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REVIEW

Organosilicon sonochemistry

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Sonochemical reactions involving organosilicon compounds are reviewed. Possible applications of ultrasonic irradiation for acceleration and initiation of various types of reactions are demonstrated along with examples from organic synthesis using organosilicon compounds. Also described are the sonochemical reactions of organic compounds containing the Group IVB elements germanium and tin, chemically related to silicon.

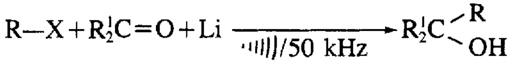
Keywords: Sonochemistry, organosilicon compounds, sonolysis, ultrasound

CONTENTS

1 INTRODUCTION

Ultrasound is the name given to sound waves having frequencies above 16 kHz, i.e. exceeding those to which the human ear can respond. The upper limit of ultrasonic frequency is not sharply defined but is usually taken to be 5 MHz for gases and 500 MHz for liquids and solids.[1] Normally, sonochemical reactions are effected over the frequency range 20–55 kHz.

The chemical effects of ultrasonic waves have been known for more than 50 years. The early examples of organic and inorganic, homogeneous and heterogeneous sonochemical reactions have been well-documented in a number of monographs[2–5] and review articles.[6–12] The chemical effects of ultrasonication (sonolysis) have been generally associated with acoustic cavitation of liquids, i.e. the generation, growth and implosive collapse of vapour–gas bubbles accompanied by release of energy. As a result, short-lived ($\sim 10^{-9}$ s) local 'hot spots' occur in the system with the temperature reaching several thousand degrees and the pressure hundreds of atmospheres.[1,10] Thus, the process of cavitation temporarily creates a high-energy environment responsible for chemical conversions. The physical aspects of sonochemistry and the mechanism of chemical effects of sonolysis in the homogeneous and heterogeneous environment have been surveyed by Suslick,[5,10,11] Margulis[3,4,13] and Lorimer and Mason.[1] Intensive investigation of the effects of ultrasonic waves on chemical systems and the use of sonolysis in organic synthesis began in 1980 after the work of Luche and Damiano.[14] It has been demonstrated that the sonication of a lithium suspension in tetrahydrofuran containing a carbonyl compound and an alkyl or aryl halide considerably accelerates the Barbier reaction, the products being formed rapidly in less than one hour in high yield (76–100%) (Eqn [1]).


$$\mathrm{R{-}X + R^1_2C{=}O + Li \xrightarrow[\text{)))/50 kHz}]{} R^1_2C\begin{smallmatrix}\nearrow R\\ \searrow OH\end{smallmatrix}} \qquad [1]$$

The publication of this result prompted a series of investigations in organic sonochemistry aimed at the solution of synthetic problems (mainly concerned with the intensification of heterogeneous processes) and at elucidation of the mechanism of action of ultrasound on chemical systems.

A vast variety of sonochemical reactions involving different classes of organic compounds have been examined over the past seven years. Ultrasonic cleaning baths have been commonly used as a source of

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ultrasound, except for some rare cases when sonic horns have been applied. Experimental findings have been surveyed in a number of books and review papers.[3–5, 7–12, 15,16] Particularly encouraging is the use of ultrasound in organometallic chemistry, where the heterogeneity of reaction systems is an urgent issue both in the synthesis of organometallic compounds and in many catalytic procedures.[10,11]

The present paper surveys sonochemical reactions involving organosilicon compounds as well as compounds containing the chemically related Group IVB elements, germanium and tin. It should be noted, however, that sonolysis is not the only means of intensification of heterogeneous reactions. For instance, the vigorous development of organometallic sonochemistry in recent years coincides with an equally extensive application of phase-transfer catalysis in organometallic chemistry,[17–20] specifically in organosilicon chemistry.[21] In some cases these basically different approaches used to accelerate or initiate heterogeneous reactions have the same objective and lead to similar results. For this reason, it appears worthwhile to compare, whenever possible, the application of sonochemical and phase-transfer catalysis methods for the enhancement of organosilicon reactions.

2 HOMOGENEOUS SONOCHEMICAL REACTIONS

The first reported application of ultrasound in organosilicon chemistry was the cleavage of the siloxane bond with thionyl chloride under sonication[22] (Eqn [2]).

$$R_3SiOSiR_3 + SOCl_2 \xrightarrow[\text{)))/20 kHz}]{} 2R_3SiCl + SO_2$$

$$R = \text{Me, Et} \qquad [2]$$

Sonication of a mixture of hexamethyldisiloxane and thionyl chloride in the molar ratio 2:7 for two hours yields trimethylchlorosilane (Me_3SiCl) (27.5%). Under the same conditions, only 2% of hexaethyldisiloxane undergoes cleavage by thionyl chloride. The cleavage of the silicon–oxygen–silicon bonds with thionyl chloride occurs similarly under UV irradiation. Without UV irradiation or sonolysis these reactions require the presence of a catalyst and follow a heterolytic pathway. Similar effects noted for sonolysis and UV irradiation have led to the conclusion that in both cases the reaction proceeds by a free-radical mechanism.[22]

Under ultrasonic irradiation each reagent is capable of entering the gaseous phase within the cavitation bubble, where its molecules become excited. This process may be accompanied by the formation of chlorine radicals which break the siloxane bond in the molecule $R_3SiOSiR_3$. The latter molecule is itself in an excited state or even undergoes fragmentation to radicals (Scheme 1).

