The Thermal Rearrangement of α-Substituted Silanes

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The thermal rearrangement of α-substituted silanes ($R_3SiCHXR'$), in which there is exchange of X and R between the silicon atom and the adjacent carbon atom, has been studied. Kinetic parameters for two compounds ($Me_3SiCBrPh_2$ and $Ph_3SiCHOAcPh$) have been measured. Migratory aptitudes of both X and R have been examined. A mechanism involving initial migration of X to silicon, to form an "inverse ylid" ($R_3\bar{S}iX—\overset{+}{C}HR'$) is proposed.

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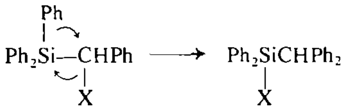
On a étudié le réarrangement thermique de silanes α-substitués ($R_3SiCHXR'$) dans lesquels il y a un échange de X et de R entre l'atome de silicium et l'atome de carbone adjacent. On a mesuré les paramètres cinétiques pour la réaction de deux composés le ($Me_3SiCBrPh_2$ et $Ph_3SiCHOAcPh$). On a examiné les aptitudes migratrices des groupes X et R. On propose un mécanisme impliquant une migration initiale du X vers le silicium formant un "ylide inverse" du type ($R_3\bar{S}iX—\overset{+}{C}HR'$).

[Traduit par le journal]

Introduction

We have previously reported, in a brief communication, that certain α-substituted benzyltriphenylsilanes undergo the following thermal rearrangement (1)

[1] 

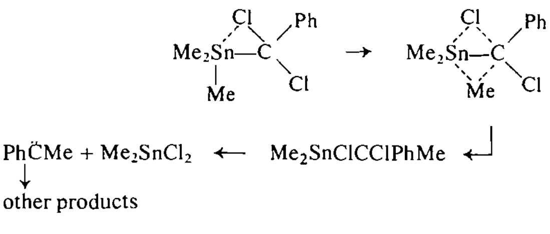
$$Ph_2Si(Ph)—CH(X)Ph \longrightarrow Ph_2Si(X)CHPh_2$$

(X = F, Cl, OAc, OTos)

The present study represents a more detailed examination of this rearrangement together with some extension in its scope.

Other examples of this kind of thermal rearrangement are known. Seyferth and coworker (2) reported that dimethyldichlorostannane was one of the products of the thermolysis of trimethyl(α,α-dichlorobenzyl)tin at 150° in cyclohexene. The reaction course proposed was

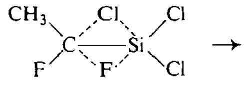
[2] $Me_3SnCCl_2Ph \rightarrow$



$$Ph\ddot{C}Me + Me_2SnCl_2 \longleftarrow Me_2SnClCClPhMe$$

other products

Haszeldine and co-workers (3, 4) have described a similar rearrangement involving halogen exchange between the adjacent carbon and silicon atoms

[3] $CH_3CF_2SiCl_3 \rightarrow$ 

$CH_3CClFSiFCl_2$
↓
$CH_3CCl_2SiF_2Cl$

which they considered to involve a cyclic transition state of the type shown. Such a doubly-bridged transition state is of the type encountered in a symmetry-allowed, type-I dyotropic rearrangement (5); however, at present there is no unambiguous mechanistic evidence for a simultaneous double σ-shift. It was, therefore, of considerable importance to determine the activation parameters E_a, $\Delta S^{\ddagger}$, and A for the thermal rearrangement of these α-substituted silanes and we have measured these for two representative examples. As an additional aid to the interpretation of the mechanism the relative migratory aptitudes of a variety of groups on both silicon and the α-carbon have been studied.

