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Journal of Organometallic Chemistry 500 (1995) 325–329

Journal of Organometallic Chemistry

Invited review

From ephemers [☆] to monomers, oligomers and polymers. New methods for the generation and transformation of silanones

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Received 28 March 1995

Abstract

New efficient routes to the generation of silanones at relatively low temperatures are based on the following reactions:

(1) reaction of linear and branched perhydrocarbyldisiloxanes and oligosiloxanes, and of some of their C-functional derivatives, with gallium or indium iodides or bromides;

(2) reaction of hydrocarbylchlorosilanes $R_{4-n}SiCl_n$ ($n = 2$–4) and $SiCl_4$ with dimethylsulphoxide (with or without Mg or Zn);

(3) Autodecomposition of organosilicon compounds containing $\geqslant$ISiOSi$\leqslant$ and $\geqslant$ISiOC$\leqslant$ groups;

(4) reaction of $R_{4-n}SiCl_n$ with metal oxides of high redox potential (with or without the presence of CH_3CN).

Insertions of dialkylsilanones into Si–O–Si and Si–O–C linkages as well as into the Si–Cl bond have been studied.

Keywords: Silicon; Silanones

Silanones RR′Si=O where R,R′ = hydrocarbyl (hydrocarbon radical), chlorine, hydrogen, etc. are transient highly reactive intermediates most often formed during high-temperature reactions of organosilicon compounds containing Si–O siloxane bonds [1–3].

These transient species were encountered quite unexpectedly when we started our research on the reactions of gallium and indium iodides and bromides with permethyloligosiloxanes [4–7]. At that time the idea that hexamethyldisiloxane, as a monomer, could be transformed into linear permethylsiloxanes (including high-molecular-weight elastomers and even solid polymers) or to cyclic permethylsiloxanes seemed fantastic. No less unreal appeared the prospect of obtaining tetramethylsilane from hexamethyldisiloxane in the absence of any methylating agent. Nevertheless, we were able to perform all these conversions and extend them to other perhydrocarbylsiloxanes and some of their C-functional derivatives.

During this research we found out that the dihydrocarbylsilanones were ephemeral intermediates ("ephemers") in these conversions. This caused us to pay special attention to these species, to develop some new methods for their generation at low and moderate temperatures and to examine some of their conversions. But let us not get ahead of the story.

Some time ago one of us began a systematic research on heterolytic cleavage reactions of the siloxane bond. He was the first to observe the high reactivity of the Si–O–Si group [8–10], which contradicted the ideas current at that time. The research was initiated by the discovery of cleavage of hexaalkyldisiloxanes by aluminium halides, which provided a widely accepted simple route to trialkylsilyl halides [8–12]. During this investigation it was shown that not only individual AlI_3 itself but also a mixture of elementary aluminium and iodine could be used for the synthesis of trialkyliodosilanes [13].

Recently, in continuation of this research, we have examined the reaction of permethyloligosiloxanes of

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[☆] Editor's note. "Ephemer" is not a known word in English (the correct word for "that which lasts a short time" is " ephemera") but its use here makes an attractive title. However, the "mer" in ephemera is not related by origin to that in monomer or polymer.

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Elsevier Science S.A.
SSDI 0022-328X(95)00523-4

general formula $Me_{4-n}Si(OSiMe_3)_n$ ($n = 1$–4) with gallium triiodide and tribromide and also with gallium or indium metals and iodine or bromine.

Earlier it had been reported [14–16] that gallium trichloride reacts with hexamethyldisiloxane (1 : 1 molar ratio) according to the following equation:

$$Me_3SiOSiMe_3 + GaCl_3 \longrightarrow MeGaCl_2 + Me_3SiCl + 1/n(Me_2SiO)_n \quad (1)$$

We found that, in contrast to gallium trichloride, gallium tribromide, and especially gallium triiodide or gallium metal–iodine or metal–bromine systems, react with an excess of hexamethyldisiloxane (1 : 1.5–10) under reflux to give tetramethylsilane in high yield along with cyclic and linear permethyloligosiloxanes.

