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DEOXYMETALATION REACTIONS. THE MECHANISMS OF DEOXYSILYLATION OF MONO-TRIMETHYLSILYL- AND BIS-TRIMETHYLSILYL-SUBSTITUTED ALCOHOLS AND A COMPARISON TO THE MECHANISM OF DEOXYSTANNYLATION AND DEOXYPLUMBYLATION

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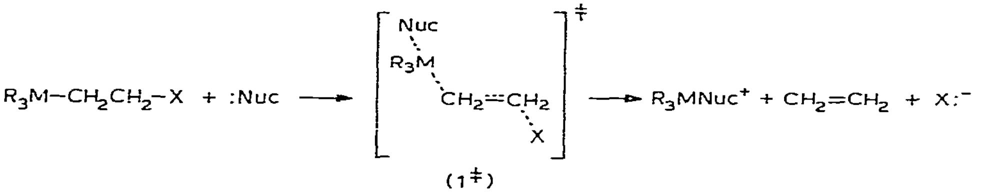
Summary

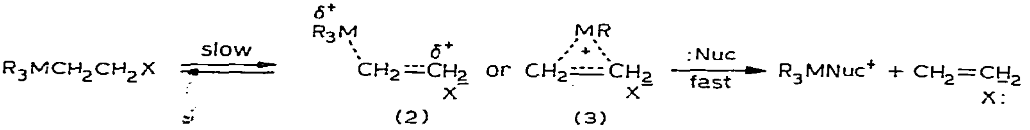
The relative rates of acid-catalyzed deoxysilylation of 2-trimethylsilyl-1-hydroxyethane, 4, 1-trimethylsilyl-2-hydroxypropane, 5, 1,3-bis(trimethylsilyl)-2-hydroxypropane, 6, and 1-trimethylsilyl-2-methyl-2-hydroxypropane, 7, were found to be 1 : $10^{3.30}$: $10^{5.92}$: $10^{6.77}$, respectively, in 9 vol % aqueous-methanol at 40°C. These rates are directly proportional to the sum of the σ^+ constants of the substituents on the carbon bearing the nucleofuge ($\rho^+ = -11$). The additive rate-accelerating effect of two trimethylsilyl groups requires equal conjugative stabilization by each trimethylsilyl group, and a mechanism involving a hyperconjugatively-stabilized carbocation intermediate is proposed. In contrast, the deoxymetalation reactions of the triphenyltin-, triphenyllead-, and iodomercury-analogs exhibit very different structure-reactivity relationships and have been described as proceeding through concerted E_2-like or bridged-ion mechanisms. These mechanistic regimes are reconciled by considering the conjugative interactions, electrofugalities and nucleophilic solvent assistance at the organometal-leaving groups in terms of Thornton's Reacting Bond Rules. This analysis suggests a spectrum of merging mechanisms, the acid-catalyzed deoxysilylation representing one extreme, the E_1M (carbocation intermediate) mechanism and the other Group IV deoxymetalation reactions more nearly concerted E_2M-paths.

Introduction

The mechanisms of the elimination and substitution reactions of β-substituted Group IV organometallics have intrigued chemists since the exceptional reactivity of β-halogenoalkylsilanes, $R_3SiCH_2CH_2X$, was originally noted by Ushakov and Itenberg in 1937 [1]. A review by Jarvie [2] in 1970 dealt exclusively with the "β-silicon effect" and yet, despite the insights provided by Eaborn [3], Traylor [4], Pitt [5] and others [6] a number of questions still remain. These pertain to the concertedness of the reaction and the nature of the intermediates, if any, which may be involved. The reaction of β-halogenoalkyl organometallics with basic reagents, $AlCl_3$ and Grignard reagents [7] leads to elimination products almost exclusively. Under acid catalysis the alcohols, $R_3M{-}CH_2CH_2OH$, also give elimination products [8] although substitution (with rearrangement) [3b] has been noted in the reaction of $(CH_3)_3SiCH_2CH_2OH$ with $SOCl_2$ and PBr_3 [9]. A spectrum of mechanisms has been proposed to account for these results, the limiting types being: an E_2-type reaction with nucleophilic attack at the electrofugal group and concurrent elimination [10], eq. 1; or rate-limiting formation of an intermediate carbonium ion [11] which aside from its classical structure may also claim stabilization from carbon—metal hyperconjugation (vertical stabilization) [4,12] or by bridging, (non-vertical stabilization) [13] eq. 2. The gas-phase and base-promoted reactions require other mechanistic explanations and are not considered here [2].



(1)



(2)

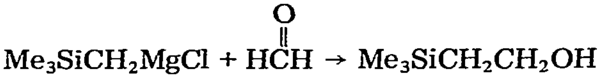
An interesting feature of the structures shown above is the involvement of C—M bond stretching in the transition states for eq. 1 and 2. In the former the organometallic moiety is the leaving group, while in the latter it supplies conjugative stabilization to the intermediate cations. Thus the effect on the reaction of changing the organometallic group should be dependent upon the mechanism and involve both leaving group ability (electrofugality) and conjugative stabilization in $1^{\ddagger}$, but primarily conjugative stabilization of the transition states leading to 2 and 3. In this work we demonstrate that vertical conjugative stabilization by β-$SiMe_3$ groups is the dominant feature in the acid-catalyzed elimination reactions of a series of β-trimethylsilyl alcohols, whereas other additional factors, primarily leaving group abilities, are involved in the elimination reactions of the corresponding β-triphenylstannyl-, β-triphenylplumbyl- and β-iodomercuri-alcohols.

Results

The rates of the acid-catalyzed elimination reactions of a series of β-hydroxyalkylsilanes in 9 vol. % water in methanol were determined at 40°C.

