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# Organosilicon Ketones

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One of the most important fields in the chemistry of organosilicon compounds at the present time is the chemistry of organic silanes and siloxanes with carbon-containing functional groups[1-6]. Polysiloxanes with vinyl, nitrile, hydroxy- and other functional groups in the silane exhibit enhanced mechanical strength compared with alkylsiloxanes, are satisfactorily compatible with many materials, and have already found industrial application. Organic silanes and siloxanes with carbonyl groups in the organic substituents are also used in the manufacture of new products[7-11]. Patent data show that polyketoalkylsiloxanes exhibit improved adhesion to metallic surfaces[12]. The aim of the review is to describe methods for the preparation and the properties of silicon-containing ketones. In earlier monographs[3,13] and a review[14] on organic silanes with carbon-containing functional groups, the sections dealing with organosilicon ketones are very fragmentary and incomplete.
The bibliography includes 180 references.

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## I. INTRODUCTION

The first information about organosilicon compounds with carbonyl groups appeared in 1903.[15] However, vigorous studies in this field were begun only after 1950 by Sommer, Andrianov, Petrov, Brook, Gilman, and many other investigators. The names of these compounds are usually derived from the name of the organic ketone with an indication of the position of the silyl group. For example, the compound $(CH_3)_3SiCH_2COCH_3$ is called 1-trimethylsilyl-2-propanone or trimethylsilylacetone. Sometimes the silane serves as a basis for the name, for example, benzoyltrimethylsilane $(CH_3)_3SiCOC_6H_5$.

Depending on the relative positions of silicon and the carbonyl group, silyl-substituted ketones of the type $R_3SiCOR'$, $R_3SiCH_2COR'$, $R_3Si(CH_2)_2COR'$, $R_3Si(CH_2)_3COR'$, $R_3Si(CH_2)_4COR'$, etc. are called respectively $\alpha$-, $\beta$-, $\gamma$-, $\delta$-, $\epsilon$-, etc. organosilicon ketones. An aromatic or a heterocyclic group may also be interposed between the silyl and keto-groups, for example:

$$R_3Si(CH_2)_nC_6H_4COR',\ n = 0, 1, 2 \ldots \text{ or } R_3Si-\langle\!\rangle\!\!\langle O \rangle\!\rangle-COR'.$$

Silicon-containing $\beta$-diketones and ketoesters of the type

$$R_nSi[OC(R') = CHCOR']_{4-n} \text{ and } R_nSi[CH(COCH_3)COOR']_{4-n}, n = 1, 2, 3.$$

are also known.

## II. METHODS OF SYNTHESIS OF ORGANOSILICON KETONES

The majority of the synthetic methods do not differ fundamentally from those for the preparation of organic ketones, although the presence of a silicon atom undoubtedly influences the type of reaction. The only general method, whereby organosilicon ketones with a wide variety of structures may be obtained, is organometallic synthesis. Among other methods, the Friedel–Crafts reaction, the acetoacetic ester synthesis, the Kharasch reaction, and the oxidation of silicon-containing alcohols and hydrocarbons have been widely employed.

### 1. Organometallic Synthesis

Organosilicon ketones are obtained with the aid of organolithium, organosodium, organopotassium, organocadmium, and organomagnesium compounds, the organomagnesium synthesis being most widely used.

As early as 1947 Whitmore et al.[16] attempted to prepare trimethylsilylacetone by the reaction of acetyl chloride with trimethylsilylmethylmagnesium chloride. However, only the decomposition products, including acetone, were obtained. The compound was later prepared by Hauser and Hance[17] by the reaction of acetic anhydride with trimethylsilylmethylmagnesium bromide under milder conditions:

$$(CH_3)_3SiCH_2MgBr \xrightarrow[2.\ H_2O,\ NH_4Cl]{1.\ (CH_3CO)_2O,\ -70^\circ} (CH_3)_3SiCH_2COCH_3.$$

4-Trimethylsilyl-2-butanone was synthesised from the chloride of trimethylsilylpropionic acid and methylmagnesium bromide in the presence of ferric chloride[18]:

$$(CH_3)_3SiCH_2CH_2COCl \xrightarrow[FeCl_3]{CH_3MgBr} (CH_3)_3SiCH_2CH_2COCH_3.$$

This ketone was also obtained using an organocadmium compound[19]:

$$(CH_3)_3SiCH_2CH_2COCl \xrightarrow{(CH_3)_2Cd} (CH_3)_3SiCH_2CH_2COCH_3.$$

$\gamma$-Silylketones are also obtained in high yields by the action of organomagnesium compounds on the nitriles of silicon-containing carboxylic acids[20-23]:

$$Cl_3SiCH_2CH_2CN \xrightarrow{RMgHal} R_3SiCH_2CH_2COR,$$

where R = $CH_3$ and $C_6H_5$.

$\delta$- and $\epsilon$-Silyl-substituted ketones[24,25], silicon-containing ethynyl ketones[26,27], and aromatic and heterocyclic silyl-substituted ketones[28,29] have been obtained similarly. At the same time the reaction of chloro-$\alpha$-cyanoisopropopoxydimethylsilane $(CH_3)_2ClSiOC(CH_3)_2CN$ with Grignard reagents involves not only the CN group but also the Si–Cl and Si–O bonds and leads to the formation of a complex mixture of substances from which it is impossible to isolate the individual products[30]. Komarov and Yarosh[31,32] obtained $\alpha$-silylethynyl ketones by the reaction of trialkylsilylethynylmagnesium bromides with acetic anhydride:

$$R_3SiC{\equiv}CMgBr + (CH_3CO)_2O \rightarrow R_3SiC{\equiv}CCOCH_3,$$

where R = $CH_3$ or $C_2H_5$.

The same reaction with acetyl and benzoyl chlorides leads to the exclusive formation of tertiary diethynylsilylalcohols.

The reactions of *p*-triethylsilylphenylmagnesium bromide with acid anhydrides gave alkyl(aryl) *p*-triethylsilylphenyl ketones [33]:

$$p\text{-}(C_2H_5)_3SiC_6H_4MgBr + (RCO)_2O \rightarrow p\text{-}(C_2H_5)_3SiC_6H_4COR,$$

where R = $CH_3$, $C_2H_5$, n-$C_3H_7$, or $C_6H_5$.

*p*-Trimethylsilylacetophenone is formed in high yield by the reaction between the magnesium derivative of the ethyleneketal of 4-bromoacetophenone and trimethylchlorosilane in tetrahydrofuran (THF) [34]:

$$(CH_3)_3SiCl + BrMgC_6H_4CCH_3 \xrightarrow{THF} \left[(CH_3)_3SiC_6H_4CCH_3\right] \xrightarrow[HCl]{H_2O} (CH_3)_3SiC_6H_4COCH_3.$$

Silicon-containing ketoalcohols are obtained by the addition of benzil to an ethereal solution of trimethylsilylmethylmagnesium chloride [35]:

$$(CH_3)_3SiCH_2MgCl + C_6H_5COCOC_6H_5 \rightarrow (CH_3)_3SiCH_2C(OH)(C_6H_5)COC_6H_5.$$

Treatment of benzoyl chloride with a suspension of triphenylsilylpotassium in ether leads to the synthesis of benzoyltriphenylsilane in 4% yield [36]:

$$C_6H_5COCl + (C_6H_5)_3SiK \rightarrow (C_6H_5)_3SiCOC_6H_5 + KCl.$$

When triphenylsilyl-lithium reacts with an excess of acetyl chloride, acetyltriphenylsilane is also formed in a low yield [37]:

$$(C_6H_5)_3SiLi + CH_3COCl \rightarrow (C_6H_5)_3SiCOCH_3 + LiCl.$$

On the other hand, the reaction of triphenylsilyl-lithium with acetic anhydride does not yield the expected ketone [38]. A di-$\epsilon$-silylketone was obtained unexpectedly as a side product in the synthesis of an $\epsilon$-silylcarboxylic acid by the following reaction [39]:

$$(C_6H_5)_3Si(CH_2)_4Li \xrightarrow[-25^\circ]{CO_2} \xrightarrow{H_2O} (C_6H_5)_3Si(CH_2)_4COOH + [(C_6H_5)_3Si(CH_2)_4]_2CO.$$

## 2. Synthesis with the Aid of Acetoacetic Ester

The first information about the sodioacetoacetic synthesis of organosilicon ketones was obtained in 1947 when Gilman [40] attempted to prepare triethylsilylacetoacetate by the reaction of sodioacetoacetic ester with triethylchlorosilane according to the following scheme:

$$(CH_3COCHCOOC_2H_5)^-Na^+ + (C_2H_5)_3SiCl \rightarrow (C_2H_5)_3SiCH(COCH_3)COOC_2H_5.$$

However, the only product isolated under these conditions proved to be ethyl $\beta$-triethylsiloxyorotonate $(C_2H_5)_3SiOC(CH_3)=CHCOOC_2H_5$.

