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REARRANGEMENT OF β-SILYL KETONES INTO O-SILYL-SUBSTITUTED ENOLS

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In recent years many investigations of functionally-substituted organoelement compounds have been reported. Nevertheless, the question of the relative stability of isomeric organo-element *O*- and *C*-derivatives of keto-enolic systems has been little studied. For example, with regard to the elements of Group IVB and enolisable carbonyl compounds, only one of the derivatives was usually obtained, and isolation, or support for the existence, of both isomers was reported only in a few papers*. The latter cases are of particular interest, as it is here that one can expect either the rearrangement of less thermodynamically stable isomers into more stable ones or establishing equilibrium between isomers, *i.e.* elementotropy (see, for example the data on the trimethylsilylketene–trimethylsiloxyacetylene tautomeric system[4]).

Recently we have shown[5,5a] that *O*-silyl-*O*-methylketeneacetals (I) formed in the reaction of halosilanes or organohalosilanes with methyl (trialkylstannyl) acetates are rearranged into esters of silylated acetic acid under corresponding condition.

$$\underset{\text{(I)}}{CH_2{=}C(OCH_3)OSiR_3} \rightarrow \underset{\text{(II)}}{R_3SiCH_2COOCH_3} \qquad \text{(1a, b)}$$

This isomerisation accompanied by the fission of the Si–O bond and the formation of a Si–C bond occurs either (1a) by the action of HgI_2 or Et_3SiI (at $R = SiEt_3$) on (I) or (1b) on moderate heating if (I) contains at least one chlorine atom at the silicon atom.

This paper deals with the properties of other isomeric pairs of compounds –*O*-silyl-substituted enols (III) and β-silyl ketones (IV). Data on the rearrangement of (IV) into (III) with the fission of the Si–C bond and the formation of a Si–O bond are given here**. This new reaction can be regarded, to a certain extent as being the reverse of reaction (1).

$$\underset{\text{(IV)}}{R_3SiCH_2COR'} \rightarrow \underset{\text{(III)}}{R_3SiOC(R'){=}CH_2} \qquad (2)$$

O-Silyl-substituted enols (III) have been more investigated than β-silylketones (IV) and they can be easily prepared by two conventional methods:

1. By hydrosilylation of α,β-unsaturated carbonyl compounds[6].

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* Most of the known examples are concerned with the chemistry of phosphorus[1]. Krüger and Rochow[2] described the isolation of isomeric Me_3SiCH_2COOEt and $CH_2{=}C(OEt)OSiMe_3$; the mixture of isomers obtained by the action of Bu_3SnH upon $CH_3CH{=}CHCOCH_3$ also contained $Bu_3SnCH(Et)COCH_3$ and $Bu_3SnOC(CH_3){=}CHEt$[3].

** Preliminary communication, see ref. 5b.

2. By the reaction of halosilanes with α-metalated (Hg, Sn) carbonyl compounds[5,7,7a,7b] or *O*-metal-substituted (Na, Sn) enols[2,8,8a].

However, only one procedure* has so far been described (using two examples) for the synthesis of (IV)—*i.e.*, the reaction of acid anhydrides with trialkylsilylmethylmagnesium halides[11]. By observing strictly all the experimental conditions suggested by the authors (except for the order of addition) we succeeded in isolating trimethylsilylacetone** with a yield of 54 %; in addition we obtained a number of other β-silylketones (IVa–f).

$$\mathrm{R_3SiCH_2MgCl + (R'CO)_2O \rightarrow \underset{(IVa\text{–}f)}{R_3SiCH_2COR'}} \tag{3}$$

a, $R=R'=CH_3$; b, $R=Et$, $R'=CH_3$; c, $R=CH_3$, $R'=C_6H_5$; d, $R=Et$, $R'=C_6H_5$; e, $R=C_6H_5$, $R'=CH_3$; f, $R=R'=C_6H_5$

O-Silyl-substituted enols (IIIa–f) (isomeric (IVa–f)) were synthesized in high yield according to the scheme previously developed by us[7b]

$$\mathrm{R_3SiCl + R'COCH_2SnR''_3 \rightarrow \underset{(IIIa\text{–}f)}{R_3SiOC(R'){=}CH_2} + R''_3SnCl} \tag{4}$$

The isomers produced, (III) and (IV), proved to be rather stable, undergoing no isomerisation under ordinary conditions, although it might be supposed that such a conversion might take place on heating or by initiation by some chemical means. It was found, in fact, that both techniques could be employed depending upon the experimental conditions and the structure of the starting materials. Thus, on adding some molar per cent of HgI_2 to (IVa–d) we observed some evolution of heat and *O*-silyl-substituted enols (IIIa–d) isomeric with (IV) could be isolated from the reaction mixture in high yields. Ethereal solutions of ZnI_2, R_3SiI, $HgBr_2$, R_3SiBr, and to a lesser extent $HgCl_2$ and R_3SiCl, act in a similar way (see Table 1)***.

$$\mathrm{\underset{(IVa\text{–}d)}{R_3SiCH_2COR'} \xrightarrow{HgI_2} \underset{(IIIa\text{–}d)}{R_3SiOC(R'){=}CH_2}} \tag{2a}$$

The isomerisation reaction (2a) can be checked with the help of infrared spectra.

