

sweet odor. It gave a positive Baeyer unsaturation test, decolorized aqueous bromine solution, and gave a positive haloform reaction with concd. sodium hydroxide.

II. Reaction of $\text{CH}_2=\text{CHCH}_2\text{MgBr}$ and CF_3COOH yielded results similar to that obtained in I. Reaction of $\text{C}_6\text{H}_5\text{MgBr}$ and $\text{CF}_2=\text{CFCN}$ yielded about 1 g. of material boiling at 100–102° at 5-mm. Hg pressure. This product gave a positive test for unsaturation with 5% permanganate solution and decolorized bromine solution. It formed a 2,4-dinitrophenylhydrazone instantaneously which after two recrystallizations from ethanol-water mixture showed an m.p. 232–234°C.

Anal.: Calculated for $\text{C}_{15}\text{H}_9\text{F}_3\text{N}_4\text{O}_4$: C, 49.19; F, 15.56. Found: C, 49.72; F, 15.80.

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A Qualitative Test for Mono-, Di-, and Tri-substituted Silanes

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The reducing properties of Group IVB metal hydrides have been known and recognized for a long time, but only recently has any use been made of this information.

Buchner¹ reported that silane reduced aqueous silver nitrate to metallic silver. Later, Stock and Somieski² reported the reduction of iron(III), copper(II), and mercury(II) salts to iron(II), copper(I), and copper(0), and mercury(I) and mercury(0), respectively, the degree of reduction being dependent on the original metal ion to silane ratio in the aqueous solution.

Ruff and Albert,³ while investigating the properties of silicochloroform, found it also could function as a reducing agent. They report the reduction of chromium(VI) oxide to chromium(III) oxide, sulfur trioxide to sulfur dioxide, sulfur dioxide to sulfur, arsenic(III) to arsenic(0), and antimony(III) oxide to antimony(0), the latter two in the presence of catalytic amounts of sodium hydroxide. Quite similar results are recorded by Besson and Fournier.⁴

Concomitant with these reductions is the evolution of hydrogen gas. Kipping⁵ devised a method of quantitative analysis for Si-H compounds which involves measurement of the volume of hydrogen produced. His technique entails the dissolution of the silane in an organic base, such as pyridine or piperidine, and measurement of the hydrogen evolved as the mixture is warmed.

The evolution of hydrogen has also served as a

means of monitoring the kinetics of the reaction of Si-H compounds with base. Price⁶ examined the rate of hydrolysis of trialkylsilanes in aqueous alcoholic potassium hydroxide, and found his data agreed satisfactorily with a pseudo first order kinetic expression during the first three fourths of the reaction. In a similar study,⁷ the effect of substituents on the rate of hydrolysis of triarylsilanes in wet piperidine was found to agree well with the values of Hammett's for carbon compounds. The rates of hydrolysis of triphenylsilane-*d* and triphenylsilane-*t* have also been investigated.⁸

The most recent studies of the reducing power of the Group IVB metal hydrides are those reporting the reduction of fourteen different transition metal salts and seven organic acids with triethylgermane,⁹ and the reduction of certain halides and oxides of seven regular group elements and thirteen transitional elements to a lower oxidation state or, in certain cases, to the free element with triethyltin hydride.¹⁰ Another recent publication¹¹ reports the reaction of Si-H compounds with alcohols in the presence of metallic copper. In light of the low yields reported, there exists the possibility that the reaction is indeed catalyzed by oxides of copper and not the metal itself.