Andrianov [41], who achieved a similar reaction with chlorodiethoxymethylsilane, succeeded in obtaining silylacetoacetate:

$$CH_3(C_2H_5O)_2SiCl + NaCH(COCH_3)COOC_2H_5 \rightarrow CH_3(C_2H_5O)_2SiCH(COCH_3)COOC_2H_5 + NaCl.$$

When this compound is hydrolysed in an alkaline medium, the ester group is not split off from silicon and there is only partial hydrolysis of the ethoxy-groups linked to silicon. On the other hand, in an acid medium the ester group is almost completely split off and an infusible, insoluble powder is formed.

Later it was shown that silylacetoacetates can be more conveniently obtained by the condensation under mild conditions of organochlorosilanes with acetoacetic ester in the presence of triethylamine: [11]

$$(CH_3)_3SiCl + CH_2(COCH_3)COOC_2H_5 \xrightarrow[C_6H_6,\ -5^\circ]{(C_2H_5)_3N} (CH_3)_3SiCH(COCH_3)COOC_2H_5.$$

Acetoacetic ester reacts with $SiCl_4$ in the cold with formation of the hydrochloride of tri(acetylethoxycarbonylmethyl)chlorosilane as prisms [42,43]:

$$3\,CH_3COCH_2COOC_2H_5 + SiCl_4 \rightarrow (CH_3COCHCOOC_2H_5)_3SiCl \cdot HCl + 2HCl.$$

On the other hand, when the mixture is heated to 100°C and at the same time dry air is passed through it the reaction leads to the formation of the yellow crystals of di(acetyl ethoxycarbonylmethyl)dichlorosilane [44].

Organosilanes containing a halogen in the organic substituent proved to be more suitable for the sodioacetoacetic ester synthesis of organosilicon ketones. Thus Sommer [19,45] obtained 4-trimethylsilyl-2-butanone by the following reaction:

$$(CH_3)_3SiCH_2I + CH_3COCH_2COOC_2H_5 + Na \rightarrow (CH_3)_3SiCH_2CH(COCH_3)COOC_2H_5 \rightarrow$$

$$\xrightarrow[\text{or } 10\%\ NaOH]{HCl} (CH_3)_3SiCH_2CH_2COCH_3.$$

The reaction of monobromohexamethyldisiloxane with sodioacetoacetic ester and subsequent hydrolysis of the ketoester produced gave a mixture of ketosiloxanes [46]:

$$(CH_3)_3SiOSi(CH_3)_2CH_2Br \xrightarrow[Na]{CH_3COCH_2COOC_2H_5} (CH_3)_3SiOSi(CH_3)_2CH_2CH(COCH_3)COOC_2H_5 \rightarrow$$

$$\xrightarrow[8\ h]{10\%\ NaOH} (CH_3)_3SiOSi(CH_3)_2CH_2CH_2COCH_3 + O[Si(CH_3)_2CH_2CH_2COCH_3]_2.$$

The $\epsilon$-silylketone [24] $(CH_3)_3Si(CH_2)_4COCH_3$ and the aliphatic-aromatic organosilicon ketoester [47] $(CH_3)_3SiC_6H_4CH_2CH(COCH_3)COOCH_3$ were synthesised similarly.

In the reaction with sodioacetoacetic ester primary $\gamma$-silyl-substituted ethynyl chlorides also form organosilicon ketoesters [48]. When the latter are heated with 10% hydrochloric acid, silylethynylketoacids are formed. More prolonged refluxing leads to the rupture of the Si–C bond with formation of hexaethyldisiloxane as the principal product:

$$(C_2H_5)_3SiC{\equiv}CCH_2Cl + CH_3COCHNaCOOC_2H_5 \rightarrow (C_2H_5)_3SiC{\equiv}CCH_2CH(COCH_3)COOC_2H_5 \rightarrow$$

$$\xrightarrow[C_2H_4OH]{HCl} (C_2H_5)_3SiC{\equiv}CCH_2CH(COCH_3)COOH \xrightarrow[90^\circ]{HCl} (C_2H_5)_3SiOSi(C_2H_5)_3 + CO_2 + \text{resin}.$$

The expected silylethynyl ketones $R_3SiC{\equiv}CCH_2COCH_3$ could not be isolated.

Secondary $\gamma$-silylethynyl chlorides behave similarly in sodioacetoacetic ester synthesis [27].

## 3. The Friedel–Crafts Reaction

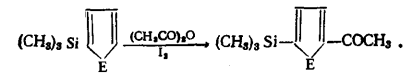
The Friedel–Crafts reaction constitutes a convenient method for the preparation of aromatic and heterocyclic organosilicon ketones, although it does not always take place successfully in consequence of the instability of the Si–Caryl bond in relation to acid reagents [49]. For example, the reaction of triethylphenylsilane [50] and also arylhalogenosilanes [51] with acid chlorides in the presence of aluminium chloride usually yields organic ketones and hexa-alkyldisiloxane instead of the expected organosilicon ketones:

$$R_3SiC_6H_5 + R'COCl \xrightarrow{AlCl_3} C_6H_5COR' + R_3SiOSiR_3.$$

Successful acylation of phenylsilanes by the Friedel–Crafts reaction [52] was achieved under mild conditions by the action of acetyl and benzoyl fluorides on trimethylphenylsilane in the presence of boron trifluoride:

$$(CH_3)_3SiC_6H_5 + RCOF \xrightarrow{BF_3} (CH_3)_3SiC_6H_4COR \quad (R=CH_3C_6H_5).$$

Acylation of 2-thienyltrimethylsilane and 2-furyltrimethylsilane with acetic anhydride takes place readily in the presence of iodine [53]:

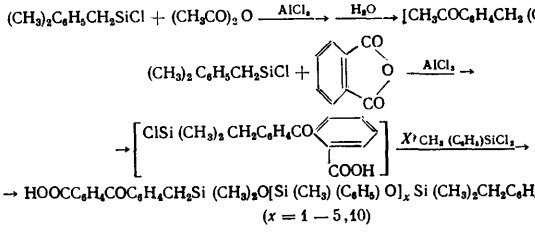


In contrast to phenylsilanes, the acylation of benzylsilanes [54] and trialkyl-β-phenylethylsilanes [55] with acyl chlorides using aluminium chloride takes place without the dissociation of the Si–C bond:

$$R_3Si(CH_2)_nC_6H_5 + R'COCl \xrightarrow{AlCl_3} R_3Si(CH_2)_nC_6H_4COR' \quad (n = 1, 2).$$

It has been established that, because of the conjugation of the Si–C bond with the aromatic ring, benzyltrimethylsilane is approximately 24 times more reactive than benzene in the acylation reaction and trimethyl-β-phenylethylsilane is 16 times more reactive.

The Friedel–Crafts reaction has been successfully used by Andrianov for the synthesis of various benzylsiloxane derivatives [10,56–59]:



Organosilicon ketones are also obtained by the Friedel–Crafts reaction from the chlorides of organosilicon carboxylic acids. Thus toluene and anisole are acylated in the *p*-position with *m*- and *p*-trimethylsilylbenzoyl chlorides [60]:

$$(CH_3)_3SiC_6H_4COCl + C_6H_5R \xrightarrow{SnCl_4} (CH_3)_3SiC_6H_4R,$$

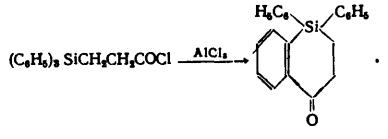
where R = $CH_3$ or $OCH_3$.

The chlorides of organosilicon carboxylic acids with alkoxy-groups at the silicon atom may be used as acylating agents. For example, the condensation of trimethoxysilylundecanoyl chloride with benzene in the presence of aluminium chloride leads to the formation of the corresponding ketone [61]:

$$(CH_3O)_3Si(CH_2)_{10}COCl + C_6H_6 \xrightarrow{AlCl_3} (CH_3O)_3Si(CH_2)_{10}COC_6H_5.$$

Ketosilanes with the composition $X_mR_{3-m}Si(CH_2)_nCOR'$, where $m = 0–3$ and $n = 2–10$, are obtained similarly [62].

It is interesting to note [63] that 3-triphenylsilylpropionyl chloride cyclises under the action of aluminium chloride to 2,3-benzo-1,1-diphenyl-1-silacyclohex-2-en-4-one:



A similar cyclisation is observed also with 4-triphenylsilylbutyryl chloride.

The condensation of β-trimethylsilylpropionyl chloride with ferrocene in the presence of aluminium chloride led to the isolation of a 76% yield of β-trimethylsilylpropionylferrocene [64]:

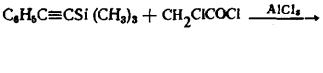
$$(CH_3)_3SiCH_2CH_2COCl + C_5H_5FeC_5H_5 \xrightarrow{AlCl_3} (CH_3)_3SiCH_2CH_2COC_5H_4FeC_5H_5.$$

A very interesting reaction was discovered by Birkofer et al. [65], who observed that the reaction of acid chlorides or anhydrides with di(trimethylsilyl)acetylene in the presence of aluminium chloride results in the formation of silylated alkynones:

$$(CH_3)_3SiC{\equiv}CSi(CH_3)_3 + RCOCl \xrightarrow{AlCl_3} (CH_3)_3SiC{\equiv}CCOR + (CH_3)_3SiCl,$$

where R = $CH_3$, $C_2H_5$, $C_6H_4NO_2$, or $CH_2Cl$. The yields of the ketones reached 90%.

