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The Synthesis and Properties of Silicon-, Germanium-, Tin-, and Lead-containing s-Triazines

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Published data on the methods of synthesis and properties of s-triazines containing group IVb elements have been summarised and systematised. The reaction mechanisms have been discussed, and various aspects of the practical application of s-triazines examined.
The bibliography contains 222 references.

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I. INTRODUCTION

The first papers on the synthesis of derivatives of s-triazine appeared about the middle of last century. Thousands of compounds of this class have now been prepared and studied, and in a number of cases have found practical applications. The interest in these compounds is related to their high inertness and chemical and thermal stability, which result from the unique electronic structure of the ring, and also to the high biological activity of some derivatives. Most published data on the methods of preparation, structure, properties, and applications of organic s-triazines and their salts have been summarised in a monograph[1] and reviews,[2,3] but there has been practically no systematisation of published data on their hetero-organic analogues, which are attracting increasing interest.

The aim of the present work was to systematise published data on the synthesis, reactivity, physicochemical properties, and applications of silicon-, germanium-, tin-, and lead-containing derivatives of s-triazine in which the element-containing fragments are joined directly to the ring.

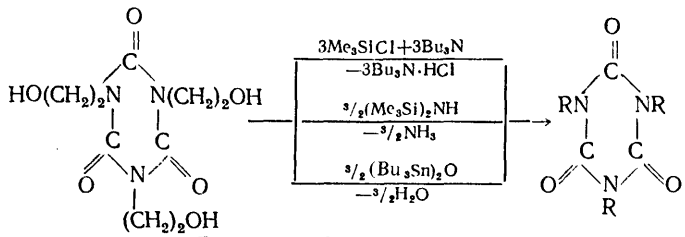
Papers dealing with carbofunctional s-triazines are not considered in detail, and are used only for comparison with data on the main group of compounds being examined, although the information on these compounds is given in full. The review includes material published in monographs, journal articles, and patents up to June 1984.

II. METHODS OF SYNTHESIS

1. The Reaction of s-Triazines with Hetero-organic Compounds

The first representative of this group of compounds, tris-(β-trimethylsiloxyethyl) isocyanurate, was synthesised in high yield by the reaction of tris(β-hydroxyethyl) isocyanurate with trimethylchlorosilane in the presence of Bu_3N [4] (scheme 1):

Scheme 1

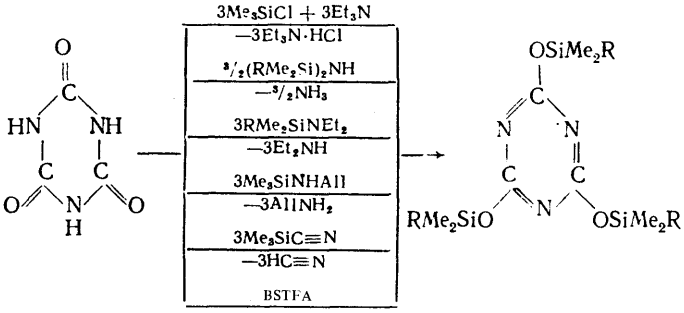


R= $(CH_2)_2OSiMe_3$, $(CH_2)_2OSnBu_3$.

The organotin analogue of the same isocyanurate was obtained in quantitative yield by the reaction with hexabutyldistannoxane,[5,6] and also by the reaction of $(Bu_3Sn)_2O$ with bis(β-iodoethyl) β-hydroxyethyl isocyanurate (yield 15%) and of tris(tributylstannyl) isocyanurate with ethylene oxide.[5]

An attempt to silylate isocyanuric acid in an autoclave at 350 °C by a shceme analogous to scheme 1 was initially unsuccessful,[7] but the use of dimethylformamide as solvent and of triethylamine (Et_3N) as HCl acceptor gave tris(trimethylsilyl) cyanurate in 74% yield[8-11] (scheme 2):

Scheme 2



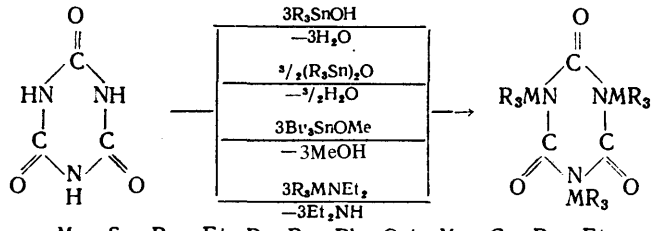
All = $-CH_2-CH=CH_2$, R = H, Me.

This cyanurate and its dimethylsilyl analogue were also obtained using the corresponding triorganosilylamines (scheme 2),[8-14] trimethylsilyl cyanide,[15] or N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA).[16]

The most promising reactions, because of their high yields and the purity of the desired products, are the reactions of isocyanuric acid with hexamethyl- or tetramethyldisilazanes (ammonium sulphate catalyst). The organosilicon cyanurates obtained can be purified by vacuum distillation, but increase in the distillation temperature or the presence of chlorine-containing impurities leads to their thermal decomposition.[12-14,17]

The first organotin s-triazines were obtained by Stamm,[18-20] again by the direct metallation of isocyanuric acid by tin-containing oxides and hydroxides (100–160 °C); with evacuation [scheme (3)]:

Scheme 3



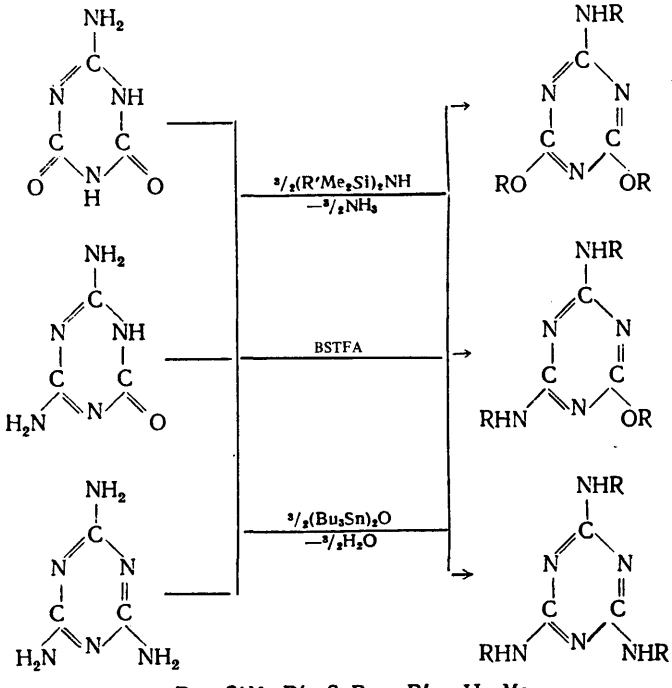
M = Sn, R = Et, Pr, Bu, Ph, Oct; M = Ge, R = Et.

The same method was later used to synthesise tris-substituted isocyanurates of triethyl- and tripropyltin.[21-23] The synthesis of these products by the reaction of cyanic acid with organotin oxides and hydroxides has been reported.[24] Under the given conditions (120–190 °C), however, the process probably involves the formation of isocyanuric acid, followed by reaction according to scheme 3.

The reaction of isocyanuric acid with methoxy- and diethylaminostannanes or diethylaminogermane gives the corresponding highly pure hetero-organic isocyanurates.[8,9,25]

Tris(organosilicon)- and tris(organotin)-derivatives of amino(hydroxy)-s-triazines were obtained similarly. Thus the reaction of the latter with hexamethyl- and tetramethyldisilazanes (HMDS and TMDS respectively) or BSTFA gave tris(trimethylsilyl)- and tris(dimethylsilyl)ammelide, -ammeline, and -melamine[9,11,16,26,27] (scheme 4):

Scheme 4



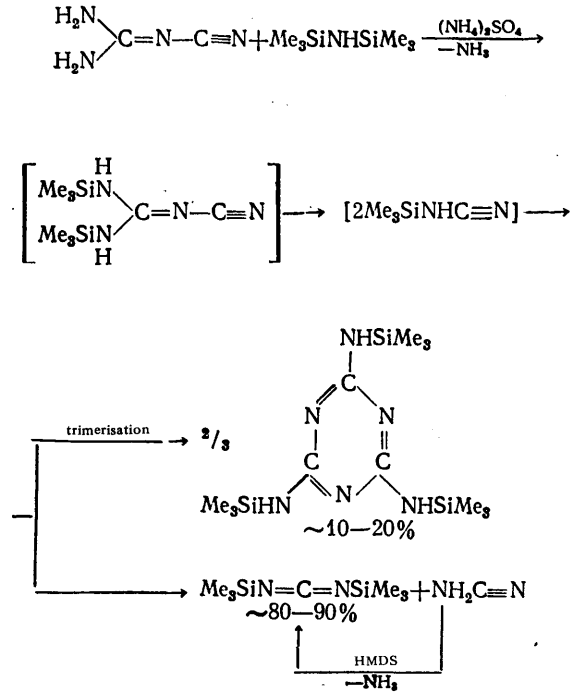
R = $SiMe_2R'$, $SnBu_3$; R' = H, Me.

The same heterocyclic compounds react with hexbutyldistannoxane to give the corresponding organotin compounds in good yield,[9,28] but they do not react with hexaethyldigermoxane.

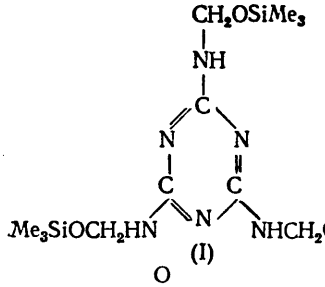
Silylation using HMDS or TMDS (ammonium sulphate catalyst) becomes increasingly difficult in the series isocyanuric acid–ammelide–ammeline–melamine, that is as the carbonyl groups are replaced by NH_2 groups. Thus the silylation of the first member of the series takes not more than 1–2 h, and a catalyst is not necessary, whereas tris-silicon-substituted melamine is obtained in 70% yield only after heating the reagents for 60 h in the presence of $(NH_4)_2SO_4$.

Other workers[29] who repeated this synthesis (H_2SO_4 catalyst, 140 °C, 6 h) were able to isolate only 2,4-bis(trimethylsilylamino)-6-amino-s-triazine in 35.5% yield, and the tris-substituted analogue was not obtained. There is no doubt that tris(trimethylsilyl)melamine exists, however, since it has been isolated in large quantities and identified as a by-product in the extended treatment of bis(trimethylsilyl)-carbodi-imide by the published methods.[30-33] A scheme for the formation of an organosilicon derivative of melamine has been proposed[33] (scheme 5):

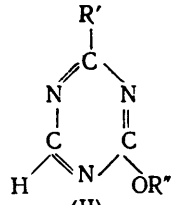
Scheme 5



Reactions analogous to those of schemes 1–4 can also be used to obtain silylated derivatives of methylol- and organo-substituted melamines (for example compound (I),[34-37] amino-(hydroxy)-s-triazines (II),[38-42] organosilicon and organotin diallyl or dicyanoethyl isocyanurates (III), (IV),[5,6,43-45] and other compounds, frequently used as intermediates in organic synthesis:

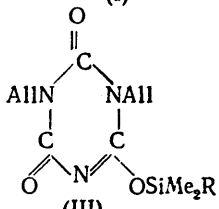


(I)



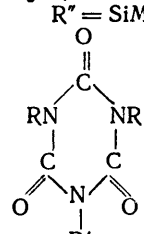
(II)

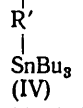
$R' = NHSiMe_3$, $OSiMe_3$; $R'' = SiMe_3$



(III)

R = H, Me



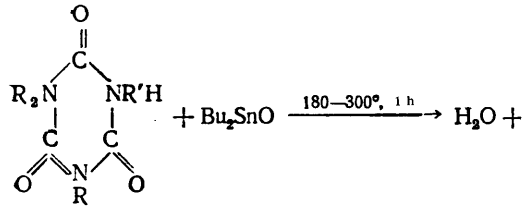


(IV)

R = All, $(CH_2)_2CN$;
R′ = $CH_2CH_2C(O)O$, CH_2CH_2O.