Results and Discussion

A series of α-substituted silanes, $R_3SiCHXR'$ (R = Ph, Me; X = F, Cl, Br, OTos, OAc;

TABLE 1. Thermal rearrangement of α-substituted silanes

Starting material	Product	Yield*	Temperature	Time (min)
$Ph_3SiCHFPh$	$Ph_2SiFCHPh_2$	100	145	6
$Ph_3SiCHOTosPh$	$Ph_2SiOTosCHPh_2$	100	150	10
		17	145	6
$Ph_3SiCHOAcPh$	$Ph_2SiOAcCHPh_2$	100	255	60
		58	230	60
		8	200	60
Ph_3SiCH_2OAc	$Ph_2SiOAcCH_2Ph$	33	254	60
		37	277	60
		0	200	60
$Ph_3SiCHCH_3OAc$	$Ph_2SiOAcCHCH_3Ph$	100	277	60
$Ph_3SiCHClPh$	$Ph_2SiClCHPh_2$	45	253	52
$Ph_3SiCHBrPh$	$Ph_2SiBrCHPh_2$	24	250	60
		23	230	270
Ph_3SiCH_2Cl	$Ph_2SiClCH_2Ph$	16	330	65
$Ph_3GeCHClPh$	$Ph_2GeClCHPh_2$	25	285	90
$Me_3SiCBrPh_2$	$Me_2SiBrCMePh_2$	100	220	27
$Et_3SiCBrPh_2$	$Et_2SiBrCEtPh_2$	100	220	2
$Ph_3SiCBrPh_2$	$Ph_2SiBrCPh_3$	95†	240	30
$Ph_2MeSiCBrPh_2$	$PhMeBrSiCPh_3$	100	240	30

*By n.m.r.
†Isolated product.

R′ = Ph, Me, H), $R_3SiCBrPh_2$ (R = Ph, Me, Et) and chlorobenzyltriphenylgermane were heated in sealed, flame dried Pyrex ampoules under a variety of conditions. The products obtained, the conditions, and the extent of reaction are given in Table 1. The reactions observed are summarized below

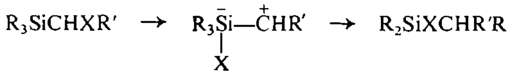
[4] $R_3SiCHXR' \rightarrow R_2SiXCHRR'$

[5] $R_3SiCBrPh_2 \rightarrow R_2SiBrCPh_2R$

[6] $Ph_3GeCHClPh \rightarrow Ph_2GeClCHPh_2$

The kinetics of the rearrangement of bromobenzyhydryltrimethylsilane (**1**) and acetoxybenzyltriphenylsilane (**2**) were studied. Both reactions were first-order in reactant to at least 90% completion.

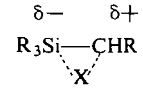
The results, as shown in Table 2, are inconsistent with a highly-ordered doubly-bridged transition state which would be expected to have a very large, negative $\Delta S^{\ddagger}$. The near-zero value of $\Delta S^{\ddagger}$ (−1.3 e.u.) for **1** is indicative of a relatively open transition state. Thus, the results in Table 1 are consistent with and strongly support the following mechanism

[7] 

$$R_3SiCHXR' \rightarrow R_3\underset{X}{\overset{-}{Si}}\text{—}\overset{+}{C}HR' \rightarrow R_2SiXCHR'R$$

3

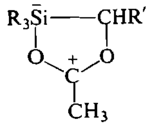
The “inverse ylid”, **3**, may be either a transition state or a discrete intermediate but our results do not allow a distinction to be made. However, the first, and rate-determining, step indicated by the study of relative migratory aptitudes appears to be the formation of the “inverse ylid” by migration of X from carbon to silicon. The transition state for this step should resemble a singly-bridged species, **4**,



$$\overset{\delta-}{R_3Si}\text{—}\overset{\delta+}{CHR}\ \ (\cdots X \cdots)$$

4

with a considerably less negative value of $\Delta S^{\ddagger}$ than expected for a doubly-bridged transition state. An acetoxy group, unlike a bromine atom, should migrate through a five-centered species, **5**,



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and the value of −20 e.u. for $\Delta S^{\ddagger}$ for **2** is consistent with this interpretation. With this alternative mode of migration the rearrangement of **2** relative to **1** should have a lower activation

TABLE 2. Kinetic data for the thermal rearrangement of bromobenzhydryltrimethylsilane and acetoxybenzyltriphenylsilane

