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SELECTIVE REDISTRIBUTION REACTIONS OF ORGANOSILANES IN THE PRESENCE OF CHLOROPLATINIC ACID *

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Summary

Tetrasubstituted silanes of the general formula $R_2SiR'_2$ undergo redistribution reactions quite selectively in the presence of $SiHCl_3$ and chloroplatinic acid. It is the smallest and seemingly the least hindered of the R groups on the tetrasubstituted silane which exchange most readily with a chloro group on trichlorosilane.

Introduction

It has been recognized for more than half a century that many organosilanes and organochlorosilanes can undergo metal halide catalyzed disproportionation or redistribution. Lewis acids such as anhydrous aluminum chloride are most often used as catalysts for such reactions [1,2]. Random cleavages of silicon–carbon bonds by platinum reagents have also been reported [3–6], wherein chloroplatinic acid was commonly used as the platinum source. Redistribution reactions are of great importance from an industrial viewpoint, since they enable inert organosilanes to be converted to reactive organochlorosilanes useful in the manufacture of silicone polymers. For example [7].

$$Ph_4Si + SiCl_4 \xrightarrow[300°C,\ press.]{CuCl} Ph_3SiCl\ (34\%) + \text{other phenylchlorosilanes}$$

Several years ago a unique and selective exchange of a chlorine atom on trichlorosilane with a methyl group on a tetraalkylsilane in the presence of chloroplatinic acid was discovered [8] in our Laboratory. Thus:

$$n\text{-}C_8H_{17}SiEt_2Me + SiHCl_3 \xrightarrow[148°C,\ 24\ h]{H_2PtCl_6} n\text{-}C_8H_{17}SiEt_2Cl\ (96\%) + MeSiHCl_2$$

It was clear from the earlier disclosure [8], and as exemplified by the above

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* Dedicated to Professor Raymond Calas on the occasion of his 70th birthday (April 8, 1984).

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equation, that a methyl group migrated preferentially, regardless of what other alkyl or aryl group was attached to the silicon atom.

It was the purpose of the present research to determine whether the methyl group is really unique, or whether, under carefully selected conditions, other groups can be made to exchange.

$$R^1R^2R^3R^4Si + SiHCl_3 \xrightarrow[\Delta]{\text{Pt cat.}} R^2R^3R^4SiCl + R^1SiHCl_2$$

The results described herein indicate that a wide variety of other groups can be made to exchange, but that again the exchange is quite selective.

In order to study the selectivity between two alkyl groups toward alkyl–chloro exchange, compounds like $R_2SiR'_2$ were chosen as starting materials to eliminate any statistical effects of the alkyl groups (See Table 1; entries 1–4). It is evident from entries 1–3 in Table 1 ($Et_2SiR'_2$) that, when R′ is a group larger than ethyl, quite a selective ethyl–chloro exchange is observed. The yields of the corresponding $EtClSiR'_2$ were above 80%. It should also be noted that tetra-n-propylsilane (Table 1; entry 5) was converted to tri-n-propylchlorosilane in 78% yield, whereas diethyldi-n-propylsilane gave diethyl-n-propylchlorosilane in only a 9% yield (Table 1; entry 1). Unfortunately, a precise selectivity between the n-propyl and the i-propyl group (Table 1; entry 4) could not be ascertained because of the analytical difficulties encountered in the separation of the isomers of the tripropylchlorosilanes. Analysis of the product of this reaction by VPC showed seven components. One of the major components (53%) was shown by GC-MS to consist of two isomers with a molecular ion (m/e) at 192. The elemental analysis of this mixture agreed well with the composition $C_9H_{21}SiCl$. We have tentatively assigned the structures of these two isomers as $n\text{-PrClSi-i-Pr}_2$ and $n\text{-Pr}_2\text{SiCl-i-Pr}$.