$$\begin{aligned}
SOCl_2 &\xrightarrow{\qquad} SOCl\cdot + Cl\cdot \\
\equiv Si{-}O{-}Si\equiv &\xrightarrow{\qquad} \equiv Si\cdot + \cdot O{-}Si\equiv \\
\equiv Si{-}O\cdot &\xrightarrow{Cl\cdot} \equiv SiCl + O\cdot \\
SOCl\cdot &\xrightarrow{O\cdot} SO_2 + Cl\cdot \\
\equiv Si\cdot &\xrightarrow{Cl\cdot} \equiv SiCl
\end{aligned}$$

Scheme 1

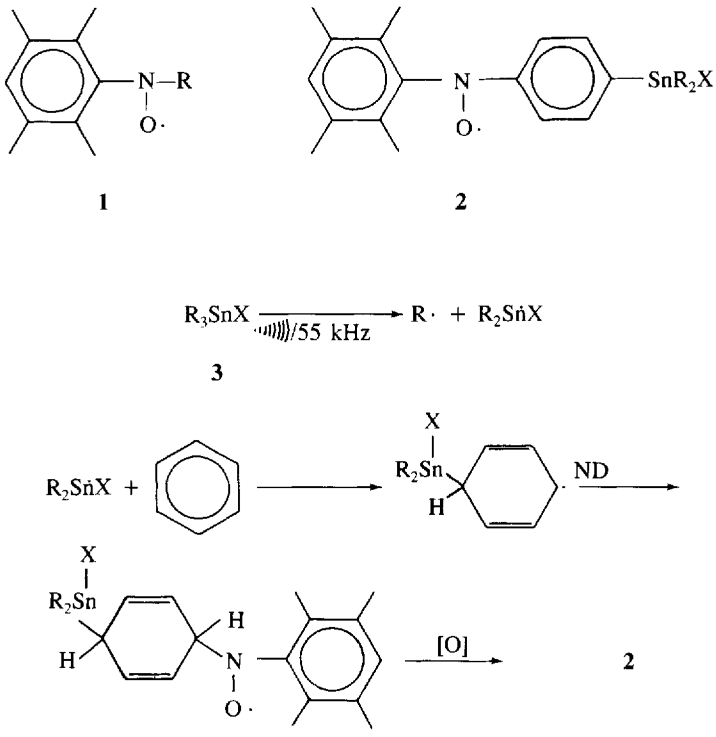
That this reaction occurs in the gas phase is confirmed by the extremely low yield of triethylchlorosilane (Et_3SiCl) resulting from the interaction of $SOCl_2$ and $Et_3SiOSiEt_3$. The latter has a higher boiling point (231 °C) and is less readily evaporated during sonolysis than hexamethyldisiloxane, which boils at 100°C.[22]

Conversions of organotin compounds under ultrasonic irradiation have been also examined.[23] Solutions of alkyl or aryl stannanes in benzene were subjected to ultrasonic irradiation for 20 minutes and the radicals formed were trapped with nitrosodurene ($(CH_3)_4C_6HNO$; ND) used as the spin trap and identified with the aid of ESR spectra.

During irradiation the ESR spectra of hexabutyldistannane (Bu_6Sn_2) solutions revealed signals assigned to two different aminoxyl radicals, viz. the spin adduct of an n-butyl radical with ND structure (**1**, R = Bu) and the tin-substituted arylaminoxyl radical structure (**2**, R = X = Bu). Similar results were obtained with other organotin compounds.

The formation of alkyl radicals suggests a sonochemical cleavage of the tin–carbon bond (and possibly tin–tin). As to the radicals of type **2**, their generation is apparently due to the addition of stannyl radicals to benzene,[23] the resultant cyclohexadienyl adduct (Scheme 2) being trapped by ND and oxidized to radical **2** (the oxidation source is unknown).

No quantitative data were given. The authors merely point out that the highest intensity of signals is observed during the sonolysis of butyl-, ethyl- and benzyl-substituted stannanes.[23] The generation of free radicals allegedly occurs in the gas phase of cavita-



R = Me, Et, Bu, Ph, CH_2Ph; X = SnR_3, Me, Et, Ph, Cl

Scheme 2

tion bubbles, whereas the reaction takes place in the solvent shell or in bulk.[23] It is noteworthy that the photolysis ($\lambda > 310$ nm) of stannane **3** (R = Bu) in the presence of ND yields exclusively radical **1** (R = Bu). Under thermolysis (boiling of the benzene solution) this radical could not be detected, a fairly intense signal corresponding to radical **2** (R = Bu) being present instead. These differences apparently reflect variation in the stability of aminoxyl spin adducts rather than the various reaction mechanisms.[23]

3 HETEROGENEOUS REACTIONS UNDER ULTRASONIC IRRADIATION

3.1 Synthesis and reactions of organosilicon (-tin) compounds in the presence of lithium, magnesium and zinc

The beneficial effects (higher reaction rate and product yields, lower temperature and lower impurities) of sonication become particularly manifest in chemical reactions with metals. The cavitation phenomenon occurring when ultrasonic waves are transmitted through a solvent helps to clean the metal surface of the oxide film and impurities formed in the course of reaction.

$$2R_3MCl \xrightarrow[)))]{2Li/THF} R_3M{-}MR_3 + 2LiCl \qquad [3]$$

$R_3 = Me_3, Et_3, Bu_3, Ph_3, Ph_2H$; $M = Si, Sn$

Ultrasound has been successfully applied in the preparation of disilanes and distannanes by reacting alkylchloro-silanes and -stannanes with lithium (after the Wurtz-type reaction)[24] (Eqn [3]).