It can be assumed that rearrangements (1a) and (2a) initiated by HgI_2 are heterolytic processes consisting of some reversible steps with transfer of reaction centre:

$$\mathrm{R_3SiCH_2COR' + HgI_2 \xrightleftharpoons{(a)} R_3SiI + IHgCH_2COR' \xrightleftharpoons{(b)} R_3SiOC(R'){=}CH_2 + HgI_2} \tag{5}$$

$$\mathrm{R_3SiCH_2COR' + R_3SiI \xrightleftharpoons{(c)} R_3SiOC(R'){=}CH_2 + R_3SiI \qquad (R'=CH_3,\ C_6H_5,\ OCH_3)}$$

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* Recently, Brook[9] reported that α-silyl ketones, $R_3SiC(O)R'$, with CH_2N_2 yield a mixture of (III) and (IV), and Musker and Ashby[10] synthesized Me_3SiCH_2COEt by the method of Hauser and Hance[11].

** For the synthesis of this compound, see also refs. 2 and 12.

*** It is more convenient to carry out the isomerisation using HgX_2 since, on account of the polymerisation of the end products in the presence of R_3SiX, they must be removed immediately the reaction has been completed.

In each case, the equilibrium shifts toward the more stable isomer and the rate of a practically irreversible rearrangement is, in general, determined by the relationship of the rates of the separate steps (5a, 5b or 5c).

The essential point in scheme (5) is the formation of trialkyliodosilane which can react both with the α-mercurated carbonyl compound, $IHgCH_2COR'$, and with the original O (at $R'=OCH_3$), or C (at $R'=CH_3$, C_6H_5)-isomers to give an end product. Reactions (6)[13] and (7)[7b] previously studied by us prove the possibility of both courses,

$$IHgCH_2COOCH_3+R_3SiI \rightarrow R_3SiCH_2COOCH_3+HgI_2 \qquad (6)$$

$$IHgCH_2COCH_3+R_3SiI \rightarrow R_3SiOC(CH_3){=}CH_2+HgI_2 \qquad (7)$$

and it is supported by the easy isomerisation of (I) and (IV) when a trialkyliodosilane

$$\underset{(Ib)}{CH_2{=}C(OCH_3)OSiEt_3} \xrightarrow{Et_3SiI} \underset{(IIb)}{Et_3SiCH_2COOCH_3} \qquad (8)$$

$$\underset{(IVa\text{–}d)}{R_3SiCH_2COR'} \xrightarrow{R_3SiI} \underset{(IIIa\text{–}d)}{R_3SiOC(R'){=}CH_2} \qquad (9)$$

is present.Therefore, from a formal point of view the most essential feature of the suggested mechanism is catalysis by intermediate products.

The fact that rearrangements (1a) and (2a) are intermolecular in the presence of HgI_2 is indicative of the advantage of scheme (5).

Thus, by treating a mixture of (IVc) and (IVb) with HgI_2 (or R_3SiI) all four possible products were proved (by gas–liquid chromatography) to be present in the rearrangement products.

$$\begin{array}{c} Me_3SiCH_2COC_6H_5 \\ (IVc) \\ Et_3SiCH_2COCH_3 \\ (IVb) \end{array} \xrightarrow[\text{or } Me_3SiI]{HgI_2} \begin{array}{l} Me_3SiOC(CH_3){=}CH_2 \text{ (IIIa)} \\ Et_3SiOC(CH_3){=}CH_2 \text{ (IIIb)} \\ Me_3SiOC(C_6H_5){=}CH_2 \text{ (IIIc)} \\ Et_3SiOC(C_6H_5){=}CH_2 \text{ (IIId)} \end{array} \qquad (10)$$

A similar result was obtained by the combined isomerisation of (Ib) and (IVc).

$$\begin{array}{c} Me_3SiCH_2COC_6H_5 \\ (IVc) \\ CH_2{=}C(OCH_3)OSiEt_3 \\ (Ib) \end{array} \xrightarrow[\text{or } Me_3SiI]{HgI_2} \begin{array}{l} Me_3SiCH_2COOCH_3 \text{ (IIa)} \\ Et_3SiCH_2COOCH_3 \text{ (IIb)} \\ Me_3SiOC(C_6H_5){=}CH_2 \text{ (IIIc)} \\ Et_3SiOC(C_6H_5){=}CH_2 \text{ (IIId)} \end{array} \qquad (11)$$

The qualitative dependence of the ease of rearrangement on the nature of the halogen in HgX_2 or R_3SiX (Table 1) is in agreement with the above scheme. It is obvious from the data in Table 1, that iodides initiate the isomerisation to a more considerable degree than bromides and the latter to a far greater degree than chlorides and trialkylhalosilanes more readily than triarylhalosilanes*. This is in accordance with the relative reactivity of halosilanes in the reactions of nucleophilic substitution of halogens[14,15]. The obvious increase of isomerisation when Et_3SiCl and $HgCl_2$

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* The action of HgX_2 on $(C_6H_5)_3SiCH_2COR'$ does not result in rearrangement products probably owing to the fact that HgX_2 can strip off the aryl radical from arylsilanes (see ref. 14, pp. 229, 231).

