The Preparation of Organosilanols *via* the Metal-Catalyzed Reaction of Organosilicon Hydrides with Water

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Hydrolysis of organosilicon hydrides with catalysts such as palladium on charcoal, palladium on alumina, and ruthenium on charcoal was found to be an excellent method of preparing the corresponding organosilanols. The method was applicable to silanols sensitive to condensation and to silanols containing siloxane linkages without cleavage or rearrangement of these linkages.

Organosilicon hydrides have been oxidized to the corresponding organosilanols with metallic oxides or salts such as silver oxide,[2,3] silver nitrate,[2,3] and silver nitrite,[3] or with gaseous oxygen in the presence of a tertiary amine and a cuprous salt.[4] An indirect hydrolysis method has been reported[5] from this laboratory in which the organosilicon hydride was first converted to the sodium silanolate by dissolving in strong sodium hydroxide in mixed water–alcohol solvent and the resulting solution was neutralized by adding it to an excess of a buffered aqueous solution. The optically active silicon hydride of Sommer[6] has been converted to the optically active silanol either by powdered potassium hydroxide in xylene followed by hydrolysis of the intermediate potassium silanolate or by direct oxidation with perbenzoic acid.

The method reported in this publication, based on the catalytic hydrolysis of organosilicon hydrides as in eq 1, gives good yields of silanols with a variety of

$$\equiv\text{SiH} + \text{H}_2\text{O} \longrightarrow \equiv\text{SiOH} + \text{H}_2 \qquad (1)$$

silicon hydrides as may be seen in Table I. The method is convenient, does not use expensive reagents, and gives good yields of silanols that are sensitive to condensation to siloxanes and of silanols that contain siloxane linkages without cleavage or rearrangement of these linkages.

This method is of such utility that an organosilicon hydride may be a better choice of intermediate than the more commonly employed intermediates: organosilicon halides, alkoxides, silazanes, etc.[7]

Of the literature methods cited, only the one using silver oxide[3] seems to be a possible route to sensitive silanols or to silanols containing siloxane linkages because of the necessary condition that the reaction mixture remain neutral. The indirect hydrolysis method[5] might be successful with some sensitive silanols but would not be applicable to siloxanes because extensive rearrangement of siloxane linkages would be certain.

Eight metal-on-carrier catalysts have been successfully employed in the present work: palladium, ruthenium, platinum, and rhodium on both charcoal and alumina supports. Three of these commercially available catalysts (5% palladium on charcoal, 5% palladium on alumina, and 5% ruthenium on charcoal) most consistently led to the best yields of silanols. Also because these were the most active, many experiments proceeded at room temperature, which may be an important advantage with sensitive silanols.

All reactions listed in Table I were carried out using a buffer solution rather than pure water in an effort to prevent mixtures from becoming either acidic or basic. Acids or bases known to be present in reagents should be removed prior to reaction. Removal of base from the 5% palladium on charcoal and acids from the triethylsilane and *p*-bis(dimethylsilyl)benzene samples are reported in the Experimental Section. Impurities[8] in the silicon hydride that may be converted to acid (or base) under the experimental conditions should also be removed.

The importance of avoiding acidity even with a comparatively insensitive silanol, diphenylmethylsilanol, is exemplified in the reactions listed in Table II. Finely divided nickel has been reported[9] as a catalyst for the hydrolysis of organosilicon hydrides, yielding the corresponding organosiloxanes as the only products. The method of preparation of the nickel led us to suspect that traces of hydrochloric acid were being introduced into the reaction mixtures. Reaction 1 was an attempt to duplicate one of the reported examples[9] (bottom line of Table II) and was reasonably successful to judge by the yield values. A small yield of silanol was the only difference. Reaction 2 was carried out with our buffer solution replacing the water, whereupon the silanol yield was increased to the extent that it became the major product. In reaction 3 a finely divided nickel obtained by the reduction of nickel chloride with sodium borohydride[10] was employed in conjunction with the buffer solution. This combination probably resulted in the closest approach to neutral conditions of the three reactions and in fact the highest yield of silanol was realized.

