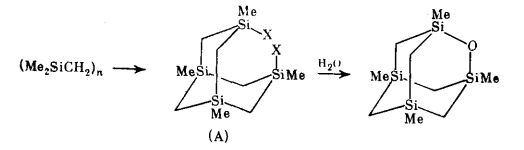
However, a final conclusion concerning the structure of $Si_{10}Me_{16}$ will be possible only after careful studies and X-ray diffraction analysis.

Sila-adamantanes in which one or several carbon atoms have been substituted by oxygen, sulphur, selenium, and phosphorus atoms have now been obtained. One such compound, 1,3,5,7-tetrasila-8-oxa-adamantane (LV), has been isolated by Fritz and coworkers[112,118] from the pyrolysis products of tetramethylsilane and characterised in terms of its mass and ^1H NMR spectra.



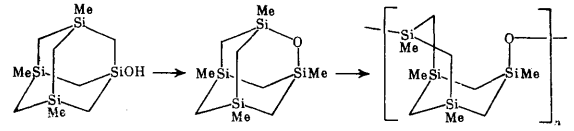
(LV)

The same compound as well as its chloro- and bromo-derivatives have been synthesised by Klosowski[149], who used Frye's method for this purpose[104]—the catalytic rearrangement of silmethylene derivatives of the type $(Me_2SiCH_2)_n (n \geq 2)$ and $(Me_2XSi)_2CH_2$ (X = Cl, Br, or Me) in the presence of aluminium halides. In his paper[149] and also in Frye's review[96] it is stated that in certain cases (these are not specified) the reaction mixture contains after rearrangement a side product having a postulated structure A, which leads to oxasila-adamantanes after hydrolysis:



(A)

According to Frye and Klosowski[96], oxasila-adamantanes can be formed in certain cases also as a result of the rearrangement of Me_3CbOH:

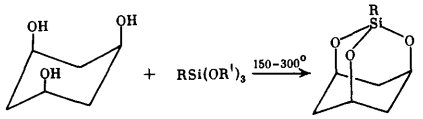


Their attempts[96] to obtain the silanol Me_3CbOH by heating $Me_3CbOCH_2CH_2NEt_2HCl$ in a highly acid medium led to a polymeric product, which may be formed as a result of the above reactions[96].

Klosowski[149] claims that the content of oxatetrasila-adamantanes in the mixture can be increased by carrying out the reaction in the presence of halogenating agents of the type of MeCOX (X = Cl, or Br) and Me_nSiX_{4-n} (X = Cl or Br, n = 1–3). It is suggested that these additives increase the yield of the products (A) and lead to oxasila-adamantanes in which one of the substituents at the silicon atom is chlorine or bromine. The authors note that, in contrast to the structure of the usual tetrasila-adamantanes, the structure of oxasila-adamantanes is apparently not free from strain, since the vibrational frequency of the Si–O–Si linkage is appreciably reduced. It is extremely likely that this structure will be readily polymerised with ring opening[96,149].

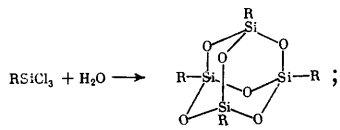
A method of synthesis of 3-substituted 2,4,10-trioxa-3-sila-adamantanes, consisting in the interaction of *cis*-phloroglucitol with trialkoxysilanes in the presence of triethylamine

on heating has been described[150,151]:



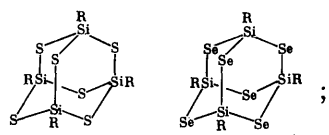
R = Me, Ph, or CH_2=CH; R' = Me or Bu.

Adamantanes of the purely siloxane type have been obtained by the hydrolysis of t-butyl and isopropyl-trichlorosilanes[152]; as a result of their high volatility, these compounds were isolated by sublimation from solid polymeric hydrolysis products. Their compositions and structures were established by elemental analysis and by molecular weight determinations (cryoscopically):



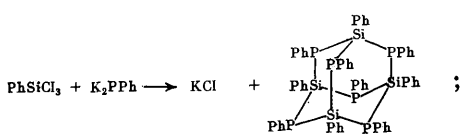
R = iso-Pr or t-Bu .

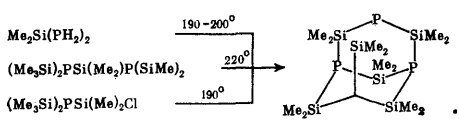
Analogous thiatetrasila- and selenatetrasila-adamantanes have been obtained under severe conditions from alkylsilanes or alkyltrichlorosilanes and hydrogen sulphide and hydrogen selenide respectively[153] and also from phenylsilane and sulphur[154].



R = Me or Et.

The crystal and molecular structures of the methyl derivative $(MeSi)_4S_6$ have been studied[155,156]. Compounds with a silicon–phosphorus adamantane nucleus have been obtained[157,158] by the reactions





IV. GERMYL- AND GERMA-ADAMANTANES

The first representative of germyladamantanes was obtained in 1973 [19]:

$$AdX + GeX_4 \xrightarrow{Na} AdGe\ (26\%)\ .$$

However, the Wurtz reaction, used successfully in this instance, proved to be relatively unsuitable for the synthesis of other germyladamantanes.

The unexpectedly easy condensation of 1-halogenoadamantanes with trihalogenogermane etherates was discovered in 1974 [87,159]:

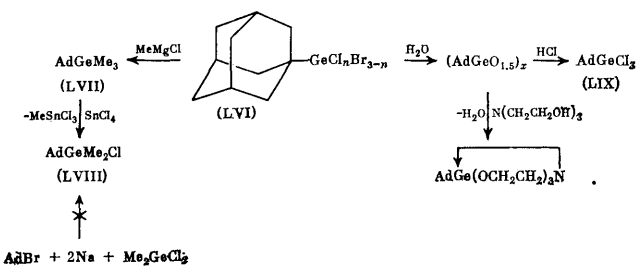
$$AdX + HGeX_3 \cdot 2Et_2O \xrightarrow[-HX]{50^\circ} AdGeX_3 + Et_2O \quad ;$$

X = Cl or Br.

