The Surprising Reactivity of Alkoxyhydrosilanes toward ⌐ Hydroxy Carboxylic Acids[1]

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Summary: Although in the absence of base or transition-metal catalysts hydrosilanes do not normally react with alcohols or carboxylic acids, the combination of α- or β-hydroxy carboxylic acids with alkoxyhydrosilanes (HSi(OEt)₃ or MeHSi(OEt)₂) was shown to lead to the rapid evolution of hydrogen gas. This was demonstrated by examining the reactions of a series of carboxylic acids, α- or β-hydroxy acids (malic, tartaric, glycolic), alcohols, and glycols with hydrosilanes (alkyl and alkoxy) in the absence of additional catalysts. This unusual reactivity is interpreted to arise from the cooperative nucleophilic attack of the hydroxy group at silicon and the electrophilic attack of the acid proton at the Si–H bond.

Introduction. Hydrosilanes are reactive compounds that are often the reagent of choice for the introduction of silicon into an organic molecule. In addition to the synthetically important hydrosilation of carbon–carbon double and triple bonds, hydrosilanes will also reduce carbon–heteroatom multiple bonds such as carbonyl groups.[3] A related silylation is, furthermore, observed in the reaction of hydrosilanes with alcohols leading to the formation of H₂ and an alkoxysilane (eq 1).[4] Although the

$$R_3SiH + R'OH \rightarrow H_2 + R_3SiOR' \qquad (1)$$
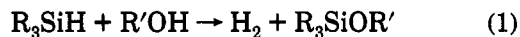
H–Si bond is rather weak,[5] these reactions normally require catalysis by transition metals[3,6] or base;[4,7] acidic catalysis is known to be effective only in the presence of concentrated strong acids.[4,7,8] Nucleophilic substitution at silicon can be catalyzed by the presence of silaphilic nucleophiles such as HMPA, DMSO, and DMF.[9–11] However, in

substitution reactions involving Si–H bonds, such catalysis has only been clearly demonstrated with intramolecular activation in systems such as 1.[10]

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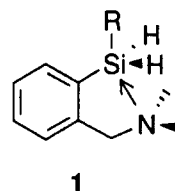
During the course of an alkoxy group exchange reaction between tartaric acid and triethoxysilane in THF[12] in the absence of catalysts, we were surprised to observe the effervescence of hydrogen. The reaction was subsequently shown to occur much more rapidly in DMSO and not occur to any observable extent in less polar solvents such as chloroform.[13] The alcoholysis of a hydrosilane under such mild acidic conditions is, to our knowledge, unprecedented. We have, therefore, examined this reaction in detail and report herein the factors necessary for the reaction to occur and propose a mechanism to explain our observations.

Results and Discussion. When a solution of triethoxysilane in DMSO or THF was subjected to the addition of acetic acid (pK_a = 4.76) or Cl₃CCOOH (pK_a = 0.65),[14] no evolution of hydrogen was observed over 24 h, as was expected from previous reports. The addition to either of these solutions of a nucleophilic alcohol, EtOH or *t*-BuOH, led only to slow exchange of alkoxy groups (observable only in the latter case); simple acid-catalyzed alcoholysis did not occur even in the presence of excess DMSO (solvent). The related reaction of the silane with the alcohols in DMSO *or THF* in the absence of carboxylic acids similarly led only to recovered starting materials or products of transesterification.

In contrast, under otherwise identical conditions, a rapid evolution of hydrogen gas was observed when tartaric acid was allowed to react with triethoxysilane or methyldiethoxysilane. In order to demonstrate that there were no

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(2) Natural Sciences and Engineering Research Council of Canada University Research Fellow, 1985–1995.

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(11) Corriu, R. J. P.; Perz, R.; Reye, C. *Tetrahedron* 1983, 39, 999.

(12) THF is not a very good activator for nucleophilic attack at Si. For example, racemization of chlorosilanes does not rapidly occur in THF in the absence of such nucleophilic activators such as HMPA, DMF, and DMSO: Corriu, R. J. P.; Dabosi, G.; Martineau, M. *J. Organomet. Chem.* 1978, 150, 27.

(13) It was, however, difficult to perform this reaction due to the very low solubility of tartaric acid in chloroform.

(14) Typical experimental procedure given for the reaction between tartaric acid and HSi(OEt)₃ (1:1): In a flame-dried test tube equipped with a stirring bar and a small Teflon tube leading to an inverted, paraffin-filled buret (to measure H₂ production) was placed DMSO (dried by distillation under reduced pressure from CaH₂, 2.27 mL) and the acid (0.1550 g, 1.03 mmol [2.5 mM in acid]). The tube was sealed with a septum under an N₂ atmosphere at room temperature. After the material had dissolved, the silane (0.03 mL, 1.0 mmol [2.5 mM in silane]) was added via syringe and the rate of evolution of H₂ was recorded over 10 h at 30-s intervals for 10 min and at 30-min intervals thereafter.

