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THE MECHANISM OF THE β-KETOSILANE TO SILOXYALKENE THERMAL REARRANGEMENT

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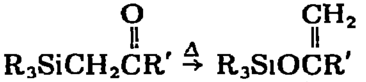
Summary

The mechanism of the β-ketosilane to siloxyalkene rearrangement has been investigated. The reaction followed first order kinetics for a wide variety of compounds. Activation parameters have been determined for six compounds. For a series of *p*-substituted triphenylsilylacetophenones log *k* vs. σ_p gave a Hammett ρ value of −0.78. The data are consistent with an intramolecular concerted rearrangement involving a four-centre transition state where silicon—oxygen bond formation cannot significantly precede silicon—carbon bond breaking. Molecular orbital calculations were consistent with this view.

Several years ago we reported that a number of β-ketosilanes I were thermally isomerized at 100-180° to the corresponding siloxyalkenes II [1].



$$\mathrm{R_3SiCH_2\overset{\overset{\displaystyle O}{\|}}{C}R'} \xrightarrow{\Delta} \mathrm{R_3SiO\overset{\overset{\displaystyle CH_2}{\|}}{C}R'}$$

(I) (II)

(R or R' = Me, Ph)

Our preliminary studies indicated that the rearrangement followed first order kinetics, that it occurred with a wide variety of types of β-ketosilane and that when a compound asymmetric at silicon was employed the rearrangement occurred with high stereospecificity involving retention of configuration at silicon.

We have now broadened the scope of this investigation and wish to report kinetic data for a number of examples of this thermal rearrangement.

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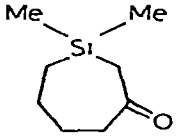
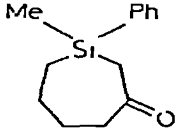
* The experimental part of this paper is derived largely from the Ph. D. Thesis of D.M. MacRae, University of Toronto, 1972.

TABLE 1

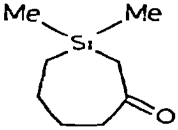
THE ISOMERIZATION OF SOME β-KETOSILANES

β-Ketosilane	Conditions (°C/h)	Yield (%)
Ph_3SiCH_2COPh	cyclohexane, 81/18	10 [a]
	toluene, 110/18	100
Ph_3SiCH_2COMe	toluene, 110/24	≈0
	xylene, 175/18	100
Me_3SiCH_2COPh	neat, 100/24	16 [a]
	neat, 150/36	100
Me_3SiCH_2COMe	neat, 140/36	100
	neat, 170/20	100 [b]
	neat, 170/20	100 [b]
	GLPC at 275°	100
Ph_3SiCH_2CHO	melt, 150/18	50 [a]
	melt, 150/92	100
1-$NpPhMeSiCH_2COPh$	toluene, 110/52	100

[a] Unreacted starting material was recovered in good yield. [b] The product contained some isomeric endocyclic alkene.

TABLE 2

KINETIC PARAMETERS FOR THE ISOMERIZATION OF SOME β-KETOSILANES

	Temp. (°C)	k (min^{-1}) (X 10^{-3})	E_{act} (kcal/mol)	$\Delta S^{\ddagger}$ (cal/mol. K)	k (150°) (X 10^{-3})	k_{rel}
Ph_3SiCH_2COPh [a]	100.1	1.25	28.1 ± 0.4	−7.3 ± 1	126 (*E*)	174
	125.0	13.5				
Ph_3SiCH_2COPh [b]	105	2.06	28.4 ± 0.8	−6.4 ± 2		
	125	13.5				
Me_3SiCH_2COPh [c, d]	133	2.61	26.1 ± 0.7	−16.9 ± 1.6	10.0 (*I*)	13.8
	152.7	11.5				
Ph_3SiCH_2COMe [c, e]	148	7.03	31.7 ± 0.9	−4.2 ± 2	8.12 (*I*)	11.2
	173	56.4				
Me_3SiCH_2COMe [c, f]	159	7.03	30.1 ± 0.3	−9.8 ± 0.8	3.27 (*E*)	4.5
	180	34.8				
 [c,g]	175	5.41	33.0 ± 1.2	−6.4 ± 0.4	0.733 (*E*)	1.07
	195	27.2				
Ph_3SiCH_2CHO [c]	150	0.723			0.723	1.00