Organotin bis-triazine derivatives are formed according to a scheme which does not differ fundamentally from scheme 3 [5,6,46,47] (scheme 6):

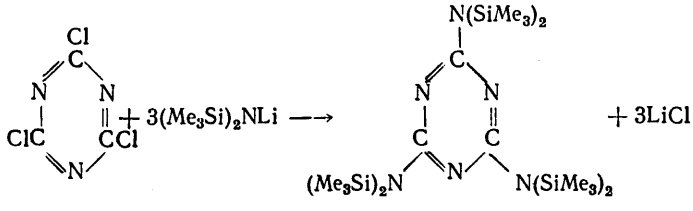
Scheme 6



R = All, CH_2—CH_2—C≡N, R′ = —; R = All, R′ = $CH_2CH_2C(O)O$, CH_2CH_2O

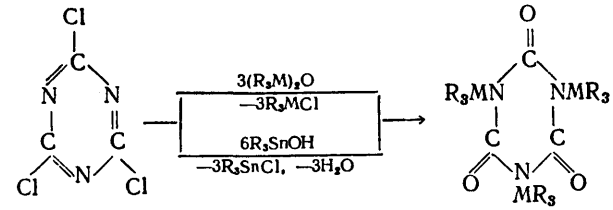
Mono-, di-, and trimethylsilyl derivatives of melamine can be synthesised using cyanuric chloride as the original s-triazine, and hexakis(trimethylsilyl)melamine has been obtained in low yield by the reaction of the latter with $(Me_3Si)_2NLi$ [29, 32,48–50] (scheme 7):

Scheme 7



Cyanuric chloride has also been used to obtain other hetero-organic s-triazines. Thus the organogermanium s-triazine tris(triethylgermyl) isocyanurate was first synthesised according to scheme 8 by heating a mixture of the reagents in dibutyl ether for a long time. The yield was 73%. [51]

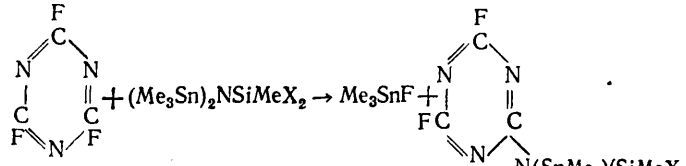
Scheme 8



M = Ge, R = Et; M = Sn, R = Et, Bu, $PhCH_2$— .

Cyanuric chloride reacts similarly with triethyltin and tribenzyltin hydroxides and hexabutyldistannoxane. [51] The use of cyanuric chloride to obtain various carbofunctional organosilicon s-triazines [48,52–57] (including trimethylsilylethynyl, [52] trimethylsilylphenyl, [53] and other derivatives) and triazine-containing polysiloxanes [58–66] has also been described. Cyanuric fluoride can be used instead of cyanuric chloride. Thus the reaction of cyanuric fluoride with mixed organosilicon–tin amines has been used to synthesise a number of corresponding mono-substituted s-triazines [67] (scheme 9):

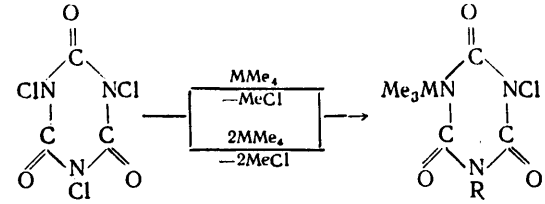
Scheme 9



X = Me, Cl, F

Trichloroisocyanuric acid has been used to synthesise hetero-organic compounds of this class. A method has been described [68] for obtaining mono- and di-substituted organotin isocyanurates and a dialkyltin bis-isocyanurate derivative using the above chlorine-containing heterocyclic compound. The same method was used to prepare the only mono- and di-substituted organolead s-triazines which have been obtained up to the present, namely dimethylplumbyl dichloroisocyanurate and bis(trimethylplumbyl) chloroisocyanurate [68] (scheme 10):

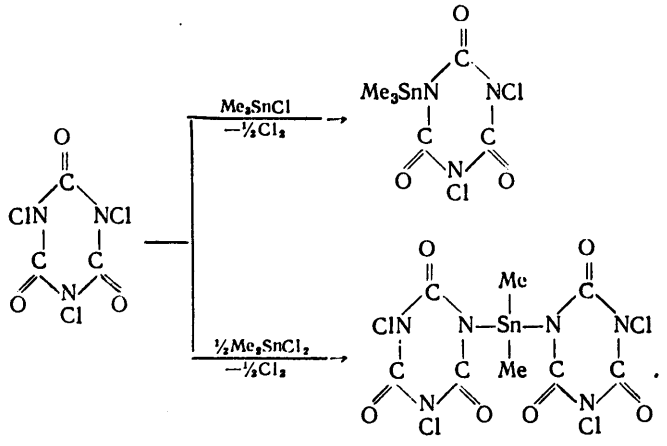
Scheme 10



M = Sn, Pb; R = Cl, MMe_3 .

If the metallating reagent contains a chlorine atom, molecular chlorine is liberated instead of methyl chloride. For example, in the case of trimethylchloro- or dimethyldichlorostannanes, the products were chlorine and trimethylstannyl dichloroisocyanurate or bis(di-chloroisocyanurato)dimethylstannane respectively (scheme 11):

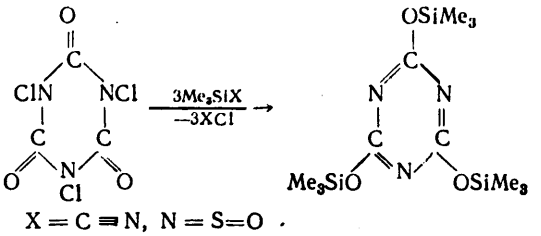
Scheme 11



The analogous organosilicon derivatives, trimethylsilyl and dimethylsilyl dichloroisocyanurates, have been described.[69]

The reaction of trichloroisocyanuric acid with trimethylsilyl cyanide and sulphinyl imide,[15] in which exchange of trimethylsilyl fragments and chlorine atoms takes place to give tris-(trimethylsilyl) cyanurate, was studied later (scheme 12):

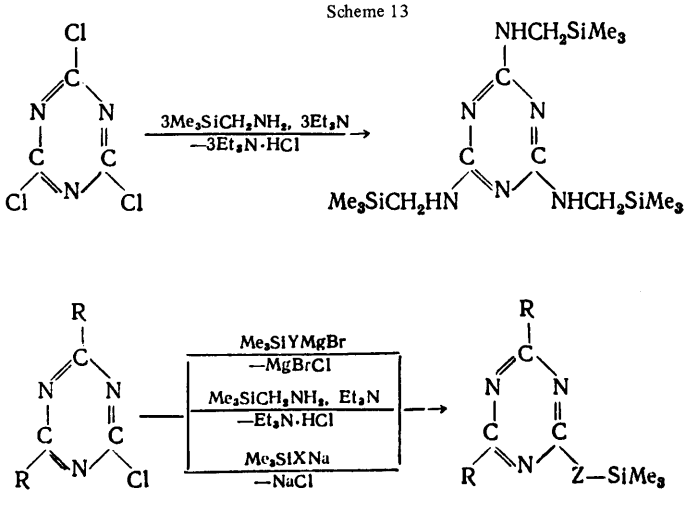
Scheme 12



X = C ≡ N, N = S=O .

The routes by which cyanuric chloride and other halogenotriazines are converted into their hetero-organic analogues are extremely varied. For example, the above trimethylsilylethynyl[52] or trimethylsilylphenyl[53] heterocycles are obtained using a Grignard reagent, and a number of carbofunctional derivatives are obtained by the reaction with Me_3SiCH_2L (L = NH_2, ONa, SNa; boiling benzene, 6 h)[51] (scheme 13):

Scheme 13

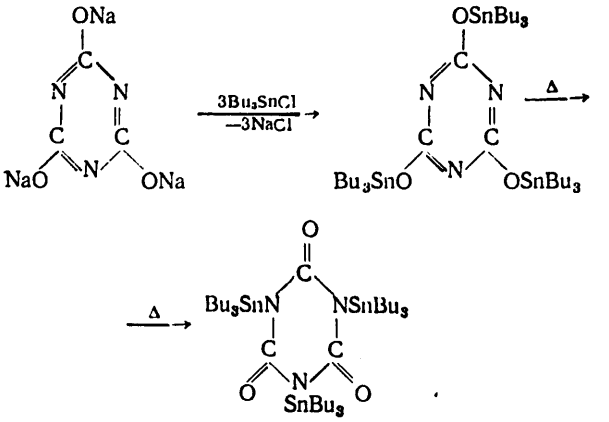


R = Cl, Y = Z = —C ≡ C—, —C_6H_4—; R = Ph,
X = Z = CH_2O, CH_3S; R = Ph, NH_2, Z = CH_2NH.

In contrast to this scheme, the reaction of cyanuric chloride with sodium triethylsilanolate (160–200 °C, 1 h, without solvent) gave not tris(triethylsilyl) cyanurate but its decomposition product Et_3SiNCO and NaCl.[17]

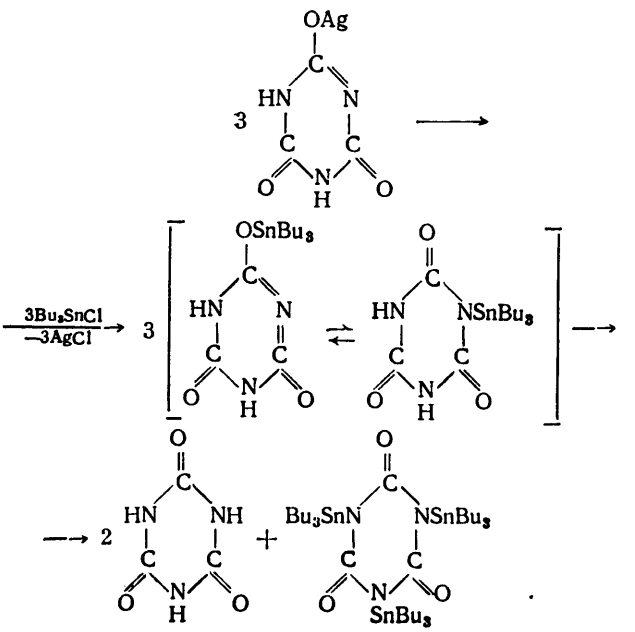
Sodium chloride is also formed in the reaction of sodium isocyanurate with tributylstannyl chloride (50 °C, 5 h), and the yield of the desired product, tris(tributylstannyl) isocyanurate, reaches only 18%.[51] The authors proposed and confirmed by infrared (IR) spectroscopy a reaction scheme involving the intermediate formation of the comparatively unstable cyanurate isomer (scheme 14):

Scheme 14



The transformations involving tributylstannyl chloride and various salts of isocyanuric acid were studied in more detail in Ref.70. The addition of moist solvents (acetonitrile, dimethylformamide) to the reaction system increases the yield of the Sn-s-triazine to 37%. In dry dimethylformamide the yield was 15%. The influence of moisture is attributed to the partial hydrolysis of the original salt to give isocyanuric acid, which is then stannylated by the hexabutyldistannoxane formed to give the tris-substituted isocyanurate according to scheme 3. The reaction of tributylstannyl chloride with thoroughly dried monosilver isocyanurate, contrary to expectations, also gave tris(tributylstannyl) isocyanurate (yield 79%) (scheme 15):

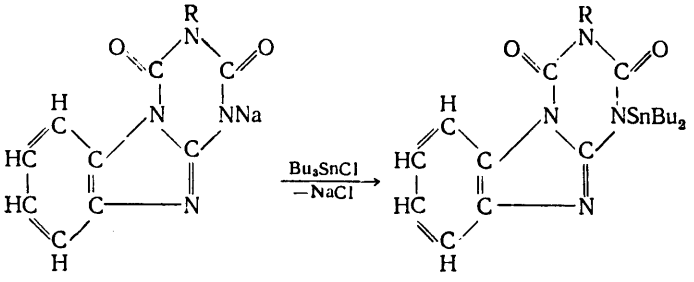
Scheme 15



Treatment of the unseparated reaction mixture with hexabutyldistannoxane gave an additional quantity of organotin isocyanurate. Similar treatment of monocalcium isocyanurate gave the same product in 70% yield.