This reaction provides the most convenient and cheapest route to tetramethylsilane, which was comparatively difficult to make. With gallium bromide the yield of tetramethylsilane was slightly lower, but still high (up to 80%). The processes involved are shown in the following equations:

$$Me_3SiOSiMe_3 \xrightarrow{GaX_3} Me_4Si + [Me_2Si{=}O]$$

$$X = I \text{ or } Br \quad (2)$$

$$n[Me_2Si{=}O] \longrightarrow (Me_2SiO)_n \quad n = 4\text{–}14 \quad (3)$$

$$m[Me_2Si{=}O] + (Me_2SiO)_n \longrightarrow (Me_2SiO)_{n+m} \quad (4)$$

$$m[Me_2Si{=}O] + Me_3SiOSiMe_3 \longrightarrow Me_3SiO(Me_2SiO)_mSiMe_3 \quad (5)$$

$$m = 1\text{–}14$$

The m and n values reported here are those that were experimentally determined but they can be much higher.

The dimethylsilanone formed during the reaction either undergoes polymerization (cf. Refs. [1–3], [17–18]) to oligocyclodimethylsiloxane (Eq. (3)) or insertion into the Si–O bond of linear or cyclic permethyloligosiloxanes (cf. Refs [1–3]) according to Eqs. (4) and (5).

Analysis by GLC indicates that the production of linear and cyclic permethylsiloxanes starts with the formation of linear oligomers $Me_3SiO(Me_2SiO)_mSiMe_3$, $m = 1$ or 2, as in Eq. (5), and only after this do cyclic oligomers $(Me_2SiO)_n$, $n = 3$ or 4, formed by reactions (3) and (4), appear. Furthermore, the concentration of hexamethylcyclotrisiloxane ($n = 3$) falls abruptly as a result of reaction (4). Thus, the formed dimethylsilanone inserts into a molecule of hexamethyldisiloxane or octamethyltrisiloxane more readily than it generates cyclic oligomers.

The GaI_3 used as a catalyst facilitates the conversion of hexamethyldisiloxane into high-molecular-weight linear permethylpolysiloxanes, and even insoluble rubbery and hard polymers. In this way a polymer of 12 300 MM (as determined obullioscopically), soluble in toluene, was obtained. It is noteworthy that upon prolonged heating of GaI_3 with a liquid linear permethylpolysiloxane PMS-200 (200 cSt) the latter does not undergo much change. This can be attributed to the very low concentration of end trimethylsiloxy groups that generate dimethylsilanone. At the same time, in the reaction of GaI_3 with this permethylsiloxane in the presence of hexamethyldisiloxane as a disilanone donor, conversion into a high-molecular-weight rubbery permethylpolysiloxane occurs. Thus, in addition to the two well established ways of constructing a macromolecular chain, involving polyaddition or polycondensation reactions, there is a third one, that involving polyinsertion.

In the reaction of hexamethyldisiloxane with GaI_3 in the presence of tetraethoxysilane as a dimethylsilanone trap 1,1,1,3-tetraethoxy-3,3-dimethyldisiloxane was isolated in addition to the oligomers formed by reactions (3)–(5) and tetramethylsilane:

$$(EtO)_3Si\text{–}OEt + [O{=}SiMe_2] \longrightarrow (EtO)_3Si\text{–}OSiMe_2OEt \quad (6)$$

This reaction provides yet more evidence for the intermediate generation of dimethylsilanone according to reaction (2).