Table 1. Relative Rates of Reaction of Various Carboxylic Acids and Alcohols with HSi(OEt)$_3$[14]

Group 1: Reaction within 5–10 Min

| entry no. | solvent | amt, equiv | | | acid | amt, mmol | | | | % H$_2$ recov |
		acid	TES	H$_2$ prod.		acid	TES	H$_2$ calcd	H$_2$ found	
1	THF	1	1	1.0	tartaric	0.93	0.93	0.93	0.89	96.1
2	DMSO	1	1	1.1	tartaric	1.03	1.03	1.03	1.05	101.9
3	DMSO	1	1	1.0	tartaric	0.84	0.84	0.84	0.82	97.4
4	DMSO	1	2	2.2	tartaric	0.72	1.44	1.44	1.42	98.4
5	DMSO	1	3	3.0	tartaric	0.57	1.70	1.70	1.59	93.5
6	DMSO	1	4	4.0	tartaric	0.34	1.36	1.36	1.25	91.9
7	DMSO	1	10	5.0	tartaric	0.12	1.20	0.48 (4 equiv)	0.43	89.6
8	DMSO	2	1	1.1	tartaric	1.51	0.76	0.76	0.80	106.4
9	DMSO	3	1	1.1	tartaric	1.93	0.65	0.65	0.65	100.7
10	DMSO	4	1	1.0	tartaric	3.05	0.76	0.76	0.72	94.6
11	DMSO	1	1	1.1	malic	1.13	1.13	1.13	1.15	101.9
12	DMSO	1	2	2.2	malic	0.78	1.57	1.57	1.45	92.5
13	DMSO	2	1	1.1	malic	1.46	0.73	0.73	0.77	105.6
14	DMSO	1	1	1.1	glycolic	1.63	1.63	1.63	1.63	100.0
15	DMSO	1	2	2.0	glycolic	0.97	1.95	1.95	1.80	92.4
16	DMSO	2	1	1.1	glycolic	2.04	1.02	1.02	1.07	105.0

Groups 2 and 3

entry no.	solvent	acid or alcohol	entry no.	solvent	acid or alcohol
		Group 2: Very Slow Reaction (within 2 h)			
17	DMSO or THF	ethylene glycol			
		Group 3: No Reaction within 7 Days			
18	DMSO or THF	succinic acid	24	DMSO or THF	trichloroacetic acid/t-BuOH
19	DMSO or THF	malonic acid	25	DMSO or THF	acetic acid
20	DMSO or THF	glutaric acid	26	DMSO or THF	acetic acid/EtOH
21	DMSO or THF	1,1,1-tris(hydroxymethyl)ethane	27	DMSO or THF	acetic acid/t-BuOH
22	DMSO or THF	trichloroacetic acid	28	DMSO or THF	EtOH
23	DMSO or THF	trichloroacetic acid/EtOH	29	DMSO or THF	t-BuOH

contaminants present in the glass acting as catalysts, we performed the reaction in Teflon and in acid-treated, base-treated, and silanized (HN(SiMe$_3$)$_2$) glass with similar results.

Unlike simple alcohols or acids, tartaric acid can bind to the silicon in a multidentate fashion. α-Hydroxy acids have been previously reported to react with activated dihydrosilanes, leading to cyclic products.[15,16] Further, it is well-known that catecholates, for instance, react rapidly with difunctional silanes to form dioxasilacyclopentanes.[17] In order to assess whether such multidentate coupling was occurring and was responsible for the reaction observed and, if so, whether this was coupling of (i) an α-diol, (ii) an α- or β-hydroxy acid, or (iii) an α,β-diacid, we examined the reaction of a series of appropriately substituted compounds with triethoxysilane and methyldiethoxysilane. The rates of reaction could not be conveniently followed by ^{1}H NMR or IR, and we therefore used the rate of evolution of hydrogen gas for this purpose.

The results are shown in Table 1, indicating three classes of compounds; those which reacted vigorously (reaction complete within 5–10 min),[18] those that showed no reactivity within 7 days; and a compound that showed intermediate reactivity (ethylene glycol), for which the reaction was complete within 2 h. It can clearly be seen
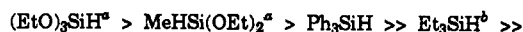
Chart 1

(EtO)$_3$SiH^a > MeHSi(OEt)$_2$^{a} > Ph$_3$SiH >> Et$_3$SiH^b >>

HSiMe$_2$Ph, H$_2$SiPh$_2$, HSiMePh$_2$, –[–HSiMeO–]$_n$–^{c}

^{a} The same reaction order for these two silanes has been previously reported.[10] ^{b} Reaction only proceeded to about 5% completion within 7 days. ^{c} The latter group of silanes did not react to any observable extent within 7 days.

that the fastest reactions were observed with α- or β-hydroxy acids.[19,20]

If an excess of silane was allowed to react with the polyfunctional molecules malic and tartaric acid, 2 and 4 equiv, respectively, of hydrogen were produced. This indicates that a pair of functional groups on the same molecule (OH + COOH) is required for the formation of H$_2$, and each OH leads to the production of an H$_2$ molecule.

