Palladium-Catalyzed Reactions of Triorganosilicon Hydrides with Halocarbons

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The palladium-catalyzed reactions of silicon–hydrogen bonds with a wide variety of halocarbons produces silicon halides (except fluorides) in high yields. The method is fast and convenient, and has the advantage of not involving contact with either elemental halogen or (free) hydrogen halide. The other products of the reaction depend upon the halocarbon used, but generally all of the halogen atoms are removed from the halocarbon molecules that react. Discussion of the mechanism of the reaction is based on the nature of the reaction products, and the stereochemistry at asymmetric silicon, which is retention of configuration.

In a recent paper[2] from this laboratory we reported that halosilanes could be prepared by the group VIII metal catalyzed reaction of HX (X = halogen) with silicon–hydrogen bonds. Continuing our work in this area, we now report a new general catalytic reaction[3] for the preparation of halosilanes.[4]

Use of a wide variety of halocarbons has revealed some very interesting mechanistic facets of reactions

$$\equiv\mathrm{CX} + \equiv\mathrm{SiH} \xrightarrow{\mathrm{Pd-C}} \equiv\mathrm{SiX} + \equiv\mathrm{CH} \qquad (1)$$

of type 1. This route to the preparation of halosilanes had advantages over direct halogenation, particularly for compounds sensitive to halogen or hydrogen halide. The catalyst used is clearly preferable to Lewis acids such as AlX_3 which have previously been reported to catalyze type-1 reactions.[5]

In Table I are given the results of type-1 reactions. Table I shows that they comprise an excellent method for preparation of chloro- and bromosilanes (and probably iodosilanes). In all cases where reaction occurred, high yields of halosilanes were obtained, and no organosilicon side products were found. The reactions are easily performed, are fairly rapid, and the halosilane products were easily isolated by distillation or crystallization. Owing to the highly exothermic nature of the reaction when using the more reactive compounds, it is necessary to provide adequate cooling, or to add the silane slowly.

The reactions with tribenzylsilane illustrate the value of this method. The reaction of tribenzylsilane with chlorine is reported to yield tribenzylchlorosilane in <60% yield,[6] although this can be improved by doing the reaction in darkness.[7] Using the catalytic reaction (reaction no. 12 and 13 in Table I), pure tribenzylchlorosilane was obtained in almost quantitative yields.

A very interesting facet of this reaction is provided by the nonsilane products. With few exceptions, partially reduced halocarbons could not be isolated from the reaction mixtures. For example, in the reactions of CCl_4 (reaction no. 3 and 12 in Table I), $CHCl_3$, CH_2Cl_2, CH_3Cl, or C_2Cl_6 were not detected as products (vapor phase chromatography and mass spectrum, see Experimental Section). Partially reduced products were also not found in the reactions of $CHCl_3$ (reaction no. 4), CH_3CCl_3 (no. 6), and $PhCCl_3$ (no. 8) (except for a dimer). Instead, completely reduced or coupled products are formed. For CCl_4 and Et_3SiH, eq 2

$$\mathrm{CCl_4 + Et_3SiH \xrightarrow{10\%\ Pd-C} \underset{85\%}{Et_3SiCl} + \underset{15\%}{CH_4} + \underset{40\%}{H_2} + C_nH_{2n+2}} \qquad (2)$$

applies. This complete reduction does not occur in either the uncatalyzed reaction[8] (eq 3) or in the palladium-catalyzed hydrogenolysis of CCl_4 (eq 4).[9] In

$$\mathrm{(Me_3Si)_3SiH + CCl_4 \xrightarrow[2\ hr]{reflux} (Me_3Si)_3SiCl + CHCl_3} \qquad (3)$$

$$\mathrm{CCl_4 + H_2 \xrightarrow{Pd-pumice} CHCl_3 + C_2Cl_6 + HCl} \qquad (4)$$

the present reaction, the order of reactivity as shown in Table I is $CCl_4 > CHCl_3 \gg CH_2Cl_2 > n\text{-BuCl}$. Thus it is obvious that *the production of methane (or other hydrocarbon) in eq 2 does not occur by simple stepwise reduction of CCl_4.* Indeed, it seems clear that *a halocarbon molecule gives an activated or reactive species which stays on the catalyst surface until all of the halogen is stripped away.*