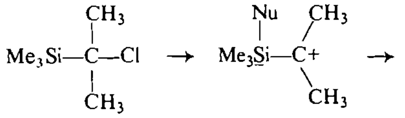
T (°C)	$k_1 \times 10^3$ (min^{-1})	E_A (kcal mol^{-1})	$\Delta S^{\ddagger}$ *(e.u.)	$\log_{10} A$ (s)
$Me_3SiCBrPh_2$				
164	1.44 ± 0.14	37 ± 3	− 1.3 ± 3	13.9
184	7.61 ± 0.5			
200	30.3 ± 1.0			
220	185 ± 15			
$Ph_3SiCHOAcPh$				
210	5.9 ± 0.4	30 ± 3	−20 ± 4	9.1
220	10.6 ± 1			
230	19 ± 1			
242	41.8 ± 0.4			

*500 °K.

energy, a more negative $\Delta S^{\ddagger}$ and a smaller A value. These trends are clearly illustrated by the data in Table 2, where comparison shows lowering of the activation energy from 37 to 30 kcal mol^{-1}, change of $\Delta S^{\ddagger}$ from -1.3 to -20 e.u., and lowering $\log_{10} A$ from 13.9 to 9.1, for **2** relative to **1**. The comparison must be qualitative rather than quantitative since R and R′ differ in the two compounds but the kinetic parameters indicate that a dyotropic mechanism is most unlikely, and the transition state is not significantly bridged but resembles the "inverse ylid" **3**.

Recently O'Brien and co-worker (6) have obtained good kinetic evidence for the intermediacy of an "inverse ylid" in the SbF_5-catalyzed rearrangement of 2-chloro-2-trimethylsilylpropane

[8]



Products (Nu = nucleophile)

This is, of course, the catalyzed equivalent of the present rearrangement and is well known in organosilicon chemistry. The aluminum chloride catalyzed isomerization of (chloromethyl)trimethylsilane to chlorodimethylethylsilane was reported by Sommer and co-workers in 1947 (7).

Based on the results given in Table 1 the relative ease of migration of X from carbon to silicon appears to decrease in the following order: F > OTos > OAc > Cl > Br ≫ OMe. This coincides with the expected order of stabilization of a penta-coordinated silicon atom, based on bond energies, and the electronegativities of X, with the exception that since alkoxy compounds do not thermally rearrange, other factors not yet fully understood must be involved at least in these cases.

The ease of migration of R from silicon to carbon decreased in the order Ph > Me, Et. Thus bromobenzhydryldiphenylmethylsilane on heating rearranged to triphenylmethylphenylmethylbromosilane as a result of exclusive phenyl migration

$$[9] \qquad Ph_2MeSiCBrPh_2 \rightarrow PhMeSiBrCPh_3$$

After 1 h at 253° a sample of bromobenzyltrimethylsilane contained no 1-phenylethyldimethylbromosilane (although the n.m.r. spectrum did show a substantial amount of benzyltrimethylsilane, presumably due to redistribution[1]). Under the same conditions bromobenzyltriphenylsilane rearranged to benzhydryldiphenylbromosilane to the extent of 30%. (Redistribution products were also present.) The migration of a phenyl group to a carbonium ion center is generally faster than alkyl migration (8). If the inverse ylid was a true intermediate formed in the rate determining step then the rate of

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[1] The rate of rearrangement of α-bromo compounds was difficult to duplicate. In addition they sometimes underwent redistribution reactions concurrently with rearrangement, according to the reaction

$$R_3SiCHBrR' \rightarrow R_2SiBrCHRR' + R_3SiCH_2R' + R_3SiCBr_2R'$$

The extent of redistribution was variable and may have been catalyzed by traces of unknown impurities. However, a sample of bromobenzyltriphenylsilane containing 5% by weight of dibenzoyl peroxide rearranged at the same rate to give the same product mixture as a sample without added peroxide. Therefore, free radical intermediates in either rearrangement or redistribution reactions appear unlikely.

migration of R from silicon to carbon would be relatively fast and should not affect the overall reaction rate. Therefore the reactivity series observed does not necessarily reflect migratory aptitudes of aliphatic and aromatic moieties, but rather the ability of R to stabilize the ylid through delocalization of the positive charge on the carbon atom.