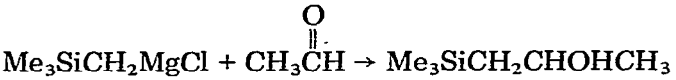
$$Me_3SiCR_2CR_2\text{-}OH \xrightarrow[CH_3OH/H_2O]{H^+} R_2C{=}CR_2 + Me_3SiOH + (Me_3Si)_2O \qquad (3)$$

The series of compounds investigated contained various groups about the carbinol carbon: $\mathrm{Me_3SiCH_2CH_2OH}$ (4), $\mathrm{Me_3SiCH_2CHOHCH_3}$ (5), and $\mathrm{Me_3SiCH_2C(CH_3)_2OH}$ (7), allowed the effects of one trimethylsilyl substituent at the β-position and either, 0, 1, or 2 methyl groups about the carbinol carbon (primary, secondary, and tertiary alcohols) to be studied. A second trimethylsilyl group at the β-position in $\mathrm{(Me_3SiCH_2)_2CHOH}$ (6), enabled the additivity of the effects of the silicon-containing groups to be compared to the effects of the methyl groups. The β-hydroxyalkyltrimethylsilanes were prepared from the Grignard reagent of chloromethyltrimethylsilane and the appropriate carbonyl compound and provided the desired compounds in reasonable yields:



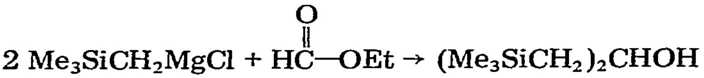
$$\mathrm{Me_3SiCH_2MgCl} + \mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} \rightarrow \mathrm{Me_3SiCH_2CH_2OH} \qquad 37\% \tag{4}$$

(4)



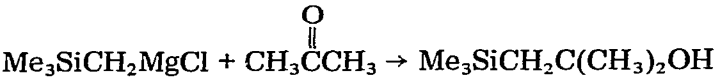
$$\mathrm{Me_3SiCH_2MgCl} + \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{H} \rightarrow \mathrm{Me_3SiCH_2CHOHCH_3} \qquad 24\% \tag{5}$$

(5)



$$2\ \mathrm{Me_3SiCH_2MgCl} + \mathrm{H}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{{-}OEt} \rightarrow \mathrm{(Me_3SiCH_2)_2CHOH} \qquad 42\% \tag{6}$$

(6)



$$\mathrm{Me_3SiCH_2MgCl} + \mathrm{CH_3}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{CH_3} \rightarrow \mathrm{Me_3SiCH_2C(CH_3)_2OH} \qquad 43\% \tag{7}$$

(7)

Kinetic technique

The rates of the acid-catalyzed elimination reactions were determined by monitoring the decay of a characteristic NMR peak of the starting material. The peaks monitored (**4**, triplet, δ 0.94 ppm; **5**, doublet, δ 1.23 ppm; **6**, doublet, δ 0.92 ppm; **7**, singlet, δ 1.29 ppm) were chosen because they were well isolated from other peaks occurring in the spectra of the starting materials, solvents, and products. The reactions are first-order in silane, however the relationship of rate to acidity is not so straightforward. Although the H_0-function for the medium has been established by Eaborn [14], it did not extend over the complete range of acidities studied. Examination of Table 1 reveals that k_ψ ($k_\psi = k_{\mathrm{obs}}/[\mathrm{H}^+]$) shows a steady drift upward for **5** as $[\mathrm{H}^+]$ increases from 0.0562 to 0.446 *M*. From the relationship $\log(k_{\mathrm{obs}}) = \log(k) + (n) \log [\mathrm{H}^+]$ it was found that the rate observed was dependent on $[\mathrm{H}^+]^{1.4}$. This is not surprising since the actual acidity of the medium would not be expected to follow $[\mathrm{H}^+]$ except at very low acid concentrations. In the absence of a useable acidity function, the data are listed with respect to $[\mathrm{H}^+]$. Compounds **6** and **7** were reacted at low acid concentrations and the acidity of the medium was taken as proportional to $[\mathrm{H}^+]$.

The acid-catalyzed elimination of bis-1,3-trimethylsilyl-2-hydroxypropane, **6**,

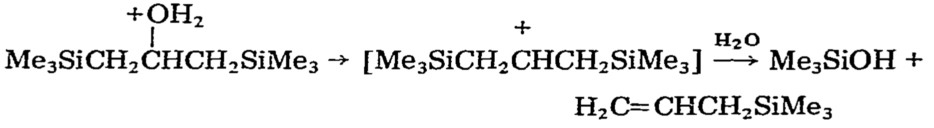
TABLE 1

RATES OF ELIMINATION OF β-HYDROXYALKYLSILANES IN METHANOL CONTAINING 9 VOL % AQUEOUS HCl AT 40°C

Compound	$[H^+]$	k_{obs} (sec^{-1}) [a]	k_ψ, [b] $(M^{-1}\ sec^{-1})$
$(CH_3)_3SiCH_2CH_2OH$	1.11	8.23×10^{-6}	7.40 ± 10^{-6} [d]
(4)			
$(CH_3)_3SiCH_2CH(CH_3)OH$	1.11	(1.66×10^{-2}) [c]	(1.49×10^{-2})
(5)	0.446	4.85×10^{-3}	$1.09 \pm 0.05 \times 10^{-2}$
	0.223	1.57×10^{-3}	$7.04 \pm 0.09 \times 10^{-3}$
	0.112	6.93×10^{-4}	$6.18 \pm 0.01 \times 10^{-3}$
	0.0562	3.16×10^{-4}	$5.63 \pm 0.44 \times 10^{-3}$
	0.011	5.64×10^{-5}	$5.07 \pm 0.10 \times 10^{-3}$
$(CH_3)_3SiCH_2)_2CHOH$	0.0111	2.71×10^{-2}	2.44 ± 0.06
(6)	0.00562	1.21×10^{-2}	2.15 ± 0.09
	0.00281	6.70×10^{-3}	2.38 ± 0.25
	0.00111	2.49×10^{-3}	2.20 ± 0.35
$(CH_3)_3CH_2C(CH_3)_2OH$	0.00281	4.47×10^{-2}	15.9 ± 0.5
(7)	0.00111	1.95×10^{-2}	17.6 ± 0.7
	0.00056	7.66×10^{-3}	13.7 ± 0.4