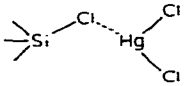
TABLE I

THE RELATIVE CAPACITY OF β-SILYLKETONES (IV) TO REARRANGE TO *O*-SILYL-SUBSTITUTED ENOLS (III)

Catalyst	$Me_3SiCH_2COCH_3$ (*IVa*)				$Et_3SiCH_2COCH_3$ (*IVb*)				$Me_3SiCH_2COC_6H_5$ (*IVc*)				$Et_3SiCH_2COC_6H_5$ (*IVd*)				$(C_6H_5)_3SiCH_2COCH_3$ (*IVe*)				$(Ph)_3SiCH_2COPh$ (*IVf*)			
	t (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)	*t* (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)	*t* (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)	*t* (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)	*t* (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)	*t* (*h*)	*T* (°C)	*Cat.* (*g*)	*Comp.* (*g*)
HgI_2	0.3	50^a	0.05	4.8	0.15	70^a	0.1	12	0.5	80	0.1	2.8	1	80	0.1	2.6		^{b}				^{b}		
$HgBr_2$					0.15	50^a	0.05	2																
$HgCl_2$					25^c	90	0.05	2																
Me_3SiI	0.05	50^a	0.02	0.5	0.05	60^a	0.05	2	0.2	40^a	0.05	2												
Et_3SiI	0.2	40^a	0.05	0.5	0.08	40^a	0.1	2.5	1	60	0.05	2	1	90	0.05	1.5		^{b}				^{b}		
Et_3SiI/Py					20^c	90	0.05/ 0.1	2																
Et_3SiBr					1.5	90	0.03	0.3																
Me_3SiCl	7	140	1	5																				
Et_3SiCl					20^c	90	0.05	0.3																
$Et_3SiCl/HgCl_2$ (1 : 1)					1.5	90	0.03	0.3																
ZnI_2^{d}					0.3	40	1	2																
None			^{e}		4	160		4.5	2	160	3.2		2	160		3.8	2		160	0.8	3	160		0.7

^{a} Exothermic reaction; ^{b} no rearrangement; ^{c} about 75% conversion; ^{d} 10% soln. in ether; ^{e} only by distillation through column at atmospheric pressure.

act jointly on (IVb) as well as the more rapid isomerisation of (IVb) in the presence of $HgBr_2$ (which acts essentially as a mixture of $HgBr_2$ and Et_3SiBr) than Et_3SiBr seems to indicate the importance of electrophilic catalysis in step (5c) which is a typical case of nucleophilic substitution of halogen at silicon.



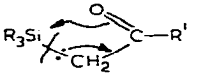
(12)

The addition of nucleophilic substances has the opposite effect. Thus, isomerisation of (IVb) due to Et_3SiI in the presence of pyridine becomes noticeable only after heating for 3 h at 80° whereas isomerisation of (IVb) proceeds practically instantly when only Et_3SiI takes part in the reaction.

Further examination of the properties of isomers (III) and (IV), showed that β-silylketones (IV) can rearrange into *O*-silyl-substituted enols (III) even if (IVb–f)* are heated to 160–180° for 2–3 h**. It should be noted that, unlike reaction (2a), even (IV) compounds containing phenyl groups at silicon rearrange by such a method.

$$\underset{\text{(IVb–f)}}{R_3SiCH_2COR'} \xrightarrow{160-180°,\ 2-3\ h} \underset{\text{(IIIb–f)}}{R_3SiOC(R'){=}CH_2}^{***} \tag{2b}$$

Preliminary data indicate the intramolecular character of the thermal isomerisation of (2b). Thus, on isomerising (IVb) and (IVc) together as well as (Ib) and (IVc) we could not confirm the formation of an intermolecular rearrangement product. In this case the reaction appears to proceed via a four-centered activated complex (13).



(13)

This is in agreement with recently reported data on the existence of the *intra*-molecular interaction Si···O in the molecule of (IVa)[12] and other β-silyl ketones[10].

It is interesting to note that by treating triethylstannylacetone (V) with (Ib), methyl(triethylstannyl) acetate (VI) and (IIIb) have been isolated *i.e.*, by substituting silicon for tin there has been an intermolecular reaction. Both partners of this reaction react with transfer of the reaction centre.

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* Concerning (IVa) see p. 45.

** We have shown earlier that (Ib) does not rearrange into (IIb) on heating to 160–180° but decomposes[5]. This decomposition can be expressed as follows:

$$2\,CH_2{=}C(OCH_3)OSiEt_3 \rightarrow Et_3SiOCH_3 + CH_2{=}C(OSiEt_3)CH_2COOCH_3$$