[a] In toluene. Other k(T°C) were: 2.00 X 10^{-3} (105.1°); 3.84 X 10^{-3} (111°); 5.38 X 10^{-3} (115.5). [b] In decalin. Other k(T°C) were: 3.65 X 10^{-3} (110.1°); 5.10 X 10^{-3} (115°). [c] Neat or melt. [d] Other k(T°C) were: 4.31 X 10^{-3} (139°); 7.45 X 10^{-3} (145.8°). [e] Other k(T°C) were: 1.00 X 10^{-2} (153°); 1.57 X 10^{-2} (159°); 2.76 X 10^{-2} (164°). [f] Other k(T°C) were: 1.03 X 10^{-2} (164°); 1.55 X 10^{-2} (169°); 2.49 X 10^{-2} (175°). [g] Other k(T°C) were: 8.12 X 10^{-3} (180.1°); 1.06 X 10^{-2} (185°); 1.67 X 10^{-2} (190°).

TABLE 3

RATES OF REARRANGEMENT OF *p*-SUBSTITUTED TRIPHENYLSILYLACETOPHENONES AT 120° IN TOLUENE

$Ph_3SiCH_2C(O)C_6H_4$-*p*-X	k (min^{-1}) (× 10^{-3})	σ_p
Br	8.57	0.232
Cl	8.69	0.227
F	10.1	0.062
H	13.5	0.000
t-Bu	18.6	−0.197
OMe [a]	27.1	−0.268

[a] As a melt, $k = 2.72 \times 10^{-2}$; in dimethylformamide as solvent $k = 2.08 \times 10^{-2}$. Dielectric constant of toluene is approx. 2.39; of DMF about 36.7.

Results

The data consist of two sorts. On the one hand a series of preparative experiments, summarized in Table 1, were run to determine approximate conditions required to effect essentially complete conversion of a β-ketosilane to the isomeric siloxyalkene. The second type of data come from rearrangements carried out under controlled conditions in sealed tubes, whereby the reactions were followed using NMR techniques in order to determine the first order rate constants. In most cases the rates were measured at several temperatures over a twenty to twenty-five degree range in order that E_{act} and $\Delta S^{\ddagger}$ could be determined. These data are given in Table 2 together with the standard deviations for E_{act} and $\Delta S^{\ddagger}$. The rates were calculated for each compound at 150°, by interpolation or extrapolation and relative rates of rearrangement were thereby established.

Finally, Table 3 contains rate data for a series of *p*-substituted triphenylsilylacetophenones. A plot of these data vs. σ_p gives a good straight line through the points for the *p*-Br, Cl, H and t-Bu compounds and a value for ρ of −0.78. The points for *p*-fluoro and *p*-methoxy fell somewhat off this line.

Discussion

It is clear from the data in Tables 1 and 2 that the rearrangement of β-ketosilanes can be effected relatively readily and cleanly regardless of structural features (acyclic or cyclic) or substitution (acyl or alkyl substituents). The kinetic data showed in every case good first order kinetics over several half lives. Great care was taken to ensure the absence of catalysts in the system, since Lutsenko, Baukov and Litvinova [2] had reported catalysis (and hence bimolecular kinetics) of comparable rearrangements by mercuric iodide or silyl iodides. Subsequently the authors also observed [3] thermal uncatalyzed rearrangements similar to those reported by us.