[a] Average of three kinetic runs. [b] $k_\psi = k_{obs}/[H^+]$. [c] Extrapolated from $\log k_{obs} = \log k + 1.41 \log [H^+]$, highest three acid concentrations used to estimate slope. [d] Errors are deviations from the mean.

should involve the intermediate formation of allyltrimethylsilane, 8. Subsequent addition of H^+ or HCl to the double bond to form the ion $Me_3SiCH_2\overset{+}{C}HCH_3$, of



$$\underset{}{Me_3SiCH_2\overset{\overset{+OH_2}{|}}{C}HCH_2SiMe_3} \rightarrow [Me_3SiCH_2\overset{+}{C}HCH_2SiMe_3] \xrightarrow{H_2O} Me_3SiOH + H_2C{=}CHCH_2SiMe_3 \qquad (8)$$

(8)

the β-chloro compound, would easily lead to a further elimination reaction to form propylene [15]. Propylene was found to be present in 85% yield in the product analysis.

$$H_2C{=}CHCH_2SiMe_3 \xrightarrow{H^+} [H_3C{-}\overset{+}{C}HCH_2SiMe_3] \xrightarrow{H_2O} H_3C{-}CH{=}CH_2 + Me_3SiOH \qquad (9)$$

The rate of elimination of 4 has been determined previously by Sommer [8a] in 50% methanol with 4 M H_2SO_4 at 25°C. A rate constant of 4.04×10^{-3} sec^{-1} was observed. Corrected for acidity, k'_ψ is 5.84×10^{-5} sec^{-1} M^{-1}. This compares favorably with the value reported here, $k'_\psi = 1.25 \times 10^{-5}$ sec^{-1} M^{-1}, ($\log k'_\psi = \log k_{obs} + H_0$) considering the difference in conditions.

Discussion

The relative reactivities of the substituted β-hydroxylaklylsilanes 4—7, listed in Table 2, show great sensitivity to substitution at the carbinol carbon. The α-CH_3/H ratio is $10^{3.3}$, both in the change from primary to secondary alcohol and in the change from secondary to tertiary alcohol. This additivity in substituent effect at the carbinol carbon can be quantitated by considering the sum of the σ^+-values on the carbinol carbon, $\Sigma\sigma^+$. Figure 1 shows this linear free energy relationship in which a ρ^+ of —11.0 is obtained. Two important features of this data need emphasis: a α-CH_3/H ratio of $10^{3.3}$ in this case compared to $10^{4.7}$ for t-butyl/isopropyl chloride in ethanol [16] suggests a similar and high degree of carbonium ion character in the transition state; secondly, the fact that a second $(CH_3)_3SiCH_2$— group results in an increment of rate acceleration, $10^{5.92}$, equal to $\rho^+\sigma^+$, $(-11 \times (-0.54) = 5.94)$, is strong evidence against bridging and favors a vertical conjugative stabilization mechanism. The principle of multiple substitution has been utilized to demonstrate the necessity for bridging in 2-phenethyl systems [17] and to show the lack of bridging, and hence vertical conjugative stabilization, in cyclopropyl-substituted systems [18]. An earlier experiment by Traylor [11] led to a rather puzzling rate acceleration of less than 80 in the relative reactivities of tetraethyltin and bis-1,3-trimethylstannylpropane toward trityl tetrafluoroborate compared to an expected statistical factor of two or a much larger factor ($>10^6$) due to conjugative interaction of a second Me_3Sn— group. The additivity in our work implies either an additive electronic effect (vertical stabilization) or a bridging effect which allows either one or two trimethylsilyl groups to bridge to their full extent. Vertical stabilization is favored because the bridging of two groups simultaneously, 9a, b, would be less sterically favorable and the central carbon would be approaching a six-coordinate structure (including the leaving group).

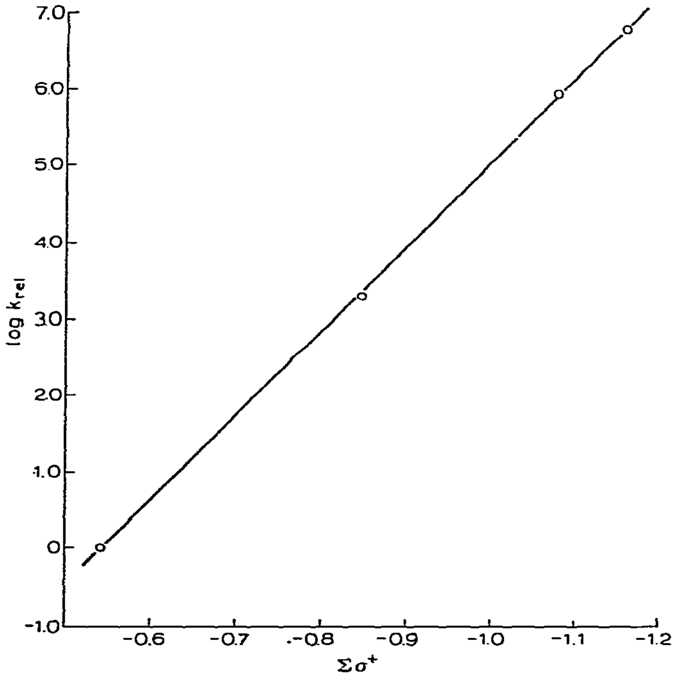
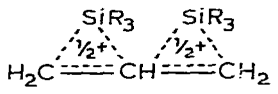
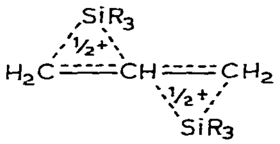


Fig. 1. Hammett plot for the acid-catalyzed elimination of β-Me_3Si-substituted alcohols; $\rho^+ = -11.0$.