The reaction of GaI_3 with the octamethyltrisiloxane $Me_2Si(OSiMe_3)_2$ occurs analogously to that with hexamethyldisiloxane, but considerably faster, and leads mainly to the products formed by reactions (2)–(5).

$$Me_2Si(OSiMe_3)_2 \xrightarrow{GaI_3} Me_4Si + 2\,[Me_2Si{=}O] \quad (7)$$

The reaction of GaI_3 with methyltris(trimethylsiloxy)silanes and tetrakis(trimethylsiloxy)silane also affords tetramethylsilane in high yield. In this case all the trimethylsiloxy groups are involved.

$$2MeSi(OSiMe_3)_3 \xrightarrow{GaI_3} 3Me_4Si + 3[Me_2Si{=}O] + 2/n(MeSiO_{1.5})_n \quad (8)$$

$$Si(OSiMe_3)_4 \xrightarrow{GaI_3} 2Me_4Si + 2[Me_2Si{=}O] + SiO_2 \quad (9)$$

The reactivity of methyltris(trimethylsiloxy)silanes $Me_{4-n}Si(OSiMe_3)_n$ with respect to GaI_3 enhances with increasing the n value. This is not related to the increasing boiling point of $Me_{4-n}Si(OSiMe_3)_n$. Thus, $Si(OSiMe_3)_4$ reacts vigorously with GaI_3 to form tetramethylsilane at temperatures as low as 35–40°C. The dimethylsilanone formed according to reactions (8) and (9) is involved in the formation of hard three-dimensional polymers. Along with them, minor quantities of linear permethyloligosiloxanes $Me_3Si(OSiMe_2)_mMe$, $m = 1$–5, and $(Me_2SiO)_5$ were also identified (GLC–MS) during reaction (9).

A general representation of the reaction of the permethyloligosiloxanes studied with triiodide or tribromide is shown in Eq. (10):

$$Me_{4-n}Si(OSiMe_3)_n \xrightarrow{GaI_3} n/2Me_4Si + n/2[Me_2Si{=}O] + Me_{4-n}SiO_{n/2} \quad (10)$$

The interaction of GaI_3 with hexaalkyldisiloxanes is an example of a more general reaction. Thus, for example, the reaction of gallium triiodide with hexaethyldisiloxane affords tetraethylsilane in ca. 60% yield 60%, and some octaethyltrisiloxane $Et_2Si(OSiEt_3)_2$ and perethylcyclosiloxanes $(Et_2SiO)_n$ $n = 2–7$ were also isolated.

The reaction of 1,1,3,3-tetramethyldisiloxane with GaI_3 (10 : 1) occurred exothermically even at room temperature to give a quantitative yield of dimethylsilane, which was further converted to dimethylbromosilane. Along with dimethylsilane linear and cyclic polymethylsiloxanes are formed.

$$HMe_2SiOSiMe_2H \xrightarrow{GaI_3} Me_2SiH_2 + [O{=}SiMe_2] \quad (11)$$

Reaction (11) provides a convenient method for the preparation of dimethylsilane. When reaction (11) is carried out in the presence of an excess of hexamethyldisiloxane (1 : 10) along with dimethylsilane, linear and cyclic permethyloligosiloxanes are formed, providing evidence for the mechanism of reaction (11):

$$(Me_2SiH)_2O + (Me_3Si)_2O + (Me_2SiO)_n \xrightarrow{GaI_3} Me_2SiH_2 + Me_3SiO(Me_2SiO)_mSiMe_3$$

$$m = 1–4,\ n = 4–8 \quad (12)$$

1,3-Bis(chloromethyltetramethyldisiloxane reacts with GaI_3 (5 : 1) though only upon long boiling according to the following equation:

$$ClCH_2Me_2SiOSiMe_2CH_2Cl \xrightarrow{GaI_3} [Me_2Si{=}O] + Me_2Si(CH_2Cl)_2 \quad (13)$$

The reaction is accompanied by partial exchange of chlorines for iodine atoms in both the initial siloxane and dimethylbis(chloromethyl)silane formed. In addition, some $Me_2Si(CH_2Cl)CH_2I$, $ClCH_2Me_2SiOSiMe_2CH_2I$ and $ICH_2Me_2SiOSiMe_2CH_2I$, as well as permethylcyclosiloxanes $(Me_2SiO)_n$ with $n = 3–5$, were isolated.

