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HYDROGENOLYSIS OF SOME ORGANOPOLYSILANES

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The hydrogenolysis of organic derivatives of many metals and metalloids is well established[1–9][**] and, in general, proceed according to one of the following reaction paths. The experimental conditions of time, temperature, pressure and catalysts

$$R_nM + n\,H_2 \rightarrow n\,RH + MH_n \quad M = Li, Na, K, Rb, Cs, Mg, Ca, Zn, B \qquad (1)$$

$$R_nM + x\,H_2 \rightarrow x\,RH + R_{n-x}MH_x \quad M = Al \qquad (2)$$

$$R_nM + \tfrac{1}{2}n\,H_2 \rightarrow n\,RH + M \quad M = Zn, Sn, Pb, As, Sb, Bi \qquad (3)$$

$$2\,R_nM + \tfrac{1}{2}n\,H_2 \rightarrow n\,RH + 2\,M \quad M = Zn, Sn, Pb \qquad (4)$$

under which these reactions occur vary from extremely mild for derivatives of the alkali metals to quite vigorous for compounds of the less metallic elements. In fact, the rates of hydrogenolysis have been suggested as a means to determine the relative reactivities of organometallic compounds[2,4,5].

In addition to the reactions of compounds containing only one metal atom, the hydrogenolysis of hexaphenyldilead has also been investigated[2]. Instead of a simple cleavage of the lead–lead bond, which would have afforded triphenyllead hydride, the reaction provided tetraphenyllead and the free metal.

Organosilicon compounds have also been treated with hydrogen under a variety of conditions. Tetraethylsilane, when passed over an aluminosilicate catalyst in a stream of hydrogen at a temperature of 550°, yielded triethylsilane and some ethane[10], in a manner analogous to reaction (2). However, when heated at 350° under 100 atmosphere of hydrogen pressure, ethane and hexaethyldisilane are formed[11]. Similarly, triethylphenylsilane reacts to give benzene, hexaethyldisilane, diethyldiphenylsilane and tetraethylsilane[12], while tetraphenylsilane[11] and tetrabenzylsilane[12] are stable towards hydrogen at temperatures above 400°. In the presence of Raney nickel, the benzene nucleus attached to silicon can be hydrogenated to yield the corresponding cyclohexyl derivatives at temperatures of 100° and hydrogen pressures of about 50 atm.[13]. Thus, it can be seen that organosilanes are somewhat resistant toward cleavage of silicon–carbon bonds by hydrogen. However, we have found that certain silicon–silicon bonds undergo hydrogenolysis in the presence of copper oxide catalysts.

It was considered likely that the chemically labile silicon–silicon bonds in

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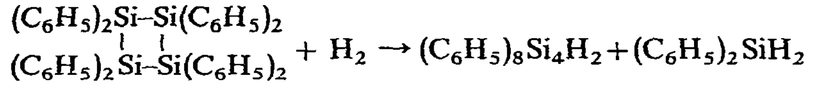
[**] For general surveys to hydrogenation and hydrogenolysis reactions, see ref. 1. We have just learned of a paper which just appeared on some aspects of hydrogenolysis of some phenyl derivatives of monosilicon by Raney nickel[20].

octaphenylcyclotetrasilane (I)[14] might react readily with hydrogen. At low temperatures and pressures, no reaction was observed. However, extensive cleavage occurred when this compound was treated with hydrogen under 800 p.s.i.g. pressure and at 150° in the presence of "copper chromite", according to reaction (5).



$$\begin{matrix}(C_6H_5)_2Si{-}Si(C_6H_5)_2\\ |\quad\quad | \\ (C_6H_5)_2Si{-}Si(C_6H_5)_2\end{matrix} + H_2 \rightarrow (C_6H_5)_8Si_4H_2 + (C_6H_5)_2SiH_2 \quad (5)$$

(I) (II) (10%) (50%)

The yields of the two isolated products were not greatly affected by the time of reaction, which varied from one to five hours. The remainder of the products consisted of complex mixtures containing disiloxane linkages. Various attempts to increase the yield of 1,1,2,2,3,3,4,4-octaphenyltetrasilane (II)[15], the product of a single cleavage, were unsuccessful (see Table 1 in the *experimental part*). It is likely that the rate of dissolution of the quite insoluble starting material is slower than the rate of secondary cleavage. It is somewhat surprising that Raney nickel or palladium-on-charcoal did not appear to effect the hydrogenolysis of silicon–silicon bonds at relatively high temperatures and pressures.