The coupling products are also of some interest. When C_2Cl_6 was isolated from the hydrogenation of CCl_4,[9] it was attributed to dimerization of $\cdot CCl_3$. In an analogous way, formation of $(PhCCl_2)_2$ from $PhCCl_3$ and $(Ph)_2$ from PhCl and PhBr strongly suggests that these products derive *formally* from dimerization of $Ph\dot{C}Cl_2$ and $Ph\cdot$, although the latter most probably are not present as "free" radicals. Likewise, formation of higher hydrocarbons (consisting mostly of CH_2 and CH_3 groups) from CCl_4 suggests

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[2] L. H. Sommer and J. D. Citron, *J. Org. Chem.*, **32**, 2470 (1967).

[3] A reaction employing a mixture of an α-halo ester (a highly activated halide) and colloidal nickel has been used to prepare halosilanes from organosilicon hydrides: N. F. Orlov, R. A. Bogatkin, Z. I. Sergeeva, and M. G. Voronkov, *Zh. Obshch. Khim.*, **33**, 1934 (1963); N. F. Orlov and L. N. Slezar, *ibid.*, **36**, 1078 (1966).

[4] After this study was completed, it came to our attention that a very limited investigation of a similar reaction using metal catalysts (Ni, Co, Pd, Pt) with halobenzenes had been reported to yield halosilanes in high yield [Yu. I. Khudobin, B. N. Dolgov, and N. P. Kharitonov, *Khim. i. Prakt. Primenenie Kremnorgan. Soedin., Tr. Konf., Leningrad*, **1958**, 155 (1961); *Chem. Abstr.*, **56**, 8737 (1962); Yu. I. Khudobin, M. G. Voronkov, and N. P. Khartonov, *Latvijas PSR Zinatnu Akad. Vestis Kim. Ser.*, 595 (1967); *Chem. Abstr.*, **68**, 69070 (1968)]. The general reaction is

$$\mathrm{R_3SiH + PhX \xrightarrow[\Delta]{metal} \underset{99\%}{PhH} + \underset{90\text{–}98\%}{R_3SiX}}$$

$$\mathrm{X = Cl, Br, I}$$

[5] C. Eaborn, "Organosilicon Compounds," Butterworth and Co. Ltd., London, 1960, p 212.

[6] J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 556 (1950).

[7] Reference 5, p 169.

[8] H. Gilman and R. L. Harrell, *J. Organometal. Chem.*, **5**, 199 (1966). The example cited here is an exceptionally good one. It has been reported [Y. Nagai, *et al.*, *J. Organometal. Chem.*, **9**, P21 (1967)] that R_3SiH does not react with CCl_4, even after 10 hr at 80°. This illustrates the value of the palladium catalyst.

[9] M. A. Besprozvannyi, N. F. Kononov, and V. V. Kharlamov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1345 (1965).