*** (III) were the main products. Other products formed by heating (IV) will be reported in a following paper.

TABLE 2

SOME SPECTRAL DATA FOR β-SILYLKETONES (IV) AND O-SILYL-SUBSTITUTED ENOLS

Compound	*Infrared spectra* (ν *cm*$^{-1}$, *liquid*) *C=O absorption*	*C=C absorption*	*Ultraviolet spectra* (λ_{max}, $m\mu(\varepsilon_{max})$) *Solvent*[a]	*n-π* transition*	^1H *NMR spectra* *Chemical shifts (ppm) and J-values* CH_2= $J(AB)$	$\delta(A)$	$\delta(B)$	$\delta(Si\text{-}CH_2\text{-})$	$\delta(\text{-}CH_3)$
CH_3COCH_3	1715[b]		HP	277 (12)[c]					
$Me_3CCH_2COCH_3$	1710[d]		CY	287 (20)[e]					
$Me_3SiCH_2COCH_3$ (IVa)	1695 (1698)[c]		IO	282 (57.5)				2.1	1.9
$Et_3SiCH_2COCH_3$ (IVb)	1697		IO	282 (72.5)				2.15	2.05
$Et_3GeCH_2COCH_3$[f]	1695		IO	283 (120)					
$Et_3SnCH_2COCH_3$[g]	1684			277–280 (219)					
$Hg(CH_2COCH_3)_2$[g]	1660 (solid)			290 (631)					
$Ph_3SiCH_2COCH_3$ (IVe)	1697 (in CCl_4)								
$PhCOCH_3$	1687[b]		HP	325 (54)[c]					
Ph_3CCH_2COPh[h]	1698		ET	323 (95)					
Me_3SiCH_2COPh (IVc)	1667		IO 235–238 (11480), 278 (758), 285 (646)	310 (138), 320 (151), 331 (129)				2.99	
Et_3SiCH_2COPh (IVd)	1665		IO 238 (11750), 275–278 (724)	321 (126)				2.68	
Ph_3SiCH_2COPh (IVf)	1670 (in CCl_4) (1667[h])		IO 240 sh(12590) 265 (1585), 271 (1380)	318–321 (174)				3.38 (3.34[i])	
$Me_3SiOC(CH_3)=CH_2$ (IIIa)		1635–1650				3.98	3.98		1.63
$Et_3SiOC(CH_3)=CH_2$ (IIIb)		1640–1658				3.92	3.92		1.8
$Me_3SiOC(Ph)=CH_2$ (IIIc)		1630			2	4.38	4.98		
$Et_3SiOC(Ph)=CH_2$ (IIId)		1625			2	4.4	4.8		
$Ph_3SiOC(CH_3)=CH_2$ (IIIe)		1655							
$Ph_3SiOC(Ph)=CH_2$ (IIIf)		1620			2	4.34 (4.34[i])	4.78 (4.77[i])		

[a] HP = heptane; CY = cyclohexane; IO = *iso*-octane; ET = ethanol. [b] Compiled by Bellamy and Williams[19]. [c] Compiled by Rao[20]. [d] Ref. 12. [e] Ref. 10. [f] Ref. 7b. [g] Ref. 17. [h] Compiled by Brook and Pierce[21]. [i] Compiled by Brook[9].

$$\underset{\text{(Ib)}}{\mathrm{CH_2{=}C(OCH_3)OSiEt_3}} + \underset{\text{(V)}}{\mathrm{Et_3SnCH_2COCH_3}} \rightarrow$$

$$\underset{\text{(IIIb)}}{\mathrm{Et_3SiOC(CH_3){=}CH_2}} + \underset{\text{(VI)}}{\mathrm{Et_3SnCH_2COOCH_3}} \qquad (14)$$

The structure of β-silylketones (IV) and their rearrangement products is proved by chemical means as well as by IR, UV and ^{1}H NMR spectra (see Table 2). Thus, the reduction of (IV) by $LiAlH_4$ proceeds without fission of the Si–C bond and proves their C-structure.

$$\underset{\text{(IVa–f)}}{\mathrm{R_3SiCH_2COR'}} \xrightarrow{\mathrm{LiAlH_4}} \underset{\text{(VIIa–f)}}{\mathrm{R_3SiCH_2CH(OH)R'}} \qquad (15)$$

The synthesis of *O*-silyl-substituted enols (III) from β-stannylketones and chlorosilanes was mentioned earlier (see reaction 4). The constants and spectra of (III) obtained by two independent methods [reactions (2) and (4)] were in agreement.

In the IR spectra of (IIIa–f), intensive absorption bands were detected at 1620–1655 cm^{-1} corresponding to the C=C stretching vibration[16]. (IVa–f) exhibit intensive absorption at 1670–1700 cm^{-1} in infrared spectra and at 282–335 mμ in ultraviolet spectra (see Table 2 and examples of infrared spectra on Fig. 1). This lowering of the infrared stretching frequency of the carbonyl band and the intensification of the n–π^* transition in (IV) compared with the usual values (see for example values for acetone and acetophenone in Table 2) is characteristic of α-metalated carbonyl compounds and places (IV) in line with those compounds that are typical of σ,π-conjugated systems. The spectral properties of such systems can also be accounted for by σ,π-conjugation[17]. It should be noted that the reasons for the spectra "anomalies" observed in α-metalated carbonyl compounds (which may be different for IR and UV spectra) will be rather complicated. Besides σ,π-conjugation, there is also the possibility of the presence of both intramolecular coordination (between the atom of the element and the oxygen atom[10,12]) and intermolecular association[18].

^{1}H NMR spectra* are also in agreement with the suggested structures. Signals of vinyl protons of the CH_2= terminal group (a typical AB pattern) having values of chemical shifts (in ppm) of 3.9–5.0 were detected in the (IIIa–f) spectra. Signals of protons of the methylene group immediately connected to the silicon atom having values of chemical shifts of 2.1–2.15 for (IVa, b) and 2.7–3.4 for (IVc–f) were detected in the spectra of (IVa–f).