The AlI_3-assisted exchange of the chlorine atom in the $ClCH_2$-Si group by iodine was described by us previously [19,20]. The formed dimethylsilanone does not insert into the initial 1,3-bis(chloromethyl)tetramethyldisiloxane, apparently owing to the greater strength of the Si–O bond in the latter compared with that in hexaalkyldisiloxanes.

Indium triiodide and tribromide react with permethyloligosiloxanes in the same way as the corresponding gallium halides (i.e. by reactions (2)–(5)), but less efficiently. Thus, for example, the reaction of boiling excess hexamethyldisiloxane with indium triiodide (1 : 1.5–2) gives tetramethylsilane in 60% yield along with linear and cyclic permethyloligosiloxanes. These reactions can also be accomplished with the use of gallium–indium liquid alloys in combination with iodine and bromine.

Thallium triiodide (or, more exactly, $TlI \cdot I_2$) and the iodides of Zn, Sn, Sb and Fe undergo practically no reaction with hexamethyldisiloxane under the conditions used.

There is no doubt that reaction (2) and similar reactions start with cleavage of the Si–Me bond by gallium or indium trihalide (evidently through a six- or four-centred transition state).

$$GaX_3 + Me_3SiOSiMe_3 \longrightarrow MeGaX_2 + XMe_2SiOSiMe_3 \quad (14)$$

As pentamethylhalosiloxanes formed by reaction (14) have not been found in the reaction mixture, they are supposed to disproportionate according to the Eq. (15):

$$XMe_2SiOSiMe_3 \longrightarrow [Me_2Si{=}O] + XSiMe_3 \quad (15)$$

This is followed by methylation of Me_3SiX:

$$Me_3SiX + X_2GaMe \longrightarrow Me_4Si + GaX_3 \quad (16)$$

The occurrence of reaction (15) accounts for the GaX_3 catalytic effect of GaX_3 and seems highly probable since our studies have shown that organosilicon compounds containing $R_2ISiOSi\langle$ and $R_2ISiOC\langle$ groups are readily cleaved [15] according to Eq. (17)

$$R_2ISiOM\lessgtr \longrightarrow [R_2Si{=}O] + IM\lessgtr \quad (17)$$

$$M = Si \text{ or } C$$

Peralkyliodosiloxanes, $R_3Si(OSiR_2)_nI$ and $IR_2Si(OSiR_2)_nI$ ($n > 1$) are not known at the present time. We attempted to synthesise pentamethyliododisiloxane, as the first representative of this type of compound by exchange between pentamethyl(chloro)disiloxane and NaI in acetonitrile. In the absence of this solvent there is no reaction. When the reaction was carried out at 20°C (18–20 h) or at the boiling point of the solvent (2–3 h), octamethylcyclotetrasiloxane (yield up to 10%), 1,1,1,3,3,5,5-heptamethy 1-5-chlorotrisiloxane, 1,1,1,3,3,5,5,7-nonamethyl-7-chlorotetrasiloxane and trimethyliodosilane were formed instead of the expected pentamethyl iododisiloxane [21].

The course of the reaction can be represented by the following equations:

$$Me_3SiOSiMe_2Cl + NaI \xrightarrow[-NaCl]{MeCN} [Me_3SiOSiMe_2I] \longrightarrow [Me_2Si{=}O] + ISiMe_3 \quad (18)$$

$$Me_3SiOSiMe_2Cl + n[Me_2Si{=}O] \longrightarrow Me_3SiO(Me_2SiO)_nSiMe_2Cl \quad (19)$$

$$4[Me_2Si{=}O] \longrightarrow (Me_2SiO)_4 \quad (20)$$

The intermediate pentamethyliododisiloxane could not be isolated because upon heating it decomposes according to Eq. (18). The trimethyliodosilane formed is taken up by acetonitrile to form a solid complex which dissociates upon heating.