With changes in R′ the ease of rearrangement decreases in the order Ph > Me > H. This order is consistent with a build up of positive charge on the α-carbon and reflects the ability of the groups to stabilize a carbonium ion.

Finally it was observed that α-chlorobenzyltriphenylsilane rearranged faster than the analogous germanium compound. This probably reflects the greater bond energy of Si—X compounds and the lower energy of the silicon d orbitals.

As a further test of the proposed mechanism equimolar solutions of α-fluorobenzyltriphenysilane (**6**) in $CDCl_3$ and DMSO-d_6 were heated to 140° for $4\frac{1}{2}$ h. The solution in DMSO-d_6 was 32% rearranged to benzhydryldiphenylfluorosilane (**7**), the remaining material being unreacted **6**. The solution in $CDCl_3$ contained only unreacted **6**. The faster reaction in polar solvents is evidence of substantial charge separation in the transition state.

In summary, the available evidence strongly supports the open-chain mechanism for rearrangement of α-substituted silanes, where Si—X bond formation is significantly developed in the transition state. The transition state thus resembles an inverse ylid.

Experimental

Experiments involving reactive organometallic reagents were carried out under nitrogen using dried, purified solvents. Infrared spectra were recorded on a Perkin–Elmer 237B instrument. Nuclear magnetic resonance spectra were determined using Varian T-60 or A-60 spectrometers. Melting points were measured on a Fisher–Johns apparatus and are recorded uncorrected. Analyses were carried out by A. B. Gygli, Toronto.

Preparation of Starting Materials

Known compounds were prepared by the standard literature preparations. All benzyltriphenylsilyl derivatives were prepared by the action of HX on phenyltriphenylsilydiazomethane (1). The general method is given below and the results of individual preparations are given in Table 3.

The experimental procedure was as follows. A solution of diazoalkane and excess acid in an organic solvent was allowed to stand at ambient temperature, in the dark, until the color of the diazoalkane was completely discharged. With HCl the gas was bubbled through the reaction mixture until decolorization occurred. The workup procedure involved washing the reaction mixture several times with water, drying the organic layer over $MgSO_4$, removing the solvent on a rotary evaporator, and then recrystallizing the product. Reaction conditions and other information are given in Table 3. The n.m.r. spectra of starting materials and products are shown in Table 4.

Rearrangement Studies

Samples of the α-substituted silanes were sealed in carefully flame-dried Pyrex ampoules which were then immersed in an oil bath. After a given time, the sample was removed and the contents analyzed. The results are given in Table 1.

Synthesis of Previously Unknown Rearrangement Products

Acetoxybenzhydryltriphenylsilane

A mixture of benzhydryldiphenylchlorosilane (5 g, 13 mmol) and silver acetate (2.16 g, 13 mmol) in benzene (50 ml) was stirred for 16 h at ambient temperature, filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from pentane to yield acetoxybenzhydryldiphenylchlorosilane 2.55 g (48%), m.p. 113–115°.

Anal. Calcd. for $C_{27}H_{24}O_2Si$: C, 79.37; H, 5.92. Found: C, 79.70; H, 6.03.

Tosyloxybenzhydryldiphenylsilane

A mixture of benzhydryldiphenylchlorosilane (5 g, 13 mmol) and silver tosylate (3.62 g, 13 mmol) in benzene (50 ml) was stirred for 16 h at ambient temperature, filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from pentane to afford tosyloxybenzhydryldiphenylsilane 2.65 g (40%), m.p. 162–163°.

Anal. Calcd. for $C_{33}H_{28}O_3SSi$: C, 74.40; H, 5.30. Found: C, 74.27; H, 5.49.

(Triphenylmethyl)diphenylbromosilane

Bromobenzhydryltriphenylsilane (4 g, 7.9 mmol) was sealed in a glass ampoule and heated at 240° for 1 h. A black solid was obtained which was dissolved in benzene, clarified with activated charcoal, and recrystallized from hexane to yield pure (triphenylmethyl)diphenylbromosilane, m.p. 214–215°.

Anal. Calcd. for $C_{31}H_{25}BrSi$: C, 73.64; H, 5.05; Br, 15.81. Found: C, 73.51; H, 4.98; Br, 15.83.

