Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE REARRANGEMENT OF (2-HYDROXYALKYL)SILANES WITH THIONYL CHLORIDE AND PHOSPHOROUS TRIBROMIDE

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(Received April 20th, 1970)

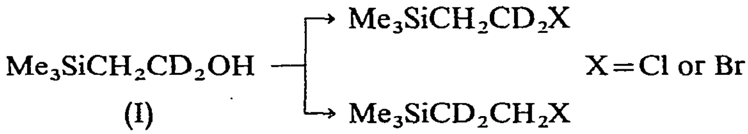
SUMMARY

The addition of phosphorous tribromide or thionyl chloride to compounds of the type $R_3SiCH_2CD_2OH$ (where $R_3 = Me_3$, $PhMe_2$, Ph_2Me or Ph_3) gave rise to approximately the same proportion of the α-deuteriated product $R_3SiCH_2CD_2X$ and the β-deuteriated product $R_3SiCD_2CH_2X$ in all cases. Fragmentation accompanied the rearrangement, the yields of breakdown products R_3SiX, decreased with successive phenyl substitution on silicon and little or no decomposition was observed with (2-hydroxyethyl-2,2-d_2)triphenylsilane, $Ph_3SiCH_2CD_2OH$.

The compounds trimethyl(2-methyl-2-hydroxypropyl)silane ($Me_3SiCH_2CMe_2OH$) and trimethyl(2,2-diphenyl-2-hydroxyethyl)silane ($Me_3SiCH_2CPh_2OH$) did not give the expected products with phosphorous tribromide or thionyl chloride, complete decomposition to trimethylsilyl halide and olefin being observed.

INTRODUCTION

It has been shown previously[1] that rearrangement occurs on addition of thionyl chloride or phosphorous tribromide to the compound (2-hydroxyethyl-2,2-d_2)trimethylsilane (I).



$$\underset{\text{(I)}}{Me_3SiCH_2CD_2OH} \rightarrow \begin{cases} Me_3SiCH_2CD_2X \\ Me_3SiCD_2CH_2X \end{cases} \quad X = Cl \text{ or } Br$$

Fragmentation accompanies the rearrangement,

$$Me_3SiCH_2CH_2OH \xrightarrow[\text{or } SOCl_2]{PBr_3} Me_3SiX + CH_2{=}CH_2 \qquad X = Cl, Br$$

It was proposed that the rearrangement might proceed by the following mechanism:

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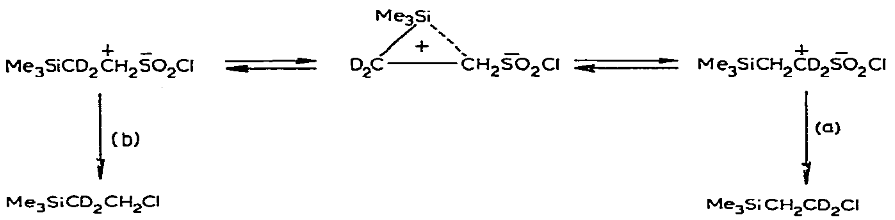


Since rearrangement of this compound was suggested to involve interaction of silicon with the developing positive charge at the β-carbon atom, it was of interest to study the effect of introducing electron-withdrawing groups at the silicon atom. The effect of substituents at the β-carbon atom on the fragmentation/rearrangement ratio was also investigated.

RESULTS AND DISCUSSION

Introduction of phenyl groups at the silicon atom had little effect upon the rearrangement and approximately the same proportion of rearranged and unrearranged products were obtained from the reactions of all the 2-hydroxyethyl compounds, $Ph_nMe_{3-n}SiCH_2CH_2OH$ with both phosphorous tribromide and thionyl chloride.

In contrast, introduction of successive phenyl groups at silicon retards the elimination reaction so that little or no breakdown is oberved for the triphenyl compound. The results are summarised in Table 1.

TABLE 1

PERCENTAGE REARRANGEMENT AND ELIMINATION

Alcohol	$SiCH_2$ (%)	CH_2X (%)	Breakdown (%)	$SiCH_2/CH_2X$
Reaction with thionyl chloride ($X = Cl$)				
$Me_3SiCH_2CD_2OH$	29	27	44	1.07
$Me_2PhSiCH_2CD_2OH$	33	29	38	1.14
$MePh_2SiCH_2CD_2OH$	38	36	26	1.06
$Ph_3SiCH_2CD_2OH$	49	47	4^a	1.05
Reaction with phosphorous tribromide ($X = Br$)				
$Me_3SiCH_2CD_2OH$	30	27	43	1.11
$Me_2PhSiCH_2CD_2OH$	31	28	41	1.11
$MePh_2SiCH_2CD_2OH$	40	36	24	1.11
$Ph_3SiCH_2CD_2OH$	33^b	27^b	0^a	1.22

[a] Determined as the difference between observed and theoretical aromatic intensity. [b] Overlap of integrals at approximately τ 8.0 permitted only approximate calculation, the third peak at τ 8.1 accounted for 40% of the total methylene absorption.