The use of a solvent such as toluene as in Table II is considered a poorer choice than a solvent such as dioxane used in Table I or tetrahydrofuran, which produce a single organic–aqueous phase. The single phase would logically be expected to allow better control of the neutrality of the reaction mixture.

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[1] Multiple Fellowship on Silicones sustained by Dow Corning Corp. and Corning Glass Works.

[2] H. H. Anderson, *J. Am. Chem. Soc.*, **80**, 5083 (1958).

[3] N. Duffaut, R. Calas, and J. Mace, *Bull. Soc. Chim. France*, 1971 (1959).

[4] A. S. Hay, U. S. Patent 3,099,640 (1963); *Chem. Abstr.*, **60**, 552e (1964).

[5] R. L. Merker and M. J. Scott, *J. Polymer Sci.*, **A2**, 15 (1964).

[6] L. H. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1965, pp 104 and 110.

[7] C. Eaborn, "Organosilicon Compounds," Academic Press Inc., New York, N. Y., 1960, p 228.

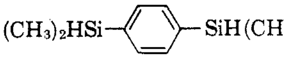
[8] For example, aromatic bromides are efficiently reduced in such mixtures to hydrobromic acid.

[9] N. F. Orlov and B. N. Dolgov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **125**, 817 (1959).

[10] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956.

TABLE I

SILANOL PREPARATIONS WITH PALLADIUM, RUTHENIUM, RHODIUM, AND PLATINUM CATALYSTS

Reaction no.	Starting material	Silicon hydride, mole	Dioxane, ml	Buffer soln,[a] ml	Catalyst (g-atom of metal)	Reaction temp, °C	Reaction time, hr	Yield of silanol, %
1		0.025	50	4.5	5% Pd-C (2.3×10^{-4})	25	1.0	81
2		0.025	50	4.5	5% Pd-Al_2O_3 (2.3×10^{-4})	25	2.0	88
3		0.025	50	4.5	5% Pt-C (2.3×10^{-4})	85	18	40
4		0.025	50	4.5	5% Pt-Al_2O_3 (2.3×10^{-4})	85–88	4.0	30
5		0.025	50	4.5	5% Ru-C (2.3×10^{-4})	70–88	2.0	65
6		0.025	50	4.5	5% Ru-Al_2O_3 (2.3×10^{-4})	88	30	26
7		0.025	50	4.5	5% Rh-C (2.3×10^{-4})	*Ca.* 88	18	53
8		0.025	50	4.5	5% Rh-Al_2O_3 (2.3×10^{-4})	88	9.0	53
9	$(CH_3)_2HSiOSiH(CH_3)_2$	0.05	62	9.0	5% Ru-C (2.0×10^{-4})	24–29	4.0	60
10	$(C_6H_5)_3SiH$	0.025	25	2.3	5% Ru-C (2.0×10^{-4})	85–8	7.5	97
11		0.025	25	2.3	5% Pd-Al_2O_3 (1.9×10^{-4})	29–35	4.5	100
12	$(CH_3)_2C_6H_5SiH$	0.10	73	9.0	5% Pd-Al_2O_3 (1.1×10^{-4})	30–35	11	95
13		0.10	73	9.0	5% Ru-C (2×10^{-4})	25–31	23.5	92
14	$CH_3(C_6H_5)_2SiH$	0.075	64	6.7	5% Ru-C (1.5×10^{-4})	88	23	78
15	$(C_2H_5)_3SiH$	0.15	125	13.5	5% Ru-C (3×10^{-4})	57–90	6	86
16	$CH_3CH_2(CH_3)_2SiOSi(CH_3)_2H$	0.10	100	9.0	4% Pd-C (7.5×10^{-5})	25–32	3	79
17	$[(CH_3)_3SiO]_2CH_3SiH$	0.10	105	9.0	4% Pd-C (1.12×10^{-4})	25–30	3	87

[a] The buffer solution contained 0.65 g of $NaH_2PO_4 \cdot H_2O$ plus 39.80 ml of 0.100 *N* NaOH per liter.