When decaphenylcyclopentasilane[16] was treated with hydrogen in the presence of "copper chromite" under 860 p.s.i.g. pressure and at 160° for two hours, or under the more vigorous conditions at 1000 p.s.i.g. and 200° for four hours, a high recovery of starting material was realized, and only traces of impure diphenylsilane were obtained. Perhaps steric factors combined with a lower reactivity prevented extensive reaction. Some material containing siloxane bonds was obtained.

The hydrogenolysis reaction was also investigated on compounds containing only one silicon–silicon bond. Thus hexaphenyldisilane, when subjected to hydrogen over "copper chromite" catalyst for two hours at 150° and 850 p.s.i.g. pressure, gave a 17% yield of triphenylsilane (reaction 6).

$$(C_6H_5)_3SiSi(C_6H_5)_3 + H_2 \rightarrow 2\,(C_6H_5)_3SiH \quad (6)$$

In addition to a high recovery of starting material, there was isolated 10% of hexaphenyldisiloxane (impure). After five hours under similar conditions, no triphenylsilane was obtained; however, the yield of disiloxane increased. Starting material was recovered to the extent of 68%. These results are understandable in view of the fact that, in a separate experiment under similar conditions, triphenylsilane was converted into the disiloxane, with no trace of recovered starting material being detected. Evidently, the silicon–hydrogen bond was hydrolyzed according to the following, well-established reaction. The amount of water needed for the hydrolysis of the triphenylsilane used was only 0.18 g (0.01 mole).

$$2\,R_3SiH + 2\,H_2O \xrightarrow{-H_2} 2\,R_3SiOH \xrightarrow{-H_2O} R_3SiOSiR_3 \quad (7)$$

The autoclave system undoubtedly contained sufficient moisture for these reactions to occur. Also some water may have come by reaction with the catalyst.

In contrast to the high recovery of hexaphenyldisilane in the preceding reactions, 1,2-dimethyl-1,1,2,2-tetraphenyldisilane underwent hydrogenolysis to give a 73.4% yield of methyldiphenylsilane after 2 hours at 150° and 810 p.s.i.g. pressure in the presence of "copper chromite". Also, 1,1,2,2-tetramethyl-1,2-diphenyldisilane was cleaved under comparable conditions to give a 21.7% yield of impure dimethylphenylsilane, and a mixture of recovered starting material and disiloxane. However, hexaethyldisilane, similarly treated, was recovered in high yield, with no present evidence of the formation of triethylsilane.

Thus, it appears that the disilane bond must be activated by the presence of phenyl groups for hydrogenolysis to occur under the conditions described. On this basis, hexaphenyldisilane might be expected to undergo extensive cleavage. However, steric factors combined with the low solubility of hexaphenyldisilane, might account for the lesser amount of cleavage. A similar phenomenon is observed for the cleavage of the aliphatic carbon–carbon bonds in phenyl-substituted ethanes[17]. For example, pentaphenyl-1,1,2,2- and 1,1,1,2-tetraphenyl-, and even to some extent, 1,1,2-triphenylethane are cleaved by hydrogen under conditions similar to those described above. In the presence of "copper chromite", these compounds give the phenyl-substituted methanes, whereas aliphatic compounds are unaffected[17]. The use of a nickel catalyst provided the respective cyclohexylethanes, without appreciable cleavage of the carbon–carbon bonds except in the case of pentaphenylethane[17], which may have been due in part to dissociation into free radicals.

As mentioned previously, Raney nickel was ineffective in bringing about the cleavage of octaphenylcyclotetrasilane. Furthermore, 1,1,2,2-tetraphenyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane were recovered in high yields when treated with hydrogen under 800 p.s.i.g. pressure at 150° for 3 hours over Raney nickel. Even under more forcing conditions, 220° and 1630 p.s.i.g. pressure for 11 hours in the presence of Raney nickel, the latter compound was recovered in a yield of 69.4%; a small amount of material was obtained which contained silicon–hydrogen bonds, while the remainder of the products showed a strong absorption band for the disiloxane grouping in its infrared spectrum. Both of these fractions also contained phenyl groups and cyclohexyl and/or cyclohexenyl groups. To make sure that the catalyst was active and that the solvent did not contain a catalyst poison, the same reagents were used to successfully hydrogenate tetraphenylsilane to give the tetracyclohexyl derivative[13].

Since the series of methylphenyl-substituted monosilanes can be hydrogenated over Raney nickel catalyst to give the corresponding cyclohexyl compounds[13], it does not seem likely that the presence of methyl groups in 1,2-dimethyl-1,1,2,2-tetraphenyldisilane is the cause of the apparent inability of this compound to undergo hydrogenation. It appears that one of the methyldiphenylsilyl groups prevents the aromatic nuclei on the other from undergoing hydrogenation. The mode of this inhibition is not known, but it may be that steric factors prevent the proper adsorption on the catalytic surface.