It is generally observed[2] that electron deficiency at a β-carbon atom promotes cleavage of the silicon–carbon bond and the effect of phenyl substituents in stabilising the silicon–carbon bond may be due to the ability of the phenyl rings to delocalise the positive charge transferred to silicon in the carbonium ion and thus prevent a build up of positive charge at silicon. Normally fragmentation and rearrangement do not occur in the same reaction[3] and it is possible that the fragmentation process is a reaction of the (2-haloalkyl)silane products rather than of the carbonium ion intermediates. This proposal seems unlikely since approximately the same yields of elimination products are obtained from the reaction of any one of the silyl alcohols with both thionyl chloride and phosphorous tribromide and it is known[4] that the bromo compounds undergo desilicohalogenation more rapidly than the chloro compounds.

The NMR spectrum of the reaction product from the triphenyl compound and phosphorous tribromide showed in addition to absorptions due to methylene protons adjacent to silicon and bromine, another absorption at τ 8.1. The latter peak was the main one observed in the spectrum immediately after addition of reagents and then decreased with time whilst the other methylene absorptions increased. The peaks assumed a constant ratio after about 60 minutes and remained unchanged even after a period of one week. The mechanism of reaction of alcohols with phosphorous tribromide has been suggested by Gerrard[5] to proceed through the following stages:

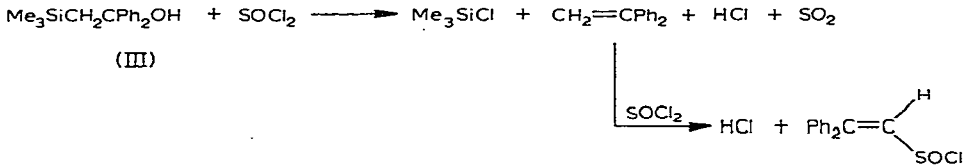
$$\mathrm{ROH + PBr_3 \rightarrow ROPBr_2 + HBr}$$

$$\mathrm{ROH + PBr_3 \rightarrow (RO)_2PBr + HBr}$$

$$\mathrm{ROH + PBr_3 \rightarrow (RO)_3P + HBr}$$

and it seems possible that this additional peak may be due to one of the higher phosphate esters. The presence of phenyl groups on silicon would tend to make this compound more stable then its trimethyl analogue which probably undergoes decomposition relatively quickly.

Reactions of the tertiary alcohols $Me_3SiCH_2CMe_2OH$ (II) and $Me_3SiCH_2CPh_2OH$ (III) were also studied and in contrast to the primary compounds underwent complete elimination. The NMR spectrum of the products from reaction of the carbinol (II) with phosphorous tribromide indicated formation of trimethylbromosilane and tert-butyl bromide. Similarly reaction with thionyl chloride gave a mixture of trimethylchlorosilane and tert-butyl chloride. The compound (III) reacted with phosphorous tribromide to give 1-bromo-1,1-diphenylethane and trimethylbromosilane. Reaction of (III) with thionyl chloride at first appeared irregular but further investigation indicated that decomposition to diphenylethylene had occurred followed by reaction with thionyl chloride in a manner similar to that described by Patai and co-workers[6].



It is possible to explain the greater tendency of the tertiary alcohols to undergo fragmentation rather than rearrangement in terms of steric or electronic effects. Carey and Tremper[7] found that the more highly substituted cyclopropylmethyl cations exhibit a greater tendency to ring open than the less substituted ones and attribute this to interactions between the substituents on the carbonium ion centre and the cyclopropyl group. Similarly interactions between the substituents on the carbonium ion and silyl groups may explain the results obtained with the tertiary compounds. An alternative explanation is that the more branched cations undergo fragmentation rather than rearrangement because the substituents stabilize the incipient double bond of the transition state either by conjugation or hyperconjugation. This argument has previously been suggested to explain why tertiary carbonium ions undergo elimination in preference to substitution in solvolysis reactions[3].

EXPERIMENTAL

IR spectra were recorded using a Perkin–Elmer Infracord 237, and NMR spectra with a Varian Associates A60, Spectrometer. Elemental Analysis of liquid materials was carried out at the Alfred Bernhardt Laboratory (W. Germany). The lithium aluminium deuteride (99% isotopic purity) was obtained from CIBA and the chlorosilanes from Midland Silicones.

Preparation of acetates

The compounds ethyl (trimethylsilyl)acetate, ethyl (diphenylmethylsilyl)-acetate and ethyl (triphenylsilyl)acetate were prepared by the method outlined by Pratt[8] from chlorosilane and ethylbromoacetate.