TABLE II

SILANOL PREPARATIONS WITH NICKEL CATALYSTS

Reaction no.	$MePh_2SiH$, mole	Water, mole	Toluene, ml	Nickel, g-atom	Reaction temp, °C	Reaction time, hr	% yield MePh$_2$-SiOH	% yield MePh$_2$-Si$_2$O
1	0.10	0.20	30	8.4×10^{-5}	102	22.0	5.0	64.0
2	0.10	Buffer[b] 0.20	30	8.4×10^{-5}	110	22.0	50.0	32.0
3	0.10	Buffer[b] 0.20	30	6.6×10^{-4}	110	20.0	85.0	<10.0
...[a]	0.10	0.10	30	8.4×10^{-5}	Reflux	4.0	...	83.0

[a] Reference 9. [b] See footnote *a* in Table I.

Experimental Section

Starting Materials.—The 5% metal-on-carrier catalysts were purchased from Engelhard Industries; the 4% palladium on charcoal was prepared in this laboratory. The 5% palladium on charcoal was neutralized by suspending 15.0 g in 200 ml of water and over a period of several hours adding 0.1 *N* HCl until the pH remained at 7.0. After filtration the catalyst was dried at 60° under vacuum.

p-Bis(dimethylsilyl)benzene obtained from the *in situ* Grignard reaction of *p*-dibromobenzene and dimethylchlorosilane[5] 4 years previously was dissolved in ethanol and neutralized with 0.1 *N* ethanolic sodium hydroxide to a pH of 6.5. After evaporation of the water and ethanol, the sodium salt was removed by filtration and the filtrate was then redistilled: bp 142.5° (78 mm), $n^{25}D$ 1.4991–1.4992. Analysis by glpc on an 8-ft 20% Carbowax 1500 column at 175° showed 5.5% of an unknown impurity (4.0 min), 94.5% *p*-bis(dimethylsilyl)-benzene (5.1 min), and no trace of *p*-(dimethylsilyl)bromobenzene (9.5 min) or *p*-dibromobenzene (17.8 min). The impurity also had a shorter retention time than the main component on a silicone column.

1,1,3,3-Tetramethyldisiloxane was prepared by the hydrolysis of dimethylchlorosilane; ethyl-1,1,3,3-tetramethyldisiloxane from the cohydrolysis of ethyldimethylchlorosilane and dimethylchlorosilane; 1,1,1,5,7,7,7-heptamethyltrisiloxane from the cohydrolysis of trimethylchlorosilane and methyldichlorosilane. All chlorosilanes were obtained from Dow Corning Corp. Triphenylsilane, phenyldimethylsilane, and diphenylmethylsilane were prepared by reduction of the corresponding chlorosilanes with lithium aluminum hydride. Triethylsilane from Peninsular ChemResearch, Inc., was washed with water to remove a trace of acid, dried, and redistilled.

General Procedure for Reactions 1–17 in Table I.—In a typical procedure (reaction 1), 4.8 g of *p*-bis(dimethylsilyl)benzene was added over a period of a few minutes to a stirred flask containing 4.5 g of buffer solution, 50 ml of dioxane, and 0.5 g of 5% Pd–C. One neck of the flask was connected through a condenser to a gas collector filled with saturated brine and arranged so that the displaced brine could be measured. After 1 hr the gas evolution stopped. The final gas volume was 1280 cc (uncor) (calcd 1260 cc). The volumes usually were 92 to 100% of theory. A drop of the reaction mixture did not give a white, amorphous precipitate when tested with 1 ml of 0.1 *M* mercuric chloride solution in ethanol, so Si–H was absent. (Dioxane forms a white, crystalline complex with mercuric chloride[11] after a few minutes and this should not be confused with the Si–H test). The reaction mixture was filtered to remove catalyst.

Typical isolation procedures for the various silanols are described below.

***p*-Bis(dimethylhydroxysilyl)benzene.**—In reaction 1 the filtered mixture was stripped of solvent on a rotary film evaporator, and the solid residue was recrystallized from 30 ml of toluene to give 4.6 g (81%), mp 138–139°, of the title compound.