In this laboratory, we have had the occasion to synthesize a large number of partially substituted silanes and, while investigating their chemical and physical properties, have developed a sensitive test for the degree of substitution at the silicon atom. Essentially, the test entails treatment of a mixture of one milliliter of a basic solvent, such as pyridine, and two drops of an approximately 5% aqueous solution of copper(II) chloride with one drop of the silane. Monosubstituted silanes discharge the blue color of the test solution within a few seconds and very rapidly thereafter develop a yellow coloration. Disubstituted silanes are somewhat slower in discharging the blue color, giving a final green coloration. The trisubstituted silanes do not discharge the blue color over a period of three minutes. In all cases where color changes were observed, the aryl compound underwent these changes at a more rapid rate than the similarly substituted alkyl compounds. It is possible to differentiate between monoalkyl and monoarylsilanes using nickel(II) salts. Mercury(II) chloride, potassium permanganate, and silver nitrate, more powerful

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TABLE I
RATE OF REACTION IN PYRIDINE

Oxidant	Color of Complex	Phenylsilsilane		Diphenylsilsilane		Triphenylsilsilane		<i>n</i> -Hexylsilsilane		Di- <i>n</i> -butylsilsilane		Triethylsilsilane	
		Color	Time, Sec.	Color	Time, Sec.	Color	Time, Min.	Color	Time, Sec.	Color	Time, Sec.	Color	Time, Min.
CuCl ₂ ·2H ₂ O	Dk. blue	Green	4	Green	50	Dk. blue	3	Green	6	Green	80	Dk. blue	3
Cu(NO ₃) ₂ ·3H ₂ O	Blue	Yellow	11	Lt. blue	60	Blue	3	Yellow	70	Lt. blue	3 (min.)	Blue	3
		Lt. green	13			Lt. blue	15	Lt. green	60				
CuAc ₂ ·H ₂ O	Blue	Yellow	30	Green	4	Blue	3	Lt. green	60	Green	50	Blue	3
		Brown	2										
NiCl ₂ ·6H ₂ O	Lt. blue	Brown	12	Blue	3 (min.)	Blue	3	Blue	3 (min.)	Blue	3 (min.)	Blue	3
		Brown	6										
Ni(NO ₃) ₂ ·6H ₂ O	Lt. blue	Brown	1	Grey	1	Grey	1	Grey	1	Grey	1	Grey	1
HgCl ₂	Colorless	Brown	1	Brown	2	Brown	5 (sec.)	Brown	1	Brown	2	Brown	2
AgNO ₃	Colorless	Brown	1	Brown	2	Brown	5 (sec.)	Brown	1	Brown	2	Brown	2
KMnO ₄	Deep purple	Brown	2	Brown	2	Brown	5 (sec.)	Brown	2	Brown	2	Brown	2

TABLE II
RATE OF REACTION WITH CuCl₂ IN OTHER SOLVENTS

Solvent	Color of Complex	Phenylsilsilane		Diphenylsilsilane		Triphenylsilsilane		<i>n</i> -Hexylsilsilane		Di- <i>n</i> -butylsilsilane		Triethylsilsilane	
		Color	Time, Sec.	Color	Time, Min.	Color	Time, Min.	Color	Time, Sec.	Color	Time, Min.	Color	Time, Min.
Tetrahydrofuran	Lt. green	Colorless	4	Colorless	3	Lt. green	3	Colorless	9	Lt. green	3	Lt. green	3
		Yellow	30										
Ethylene glycol dimethyl ether	Green	Turbid	60	Green	5	Green	3	Turbid	70	Green	3	Green	3
		Colorless	5										
1,4-Dioxane	Lt. blue	Yellow	22	Lt. blue	3	Lt. blue	3	Yellow	22	Lt. blue	3	Lt. blue	3
		Turbid	30										
Piperidine	Dk. green	Colorless	9	Brown	2 (sec.)	Brown	2.5	Yellow	21	Brown	1	Dk. green	3
		Yellow	15										

oxidants, give positive tests with trisubstituted silanes. Further differentiations are also possible if the time for color change is observed as well as the final color attained.