The *p*-tolyl group on tetra-*p*-tolylsilane was also found to undergo exchange with a chloro group on trichlorosilane (Table 1; entry 6). Previously [8] it was observed that under identical conditions phenyltrimethylsilane was converted to dimethylphenylchlorosilane in 70% yield. These examples again illustrate the propensity for methyl migration.

One rather surprising conclusion can be drawn from the data in Table 1. There is nothing unique about the methyl group in these exchanges except for its size. Table 1

TABLE 1

EXCHANGE REACTIONS BETWEEN ORGANOSILANES AND TRICHLOROSILANE

Organosilanes	Reaction conditions (°C/h)	Products
		$ClSiRR'_2$ (Yield %)+$HSiCl_2R$
1. $Et_2Si\text{-n-}Pr_2$	153/72	$ClSiEt\text{-n-}Pr_2$ (81) $HSiCl_2Et$ $ClSiEt_2\text{-n-}Pr$ (9) $HSiCl_2\text{-n-}Pr$
2. $Et_2Si\text{-i-}Pr_2$	161/72	$ClSiEt\text{-i-}Pr_2$ (85) $HSiCl_2Et$
3. $Et_2Si\text{-n-}Bu_2$	164/72	$ClSiEt\text{-n-}Bu_2$ (83) $HSiCl_2Et$
4. $n\text{-}Pr_2Si\text{-i-}Pr_2$	165/72	mixture of $HSiCl_2\text{-n-}Pr$ + $(C_3H_7)_3SiCl$ isomers
5. $n\text{-}Pr_4Si$	166/24	$ClSi\text{-n-}Pr_3$ (78) $HSiCl_2\text{-n-}Pr$
6. (p-tolyl)$_4$Si	145/48	ClSi-p-tolyl$_3$ (65)[a]

[a] Based on ClSi-*p*-tolyl$_3$/(*p*-tolyl)$_4$Si ratio in product mixture.

demonstrates that there is a decided preference for the smallest and probably the least hindered of the alkyl groups attached to silicon to exchange. Even aryl groups like the *p*-tolyl can be made to exchange.

Efforts are presently underway to attempt to recycle the platinum in these exchanges. We are presently assuming that Pt^{II} is the active catalyst species in these reactions. It would follow that Pt^{IV} is being reduced to Pt^0 during the course of the group exchanges. We have ascertained that Pt black does form during the course of these reactions but is completely inactive as a catalyst for the exchange sequence. Various ways of oxidizing Pt^0 to higher valence states during the course of the exchange reaction are presently being examined.

Experimental

Chloroplatinic acid (J.T. Baker) was used as received. Trichlorosilane was distilled from quinoline prior to use. Routine VPC work was carried out on an F and M model 720 gas chromatograph. The ratio of each component was determined by triangulation of the integration peaks. Nuclear magnetic resonance (NMR) spectra were obtained from a Varian A-60 or Perkin–Elmer R-32 spectrometer. The GC-MS (70 eV) data were recorded on a Finnigan 4000 mass spectrometer, utilizing a Nova 4 data system, interfaced with a Finnigan 9610 gas chromatograph. Elemental analyses were performed by Dr. C.S. Yeh and Dr. D. Lee in the Microanalytical Laboratory of the Department of Chemistry, Purdue University.

Preparation of organochlorosilanes

The organochlorosilanes were prepared in essential accordance with standard methods [9,10]. Ethyldichlorosilane [9] and n-propyldichlorosilane [11] were prepared from trichlorosilane and the corresponding alkylmagnesium bromide. Tri-*p*-tolylchlorosilane [12] was prepared from tetrachlorosilane and *p*-tolylmagnesium bromide. It melted at 116–117°C; (lit. [12] m.p. 115–116°C). Tri-n-propylchlorosilane [13] was prepared by reaction of 1 equiv. of silicon tetrachloride and 3 equiv. of n-PrLi in 78% yield. Ethyldi-n-propylchlorosilane [14] was prepared from 1 equiv. of ethylmagnesium bromide and 0.9 equiv. of di-n-propyldichlorosilane in 43% yield; (b.p. 176–178°C; lit. [14], 181°C). Di-i-propyl-n-propylchlorosilane was prepared in 51% yield from 1 equiv. of n-$PrSiCl_3$ and 2.5 equiv. of i-PrLi. Diethyl-n-propylchlorosilane was obtained by treating n-propyltrichlorosilane with ethylmagnesium bromide (b.p. 168–170°C; lit. [15] 166°C).