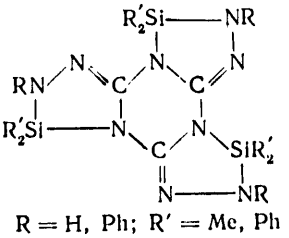
In contrast to this, the monosodium salts of triazine benzimidazoles react with tributylstannyl chloride to give the corresponding mono-substituted organotin compounds[71,72] according to scheme 16:

Scheme 16



R = $(CH_2)_5CN$, $(CH_2)_5CO_2Me$, $(CH_2)_5CO_2Et$, NMe_2, Alk, Ar etc.

A series of substituted organosilicon triazoles containing triazine rings were obtained similarly.[73]

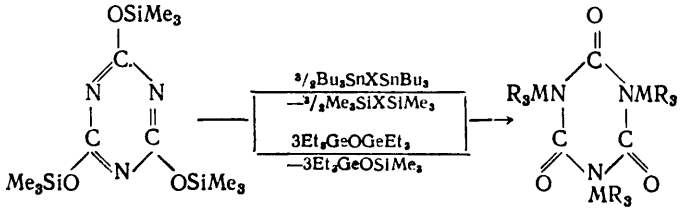


R = H, Ph; R′ = Me, Ph.

A promising method for obtaining hetero-organic s-triazines is provided by remetallation, which gives high yields and pure products. The chief condition for success is the continuous vacuum distillation of the volatile products.

This method was used to synthesise tris(triethylgermyl) and tris(tributylstannyl) isocyanurates; the substrate used was tris(trimethylsilyl) cyanurate, and hexaethyldigermoxane was remetallated to $Et_3GeOSiMe_3$ [9,33,74] (scheme 17):

Scheme 17

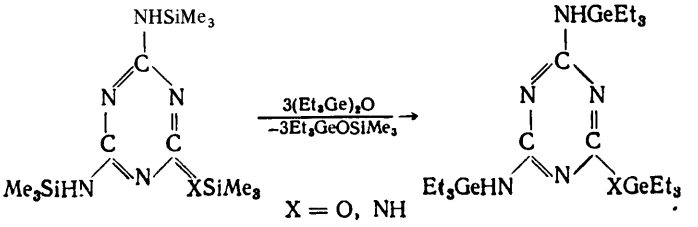


M = Ge, Sn; X = O, N=C=N.

The remetallation is reversible, and without evacuation gives a mixture of the starting materials and final products[75] (see scheme 43 in section IV).

By analogy with scheme 17, the corresponding organosilicon compounds gave for the first time tris-substituted organogermanium derivatives of ammeline and melamine[9,28] (scheme 18):

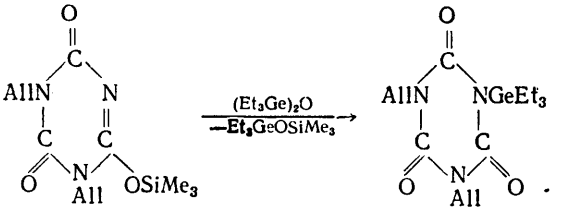
Scheme 18



X = O, NH

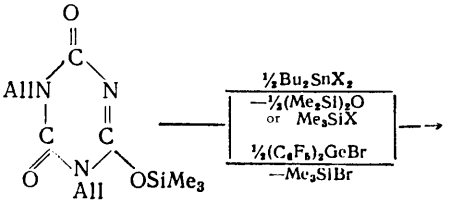
Remetallation also proved successful for the synthesis of triethylgermyl diallyl isocyanurate, since diallyl isocyanurate undergoes practically no direct reaction with hexaethyldigermoxane (200 °C, yield <5%)[43] (scheme 19):

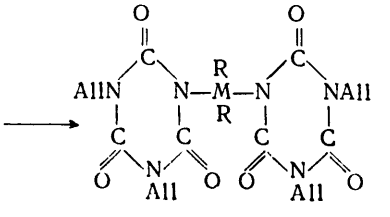
Scheme 19



This method has been used to synthesise a number of hetero-organic derivatives of polydiallyl isocyanurates. Thus the reaction of two moles of trimethylsilyl diallyl isocyanurate with dichloro-, dibromo-, or dimethoxydibutylstannanes or dibutylstannoxane under comparatively mild conditions (100–120 °C, 0.5 h) gave bis(diallyl isocyanurato)dibutylstannane[46,76] according to scheme 20:

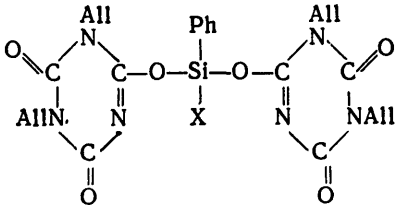
Scheme 20



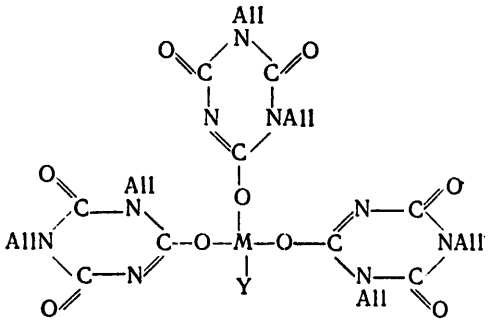


X_2 = O, $O(Me)_2$, Cl_2, Br_2; M = Ge, R = C_6F_5; M = Sn, R = Bu

The use of the corresponding hetero-organic halides and reagent ratios gave quantitative yields of bis(diallyl isocyanurato)methylphenyl- and -diphenylsilanes [compounds (V) and (VI)] and also tris(diallyl isocyanurato)chlorogermane and -vinylsilane (VII) and (VIII):[76]



X = Me(V), Ph(VI)

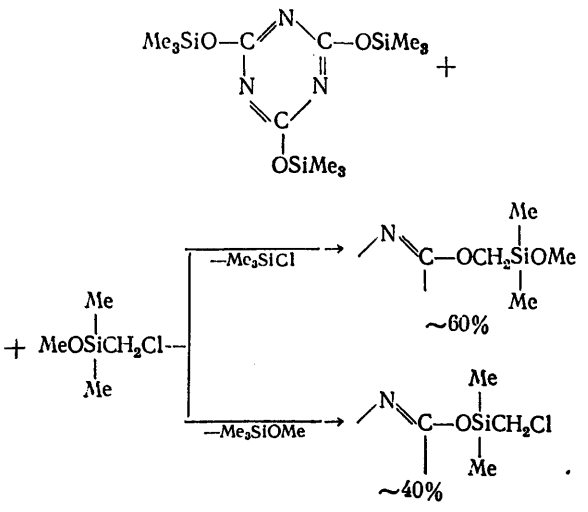


M = Ge, Y = Cl(VII); M=Si, Y=Vin(VIII)

It should be emphasised that organogermanium s-triazines are becoming accessible as a result of remetallation, since the most widely encountered starting materials, namely isocyanuric acid, ammelide, ammeline, melamine, and their many derivatives do not react with hexaethyldigermoxane under real conditions. The use of other germylating agents gives low yields of product.[9]

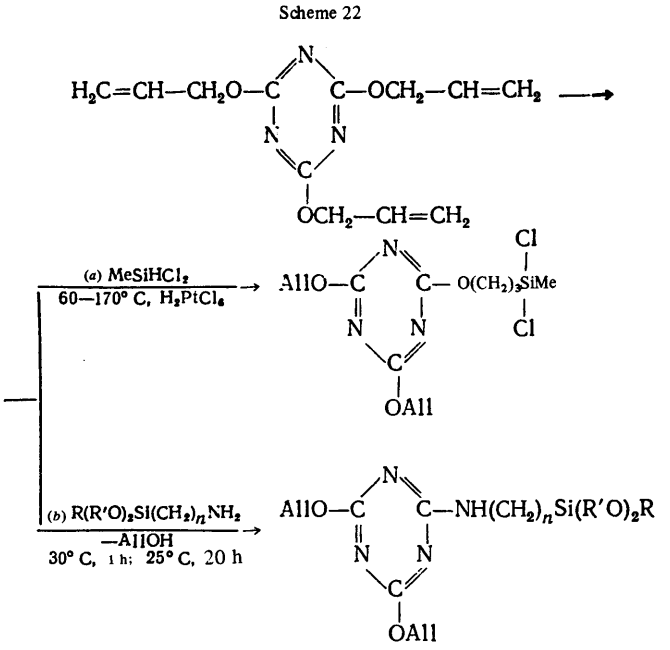
Tris(trimethylsilyl) cyanurate can react with α-chloromethylsilanes such as $(MeO)Me_2SiCH_2Cl$, $(EtO)_2MeSiCH_2Cl$, $(EtO)_3SiCH_2Cl$, etc. both in the direction of resilylation to give the alkoxytrimethylsilane and in the direction of silicoalkylation to give trimethylchlorosilane. This gives a mixture of organosilicon cyanurates containing two types of substituent in different combinations in the triazine ring[48] (scheme 21):

Scheme 21



Analogous compounds can also be obtained by the hydrosilylation of triallyl isocyanurate by chlorohydrosilanes, which, depending on the reagent ratio and the reaction conditions, gives the products of mono-, di-, and tris-addition, for example according to scheme 22a:[48]

Scheme 22



R = Me, R'O; R' = Me, Et; n = 2,4 .

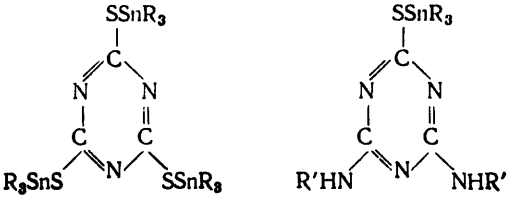
The same original s-triazine on partial ammonolysis under the influence of silylamines such as $R(R'O)_2Si(CH_2)_nNH_2$ is converted into the corresponding mono-substituted aminosilyl derivatives (scheme 22b).[77,78]

Hydrosilylation has also been used to prepare fluorosilicone-triazine polymers.[79-82]

Here it may be noted that the s-triazines synthesised according to schemes 21 and 22 [49,77,78,83] are as yet the only carbofunctional cyanurates, since other known analogues of this series exist in the oxo-form. In particular, Berger[84-87] showed by IR and NMR spectroscopy that the carbofunctional mono-, di-, and trialkyoxyorganosilicon heterocycles of this class, obtained by the reaction of triallyl isocyanurate with alkoxyhydrosilanes (100 °C, H_2PtCl_6), are isocyanurates.

A carbofunctional oxo-compound, tris[β-trimethylsilyl)-propionyl] isocyanurate, was synthesised by the reaction of tris(trimethylsilyl) cyanurate with β-(trimethylsilyl)propionyl chloride[17] (see scheme 39b, section IV).

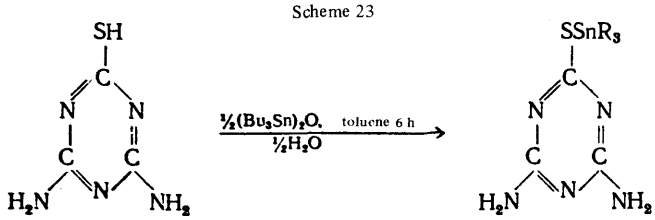
Sulphur-containing derivatives of organotin s-triazines have been obtained in good yields by the reaction of the appropriate thio-derivatives with various metallating agents according to schemes analogous to schems 1–4.[88-92] Examples of these compounds are tris[trialkyl(aryl)stannyl] trithiocyanurates and substituted trialkyl(aryl)stannylthioammelines



R = Pr, Bu, Ph, $PhCH_2$; R' = Et, Pr, iso-Pr, Bu, All, $MeO(CH_2)_2$, $MeO(CH_2)_3$ etc.