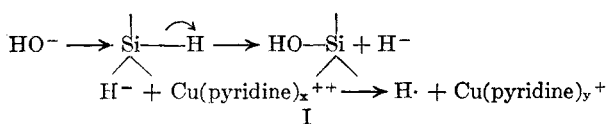
As could be predicted from the previously mentioned kinetic studies,^{6,7} there is a slight substituent effect on the rate of reaction. In the tables, the times recorded are for the specific compounds mentioned. However, time variations due to the substituent effect are small when compared with the variations due to degree of substitution at the silicon atom itself and this factor does not, therefore, reduce the applicability of the test. This was demonstrated more precisely when, after testing a total of seventy-two silanes containing either one, two or three hydrogen atoms attached to silicon, all were found to conform to the specifications of this test.¹²

In Table I are listed the various oxidants tested as possible indicators. In addition to those shown, copper(II) sulfate, vanadium(IV) sulfate, nickel(II) sulfate, iron(III) chloride, sodium chromate, chromium(VI) oxide, chromium(III) chloride, and cobalt(II) chloride were also investigated. The first three, all sulfates, and the iron(III) chloride gave precipitates in pyridine which obscured the color changes. The other four compounds underwent little or no color change over the three-minute period.

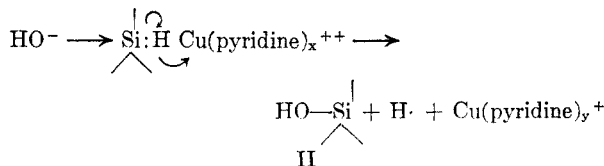
Other polar solvents were investigated as well, and the results, using copper(II) chloride as the oxidant, are assembled in Table II. All are capable of complexing the copper(II) ion somewhat, as evidenced by the various colors observed. It appears that a solvent of basicity and polarity close to that of pyridine is necessary. Piperidine, with its high basicity, is too reactive to be selective; while tetrahydrofuran, ethylene glycol dimethyl ether, and dioxane are not basic and/or polar enough. For intensity of original color and sharpness of color changes, none was as good as pyridine.

Completely nonaqueous systems were investigated also. Suspensions of chloranil, quinone, and azobenzene in pyridine underwent no reaction when treated with the various silanes. However, upon the addition of two drops of water, the evolution of hydrogen was observed and the colors of the solutions were slowly discharged.

These results indicate that hydroxide ion attack on the silane is the first step of the reaction, and the resultant reduction of the oxidant is either by hydride ion in a two step reaction (I) or by a concurrent one electron transfer (II). No attempt



(12) Some correlations between infrared spectra and the number of hydrogens attached to a silicon atom in organosilanes will be reported later



was made to ascertain which mode of reduction is actually followed.

EXPERIMENTAL

Oxidant solutions. Approximately 5% by weight solutions of all salts were prepared by dissolving 0.5 g. of the hydrated salt in 9.5 ml. of distilled water.

Solvents. All the solvents used were distilled and dried over sodium metal before use, except the pyridine and piperidine. The pyridine employed was a fresh bottle of Baker and Adamson purified grade and the piperidine was Eastman White Label.

Silanes. The times recorded in Tables I and II are for the silanes indicated. In the experiments involving pyridine, the triphenylsilane was added as a 50% by weight solution in pyridine. For the reactions involving other solvents a 50% solution of triphenylsilane in benzene was used for convenience.

Procedure. To one milliliter of the organic solvent was added 2 drops of the oxidant solution and the mixture was shaken until the color became uniform. One drop of the silane or silane solution was then introduced with shaking after which the reaction mixture was allowed to stand while the color changes were observed. The results are summarized in Tables I and II.

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o-(2,4-Dihydroxybenzhydryl)benzyl Alcohol

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Since *o*-(4,4'-dihydroxybenzhydryl)benzyl alcohol, which Baeyer called phenolphthalol, was found to be a good laxative,¹ it was decided to prepare and test its isomer, the *o*-(2,4-dihydroxybenzhydryl)benzyl alcohol (VI).

The starting material for its synthesis, the 3-phenyl-3-(2,4-dihydroxyphenyl)phthalide (I) has already been described, but neither of the two methods of preparation is satisfactory. Pech-

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