In contrast to the condensation reactions with acyclic tertiary halides, the interaction of the etherates with 1-halogenoadamantanes proceeds slowly after prolonged refluxing of the reaction mixture. This factor is the cause of the low yield of 1-tribromogermyladamantane, since the etherate $HGeBr_3$ decomposes to ethanol and $C_2H_5GeBr_3$ after prolonged heating. Use of the more stable etherate $HGeCl_3$ leads to a high yield of the product (75%). When the etherate $HGeCl_3$ reacts with 1-bromoadamantane, a mixture of chloro(bromo)germyladamantanes $AdGeCl_nBr_{3-n}$ ($n = 0-3$) is formed in ~70% yield. When the etherate of trichlorogermane is replaced in this reaction by its aminate $Et_3N.HGeCl_3$, the yield is sharply reduced (to 10%) after the same reaction time and at the same temperature[87,159].

Certain reactions of trihalogenogermyladamantanes have been carried out (Scheme 14).

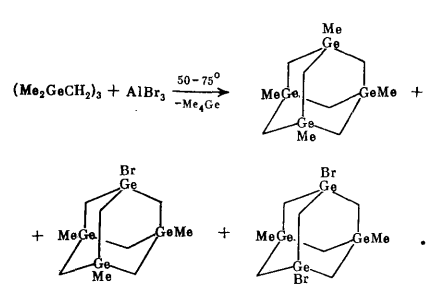
Scheme 14



It was found[87] that the presence of the adamantyl group does not introduce significant changes into the chemical behaviour of the functional groups linked to the germanium atom. The unusually slow and incomplete reaction involving the formation of 1-adamantylgermatrane compared with the synthesis of alkyl- and phenylgermatranes by a similar method is noteworthy[160]. The reaction between compound (LVII) and $SnCl_4$ takes place very selectively, leading to the elimination of the methyl and not the adamantyl group under relatively mild conditions. Thus a compound with the Ad–Sn bond could not be obtained. In the synthesis of compound (LVIII) by an independent method via the Wurtz reaction mainly the reduction of the bromoadamantane to adamantane was observed. Traces of compound (LVIII) were detected only chromatographically.

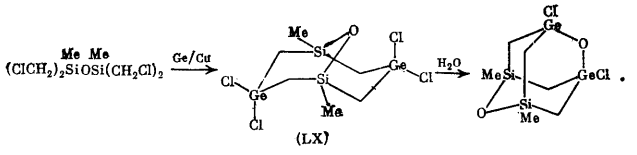
The structure of the germyladamantanes obtained was investigated by NMR[87]. Since the proton spectrum of the adamantane group is extremely complex and cannot be interpreted, ^{13}C NMR was used to investigate compounds (LVI)–(LIX).

The first representatives of 1,3,5,7-tetragerma-adamantanes have been obtained by a method analogous to that for the synthesis of carborundanes[161,162]:



It was established that, with increase of temperature and the reaction time, the monobromo-derivative is formed almost exclusively, with a slight admixture of the dibromo-compound. When bis(trimethylgermyl)methane was used as the starting material, the product proved to be a mixture of all three germa-adamantanes.

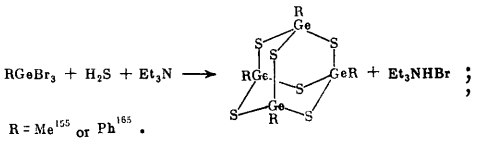
The attempts to synthesise a mixed oxasilagerma-adamantane have been reported[162-164]:



(LX)

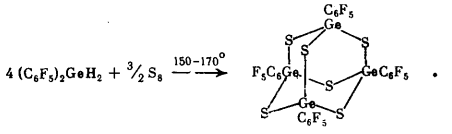
However, the products obtained in the last reaction stage contained only traces of the required compound, which were detected mass-spectrometrically. This is probably due to the steric structure of the intermediate bicyclic compound (LX) which is unfavourable for ring closure; the compound has the "chair–boat" conformation in the crystalline state[164].

Sulphur-containing germa-adamantanes have been obtained by the reaction

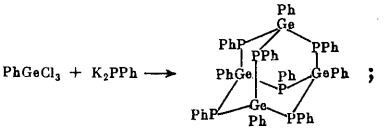


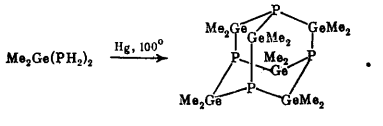
R = Me[155] or Ph[165].

The adamantane-like structure of the high melting crystalline products isolated was demonstrated by mass-spectrometric, infrared spectroscopic, and ^{1}H NMR data as well as X-ray diffraction[155,165]. An analogous derivative has been synthesised by Bochkarev et al.[166]:



Two-different phosphorus-containing germa-adamantanes have been synthesised[157,167]:





V. STANNYL- AND STANNA-ADAMANTANES

An adamantyl derivative of tin was obtained for the first time simultaneously by two groups of investigators[168,169], who studied the stereochemistry of the interaction of Me_3Sn anions with different organic halogeno-derivatives:

$$Me_3SnM + AdBr \longrightarrow Me_3SnAd \ ;$$

Me = Na, K, or Li.