In order to assess the requirements of the silane for reaction to occur, we examined a series of different hydrosilanes in DMSO with glycolic acid, the simplest and most reactive of the acids examined. The results in Chart 1 show the reaction to be particularly facile with alkoxyhydrosilanes: we were unable to examine other functional silanes such as the halohydrosilanes, because

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(16) For a review, see: Cragg, R. H.; Lane, R. D. *J. Organomet. Chem.* **1984**, *267*, 1; **1985**, *289*, 23.

(17) Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Organometallics* **1988**, *7*, 1165; Wolff, B.; Weiss, A. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 162.

(18) This was determined by loss of the Si–H signal in the ^{1}H NMR (δ 4.14 HSi(OEt)$_3$, 4.38 HMeSi(OEt)$_2$) and IR (2195 cm^{-1} HSi(OEt)$_3$, 2163 cm^{-1} HMeSi(OEt)$_2$) spectra.

(19) We have not established in detail the structures of these materials. The precipitates formed (after removal of solvent by evaporation under reduced pressure) were insoluble in normal organic solvents; decomposition was observed in water. IR and solid-state ^{29}Si NMR spectroscopy showed very broad peaks, leading us to conclude that, unlike related work with salicylic acid,[20] polymeric rather than monomeric materials are being produced. The solid-state ^{29}Si NMR of compounds prepared in entries 3, 4, and 8 (Table 1) showed very broad Q peaks at –93, –100, and –118 ppm. The product in entry 4 also showed a broad peak at –142 ppm, lending support for the proposal of pentacoordinate intermediates in the reaction mechanism.

(20) Narain, R. P.; Kaur, A. *J. Indian J. Chem.* **1978**, *16A*, 355.

they react with DMSO to form polysiloxanes.[21] In the case of phenylsilane, the reaction was extremely rapid after an initial delay. This is consistent with an increasing reaction rate of the silane as the hydrogens are sequentially replaced by alkoxy groups.[4]

From the ^{1}H NMR and IR data of the reactions of α- or β-hydroxy acids with hydrosilanes, it is clear that the loss of the Si–H signal from the silane occurs more rapidly than transesterification of the ethoxy groups with the hydroxy groups on the added α- or β-hydroxy acid.

The data presented above can be accounted for by invoking a cooperative transition state or intermediate in which the more basic hydroxy group (with respect to the acid OH group) or the carbonyl group attacks Si nucleophilically, perhaps aided by hydrogen bonding from the silylalkoxy group, while the acidic H is delivered from the α- or β-acid. In THF as solvent, a poor nucleophile for silicon, this could occur in a concerted fashion (2) or via the intermediacy of a pentacoordinate intermediate such as 3 or 4[22] (Scheme 1). In the presence of DMSO, the faster reaction rate could be simply a consequence of a more polar solvent stabilizing a more polar intermediate or transition state. However, as is frequently the case in nucleophilic substitutions at silicon, DMSO may activate the silicon center, followed by further coordination expansion to the hexacoordinate species corresponding to 3 or 4 (5 or 6, respectively). The possibility of coordination expansion is reasonable in that it is known that the ease of expansion from 4- to 5- or 6-coordinate silicon increases with the number of electron-withdrawing groups on silicon; the alkylsilanes that do not readily expand their coordination shell did not react with α-hydroxy acids. Moreover, it has been clearly shown that pentacoordinate alkoxyhydrosilicates are much more potent reducing agents than the corresponding tetracoordinate species.[23] Such a cooperative transition state explains why reaction with

(21) To be submitted for publication; see however: Chan, T.-H.; Melnyk, A.; Harpp, D. N. *Tetrahedron Lett.* **1969**, 201. Chan, T.-H.; Melnyk, A. *J. Am. Chem. Soc.* **1970**, *92*, 3718.

(22) We thank a reviewer for this suggestion.

Scheme 1
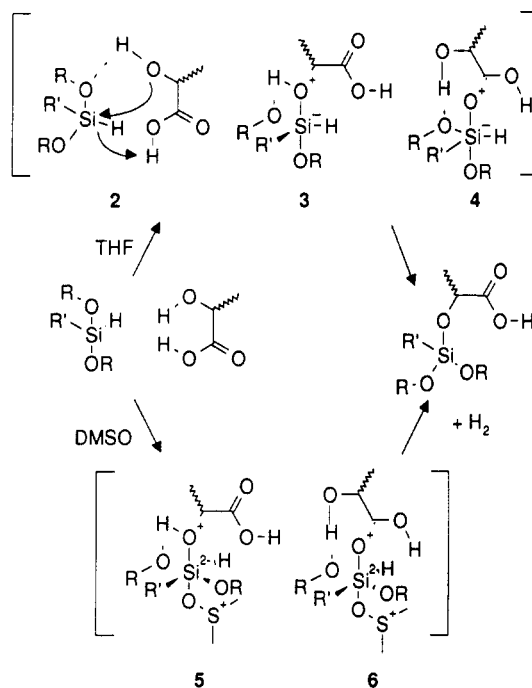
the more acidic Cl₃CCOOH and/or EtOH and triethoxysilane was not observed: the probability of forming a ternary complex is low.

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