TABLE I

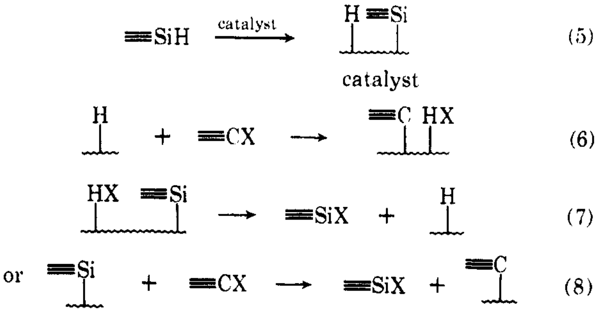
10% Pd–C CATALYZED REACTIONS OF HALOCARBONS WITH SILICON–HYDROGEN BONDS

Type-1 reactions, no.	Silane	Halocarbon	Reaction time,[a] min	Products: Halosilanes[b]	Products: Other solids and liquids[b]	Products: Gases (ratio,[c] volume[d])
1	Et_3SiH	$PhCF_3$	(1440)	No reaction (ir)		
2	Et_3SiH	PhF	(1000)	No reaction (ir)		
3	Et_3SiH	CCl_4	<1	Et_3SiCl (85%, i)	C_nH_{2n+2} (ir, nmr)	H_2, CH_4 (1.0:0.18, 5.3 ml)
4	Et_3SiH	$CHCl_3$	20	Et_3SiCl (glpc)	$Cl_2C{=}CCl_2$ (glpc)	H_2, CH_4 (1.0:1.5, 6.7 ml)
5	Et_3SiH	CH_2Cl_2	(2300)	Little or no reaction (ir)		
6	Et_3SiH	CH_3CCl_3	150	Et_3SiCl (glpc)		H_2, C_2H_6 (1.0:2.2, 4.5 ml)
7	Et_3SiH	$PhCH_2Cl$	<1	Et_3SiCl (glpc)	$PhCH_3$ (glpc)	None
8	Et_3SiH	$PhCCl_3$	<1	Et_3SiCl (glpc)	$(PhCCl_2)_2$[e] (72%, i) $PhCH_3$ (20%, glpc)	H_2 (5.5 ml)
9	Et_3SiH	*n*-BuCl	(1400)	No reaction (ir)		
10	Et_3SiH	PhCl	7	Et_3SiCl (ir, glpc)	PhH (78%, glpc) PhPh (31%, glpc)	Gas evolved
11	Et_3SiH	*o*-$Cl_2C_6H_4$	1800	Et_3SiCl (ir)	*f*	Gas evolved
12	$(PhCH_2)_3SiH$	CCl_4	(1200)	$(PhCH_2)_3SiCl$[g] (99%, i)		Gas evolved
13	$(PhCH_2)_3SiH$	$PhCH_2Cl$	(1200)	$(PhCH_2)_3SiCl$[g] (99%, i)		None
14	α-NpPhMeSiH	CCl_4	15	α-NpPhMeSiCl (95%, i)		Gas evolved
15	α-NpPhMeSiH	$CHCl_3$	1560	α-NpPhMeSiCl (93%, i)		Gas evolved
16	α-NpPhMeSiH	$PhCH_2Cl$	(2880)	α-NpPhMeSiCl (90%, i)		None
17	Et_3SiH	$CHBr_3$	105	Et_3SiBr (ir)		H_2, CH_4 (1.0:0.88, 6.8 ml)
18	Et_3SiH	$PhCH_2Br$	2	Et_3SiBr (ir)		None
19	Et_3SiH	PhBr	4	Et_3SiBr (ir, glpc)	PhH (79%, glpc) PhPh (24%, glpc)	Gas evolved
20	Et_3SiH	PhI	25	Et_3SiI(?)[h]		Gas evolved

[a] Based upon length of time of gas evolution or until reaction started to cool. When these were not observed, time of work-up is given in parentheses. [b] Identified by the following methods: i, isolated; ir, infrared spectrum; nmr, nuclear magnetic resonance spectrum; glpc, gas–liquid partition chromatography. [c] Molar ratio, determined by mass spectrum. [d] Total volume of gas per mmole of Si–H bond, corrected for vapor pressure of the solvent and to STP. [e] Mp 159–161°. [f] An unidentified white solid precipitated during the reaction, which, by analogy with the preceeding reaction, was probably a mixture of poly-*o*-phenyls. [g] Mp 140.5–141.5°. [h] Owing to the highly corrosive nature of the reaction mixture [it gave off acidic fumes (HI?) and had a purple color (I_2?)], it was not examined spectroscopically.

coupling of $\cdot CCl_3$, $:CCl_2$, and $:\dot{C}Cl$ units with subsequent reduction, or alternately the coupling of the corresponding hydrocarbon units. Since these reactions do not occur without the silane being present (see Experimental Section), the silane must be intimately involved in one of the first steps of the reaction.

In view of the above evidence, the mechanism in eq 5–8 seem reasonable. Repetition of steps similar to eq 6 or 8 would remove more halogens from the adsorbed carbon species, and carbon–carbon, carbon–hydrogen, and/or hydrogen–hydrogen coupling concurrent with or after the halogen stripping would account for the products observed. The cleavages are meant to be homolytic, but "free radicals" are not necessarily implied.



The question as to whether hydrogen abstracts halogen (eq 6 above), with the resulting "hydrogen halide" halogenating the silicon, or silicon directly combines with halogen (eq 8 above) is a difficult one. Although the problem cannot be resolved at this time, there is circumstantial evidence supporting both hypotheses. Δ*H* for both reactions, at least in the gas phase, is favorable, being −34 kcal/mol for eq 6, and −58 kcal/mol for eq 8, both using CCl_4 as the halocarbon.[10] The uncatalyzed tin hydride reduction of carbon–halogen bonds is believed[11,12] to proceed through a step similar to eq 8, but the over-all reaction is a stepwise reduction. Finally, the stereochemistry (Table II) is retention of configuration at asymmetric silicon, which is the same stereochemistry observed in the palladium-catalyzed reaction of hydrogen chloride with silicon–hydrogen bonds.[2] Thus the reaction *could* proceed through adsorbed hydrogen chloride molecules.

