Journal of Organometallic Chemistry, 371 (1989) 19–30
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

The interaction of fluoride ion with organosilicons: facile isomerizations and new reactions of silicon hydrides

Craig Blankenship * and **Sheldon E. Cremer**

Department of Chemistry, Marquette University, Milwaukee, WI 53233 (U.S.A.)

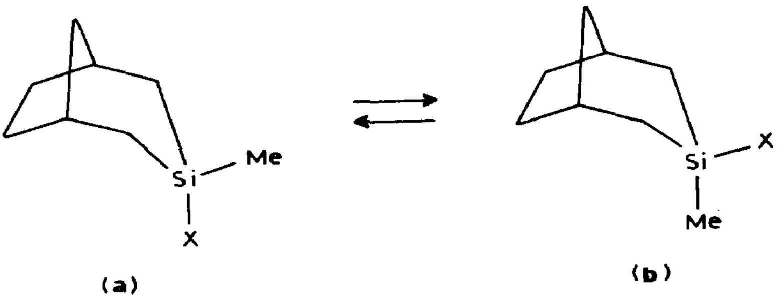
(Received August 18th, 1988)

Abstract

Cesium fluoride isomerization of several derivatives of 3-silabicyclo[3.2.1]octane and 2-silabicyclo[2.2.1]heptane as well as chiral α-NpPhMeSiH are described. The effect of solvent, 18-crown-6 ether, and other salts is discussed. Associated side reactions prompted study of the conversion of Ph_3SiH to Ph_3SiF by CsF and the identification of the products formed from the reaction of Ph_3SiH with DMF, *N*-methylformanilide, and benzamide in the presence of metal fluorides.

Introduction

We have described the equilibration of the isomers of 3-methyl-3-silabicyclo-[3.2.1]octane (**1**) (eq. 1) in a previous communication [2]. This was accomplished by treatment of either pure isomer with fluoride ion in dimethylformamide (DMF). Here we report that this method can be generalized to equilibrate other organosili-



(1)

(**1**, X = H; **2**, X = OCH_3; **3**, X = C_6H_5; **4**, X = F; a = *exo*-Me, b = *endo*-Me)

---

* Taken in part from the dissertation of C.B. [1]. Present address: Petrarch Systems, Hüls America, Inc., Bristol, PA. 19007.

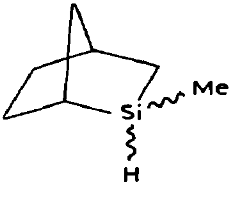
0022-328X/89/$03.50 © 1989 Elsevier Sequoia S.A.

con isomers, including the first example of the isomerization of a tetraorganosilane, **3**. The extremely facile racemization of chiral methyl(α-naphthyl)phenylsilane (**5**) is also described. Previously, nucleophile-induced isomerizations and racemizations at a silicon center have been limited to compounds that have halides bonded to silicon [3*–5*]. The reactions presented here represent the best documented examples of nucleophile-induced isomerizations of organosilanes which do not possess Si–halide bonds [6*,7*].

The mechanism for these isomerization reactions likely involve short lived pentacoordinate siliconate or hexacovalent silicate intermediates [8*]. These intermediates can undergo intramolecular stereomutation of substituents about the silicon center. Siliconate intermediates were not directly observed in these studies, but this would be expected based upon previous investigations of discrete, stable siliconates [9*], particularly the classic studies of Klanberg and Muetterties [10] and the more recent ones of Damrauer [11] and Holmes [12]. In our systems there are no substituents that allow for the effective dispersal of the formal negative charge on silicon, nor are there other structural features which impart stability to the intermediate. Siliconate intermediates have been proposed for synthetically important reactions of allylsilanes promoted by fluoride ion [13]. Nucleophilically-activated silyl hydrides can be used as reducing agents [14], and the stereochemistry of reduction of prochiral ketones by chiral silane **5** activated by fluoride ion has been examined by Fry and McAdam [15]. Several new reactions of fluoride-activated silyl hydrides were uncovered in our studies, described herein, which provide evidence for the intermediacy of the pentacoordinate siliconate. The significance of the isomerizations described here, aside from the thermodynamic information that can be obtained, is the implication in the mechanism of nucleophilic substitution reactions at silicon. Short-lived pentacoordinate intermediates are often invoked in such substitutions, but the stereomutations of substituents about the siliconate centers often are not considered important in the overall mechanisms [3*,4]. This view has been challenged most recently by Deiters and Holmes [16*], who have carried out computational studies for modeling nucleophilic displacements at silicon. It was suggested that intramolecular stereomutations of substituents about silicon via pseudorotation in the intermediate is important for reactions that occur with retention of configuration at silicon [16*].