The following reaction takes place similarly:



## 4. The Kharasch Reaction [66]

Sommer [67] and then Petrov and Chernyshev [68,69] obtained silicon-containing ketones by the addition of butyraldehyde and benzaldehyde to vinyl- and γ-butenyl-silanes in the presence of diacetyl and benzoyl peroxides:

$$R_3SiCH{=}CH_2 + R'CHO \xrightarrow{peroxide} R_3SiCH_2CH_2COR',$$

where R = $CH_3$ or $C_2H_5$ and $R^1$ = $C_3H_7$ or $C_6H_5$.

Organosilicon ketones are also formed in low yields on heating equimolar mixtures of tri(trimethylsiloxy)vinylsilane with aldehydes in an autoclave in the presence of t-butyl peroxide [70]:

$$[(CH_3)_3SiO]_3SiCH{=}CH_2 + RCHO \xrightarrow[150°,\ 4\ h]{peroxide} [(CH_3)_3SiO]_3SiCH_2CH_2COR,$$

where R = $CH_3$, $C_6H_5$, or *o*-$HOC_6H_4$.

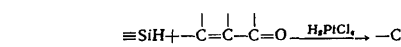
Brook [71] added benzaldehyde to triphenylvinylsilane with ultraviolet irradiation and obtained a corresponding ketone in 12% yield. We showed that the photochemical reaction of aldehydes with alkylvinyl- and alkoxyvinyl-silanes is general and may serve as a convenient method for the synthesis of γ-silyl-substituted ketones with various structures, including ketones containing readily hydrolysable alkoxy-groups at the silicon atom [72–73]:

$$R_3SiCH{=}CH_2 + R'CHO \xrightarrow{h\nu} R_3SiCH_2CH_2COR',$$

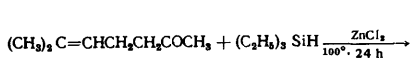
where R = $CH_3$, $C_2H_5$, or $C_2H_5O$ and R′ = $CH_3$, $C_2H_5$, $C_3H_7$, iso-$C_4H_9$, $C_6H_5$, etc. The yields of ketones reach 90%. On the other hand, the reaction involving the radical addition of aldehydes to allylsilanes could not be achieved.

## 5. Interaction of Silanes Containing Unsubstituted Hydrogen Atoms with Unsaturated Ketones

Petrov and Sadykh-Zade [74,75] showed that the addition of partially substituted silanes bearing organic substituents to αβ-unsaturated ketones in the presence of a Speier catalyst does not yield the expected organosilicon ketone. The reaction involves the 1,4-position with formation of silicon-containing vinyl ethers:



Calas [76] investigated the reaction between silanes with free hydrogen atoms and unsaturated ketones having an isolated double bond. The reaction of triethylsilane with 2-methylhept-2-en-6-one in the presence of zinc chloride as a catalyst does not lead to the formation of a ketone:



We investigated [77,78] the reaction between silanes with free hydrogen atoms and allylacetone under the influence of chloroplatinic acid and showed that it is suitable for the synthesis of ϵ-silyl-substituted ketones:

$$R_3SiH + CH_2{=}CHCH_2CH_2COCH_3 \xrightarrow{H_2PtCl_6} R_3Si(CH_2)_4COCH_3.$$

The yields of ketones reached 75–85%. Recently Khudobin and Kharitonov [79] obtained ϵ-silyl-substituted ketones by the addition of trisubstituted silanes to unsaturated ketones with an isolated double bond, the mixture being heated in the presence of colloidal nickel. Klotz and Kuckertz [12] synthesised siloxanes with two keto-groups in the ϵ-positions in 42% yield by the reaction of *sym*-tetramethyldisiloxane with allylacetonylacetone in the presence of platinum in an autoclave:

$$2H(CH_3)_2SiOSi(CH_3)_2H + 2CH_2{=}CHCH_2CH(COCH_3)_2 \xrightarrow{Pt,\ 160^\circ} \rightarrow (CH_3CO)_2CH(CH_2)_3Si(CH_3)_2OSi(CH_3)_2(CH_2)_3CH(COCH_3)_2.$$

Mashlyakovskii and Chelpanova [80] investigated the reaction of 2-butynone with diethylmethylsilane and established that, in contrast to methyl vinyl ketone, the reaction involves the 1,2-position with formation of a mixture of the *cis*- and *trans*-isomers. On the basis of infrared and PMR-spectroscopic studies, gas–liquid and thin-layer chromatography, and also by synthesis, Komarov and Pukhnarevich [81] showed that, under the conditions of this reaction, a mixture of β- and γ-silylvinyl ketones is in fact obtained:

$$CH_3(C_2H_5)_2SiH + HC{\equiv}CCOCH_3 \xrightarrow{H_2PtCl_6} \begin{cases} \rightarrow CH_3(C_2H_5)_2SiCH{=}CHCOCH_3 \\ \rightarrow CH_3(C_2H_5)_2SiC(COCH_3){=}CH_2. \end{cases}$$

The use of polar aprotic solvents (tetrahydrofuran, dioxane) permits the selective hydroxylation of ethyl methyl ketone and the isolation of chromatographically pure γ-substituted ketone derivatives [82].

## 6. Oxidation of Silicon-containing Alcohols and Hydrocarbons

Organosilicon ketones may be obtained by the oxidation of silicon-containing secondary alcohols and aliphatic-aromatic silicon-containing hydrocarbons. Potassium permanganate, the chromic acid mixture, anddicyclohexylcarbodi-imide are used as oxidising agents. α-Silyl-substituted ketones [83–87] $R_3SiCOR'$ and β-silyl-substituted ketones [71,87] $R_3SiCH_2COR'$ have been obtained in this way. By oxidising secondary silicon-containing ethynyl- and vinyl-alcohols with chromium trioxide, one of the present authors [88,89] synthesised for the first time organosilicon ethynyl ketones:

$$(CH_3)_3SiC{\equiv}CCHOHR \xrightarrow{CrO_3} (CH_3)_3SiC{\equiv}CCOR,$$

where R = $CH_3$, $C_2H_5$, or $CH{=}CH_2$. Organosilicon ketones of the ethylene series $R_3SiCH{=}CHCOR^1$ were obtained similarly [90].

The oxidation of *o*-, *m*-, and *p*-trimethylsilylethylbenzenes with oxygen in the presence of chromium trioxide and calcium carbonate gives a mixture of trimethylsilylacetophenones with trimethylsilylbenzoic acids [91]:

$$(CH_3)_3SiC_6H_4C_2H_5 \xrightarrow[200^\circ]{O_2/CrO_3+CaCO_3} (CH_3)_3SiC_6H_4COCH_3 + (CH_3)_3SiC_6H_4COOH.$$

The yields of ketones are 15–20%.

When secondary silicon-containing aromatic alcohols were heated with an excess of acetone in the presence of aluminium t-butoxide, the corresponding ketones were isolated in yields of 19–42% (Oppenauer reaction) [33]:

$$p\text{-}R_3SiC_6H_4CHOHR' + CH_3COCH_3 \underset{200^\circ}{\overset{Al(OC_4H_9\text{-}t)_3}{\rightleftarrows}} p\text{-}R_3SiC_6H_4COR' + CH_3CHOHCH_3,$$

where R = $CH_3$ or $C_2H_5$ and R′ = $CH_3$, $C_2H_5$, $C_3H_7$, or $C_6H_5$.

## 7. Hydrolysis of Organosilicon Dihalogeno-derivatives

The hydrolysis of silicon-containing dihalogeno-derivatives of hydrocarbons is an important method for the synthesis of α-silyl-substituted ketones. The first α-silyl-substituted ketones was obtained in 1957 by Brook [36] from benzyltriphenylsilane by the reaction

$$(C_6H_5)_3SiCH_2C_6H_5 \xrightarrow{2\,CH_2CO\rangle NBr\ (CH_2CO)} (C_6H_5)_3SiCBr_2C_6H_5 \xrightarrow[CH_3COOAg]{H_2O} (C_6H_5)_3SiCOC_6H_5.$$

Benzoylhydroxy- and benzoylmethoxy-silanes $C_6H_5COSi(C_6H_5)_2OR$ (R = H or $CH_3$), benzoyl(halogenobenzyl)silanes $C_6H_5COSi(C_6H_5)_2CXYC_6H_5$ (Y = Cl or Br: X = H, Cl, or Br), dibenzoylsilanes $(C_6H_5CO)_2SiR_2$ (R = $CH_3$ or $C_6H_5$), and benzoylmethyl-α-naphthylphenylsilane $CH_3(C_6H_5)(C_{10}H_7)SiCOC_6H_5$ were synthesised analogously [92,93]. All the reactions take place with satisfactory yields. The synthesis of a γ-silyl-substituted ketone was achieved similarly [71]:

$$(C_6H_5)_3SiCl + Li(CH_2)_3C_6H_5 \rightarrow (C_6H_5)_3Si(CH_2)_3C_6H_5 \xrightarrow[H_2O]{Br_2} (C_6H_5)_3SiCH_2CH_2COC_6H_5.$$

A β-silyl-substituted ketone could not be obtained by this method, only the decomposition products being isolated.