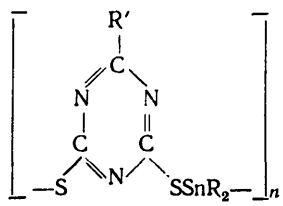
Unlike ammeline, thioammeline can undergo selective stannylation of the thiol group (scheme 23):[88]

Scheme 23



R = Pr, Bu, Ph, $PhCH_2$.

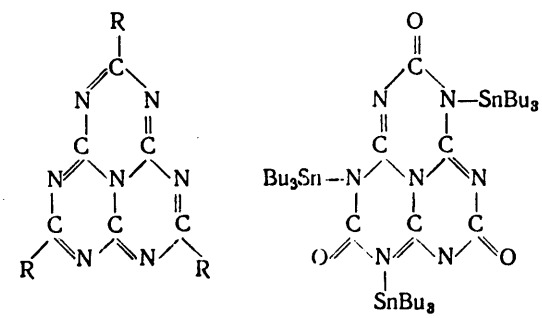
The reaction of thiotriazines or their sodium salts with dialkylstannoxanes and dichlorostannanes respectively gave oligomeric and polymeric s-triazine derivatives:[93]



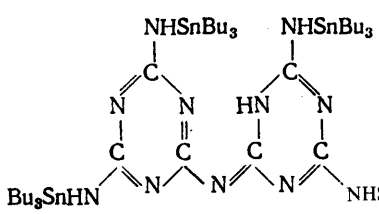
R = Me, Bu, Oct, Ph; R' = PhO, PhNH, EtNH, Et_2N, MeO etc.; n = 5—293 .

In addition to the data on organosilicon sulphur-containing s-triazines given in scheme 13,[57] data on the preparation and uses of a number of their analogues have also been published.[94,95]

This group of methods can also be used to synthesise condensed and other complex hetero-organic systems containing s-triazine rings. Thus the reaction of hexabutyldistannoxane with cyameluric acid, melem, and melam gives tris-(tributylstannyl) cyamelurate, tris(tributylstannyl)melem, and tetra(tributylstannyl)melam respectively.[27,96,97] HMDS has been used to synthesise tris(trimethylsilyl) cyamelurate in high yield, but melem and melam do not undergo this reaction.



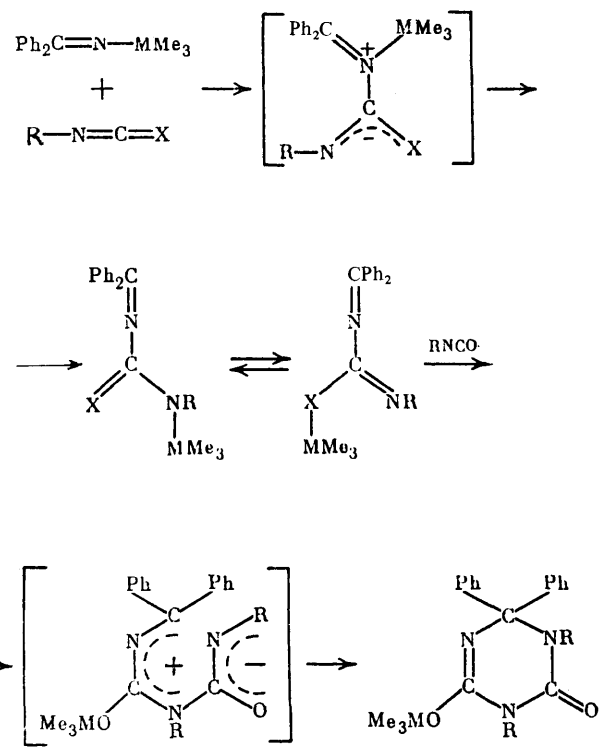
R = $OSiMe_3$, $NHSnBu_3$



2. The Cyclo-addition of Isocyanates to Substances with C=N Bonds

An extremely interesting and original method for obtaining hetero-organic s-triazines is provided by the cyclo-addition of isocyanates to the double bonds of nitrogen-containing hetero-organic compounds. In this case the s-triazine ring is formed in the reaction, and is not introduced into the system in the "prepared" form. Thus in the reaction of isocyanates with organosilicon and organotin derivatives of ketimines, a two-stage process gives the corresponding hetero-organic s-triazines (the reaction conditions are different for different M, R, and X)[98—100] (scheme 24):

Scheme 24



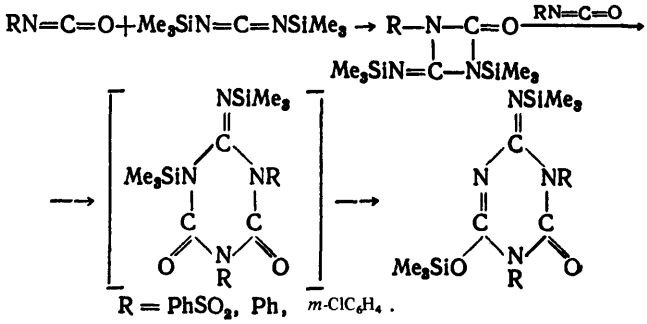
M = Si, Sn; R = Me, Ph; X = O, S .

In the first stage, the isocyanate is inserted at the element—nitrogen bond; the 1 : 1 adduct exists in two tautomeric forms (in the case of isocyanate the reaction is complete at this stage). In the second stage the next isocyanate molecule undergoes cyclo-addition with the 1 : 1 adduct.

The formation of similar s-triazines as intermediate compounds has been established in the reaction of $Ph_2C{=}N{-}S(O){-}PhSiMe_3$ with methyl isocyanate or $Cl_3CC{\equiv}N$.[101]

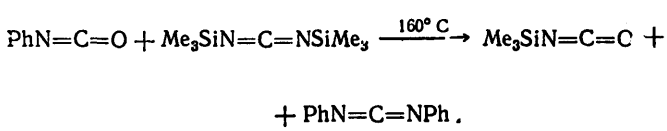
The reactions of isocyanates with organosilicon, -germanium, and -tin carbodi-imides is characteristic. The reaction of benzenesulphonyl isocyanate with bis(trimethylsilyl)carbodi-imide takes place on heating to 100—150 °C to give, depending on the conditions, four- or six-membered silicon-containing heterocycles according to scheme 25:[32,33,102]

Scheme 25



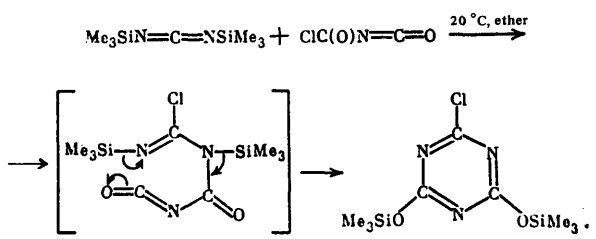
A similar scheme was proposed for the reaction of isocyanates with organic carbodi-imides.[103,104] The corresponding reactions of phenyl and *m*-chlorophenyl isocyanates take place under more severe conditions (190–250 °C, 3 h) to give as main products the corresponding organo-silicon s-triazines (yields 82–90%).[8,17,32,33,105] According to Ref. 106, the reaction of PhNCO with bis(trimethylsilyl)carbodi-imide with distillation of the volatile product (Me_3SiNCO) takes place as an exchange reaction, but no experimental proof was given (see scheme 26):

Scheme 26



In contrast to schemes 25 and 26, chloroformyl isocyanate reacts with bis(trimethylsilyl)carbodi-imide at a reagent ratio of 1:1 under mild conditions to give 2,4-bis(trimethylsiloxy)-6-chloro-1,3,5-triazine in 64% yield according to scheme 27:[32,107]

Scheme 27

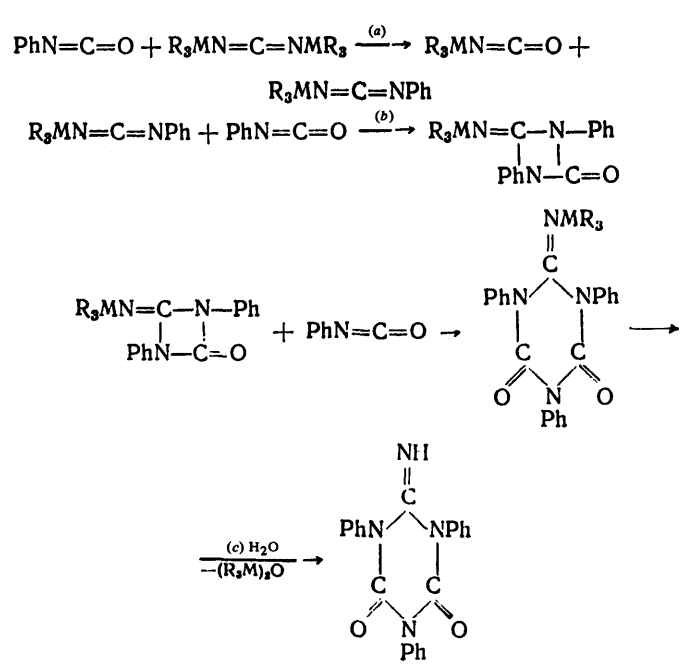


The scheme shows that the reaction begins with the electrophilic addition of isocyanate at the C=N bonds of the carbodi-imide. The product undergoes cyclisation with simultaneous migration of the Me_3Si groups from the nitrogen to the carbon atoms.

The reaction of the same isocyanate with Me_3SiNSO, instead of the expected OCN–CO–NSO and Me_3SiCl, gives tris(trimethylsilyl) cyanurate (yield 84%) and $(ClCONSO)_x$.[15]

Organogermanium and organotin s-triazines are also formed by the three-stage reaction of phenyl isocyanate with bis(tributylstannyl)carbodi-imides (scheme 28).[32,33,105,108]

Scheme 28

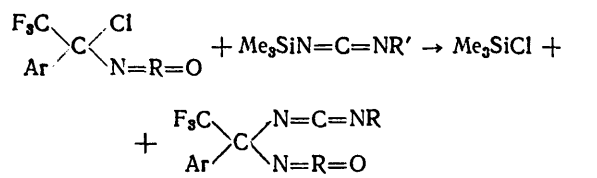


M=Ge, R=Et; M=Sn, R=Bu.

The scheme was confirmed by the IR spectra of the reaction mixtures and identification of the hydrolysis products. For example, heating phenyl isocyanate with $Bu_3SnN{=}C{=}NSnBu_3$ in the ratio 3:1 with subsequent hydrolysis of the reaction mixture gave 1,3,5-triphenyl-2-imino-4,6-dioxo-1,3,5-triazine in 61% yield. The last compound can be formed only by the hydrolytic splitting of the SnN bond of the corresponding organotin heterocycle (scheme 28c).[32,33,108]

In the case of $PhSO_2NCO$, scheme 28 is not realised, and germanium or tin s-triazines are not detected among the reaction products. The reaction involves exchange, and can be illustrated by a scheme analogous to schemes 26 and 28a. A similar result was established in a study of the reaction of unsymmetrical organosilicon carbodi-imides with α-chloroisocyanates according to scheme 29:[109–111]

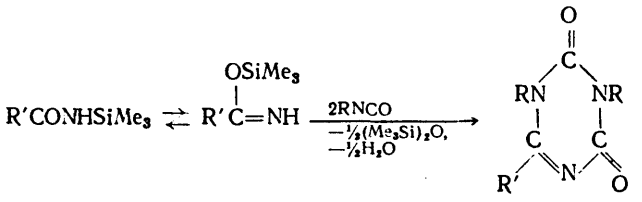
Scheme 29



R=C, S; Ar=Ph, *p*-MeC_6H_4, *p*-ClC_6H_4; R'=Ph, COOEt.