Consideration of the stereochemistry raises two other points. The first of these is that silicon "free radicals" are not present, since they would lead to racemization. Thus, even if the silicon–hydrogen bond underwent homolytic cleavage, the silyl "radical" would be strongly adsorbed or bonded to the catalyst surface. Second, while the stereochemistry could imply a simple

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[10] Calculated from values given by the following: L. A. Errede, *J. Phys. Chem.*, **64**, 1031 (1960); G. G. Hess, F. W. Lampe, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 5327 (1965).

[11] Silyl "radicals" are known to abstract halogen from halocarbons such as alkyl chlorides [(J. A. Kerr, B. J. A. Smith, A. F. Trotman-Dickenson, and J. C. Young, *J. Chem. Soc., A*, 510 (1968); R. N. Haszeldine and J. C. Young, *ibid.*, 4503 (1960)], and aryl halides [J. Curtice, H. Gilman, and G. S. Hammond, *J. Amer. Chem. Soc.*, **79**, 4654 (1957); A. G. Beaumont, C. Eaborn, R. A. Jackson, and R. W. Walsingham, *J. Organometal. Chem.*, **5**, 297 (1966)]. It has been noted (Haszeldine and Curtice) that fluorine is abstracted much less readily than either chlorine or bromine.

[12] L. W. Menapace and H. G. Kuivila, *J. Amer. Chem. Soc.*, **86**, 3047 (1964).

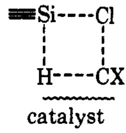
Table II

Stereochemistry of the Palladium-Catalyzed Reaction of (−)-α-NpPhMeSi*H with Chlorocarbons

Chlorcarbon	[α]D, deg, product[a]	Stereospecificity[b]
CCl_4	+4.2	83%, retention
$CHCl_3$	+3.1	75%, retention
$PhCH_2Cl$	+0.9[c]	57%, retention
$PhCH_2Cl$[d]	+1.0	58%, retention
$PhCCl_3$[d]	0.0	Racemic
$PdCl_2$[e]	+5.8	96%, retention

[a] Based upon optically pure starting material. Rotations taken in cyclohexane or heptane. [b] Based upon optically pure α-NpPhMeSi*Cl having [α]D 6.3° (*cf.* L. H. Sommer, C. L. Frye, and K. W. Michael, *J. Amer. Chem. Soc.*, **86**, 3271 (1964). [c] Rotation may have been due to impurities; crystallized material was racemic. [d] Done in heptane solvent (to reduce the possibility of solvent induced racemization) with ~10 mol % excess of chlorocarbon. [e] See Experimental Section.

four-center mechanism such as



the products obtained clearly show that the actual mechanism is more complex. Such *a simple four-center mechanism would lead to stepwise reduction, which is not observed.*

The failure of the fluorides to react is of some interest (reaction no. 1 and 2). In terms of the thermochemistry of processes analogous to eq 6 and 8, the transformation is still favorable. However, the carbon–fluorine bond energy is much higher than any of the other C–X bond energies, and this may inhibit reaction rate. Another factor which may be important would derive from a significant difference in adsorption of C–F relative to the situation for the other halogens. Perhaps C–F is adsorbed less strongly because fluorine does not have low-lying vacant d orbitals. This difference in adsorption may also account for the difference in stereochemistry between HF and HCl when allowed to react catalytically with the silicon–hydrogen bond.[2]

Experimental Section

All halocarbons were the best commercially obtainable grades, and were purified (especially dried) before use, if necessary. Triethylsilane was prepared from the reduction of triethylchlorisilane with $LiAlH_4$, bp 109°. The 10% Pd-C was obtained from Matheson Coleman and Bell.

General Procedure.—The 10% Pd-C catalyst (50 mg) was placed in an erlenmeyer flask protected from atmospheric moisture, and 10 ml of the halocarbon was added. The silane (1 ml, or 1 g in the case of solids) was added, and the reaction was allowed to proceed. In the case of larger scale runs, cooling was provided where necessary. The catalyst was then allowed to settle or was filtered from the solution.