## 8. Hydration of Silylacetylenes

The attempts to hydrate trialkylsilylacetylenes and di(trialkylsilyl)acetylenes proved unsuccessful. The reaction apparently leads to the formation of silyl-substituted ketones with the carbonyl group in the β-position, which decompose according to the mechanism [94,95]:

$$R_3SiC{\equiv}CR' + H_2O \rightarrow [R_3SiCH_2COR'] \rightarrow 2R_3SiOH + CH_3COR',$$

where R = $CH_3$ or $C_2H_5$ and R′ = $C_6H_5$, $(CH_3)_3Si$, etc.

The attempt at the Kucherov hydration of the triple bond in trialkylvinylethynylsilanes $R_3SiC{\equiv}CCH{=}CH_2$ and dialkyldi(vinylethynyl)silanes $R_2Si(C{\equiv}CCH{=}CH_2)_2$ was also unsuccessful: under mild conditions there was only partial polymerisation of the compound and under severe conditions the Si–C bond was broken [96,97]. The corresponding ketones were obtained only from monosubstituted alkynylsilanes with the triple bond in the γ-position relative to the silicon atom:

$$R_3SiCH_2CH_2C{\equiv}CH \xrightarrow[HgSO_4]{H_2O} R_3SiCH_2CH_2COCH_3,$$

where R = $CH_3$ or $C_2H_5$.

Silyl-substituted α-ketoalcohols [99] and alkenyl alkoxyalkyl ketones [100] were also synthesised from the corresponding silyl-substituted ethynyl and vinylethynyl-alcohols:

$$R_3Si(CH_2)_nCOH(CH_3)C{\equiv}CH \xrightarrow[HgSO_4]{H_2O} R_3Si(CH_2)_nCOH(CH_3)COCH_3,$$

$$R_3Si(CH_2)_nCOH(CH_3)C{\equiv}CCH{=}CH_2 \xrightarrow[HgSO_4+H_2SO_4]{CH_3OH} R_3Si(CH_2)_nC(CH_3){=}CHCOCH_2CH_2OCH_3,$$

where $n$ = 2–4 and R is an alkyl group.

### 9. Condensation of Silanes Containing Functional Groups with β-Diketones

Dilthey [15] found in 1903 that acetylacetone readily reacts with silicon tetrachloride to form a crystalline hydrochloride. The reaction usually results in the substitution of three chlorine atoms according to the mechanism:

$$3\,(CH_3CO)_2CH_2 + SiCl_4 \rightarrow [(CH_3CO)_2CH]_3SiCl\cdot HCl + 2HCl.$$

The fourth chlorine atom is not substituted even in the presence of an excess of the diketone. Subsequently this reaction was extended to benzoylacetone and dibenzoylmethane [101] and also silicon tetrabromide [102].

The condensation of tetra-acetoxysilane with acetylacetone in molar proportions of 1 : 2 leads to the formation of diacetoxydi-(2,4-dioxopentyl)silane $[CH_2(CH_3CO)_2]_2.Si(OCOCH_3)_2$. [103,104] West [105] obtained a number of mono-, di-, and tri-alkylsilyl derivatives of acetylacetone:

$$R_nSiCl_{4-n} + (4-n)\,CH_3COCH_2COCH_3 \rightarrow R_nSi[CH(COCH_3)_2]_{4-n} + (4-n)\,HCl,$$

where $n = 1-3$ and R = $CH_3$, $C_2H_5$, or $C_6H_5$. The trimethylsilyl derivative of acetylacetone is also obtained by the following reaction [106]:

$$R_3SiN(C_6H_5)CONHC_6H_5 + CH_3COCH_2COCH_3 \rightarrow R_3Si[CH(COCH_3)_2] + C_6H_5NHCONHC_6H_5.$$

The reaction of chlorodiethylmethoxysilane with sodium acetylacetonate gave a silyl ether of the enolic form of acetylacetone [107]:

$$(C_2H_5)_2(CH_3O)SiCl + CH_3COCHNaCOCH_3 \rightarrow (C_2H_5)_2(CH_3O)SiOC(CH_3)=CHCOCH_3.$$

### 10. Ester, Crotonic, and Benzoin Condensations

Esters of the type $R(CH_3)_2Si(CH_2)_nCOOR'$ condense in the presence of sodamide, sodium alkoxides [108], di-isopropylaminomagnesium bromide [108,109], and $(CH_3)_2NMgBr$ [110] to silicon-containing β-ketoesters. The latter are hydrolysed to ketones on treatment with a strong inorganic acid [108-111,180]:

$$2R(CH_3)_2Si(CH_2)_nCOOR' \xrightarrow{C_2H_5ONa}$$

$$\rightarrow R(CH_3)_2Si(CH_2)_{n-1}CH(COOR')CO(CH_2)_nSiR(CH_3)_2 \xrightarrow{H_2SO_4} [R(CH_3)_2Si(CH_2)_n]_2CO.$$

Ethyl trimethylsilylpropionate condenses with acetone in the presence of sodamide to the corresponding β-diketone [18]:

$$(CH_3)_3SiCH_2CH_2COOC_2H_5 + CH_3COCH_3 \xrightarrow{NaNH_2} (CH_3)_3SiCH_2CH_2COCH_2COCH_3.$$

The condensation of *p*-trimethylsilylbenzaldehyde with acetone, pinacol, acetophenone, and cyclohexanone has been achieved [28,112]. When the ketone contains one active methylene group, the reaction takes place unambiguously according to the mechanism:

$$p\text{-}(CH_3)_3SiC_6H_4CHO + CH_3COR \xrightarrow{-H_2O} p\text{-}(CH_3)_3SiC_6H_4CH=CHCOR,$$

where R = $C_6H_5$ or $C(CH_3)_3$. In the presence of two active methylene groups, further condensation involving this group is possible.

When an alcoholic solution of *p*-trimethylsilylbenzaldehyde is heated with potassium cyanide, benzoin condensation takes place and leads to the formation of a disilyl-substituted aromatic ketoalcohol [28]:

$$(CH_3)_3SiC_6H_4CHO + OHCC_6H_4Si(CH_3)_3 \xrightarrow{CN^-} (CH_3)_3SiC_6H_4COCH(OH)C_6H_4Si(CH_3)_3.$$

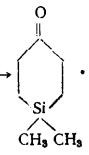
### 11. Pyrolysis of Salts of Organosilicon Acids

Dry distillation of the calcium salts of organosilicon acids and their mixtures with organic acid salts leads to the formation of silicon-containing ketones with symmetrical and asymmetric structures [113]:

$$(R_3SiCH_2CH_2COO)_2Ca \rightarrow (R_3SiCH_2CH_2)_2CO + CaCO_3,$$
$$(R_3SiCH_2CH_2COO)_2Ca + (R'COO)_2Ca \rightarrow R_3SiCH_2CH_2COR' + CaCO_3,$$

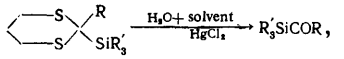
where R = $CH_3$ or $C_2H_5$ and R' = $(CH_3)_2CH$. The yields of ketones amount to 13-28%. Dimethylsilacyclohexanone was obtained in 35% yield by the pyrolysis of the thorium salt of a dibasic organosilicon acid [114]:

$$(CH_3)_2Si(CH_2CH_2COOH)_2 \xrightarrow[\text{2. } Th(NO_3)_4,\ 360^\circ,\ 25\text{ mm}]{\text{1. NaOH}}$$



### 12. Other Methods

Many α-silyl-substituted ketones have been prepared by the hydrolysis of 2-silyl-1,3-dithianes [84,115]:



where R = R' = $CH_3$, $C_6H_5$, etc.

The reaction of the chloride of β-(trimethylsilyl)propionic acid with diazomethane results in the formation of diazomethyl β-(trimethylsilyl)ethyl ketone [116,117]:

$$(CH_3)_3SiCH_2CH_2COCl + CH_2N_2 \rightarrow (CH_3)_3SiCH_2CH_2COCHN_2.$$

The latter reacts with hydrogen halides and acetic acid to form halogeno- and acetoxy-substituted organosilicon ketones and these can be converted into 4-trimethylsilyl-2-butanone:

$$(CH_3)_3SiCH_2CH_2COCHN_2 \xrightarrow{HX} (CH_3)_3SiCH_2CH_2COCH_2X,$$
$$\xrightarrow{HI} (CH_3)_3SiCH_2CH_2COCH_3,$$

where X = Cl, Br, or $OCOCH_3$.