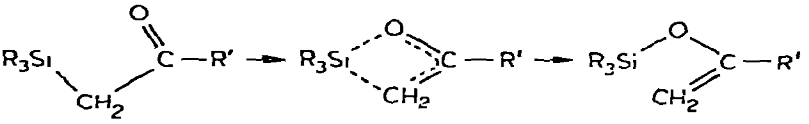
The kinetic data in Table 2 reveal some variation in ease of rearrangement depending on structural features. Thus benzoyl compounds [PhC(O)—] rearrange rather more readily than their acetyl [$CH_3C(O)$—] analogs, substitution of phenyl by methyl raising E_{act} by 3.5 to 4 kcal/mol for the two comparable pairs of compounds. On the other hand, changing the substituents on silicon has the opposite effect, and trimethylsilyl compounds have E_{act} about 2 kcal/mol lower than their triphenylsilyl analogs. This latter effect might reasonably be associated with increased steric requirements of a triphenylsilyl group compared to a trimethylsilyl group; the former effect may be associated with increased stabilization of a partially polarized carbonyl group by an adjacent aromatic ring (but see later). Cyclic β-ketosilanes have the largest E_{act} and rearrange most slowly of the β-ketosilanes studied, presumably because of unfavourable steric interactions in the transition state, attributable to non-bonded interactions of eclipsed hydrogens or bond angle strain.

The values of $\Delta S^{\ddagger}$, believed to be accurate to about 1-2 eV (see Table 2) are all negative, and of a magnitude consistent with the previously proposed four-centre transition state [1]. Within the possible limits of comparisons, trimethylsilyl compounds have significantly larger $\Delta S^{\ddagger}$ (−16.9, −9.8 cal/mol · K for benzoyl and acetyl species respectively) than do the corresponding triphenylsilyl compounds (−7.3, −4.2 cal/mol · K respectively). This may simply reflect that a somewhat sterically crowded and ordered situation already exists in the triphenylsilyl species, compared to the trimethylsilyl analogs where more ordering takes place in achieving the transition state geometry required.

The effect of solvent on the rate of rearrangement was briefly investigated. Triphenylsilylacetophenone rearranged at the same rates in toluene or in decalin, solvents having a small difference in dielectric constant, and the *p*-methoxy derivative rearranged at virtually identical rates in toluene or as a melt, and at a slightly slower rate in the very polar solvent dimethyl formamide. This apparent insensitivity of the reaction to the polarity of the solvent indicates that there is little solvation of the transition state and little development of charge separation in going from reactants to transition state.

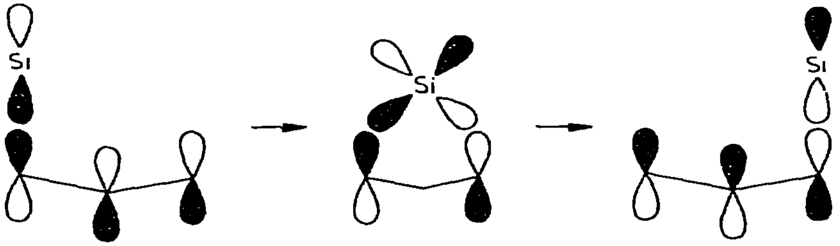
This conclusion is confirmed by the rate data in Table 3 for a series of *p*-substituted triphenylsilylacetophenones where a log k vs. σ_p plot gives a Hammett ρ value of −0.78. While the sign of ρ is consistent with some development of positive charge on the carbonyl carbon during the formation of the transition state, (which can be stabilized better by adjacent phenyl groups than methyl groups, thus lowering the E_{act}) the very small magnitude of ρ indicates relative insensitivity of the reaction to electronic effects.

All of the preceding data are fully consistent with, and indicative of, an intramolecular concerted rearrangement involving a four-centre transition state:



where silicon—oxygen bond formation cannot significantly precede silicon—carbon bond breaking to be consistent with the observed ρ.