Cyclo-addition involving trimethylsilylformamides and isocyanates, leading to the intermediate formation of the corresponding organosilicon s-triazines, has been used to prepare their organic analogues, which are not readily obtainable[112] (scheme 30):

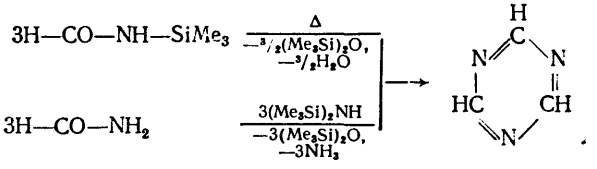
Scheme 30



R=Alk, Ph, $AlkSO_2$, $PhSO_2$; R'=H, Alk .

A similar process apparently forms the basis of the synthesis of s-triazine according to scheme 31:[113]

Scheme 31



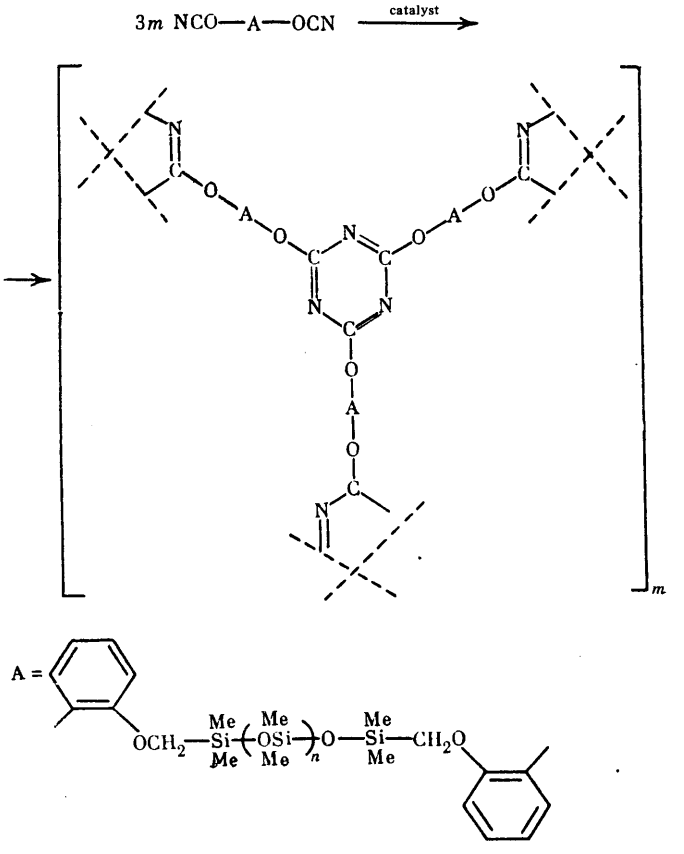
In contrast to the previous systems the analogous reactions of carbofunctional organosilicon imines give organosilicon s-triazines stable under ordinary conditions. Thus $Me_3Si(CH_2)_2C(OEt)=NH$ has been used to synthesise 2,4,6-tris-[β-(trimethylsilyl)ethyl]-1,3,5-triazine in quantitative yield.[114] The reaction of aminosilanes $R_3Si(CH_2)_3NH_2$ (R = Me, Et, Bu, EtO) with formaldehyde or paraform gave a number of other carbofunctional organosilicon analogues of the latter.[115–118] The aminosilane apparently first reacts with CH_2O by an A_N–E mechanism to give Schiff bases $R_3Si(CH_2)_3N=CH_2$, which subsequently trimerise to the corresponding s-triazines.

The addition of formaldehyde to trimethylisocyanatosilane gave as final product tris-[(trimethylsilyloxy)methyl] isocyanurate instead of its monomer $Me_3SiOCH_2N=C=O$ (CH_2O was bubbled through Me_3SiNCO at 80–83 °C.[119]

The formation of isocyanurates was also observed in the preparation of carbofunctional and organosilicon isocyanates by the reactions of KOCN with chlorine-containing siloxanes in dimethylformamide (DMF).[120–122] The improvement of the method has been protected by a series of patents devoted to the synthesis of carbofunctional s-triazines by heating mixtures of metal cyanates with various organosilyl halides in aprotic solvents (3–10 h, 90–140 °C, yield 90–95%).[123–130]

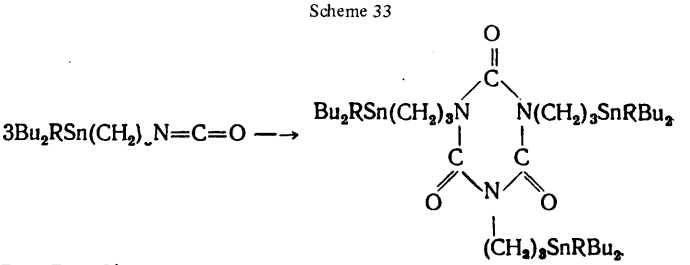
The trimerisation of isocyanates such as $Me_3SiO(CH_2)_4NCO$ by heating for a short time in DMF in the presence of $PhCO_2Na$,[131] and the preparation of polymeric cyanurate-containing siloxanes by the polycyclotrimerisation of the corresponding dicyanates according to scheme 32,[132,133] have been reported:

Scheme 32



The trimerisation of isocyanates is widely used to produce organic isocyanaurates.[134,135] In the chemistry of the heteroorganic compounds of group IVb, however, practically no use is made of this reaction, since the isocyanates R_3MNCO do not trimerise, and the corresponding data on their carbofunctional analogues are limited to the papers cited above[120–133] for the organosilicon and organotin derivatives.[136,137] In the last papers it is reported that the cyclotrimerisation of $Bu_2RSn.(CH_2)_3N=C=O$ takes place at room temperature to give high yields of the corresponding products (scheme 33):

Scheme 33



R = Bu, Cl .

Data have been published[138,139] on the analogous monosubstituted heterocycle, 2-[γ-(bromodiphenylstannyl)propoxy]-4,6-dichloro-1,3,5-triazine.

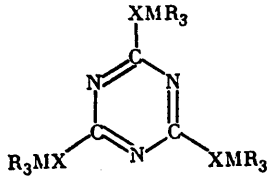
There are no published data on the synthesis and properties of germanium- and lead-containing carbofunctional s-triazines.

III. PHYSICOCHEMICAL PROPERTIES AND STRUCTURE

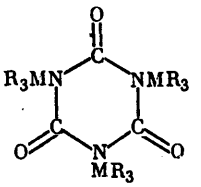
The hetero-organic compounds being considered are glycerol-like colourless or weakly coloured liquids, which boil at high temperatures or cannot be distilled in a vacuum, or vaseline-like or solid products. They are generally soluble in ether, dioxan, benzene, toluene, chloroform, and carbon tetrachloride, and insoluble in water; most hetero-organic s-triazines (except the carbofunctional compounds) are hydrolysed by water. The compounds can be kept practically unchanged for many months in an air-tight vessel. They are extremely stable to heat,[18-21,24] and can be vacuum-distilled with gentle heating. Some of these substances, however, decompose rapidly when heated strongly[12-14,17,49,50] or polymerise.[43,46,76] There are practically no specific published data on these processes, apart from data on the thermal decomposition of tris(trimethylsilyl) cyanurate, which at 280 °C in the pure state[12-14,17] or at 200–230 °C in the presence of chlorine-containing substances[17] decomposes to the monomer, trimethylisocyanatosilane, in quantitative yield. The reaction takes place so cleanly that it can be used to prepare $Me_3SiN{=}C{=}O$. As noted above, an attempt to obtain tris(triethylsilyl) cyanurate from cyanuric chloride and Et_3SiONa (160–200 °C, 1 h) also gave chiefly $Et_3SiN{=}C{=}O$.[17] In contrast to this, heating carbofunctional isocyanates in aprotic solvents gives the opposite result, that is the trimer is formed.[119-131]

Most workers have used IR spectroscopy to prove the structures of the hetero-organic s-triazines obtained. Some information has also been obtained from the NMR,[11,15,29,36,37,84-87,98,115,140] Raman,[15] and mass spectra[15,16,122] of these compounds. Since practically no use has been made of other instrumental methods (ultraviolet spectroscopy, X-ray diffraction), the conclusions reached from the IR and NMR spectra are extremely important. The structure of hetero-organic amino(hydroxy)-derivatives of isocyanuric acid depends chiefly on the nature of the substituent element and also on the volume of the organic groups joined to it. Thus all silicon-substituted non-carbofunctional s-triazines exist in the hydroxy-from (A) (O–Si), and the number of C=N double bonds in the ring corresponds to the number of R_3Si groups.[8-16,26,27,32,33,43,74,76,98-100,107] The explanation is probably that silicon has a higher affinity for oxygen than the other elements of group IVb; this is the reason for the high thermodynamic stability of the Si–O bond.

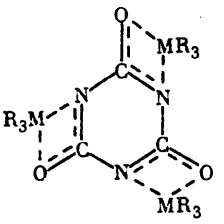
In contrast to this, the organogermanium, -tin, and -lead analogues for all degrees of substitution have the isocyanurate structure (B) (M–N), characterised by the presence of free carbonyl groups, whose IR bands lie in the range 1720–1620 cm^{-1}. Exceptions are the derivatives of ammeline[9,28,33] and ammelide,[99,100] since their R_3M groups (M = Ge, Sn) are joined to the ring through the oxygen atom, as in the organosilicon cyanurates. Tris(benzoyl)ammeline has a similar structure.[17] The fact that these compounds exist only in the form indicated is apparently due to steric hindrance in the formation of the corresponding nitrogen-functional isomers and hence their forced symmetrisation. The structure of the oligodiallyl isocyanurate hetero-organic compounds in Ref.76 can be explained similarly.



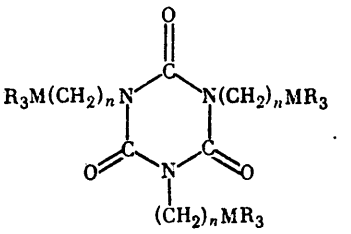
(A) X = O, NH



(B)



(C)



(D)

In addition to the above-mentioned bands due to carbonyl groups, the IR spectra of the organogermanium and organotin isocyanurates also contain bands due to the triazine ring with substituents on the nitrogen atom at 1480–1460 cm^{-1} and 780–760 cm^{-1}.[2,9,17,51] The marked decrease in the C=O stretching wavenumbers in the IR spectra of the organogermanium and organotin s-triazines[9,20,76] is probably due to the decrease in the strength of the C=O bonds as a result of the coordination of adjacent ring nitrogen atoms to the metal atoms, as in organotitanium isocyanurates [form (C)].[141-144] The IR spectra of s-triazines of type (A) contain bands due to the skeletal vibrations of the cyanurate ring at 1580–1515, 1460–1400, and 815–810 cm^{-1}, but do not contain carbonyl group bands.[2,8,9,11,26,28,33,43,74] The hydroxy-structure of the silicon-containing compounds is confirmed by the presence of Si–O–C group bands with a maximum at 1140–1110 cm^{-1}.[8,9,11,15,26]

The hydroxy-form of organosilicon amino(hydroxy)-s-triazines was proved convincingly in an IR and ^1H NMR spectroscopic study of their tri-substituted dimethylsilyl derivatives.[8,11] The ν(Si–H) bands in the IR spectra of these compounds are displaced to higher wavenumbers and increase in the derivative order: melamine–ammeline–ammelide–cyanuric acid. Thus in the first case ν(Si–H) lies at 2140 cm^{-1}, whereas in the last case the wavenumber is increased to 2180 cm^{-1}. This indicates that the Si–H bond in the oxygen-containing organosilicon s-triazines is stronger than that in related compounds containing $H{-}\overset{|}{\underset{|}{Si}}{-}N{=}$ fragments. One reason for this phenomenon is apparently the difference in the degree of conjugation of the Si–O and Si–N bonds. The ν(Si–H) bands of the $Me_2HSiOC{\equiv}$ (E) and $Me_2HSiNH{-}$ (F) groups of tris(dimethylsilyl)ammelide and tris(dimethylsilyl)ammeline were distinguished; they lie at 2170 cm^{-1} and 2160 cm^{-1} for (E) and at 2130 cm^{-1} and 2135 cm^{-1} for (F). The numbers of these fragments can also be estimated from the intensity ratio of the signals of the silyl protons in the ^1H NMR spectra (the chemical shifts for (E) and (F) are 4.92 p.p.m. and 4.60 p.p.m. respectively). Thus the rearrangement of the isocyanurate to the cyanurate system and vice versa may be due either to the introduction of the organosilicon substituents into the isocyanuric acid structure or to the replacement of the latter by other hetero-organic fragments containing group IVb elements[74,75] (section IV, scheme 43). The isomeric transformation of the individual hetero-organic s-triazines is generally irreversible, and in some cases it can be followed by instrumental methods. Thus scheme 14, given in Ref.51, was proved by the IR spectra of the reaction mixtures (50 °C, 5 h), which contain bands due to tris(tributylstannyl) cyanurate [form (A)] at 1560 cm^{-1} and 820 cm^{-1}. When heated to 100–150 °C, the cyanurate is converted into the isocyanurate, as shown by the appearance of bands due to the isocyanurate ring at 1480 cm^{-1} and 780 cm^{-1}, and bands due to the carbonyl groups at 1680–1620 cm^{-1} [form (B)]; the bands characteristic of form (A) disappear. In Refs.23 and 145, the tripropyl- and tributylstannyl derivatives of isocyanuric acid were erroneously assigned to hydroxy-form (A).