Ethyl (trimethylsilyl)acetate. Yield 47%; b.p. 74–76°/42 mm; IR (neat liquid): carbonyl absorption 1720 cm^{-1}; NMR (neat liquid); quartet τ 6.1 (intensity 2), singlet τ 8.2 (intensity 2), triplet τ 8.9 (intensity 3), singlet τ 10.0 (intensity 9).

Ethyl (diphenylmethylsilyl)acetate. Yield 62%; b.p. 143–148°/0.1 mm; IR (neat liquid): carbonyl absorption 1720 cm^{-1}; NMR (neat liquid): multiplet τ 2.6 (intensity 10), quartet τ 6.1 (intensity 2), singlet τ 7.6 (intensity 2), triplet τ 9.1 (intensity 3), singlet τ 9.4 (intensity 3). (Found: C, 71.88; H, 7.03; Si, 9.62. $C_{17}H_{20}O_2Si$ calcd.: C, 71.80; H, 7.09; Si, 9.88%.)

Ethyl (triphenylsilyl)acetate. The ethyl (triphenylsilyl)acetate was separated from triphenylsilanol by column chromatography; m.p. 74–76°; IR (KBr disc): carbonyl absorption 1712 cm^{-1}; NMR: multiplet τ 2.5 (intensity 15), quartet τ 6.2 (intensity 2), singlet τ 7.4 (intensity 2), triplet τ 9.1 (intensity 3). (Found: C, 75.50; H, 6.30. $C_{22}H_{22}O_2Si$ calcd.: C, 76.25; H, 6.40%.)

Ethyl (dimethylphenylsilyl)acetate. This was prepared by the method of Gold *et al.*[9]. Reaction of phenylmagnesium bromide and (chloromethyl)dimethylchlorosilane gave (chloromethyl)dimethylphenylsilane in 72% yield; b.p. 87–90°/6 mm (lit.[10] b.p. 106°/15 mm). The Grignard reagent of this compound reacted with ethylchloroformate to give the desired ester in 53% yield distilling at 93–99°/3 mm.

Reduction of esters with $LiAlD_4$

Reduction in diethyl ether as described previously[1] gave the deuterated alcohols.

(2-Hydroxyethyl-2,2-d_2)trimethylsilane. B.p. 68°/30 mm; NMR (neat liquid): singlet τ 5.1 (intensity 2), singlet τ 10.0 (intensity 9). (Found: C, 50.65; H, 11.71; Si, 23.55. $C_5H_{12}D_2OSi$ calcd.: C, 50.01; H, 11.86; Si, 23.35%.)

(2-Hydroxyethyl-2,2-d_2)dimethylphenylsilane. B.p. 96–100°/4 mm; NMR (neat liquid): multiplet τ 2.6 (intensity 5), singlet τ 5.9 (intensity 1), singlet τ 8.8 (intensity 2), singlet τ 9.8 (intensity 6). (Found: C, 66.83; H, 8.72; Si, 15.27. $C_{10}H_{14}D_2OSi$ calcd.:

C, 65.90; H, 8.85; Si, 15.41%.)

(2-Hydroxyethyl-2,2-d_2)diphenylmethylsilane. B.p. 145–8°/0.2 mm; NMR (neat liquid): multiplet τ 2.6 (intensity 10), singlet τ 6.5 (intensity 1), singlet τ 8.6 (intensity 2), singlet τ 9.5 (intensity 3). (Found: C, 74.33;H, 7.47; Si, 11.41. $C_{15}H_{16}D_2OSi$ calcd.: C, 73.77; H, 7.42; Si, 11.49%.)

(2-Hydroxyethyl-2,2-d_2)triphenylsilane. M.p. 97–98°; NMR multiplet τ 2.6 (intensity 15), singlet τ 7.7 (intensity 1), singlet τ 8.3 (intensity 2). (Found: C, 77.85; H, 6.53. $C_{20}H_{18}D_2OSi$ calcd.: C, 78.43; H, 6.54%.)

Trimethyl(2-methyl-2-hydroxypropyl)silane

Reaction of ethyl (trimethylsilyl)acetate and methylmagnesium iodide in ether gave product in low yield; b.p. 85–90°/90 mm (lit.[10] 91–92°/98 mm); NMR (neat liquid): singlet τ 10.0 (intensity 9), singlet τ 9.0 (intensity 2), singlet τ 8.8 (intensity 6), and singlet τ 6.6 (intensity 1). (Found: C, 57.31; H, 12.22. $C_7H_{18}OSi$ calcd.: C, 57.46; H, 12.40%.)