In addition, it has been claimed[169] that not only 1-bromoadamantane but also the 2-bromo-derivative forms readily the corresponding adamantyltrimethylstannane under analogous conditions. Evidently in the case of the sterically rigid 1-adamantyl group the reaction proceeds with retention of configuration. To account for this finding, a two-stage reaction mechanism has been proposed[168,169]:

$$Me_3SnM + AdBr \xrightarrow{\text{slow}} Me_3SnBr + AdM$$
$$\downarrow \text{fast}$$
$$M = Na \text{ or } K. \qquad Me_3SnAd + MBr$$

According to Koermer et al.[168], nucleophilic S_N2 substitution at the halogen atom takes place in this instance. Later Roberts[19] repeated the synthesis of Me_3SnAd with the aid of an analogous reaction. Other derivatives (Me_2SnAd_2, Ph_2.$SnAd_2$) could not be obtained by this method, but the Wurtz reaction has been used successfully[19]:

$$Ph_3SnCl + Na + AdCl \longrightarrow Ph_3SnAd \ (19\%) \ ;$$
$$SnCl_4 + Na + AdCl \longrightarrow Ad_4Sn \ (20\%) \ .$$

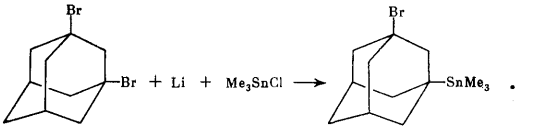
The compounds obtained were characterised in detail by elemental analysis, melting point measurements, infrared spectra, and NMR.

According to Roberts' hypothesis[19], the Wurtz reaction takes place in this instance via a radical mechanism involving electron transfer from sodium to R_3SnX and AdX:

$$R_3SnX + Na^{\cdot} \longrightarrow R_3Sn^{\cdot} + NaX \ ;$$
$$AdX + {}^{\cdot}Na \longrightarrow Ad^{\cdot} + NaX \ ;$$
$$R_3Sn^{\cdot} + Ad^{\cdot} \longrightarrow R_3SnAd \ .$$

It has been stated[19] that the process is accompanied by side reactions involving the dimerisation of the radicals with formation of Ad_2 and R_3SnSnR_3. The attempts to synthesise 1-adamantyltrichlorostannane by refluxing 1-chloroadamantane and $SnCl_2$ in diglyme (with and without the addition of amine salts as catalysts) were unsuccessful: mainly the reduction of chloroadamantane to adamantane was observed[87].

3-Bromo-1-trimethylstannyladamantane has also been synthesised[170]:



Certain chemical properties of adamantyl derivatives of tin have been investigated[19,171], mainly in reactions with electrophiles. The tetra-adamantane compound proved to be extremely inert with respect to bromine and $HgCl_2$. However, the same reagents interact vigorously with monoadamantyl derivatives:

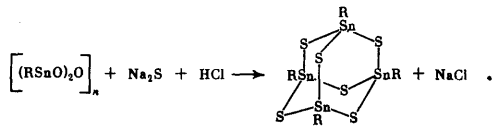
$$Me_3SnAd + X_2 \longrightarrow Me_2XSnAd \ ;$$
$$Me_3SnAd + HgCl_2 \longrightarrow Me_2ClSnAd \ ;$$

X = Cl or Br.

Triphenyladamantyltin reacts with bromine exclusively with the dissociation of the tin–phenyl bond.

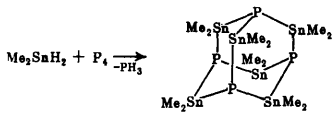
The physical properties of adamantylstannanes have so far been studied inadequately. Roberts[19] quotes the wavelengths of the infrared absorption bands of Me_3SnAd and Ph_3SnAd as well as ^{1}H and ^{13}C NMR data for the compounds synthesised (certain features of the proton spectra are also discussed). Several sulphur-containing adamantane-like compounds of tin have also been obtained. Komura and Okawara[172] investigated the reactions of methyl-, n-propyl-, and n-butyl-tin oxides with sodium sulphides in hydrochloric acids. The reaction of

the n-butyl compound yielded a product soluble in benzene, which made it possible to determine its molecular weight and to study some of its chemical properties:

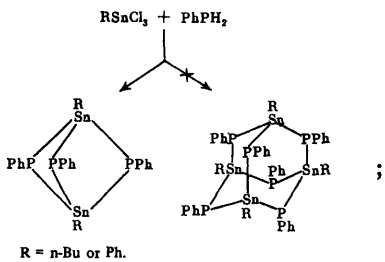


Later this compound was suggested as a stabiliser of PVC.[173] The methyl derivative (R = Me) obtained from $MeSnCl_3$ and Na_2S has an analogous structure[174] However, the adamantane-like structure of the compound obtained was established by X-ray diffraction much later[175].

Selenium- and tellurium-containing stanna-adamantanes $Me_4Sn_4X_6$ (X = Se or Te), whose structure was confirmed by infrared spectroscopic NMR, and X-ray diffraction data, were synthesised from $MeSnBr_2$ and NaHX.[176] A novel hexakis(dimethylstannyl) tetraphosphide has been obtained recently[177]:



It is noteworthy that the attempt to synthesise another phosphorus-containing stanna-adamantane was unsuccessful[155], although the analogous reactions with organosilicon and organogermanium compounds led to products with the adamantane structure:



R = n-Bu or Ph.

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During the preparation of the manuscript for the press, new reports on the chemistry of silicon-containing adamantanes were published. Among the new syntheses of silyladamantanes, the involvement of dihalogenoadamantanes and arylsilanes in the Friedel–Crafts reaction[178,179] as well as the interaction of adamantane with methylchlorosilane under the influence of lithium[180] should be mentioned. Polymers have been obtained from silyladamantanes; they exhibit improved thermal and radiation stabilities[181]. The structure of 1-methyl-1-sila-adamantane has been established by gas electron diffraction[182,183]. Studies on tin-substituted adamantanes are being continued: the methods of synthesis are being improved and the physicochemical properties (^{13}C NMR spectra) and the chemical behaviour of these compounds are being investigated[184].