(Triphenylmethyl)phenylmethylbromosilane

Bromobenzhydryldiphenylmethylsilane (4 g, 9 mmol) was sealed in a glass ampoule and heated at 240° for 1 h. The brown solid obtained was dissolved in benzene, clarified with activated charcoal, and recrystallized from hexane to afford (triphenylmethyl)phenylmethylbromosilane, m.p. 133–135°.

Anal. Calcd. for $C_{26}H_{33}BrSi$: C, 70.42; H, 5.24; Br, 18.01. Found: C, 70.51; H, 5.12; Br, 17.82.

Methylbenzhydryldimethylbromosilane

Bromobenzhydryltrimethylsilane (2 g) was heated at 240° for 22 h. After this time, the brown liquid was flash-distilled under aspirator pressure in a Kugelröhr apparatus. The resulting clear liquid, methylbenzhydryldimethylbromosilane was analyzed immediately.

TABLE 3. Reaction of Ph_3MCN_2Ph with HX (M = Si, Ge; X = F, Cl, Br, OTos, OAc) at ambient temperature

Diazoalkane	HX	Product	Solvent	Time	Yield (%)	Melting point (°C)	Analytical data (%)			
							Calculated		Found	
							C	H	C	H
Ph_3GeCN_2Ph	HCl	$Ph_3GeCHClPh$	Toluene	1 min	88	131–132*	69.90	4.93	70.14	5.30
Ph_3SiCN_2Ph	HCl	$Ph_3SiCHClPh$	Ether	1 min	94	136–138*§				
Ph_3SiCN_2Ph	HF	$Ph_3SiCHFPh$	Toluene	45 min	82	120–122*	81.49	5.75	81.04	5.93
Ph_3SiCN_2Ph	AcOH	$Ph_3SiCHOAcPh$	AcOH/toluene	90 min	89	154–155†	79.37	5.92	79.71	5.83
Ph_3SiCN_2Ph	TosOH	$Ph_3SiCHOTosPh$	Toluene	15 h	80	138–141‡	73.82	5.42	74.50	5.47
Ph_3SiCN_2Ph	HBr	$Ph_3SiCHBrPh$	Benzene	2 h	92	147–148*§				

*From MeOH.
†From EtOH.
‡From hexane.
§Mixed m.p. with authentic sample undepressed.

TABLE 4. Nuclear magnetic resonance data for α-substituted silanes (δ(CCl_4) p.p.m.)

Compound	Nuclear magnetic resonance data (p.p.m.)			
$Ph_3SiCHPhF$	6.65–7.7	(m,* 20H, aromatic)	6.13	(d, 1H, J_{FH} = 45 Hz, C*H*F)
$Ph_3SiCHPhCl$	6.85–7.75	(m, 20H, aromatic)	4.94	(s, 1H, CHCl)
$Ph_3SiCHPhBr$	7.0 –7.6	(m, 20H, aromatic)	4.88	(s, 1H, CHBr)
$Ph_3SiCHPhOAc$	6.8 –7.5	(m, 20H, aromatic)	6.41	(s, 1H, C*H*OAc) 1.90 (s, 3H, $OCOCH_3$)
$Ph_3SiCHPhOTos$	6.5 –7.5	(m, 24H, aromatic)	6.00	(s, 1H, C*H*OTos) 2.21 (s, 3H, $ArCH_3$)
$Ph_3SiCHPhOMe$	6.8 –7.7	(m, 20H, aromatic)	4.70	(s, 1H, C*H*OCH_3) 3.32 (s, 3H, OCH_3)
Ph_3SiCH_2Cl	7.2 –7.7	(m, 15H, aromatic)	3.43	(s, 2H, CH_2Cl)
Ph_3SiCH_2OAc	7.2 –7.7	(m, 15H, aromatic)	4.48	(s, 2H, C*H*$_2$OAc) 1.89 (s, 3H, $OCOCH_3$)
$Ph_3SiCHMeOAc$	7.2 –7.7	(m, 15H, aromatic)	5.58	(q, 1H, *J* = 7 Hz, C*H*Me) 1.84 (s, 3H, $OCOCH_3$) 1.41 (d, 3H, *J* = 7 Hz CH*Me*)
$Ph_3SiCBrPh_2$	6.6 –7.7	(m, aromatic)		
$Ph_2MeSiCBrPh_2$	7.0 –7.65	(m, 20H, aromatic)	0.76	(s, 3H, CH_3Si)
$Me_3SiCBrPh_2$	7.2 –7.6	(m, 10H, aromatic)	0.71	(s, 9H, CH_3Si)
$Et_3SiCBrPh_2$	7.0 –7.5	(m, 10H, aromatic)	0.90	(broad s, 15H, EtSi)
$Ph_3GeCHClPh$	6.6 –7.7	(m, 20H, aromatic)	5.08	(s, 1H, CHCl)

