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NOTE

REARRANGEMENT OF BIS(TRIORGANOSILYL)CARBINOLS

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Recently Brook, LeGrow and MacRae[1] showed that the rate of rearrangement of α-(triorganosilyl)carbinols, $R_3SiCOHR'R''$, was primarily dependent upon the ability of the groups R′ and R″ to stabilize an adjacent carbanion. In an earlier paper

TABLE 1

RATES OF REARRANGEMENT OF SILYL CARBINOLS BY DIETHYLAMINE AT 38°

Compound	Initial carbinol concentration (M)	Base concentration (M)	k_1 (sec^{-1})	k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$)
$Ph_2MeSiCHOHPh$	5.0×10^{-2}	1.94	4.1×10^{-4}	2.1×10^{-4}
	5.1×10^{-2}	0.885	2.0×10^{-4}	2.3×10^{-4}
$(Ph_3Si)_2CHOH$	5.3×10^{-2}	1.94	3.2×10^{-4}	1.6×10^{-4}
	5.4×10^{-2}	0.885	1.3×10^{-4}	1.5×10^{-4}
$(Ph_2MeSi)_2CHOH$	5.3×10^{-2}	1.94	^{a}	
$Ph_3SiCOH(CH_3)_2$	5.3×10^{-2}	1.94	^{a}	

^{a} Too slow to measure.

TABLE 2

RATES OF REARRANGEMENT OF SILYL CARBINOLS BY TMEDA AT 40°

Compound	Initial carbinol concentration (M)	Base concentration (M)	k_1 (sec^{-1})	k_2 ($l \cdot mole^{-1} \cdot sec^{-1}$)
$Ph_3SiC(CH_3)OHPh$	5.2×10^{-2}	1.76×10^{-1}	6.5×10^{-5}	3.7×10^{-4}
	5.2×10^{-2}	8.8×10^{-2}	3.5×10^{-5}	4.0×10^{-4}
	2.6×10^{-2}	8.8×10^{-2}	3.3×10^{-5}	3.7×10^{-4}
$Ph_2MeSiCHOHPh$	5.05×10^{-2}	1.76×10^{-1}	2.2×10^{-6}	1.3×10^{-5}
	5.05×10^{-2}	8.8×10^{-2}	1.2×10^{-6}	1.4×10^{-5}
$(Ph_3Si)_2CHOH$	5.2×10^{-2}	1.76×10^{-1}	5.3×10^{-6}	3.0×10^{-5}
$(Ph_2MeSi)_2CHOH$	5.2×10^{-2}	1.76×10^{-1}	^{a}	
$Ph_3SiCOH(CH_3)_2$	5.2×10^{-2}	1.76×10^{-1}	^{a}	
$Ph_3SiCHOHC(CH_3)_3$	5.2×10^{-2}	1.76×10^{-1}	^{a}	

^{a} Too slow to measure; no rearrangement was observed in 140 h.

Brook, Warner and McGrisken[2] indicated that the rate of rearrangement of 1,1-bis(triphenylsilyl)ethanol was much slower than that of 2-(triphenylsilyl)-2-propanol.

Since there is considerable interest in silicon's ability to interact with adjacent electron rich groups, it seemed valuable to investigate further the effect of the second silicon atom in the rearrangement of bissilylcarbinols.

The rates of rearrangement of three bissilylcarbinols and a number of monosilylcarbinols, with three different bases, were determined by a method analogous to that used by Brook, LeGrow and MacRae[1]. The kinetic results are reported in Tables 1, 2 and 3.

TABLE 3

RATES OF REARRANGEMENT OF SILYL CARBINOLS BY PYRROLIDINE AT 80°

Compound	Initial carbinol concentration (M)	Base concentration (M)	k_1 ($\sec^{-1}$)	k_2 ($\text{l}\cdot\text{mole}^{-1}\cdot\sec^{-1}$)
$Ph_3SiCOH(CH_3)Ph$	5.4×10^{-2}	1.1×10^{-2}	1.3×10^{-2}	1.1
$Ph_2MeSiCHOHPh$	5.1×10^{-2}	3.5×10^{-1}	1.4×10^{-2}	4.0×10^{-2}
	5.1×10^{-2}	9.2×10^{-2}	3.5×10^{-3}	3.8×10^{-2}
$(Ph_3Si)_2CHOH$	5.4×10^{-2}	4.6×10^{-2}	5.2×10^{-3}	1.1×10^{-1}
	5.3×10^{-2}	2.7×10^{-2}	3.0×10^{-3}	1.1×10^{-1}
	5.3×10^{-2}	2.3×10^{-2}	2.6×10^{-3}	1.2×10^{-1}
	2.6×10^{-2}	4.6×10^{-2}	5.4×10^{-3}	1.2×10^{-1}
	2.6×10^{-2}	2.7×10^{-2}	2.7×10^{-3}	1.2×10^{-1}
$(Ph_3Si)_2COHCH_3$	5.4×10^{-2}	4.6×10^{-2}	1.8×10^{-2}	3.9×10^{-1}
	5.3×10^{-2}	2.3×10^{-2}	9.1×10^{-3}	4.0×10^{-1}
	5.4×10^{-2}	1.1×10^{-2}	4.7×10^{-3}	4.3×10^{-1}
$(Ph_2MeSi)_2CHOH$	5.2×10^{-2}	6.8×10^{-1}	6.9×10^{-4}	1.0×10^{-3}
$Ph_3SiCOH(CH_3)_2$	5.2×10^{-2}	6.8×10^{-1}	[a]	
$Ph_3SiCHOHC(CH_3)_3$	5.2×10^{-2}	6.8×10^{-1}	[a]	

[a] Too slow to measure.