Reports of the synthesis of a new inorganic high-strength fibre from silicon carbide, suitable for the preparation of a wide variety of compound materials, have recently begun to appear in the literature[185,186]. The technology of the preparation of this fibre consists in the spinning of thread from a polymeric oxygen-free organosilicon product and its subsequent thermal carborundation[187–189].

REFERENCES

1. H.Stetter, Angew.Chem., 66, 217 (1954).
2. H.Stetter, Angew.Chem., 74, 361 (1962).
3. R.Fort and P.Schleyer, Chem.Rev., 64, 277 (1964).
4. S.Landa, Neftekhimiya, 7, 476 (1967).
5. B.M.Mikhailov and L.S.Povarov, Zhur.Vses.Khim. Obshch.im.Mendeleeva, No.12, 77 (1967).
6. R.Fort and P.Schleyer, "Advances in Alicyclic Chemistry", Acad.Press, New York–London, 1966.
7. G.Gelbard, Ann.Chim., 4, 331 (1969).
8. V.V.Sevost'yanova, M.M.Krayushkin, and A.G.Yurchenko, Uspekhi Khim., 39, 1721 (1970) [Russ.Chem.Rev., No.10 (1970)].
9. R.C.Bingham and P.V.R.Schleyer, "Fortschritte der chemischen Forschung" (Topics in Current Chemistry), Springer, New York, Vol.18, 1971.
10. T.Sasaki, Kakagu no Ryoiki, 25, No.9,27 (1971) (Translation from Japanese No.TS-36134, All-Union Translation Centre).
11. N.V.Averina and N.S.Zefirov, Uspekhi Khim., 45, 1077 (1976) [Russ.Chem.Rev., No.6 (1976)].
12. Z.Kafka and V.Galik, Chem.Listy, 509 (1978).
13. V.F.Mironov, T.K.Gar, N.S.Fedotov, and G.E.Evert, "Adamantanovye Struktury v Khimii Kremniya, Germaniya i Olova" (Adamantane Structures in the Chemistry of Silicon, Germanium, and Tin), Izd. NIITEKhIM, Moscow, 1976.
14. V.P.Ushchenko, Candidate's Thesis, Volgograd, 1973.
15. B.I.No, S.S.Novikov, Yu.V.Popov, and V.P.Ushchenko, "Funktsional'nye Organicheskie Soedineniya i Polimery, Trudy Volgogradskogo Politekhnicheskogo Instituta" (Functional Organic Compounds and Polymers. Transactions of the Volgograd Polytechnic Institute), 1973, p.63; 1978, pp.29,34,37.
16. B.I.No, V.P.Ushchenko, and A.L.Sheigerevich, "Khimiya i Tekhnologiya Elementoorganicheskikh Soedinenii i Polimerov. Mezhvuzovskii Sbornik" (The Chemistry and Technology of Organoelemental Compounds and Polymers. Intercollegiate Collection), Kazan, 1972, Nos.1 and 2, p.37.
17. B.I.No, V.P.Ushchenko, Yu.V.Popov, and S.S.Novikov, USSR P.405 901 (1971); Byul.Izobret., No.45 (1973).
18. S.S.Novikov, B.I.No, and V.P.Ushchenko, "Tezisy Dokladov na Ukrainskoi Respublikanskoi Konferentsii 'Khimiya i Perspektivy Premeneniya Uglevodorodov Ryada Adamantana i Rodstvennykh Soedinenii'" (Abstracts of Reports at the Ukrainian Republic Conference on 'The Chemistry and Prospects for the Application of Hydrocarbons of the Adamantane Series and Related Compounds'), Kiev, 1974, p.10.
19. R.M.G.Roberts, J.Organometal.Chem., 63, 159 (1973).
20. V.F.Mironov, N.S.Fedotov, and G.E.Goler, see Ref.18, p.8.
21. E.A.Chernyshev, N.G.Komalenkova, S.A.Bashkirova, N.S.Fedotov, G.E.Evert, and V.F.Mironov, Zhur. Obshch.Khim., 48, 633 (1978).
22. J.E.Dubois, P.Bauer, G.Molle, and J.Daza, Compt. rend., 284C, 145 (1977).
23. V.F.Mironov, N.S.Fedotov, G.E.Evert, M.G.Kuznetsova, and A.V.Kisin, Zhur.Obshch.Khim., 49, 361 (1979).