Trimethyl(2,2-diphenyl-2-hydroxyethyl)silane

Reaction of phenylmagnesium bromide and ethyl (trimethylsilyl)acetate gave after 48 h reflux a 37% yield of compound which distilled at 144–148°/0.1–0.2 mm and then solidified. Recrystallisation from light petroleum (b.p. 60–80°) gave a product, m.p. 67–69°; NMR multiplet τ 2.6 (intensity 10), singlet τ 7.8 (intensity 1), singlet τ 8.1 (intensity 2), singlet τ 10.0 (intensity 9). (Found: C, 76.22; H, 8.38. $C_{17}H_{22}OSi$ calcd.: C, 75.54; H, 8.15%.)

Reaction of the alcohols with phosphorous tribromide or thionyl chloride

Phosphorous tribromide or thionyl chloride was added dropwise to the alcohol at 0°, after addition was complete, NMR spectra were recorded at 40°. Normally the relative yields of rearranged and elimination products were determined from the NMR spectra and are summarised in Table 1. For the reaction of thionyl chloride with (2-hydroxyethyl-2,2-d_2)trimethylsilane and (2-hydroxyethyl-2,2-d_2)triphenylsilane the mixture of isomeric products was isolated.

(2-Chloroethyl-2,2-d_2)trimethylsilane + (2-chloroethyl-1,1-d_2)trimethylsilane. B.p. 60°/60 mm; NMR (neat liquid): singlet at τ 6.4 (intensity 1), singlet at τ 8.8 (intensity 1), singlet at τ 10.0 (intensity 9). (Found: titratable Cl, 25.9. $C_5H_{11}D_2ClSi$ calcd.: titratable Cl, 25.6%.)

(2-Chloroethyl-2,2-d_2)triphenylsilane + (2-chloroethyl-1,1-d_2)triphenylsilane. Recrystallisation from light petroleum (b.p. 60–80°) gave a white solid, m.p. 128–130°; NMR singlet τ 2.6 (intensity 15), singlet τ 6.3 (intensity 1), singlet τ 8.0 (intensity 1). (Found: C, 74.50; H, 5.90; Cl, 10.93. $C_{20}H_{17}D_2ClSi$ calcd.: C, 73.96; H, 5.86; Cl, 10.91%.)

Reaction of (2-hydroxyethyl-2,2-d_2)triphenylsilane with phosphorous tribromide

The two reactants were mixed as described previously, after addition was complete the NMR spectrum was examined and absorptions at τ 2.6, 6.4, 7.9 and 8.1 were found. The peak at τ 8.1 decreased with time whilst those at τ 6.5 and 7.9 increased until constant proportions were reached and remained unchanged after 1 week. Calculation showed that the material absorbing at τ 8.1 was present to approximately 38%.

Reaction of trimethyl(2-methyl-2-hydroxypropyl)silane (II) and trimethyl(2,2-diphenyl-2-hydroxyethyl)silane (III) with phosphorous tribomide and thionyl chloride.

Reaction of (II) with phosphorous tribromide gave a mixture whose NMR spectrum showed singlet absorptions at τ 8.2 and 9.5. (Pure samples of tert-butyl bromide and trimethylbromosilane absorbed at τ 8.2 and 9.5 respectively). Reaction of (II) with thionyl chloride gave a mixture of products showing absorptions at τ 8.4 and 9.6. (Pure samples of tert-butyl chloride and trimethylchlorosilane absorbed at τ 8.4 and 9.6 respectively).

Reaction between (III) and phosphorous tribromide gave a mixture whose NMR spectrum showed absorptions at τ 9.5 (trimethylbromosilane CH_3), τ 2.7 (aromatic CH) and τ 7.6 and 4.6. By analogy with the reaction of (II) with phosphorous tribromide these latter two peaks were assigned to 1-bromo-1,1-diphenylethane (methyl protons) and 1,1-diphenylethylene (olefinic CH) peaks respectively. It was shown by calculation[11,12] that these compounds would be expected to absorb at τ 7.6 and 4.5. Similar calculations indicated that these absorptions were not due to the rearranged and unrearranged materials, (1,1-diphenyl-2-bromoethyl)trimethylsilane (CH_2 adjacent to Br 6.0 τ) and (2,2-diphenyl-2-bromoethyl)trimethylsilylane (CH_2 adjacent to Si τ 8.0).

Reaction of (III) with thionyl chloride appeared normal at 0° but on warming to room temperature vigorous gas evolution occurred and the solution turned from yellow to dark brown. Absorptions at τ 2.7 and 9.6 (trimethylchlorosilane CH_3) were observed. Removal of trimethylchlorosilane and excess thionyl chloride under vacuum gave a product showing only complex absorption at τ 2.7. Its IR spectrum was non-superimposable on those of diphenylethylene or *cis/trans* stilbene but indicated a trisubstituted ethylene. Lassaigne tests showed the presence of sulphur and chlorine.

ACKNOWLEDGEMENT

We thank Midland Silicones for the gift of chemicals and one of us (A.J.B.) thanks the Scientific Research Council for a maintenance grant.

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