General procedure for the preparation of tetraalkylsilanes

A flame-dried, two-neck flask was equipped with a magnetic stirrer, water-cooled condenser (with drying tube) and dropping funnel (with nitrogen inlet) and then charged with the appropriate alkyllithium compound in anhydrous diethyl ether or n-pentane. The organochlorosilane was then added through the dropping funnel. The mixture was stirred at room temperature for an appropriate time and hydrolyzed. The organic residue after solvent removal was washed with concentrated H_2SO_4 several times, then with water, dilute ammonium hydroxide and finally again with water. It was then dried over anhydrous sodium sulfate. The product was obtained by fractional distillation.

Diethyldi-n-propylsilane

This compound was prepared from diethyldichlorosilane (8.0 g, 0.05 mol) and n-propyllithium (0.128 mol), following the general procedure. The mixture was refluxed for three hours before hydrolysis. There was obtained 6.5 g (75%) of diethyldi-n-propylsilane: b.p. 184°C. (lit. [16], 185–186°C); NMR (CCl_4), δ 0.40–0.70 (m, 8H), 0.90–1.12 (m, 12H), 1.19–1.62 (m, 4H). Anal. Found: C, 69.90; H, 13.74; Si, 16.00. $C_{10}H_{24}Si$ calcd.: C, 69.76; H, 13.95; Si, 16.28%.

Diethyldi-i-propylsilane

By the general method with 2.7 g (0.015 mol) of ethyldi-i-propylchlorosilane and 0.03 mol of ethyllithium, diethyldi-i-propylsilane was obtained in 67.5% yield: b.p. 184°C, NMR (CCl_4), δ 0.50–0.75 (m, 4H), 0.90–1.15 (m, 20H). Anal. Found: C, 69.38; H, 14.02; Si, 16.03. $C_{10}H_{24}Si$ calcd.: C, 69.76; H, 13.95; Si, 16.28%.

Diethyldi-n-butylsilane

From diethyldichlorosilane (8.0 g, 0.05 mol) and 0.152 mol of n-butyllithium following the general procedure, was obtained 5.1 g (51%) of diethyldi-n-butylsilane: b.p. 84.5°C/6.5 Torr.. (lit. [17] 68–70°C/2 Torr.); NMR (CCl_4), δ 0.30–0.60 (m, 8H), 0.70–1.02 (m, 12H), 1.10–1.40 (m, 8H). Anal. Found: C, 72.12; H, 14.35; Si, 13.98. $C_{12}H_{28}Si$ calcd.: C, 72.00; H, 14.00; Si, 14.00%.

Di-n-propyldi-i-propylsilane

This compound was prepared from di-i-propyl-n-propylchlorosilane (7.5 g, 0.039 mol) and n-propyllithium (0.06 mol), following the general procedure. The reaction mixture was refluxed for three hours before hydrolysis. Crude product (5.7 g) consisting of di-n-propyldi-i-propylsilane and di-i-propyl-n-propylchlorosilane was obtained. This mixture was allowed to react with another 0.03 mol of n-propyllithium. After sixteen hours of reflux, the product was worked-up as usual. There was obtained 3.9 g (50% yield overall) of di-n-propyldi-i-propylsilane: b.p. 216–217°C; NMR (CCl_4), δ 0.40–0.70 (m, 4H), 0.90–1.05 (m, 20H), 1.20–1.45 (m, 4H). Anal. Found: C, 71.93; H, 14.25. $C_{12}H_{28}Si$ calcd.: C, 72.00; H, 14.00%. The mass spectrum gave a molecular ion, *m/e* at 200.