In addition, the disiloxane grouping is evidently quite stable towards hydrogenolysis, as hexaphenyldisiloxane was recovered nearly quantitatively after treatment at 150° for two hours under 800 p.s.i.g. of hydrogen pressure in cyclohexane with "copper chromite" as catalyst. There was no evidence of the formation of triphenylsilane or triphenylsilanol.

EXPERIMENTAL

All temperatures recorded are uncorrected. The hydrogenation apparatus was manufactured by the American Instrument Co., Silver Springs, Maryland.

General procedure for high pressure reactions

The reactions were carried out in a pyrex container placed in a steel bomb, which was heated by an external heater, and agitated by a rocking assembly. The system was flushed two or three times with hydrogen by filling to *ca.* 800 p.s.i.g. and releasing to atmospheric pressure before filling to the desired pressure. Agitation and heating were begun at the same time. About 30 min were required to reach a temperature of 100°, and approx. 5 min for each additional 30° rise. The temperature was measured by means of an iron–constantan thermocouple placed in the bottom of the bomb. The temperature was maintained within ±10° of that recorded. The duration of heating was measured from the time the reported temperature was reached until the heater was turned off and agitation stopped. Cooling to room temperature usually required about 8 h. The solids were removed by filtration, and washed with a few ml of benzene. After removal of the solvents by distillation, the products were isolated by crystallization and/or distillation under reduced pressure. The products were identified by their infrared spectra and, in the case of solids, by melting points, and mixed melting points with authentic samples; liquids were also identified by refractive indices.

Octaphenylcyclotetrasilane

The results of the high temperature and pressure reactions are listed in Table 1.

TABLE 1

HYDROGENOLYSIS OF OCTAPHENYLCYCLOTETRASILANE[a]

Catalyst	*Time* (*h*)	*Temp.* (°*C*)	*Pressure* (*p.s.i.g.*)	R_2SiH_2 (%)	$R_8Si_4H_2$[b] (%)	*Starting material* (%)
none added[c]	2	150	800			94[d]
[e]	4	250	1450	trace[f]	2	86
CuCr[g]	1	150	750	46	8	2
	2	150	890	42	5	
	5	150	800	48	12	2
[c]	1	160	100		4	44
CuO/Cr_2O_3[h]	1	150	800	14		72
	1	150–260	750–1000	8		
	3.5	150	975	50		
	2	150	160			98
Ni[i]	1	150	870			94
Pd/C (10%) (0.5 g)	2	150	830			96
C[e,j]	3	150–240	1150–1540			94[d]

[a] R is phenyl in all cases. In all cases, there was also obtained an intractable material which showed strong infrared absorption bands characteristic of siloxane linkages. [b] 1,1,2,2,3,3,4,4-Octaphenyltetrasilane. [c] Reagent-grade xylene was the solvent used. [d] A trace of soluble material containing SiH absorption bands in its infrared spectrum was also obtained. [e] The solvent was reagent-grade toluene. [f] Trace of volatile material with the characteristic odor of diphenylsilane. [g] CuCr is used as the abbreviation for "copper chromite", which was prepared according to the directions of ref. 18. [h] A mixture of 0.3 g of CuO and 0.2 g of Cr_2O_3, which was ground together in a mortar and dried at 130° for 3 h. [i] Raney nickel of W-2 activity. Approx. 1 g was used. [j] One gram of Norite "A" charcoal.

Five grams (0.006 mole) of octaphenylcyclotetrasilane was used in each run. Unless otherwise indicated, the reactions were carried out in *ca.* 100 ml of a purified grade of cyclohexane, m.p. 5–6°, used without further purification.