24. V.F.Mironov, N.S.Fedotov, G.E.Evert, T.E.Latysheva, E.A.Chernyshev, N.G.Komalenkova, and S.A.Bashkirova, "Tezisy Dokladov na IV Mezhdunarodnym Simpoziume po Khimii Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the IVth International Symposium on the Chemistry of Organosilicon Compounds), Moscow, 1975, Vol.1, Part 2, p.68.
25. E.A.Chernyshev, N.G.Komalenkova, S.A.Bashkirova, G.M.Kuz'mina, N.S.Fedotov, and V.F.Mironov, USSR P.518 498 (1976); Byul.Izobret., No.23, (1976).
26. N.S.Fedotov, G.E.Evert, T.E.Latysheva, and V.F.Mironov, "Tezisy Dokladov na Vsesoyuznoi Konferentsii 'Khimii Poliedranov" (Abstracts of Reports at the All-Union Conference on 'The Chemistry of Polyhedranes'), Volgograd, 1976, p.97.
27. O.Zh.Zhebarov, Candidate's Thesis, Institute of Organic Chemistry, Bashkir Division of the USSR Academy of Sciences, Ufa, 1978.
28. V.V.Kaverin, Candidate's Thesis, Institute of Organic Chemistry, Bashkir Division of the USSR Academy of Sciences, Ufa, 1978.
29. V.F.Mironov, N.S.Fedotov, and T.E.Latysheva, Zhur.Obshch.Khim., 45, 2109 (1975).
30. V.F.Mironov, N.S.Fedotov, and G.E.Goler, USSR P.386 950 (1973); Byul Izobret., No.27, (1973).
31. V.F.Mironov, N.S.Fedotov, and G.E.Goler, Zhur.Obshch.Khim., 42, 1173 (1972).
32. V.F.Mironov, N.F.Fedotov, G.E.Evert, T.E.Latysheva, and V.N.Bochkarev, Zhur.Obshch.Khim., 44, 561 (1973).
33. V.F.Mironov, N.S.Fedotov, and G.E.Evert, USSR P.536 679 (1966); quoted after Ref.13.
34. S.S.Novikov, B.I.No, Yu.V.Popov, V.V.Son, and S.M.Dedov, see Ref.26, p.90.
35. S.S.Novikov, B.I.No, Yu.V.Popov, N.M.Khvoshcheva, I.S.Grigor'eva, and V.V.Son, Zhur.Obshch. Khim., 17, 1668 (1977).
36. V.V.Son, Candidate's Thesis, Volgograd Polytechnic Institute, Volgograd, 1978.
37. S.S.Novikov, B.I.No, Yu.V.Popov, V.I.Emel'yanov, V.V.Son, and P.A.Morozov, Zhur.Obshch.Khim., 47, 724 (1977).
38. B.I.No, Yu.V.Popov, and S.S.Novikov, USSR P.448 172 (1974); Byul.Izobret., No.40
39. V.F.Mironov and N.S.Fedotov, Zhur.Obshch.Khim., 42, 166 (1972).
40. K.F.Krasil'nikova, B.I.No, S.S.Novikov, Yu.V.Popov, and V.P.Ushchenko, see Ref.15, 1973 p.71.
41. K.F.Krasil'nikova, B.I.No, and S.S.Novikov, see Ref.15, 1973, p.63.
42. S.S.Novikov, B.I.No, Yu.V.Popov, and K.F.Krasil'nikova, see Ref. 18, p.12.
43. B.I.No, K.F.Krasil'nikova, I.R.Baranova, and S.S.Novikov, see Ref.15, p.94.
44. B.I.No, Yu.V.Popov, L.A.Kruglova, and S.S.Novikov, Zhur.Obshch.Khim., 46, 928 (1976).
45. M.P.Doyle, C.C.McOsker, and C.T.West, J.Org. Chem., 41, 1393 (1976).
46. W.Adam and J.del Fierro, J.Org.Chem., 43, 1158 (1978).
47. S.S.Novikov, B.I.No, Yu.V.Popov, and T.K.Korchagina, see Ref.26, p.96.
48. J.Schraml, J.Vcelak, V.Chvalovski, G.Engelhardt, H.Jancke, L.Vodicka, and J.Hlavaty, Coll.Czech. Chem.Comm., 43, 3179 (1978).