Consideration of the pseudo first order rate constants obtained indicates that the second silicon containing group does facilitate the carbinol rearrangement and that a triphenylsilyl group is more effective than a diphenylmethylsilyl group.

Probably steric factors influence the difference in rates of 1,1-bis(triphenylsilyl)ethanol compared to bis(triphenylsilyl)methanol and of bis(triphenylsilyl)methanol compared to bis(diphenylmethylsilyl)methanol. However, it is unlikely that steric factors are the only ones involved since 1-(triphenylsilyl)-2,2-dimethyl-1-propanol, which is a sterically hindered carbinol, showed no rearrangement under the conditions employed.

The inductive effect of a triphenylsilyl group should destabilize an adjacent carbanion by electron release[3-5].

One reasonable method by which a silicon atom could stabilize an adjacent carbanion is by d_π–p_π bonding involving the vacant d orbitals of silicon. Recently Peterson invoked d_π–p_π bonding involving the d orbitals of silicon and an adjacent carbanion to explain the acidity of the protons in tetramethylsilane[6,7]. Although such carbanion stabilization by $3d$ orbital participation has not been extensively studied in the case of silicon compounds, a great deal of work has been done in the cases of phosphorus and of sulfur compounds[6,8].

Thus the facile rearrangement of bissilylcarbinols suggests another system in which d_π–p_π bonding is important*.

EXPERIMENTAL

General

All reactions were performed under an atmosphere of dry nitrogen. Melting points are uncorrected. Elemental analyses were by Galbraith Laboratories, Inc., Knoxville, Tennessee or by Mrs. D. Roberts, Department of Chemistry, University of Alberta, Edmonton. The NMR data was obtained on a Varian Associates A56-60A spectrometer with a variable temperature accessory V4341. DMSO-d_6 was obtained from Merck, Sharp and Dohme of Canada Ltd.

Of the carbinols studied 1,1-bis(triphenylsilyl)ethanol[2], 2-(triphenylsilyl)-2-propanol[12] and 1-(triphenylsilyl)-1-phenylethanol[2] are known and were prepared as previously reported. Bis(triphenylsilyl)methanol and bis(diphenylmethylsilyl)-methanol were prepared in the course of other studies and their preparation will be published shortly in relation to that work[11,13].

(Diphenylmethylsilyl)phenylmethanol was prepared by the lithium aluminium hydride reduction of benzoyldiphenylmethylsilane[14] followed by acid workup. Recrystallization from ethanol gave a solid m.p. 66–67.5°. (Found: C, 78.8; H, 6.55. $C_{20}H_{20}OSi$ calcd.: C, 78.9; H, 6.62%.)

The NMR spectrum (CCl_4) consisted of singlets at τ 5.21, 8.28 and 9.63 ppm and a multiplet from τ 2.4–3.3 ppm with relative areas of 1 : 1 : 3 : 15, respectively. The singlet at τ 8.28 ppm disappeared when deuterium oxide and acid were added.

Similarly, lithium aluminium hydride reduction of pivalyltriphenylsilane gave 1-(triphenylsilyl)-2,2-dimethyl-1-propanol, m.p. 92–94°. (Found: C, 79.4; H, 7.61. $C_{23}H_{26}OSi$ calcd.: C, 79.7; H, 7.56%.)

The NMR spectrum (CCl_4) consisted of singlets at τ 6.10, 8.72, 9.22 ppm and a multiplet from τ 2.3–2.9 ppm with relative areas of 1 : 1 : 9 : 15, respectively. The singlet at τ 8.72 disappeared when deuterium oxide and acid were added.

Kinetic measurements

The method followed was similar to that used by Brook, LeGrow and MacRae[1].

A standard solution of carbinol was filtered and then 0.40 ml aliquots of the filtrate were introduced into NMR tubes. The tubes were sealed with a serum cap and introduced into a constant temperature bath maintained at the same temperature as the NMR probe. After allowing for temperature equilibration the sample was introduced into the NMR probe and its spectrum was checked. The sample was

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* A referee suggested that the carbanion stabilization may be due to a "phenanion" contribution. The evidence for such stabilization in the case of carbon compounds is not extensive and Cram notes[9] that results attributed to "phenanion" contributions may be due to an inductive effect. The failure to observe rearrangement in reactions involving Ph_3SiCH_2X with lithium[10] or sodium[11] also indicates that "phenanion" intermediates are not important.

withdrawn and the base was injected through the serum cap. After mixing, the sample was returned to the probe and the peak or peaks whose decay or growth were to be followed were rapidly scanned (approximately every 10 sec) for several min. If a half-life of about an hour or less was indicated, the sample was left in the probe and scanning was continued. If no change was observed, the sample was returned to the constant temperature bath and scanned every few hours, occasionally for as long as 5 days.

The logarithm of peak height was plotted *versus* time and the pseudo first order rate constant determined by measuring the slope of the line obtained.

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