In addition to the high pressure reactions, several low pressure reactions were

TABLE 2

HYDROGENOLYSIS OF OTHER ORGANOSILANES[a]

Compound (*g*)	*Catalyst* (*g*)	*Time* (*h*)	*Temp.* (°*C*)	*Pressure* (*p.s.i.g.*)	*Product* (%)
$(C_6H_5)_{10}Si_5$[b] (7.5)	CuCr[c] (0.7)	2	150	850	$(C_6H_5)_2SiH_2$ (trace); starting material (80); polysiloxane (15)[d]
		4	200	1000	starting material (66); polysiloxane[d] (24)
$(C_6H_5)_6Si_2$ (5.2)	CuCr[c] (0.5)	2	150	850	$(C_6H_5)_3SiH$ (17); $(C_6H_5)_6Si_2O$ (10); starting material (59.1)
		5	150	820	$(C_6H_5)_6Si_2O$ (22); starting material (68)
sym-$(CH_3)_2(C_6H_5)_4Si_2$ (6.0)	CuCr[c] (0.5)	2	150	810	$CH_3(C_6H_5)_2SiH$ (73.3); siloxane[d]
(12.2)	Ni(W-5) (1)	8	150–170	1000–1220	starting material (91.2); other products[e,f]
(11.8)	Ni(W-5) (1)	11	200–220	1550–1650	starting material (69.4); other products[k]
sym-$(CH_3)_4(C_6H_5)_2Si_2$ (6.0)	CuCr[c] (0.5)	2	150	800	$(CH_3)_2(C_6H_5)SiH$, (21.7 impure); mixture of starting material and siloxane (50)
sym-$(C_6H_5)_4Si_2H_2$ (12.2)	Ni(W-2) (1)	3.5	150	800	starting material (84.4); $(C_6H_5)_2SiH_2$ (trace); siloxane[d]
$(C_2H_5)_6Si_2$ (8.3)	CuCr[c] (0.5)	2	150	800	starting material (90.4)[g]
$(C_6H_5)_6Si_2O$ (6.0)	CuCr[c] (0.5)	2	150	800	starting material (98.4)[h]

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[a] The solvent used in each reaction was *ca.* 80 ml of a purified grade of cyclohexane, m.p. 5–6°, used without further treatment. [b] Decaphenylcyclopentasilane. [c] "Copper chromite": see footnote *g*, Table 1. [d] An infrared spectrum on the distillation residue contained a strong absorption band between 9 and 10 μ, indicative of SiOSi groups. [e] Distillation of the material remaining in the mother liquor gave 6% of material, b.p. 60–80° (0.12 mm), the infrared spectrum of which showed absorption bands due to aromatic and aliphatic C–H bonds, C=C, and SiH bonds. [f] The infrared spectrum of the distillation residue was similar to that described in footnote *e*, except that there was no band for SiH bonds, and there was an additional band due to SiOSi groups. [g] The solvent was carefully distilled through an 18" spinning band column, with a 6 mm bore, rated 23 theoretical plates. No material boiling higher than 66° was obtained. Also, infrared spectra of the solvent fractions and undistilled hexaethyldisilane showed no absorption bands at 4.7 μ, indicating the absence of any triethylsilane. [h] An infrared spectrum of the material remaining in the mother liquor did not contain absorption bands for SiOH or SiH groups.

attempted, from which nearly quantitative recovery of starting material was realized, and no evidence of any products containing silicon–hydrogen bonds was found. The conditions for these reactions were as follows, with the catalyst, solvent, time, temperature and pressure listed, respectively: (1) "copper chromite[18]" (see footnote *g* of Table 1), xylene, 3 h, 130°, 1 atm; (2) "copper chromite[18]", xylene, 24 h, 50°, p.s.i.g.; (3) 10% Pd/C, benzene, 18 h, 80°, 50 p.s.i.g.; (4) W-2 Raney nickel, tetrahydrofuran, 24 h, 80°, 53 p.s.i.g.

Triphenylsilane, conversion to hexaphenyldisiloxane under hydrogenolysis conditions

Five grams of "copper chromite[18]", 5.2 g (0.02 mole) of triphenylsilane, and 100 ml of cyclohexane were heated for 3.5 h at 150° under 800 p.s.i.g. pressure of hydrogen. Work-up of the reaction mixture and concentration of the solvent gave 3.1 g (60%) of impure hexaphenyldisiloxane, m.p. 205–216°. One recrystallization from a mixture of benzene and petroleum ether (b.p. 60–70°) raised the melting point to 222–224°. An infrared spectrum of the residue remaining in the mother liquor showed a strong band between 9 and 10 μ, due to Si–O–Si bonds; there was no band at 4.7 μ, indicating the absence of Si–H bonds.