49. A.H.Alberts, H.Wynberg, and J.Strating, Tetrahedron Letters, 543 (1973).
50. B.I.No, Yu.V.Popov, and S.S.Novikov, Zhur. Obshch.Khim., 44, 2359 (1974).
51. Yu.V.Popov, Candidate's Thesis, Volgograd Polytechnic Institute, Volgograd, 1975.
52. B.I.No, L.A.Kruglova, Yu.V.Popov, and S.S.Novikov, Zhur.Obshch.Khim., 46, 929 (1976).
53. B.I.No, N.D.Sandigurskii, and E.V.Andrianova, see Ref.26, p.94.
54. W.Ando, M.Ikeno, and A.Sekiquchi, J.Amer.Chem. Soc., 100, 3613 (1978).
55. S.S.Novikov, B.I.No, Yu.V.Popov, and V.V.Son, see Ref.26, p.88.
56. S.S.Novikov, B.I.No, and V.P.Ushchenko, Zhur. Obshch.Khim., 45, 2029 (1975).
57. S.S.Novikov, B.I.No, V.P.Ushchenko, and V.S.Nikolenko, see Ref.26, p.92.
58. S.S.Novikov, B.I.No, Yu.V.Popov, and V.V.Son, Zhur.Obshch.Khim., 46., 2753 (1976).
59. B.I.No, V.P.Ushchenko, V.S.Nikolenko, and S.S.Novikov, Zhur.Obshch.Khim., 47, 2633 (1977).
60. S.S.Novikov, B.I.No, Yu.V.Popov, N.M.Khvoshcheva, and V.V.Son, Zhur.Obshch.Khim., 48, 234 (1978).
61. B.I.No, T.K.Korchagina, A.M.Beskopyl'nyi, Yu.V.Popov, and S.S.Novikov, Zhur.Obshch Khim., 1669 (1977).
62. S.S.Novikov, B.I.No, and V.P.Ushchenko, Zhur. Obshch.Khim., 45, 2029 (1975).
63. B.I.No, Yu.V.Popov, S.S.Novikov, and K.F.Krasil'nikova, Zhur.Obshch Khim., 44, 2358 (1974).
64. S.S.Novikov, B.I.No, Yu.V.Popov, and K.F.Krasil'nikova, see Ref.18, p.12.
65. B.I.No, K.F.Krasil'nikova, and S.S.Novikov, see Ref.15, p.51.
66. S.S.Novikov, B.I.No, K.F.Krasil'nikova, and G.N.Zipunnikova, see Ref.26, p.86.
67. S.S.Novikov, B.I.No, K.F.Krasil'nikova, and V.I.Platonova, see Ref.26, p.87.
68. B.I.No and K.F.Krasil'nikova, see Ref.15, p.43.
69. B.I.No, Yu.V.Popov, K.F.Krasil'nikova, and S.S.Novikov, USSR P.413 134 (1973); Byul Izobret., No.4 (1974).
70. B.I.No, Yu..V.Popov, and L.G.Shmeleva, "Khimiya i Tekhnologiya Elemento-organicheskikh Soedinenii i Polimerov. Mezhvuzovskii Sbornik" (The Chemistry and Technology of Organoelemental Compounds and Polymers. Intercollegiate Collection), Kazan, 1972, Nos.1 and 2, p.71.
71. S.S.Novikov, B.I.No, and Yu.V.Popov, see Ref.18, p.11.
72. B.I.No, Yu.V.Popov, and S.S.Novikov, USSR P.467 896 (1973); Byul Izobret., No.15 (1975).
73. B.I.No, Yu.V.Popov, and L.G.Kosenkova, see Ref.15, p.16.
74. T.Sasaki, A.Usuki, and M.Ohno, Tetrahedron Letters, 49, 4925 (1978).
75. V.F.Mironov, N.S.Fedotov, and V.L.Kozlikov, Khim.Geterotsikl.Soed., 354 (1968).
76. S.S.Novikov, B.I.No, Yu.V.Popov, N.M.Khvoshcheva, and V.V.Son, USSR P.652 182 (1977); Byul.Izobret., No.10 (1979).
77. A.M.Groult and G.G.Bellman, BRD Appl.No.2 424 765 (1974); Chem.Abs., 82, 171 878 (1975).
78. S.S.Novikov, A.P.Khardin, V.P.Ushchenko, and A.D.Kim, see Ref.26, p.93.