Results and Discussion

Preparations of the bicyclic silanes used in these studies were reported previously [17,18]. Optically-active (+)-**5** was prepared according to the procedure of Sommer and co-workers [19]. Isomers of **1–3** and **6** were equilibrated by treatment with



(**6**)

---

* Reference number with asterisk indicates a note in the list of references.

Table 1

Equilibration reactions of organosilicons with CsF/DMF [a]

Entry	Compound	CsF (equiv.)	Isomer ratios initial	(%a/%b) final	T (°C), time
1	**1a**	4	100/0	70/30	80, 2 h
2	**1**	1	40/60	70/30	80, 23 h
3	**1**	0.1	40/60	70/30	80, 5 days
4	**1b**	1	0/100	70/30	80, 24 h
5	**2a**	0.4	100/0	52/48	r.t., 24 h
6	**2b**	1	7/93	52/48	r.t., 2 h
7	**3a**	1	100/0	43/57	105, 5 days
8	**3b**	1.5	0/100	42/48	105, 5 days
9	**6**	0.6	80/20 [b]	55/45 [b]	r.t. 2 h
10	**5**	0.4	[c]	[c]	r.t., ≤15 min

[a] Reactions were run in sealed ^{1}H NMR tubes (5 mm), except for entry 10, which was run in standard glassware. [b] The "**a**" isomer is the *exo*-methyl isomer; the "**b**" designation refers to the *endo*-methyl isomer. Experiments with **6** are described more fully in ref. [18]. [c] $[\alpha]_D$(initial) 30°; $[\alpha]_D$(final) 0°.

anhydrous CsF in dry DMF under the conditions shown in Table 1. Isomer ratios were measured by integration of the Si-methyl resonances in the ^{1}H NMR spectra; for **1**–**3**, relative peak areas for each isomer in the gas chromatograms were also measured, and these were always in excellent agreement with the NMR data. The last entry of Table 1 shows the surprisingly facile racemization of acyclic silane (+)-**5**.

Thermodynamic data can be readily calculated from this table; for example, $K_{eq} = 0.43$ and ΔG (80°C) = 0.6 kcal/mole for **1**. These results can be compared with the energy differences from molecular mechanics calculations by Ouellette [20].

The isomerizations of **1**–**3** did not exhibit any significant side-reactions during equilibration. Exclusion of water was necessary for isomerizations of **1**, **2**, and **6**; increasing amounts of disiloxane by-products, $R_3SiOSiR_3$, were observed when careful drying of the solvent and salt were ignored. The only other by-product occasionally detected in the reactions of **1** was trace amounts of fluorosilane **4**, which had been prepared independently [17]. Equilibrations of the isomers of **3** were clean; no by-products were detected by gas chromatography or ^{1}H and ^{13}C NMR analyses of the product mixtures. This has significant mechanistic implications as discussed later. Qualitatively, the rates of the isomerizations were dependent upon the amount of CsF used. Entries 2 and 3 (Table 1) show that a slower reaction occured when less CsF was present. For **1**–**3**, prolonged contact (1–3 days) with CsF caused no further change in the final isomer ratios.

Silyl hydrides **1**, **5**, and **6** reacted with DMF under the reaction conditions to give siloxane by-products. Trace amounts of the disiloxane were usually observed in the isomerization of **1**. This side-reaction with **5** and **6**, although proceeding slower than isomerization, gave more disiloxane and prolonged contact with the isomerization medium led to complete conversion of the silyl hydride to the disiloxane. Isomerization of **5** and **6** were carried out more cleanly in acetonitrile (MeCN) (vide infra).

Appropriate control reactions were run for each silane in DMF in the absence of CsF. Silane **1b** was heated in DMF at 80°C for two weeks, **2a** was heated at 80°C for 36 h, **3a** was heated at 105°C for 8 days, **6** (80/20 isomer mixture) was kept at room temperature for two weeks, and (+)-**5** was stirred at 60 °C for 12 h. In each case, neither isomerization nor any decomposition of the starting silane was observed.