Tetra-n-propylsilane

By the general procedure with 7.0 g (0.04 mol) of tetrachlorosilane and 0.20 mol of n-propyllithium, tetra-n-propylsilane was obtained in 87% yield; b.p. 210–212°C. (lit. [18] 213–215°C); NMR (CCl_4), δ 0.40–0.59 (m, 8H), 0.85–1.05 (t, 12H), 1.10–1.52 (m, 8H).

Tetra-p-tolylsilane

The general procedure for the preparation of tetraalkylsilanes was followed except the residue, after removal of the solvent, was recrystallized from cyclohexane. From 0.217 mol of *p*-tolyllithium and 6.16 g (0.036 mol) of tetrachlorosilane, tetra-*p*-tolylsilane was obtained in a 57% yield as white crystals: m.p. 236–237°C. (lit. [4] 232–233.5°C); NMR (CCl_4), δ 2.37 (s, 12H), 7.17–7.56 (2 doublets, 16H).

Exchange of alkyl and chloro groups attached to silicon. General procedure

The tetraalkylsilane, trichlorosilane, and chloroplatinic acid were placed in a 10 × 200 mm Pyrex tube and cooled to −78°C while flushing with nitrogen. The tube was then sealed and heated in an oil bath for the appropriate time. The tube was cooled to −78°C then opened, and the resulting mixture was distilled under reduced pressure for analyses.

Diethyldi-n-propylsilane (Table 1, Entry 1)

Following the general procedure, Et_2Si-n-Pr_2 (1.1 g, 6.4 mmol), $HSiCl_3$ (1.9 g, 14 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 33 mg) was heated in a sealed tube at 153°C for 72 h. Distillation afforded a first fraction (1.9 g, b.p. ~ 25°C/8 Torr) and a second fraction (1.1 g, b.p. 51–54°C/8 Torr). Analysis by VPC (10%QF-1, 12′, 140°C) of the first fraction was made by coinjection and concordance of retention times with known samples of $HSiCl_3$ (44%), $EtSiHCl_2$ (36%), n-$PrSiHCl_2$ (4%), and other impurities. The second fraction was identified by a similar method to be EtClSi-n-Pr_2 (81% yield), Et_2SiCl-n-Pr (9% yield), Et_2Si-n-Pr_2 and small amount (6%) of unidentified impurities.

Diethyldi-i-propylsilane (Table 1, Entry 2)

Using the general procedure, Et_2Si-i-Pr_2 (0.7 g, 4 mmol), $HSiCl_3$ (1.1 g, 8 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 20 mg) were heated in a sealed tube at 161°C for 72 h. Distillation afforded two fractions. Analysis by VPC (10%QF-1, 12′, 140°C) of the first fraction (0.65 g, b.p. ~ 25°C/40 Torr.) by coinjection of known samples showed the presence of $HSiCl_3$, $EtHSiCl_2$, and a minor impurity. VPC analysis (10%QF-1, 12′, 200°C) of the second fraction (0.70 g, b.p. 54–55°C/7 Torr) indicated there were three components. The first component (5%) was not identified. The second component was found to be Et_2Si-i-Pr_2. The third component was collected by preparative VPC (10%QF-1, 12′, 200°C) and found to be EtClSi-i-Pr_2 (85% yield). Anal. Found: C, 53.99; H, 10.88; Cl, 19.55; Si, 15.44. $C_8H_{19}SiCl$ calcd.: C, 53.75; H, 10.71; Cl, 19.83, Si, 15.71%.