Tetramethyldisiloxane-1,3-diol.—The filtrate from reaction 9 was evaporated in a stream of air, leaving a residue of long white needles, 6.7 g. These were recrystallized from 25 ml of hexane: 5.0 g, mp 61.5–65°, a 60% yield of the diol. A second recrystallization gave 4.7 g, mp 66–67.5°, lit.[12] mp 67–68°.

Triphenylsilanol.—The filtrate from reaction 10 was evaporated in a stream of air, leaving a greyish solid, 6.7 g (97%), mp 146–151°, lit.[13] mp 150.5–151.5°. The yield was taken on this slightly impure material.

Phenyldimethylsilanol, Diphenylmethylsilanol, and Triethylsilanol.—The silanols were isolated from the respective filtrates by fractional distillation through a small Podbielniak column. The following properties were found: phenyldimethylsilanol, bp 100° (10 mm), $n^{25}D$ 1.5110 [lit.[14] bp 99–99.5° (10 mm), $n^{20}D$ 1.5120]; diphenylmethylsilanol, bp 187–188° (24 mm), $n^{25}D$ 1.5785 [lit.[15] bp 184–187° (24 mm), $n^{25}D$ 1.5777]; triethylsilanol,

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[11] E. Paterno and R. Spallino, *Gazz. Ital.*, **37**, 106 (1907).

[12] G. R. Lucas and R. W. Martin, *J. Am. Chem. Soc.*, **74**, 5225 (1952).

[13] N. Marsden and F. S. Kipping, *J. Chem. Soc.*, 198 (1908).

[14] M. F. Shostakovskii and Kh. I. Kondrat'ev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 811 (1956); *Chem. Abstr.*, **51**, 3487*a* (1957).

[15] W. H. Daudt and J. F. Hyde, *J. Am. Chem. Soc.*, **74**, 386 (1952).

bp 157° (740 mm), n^{25}_D 1.4309–1.4312 (lit.[16] bp 153.5–154.5°, n^{20}_D 1.4341).

1-Ethyltetramethyldisiloxan-3-ol and Heptamethyltrisiloxan-3-ol.—Solvents and water were removed from the filtrates from reactions 16 and 17 on a rotary-film evaporator. Fractional distillation yielded the disiloxanol, 14.0 g, a 79% yield, bp 41–42° at approximately 1 mm, and the trisiloxanol, 20.8 g, an 85% yield, bp 50.5–57.5° at approximately 1 mm. Other properties and analyses were reported previously.[17]

Procedure for Reactions 1–3 in Table II.—See Table II for additional data on reagents, conditions, and yields.

Reactions 1 and 2.—In each reaction an *in situ* catalyst was prepared by heating 0.02 g (8.4×10^{-5} mole) of $NiCl_2 \cdot 6H_2O$ with 19.8 g (0.10 mole) of diphenylmethylsilane at 130–180° until the original green color passed through yellow and became black. After cooling to room temperature, the toluene was added, followed by either water in reaction 1 or buffered solution in reaction 2. The mixtures were heated under a reflux condenser for the time indicated in Table II. Tests for remaining Si–H by the mercuric chloride method were negative. The toluene layers were separated and dried, and the products were isolated by fractional distillation under vacuum.

Reaction 3.—The catalyst was prepared by adding dropwise a solution of 1.0 g (2.6×10^{-2} mole) of sodium borohydride in 20 ml of water to 4.0 g (1.68×10^{-2} mole) of $NiCl_2 \cdot 6H_2O$ in 20 ml of water. The resulting black precipitate was washed once with water and once with dioxane and stored under dioxane until used.

Approximately 0.039 g of this catalyst was added to the flask containing the three other reagents and the remainder of the procedure closely followed the procedure for reactions 1 and 2.

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[16] M. F. Shostakovskii, *et al.*, *J. Gen. Chem. USSR*, **24**, 2202 (1954); *Chem. Abstr.*, **50**, 3270 (1956).

[17] G. H. Barnes and N. E. Daughenbaugh, *Anal. Chem.*, **35**, 1308 (1963).