In the case of triphenyl- and diphenyl-chlorosilanes the reaction was conducted by using lithium wire, the yield of hexaphenyl- and tetraphenyl-disilanes after 10 hours of sonication amounting to 73 and 68%, respectively. Trialkylchlorosilanes are less reactive, the corresponding hexamethyl- and hexaethyl-disilanes being formed only in 9 and 15% yield despite the long sonication time (24–60 hours); n-propyl chloride reacts more readily resulting in a 72% yield of hexane.[25] The yield of hexa-alkyldisilanes can be raised to 42–58% and the time of reaction can be brought down to two hours by using a 30% lithium suspension in mineral oil supplemented with small amounts of anthracene.[24] Trialkylchlorostannanes (Me_3SnCl, Bu_3SnCl) are more active in the Wurtz reaction than the silicon-containing analogues and undergo conversion to hexamethyldistannane (60%) and hexabutyldistannane (94%) in the presence of lithium wire.

The reaction of dichlorosilanes with lithium under ultrasonic irradiation mainly proceeds via oligomerization to give cyclopolysilanes in high (70–95%) yield[24] (Eqn [4]).

$$n\mathrm{R_2SiCl_2} \xrightarrow[)))]{2n\mathrm{Li/THF}} (\mathrm{R_2Si})_n + 2n\mathrm{LiCl} \qquad [4]$$

$$\mathrm{R} = \mathrm{Me},\ n = 6;\quad \mathrm{R} = \mathrm{Ph},\ n = 4.$$

In both cases, cyclopentasilanes were also present in the reaction mixture; silylene intermediates did not appear to be involved in the process as the silylene insertion product ($Et_3SiSiMe_2H$) was not observed when Me_2SiCl_2, Et_3SiH, Li and anthracene were sonicated.[24]

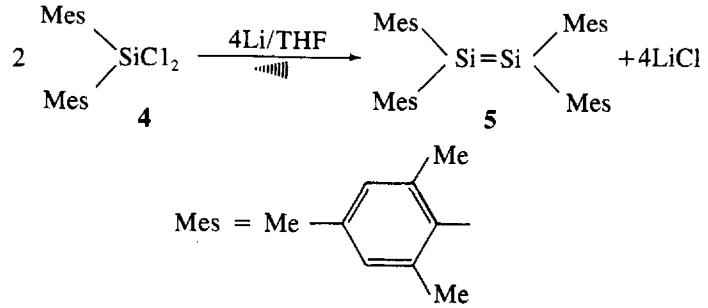
Since the presence of four mesityl groups stabilizes the silicon–carbon double bond in tetramesityldisilene (**5**),[26] it has been assumed[27] that the extension of the lithium-induced reaction of chlorosilane coupling to dimesytyldichlorosilane (**4**) may yield compound **5** (Eqn [5]).

During ultrasonic irradiation of a THF solution of silane **4** in the presence of lithium wire, a yellow coloration appeared immediately, the complete transformation of **4** and lithium taking 20 minutes to give product **5** in *ca* 90% yield (prior to purification).

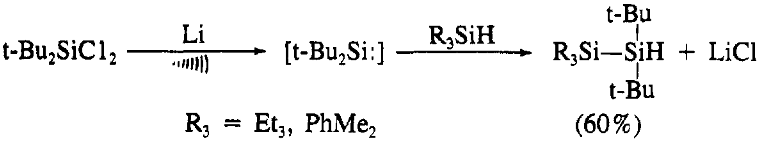
The sonochemical synthesis of disilene **5** is said to be a very simple and convenient procedure (e.g. the yield of disilene **5** in the electroreductive coupling of silane **4** was equal to only 20%,[27] whereas the preparation of compound **5** by 2,2-dimesitylhexamethyltrisilane photolysis only required temperatures below about 100°C[26]). Later, however, Boudjouk[9] reported that comparable results are difficult to obtain for the reaction of $(Mes)_2SiCl_2$ with lithium under ultrasonication because disilene (or its precursor) reacts with lithium. The reaction of **4** and lithium generally affords hexamesitylcyclotrisilane in excellent yield.[28]

Another sterically hindered silane ($t\text{-}Bu_2SiCl_2$) reacts with lithium under ultrasonic irradiation at room temperature and gives a reactive intermediate, di(t-butyl)silylene, capable of insertion at the silicon–hydrogen bond[9] (Eqn [6]).