The diazo-method can also be used to synthesise a di[oxoalkyl(alkyl)]siloxane by the reaction

$$ClSi(CH_3)_2CH_2CH_2COCl \xrightarrow{CH_2N_2} ClSi(CH_3)_2CH_2CH_2COCHN_2 \xrightarrow[H_2O]{HI}$$
$$\rightarrow O[Si(CH_3)_2CH_2CH_2COCH_3]_2.$$

The synthesis of 2-benzoyl-1-(*p*-trimethylsilylphenyl)-epoxyethane by the Darzens condensation has been reported [118]:

$$(CH_3)_3SiC_6H_4CHO + ClCH_2COC_6H_5 \xrightarrow{C_2H_5ONa} (CH_3)_3SiC_6H_4\underset{\diagdown\,O\,\diagup}{CH{-}CH}COC_6H_5.$$

The present authors synthesised a δ-silyl-substituted ketone by the pinacol rearrangement of an organosilicon glycol [99]:

$$(C_2H_5)_3SiCH_2CH_2\underset{CH_3}{\underset{|}{COH}}\underset{CH_3}{\underset{|}{COH}}CH_3 \xrightarrow[t^\circ]{H^+} (C_2H_5)_3SiCH_2CH_2C(CH_3)_2COCH_3.$$

Silicon-containing ketones can also be obtained by the silylation of hydroxyketones [119]:

$$(CH_3)_3SiCl + C_2H_5CHOHCOC_2H_5 \xrightarrow{C_5H_5N} (CH_3)_3SiOCH(C_2H_5)COC_2H_5.$$

## III. PROPERTIES OF ORGANOSILICON KETONES

The properties of organosilicon ketones depend to a large degree on the relative positions of the silicon atom and the carbonyl group. A characteristic feature of α- and β-silyl-substituted ketones is the instability of the Si-C bond in relation to the majority of the nucleophilic

and electrophilic reagents. Silicon-containing ketones in which the silicon atom is further away from the C=O group enter into various reactions involving the carbonyl group without the dissociation of the silicon–carbon bond.

These features of organosilicon ketones are reflected in their ultraviolet and infrared spectra. The study of the spectra showed that the characteristic absorption of the carbonyl group in these compounds is determined, on the one hand, by the structure of the molecule as a whole and, on the other hand, depends on the relative positions of the carbonyl group and the silicon atom. The carbonyl groups of α-silyl-substituted ketones exhibit an anomalous polarity, resembling that of a carboxylate ion rather than a β-diketone (6.2–6.45 μm).[120]

Polarity of C=O bond, μm (infrared spectra)

$CH_3COCH_3$ — 5.81
$C_6H_5COC_6H_5$ — 6.01
$(C_6H_5)_3SiCOCH_3$ — 6.08
$(C_6H_5)_3SiCOC_6H_5$, $(CH_3)_3SiCOCH_3$ } — 6.18

It has been suggested[71,121] that the anomalous spectroscopic effects of α-silyl-substituted ketones can be explained by the interaction of the unpaired electron of the oxygen atom in the carbonyl group with the vacant *d*-orbitals of silicon. As the silicon atom is removed further away from the carbonyl group, the effect of the silyl group diminishes and the absorption band associated with the carbonyl group in α-silyl-substituted ketones (1618 $cm^{-1}$ for benzoylsilanes and 1645 $cm^{-1}$ for acetyl- and propionylsilanes) rises to 1667 $cm^{-1}$ in the spectra of β-silyl-substituted ketones and reaches 1716 $cm^{-1}$ in the case of γ-silyl-substituted ketones, a value which is usual for aliphatic ketones[116,122–124]. Yates and Agolini[125] believe that the fundamental cause of the lower absorption frequency of the carbonyl group in α-silyl-substituted ketones is the inductive effect of the silicon atom, which increases the electron density at the carbonyl oxygen, thereby enhancing the basicity of the carbonyl group in ketones of the $R_3SiCOC_6H_5$ series compared with their hydrocarbon analogues.

Since the properties of α- and β-silyl-substituted ketones differ appreciably from those of ketones with the silicon atom more remote from the carbonyl group, we combined them into separate classes. Aromatic silyl-substituted ketones, silylethynylketones with the formula $R_3SiC{\equiv}CCOR'$, and complexes of silicon halides with β-diketones and β-ketoesters also exhibit a number of characteristic features because of the mutual effects of the silicon atom and the carbonyl group.

## 1. α-Silyl-substituted Ketones

In contrast to their hydrocarbon analogous, α-silyl-substituted ketones are coloured yellow, orange, or red[36,83]. Evidently the silicon atom behaves as a chromophore[120]. These ketones are thermally stable. For example, benzoyltriphenylsilane scarcely changes on heating to 250°C. At 365°C there is some decomposition, but 70% of the initial compound is recovered[36]. Alkylsilyl ketones and alkylarylsilyl ketones are liquid, while arylsilyl ketones are solid crystalline substances.

The chemical properties of α-silyl-substituted ketones were investigated Brook. The principal characteristic feature is high lability in relation to chemical reagents. The majority of benzoylsilanes are readily hydrolysed in air[92]. In consequence of the interaction of the unshared electrons of the oxygen atoms in the carbonyl group with the vacant *d*-orbitals of silicon, nucleophilic reagents usually cause the decomposition of the ketone molecule at the Si–C bond. Similar decomposition takes place also when benzoylsilanes are irradiated with ultraviolet light. Only hydrogenation and reactions with phenylhydrazine and certain Grignard reagents take place without the rupture of the carbon–silicon bond.

When α-silyl-substituted ketones are treated with ethanol in the presence of aqueous alkali, the yellow colour of the ketone disappears after several minutes and silanol and an aldehyde are formed[36,126]:

$$(C_6H_5)_3SiCOC_6H_5 \xrightarrow[H_2O]{\overline{O}H} (C_6H_5)_3SiOH + C_6H_5CHO.$$

A similar reaction takes place in the chromatographic separation of α-silyl-substituted ketones on activated alumina.

When sodium ethoxide is allowed to act upon benzoyltriphenylsilane, the main product is ethoxydiphenyl(diphenylmethoxy)silane $(C_6H_5)_2CHOSi(OC_2H_5)(C_6H_5)_2$ together with small amounts of cleavage products—diphenylmethanol and diethoxydiphenylsilane[126,127].

Treatment of benzoyltriphenylsilane with phenyl-lithium does not lead to the expected alcohol: only the decomposition products, including triphenylsilanol and tetraphenylsilane, were isolated[36]. Methyl–magnesium iodide and benzylmagnesium chloride interact with benzoyltriphenylsilane in a normal manner with formation of alcohols[120,128]:

$$(C_6H_5)_3SiCOC_6H_5 \xrightarrow{CH_3MgI} (C_6H_5)_3SiC(OH)(CH_3)C_6H_5.$$

At the same time Grignard reagents with β-hydrogen atoms ($C_2H_5MgBr$, $C_3H_7MgBr$) behave mainly as reducing agents. There is no reaction between benzoyltriphenylsilane and t-butylmagnesium chloride and only cleavage at the Si–C bond takes place when this ketone interacts with phenylmagnesium bromide.

The attempts to prepare the oxime of benzoyltriphenylsilane were unsuccessful because of its decomposition into triphenylsilanol and benzaldehyde[36]. However, benzoyltriphenylsilane does form crystalline hydrazones[129]. It is readily reduced by lithium aluminium hydride[120] to the carbinol $(C_6H_5)_3SiCHOHC_6H_5$. On being irradiated with ultraviolet light in methanol solution for 2 h, benzoyltriphenylsilane is converted into methoxytriphenylsilane[130,131]:

$$(C_6H_5)_3SiCOC_6H_5 \xrightarrow[CH_3OH]{h\nu} (C_6H_5)_3SiOCH_3 + C_6H_5CH(OCH_3)_2.$$

The treatment of α-silyl-substituted ketones with diazomethane leads to the formation of a mixture of β-silyl-substituted ketones with isomeric siloxyalkenes[132]:

$$R_3SiCOR' + CH_2N_2 \rightarrow R_3SiCH_2COR' + R_3SiOCR'{=}CH_2.$$

The Wittig reaction with α-silyl-substituted ketones has been investigated[133]. Benzoylsilanes form siloxyalkenes and alkyl silyl ketones undergo the normal Wittig reaction.