79. S.S.Novikov, B.I.No, V.P.Ushchenko, and N.S.Nikolenko, see Ref.26, p.91.
80. S.S.Novikov, A.P.Khardin, V.P.Ushchenko, A.K.Kim, and V.K.Brel', see Ref.26, p.89.
81. V.P.Ushchenko, A.D.Kim, A.P.Khardin, and V.K.Brel', Zhur.Obshch.Khim., **46**, 2157 (1976).
82. V.P.Ushchenko, A.D.Khim, A.P.Khardin, and V.K.Brel', Zhur.Obshch.Kim., **47**, 1371 (1977).
83. S.S.Novikov, B.I.No, V.P.Ushchenko, and V.S.Nikolenko, Zhur.Obshch.Khim., 231 (1977).
84. V.V.Severnyi, N.V.Varlamova, T.N.Sunekants, N.A.Suvorovskaya, Yu.D.Zyuzina, N.S.Fedotov, G.E.Evert, and V.F.Mironov, USSR P.535 322 (1976); Byul.Izobret., No.42 (1976).
85. Yu.A.Yuzhelevskii, N.N.Fedoseeva, V.P.Mileshkevich, V.F.Mironov, N.S.Fedotov, E.A.Galbovskii, and G.E.Evert, Vysokomol.Soed., **19**, 476 (1977).
86. G.I.Oleneva, M.M.Krayushkin, B.V.Sevost'yanova, A.G.Yurchenko, G.I.Danilenko, N.O.Cherskaya, and S.S.Novikov, Article deposited at the All-Union Institute of Scientific and Technical Information (VINITI) (No.1023-69, 1969).
87. V.F.Mironov, T.K.Gar, and A.V.Kisin, Symposium, "Khimiya Elementoorganicheskikh Soedinenii" (The Chemistry of Organoelemental Compounds), Izd.Nauka, Leningrad, 1976, p.33.
88. T.Pehk, E.Lippinaa, V.V.Sevostjanova, M.M.Krajuschkin, and A.J.Tarasova, Org.Magn.Res., 3, 783 (1971).
89. V.M.Kuznetsova, A.A.Sokolova, N.S.Fedotov, V.D.Petukhov, G.E.Evert, E.A.Bondarevskaya, and V.F.Mironov, see Ref.26, p.83.
90. Z.Dolejsek, S.Hala, V.Hanus, and S.Landa, Coll. Czech.Chem.Comm., 31, 435 (1966).
91. S.S.Novikov, B.I.No, I.A.Novakov, Yu.V.Popov, S.S.Radchenko, A.P.Khardin, O.A.Zauer, and V.V.Takhistov, see Ref.26, p.76.
92. N.F.Karpenko, O.S.Chizhov, S.S.Novikov, A.N.Yurchenko, and G.I.Danilenko, Izv.Akad.Nauk SSSR, Ser.Khim., 337 (1972).
93. V.E.Derbisher, Khimiya i Zhizn', No.4, 15 (1976).
94. G.Fritz, Chem.Z., 97, 111 (1973).
95. G.Fritz, Rheinisch-Westfalische Academia der Wissenschaften Vortrage, Westdeutscher Verlag Opladen, 1971, p.45.
96. C.L.Frye and J.M.Klosowski, Intra-Sci.Chem.Repts., 7, 147 (1973).
97. E.Osava and P.v.Schleyer, Kagaku no Ryoiki, 27, 365 (1973).
98. N.S.Nametkin, V.M.Vdovin, and K.S.Pushchevaya, Dokl.Akad.Nauk SSSR, 150, 562 (1963).
99. Yu.P.Egorov, K.S.Pushchevaya, E.D.Lubuzh, V.M.Vdovin, and A.D.Petrov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 822 (1963).
100. K.S.Pushchevaya, Candidate's Thesis, Topchiev Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, 1965.
101. V.F.Mironov, E.S.Sobolev, and L.M.Antipin, Zhur. Obshch.Khim., 37, 2573 (1967).
102. V.F.Mironov and A.L.Kravchenko, Izv.Akad.Nauk SSSR, Ser.Khim., 763 (1964).
103. C.L.Frye and D.R.Weyenberg, J.Amer.Chem.Soc., 92, 6379 (1970).
104. C.L.Frye and D.R.Weyenberg, US P.3 631 195 (1971).
105. G.Fritz and K.Kreilein, Z.anorg.Chem., 433, 61 (1977).
106. E.D.Babich, V.N.Karel'skii, V.M.Vdovin, and N.S.Nametkin, Izv.Akad.Nauk SSSR, Ser.Khim.,953 (1975).
107. V.F.Mironov, T.K.Gar, E.M.Berliner, and V.M.Nosova, see Ref.26, p.98.
108. V.V.Korshak, A.M.Polyakova, A.A.Sakharova, V.F.Mironov, and E.A.Chernyshev, Vysokomol. Soed., 2, 1370 (1960).
109. N.S.Nametkin, V.M.Vdovin, S.I.Zav'yalov, and P.N.Grinberg, Izv.Akad.Nauk SSSR, Ser.Khim., 929 (1965).
110. A.Smith and H.A.Clark, J.Amer.Chem.Soc., 83, 3345 (1961).
111. J.M.Klosowski and A.J.Barry, US P.3 631 197 (1971).
112. G.Fritz and J.Grobe, Z.anorg.Chem., 315, 157 (1962).
113. G.Fritz, F.Diem, H.Köhler, D.Kummer, and H.Scheer, Angew.Chem., 82, 445 (1970).
114. G.Fritz, H.Köhler, and D.Kummer, Z.anorg.Chem., 374, 54 (1970).
115. G.Fritz and N.Götz. Z.anorg.Chem., 375, 171 (1970).
116. G.Fritz, R.Haase, and D.Kummer, Z.anorg.Chem., 365, 1 (1969).
117. G.Fritz, W.König, and H.Scheer, Z.anorg.Chem., 377, 240 (1970).
118. G.Fritz and G.Marquardt, Z.anorg.Chem., 404, 1 (1974).
119. G.Fritz, Fortschr.Chem.Forsch., 4, 459 (1964).
120. G.Fritz, J.Grobe, and D.Kummer, Adv.Inorg. Chem.Radiochem., 7, 349 (1965).
121. G.Fritz, Angew.Chem., 79, 657 (1967).
122. V.F.Mironov, T.K.Gar, and A.A.Buyakov, Zhur. Obshch.Khim., 42, 1361 (1972).
123. L.H.Sommer, "Stereochemistry, Mechanisms and Silicon Compounds" (Translated into Russian), Izd. Mir, Moscow, 1966.
124. C.L.Frye and J.M.Klosowski, J.Amer.Chem.Soc., 94, 7186 (1972).
125. G.D.Homer and L.H.Sommer, J.Organometal. Chem., 49, C13 (1973).
126. L.H.Sommer, Intra-Sci.Chem.Rept., 7, 1 (1973).
127. G.D.Homer and L.H.Sommer, J.Amer.Chem.Soc., 95, 7700 (1973).
128. C.L.Frye and J.M.Klosowski, US P.3 890 334 (1975).
129. G.D.Homer and L.H.Sommer, J.Organometal.Chem., 46, C7 (1972).
130. G.D.Homer and L.H.Sommer, Chem.Comm., 1249 (1972).
131. G.Fritz, M.Berndt, and R.Huber, Z.anorg.Chem., 391, 219 (1972).
132. G.Fritz and M.Berndt, Angew.Chem.Int.Ed., 10, 510 (1971).
133. E.W.Krahé, R.Mattes, K.-F.Tebbe, H.G.Schnering, and G.Fritz, Z.anorg.Chem., 393, 74 (1972).
134. S.N.Gurkova, A.I.Gusev, V.A.Sharapov, and T.K.Gar, see Ref.26, p.82.
135. S.N.Gurkova, A.I.Gusev, V.A.Sharapov, T.K.Gar, and N.V.Alekseev, Zhur.Strukt.Khim., 20, 356 (1979).
136. M.Eckert-Maksić, K.Kovacević, and Z.B.Maksić, J.Organometal.Chem., 168, 295 (1979).
137. W.Schmidt, Tetrahedron, 29, 2129 (1973).
138. W.Schmidt, B.T.Wilkins, G.Fritz, and R.Huber, J.Organometal.Chem., 59, 109 (1973).
139. A.V.Kisin, V.F.Mironov, T.K.Gar, E.M.Berliner, and V.M.Nosova, see Ref.26, p.78.