Recently, a convenient new method has been proposed for the preparation of allylstannanes by the sonolysis of allyl chloride (**6**) and tributylchlorostannane in the presence of magnesium.[29] This is the first example of an ultrasound-enhanced process involving the cross-coupling of two halides, each of them being capable of giving homocoupling products (Eqn [7]). The procedure enables one to prepare various allylstannanes (**7**) rapidly (in less than one hour) and almost quantitatively. The reaction occurs regioselectively, with retention of configuration (stereo-isomeric

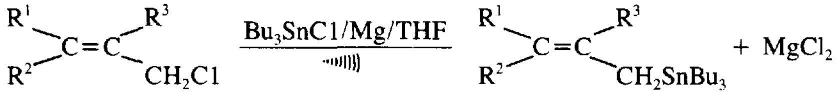


[5]



$$t\text{-}\mathrm{Bu_2SiCl_2} \xrightarrow[)))]{\mathrm{Li}} [t\text{-}\mathrm{Bu_2Si}:] \xrightarrow{\mathrm{R_3SiH}} \mathrm{R_3Si{-}\underset{t\text{-}Bu}{\overset{t\text{-}Bu}{SiH}}} + \mathrm{LiCl} \qquad [6]$$

$$\mathrm{R_3} = \mathrm{Et_3},\ \mathrm{PhMe_2} \qquad (60\%)$$



6 7 [7]

R^1 = H, Me, Ph, $CH_2{=}CH$, $MeCH{=}CH$; R^2,R^3=H, Me

purity > 90%). A near-equimolar mixture of *cis* and *trans*(7) (R^1 = Me, R^2 = R^3 = H) (45/55) and isomeric allylstannane ($Bu_3Sn(Me)CHCH{=}CH_2$) is solely gained from the β-methallyl chloride. The same method provides quantitative yields of benzyltributylstannane (from $PhCH_2Cl$ and Bu_3SnCl) and tetra-allylstannane (from $CH_2{=}CHCH_2Cl$ and $SnCl_4$). The rate of cross-coupling is considerably enhanced by ultrasonic irradiation. Without sonication, appreciable amounts of homocoupling products (after Wurtz) are formed. In terms of ease of manipulation, the yield and isomeric purity of products with the method employing sonication is superior to other known procedures employed for the preparation of allylstannanes.[29] In contrast to chlorostannanes, trimethylchlorosilane fails to yield allylsilanes under similar conditions.

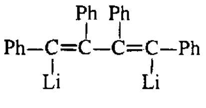
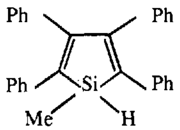
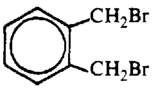
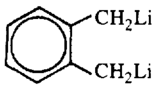
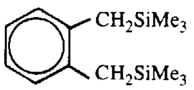
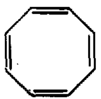
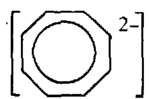
The use of ultrasound enhances drastically the synthesis and use of organolithium compounds whose reactions with methylchlorosilanes afford various organosilicon derivatives in good yield (Table 1).[30]

The synthesis of 1,4-dilithio-1,2,3,4-tetraphenylbutadiene without sonication requires stirring for 16 hours,[31] that of cyclo-octatetraenyldilithium for 12–36 hours,[32] whereas in the case of sonolysis the same lithium compounds are formed within 10 minutes. The stirring of dilithiotetraphenylbutadiene together with methyldichlorosilane for 30 minutes at room temperature leads to the five-membered silacyclane, 1-methyl-2,3,4,5-tetraphenylsilacyclopentadiene (Table 1). Equally rapidly the reaction between cyclo-octatetraenyldilithium and trimethylchlorosilane occurs to give bis(trimethylsilyl)cyclooctatetraenes. An attempt to obtain α,α′-bis(trimethylsilyl)-*o*-xylene by reacting α,α′-dibromo-*o*-xylene with trimethylchlorosilane in the presence of zinc using sonication proved unsuccessful[30,33] due to *o*-xylylene formation. But this reaction occurs rather rapidly (60–90 minutes) in the presence of lithium (Table 1). On the other hand, the preparation of $o\text{-}(Me_3SiCH_2)_2C_6H_4$ from dichlorobenzene and the Grignard reagent (Me_3SiCH_2MgCl) in the presence of $Ni[Ph_2P(CH_2)_3PPh_2]Cl_2$ requires stirring for 20 hours.[34]

Reactions of the Barbier type involving synthetically available 3-bromo-2-trimethylsilyl-1-propene (**8**) and various electrophiles (terminal alkynes, aldehydes, ketones, nitriles) in the presence of zinc offer ample possibilities for the preparation of functionally substituted vinylsilanes.[35] Addition of terminal alkynes to vinylsilane **8** under sonolysis (30 W, 48 kHz) proceeds at room temperature during 15–30 minutes to give dienes **9** in good yield (Eqn [8]).