## 2. β-Silyl-substituted Ketones

A distinctive feature of β-silyl-substituted ketones is also chemical instability. They decompose under the action of both nucleophilic and electrophilic reagents[18]. β-Silyl-substituted ketones formed on hydration of trialkylsilylacetylenes cannot be isolated because of their decomposition into trialkylsilanol and a non-silylated ketone[95]:

$$R_3SiC{\equiv}CR' \xrightarrow{H_2O} [R_3SiCH_2COR'] \xrightarrow{H_2O} R_3SiOH + CH_3COR'.$$

β-Ketosilanes isomerise to siloxyalkenes on heating to 80–175°C and also in the presence of mercuric iodide[134–137]:

$$R_3SiCH_2COR' \rightarrow R_3SiOCR'{=}CH_2.$$

When trimethylsilylacetone is treated with 2,4-dinitrophenylhydrazine in 85% ethanol containing sulphuric acid, the Si–C bond is ruptured and a 2,4-dinitrophenylhydrazone of acetone is formed [17]. This ketone also decomposes on being refluxed with ethanol:

$$(CH_3)_3SiCH_2COCH_3 \xrightarrow[t^\circ]{C_2H_5OH} (CH_3)_3SiOC_2H_5 + CH_3COCH_3 .$$

Trimethylsilylphenylacetone $(CH_3)_3SiCH(C_6H_5)COCH_3$ is more stable and does form a 2,4-dinitrophenylhydrazone. Triphenyl(phenylacetyl)silane $(C_6H_5)_3SiCH_2COC_6H_5$, obtained by the oxidation of the corresponding carbinol with a mixture of chromium trioxide and sulphuric acid, is even more stable [71].

### 3. γ-, δ-, and ε-Silyl-substituted Ketones

The Si–C bonds in γ-, δ-, and ε-silyl-substituted ketones are stable in relation to nucleophilic and electrophilic reagents, in contrast to the α- and β-substituted ketones. In oxidation, reduction, and condensation reactions they behave similarly to non-silylated ketones. In addition they undergo certain specific reactions due to the presence of the silicon atom.

The reduction of γ-silyl-substituted ketones with lithium aluminium hydride leads to the formation of silicon-containing secondary alcohols [71,138–140]. The oxidation of 4-trimethylsilyl-2-butanone [19] and 5-trimethylsilyl-2-pentanone [24] with sodium hypobromite yields organosilicon acids:

$$(CH_3)_3Si(CH_2)_nCOCH_3 \xrightarrow{NaBrO} (CH_3)_3Si(CH_2)_nCOOH \ (n=2–3).$$

The reaction with alkylmagnesium bromides results in the formation of tertiary organosilicon alcohols [19,20,22,24,140]:

$$(CH_3)_3Si(CH_2)_nCOR \xrightarrow{R'MgBr} (CH_3)_3Si(CH_2)_nCR'(OH)R',$$

where R = $CH_3$ or $C_6H_5$, R′ = $CH_3$, $C_2H_5$, or $C_6H_5$, and $n$ = 2 and 4.

The reaction of vinylethynylmagnesium bromide with γ-, δ-, and ε-silyl-substituted ketones takes place normally with formation of silicon-containing vinylethynylalcohols [100]:

$$R_3Si(CH_2)_nCOCH_3 + BrMgC{\equiv}CCH{=}CH_2 \rightarrow R_3Si(CH_2)_nC(CH_3)(OH)C{\equiv}CCH{=}CH_2 ,$$

where R = $CH_3$ or $C_2H_5$ and $n$ = 2–4.

These alcohols have also been synthesised in yields up to 80% by the reaction of organosilicon ketones with vinylacetylene in the presence of potassium hydroxide:

$$R_3Si(CH_2)_nCOCH_3 + HC{\equiv}CCH{=}CH_2 \xrightarrow{KOH} R_3Si(CH_2)_nC(CH_3)(OH)C{\equiv}CCH{=}CH_2 .$$

γ-, δ-, and ε-Silyl-substituted ketones enter into the Favorskii reaction with acetylene and also react with sodioacetylene and its derivatives to form silylethynylmethanols and silylethynylglycols [99,141–142] in high yields:

$$(CH_3)_3SiCH_2CH_2COCH_3 + HC{\equiv}CH \xrightarrow[ether]{KOH} (CH_3)_3SiCH_2CH_2C(CH_3)(OH)C{\equiv}CH +$$
$$+ (CH_3)_3SiCH_2CH_2C(CH_3)(OH)C{\equiv}CC(OH)(CH_3)CH_2CH_2Si(CH_3)_3 ,$$

$$R_3Si(CH_2)_nCOCH_3 + HC{\equiv}CNa \rightarrow R_3Si(CH_2)_nC(CH_3)(OH)C{\equiv}CH ,$$

$$R_3Si(CH_2)_nCOCH_3 + (CH_3)_3SiC{\equiv}CNa \rightarrow R_3Si(CH_2)_nC(CH_3)(OH)C{\equiv}CSi(CH_3)_3 ,$$

where R = $CH_3$ or $C_2H_5$ and $n$ = 2–4.

The reaction with 2,4-dinitrophenylhydrazine [20,22,24,68,98,113,140], 3,5-dinitrobenzoylhydrazide [143], hydroxylamine [20,108,144,145], and semicarbazide [67,68,140] leads to the formation of crystalline silicon-containing hydrazones, oximes, and semicarbazones.

The condensation of silicon-containing ketones with secondary amines and formaldehyde by the Mannich reaction requires comparatively severe conditions and the use of a solvent—dioxane or alcohol—is obligatory [146,147]:

$$R_3Si(CH_2)_nCOCH_3 + (C_2H_5)_2NH \cdot HCl + CH_2O \xrightarrow[H^+]{\text{dioxane}} R_3Si(CH_2)_{n-1}CH(CH_2N(C_2H_5)_2)COCH_3 ,$$

where R = $CH_3$ or $C_2H_5$ and $n$ = 2–4.

The yields of organosilicon aminoketones amount to 40–45%. Their water-soluble hydrochlorides are physiologically active: they reduce blood pressure, stimulate respiration, and exhibit a spasmolytic activity. Their toxicity is in the range 250–320 mg $kg^{-1}$.

The Fischer reaction between phenylhydrazine hydrochloride and γ-, δ-, and ε-silyl-substituted ketones leads to the formation of indole derivatives with a silyl substituent in the β-position [148]:

$$R_3Si(CH_2)_nCOCH_3 + C_6H_4(NH{-}NH_2HCl) \xrightarrow[170–200^\circ]{Cu_2Cl_2} C_6H_4(C(CH_3)=N(H)-)C(CH_2)_{n-1}SiR_3 + NH_4Cl .$$

γ-Silyl-substituted ketones are capable of condensation with esters in the presence of sodamide, whereby they are converted into silicon-containing β-diketones [18,149,150]:

$$(CH_3)_3SiCH_2CH_2COCH_3 + RCOOC_2H_5 \xrightarrow{NaNH_2} (CH_3)_3SiCH_2CH_2COCH_2COR,$$

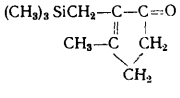
where R = $CH_3$ or $(CH_3)_3SiCH_2CH_2$.

According to their dissociation constants, organosilicon β-diketones are weaker acids than acetylacetone because of the inductive effect of the trimethylsilyl group. Like their non-silylalated analogues, they are effective chelating agents and readily form complexes with copper(II), nickel, and barium salts [18,149,151,152]. The chelates usually contain two molecules of the ketone per metal ion.

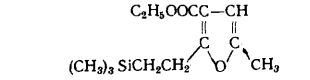
When 4-trimethylsilyl-2-butanone is heated with diethyl carbonate in the presence of sodium hydride, the product is a β-ketoester the subsequent treatment of which with bromoacetone and sodium gives a silicon-containing diketoester [18,153,154]:

$$(CH_3)_3SiCH_2CH_2COCH_3 + (C_2H_5O)_2CO \xrightarrow{NaH} (CH_3)_3SiCH_2CH_2COCH(COOC_2H_5)COOC_2H_5 \rightarrow$$
$$\xrightarrow[Na]{BrCH_2COCH_3} (CH_3)_3SiCH_2CH_2COCH(COOC_2H_5)CH_2COCH_3 .$$

The latter, on being refluxed with aqueous sodium hydroxide, cyclises to 3-methyl-[2-(trimethylsilyl)methyl]cyclopent-2-enone:



and on treatment with a mixture of sulphuric and acetic acids gives rise to a mixture of silicon-containing furan derivative:



Organosilicon β-ketoesters condense with hydrazine hydrate to crystalline pyrazolones [18]:

$$(CH_3)_3SiCH_2CH_2COCH_2COOC_2H_5 + NH_2{-}NH_2 \rightarrow (CH_3)_3SiCH_2CH_2C(=N{-}NH{-}CO{-})CH_2 + C_2H_5OH + H_2O .$$

The sodio-derivative of a silicon-containing β-ketoester adds to methyl vinyl ketone with formation of a δ-diketone (the Michael reaction):[18,155]

$$(CH_3)_3SiCH_2CH_2COCH_2COOC_2H_5 + CH_3COCH{=}CH_2 \xrightarrow{NaOC_2H_5} \rightarrow (CH_3)_3SiCH_2CH_2CO(CH_2)_3COCH_3.$$

The diketone thus obtained cyclises on treatment with alcoholic alkali to 3-[2-(trimethylsilyl)ethyl]cyclohex-2-enone:

$$(CH_3)_3SiCH_2CH_2CO(CH_2)_3COCH_3 \xrightarrow[C_2H_5OH]{NaOH} (CH_3)_3SiCH_2CH_2C{=}CH(CH_2)_2CH_2.$$