Finally, it should be emphasized that the cases of irreversible rearrangements of isomeric organosilicon *O*- and *C*-derivatives of keto-enolic systems discovered, substantiates the scheme for the formation of end products in the reaction of compounds tending to dual reactivity. The action of corresponding reagents on σ,π-conjugated organoelement compounds results in the production of *O*- or *C*-isomer derivatives or their mixture. It can be inferred from the data cited in this paper that when silicon halides take part in such reactions (even as intermediates) there is a possibility of establishing equilibrium between isomers (leading to the formation

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* This will be discussed in a separate report.

of the more thermodynamically stable isomer). Hence, the main factor determining the structure of the reaction product is, in this case, the relative stability of the isomer produced. Yet the available practical material is inadequate for discussing the causes of this different stability.

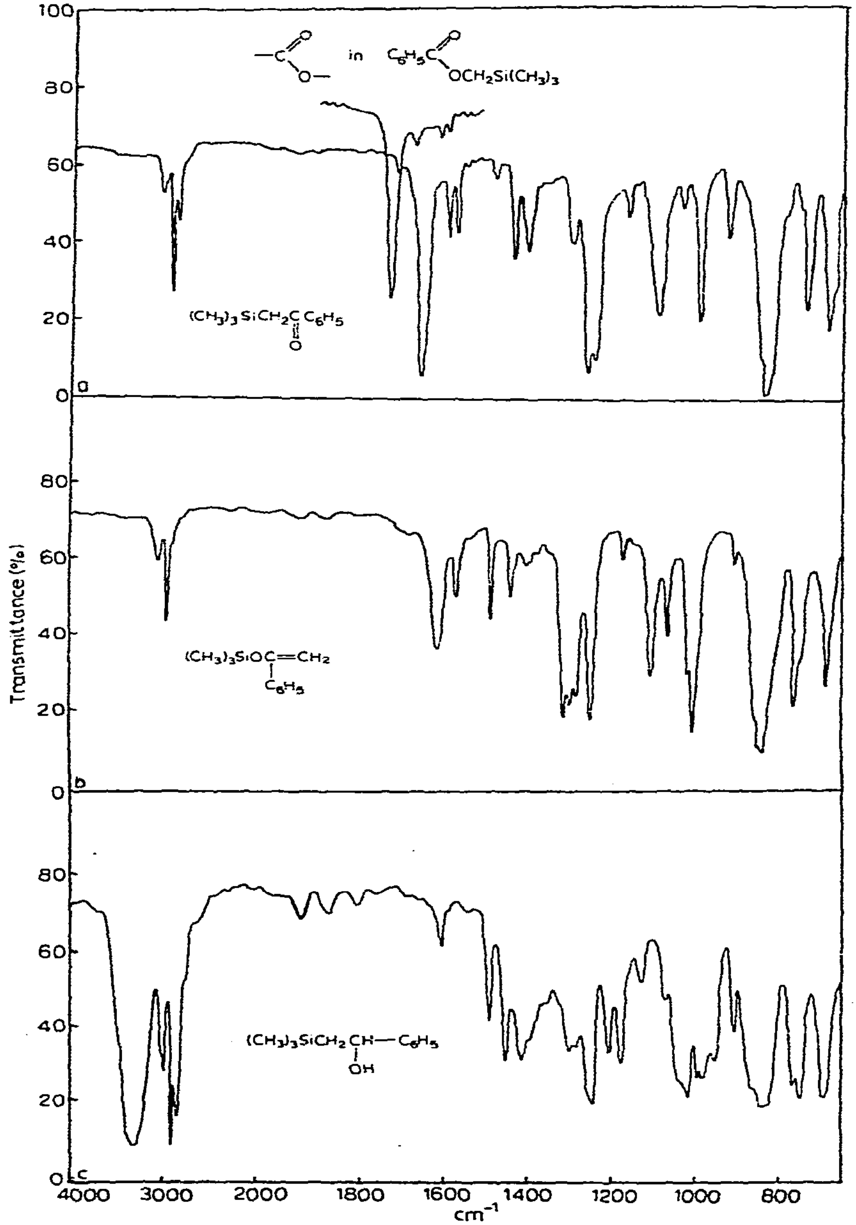

Fig. 1. IR spectrum of: (a), α-trimethylsilylacetophenone; (b), α-(trimethylsiloxy)styrene; (c), β-trimethylsilyl-α-phenylethanol.

EXPERIMENTAL

The IR spectra were taken in thin films using a spectrometer IKS-22(NaCl), calibrated with a polystyrene film. The error in the absorption maximum is estimated to be $\pm 3\ \text{cm}^{-1}$. The ^{1}H NMR spectra were obtained in carbon tetrachloride solution, with hexamethyldisiloxane as internal reference, with a Hitachi H-60 spectrograph.

1. *Reaction of trimethylsilylmethylmagnesium chloride with benzoic anhydride*

α-Trimethylsilylacetophenone, $Me_3SiCH_2COC_6H_5$ (IVc) was synthesized by a modification of the procedure outlined by Hauser and Hance[11]. The Grignard reagent, was prepared by dissolving 5 g (0.0206 mole) of magnesium and 25.5 g (0.208 mole) of trimethylchloromethylsilane in 100 ml of ether under an atmosphere of nitrogen; benzoic anhydride (25.8 g, 0.12 mole) in 100 ml of ether was added at a temperature not above −60° for 3 h. The temperature was allowed to rise to −20° and a 10% solution of NH_4Cl was added to the mixture at −20 to −30°*. The ether layer was separated and dried. Fractionation yielded 8.3 g (42%) of (IVc), b.p. 78.5–79°/1 mm. For the IR spectrum of (IVc) see Fig. 1.