A still greater yield of addition products **10**

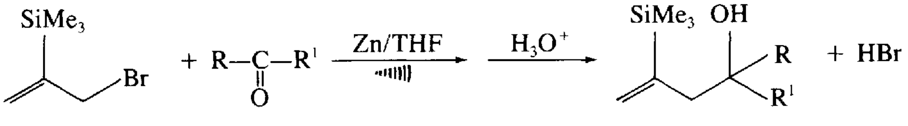
Table 1 Synthesis of organosilicon derivatives based on ultrasonically enhanced reactions of lithiation[30]

Substrate	Organolithium	Time (min)	Electrophile	Product	Yield (%)
PhC≡CPh	 $Ph{-}C(Li){=}C(Ph){-}C(Ph){=}C(Li){-}Ph$	10	$MeHSiCl_2$		68
		60–90	Me_3SiCl		45
	 $2Li^+$	10	Me_3SiCl	$c\text{-}C_8H_6(SiMe_3)_2$	82

[8]

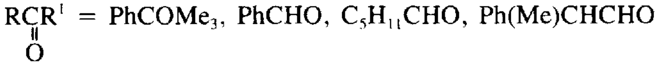
8 **9**

R = C_6H_{13} (50%), CH_2OSiMe_3 (60%), $CH_2CH_2OSiMe_3$ (60%)



[9]

8 **10**



$\underset{\underset{O}{\|}}{RCR^1}$ = $PhCOMe_3$, PhCHO, $C_5H_{11}CHO$, Ph(Me)CHCHO

(75–80%) can be attained by the reaction of **8** with aldehydes and ketones (Eqn [9]).

Aromatic and aliphatic nitriles react with alkenylsilane (**8**) with equal ease; the resultant iminovinylsilanes after hydrolysis give β,γ-unsaturated ketones (**11**). The latter can be used as suitable starting compounds for the preparation of 2-substituted 4-trimethylsilylfurans[35] (Eqn [10]).

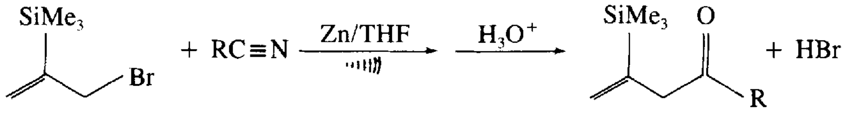
Reductive silylation of dicarbonyl compounds with trimethylchlorosilane in the presence of zinc can be mentioned as another example of the benefits of ultrasound application to heterogeneous reactions of organosilicon compounds using metals.[36] Ultrasonic irradiation (150 W, 55 kHz) drastically enhances the rates of reaction and increases product yields (Table 2). Tetrahydrofuran is a more suitable solvent than diethyl ether for the silylation of dicarbonyl compounds under sonolysis conditions, as is clearly demonstrated by the reaction of benzoquinone.

Kitazume[38] has developed a method for the preparation of practically useful fluorine-containing β-keto-γ-butyrolactones (**13**), which are otherwise difficult to obtain synthetically, i.e. by Reformatsky-type reactions conducted under ultrasonic irradiation (Scheme 3).

A mixture of *O*-trimethylsilylated cyanohydrin (**12**), ethyl α-fluoro (trifluoromethyl)bromoacetate and zinc in THF has been subjected to sonolysis. The reactions occur at room temperature to give lactones (**13**) in good yield (48–69%). Without sonication the products **13** fail to form at all. It is noteworthy that with ultrasonic irradiation the reaction proceeds by using commercially available zinc powder without prior activation, whereas without sonication acceptable yields in the Reformatsky reaction can be reached only with freshly prepared zinc powder obtained by reducing anhydrous zinc chloride ($ZnCl_2$) with active metal.

3.2 Reduction reactions

The reduction of halogen, alkoxy and amino derivatives of Group IVB elements is used for preparative purposes in the synthesis of corresponding hydrides.[39] Typically, the reduction of compounds R_3MX (M = Si, Ge, Sn; X = halogen, alkoxy, amino; R = alkyl, aryl) involves their reaction with $LiAlH_4$ in ether or THF.[39] Bearing in mind that lithium aluminium

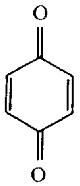
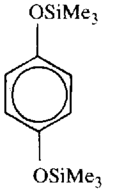
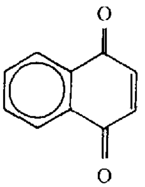
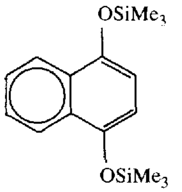
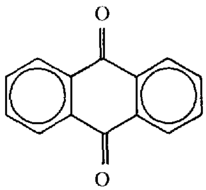
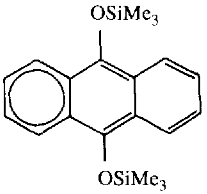
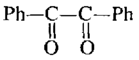
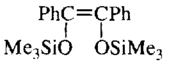
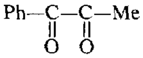
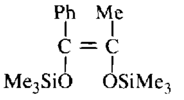
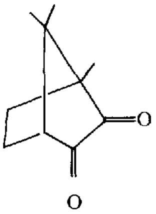
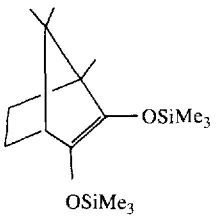


[10]

8 **11**

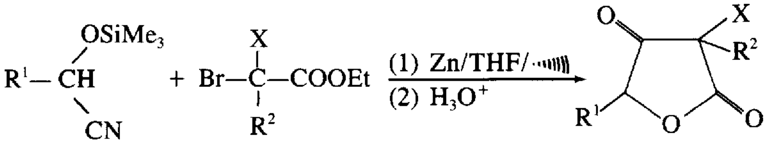
R = n-C_3H_7 (80%), n-C_7H_{15} (82%), c-C_6H_{11} (74%), Ph (61%)

Table 2 Reductive silylation of dicarbonyl compounds[36]