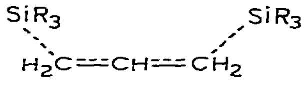
(9a)

or



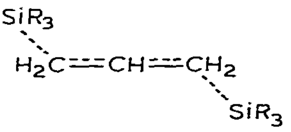
(9b)

The stereoelectronic and coordinative requirements for hyperconjugation of two groups simultaneously, **10a, b**, would not be as unfavorable.



(10a)

or



(10b)

The proportionality of the rate of elimination to $[H^+]$ or H_0 suggests the following general mechanistic scheme:

$$ROH + H^+ \overset{K_{eq}}{\rightleftharpoons} ROH_2^+ \tag{10}$$

$$ROH_2^+ \xrightarrow{k_2} \text{products} \tag{11}$$

for which the observed rate = $k_{obs}[ROH]$. From the above mechanism, the rate of product formation is $k_2[ROH_2^+]$, which then must equal $k_{obs}[ROH]$ since no intermediates of long life were observed.

$$k_{obs}[ROH] = k_2[ROH_2^+] = k_2K_{eq}[H^+][ROH] \tag{12}$$

thus

$$k_{obs} = k_2K_{eq}[H^+] \tag{13}$$

or

$$k_{obs}/[H^+] = k_2K_{eq} = k\psi \tag{14}$$

TABLE 2

RELATIVE RATES OF ELIMINATION OF β-HYDROXYALKYLSILANES IN METHANOL WITH 9 VOL % AQUEOUS HCl AT 40°C

Compound	k_ψ (M^{-1} sec^{-1})		k_ψ(rel)	log $k_\psi$rel	$\Sigma\sigma^+$
$(CH_3)_3SiCH_2CH_2OH$ (4)	7.4×10^{-6}	(4.96×10^{-4})	1.0	0	−0.54
$(CH_3)_3SiCH_2CH(CH_3)OH$ (5)	1.49×10^{-2} [a] $5.36 \pm 0.48 \times 10^{-3}$ [b]	(1.0) 1.0	2.01×10^3	3.30	−0.85
$((CH_3)_3SiCH_2)_2CHOH$ (6)	2.20 ± 0.35	4.1×10^2	8.26×10^5	5.92	−1.08
$(CH_3)_3SiCH_2C(CH_3)_2OH$ (7)	15.8 ± 1.7 [b]	2.9×10^3	5.84×10^6	6.77	−1.16

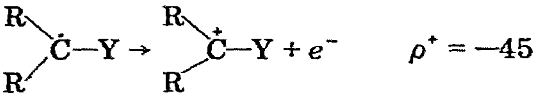
[a] At [HCl] = 1.11. [b] Average of k_ψ between 5.6×10^{-2} and 5.6×10^{-4} M HCl.

since

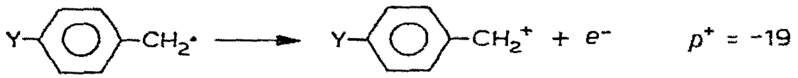
$$K_{eq} = 1/K_a\ ,\ k_2 = k\psi K_a\ . \tag{15}$$

Some of the observed rate differences could be accounted for by a shift in the prior equilibrium. The acidity equilibrium constants, K_a, for this series of alcohols have not been determined, but the method of Levitt and Widing [19] allows an estimate of the relative acidities [20]. The calculated K_a values for the alcohols 4—7 differ by only a factor of three, Table 3, and reconstruction of the linear free energy relationship, $\log k_{rel} = \rho^+(\Sigma\sigma^+)$ using k_2-values instead of k_ψ-values has the effect of lowering ρ^+ to —9.5.

By comparison, gas-phase values of ρ^+ for the ionization potentials of substituted-alkyl [21] and -benzyl [22] radicals are —45 and —19 respectively.

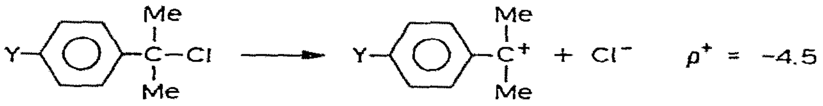


(16)



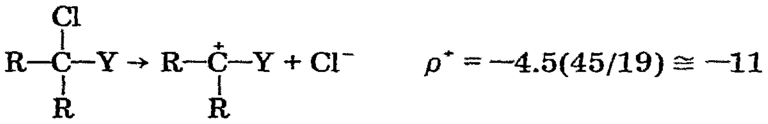
(17)

Solvolysis of p-substituted cumyl chlorides in 90% aq. acetone [22] gives ρ^+ = —4.5.