140. R.Mattes, J.Mol.Struct., 16, 53 (1973).
141. R.S.Gohlke and R.J.Robinson, Org.Mass.Spectrom., 3, 967 (1970).
142. G.D.Homer and L.H.Sommer, J.Organomet.Chem., 67, C10 (1974).
143. G.Fritz, G.Marquardt, and H.Scheer, Angew. Chem., 85, 587 (1973).
144. H.G. von Schnering, G.Sawitzki, K.Peters, and K.-F.Tebbe, Z.anorg.Chem., 404, 38 (1974).
145. C.A.Kapfer and P.Boudjouk, J.Organometal.Chem., 144, C6 (1978).
146. Q.Shen, C.A.Kapfer, P.Bondjouk, and R.L.Hilderbrandt, J.Organometal.Chem., 169, 147 (1979).
147. R.West and A.Indriksons, J.Amer.Chem.Soc., 94, 6110 (1972).
148. R.West and A.Indriksons, The Vth International Congress on Organometallic Chemistry, Moscow, 1971", Vol.2, p.189.
149. J.M.Klosowski, US P.3 631 196 (1971).
150. A.I.Kuznetsov, B.A.Kamaritskii, V.Ya.Vainshtein, V.M.Mikhailov, and B.V.Unkovskii, USSR P.447 395 (1974); Byul Izobret., No.39 (1974).
151. A.I.Kuznetsov, B.A.Kamaritskii, V.Ya.Vainshtein, and B.V.Unkovskii, Zhur.Org.Khim., 12, 227 (1976).
152. E.Wiberg and W.Simmler, Z.anorg.Chem., 282, 330 (1955).
153. J.A.Forstner and E.L.Muetterties, Inorg.Chem., 5, 552 (1966).
154. F.Fehr and R.Luepschen, Z.Naturforsch. (B) 26, 1191 (1971).
155. K.Moedritzer, Inorg.Chem., 6, 1248 (1967).
156. J.C.Bart and J.J.Daly, J.Chem.Soc., 2063 (1975).
157. H.Schumann and H.Benda, Angew.Chem., 81, 1049 (1969).
158. V.G.Fritz, R.Uhlmann, and W.Hölderich, Z.anorg. Chem., 442, 86 (1978).
159. V.F.Mironov and T.K.Gar, Zhur.Obshch.Khim., 44, 464 (1974).
160. M.G.Voronkov, G.Zelcans, V.F.Mironov, J.Bleidelis, and A.Kemme, Khim.Geterotsikl.Soed., 227 (1968).
161. T.K.Gar, A.A.Buyakov, and V.F.Mironov, Zhur. Obshch.Khim., 42, 1521 (1972).
162. A.A.Buyakov, Candidate's Thesis, Moscow, 1973.
163. V.F.Mironov and T.K.Gar, see Ref.18, p.9.
164. T.K.Gar, A.A.Buyakov, A.I.Gusev, M.G.Los', A.V.Kisin, and V.F.Mironov, Zhur.Obshch.Khim., 46, 837 (1976).
165. A.Müller, P.Christophliemk, and H.P.Ritter, Z. Naturforsch., 28b, 519 (1973).
166. M.N.Bochkarev, L.P.Maiorova, N.S.Vyazankin, and G.A.Razuvaev, J.Organometal.Chem., 82, 65 (1974).
167. A.R.Dahl and A.D.Norman, J.Amer.Chem.Soc., 92, 5525 (1970).
168. G.S.Koermer, M.L.Hall, and T.G.Traylor, J.Amer. Chem.Soc., 94, 7205 (1972).
169. H.G.Kuivila, J.L.Considine, and J.D.Kennedy, J.Amer.Chem.Soc., 94, 7206 (1972).
170. W.Fischer and C.Grob, Helv.Chim.Acta, 61, 1588 (1978).
171. R.J.Ranson and R.M.G.Roberts, J.Organometal. Chem., 107, 295 (1976).
172. M.Komura and R.Okawara, Inorg.Nuclear Chem. Letters, 2, 93 (1966).
173. French P.1 537 462 (1968); Chem.Abs., 71, 13830 (1969).
174. P.Pleiffer and R.Lehnardt, Ber., 36, 3027 (1903).
175. C.Dörfelt, A.Janeck, D.Kobelt, E.F.Paulus, and A.Scherer, J.Organometal.Chem., 14, P22 (1968).
176. A.Blecher and M.Dräger, "The IXth International Conference on Organometallic Chemistry, Dijon, 1979", p.A42.
177. B.Mathiasch, "The IXth International Conference on Organometallic Chemistry, Dijon, 1979", p.A48.
178. N.S.Fedotov and G.E.Evert, "Tezisy Dokladov V Vsesoyuznoi Konferentsii po Khimii i Primeneniyu Kremniiorganicheskikh Soedinenii" (Abstracts of Reports at the Vth All-Union Conference on the Chemistry and Applications of Organosilicon Compounds), Moscow, 1980, p.43.
179. S.S.Novikov, B.I.No, Yu.V.Popov, N.N.Mamutova, and M.V.Troitskaya, Zhur.Obshch.Khim., 50. 638 (1980).
180. A.Ekouya, J.Dunogues, and R.Calas, J.Chem.Res. Synop., No.8, 296 (1978).
181. L.N.Pankratova, M.V.Zheleznikova, A.N.Goryachev, V.V.Severnyi, N.V.Varlamova, and E.A.Rogal', Khim.Vys.Energii, 501 (1979).
182. Q.Shen, C.A.Kapfer, P.Boudjouk, and R.L.Hilderbrandt, J.Mol.Struct., 54, 295 (1979).
183. Q.Shen,C.A.Kapfer, P.Boudjouk, and R.L.Hilderbrandt, J.Organometal.Chem., 169, 147 (1979).
184. H.G.Kuivila, J.L.Considine, R.H.Sarma, and R.J.Mynott, J.Organometal.Chem., 111, 179 (1976).
185. W.C.Still, J.Amer.Chem.Soc., 99, 4836 (1977).
186. S.Yajima, K.Okamura, J.Hayshi, and M.Omori, J.Amer.Chem.Soc., 59, 324 (1976).
187. S.Yajima, H.Hayashi, M.Omori, and K.Okamura, Nature, 261, 683 (1976).
188. S.Yajima, Ind.Eng.Chem.Prod.Res.Dev., 15, 219 (1976).
189. S.Yajima, H.Kayano, K.Okamura, M.Omori, J.Hayashi, T.Matsuzawa, and K.Akutsu, Bull.Am. Ceramic Soc., 55, 1065 (1976).