Dicarbonyl compound	Product	Solvent	Yield (%) Sonolysis for 10–30 min	Yield (%) Stirring for 2–3 h, no sonolysis
		Et_2O	54	63(77[a])
		THF	90	71
		Et_2O	69	49
		THF	76	50
		Et_2O	62	60
		THF	65	65
 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}Ph}$	 $\mathrm{Ph\underset{\underset{Me_3SiO}{\mid}}{C}{=}\underset{\underset{OSiMe_3}{\mid}}{C}Ph}$	Et_2O	58	53(75[a])
		THF	62	74
 $\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}Me}$	 $\mathrm{\underset{\underset{Me_3SiO}{\mid}}{\overset{\overset{Ph}{\mid}}{C}}{=}\underset{\underset{OSiMe_3}{\mid}}{\overset{\overset{Me}{\mid}}{C}}}$	THF	73	45
		THF	88	80

[a] Mechanical stirring for 15 h.[37]

hydride as a coating on silica (SiO_2) reduces carbonyl compounds in non-polar solvents (hexane, benzene)[40] and that ultrasonic irradiation accelerates heterogenic reduction of aryl halides in dimethoxyethane,[41] the possibility of $R_3MX \rightarrow R_3MH$ sonochemical conversion in non-polar medium in the presence of $LiAlH_4$ was investigated.[42,43] A $LiAlH_4$ suspension in a hydrocarbon solvent was found to reduce chloro-, methoxy- and diethylamino-silanes, chlorogermane and chlorostannane to the corresponding hydrides (Table

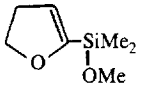
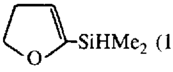
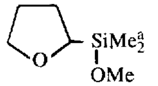
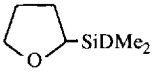


12 **13**

R^1 = Me, Ph, R^2 = H, Me, X = F, CF_3

Scheme 3

Table 3 Reduction of derivatives containing Group IVB elements with lithium aluminium hydride under sonication[42]

Substrate	Solvent	Time (h)	*T*(°C)	Product (Yield, %)
Me_3SiCl	Hexane	3	40	Me_3SiH (80)
Ph_2SiHCl	Hexane	2	40	Ph_2SiH_2 (> 95)
Et_3GeCl	Pentane	4.5	40	Et_3GeH (> 95)
Me_3SnCl	Cyclohexane	2.5	25	Me_3SnH (> 95)
Me_3SiNEt_2	Hexane	3	40	Me_3SiH (70)
	Pentane	3	25	 (100)
	Cyclohexane-d_{12}	2	25	 (100)

[a] $LiAlD_4$ as reducing agent.

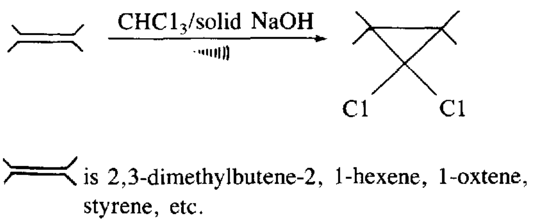
3) during ultrasonic irradiation (100 W, 55 kHz). It should be pointed out that sonolysis in this case serves to induce reactions which otherwise fail to take place.

If reduction is to be carried out in deuterated solvents, it is possible to use readily available hexane-d_{14} or cyclohexane-d_{12} instead of costly tetrahydrofuran-d_8.[42]

The demonstration of heterogeneous reduction with lithium aluminium hydride in a non-polar medium prompted the study of similar reactions under phase-transfer catalysis conditions (PTC). Soon it was reported that typical phase-transfer catalysts (crown ethers and quaternary onium salts) effectively catalyse the reduction of various functions in the two-phase system hydrocarbon/solid $LiAlH_4$.[44,45] This is a rare case when a sonochemical synthesis study has been conducted before one with phase-transfer catalysis, because generally the effects of ultrasonication on a phase-transfer reaction are examined after the process has been already effected with recourse to PTC. A comparison of the capabilities of these two synthetic routes to hydrides of Group IVB elements shows that in most cases the sonochemical and catalytic approaches yield comparable results in terms of reaction time and product output. Under PTC conditions, a two-fold excess of $LiAlH_4$ is required; under ultrasonication a three-fold excess. On the other hand, in a two-phase catalytic system the reaction occurs generally at elevated temperature (60–80°C), whereas sonolysis is conducted at room temperature.

3.3 Reactions involving carbenes and nitrenes

One of the frequently employed approaches to dichlorocarbene generation by two-phase catalysis is to treat chloroform with solid alkali in the presence of phase-transfer agents.[46] It is possible to apply ultrasound to this process instead of phase-transfer catalysis.[47] During sonolysis (35 W, 45 kHz) of a mixture of alkene, chloroform and solid NaOH the corresponding dichlorocyclopropanation products have been obtained (Scheme 4).



is 2,3-dimethylbutene-2, 1-hexene, 1-oxtene, styrene, etc.