(18)

If we consider the attenuating effect of a phenyl group to be —19/—45 then an estimate of the ρ^+ for



(19)

$$R-\overset{Cl}{\underset{R}{C}}-Y \rightarrow R-\overset{+}{\underset{R}{C}}-Y + Cl^- \qquad \rho^+ = -4.5(45/19) \cong -11$$

would be ~—11 suggesting that the cationic character in deoxysilylation is very similar to that in the solvolysis reaction in eq. 18. Implicit in the previous argument is the assumption that the effects of methyl- and trimethylsilylmethyl-substitution are relatively scaled to their σ^+-values, —0.31 [23] and —0.54 [24],

TABLE 3

CALCULATED pK_a VALUES OF Me_3SiCH_2-SUBSTITUTED ALCOHOLS

Compound	pK_a	K_a
$Me_3SiCH_2CH_2OH$ (4)	—1.83	67.6
$Me_3SiCH_2CHOHCH_3$ (5)	—1.58	38.0
$(Me_3SiCH_2)_2CHOH$ (6)	—1.44	27.5
$Me_3SiC(CH_3)_2OH$ (7)	—1.33	21.4

respectively, both measured in the defining reaction for σ^+-values. It seems reasonable to accept both of these values as primary substituent constants, however σ^+-values for other Group IV substituents containing Ge, Sn or Pb have not been determined in the defining system and are generally derived from their effect on charge-transfer spectra [25]. In considering the diverse reactants which give these elimination reactions σ^+-constants for R_3MCH_2— and $XHgCH_2$— substituents, where R = CH_3 or C_6H_5: M = Si, Ge, Sn, Pb; X = halo, alkyl, are necessary. We have used σ^+-values based upon the analysis of CT and photophysical data given by Davis [26].

Other deoxymetalations

The rates of elimination of the series of $(CH_3)_3Si$—CH_2-substituted alcohols correspond well with the extent of vertical stabilization as measured by σ^+-values. However the series of triphenylmetal—CH_2-substituted analogs (M = Sn, Pb) and the iodo mercuri-derivatives show a very different response to σ^+ as shown in Table 4 and Figure 2. The rates of elimination of Ph_3Sn-, Ph_3Pb- and IHg-substituted alcohols vary by less than a factor of 25 over a range of $\Sigma\sigma^+$-values of -0.55 to -1.32. Although a rough correlation to σ^+ can be drawn with an approximate ρ^+ of -1.5, this low and probably meaningless value clearly points out that these elimination reactions are being controlled by factors other than vertical stabilization. The —CH_2HgI and —$CH_2Si(Me)_3$ groups have nearly identical σ^+-values [26], yet compounds **16** and **4** differ in reactivity by more than 5 orders of magnitude. We conclude that the reactivities of **11**—**17** are determined only incidentally by vertical stabilization, that they react by a different mechanism and that the major factor in their reactivity is the leaving group ability of the Ph_3M— and IHg— groups. This change in mechanism must be due to the interplay between conjugative stabilization by, and electrofugality

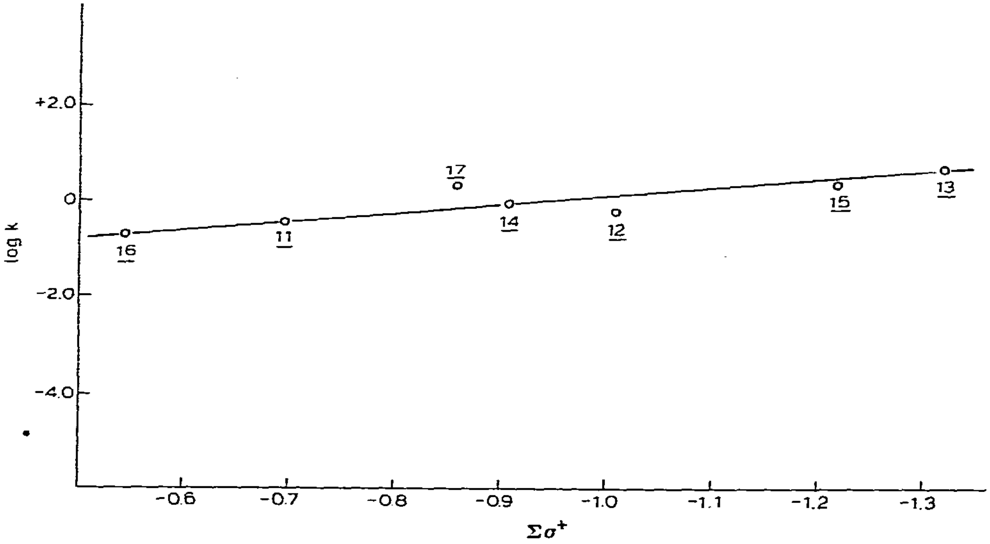


Fig. 2. Hammett plot for the acid-catalyzed elimination of β-organometallic alcohols; slope $\cong -1.5$; numbers refer to compounds listed in Table 4.

TABLE 4

ACID-CATALYZED RATES OF ELIMINATION OF β-ORGANOMETAL-SUBSTITUTED ALCOHOLS, 25°C

No.	Compound	k_ψ (M^{-1} sec^{-1})	log k_ψ	$\Sigma\sigma^{+}$ [c]
11	$Ph_3SnCH_2CH_2OH$	0.35 [a]	—0.45	—0.70
12	$Ph_3SnCH_2CH(CH_3)OH$	0.51 [a]	—0.29	—1.01
13	$Ph_3SnCH_2C(CH_3)_2OH$	4.4 [a]	0.64	—1.32
14	$Ph_3PbCH_2CH_2OH$	0.77 [a]	—0.11	—0.90
15	$Ph_3PbCH_2CH(CH_3)OH$	1.9 [a]	—0.28	—1.22
16	$IHgCH_2CH_2OH$	0.19 [b]	—0.72	—0.55
17	$IHgCH_2CH(CH_3)OH$	2.13 [b]	0.33	—0.86