If the reaction is carried out at −20°, only trimethylsilylmethylbenzoate, $Me_3SiCH_2OCOC_6H_5$, (28%), b.p. 129–130°/17 mm, n_D^{20} 1.4959, d_4^{20} 0.9844, MR_D 61.71; calcd. 60.99 (IR spectrum, see Fig. 1) is produced. (Lit.[22] b.p. 111–114°/8 mm, n_D^{20} 1.4840, d_4^{20} 0.9847.)

Other β-silylketones are produced similarly (IVa, b, d–f). Solid compounds (IV) were recrystallized without distillation.

2. *Rearrangement of β-silylketones (IV) into O-silyl-substituted enols (III)*

(*a*) *In the presence of HgI_2.* 0.05 g of HgI_2 was added to 2.6 g of (IVd). The mixture was allowed to warm up to 40–50°. After the mixture had cooled to room temperature the absorption at 1670 cm^{-1}, corresponding to the C=O stretching vibration, had disappeared, and there appeared the C=C absorption at 1620–1640 cm^{-1}**. The solution was separated from HgI_2 by decantation. Fractionation yielded 1.75 g (68%) of (IIId), b.p. 86–88°/1 mm.

The rearrangement of other β-silylketones (IVa–c) was carried out similarly.

(*b*) *In the presence of trialkyliodosilanes.* 0.1 ml of triethyliodosilane was added to 2.5 g of (IVb) under an atmosphere of nitrogen. The temperature of the mixture rose to 50°. After 15 min, 0.5 g of triethylstannylacetone*** was added to the mixture, which was heated for 15 min at 50°. Fractionation yielded 1.2 g (48%) of (IIIb), b.p. 66–67°/19 mm, n_D^{20} 1.4305, d_4^{20} 0.8368.

The rearrangement of other (IV) compounds into the corresponding (III) compounds was observed with the help of IR spectra and gas–liquid chromatography.

(*c*) *Thermal isomerisation.* 2.4 g of (IVd) was heated at 160° for 2 h (the reaction course was followed with the help of IR spectra). Fractionation yielded 2.1 g (88%) of (IIId), b.p. 109–109.5°/3 mm.

The thermal isomerisation of other (IV) compounds was carried out in the

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* If this addition is made at higher temperatures, the hydrolysis products alone are produced (IVc)—acetophenone and hexamethyldisiloxane.

** The completion of the reaction was checked by gas–liquid chromatography.

*** For separation of (IIIb) from triethyliodosilane.

TABLE 3

PROPERTIES OF THE COMPOUNDS PREPARED IN THIS INVESTIGATION

Methods: 1, *Hauser* and Hance[11]; 2, reduction with $LiAlH_4$; 3, in presence of HgI_2; 4, in presence of Et_3SiI; 5, thermal rearrangement; 6, reaction of chlorosilanes with β-stannylketones.

Compound	*Method*	*Yield (%)*	*B.p. (mm)*	n_D^{20}	d_4^{20}	MR_D		*Found (%)*			*Calcd. (%)*		
						Found	*Calcd.*	*C*	*H*	*Si*	*C*	*H*	*Si*
$Me_3SiCH_2COCH_3$[a] (IVa)	1	54	77–79° (97)	1.4220	0.8415	39.34	39.62	55.43	10.75	21.75	55.32	10.83	21.56
$Me_3SiOC(CH_3)=CH_2$[b] (IIIa)	3	55	95–96 (756)	1.3980	0.7909	39.75	39.83	55.04	10.63	21.43	55.32	10.83	21.56
$Me_3SiCH_2CH(OH)CH_3$[c] (VIIa)	2	56	86–87 (93)	1.4284	0.8301								
$Et_3SiCH_2COCH_3$ (IVb)	1	52	89–90 (10)	1.4487	0.8679	53.23	53.57	61.99	11.38	16.83	62.71	11.70	16.30
$Et_3SiOC(CH_3)=CH_2$[d] (IIIb)	3	70	56–58 (11)	1.4295	0.8354	53.24	53.77	62.61	11.82	16.73	62.71	11.70	16.30
$Et_3SiOC(CH_3)=CH_2$[d] (IIIb)	4	48	66–67 (19)	1.4305	0.8368								
$Et_3SiOC(CH_3)=CH_2$[d] (IIIb)	5	63	67–68 (18)	1.4298	0.8365								
$Et_3SiCH_2CH(OH)CH_3$ (VIIb)	2	75	101–103 (10)	1.4552	0.8670	54.59	54.95	61.65	12.64	17.20	61.99	12.66	16.21
$Me_3SiCH_2COC_6H_5$[e] (IVc)	1	42	78–79 (1)	1.5122	0.9578	59.21	60.20	68.41	8.73	14.90	68.70	8.39	14.59
$Me_3SiOC(C_6H_5)=CH_2$[f] (IIIc)	3	71	53–54 (1)	1.5040	0.9397								
$Me_3SiOC(C_6H_5)=CH_2$[f] (IIIc)	5	63	51–53 (1)	1.5038	0.9411								
$Me_3SiOC(C_6H_5)=CH_2$[f] (IIIc)	6	52	91–93 (14)	1.5038									
$Me_3SiCH_2CH(OH)C_6H_5$[g] (VIIc)	2	68	70–71 (0.5)	1.5067[m]	0.9487[m]	60.68	61.55						
$Et_3SiCH_2COC_6H_5$ (IVd)	1	39	106–107 (1.5)	1.5180	0.9768	73.15	72.73	71.77	9.56	11.86	71.72	9.46	11.97
$Et_3SiOC(C_6H_5)=CH_2$[h] (IIId)	3	68	86–88 (1.5)	1.5062	0.9520	73.39	73.17						
$Et_3SiOC(C_6H_5)=CH_2$[h] (IIId)	5	64	83–84 (1.5)	1.5077	0.9485								
$Et_3SiOC(C_6H_5)=CH_2$[h] (IIId)	6	52	89–90 (1.5)	1.5085	0.9520								
$Et_3SiCH_2CH(OH)C_6H_5$	2	50	131–133 (2.5)	1.5112	0.9615	73.53	73.7	71.86	10.46	11.62	71.10	10.23	11.87
$(C_6H_5)_3SiCH_2COCH_3$ (IVe)[o]	1	35	79–81[n]					77.96	6.38	9.19	79.74	6.37	8.87
$(C_6H_5)_3SiOC(CH_3)=CH_2$ (IIIe)	5	72	150–152 (6·10⁻²) 69–70[n]					79.92	6.47	8.89	79.74	6.37	8.88
$(C_6H_5)_3SiCH_2CH(OH)CH_3$[i] (VIIe)	2	72	86–87[n]										
$(C_6H_5)_3SiCH_2COC_6H_5$[j] (IVf)	1	31	89–91[n]					82.87	5.83	7.58	82.50	5.86	7.41
$(C_6H_5)_3SiOC(C_6H_5)=CH_2$[k] (IIIf)	5	27	80–81[n]					82.74	6.12	7.89	82.50	5.86	7.41
$(C_6H_5)_3SiCH_2CH(OH)C_6H_5$[l] (VIIf)	2	63	131–133[n]										