Scheme 4

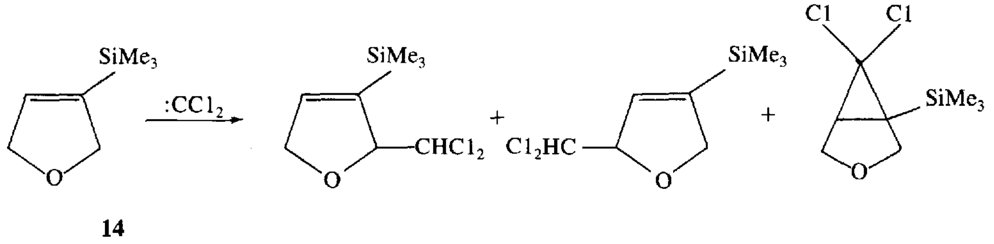
The time of reaction and product yields in most cases are improved as compared with PTC. It must be pointed out that excellent results have been reached only with small amounts of reagents (< 5 mmol alkene). The rate of conversion is low when the reaction is carried out on a larger scale, possibly due to the low power of the ultrasound source.[47] Indeed, it was demonstrated later that [3-(2,5-dihydrofuryl)]-trimethylsilane (**14**) (10 mmol) reacts very similarly with dichlorocarbene under liquid–solid PTC and under sonication (100 W)[48] (Scheme 5).

It can be seen that the total yield of insertion and addition products and their ratio are subject to little variation when catalytic and sonochemical procedures are compared.

An attempt to apply ultrasonic irradiation in place of PTC for the generation of dichlorocarbene by the trichloroacetate method was unsuccessful.[49]

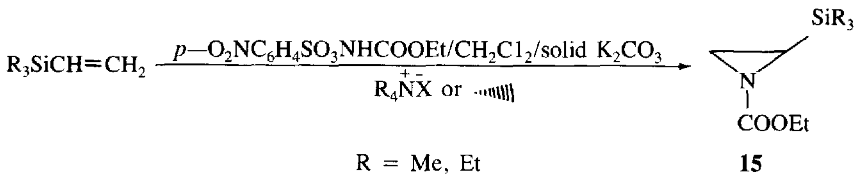
The known method for ethoxycarbonylnitrene generation by α-elimination of the *p*-nitrobenzenesulphonate anion from ethyl-*N*-(*p*-nitrobenzenesulphonyloxy)carbamate treated with base in an aqueous–organic two-phase catalytic system[50] has been recently applied to attain the addition of the :N—COOEt group to vinylsilanes leading to 1-ethoxycarbonyl-2-trialkylsilylaziridines (**15**).[51]

It is also possible to generate :N—COOEt by liquid–solid PTC; aziridines (**15**) in 30–40% yield can be obtained by this method from alkenylsilanes[52] (Scheme 6). Without phase-transfer catalysts in the system CH_2Cl_2/solid K_2CO_3, the formation of the products (**15**) is very slow and is characterized by low yields. Continuous irradiation of the reaction mixture



PTC (25°C/5 h):	20%	23%	32%
Sonolysis (40–45°C/8 h):	21%	31%	32%

Scheme 5



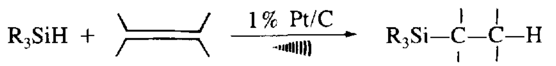
Scheme 6

with ultrasound (200 W, 45 kHz) slightly intensifies the process, whereas the use of an ultrasonic disintegrator (2000 W, 44 kHz) almost completely makes up for the absence of catalyst.

The yields of **15** are similar to those attained for PTC, but the reaction time is decreased from 2–3 hours to 15 minutes.[52]

3.4 Hydrosilylation

In hydrosilylation reactions, as in the case of other catalytic processes, it is preferable to use heterogeneous catalysts. However, in the hydrosilylation of alkenes and alkynes the highest activity is observed with the homogeneous Speier's catalyst ($H_2PtCl_6 \cdot 6H_2O$).[53] The hydrosilylation of carbon–carbon double and triple bonds in the presence of the heterogeneous catalyst platinum carbon (Pt/C) usually occurs at high temperature (150–180°C), the reaction lasting 10–20 hours for satisfactory yields to be reached.[54,55] Under ultrasonication (150 W, 55 kHz) the same reaction can be performed at 30°C in one to two hours[56] (Scheme 7).



$R_3 = Cl_3, Cl_2Me, (OEt)_3, Et_3$

Scheme 7

Hence, the hydrosilylation of alkenes with various silanes affords the corresponding adducts (Table 4) in good yield (74–95%). In the case of sterically hindered 2-methyl-1-pentene, the products of trichloro- and methyldichloro-silane addition have been gained in 71 and 30% yields respectively (30°C, two hours). Under the same conditions but without sonication the hydrosilylation does not exceed 5% even when the process occurs continuously (10–48 hours), whereas with sonolysis the carbon–carbon triple bond (C≡C) also undergoes hydrosilylation smoothly (Table 4). The advantages of sonochemical heterogeneous hydrosilylation are apparent. Apart from the advantages outlined above they include lack of exothermia, reduction in tar formation and opportunity for reutilization of the catalyst.[56]

3.5 Other reactions

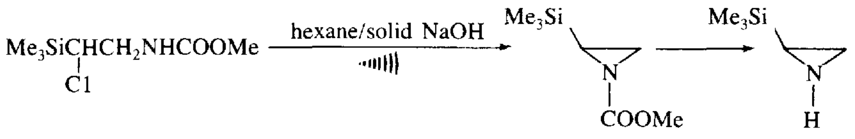
Recently, a convenient method has been proposed for the preparation of silicon-containing aziridines by intramolecular *N*-alkylation of alkyl-*N*-(2-chloro-2-trialkylsilyl)ethylcarbamates in the two phase system hexane/solid NaOH in the presence of a phase-transfer catalyst.[57,58] In the case of carbamate (**16**) this reaction proceeds slowly and in the absence of catalyst it can be considerably accelerated by ultrasonic irradiation (100 W, 55 kHz). However, after reaching a 45% yield of the desired product (aziridine, **17**) its content in the reaction mixture begins to decline due to consecutive formation of 2-silyl-substituted 1*H*-aziridine (**18**) (possibly via ultrasound-induced saponification of the ester group and decarboxylation)[58] (Scheme 8).