Analysis of the Reactions.—Where the halosilanes were isolated, they were obtained by either distillation or crystallization, and their physical constants compared with their literature values.[13]

Infrared spectra were obtained on a Beckman IR-12 using KBr optics, usually employing the solvent in which the reaction was carried out. The band at 2100 cm^{-1} identified unreacted Si–H, and the bands at 480 and 410 cm^{-1} identified the Si–Cl and Si–Br stretching vibrations, respectively.[14] Vapor phase chromatograms were obtained on a 5-ft 20% SE-30 on Chromosorb W column using helium as the carrier gas at a flow rate of 50–60 ml/min in an Aerograph A90P3 instrument. All compounds were identified by the correspondence of their retention times with known substances. In addition, certain compounds were searched for and not found, and these are listed in Table III.

Table III

Compounds Not Detected in 10% Pd–C Catalyzed Reactions

Reaction no.[a]	Vapor phase chromatography	Mass spectrum
3[b]	$CHCl_3$, CH_2Cl_2, C_2Cl_6	CH_3Cl, CH_2Cl_2
4	CH_2Cl_2, $(CHCl_2)_2$	CH_3Cl, CH_2Cl_2
6		C_2H_5Cl
7	$(PhCH_2)_2$	
8	$PhCHCl_2$, $PhCH_2Cl$	
17		CH_3Br

[a] Reaction numbers refer to those given in Table I. [b] A control experiment was run in which 0.1 ml of $CHCl_3$ was added prior to the reaction of 10 ml of CCl_4 and 1.0 ml of Et_3SiH. Analysis (glpc) before and after the reaction indicated that the amount of $CHCl_3$ present was unchanged.

Reactions in which the gases were analyzed were run in a closed system under nitrogen, and the gases produced were measured in a gas buret over mercury. The gases were then expanded into an evacuated flask, and analyzed by a CEC Model 21-104 mass spectrometer.[15] Compounds whose peaks were searched for and not found are listed in Table III. Ratios were computed from the peak intensities, after calibration with appropriate standards.

Attempted Reaction of $PhCCl_3$ with 10% Pd-C.—A mixture of $PhCCl_3$ (15 ml) and 0.15 g of 10% Pd-C was stirred for 50 hr at room temperature, and then 40–50° for 15 min. After filtration, no $(PhCCl_2)_2$ could be found in the filtrate. Therefore, $PhCCl_3$ is stable in the presence of only 10% Pd-C.

Palladium Black Catalyzed Reaction of Et_3SiH and CCl_4.—Palladium black (0.111 g) (from the reaction of α-NpPhMeSi*H and $PdCl_2$) and CCl_4 (12 ml) were mixed in a flask. Triethylsilane (1.20 ml) was added, and a very vigorous reaction (heat, gas evolution) ensued. After the reaction subsided the mixture was filtered (filtrate contained Et_3SiCl) and the catalyst was washed with pentane and then dried under vacuum (5 × 10^{-2} mm) for 30 hr. The catalyst was analyzed to see if any carbon was produced in the reaction.

Anal. Found: C, 5.2 (before reaction). C, 6.0 (after reaction).

Thus no appreciable amount of carbon was formed.

Reaction of $PdCl_2$ with α-NpPhMeSi*H.—A solution of 1.38 g of (−)-α-NpPhMeSi*H ([α]D −35°) in 50 ml of pentane was prepared, and to this was added 1.0 g of anhydrous $PdCl_2$. A vigorous reaction (gas evolution) occurred, and after 1 hr the residual palladium black was removed by filtration. After crystallization, 1.15 g (73%) of α-NpPhMeSi*Cl, [α]D +5.8°, was obtained.

Registry No.—Silane (reaction 1, Table I), 617-86-7; silane (reaction 12, Table I), 1747-92-8; silane (reaction 14, Table I), 1025-09-8; $PdCl_2$, 7647-10-1; PdC, 12313-34-7.

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[13] V. Bazant, V. Chvalovsky, and J. Rathousky, "Organosilicon Compounds," Vol. 2, Academic Press, New York, N. Y., 1965.

[14] A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960); **19**, 849 (1963).

[15] The authors wish to thank Mr. John Voth for his aid in obtaining the mass spectra.