As noted above, carbofunctional s-triazines containing group IVb elements usually exist as the isocyanurates, as shown by IR [17,33,58,84,120,122,136,137] and ^{13}C NMR [36,37] spectroscopy. For example, according to Ref.122, $\nu_{as}(C=O)$ for organosilicon s-triazines $[RC_6H_4SiMe_2CH_2NCO]_3$ (R = Hal, p-Me_3C, p-Me_3Si, p-Me_2N) lies at 1680 cm^{-1}, and that for the organotin compounds $[Bu_2Sn(CH_2)_3NCO]_3$ (R = Bu, Cl) at 1700 cm^{-1}, [136,137] that is practically in the range of the carbonyl vibrations of ordinary organic isocyanurates. Bands due to the isocyanurate ring (1470 cm^{-1} and 775 cm^{-1}) were also detected. [136,137]

Data have been published, however, indicating that carbofunctional s-triazines may be formed when tris(allyl) cyanurate is used as the original heterocyclic compound. [4,48,77,78,83] This was confirmed by the IR spectra of the products, which show bands due to the skeletal vibrations of the ring at 820–818 cm^{-1} and the allyloxy-groups at 995–990 cm^{-1} and 950–925 cm^{-1}; the C=O group bands at about 1700 cm^{-1} are not observed. [77]

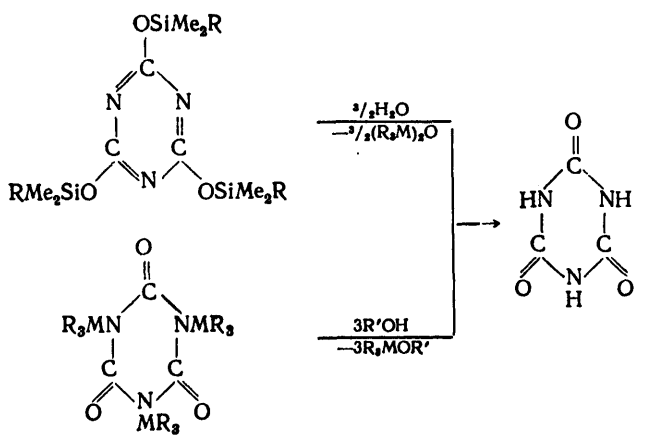
The silicon-containing derivatives of cyameluric acid, like their s-triazine analogues, exist in the O–Si form, and the tin-containing compounds exist in the N-Sn form. [96,97]

Refractometry has also been used in the synthesis and identification of hetero-organic s-triazines, and the study of a series of organosilicon, -germanium, and -tin derivatives of diallyl isocyanurate and isocyanuric acid showed that the average difference between the calculated and experimental values of the molar refraction is −1.20 cm^3 (2σ = 0.15 cm^3). This quantity can be taken as the correction for the isocyanurate ring to the refraction of compounds of this class. [146]

IV. CHEMICAL PROPERTIES

Organosilicon, -germanium, -tin, and -lead s-triazines are extremely reactive substances, but their chemical properties have been insufficiently studied. The best known reactions are those of the hetero-organic derivatives of isocyanuric acid with water and other nucleophilic reagents. Most of these substances are hydrolysed even by atmospheric moisture, so that they can be kept only in air-tight vessels or sealed ampoules. Thus tris(trimethylsilyl) cyanurate and tris(triethylgermyl) isocyanurate are hydrolysed almost instantaneously to isocyanuric acid and hexamethyldisiloxane or hexaethyldigermoxane respectively (scheme 34) [8,11,15,33,52,74] (compare with schemes 2 and 3):

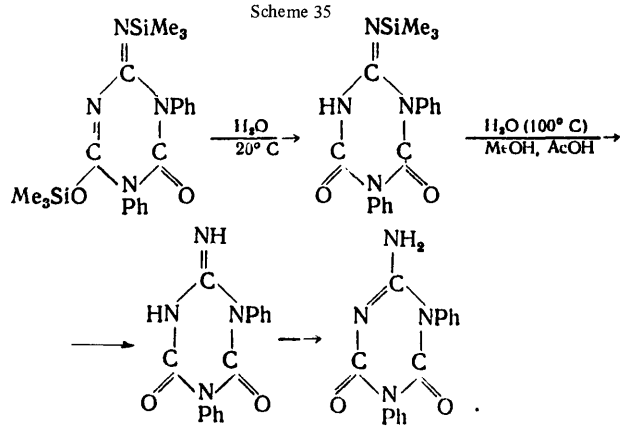
Scheme 34



M = Si, R = H, Me, R′ = H, Me, Bu, $C_{10}H_{21}$, Ph, MeCO, PhCO;
M = Ge, R = Et, R′ = H;
M = Sn, R = Bu, R′ = H, Me, Ph, o-ClC_6H_4, MeCO, PhCO.

The complete hydrolysis of tris(tributylstannyl) isocyanurate requires either a longer time or heating with water. [51] Tris(trimethylsilyl)melamine, -ammeline, and -ammelide, trimethylsilyl diallyl isocyanurate, their triethylgermyl and tributylstannyl analogues, tributylstannyl dicyanoethyl cyanurate, bis(diallyl isocyanurato)dibutylstannane, and other similar compounds are also easily hydrolysed. [9,11,26,28,33,43,105,108,147] The organosilicon imino-s-triazine obtained according to scheme 25 is hydrolysed in stages. [33,105] Its Si–O bond begins to split under the influence of moist air or ether, whereas breakdown of the Si–N bond and separation of the two trimethylsilyl groups require heating with boiling water or treatment with methanol or acetic acid. The final hydrolysis product is apparently an unstable phenyl-substituted isoammelide, which undergoes rearrangement to the corresponding ammelide [33] according to scheme 35:

Scheme 35



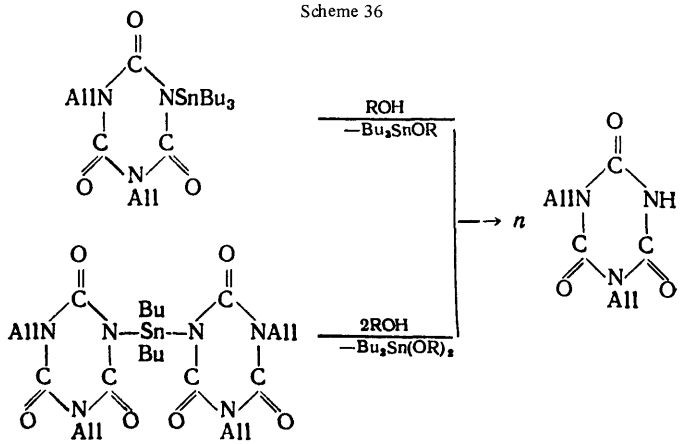
Mild hydrolysis or alcoholysis has also been used to confirm the formation of nitrogen-containing heterocycles in other cycloaddition reactions [98,99,102,108] [schemes 24, 25, and 28).

Unlike the above compounds, silatriazole trimers have an extremely high stability to hydrolysis. For example, diphenylsilyl derivatives of this group are quite stable even when boiled for 2 min with 10% HCl or NaOH. [73]

Carbofunctional s-triazines are also extremely stable to nucleophilic reagents and can even by synthesised in an aqueous-alcoholic or alcoholic medium. [115–118,123–125]

The reactions of tris(trimethylsilyl) cyanurate, [33,74] diallyl tributylstannyl isocyanurate, and bis(diallyl isocyanurato)-dibutylstannane [147] with alcohols, phenols, and carboxylic acids have also been studied (schemes 34 and 36):

Scheme 36

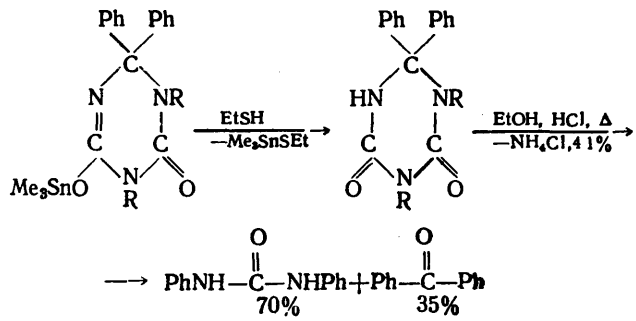


R = Et, Pr, iso-Pr, Ph, MeCO, PhCO, CCl_3CO; n = 1, 2.

The rate and extent of these reactions, and the yields of the final products, depend significantly on the nature of the central atom and the hetero-organic fragments, the reagent used, and the conditions of the process. For example, organosilicon s-triazines are much more reactive than the organotin compounds, and their reaction with hydroxyl-containing compounds is irreversible. This is because isocyanuric acid is chemically inert towards the siloxanes or alkoxy(acyloxy)silanes formed. In contrast to this, the reaction of tris(tributynylstannyl) isocyanurate with methanol is reversible.[25] The replacement of methanol by phenol, acetic acid, or benzoic acid displaced the equilibrium practically completely towards the formation of isocyanuric acid.

The reaction of 1,3,4,4-tetraphenyl-6-trimethylstannyloxy-1,3,5-triazine with ethanethiol in benzene gave the corresponding destannylated s-triazine (scheme 37):[99,100]

Scheme 37



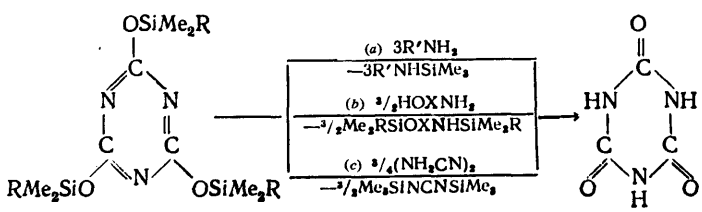
R = Me, Ph .

Subsequent hydrolysis (R = Ph; EtOH + concentrated HCl, 4 d) gave a mixture of benzophenone, N,N'-diphenylurea, and NH_4Cl.[99]

The first stage of scheme 37 has been proposed as a method for synthesising organic triazines with three different substituents on the nitrogen atoms.[99] The yields of the final heterocycles were 76–96%.

Tris(trimethylsilyl) cyanurate reacts on heating with primary amines (100–200 °C, 1–2 h)[33,74] to give isocyanuric acid and mono-substituted silylamines. An interesting feature is that the reaction is reversible. This is particularly noticeable for allylamine, which gives only 50–70% of the corresponding aminosilane (scheme 38). It is for this reason that the latter was used to prepare tris(trimethylsilyl) cyanurate[8,33] (scheme 2).

Scheme 38



R = H, Me; R' = All, Ph, n-C_7H_{15}, cyclohexyl, $Bu_3Sn(CH_2)_3$;

X = CH_2CH_2, $C_6H_4SO_2$.