Hydrogenation of tetraphenylsilane

As a check on the effectiveness of the catalyst and to establish that the solvent did not contain a catalyst poison, tetraphenylsilane, 16.8 g (0.05 mole), was hydrogenated essentially according to published directions[13]. The solvent used was cyclohexane from the same source and the Raney nickel (W-5[19]) was from the same batch as that used in the reactions of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane (Table 2). Subsequent to hydrogenation, the nickel and solids were removed by filtration and treated with excess dilute acid to dissolve the catalyst. The remaining insoluble material was washed with water and dried to give 10.0 g (57.5%) of impure tetracyclohexylsilane, m.p. 260–280°. Two recrystallizations from toluene raised the melting point to 279–281°, the reported m.p.[13]. From the original cyclohexane filtrate, there was obtained another 1.6 g (9.4%) of impure product, m.p. 240–265°, along with various fractions of material with wide melting point ranges, between 140–210°. An infrared spectrum on the oil remaining in the mother liquor showed a weak absorption band at 4.7 μ, indicative of Si–H bonds. There were no bands due to phenyl groups in the spectra of any of the material obtained. An NMR spectrum of tetracyclohexylsilane in $CDCl_3$ (saturated solution at 25°) showed only a complex of bands between τ 8.1 and 9.1 ppm, with respect to TMS, and did not contain bands due to hydrogen attached to phenyl or carbon–carbon unsaturated sites.

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SUMMARY

The disilane bonds of various organosilicon compounds were found to be

cleaved by hydrogen to give silicon hydrides when treated under conditions of relatively high temperatures and pressures in the presence of copper oxide catalysts, providing that the silicon–silicon bonds were activated by the presence of phenyl groups. Raney nickel was not effective as a catalyst for the hydrogenolysis reaction, nor could the aromatic rings be hydrogenated when attached to the disilane linkage.

REFERENCES

1 H. ADKINS, *Reactions of Hydrogen with Organic Compounds over Copperchromium Oxide and Nickel Catalysts*, University of Wisconsin Press, Madison, Wisc., 1937; H. ADKINS AND R. L. SHRINER, *Catalytic Hydrogenation and Hydrogenolysis*, in H. Gilman, *Organic Chemistry, An Advanced Treatise*, Vol. I., Wiley, New York, 2nd ed., 1943, pp. 779–834.
2 H. E. PODALL, H. E. PETREE AND J. R. ZIETZ, *J. Org. Chem.*, 24 (1959) 1222.
3 L. L. GARSHBEIN AND V. N. IPATIEFF, *J. Am. Chem. Soc.*, 74 (1952) 1540.
4 V. N. IPATIEFF, G. A. RAZUVAEV AND I. F. BOGDANOV, *Ber.*, 63B (1930) 335.
5 W. H. ZARTMAN AND H. ADKINS, *J. Am. Chem. Soc.*, 54 (1932) 3398.
6 V. N. IPATIEFF AND G. A. RAZUVAEV, *Ber.*, 63B (1930) 1110.
7 H. E. PODALL AND W. E. FOSTER, *J. Org. Chem.*, 23 (1958) 1848.
8 R. KLEIN, A. BLISS AND H. G. NADEAU, *J. Am. Chem. Soc.*, 83 (1961) 4131.
9 H. GILMAN, A. L. JACOBY AND H. LUDEMAN, *J. Am. Chem. Soc.*, 60 (1938) 2336.
10 N. G. VORONKOV, B. N. DOLGOV AND G. B. KARPENCO, *Zh. Obshch. Khim.*, 24 (1954) 269; *Chem. Abstr.*, 49 (1954) 4505.
11 V. N. IPATIEFF AND B. N. DOLGOV, *Ber.*, 62B (1929) 1220.
12 B. N. DOLGOV AND Y. VOLNOV, *Zh. Obshch. Khim.*, 1 (1931) 91; Chem. Abstr., 25 (1931) 4535.
13 M. KANAZASHI AND M. TAKAKUSA, *Bull. Chem. Soc. Japan*, 27 (1954) 269.
14 H. GILMAN, D. J. PETERSON, A. W. P. JARVIE AND H. J. S. WINKLER, *J. Am. Chem. Soc.*, 82 (1960) 2076.
15 H. GILMAN AND D. J. PETERSON, unpublished studies; see also H. GILMAN AND H. J. S. WINKLER, *J. Org. Chem.*, 27 (1962) 254.
16 H. GILMAN AND G. L. SCHWEBKE, *J. Am. Chem. Soc.*, 86 (1964) 2693.
17 W. H. ZARTMAN AND H. ADKINS, *J. Am. Chem. Soc.*, 54 (1932) 1668.
18 R. CONNOR, K. FOLKERS AND H. ADKINS, *J. Am. Chem. Soc.*, 54 (1932) 1138.
19 H. R. BILLICA AND H. ADKINS, *Org. Syn.*, 29 (1949) 24.
20 W. H. F. SASSE AND K. O. WADE, *Australian J. Chem.*, 19 (1966) 1897.