The product of the reaction of tetramethyl-1,3-dichloro-disiloxane with NaI in refluxing acetonitrile also turned out to be octamethylcyclotetrasiloxane:

$$ClMe_2SiOSiMe_2Cl + 2NaI \xrightarrow[-NaCl]{MeCN} [IMe_2SiOSiMe_2I] \longrightarrow [Me_2Si{=}O] + Me_2SiI_2 \quad (21)$$

Dimethylsilanone formed in this way undergoes tetramerization according to Eq. (20). Dimethyldiiodosilane is taken up by acetonitrile to give a solid adduct.

The reaction of pentamethyldisiloxane with I_2 (1 : 1) give permethyloligocyclosiloxanes (total yield 24%) and trimethyliodosilane (yield 57%) according to the following sequence:

$$Me_3SiOSiMe_2H + I_2 \xrightarrow[-HI]{} [Me_3SiOSiMe_2I] \longrightarrow [Me_2Si{=}O] + Me_3SiI \quad (22)$$

$$n[Me_2Si{=}O] \rightarrow (Me_2SiO)_n \quad (23)$$

$n = 3$ or 4

If a $Me_3SiOSiMe_2H : I_2$ molar ratio of 1 : 0.1–0.2 is used the yield of permethyloligocyclosiloxanes is lowered to 10%. Linear oligomethylsiloxanes of the general formula $Me_3SiO(Me_2SiO)_nSiMe_2H$, with $n = 1$–3, are formed (total yield 33%). They are the products of insertion of dimethylsilanone into the starting pentamethyldisiloxane.

$$Me_3SiOSiMe_2H + n[Me_2Si{=}O] \longrightarrow Me_3SiO(Me_2SiO)_nSiMe_2H \quad (24)$$

In the reaction of pentamethyldisiloxanes with I_2 in the presence of hexamethyldisiloxane (1 : 1 : 1) the latter reacts nearly quantitatively to generate dimethylsilanone which goes on to give linear permethyloligosiloxanes and minor amounts of permethyloligocyclosiloxanes (total yield 82%).

$$Me_3SiOSiMe_3 + n[Me_2Si{=}O] \longrightarrow Me_3SiO(Me_2SiO)_nSiMe_3 \quad (25)$$

$n = 1$–8 (normally 1–3)

The yield of trimethyliodosilane is the same with or without hexamethyldisiloxane.

In the reaction of 1,1,3,3-tetramethyldisiloxane with I_2 in the presence of hexamethyldisiloxane (1 : 1 : 1) the generated dimethylsilanone inserts into hexamethyldisiloxane to form linear permethyloligosiloxanes according to Eq. (25), $n = 1$–11, and undergoes cyclization to afford permethyloligocyclosiloxane according to Eq. (23), $n = 3$ or 4 (total yield of all siloxanes is 89%). In this case dimethylsilanone is generated according to the following equation

$$HMe_2SiOSiMe_2H + I_2 \xrightarrow[-HI]{} [IMe_2SiOSiMe_2H] \longrightarrow [Me_2Si{=}O] + Me_2SiHI \quad (26)$$

Replacement of hexamethyldisiloxane by octamethylcyclotetrasiloxane leads to the formation of oligomethylcyclosiloxanes containing between five and nine silicon atoms (total yield 35%).

$$(Me_2SiO)_4 + n[Me_2Si{=}O] \longrightarrow (Me_2SiO)_{n+4} \quad (27)$$

$n = 1$–5

In this case only about 5% of octamethylcyclotetrasiloxane was involved in the reaction and dimethyldiiodosilane was isolated (yield 10%) along with dimethyliodosilane.