Since this s-triazine is a fairly powerful silylating agent, the equilibrium for the process (scheme 38a) is determined by the comparative activity of the organosilicon reagents.

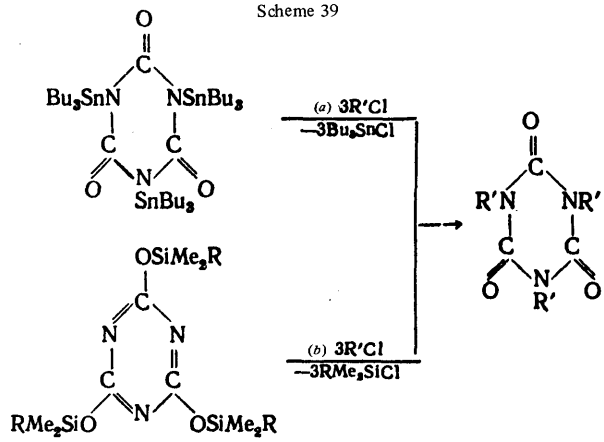
The isocyanuric acid formed when aliphatic amines are used can be removed from the reaction zone as complexes with the original amines (1:1), which decompose to their components above 240 °C.[74]

The reactions of organosilicon cyanurates with bifunctional compounds (2-aminoethanol, sulphanilic acid) do not differ fundamentally from the above reactions and take place according to the general scheme 38b.

The reaction of dicyandiamide with tris(trimethylsilyl) cyanurate gave bis(trimethylsilyl)carbodi-imide in quantitative yield (scheme 38c). The last compound can also be obtained using tris(trimethylsilyl)melamine.[31]

Organosilicon cyanurates do not react with secondary amines, and tris(tributylstannyl) isocyanurate does not react with primary amines either. It reacts readily, however, with carboxylic acid halides, forming tris(acyl) isocyanurates according to scheme 39:[17,25,33,148]

Scheme 39



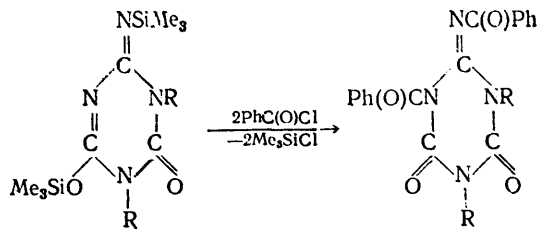
M = Sn, R' = MeCO, PrCO, PhCO, $CH_2CH(CH_3)CO$; M = Si, R = H, Me, R' = MeCO, PhCO, $Me_3Si(CH_2)_2CO$, $(CH_2)_6N{=}C{=}O$, substituted monosaccharides.

Other organotin s-triazines such as tributylstannyl and dibutylstannyl diallyl isocyanurates[147] and tris(tributylstannyl)melamine, -ammeline, and -ammelide[17] are also converted into the corresponding acylated heterocycles by the reaction with acid halides.

Scheme 39a can be used to obtain various acyl derivatives of s-triazines. It gives high yields of the products. High purity of the desired compounds is achieved by replacing the organotin s-triazines by their silicon-containing analogues.

The synthesis of various tris- and bis(acyl) isocyanurates from the corresponding organosilicon s-triazines has been described[10,17,33] (schemes 39b and 40):

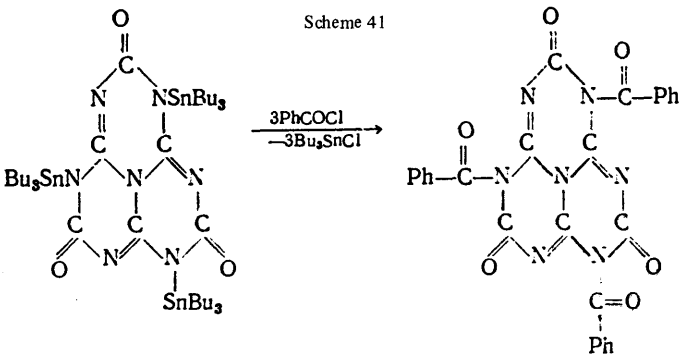
Scheme 40



R = Ph, *m*-ClC_6H_4 .

Tris(tributylstannyl) cyamelurate also reacts with benzoyl chloride, to give the corresponding tris(benzoyl)derivative[17] in up to 75% yield according to scheme 41:

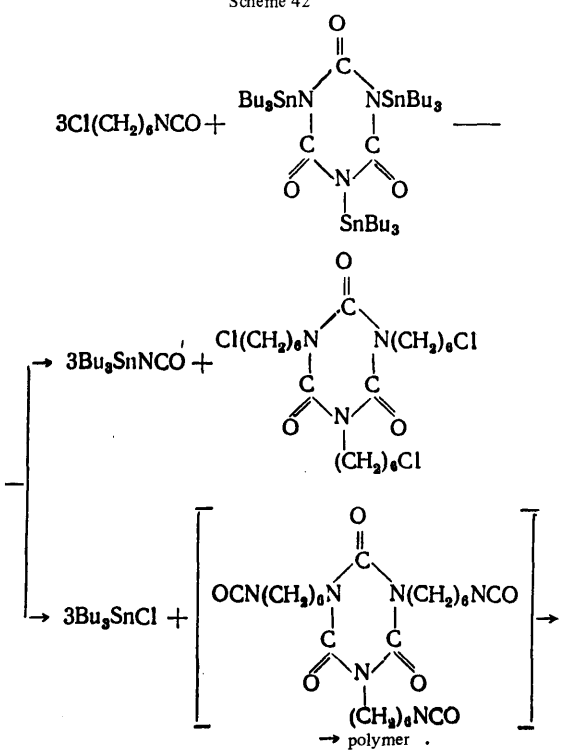
Scheme 41



Hetero-organic s-triazines do not react directly with alkyl halides or aryl halides under normal conditions or on heating,[148] but in some cases reaction takes place in polar aprotic solvents such as DMF. Thus the reaction of tris-(trimethylsilyl) cyanurate with chlorohexamethylene isocyanate gave tris(6-isocyanatohexamethylene) isocyanurate (DMF, 120–170 °C, 3–4 h, yield 96.5%).[149] An interesting feature is that heating a mixture of the same starting materials without a solvent, and heating a mixture of tris-(trimethylsilyl) cyanurate with cyanuric chloride, give exclusively trimethylsilyl isocyanate.[17] Similar splitting of the triazine ring is observed when tris(tributylstannyl) isocyanurate is heated with benzenesulphonyl chloride (120 to 160 °C). At an original reagent ratio of 1:1, tributylstannyl isocyanate is formed in high yield. Change in the ratio to 1:2 or 1:3 leads to the preferential formation of benzenesulphonyl isocyanate. The process is accompanied by considerable tar formation.[25] An attempt to carry out the reaction of tris(trimethylsilyl) cyanurate with ClC(O)NCO (reagent ratio 1:3, ether, 20 °C) gave a polymeric N-substituted tri-isocyanate, which was depolymerised at 150 °C to give 95–97% $(OCN)_2CO$.[150]

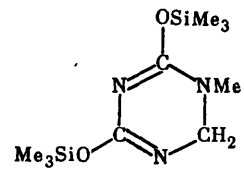
Tris(tributylstannyl) isocyanurate also reacts with $Cl(CH_2)_6NCO$ in DMF with heating to 180–210 °C for 5 h according to scheme 42:[151]

Scheme 42

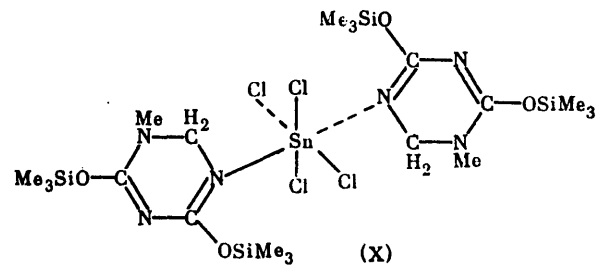


The ability of organosilicon s-triazines to react comparatively easily and quantitatively with active halogen-containing compounds has recently been widely used to synthesise nucleosides. The rate of the reaction is increased in the presence of catalytic quantities of $SnCl_4$,[140,152–158] although the reaction also takes place in its absence.[38,39] Recent investigations of the role of the catalyst[140,153] showed that it forms an intermediate compound (X), which was isolated and characterised from its ^{13}C NMR spectra. Thus the simplified scheme for the preparation of nucleosides [for example (XII)] involves the preliminary synthesis of the organosilicon s-triazine (IX), the intermediate formation of the complex (X), the reaction of the latter with the halogenosaccharide (XI) (the O-acylsaccharide), and the subsequent hydrolysis of the compound formed.[140]

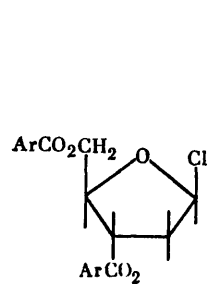
The N-glycosides obtained by these or similar operations can subsequently be methylated or deacetylated when the triazine ring contains N–H groups or the carbohydrate contains Ac–O groups respectively [for example (XIII), (XIV)].



(IX)

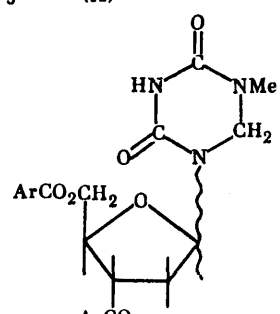


(X)

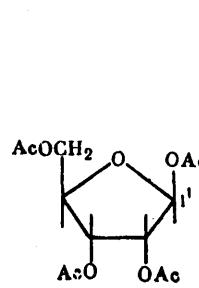


(XI)

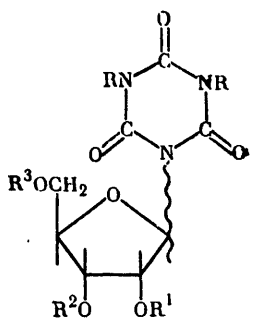
R = H, Me; R^1–R^3 = H, Ac



(XII)



(XIII)

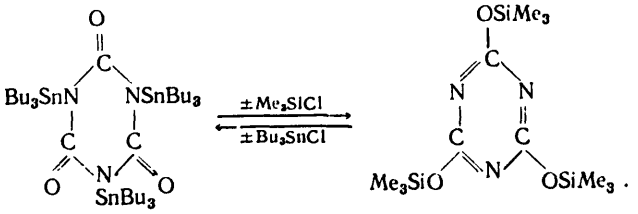


(XIV)

Instead of halogenosaccharides, their acyl derivatives,[152, 159–166] for example tetra-O-acetyl-β-D-ribofuranoside (VIII) [166] are often used. The organosilicon fragments of the s-triazines break the (1′) C–O bond of the O-glycosides and combine with the AcO groups to form compounds of the type Me_3SiOAc and the desired substituted nucleosides (XIV) (N-glycosides). The use of catalysts of the $SnCl_4$ type is necessary. New catalysts for these processes, $Me_3SiOSO_2CF_3$, $Me_3SiOSO_2C_4F_9$, and Me_3SiClO_4, have been proposed.[161] In many cases all the operations described above are carried out in a single stage by heating a mixture of all the starting materials in solvents, but here also the basis is the Gilbert–Johnson method.[161,162] In Refs. 163–166, tris(trimethylsilyl) cyanurate prepared by the method of Refs. 8 and 10 was used.

As noted above, tris(tributylstannyl) isocyanurate undergoes reversible remetallation with trimethylchlorosilane to give tributylstannyl chloride and a trimethylsilyl derivative of cyanuric acid, which exists in the hydroxy-form, according to scheme 43:[75]

Scheme 43

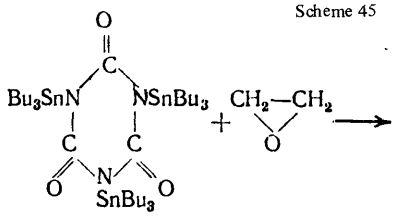


Processes similar to scheme 43 were examined in detail in section II of the present review (schemes 17–21).