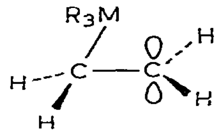
[a] Ref. 10, 73% aq. methanol. [b] Ref. 27, 98% aq. methanol. [c] Ref. 26.

of, the —MR_3 groups. Both factors are related through the common concept of bond polarizability (strength, force constant) [26], the first directly and the second, strongly, but in an as yet quantitatively unknown manner. The order of electrofugality, considering both bond strengths and ionization energy, is Hg > Pb > Sn > Ge > Si, a commonly observed order of reactivities in electrophilic organometallic reactions [28]. Since the actual leaving groups are expected to be strongly solvated, leaving group—solvent interaction, R_3M . . . solv, must be an important factor in electrofugality. Braune and Jarvie [9] have clearly shown that the proportion of elimination to substitution is a sensitive function of the nature of the leaving group. In the reaction

$$\begin{aligned}Ph_nMe_{3-n}CH_2CD_2OH &\xrightarrow{PBr_3} Ph_nMe_{3-n}SiCH_2CD_2Br + Ph_nMe_{3-n}SiCD_2CH_2Br \\ &+ Ph_nMe_{3-n}SiBr + CH_2{=}CH_2 \qquad (20)\end{aligned}$$

the introduction of successive phenyl groups at silicon retards the elimination reaction (~44% elimination $n = 0$, ~0% elimination $n = 3$) relative to substitution. The scrambling, CD_2 vs CH_2, observed above is nearly independent of the nature of substitution at silicon and shows only a slight preference (~10%) for unrearranged product. The elimination/substitution ratio is then a result of a substituent effect on the product-forming transition state, with Me_3Si a better leaving group than Ph_3Si. The intermediate(s) must allow for essentially complete randomization of the α- and β-carbons consistent with either a bridged-ion or a pair of rapidly equilibrating ions. MO calculations have suggested that the bridged ion, **3**, is more stable than the equilibrating pair, **2**, if limited-basis set *ab-initio* [29] or CNDO methods [30] are used, but the opposite conclusion is derived from MINDO calculations [31]. It would only be safe to say that the energy difference between the two structures is small, particularly if the conjugative interaction is not strictly vertical [30], **18**. There is considerable evidence for the bridged-mercurinium ion, **3**, M = HgX, as an intermediate in deoxy- and oxy-mercuration reactions [32]. The tendency of a metallogroup to bridge should impart some non-vertical character to the rate limiting transition state [32b, c].

Conjugative stabilization would contribute most to the stability of transition



(18)

state A, Fig. 3, while leaving group ability would determine the stability of transition state B. These two related factors and their effect on mechanism is best understood in terms of Thornton's Reacting Bond Rules [33] and a reaction coordinate diagram of the type developed by More O'Ferrall [34] and Jencks [35], Fig. 4. The upper-left corner represents the reactants (N = nucleophilic solvent; L = nucleofuge, in this case H_2O; M = electrofuge and conjugative stabilizing group) and the lower-right the products, the figure representing a projection of the potential energy surface from above. The upper-right and lower-left corners represent limiting structures for possible intermediates, O. Progress from reactants to products (R → P) may occur by the limiting mechanisms: $R \rightarrow *_A \rightarrow O \rightarrow *_B \rightarrow P$, a limiting E_1-like carbocation mechanism, (E_1M), whose vertical projection is shown in Fig. 3a; or $R \rightarrow *_c \rightarrow P$, a purely-concerted E_2-like mechanism, (E_2M). Following a path along the left and bottom edges (not shown) may represent a possible mechanism for the base or nucleophilic cleavage of organometallics [36] and is not being considered here [2]. Between the two limiting paths shown there exist a number of other reaction coordinates, less concerted than the direct R → P coordinate. Thornton's Reacting Bond Rules [33] describe the effects of structural changes on the location of transition states along these coordinates and may be summarized as follows: (1) a structural change which makes progress over the reaction coordinate easier will move the position of the transition state toward the reactants (Hammond's Postulate) [37]; (2) the effect of a structural change on a bound vibration will be opposite to Hammond behavior, i.e., perpendicular to the reaction coordinate and in the direction of the change. Let us follow the position of the transition states $*_A$ and $*_B$ upon increasing the conjugative stabilization and electrofugality of M: $*_A$ would move in the direction R_a and $\perp_a$ and the new position would be $*_{A'}$; $*_B$ would move in the directions R_B and $\perp_B$ to $*_{B'}$ and the inter-

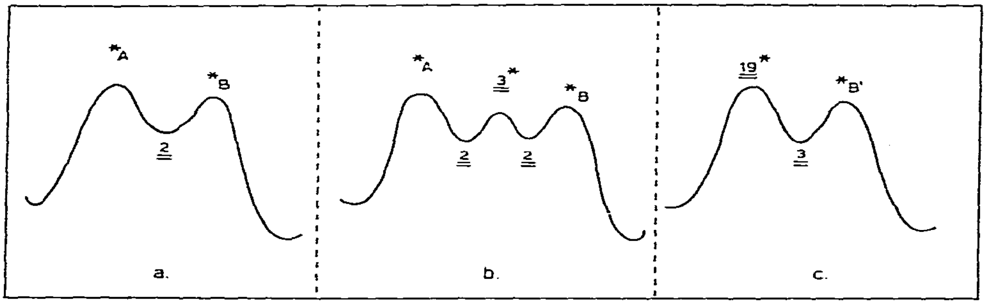


Fig. 3. Reaction coordinate diagrams for elimination reactions of β-organometal-substituted carbocations: (a) rate-limiting formation of a vertically-stabilized carbocation; (b) rate-limiting formation of a rapidly equilibrating pair through a bridged cationic transition state; (c) rate limiting formation of a distortionally-stabilized carbocation with a bridged cation intermediate.