In the reaction of 1,1,3,3-tetramethyldisiloxanes with I_2 (1 : 0.1–0.2) along with permethyloligocyclosiloxanes linear 1,1,3,3-dihydropermethyloligosiloxanes are formed (yield > 20%) according to the following equation:

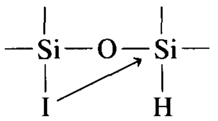
$$HMe_2SiOSiMe_2H + n[Me_2Si{=}O] \longrightarrow HMe_2SiO(Me_2SiO)_nSiMe_2H \quad (28)$$

$n = 1$–4

In contrast, when the reaction of 1,1,3,3-tetramethyldisiloxanes with I_2 is carried out at a molar ratio of 1 : 2 dimethyl-(diiodo)silane is obtained in up to 60% yield, according to Eq. (29):

$$HMe_2SiOSiMe_2H + 2I_2 \xrightarrow[-2HI]{} [Me_2Si{=}O] + Me_2SiI_2 \quad (29)$$

These results allow a new interpretation of the unexpectedly low rate constant (k_2) for the substitution of the second hydrogen atom in the iodation of 1,1,3,3-tetramethyldisiloxane, an observation that was ascribed to "a strong direct interaction of the large iodine atom with the silicon atom" (the so called "field effect") [22] as represented below



(30)

The data obtained indicate that in the reaction of 1,1,3,3-tetramethyldisiloxane with iodine the latter replaces only one hydrogen atom. The 1,1,3,3-tetramethyliodosiloxane formed in this case further decomposes to give dimethylsilane and dimethyliodosilane. It is the latter that reacts with iodine but at a much lower rate:

$$Me_2SiHI + J_2 \longrightarrow Me_2SiI_2 + HI \qquad (31)$$

However, alternative mechanisms for the above reactions based on cleavage of the SiOSi bond by GaX_3 or $RGaX_2$ are also possible [4,5].

In a search for other routes to the generation of dihydrocarbylsilanones we found that reaction of dialkyldichlorosilanes with dimethylsulphoxide gave peraalkylcyclosiloxanes (in up to 80% yield) and methyl(chloromethyl)sulphides [23] according to the following equation:

$$RR'SiCl_2 + OS(CH_3)_2 \longrightarrow 1/n(RR'SiO)_n + S(CH_2Cl)CH_3 + HCl \qquad (32)$$

R = alkyl, R′ = alkyl, alkenyl, aryl, halogen, etc.;
n = 3–6

The intermediates in reaction (32) are the corresponding organylsilanones RR′Si=O, which oligomerize to perorganylcyclosiloxanes.

When a $Me_2SiCl_2 : Me_2SO$ molar ratio of 1 : 2 was used, along with permethylcyclosiloxanes up to 10% of α,ω-dichloropermethyloligosiloxanes $ClMe_2Si(OSiMe_2)_nCl$ ($n = 2$–4) were also generated. Appropriate metals (Mg, Zn, etc.) may serve as acceptors of the generated chlorine.

The formation of dialkylsilanone was confirmed by trapping experiments as follows. In the reaction of dimethylsulphoxide with $RR'SiOCl_2$ with an excess of hexamethyldisiloxane with RR′Si=O present as a trap, linear perorganylsiloxanes (total yield 38%) were formed together with the products of reaction (32).

$$n[RR'Si{=}O] + Me_3SiOSiMe_3 \longrightarrow Me_3Si(OSiRR')_nOSiMe_3 \qquad (33)$$

Analogously, RR′Si=O inserts into the –Si–Cl and –Si–OC bonds:

$$\geqslant Si{-}Cl + n[RR'Si{=}O] \longrightarrow \geqslant Si[OSiRR']_nCl \qquad (34)$$

$$\geqslant Si{-}OC\leqslant + n[RR'Si{=}O] \longrightarrow \geqslant Si[OSiRR']_nOC\leqslant \qquad (35)$$

Diorganylsilanones are also generated during the reaction of diorganyldichlorosilanes with metal oxides of high oxidative potential (preferably in the presence of acetonitrile and metal halide) [7,24].

$$RR'SiCl_2 + OM^n_{2/n} \longrightarrow [RR'Si{=}O] + Cl_2M^n_{2/n} \qquad (36)$$

M = Ag, Cu, Hg, Pb, Cd, Zn, Mg, etc.;
R,R′ = hydrocarbyl

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