In conclusion, it should be added that ultrasound (150 W, 55 kHz) can be successfully used for the generation of silyl anions (**19** and **20**) from 1-methyl-1-silaphenalene and (1-naphthyl)vinylmethylsilane, respectively, by treating them with potassium hydride in THF[59] (Scheme 9).

Silyl anions **19** and **20** are readily formed during ultrasonic irradiation at room temperature for one hour. The use of the system potassium hydride (KH/THF) for generating $Et_3Si^-K^+$ and $Ph_3Si^-K^+$ in the absence of ultrasound requires six to twelve hours and temperatures above 40°C.[59]

CONCLUSION

Analysis of the relatively small number of publications presented in this survey demonstrates the new possibilities offered by sonochemical procedures in the chemistry of organic compounds containing silicon and related elements. This applies, first and foremost, to reactions with metal-containing reagents and catalysts.

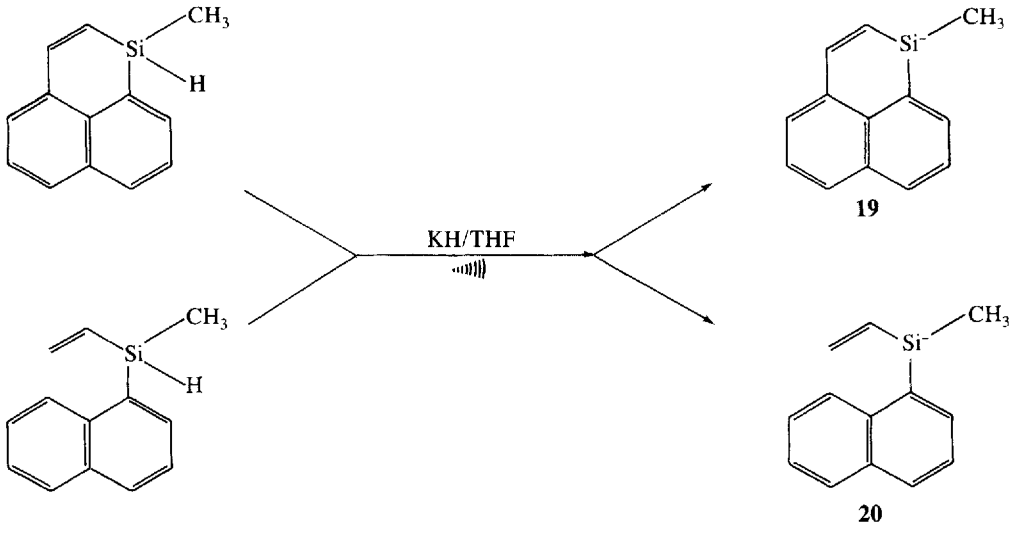


16 **17** **18**

Scheme 8

Table 4 Sonochemical hydrosilylation reactions[56]

Substrate	Hydrosilane	Time (h)	Product	Yield (%)
1-Hexene	$HSiCl_3$	1	$n\text{-}C_6H_{13}SiCl_3$	90
	$HSiCl_2Me$	1	$n\text{-}C_6H_{13}SiCl_2Me$	95
	$HSiEt_3$	2	$n\text{-}C_6H_{13}SiEt_3$	74
4-Methyl-1-pentene	$HSiCl_3$	1	$(CH_3)_2CHCH_2CH_2CH_2SiCl_3$	94
	$HSiCl_2Me$	1	$(CH_3)_2CHCH_2CH_2CH_2SiCl_2Me$	96
	$HSi(OEt)_3$	1	$(CH_3)_2CHCH_2CH_2CH_2Si(OEt)_3$	93
2-Methyl-1-pentene	$HSiCl_3$	2	$CH_3CH_2CH_2CH(CH_3)CH_2SiCl_3$	71
	$HSiCl_2Me$	2	$CH_3CH_2CH_2CH(CH_3)CH_2SiCl_2Me$	30
Styrene	$HSiCl_3$	1.5	$PhCH_2CH_2SiCl_3$	94
	$HSiCl_2Me$	1.5	$PhCH_2CH_2SiCl_2Me$	94
Phenylacetylene	$HSiCl_3$	2	$(E)\text{—}PhCH{=}CHSiCl_3$	98



Scheme 9

The mechanism of action of ultrasound on heterogeneous chemical systems is still obscure and is being studied by several teams of investigators.[1,4,5,10–13] Another interesting possibility is the use of ultrasound in two-phase reactions in lieu of or together with phase-transfer catalysts, although in this case one should consider the possibility of switching over of reaction pathways (see, for example, Refs 60, 61).

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