When concentrated sulphuric acid is allowed to act upon γ- or ε-silyl-substituted ketones, one methyl group is split off from the silicon atom and the corresponding ketosiloxanes are formed [7-9,19,109,156-160]:

$$2(CH_3)_3SiCH_2CH_2COCH_3 \xrightarrow{H_2SO_4} \xrightarrow{H_2O} O[Si(CH_3)_2CH_2CH_2COCH_3] + 2CH_4,$$

$$n[(CH_3)_3Si(CH_2)_2]_2CO \xrightarrow{H_2SO_4} \xrightarrow{H_2O} [(CH_3)_3Si(CH_2)_2CO(CH_2)_2Si(CH_3)_2O]_n + 2nCH_4.$$

γ- and ε-Oxoalkylsiloxanes with linear and cyclic structures are readily obtained by the hydrolysis of mono-, di-, and tri-ethoxy- and mono-, di-, and tri-chloro-oxoalkylsilanes [159,160]:

$$(C_2H_5O)_n(CH_3)_{3-n}SiCH_2CH_2COCH_3 \xrightarrow{H_2O,\ H^+} [O_{n/2}(CH_3)_{3-n}SiCH_2CH_2COCH_3]_x,$$

$$Cl_nR_{3-n}Si(CH_2)_4COCH_3 \xrightarrow{H_2O} [O_{n/2}R_{3-n}Si(CH_2)_4COCH_3]_x.$$

When the oxoalkylsiloxanes are refluxed with dilute alkali, water-soluble oxoalkylsiliconates (monosodium salts of oxoalkylsilanetriols) are formed:

$$[CH_3CO(CH_2)_nSiO_{1.5}]_x \xrightarrow{NaOH} x[CH_3CO(CH_2)_nSi(OH)_2]ONa,$$

where $n = 2$ and 4.

The photolysis of organosilicon ketones leads to mainly cleavage [161].

## 4. Silylethynyl ketones with the General Formula $R_3SiC{\equiv}CCOR'$

The chemistry of these ketones was investigated by Komarov and Pukhnarevich [89,162-171]. Their characteristic feature is reduced reactivity of the triple bond in reactions with nucleophilic reagents. It is due to the conjugation of the triple bond with the 3*d*-orbitals of the silicon atom and also due to influence of the silicon and carbonyl groups. The addition of electrophilic agents and reactions involving the carbonyl group take place according to the usual mechanism characteristic of non-silylated analogues [163].

a. Reactions involving the carbonyl group. The reaction of 4-trimethylsilylbut-3-yn-2-one with methylmagnesium iodide leads to the formation of a tertiary alcohol:

$$(CH_3)_3SiC{\equiv}CCOCH_3 \xrightarrow{CH_3MgI} (CH_3)_3SiC{\equiv}CC(OH)(CH_3)_2.$$

The reaction with vinylethynylmagnesium bromide results in the formation of silylethynyl homologues of Nazarov's carbinol and those with phenylethynylmagnesium bromide give organosilicon diethynylalcohols with isolated triple bonds [164,165]:

$$R_3SiC{\equiv}CCOCH_3 + BrMgC{\equiv}CR' \rightarrow R_3SiC{\equiv}CC(OH)(CH_3)C{\equiv}CR',$$

where $R = CH_3$ or $C_2H_5$ and $R' = C_6H_5$ or $CH{=}CH_2$.

Triethynyldisilylglycols with isolated triple bonds were synthesised by reaction with ethynylenedimagnesium dibromide [166]:

$$2R_3SiC{\equiv}CCOCH_3 + BrMgC{\equiv}CMgBr \rightarrow R_3SiC{\equiv}CC(OH)(CH_3)C{\equiv}CC(OH)(CH_3)C{\equiv}CSiR_3,$$

where $R = CH_3$ or $C_2H_5$.

The reaction of silyl-αβ-ethynyl ketones with magnesium derivatives of ethynylalcohols leads to the synthesis of organosilicon diethynylglycols [167]:

$$R_3SiC{\equiv}CCOCH_3 + BrMgC{\equiv}CCH_2OMgBr \rightarrow R_3SiC{\equiv}CC(OH)(CH_3)C{\equiv}CCH_2OH.$$

Silyl-α-ethynyl ketones react with 2,4-dinitrophenylhydrazine, semicarbazide, 3,5-dinitrobenzoylhydrazide, and hydrazine hydrate, forming the corresponding hydrazones [143].

The addition of phenyl azide to trimethylsilylalkynones gave silyl-substituted triazoles [65]:

$$C_6H_5N{=}N{\equiv}N + (CH_3)_3SiC{\equiv}CCOR \rightarrow (CH_3)_3Si{-}C{=}CCOR.$$

b. Reactions involving the triple bond. When hydrogen chloride is passed through a solution of a silyl-α-ethynyl ketone in glacial acetic acid, silyl-substituted β-chlorovinyl ketones are formed [168,169]:

$$R_3SiC{\equiv}CCOCH_3 + HCl \rightarrow R_3SiCCl{=}CHCOCH_3,$$

where $R = CH_3$ or $C_2H_5$. They are thick oily liquids, which rapidly darken in the light with formation of viscous polymers. Chemically they are less reactive than their non-silylated analogues. They do not enter into the Diels–Alder reaction with cyclopentadiene and hexachlorocyclopentadiene and do not exchange the chlorine atom for an alkoxy-, acetoxy-, and hydroxy-group under normal conditions. When silicon-containing β-chlorovinyl ketones were allowed to react with Grignard reagents, tertiary chloroallyl alcohols were obtained in high yields [170]:

$$R_3SiCCl{\equiv}CHCOR' + R''MgX \rightarrow R_3SiCCl{=}CHCOHR'R'',$$

where $R = R' = CH_3$ or $C_2H_5$, $R'' = CH_3$ or $C_6H_5$, and X = Br or I.

Silyl-α-ethynyl ketones can combine with both one and two bromine molecules at the multiple bond, but the addition of a second molecule takes place with considerable difficulty [89]:

$$R_3SiC{\equiv}CCOR' \xrightarrow{Br_2} R_3SiCBr{=}CBrCOR' \xrightarrow{Br_2} R_3SiCBr_2CBr_2COR'.$$

In contrast to their non-silylated analogues, silyl-substituted ketones do not combine with hydrogen under the usual conditions in the presence of Raney nickel and Lindlar's catalyst. Hydrogenation in an autoclave at 25 atm leads to the formation of saturated ketones without a silicon atom.

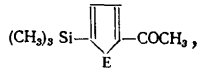
In reactions with cyclopentadiene and hexachlorocyclopentadiene adducts could be isolated only in the case of the latter and even then severe conditions were required and the yields were low, while non-silylated α-ethynyl ketones react with cyclopentadiene even at room temperature [171]:

$$R_3SiC{\equiv}CCOCH_3 + \text{hexachlorocyclopentadiene} \rightarrow \text{adduct}.$$

The reaction of silyl-$\alpha$-ethynyl ketones with alcohols and phenols in the presence of sodium ethoxide and with diethylamine is usually accompanied by the cleavage of the Si–C bond. They do not react with acetic and chloroacetic acids in the presence of $BF_3.O(C_2H_5)_2$–HgO and on irradiation with ultraviolet light. The reaction with mercaptans in the presence of sodium methoxide or on prolonged ultraviolet irradiation also does not occur, while non-silylated ethynyl ketones readily combine with one or two mercaptan molecules. The attempts to hydrate silyl-$\alpha$-ethynyl ketones in the presence of mercuric salts led only to the formation of products of decomposition at the silicon–carbon bond.

## 5. Aromatic and Heterocyclic Silyl-substituted Ketones

A characteristic feature of silicon-containing aromatic ketones of the type $(CH_3)_3SiC_6H_4COR$ is the instability of the $Si-C_{aryl}$ bond in relation to electrophilic agents such as $AlCl_3$ [50,51] and that of ketones of the type $(CH_3)_3SiCH_2C_6H_4COR$ is instability to the action of oxidising agents [56]. At the same time oxidation of heterocyclic ketones takes place without the cleavage of the Si–C bond [53,172]:



where E = O or S.