[a] lit.[11] b.p. 74°/96 mm, n_D^{26} 1.4188, d_4^{26} 0.8275. [b] lit.[7b] b.p. 92–94°/758 mm, n_D^{20} 1.3989, d_4^{20} 0.7873. [c] lit.[25] b.p. 48°/10 mm, n_D^{20} 1.4281. [d] lit.[7b] b.p. 70–71°/23 mm, n_D^{20} 1.4309, d_4^{20} 0.8336. [e] lit.[9] b.p. 104°/3.1 mm. [f] lit.[2] b.p. 94°/14 mm, n_D^{20} 1.5008. [g] lit.[11] b.p. 103–104°/3 mm, n_D^{27} 1.4984, d_4^{27} 0.9380. [h] lit.[7] b.p. 106–107°/3 mm, n_D^{20} 1.5089, d_4^{20} 0.9466. [i] lit.[24] m.p. 86–88°. [j] lit.[21] m.p. 89–91°. [k] lit.[9] m.p. 78–80°. [l] lit.[24] m.p. 131°. [m] at 27°. [n] m.p. [o] Purification of (IVe) by distillation failed. This compound was rearranged to (IIIe) by distillation at 150–152°/6·10⁻² mm.

same way. The most difficult reaction was that of (IVa). This compound was rearranged only by distillation through the column at atmospheric pressure.

4. *Reaction of triethylstannylacetone (V) with O-triethylsilyl-O-methylketeneacetal (1b)**

7.8 g (0.042 mole) of (1b) were added dropwise to 11.2 g (0.042 mole) of (V) and the mixture heated at 110–120° for 2.5 h. Fractionation yielded 5.7 g (55%) of (IIIb), $Et_3SiOC(CH_3)=CH_2$, b.p. 74–76°/33 mm, and 9.3 g (98%) of (VI), $Et_3SnCH_2COOCH_3$, b.p. 108–110°/10 mm, n_D^{20} 1.4850, d_4^{20} 1.2850, MR_D 61.81; calcd. 61.74 (lit.[23], b.p. 71–72°/2 mm, n_D^{20} 1.4833, d_4^{20} 1.2958.)

5. *Reduction of β-silylketones (IV) with lithium aluminium hydride*

β-Triethylsilyl-α-phenylethanol, $Et_3SiCH_2CH(OH)C_6H_5$ (VIId). An ethereal solution of 4.3 g (0.018 mole) of (IVd) was added to 0.9 g (0.23 mole) of $LiAlH_4$ in ether. The reaction mixture was refluxed for 2 h, hydrolysed with moist ether and then with water. The ether layer was separated, treated in the usual manner and distilled. The yield of (VIId) was 2.15 g (50%), b.p. 130–131°/2 mm.

Other (IV) compounds were reduced similarly. Solid (VII) compounds were recrystallized without distillation.

6. *Reaction of chlorosilanes with β-stannylketones*

α-(Triethylsiloxy)styrene, $Et_3SiOC(C_6H_5)=CH_2$ (IIId). Triethylchlorosilane (4 g, 0.028 mole) was added dropwise to 10.2 g (0.031 mole of α-triethylstannylacetophenone and the mixture heated at 60–80° for 2 h. Fractionation yielded 4.1 g (52%) of (IIId), b.p. 89–90°/1 mm.

Other (III) compounds were obtained similarly.

The properties of the compounds prepared in this investigation are summarized in Table 3.