*It was possible to differentiate between C-phenyl protons and Si-phenyl protons, the former being shielded by *ca.* 0.4 p.p.m. relative to the latter.

TABLE 5. Nuclear magnetic resonance data for the products of rearrangement of α-substituted silanes (δ(CCl_4) p.p.m.)

Compound	Nuclear magnetic resonance data (p.p.m.)			
$Ph_2SiFCHPh_2$	7.1 –7.3	(2 singlets, 20H, aromatic)	4.10	(d, 1H, *J* = 7 Hz $CHPh_2$)
$Ph_2SiClCHPh_2$	7.1 –7.5	(m, 20H, aromatic)	4.25	(s, 1H, $CHPh_2$)
$Ph_2SiBrCHPh_2$	7.1 –7.5	(m, 20H, aromatic)	4.34	(s, 1H, $CHPh_2$)
$Ph_2SiOAcCHPh_2$	7.05–7.5	(m, 20H, aromatic)	4.78	(s, 1H, $CHPh_2$) 1.81 (s, 3H, $OCOCH_3$)
$Ph_2SiOTosCHPh_2$	6.8 –7.5	(m, 24H, aromatic)	4.64	(s, 1H, $CHPh_2$) 2.30 (s, 3H, ArMe)
$Ph_2SiClCH_2Ph$	6.8 –7.7	(m, 15H, aromatic)	2.77	(s, 2H, CH_2Ph)
$Ph_2SiOAcCH_2Ph$	6.7 –7.7	(m, 15H, aromatic)	2.90	(s, 2H, CH_2Ph) 1.97 (s, 3H, $OCOCH_3$)
$Ph_2SiOAcCHMePh$	6.7 –7.7	(m, 15H, aromatic)	3.38	(q, 1H, *J* = 7 Hz CHPh) 1.94 (s, 3H, $OCOCH_3$) 1.41 (d, 3H, *J* = 7 Hz CH*Me*)
$Ph_2SiBrCPh_3$	6.6 –7.7	(m, aromatic)		
$Me_2BrSiCMePh_2$	7.0 –7.33	(m, 10H, aromatic)	1.76	(s, 3H, CCH_3) 0.46 (s, 6H, $SiCH_3$)
$Et_2BrSiCEtPh_2$	7.0 –7.5	(m, 10H, aromatic)	2.33 0.37–1.27	(q, 2H, *J* = 10.5 Hz, C*H*$_2$$CH_3$) (m, 13H, SiEt, CCH_2*C**H*$_3$)
$Ph_2ClGeCHPh_2$	6.6 –7.7	(m, 20H, aromatic)	4.51	(s, 1H, C*H*Ph_2)

Anal. Calcd. for $C_{16}H_{19}BrSi$: C, 60.18; H, 6.00; Br, 25.03. Found: C, 60.33; H, 5.98; Br, 24.82.

Kinetic Studies

In a typical run, ten or more aliquots of the α-substituted silane in sealed tubes were simultaneously immersed in an oil bath whose temperature was constant to within ±1°. The ampoules were removed periodically and the extent of reaction was measured by integration of suitable signals in the n.m.r. spectrum. A plot of log [reagent] *vs.* time gave a good straight line and first order rate constants were obtained with an accuracy of better than ±10%. Several runs were carried out at each temperature. The results are given in Table 2.

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