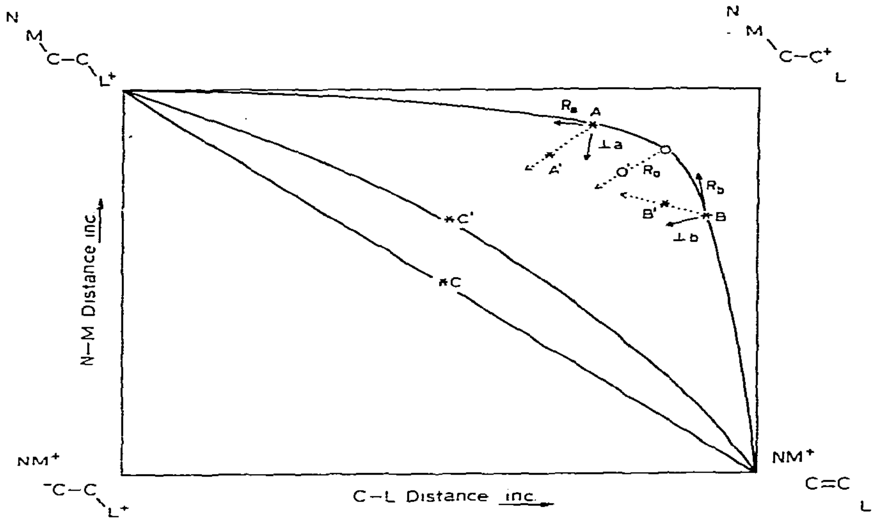


Fig. 4. More O'Ferrall-Jencks diagram for elimination reactions of β-substituted organometallics.

mediate would move along R_0 to O′, which is lower in energy than O. A series of these changes, for example from M = Me_3Si to Me_3Ge to Me_3Sn etc, would cause the transition states and intermediate to continue to move along the projections $* \rightarrow *'$ and R_0 (dotted lines). Note that the energy minimum, O, and the energy maximum, $*_B$, would merge leaving only $*_A$ on a reaction coordinate displaced slightly to the right of the fully concerted path (R → P), a reaction still best described as a concerted elimination.

Two direct consequences of this spectrum of mechanisms can be seen in Fig. 4. First, the rate-determining transition state, $*_A$, moves in the direction of decreasing C—L bond distance in the transition state implying lower charge density on C_α and hence a lower αMe/H rate effect, as is observed; αMe/H(Si) = $10^{3.4}$, αMe/H(Sn or Pb) [10] $\cong 10^{0.5}$. Second, nucleophilic assistance by N plays an integral role in the perpendicular movement of $*_A$ and $*_B$ toward the limiting structure $NM^+\bar{C}$—C—L and would be expected to have greater influence on $*_B$ (electrofugality) than on $*_A$ (conjugative stabilization). In the absence of such assistance, for example in Traylor's study of the elimination of a series of homoleptic metal alkyls in acetonitrile [11], the mechanism remains E_1M and $\rho^+ \cong -14$ *. In the more nucleophilic solvents, water and methanol, $Me_3SiCH_2CH_2OH$ undergoes acid-catalyzed elimination by an E_1M-mechanism and $Ph_3SnCH_2CH_2OH$ by an E_2M path, the merger point probably occurring with the Ge-substituted compounds for which little data is available. In a solvent of medium nucleophility, acetic acid, the direct participation of added nucleophile, H_2O, has been noted in the kinetic expression for deoxystannylation [10], suggesting E_2M behavior.

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* Rate data from ref. 11 and σ-constants from Ref. 26 show a Hammett correlation with $\rho^+ = -14$.

Experimental

General

NMR spectra were recorded using the Varian A60-A NMR spectrometer (60 MHz), gas chromatographic analyses were carried out on an F & M Scientific 700 Laboratory Chromatograph with a thermal conductivity detector. A 1/4-inch column of 10% Carbowax on Chromasorb-W with He gas at a flow of 60 ml/min effected the separation of the bromides (95° C column, 250° C detector, 285° C injection port).

Cognate preparations were used for 4—7. The syntheses of 5 and 6 are shown in detail to illustrate the method used in handling these acid-sensitive compounds. All physical and spectral properties were comparable to the literature values for these previously prepared compounds.

Procedures

Synthesis of trimethylsilyl-2-hydroxpropane, 5. A 100 ml round bottom flask, fitted with reflux condenser, dropping funnel (with drying tube), and magnetic stirrer, was dried with a heat gun and flushed with dry N_2. Into this was introduced 1.2 g (0.05 mole) Mg ("for Grignard reaction") and 25 ml of dry ethyl ether which had been previously distilled from Na and then LAH. The ether was then brought to reflux temperature using a heating mantle. The dropping funnel containing 6.1 g (0.05 mole) chloromethyltrimethylsilane and 25 ml dried ether was situated above the reflux condenser and the mixture introduced dropwise with stirring into the refluxing ether over a period of 30 minutes. The mixture was refluxed for an additional 30 minutes then allowed to cool to room temperature. The dropping funnel was then used to introduce a solution of acetaldehyde (2.2 g, 0.05 mole) in 25 ml of dry ether. This brought the temperature quickly back to reflux. The addition was continued dropwise for 30 minutes and refluxed for 15 minutes thereafter. The resultant paste was poured onto a slurry of ice and ammonium chloride and allowed to warm to room temperature. (It was found that if the mixture was hydrolyzed with stronger acid, such as cold 5% H_2SO_4, no product alcohol was obtained, thus indicating the sensitivity of the alcohol to acid even at reduced remperatures.) The water layer was separated and extracted with three 10-ml portions of ether. The combined ether layers were washed with saturated brine and dried over K_2CO_3. The ether was evaporated and the residue vacuum distilled into a dry-ice-cooled receiver. The fraction boiling over the range 31—33° C (7.5 torr) was shown by NMR to be the desired product, $(CH_3)_3SiCH_2CHOHCH_3$. The reaction gives the alcohol in 25% yield (1.6 g).