7. *Gas–liquid chromatographic analyses*

Gas–liquid chromatographic analyses were carried out with a "Tsvet 1" gas–liquid chromatograph with a flame-ionization detector, using helium as a carrier gas at 120 and 190°. In these analyses, the following column was used: the length of the column was 3 m, internal diameter, 0.4 cm; the column was packed with 7.5% Apiezon L, 2.4% FC-60, 0.1% Carbowax 3000 on Chromosorb W 60–80 mesh treated with trimethylchlorosilane.

The chromatograms for the analysis of the reaction products of (IVb) and (IVc) in the presence of catalytic quantities of HgI_2 are given in Fig. 2. In the analysis of a standard equimolar mixture of these substances, the chromatogram obtained was similar to that given in Fig. 2.

Relative retention times corresponding to the peaks of the components of the mixture were in agreement with the retention times of the separate substances. On the addition of a standard compound to the mixture, the peak corresponding to that compound in the reaction products, increased.

Table 4 lists the number and the quantity of peaks in the chromatograms of the reaction mixtures and the relative retention times coinciding with the peaks of the corresponding *O*-isomers, obtained by rearrangement.

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* In collaboration with G. S. Burlachenko.

TABLE 4

RELATIVE RETENTION TIMES OBTAINED BY GAS-LIQUID CHROMATOGRAPHY UNDER DIFFERENT CONDITIONS OF REARRANGEMENT AND ANALYSIS

Reactants	*Numbers of peaks*	*Reaction products*	HgI_2		Me_3SiI		*Heating at 160–170° for 2 h*	
			120°	190°	120°	190°	120°	190°
$Me_3SiCH_2COC_6H_5$ (IVc), $Et_3SiCH_2COCH_3$ (IVb)	1	$Me_3SiOC(CH_3)=CH_2$ (IIIa)	0.3	0.1	0.3	0.1		
	2	$Et_3SiOC(CH_3)=CH_2$ (IIIb)	3.44	0.71	3.75	0.63	3.7	0.8
	3	$Me_3SiOC(C_6H_5)=CH_2$ (IIIc)	18.1	2.7	19.8	2.3	18.9	2.9
	4	$Et_3SiOC(C_6H_5)=CH_2$ (IIId)		12.3		10.8		
$Me_3SiCH_2COC_6H_5$ (IVc) $CH_2=C(OCH_3)OSiEt_3$ (Ib)	1	$Me_3SiCH_2COOCH_3$ (IIa)	1.42	0.35		0.4		
	2	Et_3SiOCH_3[a]					2.3	0.5
	3	$Et_3SiCH_2COOCH_3$ (IIb)	14.4	2.0		1.6		
	4	$Me_3SiOC(C_6H_5)=CH_2$ (IIIc)	22.8	2.8		2.0	23.0	2.8
	5	$Et_3SiOC(C_6H_5)=CH_2$ (IIId)		12.1		10.0		

[a] Scheme of the thermal decomposition of (Ib), see p. 39.

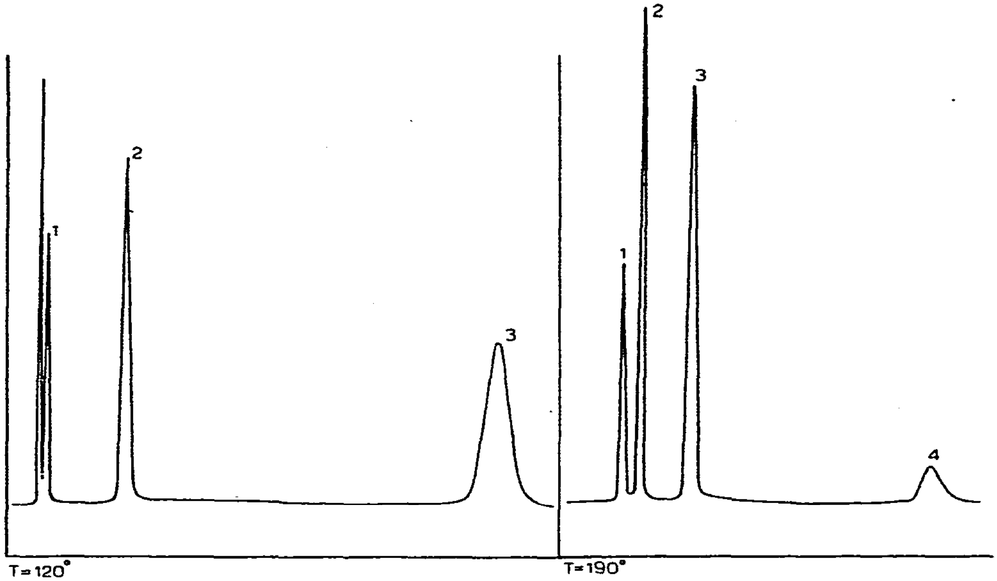

Fig. 2. Gas–liquid chromatograms for the analysis of the reaction products of (IVb) and (IVc) in the presence of HgI_2. 1, (IIIa); 2, (IIIb); 3, (IIIc); 4, (IIId).

Ether was used as the standard compound. Its relative retention time was taken as 1.

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SUMMARY

The conditions for the rearrangement of β-silylketones to *O*-silyl-substituted enols are reported. The mechanism of irreversible isomerisation of the organosilicon *O*- and *C*-derivatives of keto-enolic systems is discussed.

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