When acted upon by reducing agents, organomagnesium compounds, 2,4-dinitrophenylhydrazine, hydroxylamine, and semicarbazide and in the Mannich reaction, ketones of this class behave like their non-silylated analogues. The reduction of 4-trimethylsilylacetophenone with sodium borohydride takes place according to the usual mechanism [173]:

$$(CH_3)_3SiC_6H_4COCH_3 \xrightarrow{2H} (CH_3)_3SiC_6H_4CHOHCH_3.$$

A glycol is obtained in 91% yield by a similar procedure from the diketone $(CH_3)_2Si(C_6H_4COCH_3)_2$. The hydrogenation of the hydrochlorides of organosilicon aminoketones over Raney nickel yielded secondary aminoalcohols, the reduction being accompanied by the degradation of the aminoketones [174]:

$$(CH_3)_3SiCH_2C_6H_4COCH_2CH_2N(CH_3)_2\,HCl \xrightarrow[Ni]{H_2} (CH_3)_3SiCH_2C_6H_4CHOHCH_2CH_2N(CH_3)_2 + HCl.$$

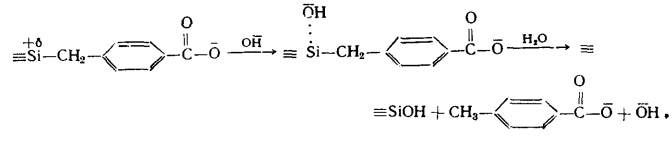
The hydrochlorides of organosilicon aminoketones react with ethylmagnesium bromide to form silicon-containing tertiary aminoalcohols. Organosilicon tertiary alcohols have also been obtained by Grignard reaction from trialkylsilylmethylphenyl and trialkylsilylethylphenyl ketones [55]:

$$R_3Si(CH_2)_nC_6H_4COCH_3 \xrightarrow{CH_3MgCl} R_3Si(CH_2)_nC_6H_4C(OH)(CH_3)_2.$$

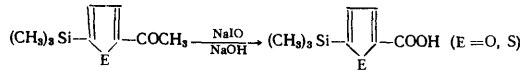
The oxidation of di(acetylbenzyl)tetramethyldisiloxane with sodium hypobromite in an alkaline medium is accompanied by the decomposition of the molecule at the silicon–carbon bond [56]:

$$[CH_3COC_6H_4CH_2(CH_3)_2Si]_2O + 6NaBrO \rightarrow 2CH_3C_6H_4COONa + [(CH_3)_2SiO]_x + 4NaOH + 2CHBr_3.$$

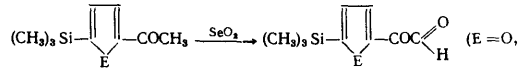
The comparatively ready elimination of the benzylcarboxy-group is probably associated with the migration of the reaction centre in a system of conjugated multiple bonds, as a result of which the electron density at the silicon atom is reduced, whereupon the Si–C bond dissociates under the action of a nucleophilic agent:



The oxidation of 2-acetyl-5-trimethylsilylfuran and 2-acetyl-5-trimethylsilylthiophen with hypoiodite takes place without the rupture of the Si–C bond and yields the corresponding acids [53]:



Selenium dioxide oxidises the above compounds to silicon-containing glyoxals in 40–70% yield [172]:



The Mannich condensation of alkyl trimethylsilylmethylphenyl ketones with dimethylamine and paraformaldehyde leads to the formation of organosilicon aminoketones [174]. However, the aminoketones were not isolated in a pure form:

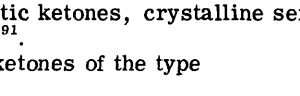
$$(CH_3)_3SiCH_2C_6H_4COR + CH_2O + (CH_3)_2NH \cdot HCl \xrightarrow[C_2H_5OH]{HCl} \rightarrow (CH_3)_3SiCH_2C_6H_4COCHR'CH_2N(CH_3) \cdot HCl,$$

where R = $CH_3$ or $C_2H_5$ and R′ = $CH_3$.

The aromatic silicon-containing ketones $R_3Si(CH_2)_nC_6H_4COR'$, where R = $CH_3$ or $C_2H_5$, R′ = $CH_3$, $C_6H_5$, $C_5H_{11}$, $C_6H_4OCH_3$, or $C_6H_4CH_3$, and $n$ = 0–2, react with 2,4-dinitrophenylhydrazine to form crystalline 2,4-dinitrophenylhydrazones [33,34,52,55,60,91]. The reaction of 2,4-dinitrophenylhydrazine with the ketodisiloxanes $O[Si(CH_3)_2CH_2C_6H_4COR]_2$ may involve both carbonyl groups [56,57].

When semicarbazide is allowed to react with silicon-containing aromatic ketones, crystalline semicarbazones are obtained [34,60,91].

Heterocyclic ketones of the type



also readily form semicarbazones. A crystalline oxime has been obtained from $p$-trimethylsilylacetophenone $(CH_3)_3SiC_6H_4COCH_3$. [34]

The polycondensation of organosilicon ketodicarboxylic acids with glycol at 170–190°C in an atmosphere of nitrogen has been reported [58]:

$$HOOCC_6H_4COC_6H_4CH_2Si(CH_3)_2OSi(CH_3)_2CH_2C_6H_4COC_6H_4COOH + n\,HOCH_2CH_2OH \rightarrow$$
$$\rightarrow [OCOC_6H_4COC_6H_4CH_2Si(CH_3)_2OSi(CH_3)_2CH_2C_6H_4COC_6H_4COOCH_2CH_2]_nOH + (n-1)\,H_2O.$$

The polycondensation of organosilicon ketoacids with more than two dimethylsiloxane rings may involve a rearrangement into cyclic polydimethylsiloxanes and polyesters with a disiloxane unit:

$$m\,HOOCC_6H_4COC_6H_4CH_2Si(CH_3)_2O[Si(CH_3)_2O]_nSi(CH_3)_2CH_2C_6H_4COC_6H_4COOH +$$
$$+ m\,HOCH_2CH_2OH \rightarrow H_2O + m[-Si(CH_3)_2O-]_n +$$
$$+ n[OCH_2CH_2OCOC_6H_4COC_6H_4CH_2Si(CH_3)_2OSi(CH_3)_2CH_2C_6H_4COC_6H_4CO]_mOH.$$

These polyesters are vitreous low-melting products readily soluble in organic solvents.

The polycondensation of silicon-containing diketodicarboxylic acids with di-($\beta$-hydroxyethoxymethyl)tetramethyldisiloxane takes place according to the mechanism [10]:

$$x\,HOOCC_6H_4COC_6H_4CH_2Si(CH_3)_2O[Si(CH_3)_2O]_nSi(CH_3)_2CH_2C_6H_4COC_6H_4COOH +$$
$$+ x\,HOCH_2CH_2OCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCH_2CH_2OH \rightarrow (x-1)\,H_2O +$$
$$+ x\,H\{OOCC_6H_4COC_6H_4CH_2Si(CH_3)_2O[Si(CH_3)_2O]_nSi(CH_3)_2CH_2C_6H_4COC_6H_4COOCH_2-$$
$$-CH_2OCH_2Si(CH_3)_2OSi(CH_3)_2CH_2OCH_2CH_2\}OH^{-}.$$

6. Complexes of Silicon Halides with β-Diketones and β-Ketoesters

West [105], Andrianov [107], and Hester [175] established by infrared and NMR spectroscopy that the complexes of acetylacetone with silicon halides have the structure of *o*-silyl derivatives:

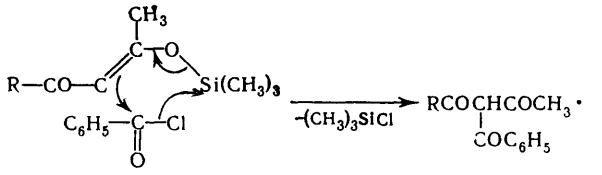
$$R_nSi[OC(CH_3)=CHCOCH_3]_{4-n},$$

where $n = 1-3$ and R = alkyl, aryl, or a halogen. For the triethylsilyl derivative of ethyl acetoacetate, Andrianov [41] proposed a structure with a C-silyl bond, i.e. $R_3Si[CH(COCH_3)COOC_2H_5]$, and Gilman [40] and West [176] suggested an enolic structure: $R_3SiOC(CH_3)=CHCOOC_2H_5$.

A characteristic property of compounds of this class is instability in both acid and alkaline media. In aqueous hydrochloric acid solutions they are slowly hydrolysed, while in an alkaline medium the hydrolysis is instantaneous [105,107,177,178]:

$$[CH_3COCH=C(CH_3)O]_3SiCl\cdot HCl \xrightarrow{H_2O} (CH_3CO)_2CH_2 + Si(OH)_4 + HCl.$$

When benzoyl chloride is allowed to act upon 2-trimethylsiloxypent-2-en-4-one, the molecule decomposes, possibly as a result of the interaction between the 3*d*-orbitals of silicon and the free electron pairs of the chlorine atom in benzoyl chloride [179]:



The interaction of complexes with heavy metal chlorides leads to the formation of crystalline double salts [15,43,102,105]:

$$[RCOCH=C(R)O]_3SiCl\cdot HCl + MCl_n \rightarrow [RCOCH=C(R)O]_3SiCl\cdot MCl_n,$$

where R = $CH_3$ or $C_6H_5$, M = Rb, Cu, Zn, Fe, Au, Pt, or Sn, and *n* is the valence of the metal.

When $[C_6H_5COCH=C(C_6H_5)O]_3SiCl.HCl$ is acted upon by sulphuric acid or silver nitrate, the crystalline sulphate $[C_6H_5COCH=C(C_6H_5)O]_3Si(HSO_4)$ and the nitrate $[C_6H_5COCH=C(C_6H_5)O]_3SiNO_3$ are formed respectively [101].

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