On the Mechanism of Metal Chelate Catalysis in the Reaction between Alcohols and Isocyanates

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Catalysis of the urethan reaction by ferric acetylacetonate [$Fe(AA)_3$] can be described or predicted quantitatively if it is assumed that alcoholysis of the chelate is the first step in the reaction sequence. The validity of this assumption is demonstrated for the following systems: (1) undiluted hexanediisocyanate and neododecanol, (2) *n*-butyl isocyanate and 1-butanol in benzene, (3) *n*-butyl isocyanate in excess 1-butanol, and (4) phenyl isocyanate in excess 1-butanol. The dependence of the rate constant on $Fe(AA)_3$ concentration is parabolic, while the addition of small amounts of acetylacetone (HAA) to the metal-catalyzed reaction causes a hyperbolic response. Both phenomena are described quantitatively by a single equation.

Metal chelate catalysis of alcohol–isocyanate reactions, although widely used in industry, has found little attention in the literature. Very little is known about the mechanism of this catalysis. The few published mechanisms are adaptions of Baker's mechanism for base catalysis[1–4]—the metal chelate essentially substituting the base.[5]

The mechanism proposed by Baker and co-workers is as shown in eq 1 plus 2 and, independent of this,

$$\text{ArNCO} + \text{base} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{complex} \tag{1}$$

$$\text{complex} + \text{ROH} \xrightarrow{k_3} \text{ArNHCOOR} + \text{base} \tag{2}$$

the uncatalyzed reaction shown in eq 3.

$$\text{ArNCO} + \text{ROH} \xrightarrow{k_0} \text{ArNHCOOR} \tag{3}$$

From the stationary state condition, the concentration of the complex is given by eq 4, and the rate of

$$\text{complex} = \frac{k_1[\text{ArNCO}][\text{base}]}{k_2 + k_3[\text{ROH}]} \tag{4}$$

formation of the product is obtained by eq 5.

$$\frac{d[\text{ArNHCOOR}]}{dt} = k_0(\text{ArNCO})(\text{ROH}) + \frac{k_1k_3[\text{ArNCO}][\text{ROH}][\text{base}]}{k_2 + k_3[\text{ROH}]} \tag{5}$$

The second-order rate constant is defined as follows.

$$\frac{d[\text{ArNHCOOR}]/dt}{[\text{ArNCO}][\text{ROH}]}$$

With this eq 5 reduces to

$$k_{\text{bi}} = k_0 + \frac{k_1k_3[\text{base}]}{k_2 + k_3[\text{ROH}]} \tag{6}$$

where k_{bi} = pseudo-second-order rate constant.[6]

If $k_2 >> k_3[\text{ROH}]$, k_{bi} reduces to eq 7 in which k_c =

$$k_{\text{bi}} = k_0 + \frac{k_1k_3}{k_2}[\text{base}] = k_0 + k_c[\text{base}] \tag{7}$$

rate constant of the catalyzed reaction.

Later, other investigators adopted this mechanism by substituting the metal chelate for the base, thus deriving an analogous expression to eq 7, *i.e.*, eq 8,

$$k_{\text{bi}} = k_0 + k_c[\text{Fe(AA)}_3] \tag{8}$$

where $Fe(AA)_3$ = ferric acetylacetonate, a widely used metal chelate catalyst.

Results

Several observations cannot be explained by eq 8. The three more important ones are (1) a marked deviation from linearity of the rate constant with $Fe(AA)_3$ concentration; (2) drastic reduction of catalytic activity by the addition of minute quantities of acetylacetone (HAA); and (3) addition of acids decreases while addition of bases increases the rate of the metal-catalyzed reaction.

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[1] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 713 (1947).

[2] J. W. Baker and J. Gaunt, *ibid.*, 9 (1949).

[3] J. W. Baker and J. Gaunt, *ibid.*, 19 (1949).

[4] J. W. Baker, M. M. Davies, and J. Gaunt, *ibid.*, 24 (1949).

[5] L. Schieler, Technical Report No. 32-129, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, Calif., July 1, 1961.

[6] The prefix "pseudo" denotes that k_{bi} is not a true constant but rather a complex function of the concentration of the reactants and environment.