That the rearrangement occurs with exclusive retention of configuration at silicon is of some theoretical importance since a 1,3 suprafacial migration should take place with inversion of configuration, according to the Woodward—Hoffmann rules [4]. Accordingly, a molecular orbital study of the rearrangement of the model compounds silylacetaldehyde to vinyloxysilane was carried out in the hope of providing further information about the rearrangement of β-ketosilanes. Calculations using CNDO/2 were made for the aldehyde, alkene and several intermediate species with geometries appropriate to both retention and inversion of configuration at silicon. The data suggested that retention of configuration at silicon was the preferred pathway, when a *d* function was included in the basis set for silicon. Zimmerman [5], in analyzing the 1,3 sigmatropic shift of a hydrogen atom (equivalent to migration with retention of configuration), by MO following, showed that if subjacent orbital overlap was included, a correlation diagram could be constructed in which the MO's of ground state reactants and products correlated directly. The reaction remains forbidden, however, since the HOMO of the reactant (π) is transformed into a non-bonding MO at half reaction (an orbital equivalent to the HOMO of an allyl anion) thus creating an energy barrier to reaction. The orbital correlation scheme obtained from our calculations for retention of configuration at silicon was almost identical to the following MO scheme for hydrogen migration, with the exception that the barrier to reaction was dramatically lowered by overlap of the termini of the allyl NBMO with the d_{xz} and d_{yz} orbitals on silicon, as shown below.



β-ketosilane HOMO — half reaction HOMO — siloxyalkene HOMO

Thus the least-motion pathway is favoured over the formally allowed route.

The calculations also confirm that there is very little change in charge distribution over the molecule at various geometries along the reaction profile, up to half-reaction. The electron density on the carbonyl carbon at half-reaction is slightly lower than in the aldehyde and is unchanged on the silicon atom. The dipole moment is very slightly lower at half-reaction. This is consistent with a negligible solvent effect on the rate and a small positive value for ρ when there is substitution at the carbonyl carbon atom. The electronic effect of substitution at the silicon atom is predicted to be negligible. A full account of the theory of sigmatropic reactions of organosilicon compounds will be presented in a forthcoming paper*.

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* Manuscript in preparation. A paper on the orbital symmetry considerations of organosilicon compounds was presented by one of us (A.R.B.) to the Symposium on Recent Advances in Orbital Symmetry Relationships at the 57th Canadian Chemical Conference, CIC, Regina, Sask., Canada, June 2-5th, 1974.

Experimental

General

All solvents were carefully dried before use in the kinetic studies. The β-ketosilanes were purified immediately prior to use, by recrystallization or distillation where appropriate.

Temperatures were measured to the nearest 0.1°C.

Procedure

The general procedure used for obtaining the rate data for the thermal rearrangement of β-ketosilanes to their isomeric siloxyalkenes was as follows:

A solution of approximately 1 g of the ketone was prepared in about 10-12 ml of dry solvent. Aliquots of 1 ml were sealed in glass vials. For those compounds which were rearranged in the absence of a solvent, approximately 100 mg of material was sealed in each glass vial. Usually ten to twelve samples were prepared. At $t = 0$ all but one of the samples were placed together in the oil bath and the clock started. At specified time intervals, a vial was withdrawn from the bath and chilled in ice-water to stop the reaction. The products were analysed by NMR spectroscopy as follows.

At least 5 or 6 scans were made of each peak to obtain an average value for the peak height. In those cases where a solvent such as toluene was used, the peak height of the solvent could be used to calibrate the instrument response. One, or in some cases two, of three methods were used for following the progress of the rearrangement.

(i) Use of the heights of peaks characteristic of the starting β-ketosilanes. This method was used for all of the substituted triphenylsilylacetophenones whose peak positions are listed in Table 4 .

In all compounds except the *p*-methoxy-substituted silylacetophenone, the methylene singlet was used as a measure of the concentration of the β-ketosilane.

In the latter case the peak position of the methoxy group in the isomeric siloxyalkene coincided with that of the methylene protons when toluene was used as the solvent. Thus the methoxy peak of the β-ketosilane was used to follow the rearrangement of this compound in toluene.

The logarithms of the peak heights were plotted against time to obtain the first order rate constant.