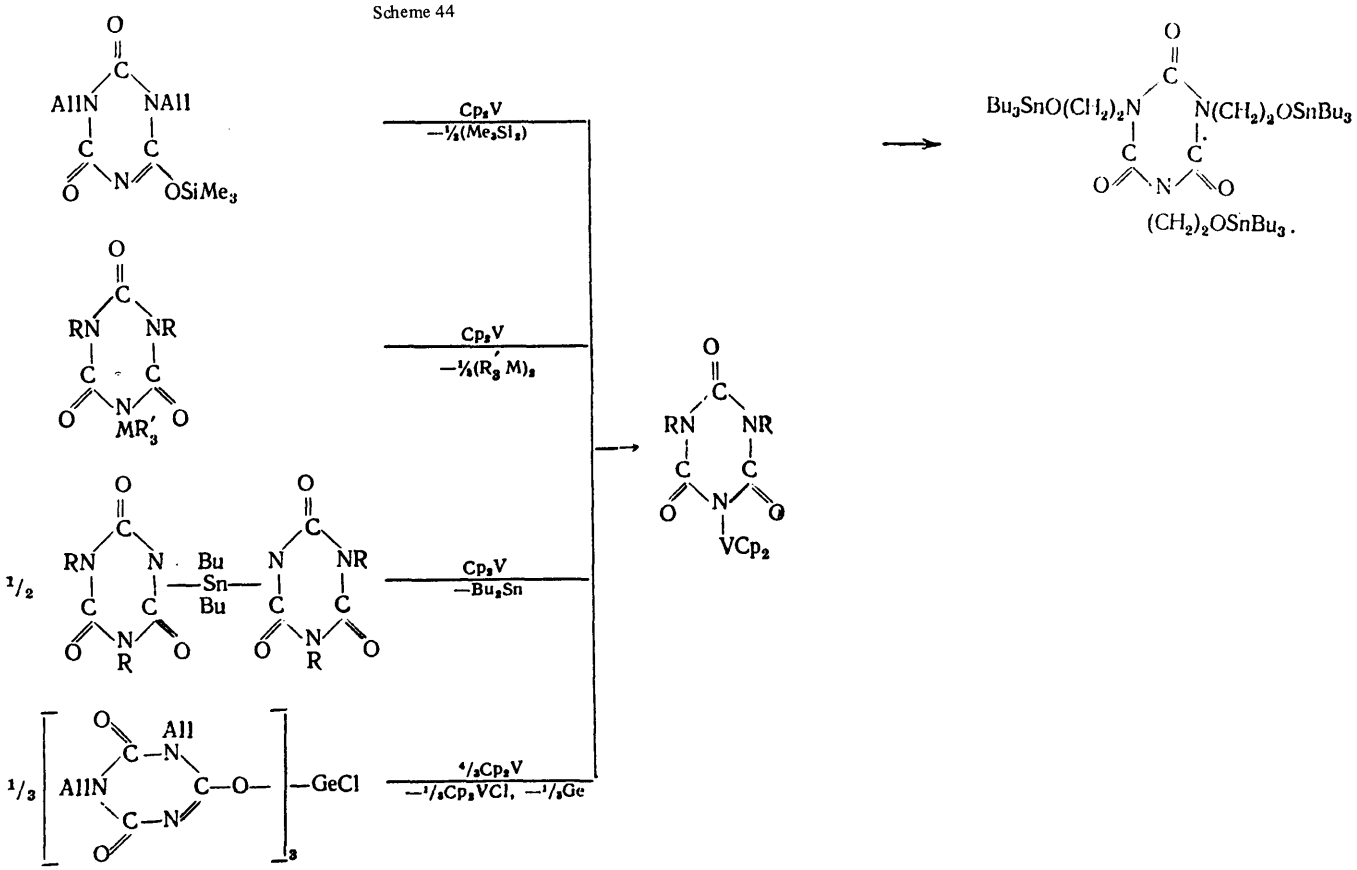
Organosilicon, -germanium, and -tin s-triazines can undergo remetallation not only with hetero-organic compounds of group IVb but also with other compounds. A group of workers including the authors of the present review published a series of papers on the reaction of Si-, Ge-, and Sn-containing derivatives of diallyl and dicyanoethyl isocyanurates with bis-(η^5-cyclopentadienyl)vanadium (Cp_2V) and of trimethylsilyl diallyl isocyanurate with vanadium tetrachloride or tris(acetyl)phosphine.[76] The use of Cp_2V as starting material led to the synthesis of the first representatives of vanadium s-triazines, which are blue–violet crystalline substances, readily oxidised by atmospheric oxygen. The reactions were therefore carried out in toluene in evacuated or argon-filled ampoules [40–50 h, 100–120 °C for the mono- and tris-triazine, and 40 h, 20 °C for the bis-triazine heterocycles (scheme 44)]. The reactivity of the compounds towards Cp_2V increases in the order Si < Ge < Sn.[147,167–170]

The insertion reaction, widely familiar for hetero-organic compounds with an element–nitrogen bond, has been little developed for s-triazines. The only example is the synthesis of tris(β-tributylstannyloxyethyl) isocyanurate using the corresponding organotin s-triazine and ethylene oxide (DMF, heating) according to scheme 45:[5]

Scheme 45



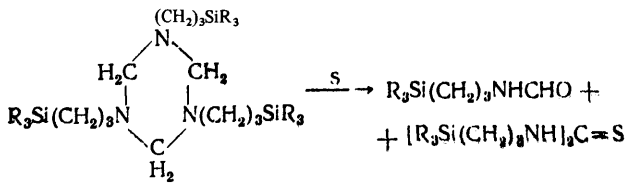
Scheme 44



M = Ge, R′ = Et; M = Sn, R′ = Bu; R = All, $(CH_2)_2Cl \equiv N$ Cp_2V = bis(cyclopentadienyl)vanadium

There are practically no published papers describing the properties of carbofunctional s-triazines. It is known only that 1,3,5-tris-(3-trialkylsilylpropyl)hexahydrotriazine, when heated with sulphur in aqueous alcohol, is converted into a 1:1.6 mixture of N-(3-trialkylsilylpropyl)formamide and N,N'-bis-(3-trialkylsilylpropyl)thiourea (scheme 46):[115-118]

Scheme 46



R = Me, Et, Bu, MeO, EtO.

Data have also been published on the reaction of 2,4-dichloro-6-[(trimethylsilyl)ethynyl]-1,3,5-triazine (scheme 13) with methanol. This reaction does not lead to the rupture of the Si—C bond of the heterocycle, but gives a good yield of the corresponding 2,4-dimethoxy-derivative, which is hydrolysed, but under more severe conditions, to 2-ethynyl-4,6-dimethoxy-1,3,5-triazine.[42]

V. PRACTICAL APPLICATIONS

s-Triazines containing group IVb elements have found extremely varied and extensive practical applications, which are continuing to expand.

The foundation for applied studies in the chemistry of compounds of this class was laid by the synthesis and successful investigation of the possible uses of carbofunctional organosilicon s-triazines and siloxane polymers based on them. They were used to improve the physical or mechanical properties of, or to give specific properties to fibrous materials (wool, viscose, cotton, nylon, glass fibre, etc.) and to prepare heat-resistant, water-resistant, and chemically resistant films and coatings for metals, wood, and various polymers.[54,55,58-66,84-87,123-131,171-182] Thus appropriate treatment of fabrics with triazine polysiloxanes gives them water-repellent properties,[60-65,123-127,182] resistance to repeated washing,[63-65] and wear-resistance.[180,181] These organosilicon products also have increased adhesive properties, so that they are often included in adhesive compositions.[84-87,171-179] The most effective adhesion promoters are isocyanurates of the type $[(RO)_{3-n}R'_nSiR''NCO]_3$, where R, R' = Alk, R'' = CH_2, and also 1,3,5-tris(trimethoxysilylpropyl) isocyanurate. These and other similar compounds are used as vulcanising additives in rubber mixtures, and also as binding and cross-linking agents in the synthesis of various polymers.[78,94,95,132,133,173-181] The synthesis of fluorosiloxanetriazine rubbers and elastomers has been patented.[79-82] These substances and their derivatives have a high thermal stability[59,128-133] and remain practically unchanged on storage.[174]

Organotin s-triazines are used as catalysts and modifying additives in the synthesis of various polymers. For example, tris(triethylstannyl) isocyanurate is used to prepare polyoxymethylene and polyethers with improved colours and transparency.[21,22] The inclusion of tris(tributylstannyl) isocyanurate, -melamine, or cyamelurate in compositions based on polyvinyl chloride gives the polymer increased stability and transparency.[27,183] The stabilising action of organotin s-triazines is increased by their ability to bind the HCl which is liberated when polyvinyl chloride is heated and which increases the rate of the thermal decomposition of this polymer. The binding of HCl by the additives is not decisive, however, since organosilicon cyanurates, which are more reactive towards HCl, are much less effective thermal stabilisers than the tin derivatives.[27] The use of the latter with familiar components (calcium and zinc stearates) gives a synergic effect.

The introduction of tris(tributylstannyl) or tris(trioctylstannyl) isocyanurates into the structures of polymers based on ε-caprolactam gives the resulting polyamide fibre bactericidal properties while preserving its strength and absence of colour.[184]

Tin-containing s-triazines have proved to be extremely effective catalysts for the reactions of isocyanates with alcohols, used in industry for the production of polyurethanes, including their film-forming organosilicon analogues.[6,47,185-193] The tributylstannyl derivatives of these heterocycles, like bis(tributylstannyl) oxide or methoxytributylstannane, have a medium catalytic activity and can be used to obtain polyurethane adhesives and coatings, an important characteristic of which is the stability of the polymer compositions.[193] In contrast to these, dibutylstannyl s-triazines, with an increased catalytic activity, can be recommended for a single-stage method for obtaining polyurethane foam, in which the process should develop vigorously from the moment when the components are mixed.[6,47]

Organotin s-triazines are active and extremely promising bactericides and pesticides with varied spheres of application. Thus they show insecticidal, acaricidal, fungicidal, and algicidal properties and are used to combat bacteria, harmful insects, mites, fungi, parasites in agricultural plants and timber, and also to prevent the fouling of fishing nets, the underwater parts of ships, etc.[19,23,71,72,88-92,138,139,145,194] According to Ref.89, thio-derivatives of tin-containing s-triazines have a low toxicity to warm-blooded animals and can therefore be used to prepare fumigants, detergents, deodorants, coatings for nylon, paper, plastics, wood, etc.

Herbicidal and fungicidal compositions based on organosilicon s-triazines have been patented.[40,195]

Hetero-organic s-triazines are often used as active intermediate compounds for preparing various analogues and derivatives, including bactericidal, pharmaceutical, and medicinal products, polymer additives,[16,34,52,196,197] fabric whiteners,[69] triazinediones,[112] bis(trimethylsilyl)carbodiimide,[49] acylated and germanium-containing analogues difficult to obtain,[9,17,25,28,74,148] and "sandwich" compounds of vanadium.[167-170]

Tris(trimethylsilyl) cyanurate, synthesised comparatively recently, has already been used to obtain trimethylisocyanatosilane,[12-14] carbonyl di-isocyanate $(OCN)_2CO$,[150] bis(trimethylsilyl) carbodi-imide, tris(triethylgermyl) and tris(tributylstannyl) isocyanurates,[74] tris(6-isocyanatohexyl) isocyanurate, which is a strating material for the synthesis of polymers,[149] triacyl isocyanurates,[10,17] and N-glycosides.[163-166]

The last group of compounds, which inlcudes other triazine-containing nucleosides,[38,39,140,152-162,198,199] is of considerable interest for the present authors. These substances are of independent interest as anti-virus, anti-bacteria, and anti-tumour products, and they can also be used in the synthesis of new macrohedral compounds of the nucleotide type.

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While the present review was being prepared for publication, additional papers were published on the synthesis,[200-208] properties,[203,208,209] and practical applications[204-207,210-222] of organosilicon and organotin s-triazines.

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