Diethyldi-n-butylsilane (Table 1, Entry 3)

Following the general procedure, Et_2Si-n-Bu_2 (1.2 g, 6 mmol) $HSiCl_3$ (1.6 g, 12 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 30 mg) were heated at 164°C for 72 h in a sealed tube. Distillation afforded two fractions. VPC analysis (10%QF-1, 12′, 140°C) of the first fraction (1.45 g, b.p. ~ 25°C/9 Torr) by coinjection with known samples indicated the presence of $HSiCl_3$, $EtHSiCl_2$, and a minor impurity. VPC analysis (10%QF-1, 12′, 210°C) in a similar way showed the second fraction (1.3 g, b.p. 75–85°C/9 Torr) was composed of $EtHSiCl_2$, Et_2Si-n-Bu_2, and a major component (79%). An analytical sample of the major component was obtained by VPC (10%QF-1, 12′, 210°C) and found to be EtClSi-n-Bu_2 (83% yield): NMR (CCl_4), δ 0.5–1.0 (m, 15H), 1.1–1.5 (m, 8H). Anal. Found: C, 58.06; H, 11.37; Cl, 17.30; Si, 13.38. $C_{10}H_{23}SiCl$ calcd.: C, 58.07; H, 11.21; Cl, 17.14; Si, 13.58%.

Di-n-propyl-di-i-propylsilane (Table 1, Entry 4)

Following the general procedure, n-Pr_2Si-i-Pr_2 (0.8 g, 4 mmol), $HSiCl_3$ (1.1 g, 8 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 20 mg) were heated in a sealed tube at 165°C for 72 h. Distillation afforded 1.3 g of material. VPC analysis (10%SE-30, 10′, 170°C) indicated seven components. The first six components were identified by coinjection of known samples to be $HSiCl_3$ (6%), n-$PrHSiCl_2$ (22%), and other impurities (19%). The seventh component (53%) was collected by preparative VPC (10%QF-1, 12′, 160°C). GC-MS analysis indicated two isomers in which both gave a molecular ion, *m/e* at 192. The structures of the two isomers were tentatively assigned to be n-PrClSi-i-Pr_2 and n-Pr_2SiCl-i-Pr (90% total yield); Anal. Found: C, 56.19; H, 11.18; Cl, 18.55. $C_9H_{21}SiCl$ calcd.: C, 56.07; H, 10.98; Cl, 18.39%.

Tetra-n-propylsilane (Table 1, Entry 5)

Using the general procedure, n-Pr_4Si (1.3 g, 6.4 mmol), $HSiCl_3$ (1.8 g, 13 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 30 mg) were heated in a sealed tube at 166°C for 24 h. Distillation afforded two fractions. The first fraction (1.5 g, b.p. ~ 25°C/8 Torr.) was identified through VPC analysis (10%QF-1, 12′, 205°C) by coinjection with known samples to be $HSiCl_3$, (62.5%) and n-$PrHSiCl_2$(37.5%). The second fraction (1.3 g, b.p. 60–66°C/8 Torr) was identified in a similar way to be n-Pr_3SiCl (78% yield), n-$PrHSiCl_2$, and n-Pr_4Si.

Tetra-p-tolylsilane (Table 1, Entry 6)

Using the general procedure, (*p*-tolyl)$_4$Si (0.35 g, 0.9 mmol), $HSiCl_3$ (0.2 g, 1.5 mmol), and $H_2PtCl_6 \cdot 6H_2O$ (ca. 15 mg) were heated in a sealed tube at 145°C for 48 h. A brown residue was isolated and tentatively assigned to be a mixture of (*p*-tolyl)$_4$Si and (*p*-tolyl)$_3$SiCl by matching the NMR spectrum with that of known samples. The yield of (*p*-tolyl)$_3$SiCl was 65% based on the (*p*-tolyl)$_3$-SiCl/(*p*-tolyl)$_4$Si ratio indicated by NMR spectrum integration. The *p*-methyl groups in an authentic sample of tri-*p*-tolylchlorosilane were shown to be slightly more downfield than the *p*-methyls of tetra-*p*-tolylsilane as might be expected. This small difference in chemical shifts was used to estimate the 65% yield of tri-*p*-tolylchlorosilane.

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