TABLE 4

NMR DATA FOR $Ph_3SiCH_2CO(C_6H_4)$-*p*-X (δ ppm FROM TMS)

p-X	CDCl₃		Toluene	
	—CH₂—	*p*-X	—CH₂—	*p*-X
Br	3.45		3.20	
Cl	3.42		3.22	
F	3.46		3.20	
H	3.48		3.30	
t-Bu	3.52	1.27	3.38	1.15
OMe	3.40	3.72	3.35	3.24

(ii) Use of the heights of peaks characteristic of both ketone and siloxyalkene. In some cases both the starting material and product gave rise to sharp singlet NMR signals which enabled the course of the reaction to be followed in terms of the ketone and siloxyalkene simultaneously. The compounds for which this was the case are listed below.

$$Ph_3SiCH_2COC_6H_4\text{-}p\text{-}t\text{-}\underline{Bu} \longrightarrow Ph_3SiOC(C_6H_4\text{-}p\text{-}t\text{-}\underline{Bu})=CH_2$$

$$\underline{Me}_3SiCH_2COPh \longrightarrow \underline{Me}_3SiOC(Ph)=CH_2$$

$$\underline{Me}_3SiCH_2COMe \longrightarrow \underline{Me}_3SiOC(Me)=CH_2$$

As an example, the rearrangement of the t-Bu-substituted silylacetophenone in addition to being followed by method (i) could also be followed by observing the t-Bu signals. The t-Bu-signal for the siloxyalkene was observed at a position 4.5 Hz downfield (δ 1.22 ppm) from that of the t-Bu in the β-ketosilane.

Similarly the compounds containing silicon-methyl groups gave rise to sharp singlets in the δ0.0 ppm region which were separated by 4-12 Hz and therefore were useful for following the reaction.

The logarithms of the percentages of ketone in the mixtures were plotted to obtain the first order rate constants.

(iii) Integration of peak areas. When β-ketosilanes were rearranged as a melt, and the product mixtures were subsequently dissolved in deuterochloroform for the purpose of following the reaction by NMR, it was difficult to assure that the total concentration of material was the same for each sample. Therefore it was imperative that the ratio of ketone and siloxyalkene be measured in each case. In the compounds listed in Table 5 the peaks characteristic of either the ketone or siloxyalkene were not sharp singlets and therefore not suitable for use by method (ii). In these cases the peak areas were integrated.

Compounds and syntheses

All the β-ketosilanes employed were obtained by treatment of appropriate

TABLE 5

β-KETOSILANES USED IN METHOD (iii)

Compound	δ(ppm) (CDCl$_3$)
$Ph_3SiC\underline{H}_2CO(C_6H_4)\text{-}p\text{-}OMe$	3.40 s (2H); 3.72 s (3H)
$Ph_3SiOC(C_6H_4)\text{-}p\text{-}O\underline{Me})=C\underline{H}_2$	4.30, 4.71, 2 d, J = 2.0 Hz; 3.67 s (3H)
$Ph_3SiCH_2CO\underline{Me}$	1.65 s
$Ph_3SiOC(\underline{Me}) = CH_2$	1.80 s (slightly broadened)
$Ph_3SiC\underline{H}_2CHO$	2.98 d J = 4.2 Hz
$Ph_3SiO\overline{C}(H)=C\underline{H}_2$	4.15, 4.58 m

acylsilanes with diazomethane in the presence of light [6]. Full synthetic details, spectroscopic data etc., will be reported in a paper now in preparation.

Siloxyalkenes obtained from the thermolyses were identified by comparison with authentic samples synthesized by the general method of Kruger and Rochow [7].

Triphenylsilylacetaldehyde

Since difficulty was experienced in reproducing the published yields of this compound [8], the conditions were modified as follows. A 50 ml benzene solution of 3.0 g (0.01 mol) of epoxyethyltriphenylsilane was treated with approximately 1 ml of magnesium bromide diethyl etherate [9]. After reflux for 5 h, an equal volume of ether was added to the cooled mixture, and this was quickly shaken with cold saturated ammonium chloride solution. The benzene—ether layer was dried ($MgSO_4$) and removal of the solvents under reduced pressure gave an oil which yielded 1.87 g (60%) of triphenylsilylacetaldehyde, m.p. 114-116°, lit.[8] 115-116°, on recrystallization from hexane. The IR and NMR spectra were identical with the published data.

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