NMR (δ, ppm): 0.04; s, 9 H, (H_3C—Si); 0.90, complex doublet, 2 H, J = 6.5 Hz, (Si—CH_2—C); 1.23, d, J = 6.5 Hz, 3 H, (C—CH_3); 1.82, s, 1 H, (COH); 4.07, sextet, 1 H, J = 6.5, (CH_2—$C$$H$OH—$CH_3$): B.P. (Lit. [38]) = 48° C (10 torr).

Synthesis of bis-1,3-trimethylsilyl-2-hydroxypropane, 6. Trimethylsilylmethylmagnesium chloride (10 g, 0.07 mole) was prepared and reacted with 2.6 g (0.07 mole) freshly distilled ethyl formate as described above. The mixture was hydrolyzed with NH_4Cl/ice and extracted with ether. The ether was evaporated and the resultant viscous liquid vacuum distilled. The fraction collected over the range 81.5—83.5 (10 torr) was shown by NMR to be the desired product, $((CH_3)_3SiCH_2)_2CHOH$. The reaction gave the alcohol in 42% yield (3 g).

NMR (δ, ppm): 0.04, s, 18 H, (H_3C—Si); 0.92, d, 4 H, J = 6.5 Hz, (Si—CH_2—C); 1.32, s, 1 H, (COH); 4.08, quintet, 1 H, J = 6.5 Hz, (CHOH): B.P. (Lit. [39]). 74.5°C (7 torr).

Trimethylsilyl-2-hydroxyethane, 4. NMR (δ, ppm) 0.01, s, 9 H, (H_3C—Si); 0.94, complex triplet, 2 H, J = 8 Hz, (Si—CH_2—C); 2.75, s, 1 H, (COH); 3.72, complex triplet, 2 H, J = 8 Hz, (CH_2—CH_2OH): B.P. (Lit. [40]) 95°C (100 torr), B.P. (obs) 61—62°C (19 torr).

Trimethylsilyl-2-methyl-2-hydroxypropane, 7. NMR (δ, ppm) 0.05, s, 9 H, (H_3C—Si); 1.03, s, 2 H, (Si—CH_2—C); 1.29, s, 6 H, (C—CH_3); 1.67, s, 1 H, (C—OH): B.P. (Lit. [41]) 91—92°C (98 torr), B.P. (obs) 35—36°C (6 torr).

Product analysis

The silicon-containing products were identified by NMR. In all cases the final mixture, after the acid-catalyzed elimination was complete, showed the same peaks in the region near δ 0.0 ppm. Two peaks, one at 0.10 and the other at 0.05 ppm (downfield from TMS, cyclohexane standard) in the ratio 1/1.5, respectively, were observed. These chemical shifts correspond to those of the methyl groups of trimethylsilanol (0.10 ppm) and hexamethyldisiloxane (0.05 ppm) [42]. Peaks with the same shifts and in the same ratio were also obtained when trimethylchlorosilane was allowed to hydrolyze under reaction conditions. These data indicate that the trimethylsilyl products are those expected from the elimination of a trimethylsilyl cation in the reaction medium.

The alkene products were identified by gas chromatography of their bromine addition products. A reaction vessel containing 0.10 ml of the silyl alcohol, 1.0 ml MeOH and a magnetic stirring bar was swept by MeOH-saturated N_2. After all the connections were made and the nitrogen circulating through the system, 0.11 ml of 1.0 M HCl was injected into the reaction mixture and stirring started. The product was swept out of the reaction mixture and into a recovery vessel which contained a slight molar excess of Br_2 and $CBrCl_3$ in CCl_4. The $CBrCl_3$ was used as an internal standard. Equal weights of it and the expected product, 1,2-dibromopropane, gave equal peak areas. Thus the amount of $CBrCl_3$ in the recovery vessel was nearly equal in weight to the weight of alkene bromide expected. The reaction was allowed to continue for 30 minutes and the excess Br_2 consumed by added 2-butene (whose dibromide did not interfere with the GC analysis). The reaction mixture was then analyzed by GC, the peak area of the product compared to the standard to give the percent yield.

The yield of propylene from trimethylsilyl-2-hydroxypropane was 98% and from bis-1,3-trimethylsilyl-2-hydroxypropane was 85%. It was shown by NMR that the product of the reaction of trimethylsilyl-2-hydroxy-2-methylpropane was isobutylene.

Allytrimethylsilane is expected to be a transient intermediate in the elimination of 6 to propylene. However, when allyltrimethylsilane was subjected to the reaction conditions the expected rapid disappearance was not observed. The NMR spectrum exhibited a rapid (less than 15 seconds) initial decrease of the —CH_2— peak (after dilution was accounted for) and remained unchanged for a period in excess of 3000 seconds. The NMR spectrum of a sample of allyltrimethylsilane showed the presence of small amounts of impurities which could not be removed by distillation or column chromatography (silica gel). It was assumed that the amount of impurity observed (2%) could easily neutralize the small acid concentration (0.00281 *M*) present and prevent the desired reaction. Two different commercially available samples (Petrarch Systems) showed the same behavior and impurities.

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