A study of the effect of the solvent medium on the isomerization of **1b** was reported in our initial communication [2]. It was found that a polar, aprotic solvent was required, and DMF was the most suitable solvent of those investigated. Measurable isomerization was also observed when MeCN was used, but the rate was slower and significant decomposition occurred in some instances. For the more reactive silanes **5** and **6**, though, MeCN became the preferred solvent because of the side-reaction in DMF mentioned above. The isomers of **6** were cleanly equilibrated with 0.5 equiv. of CsF over 7 days in MeCN; continued standing for 3 more days led to no further change. One reaction was carried out with (+)-**5** in which complete racemization was observed after stirring with 0.8 equiv. of CsF in MeCN at room temperature for 9 h. No side products were observed. Methoxysilane **2b** also isomerized in MeCN, and equilibrium was attained in 3 days with 2 equiv. of CsF at room temperature; the same equilibrium ratio of isomers was observed as in DMF.

An attractive solvent for studying the isomerization is methanol, since CsF has a greater solubility in this solvent. However, alcoholysis of silyl hydrides [14] can interfere in reactions with **1**, **5**, and **6**. In one case, **1b** was treated with CsF in methanol at 80 °C, but methanolysis occurred to give the isomers of **2** as an equilibrium mixture. The isomers of **2** could be equilibrated with CsF in methanol at room temperature over 12 h; of course, this isomerization may simply occur by methoxy exchange between **2** and the solvent. When **3a** was heated at 105 °C with CsF in methanol for 9 days, no isomerization or other reaction was observed.

Different salts had a pronounced effect on the isomerization reactions of **1b** (Table 2). The order of reactivity for the alkali-metal fluorides, Cs > K > Li, was the same as the identical to fluoride-induced alcoholyses of silyl hydrides [21]. The use of KF at higher temperatures led to a greater rate of formation of the siloxane by-product. Treatment of **2b** with KF in DMF at room temperature produced no measurable isomerization over 1 week, unlike reactions with CsF. KCN promoted the equilibration of the isomers of **2** in DMF at 80 °C over 4 days, but this salt was ineffective in the case of **1b** (entry 7) [22*]. The addition of **1b** to a mixture of AgF

Table 2

Reaction of **1b** with different salts [a]

Entry	Salt	Conditions: T (°C), time	Results
1	CsF	80, 24 h	equilibration
2	KF	80, 5 days	very slow isomerization
3	KF	120, 24 h	isomerization and decomposition
4	LiF	120, 2 weeks	no reaction
5	BaF_2	120, 2 days	no reaction
6	CaF_2	120, 2 days	no reaction
7	KCN	120, 2 days	no reaction
8	AgF	r.t.	immediate reaction, **4** formed
9	SnF_2	80, 3 days	slow reaction to give **4**, no isomerization

[a] All reactions carried out in DMF solvent in sealed ^{1}H NMR tubes (5 mm). Approximate amounts of salts were 1–1.5 eq.

in either DMF or MeCN resulted in a rapid, exothermic reaction with apparent gas evolution and deposition of a silver mirror; the isomers of fluorosilane **4** were the only silicon-containing products detected [23].

The combined results of the investigations into the solvent and salt effects may be rationalized partly on the basis of solubilities, where CsF in DMF provided the greatest amount of soluble fluoride. The bulk solubilities of alkali-metal fluorides in some organic solvents have been determined [24]. In attempts to provide a medium containing a higher proportion of soluble fluoride, several reactions of **1b** were performed with added 18-crown-6 ether. Isomerization occurred more rapidly in the presence of the crown ether. For example, with CsF/DMF, a slow isomerization occurred at room temperature over several days; no measurable isomerization was observed at room temperature in the absence of the crown ether. With KF/DMF, reaction occurred more readily at 80 ° C with added 18-crown-6; however, rates of decomposition also increased, and larger quantities of siloxane by-product were observed. When CsF or KF was combined with the crown ether in MeCN, heating at 80 ° C or above was required to effect isomerization, but significant decomposition occurred which gave complex product mixtures. When **1b** was treated with KF and 18-crown-6 in refluxing benzene, no isomerization or other reaction was observed after 6 days.

One other attempt was made at using a soluble fluoride as an isomerizing agent. Silane **3b** was treated with a commercially available solution of tetrabutylammonium fluoride in tetrahydrofuran (THF). No measurable reaction occurred at room temperature over several days. When this solution was heated to 60 ° C, a reaction took place over 4 days which produced fluorosilane **4** as an isomer mixture. This reaction is attributed to the thermal decomposition of the ammonium fluoride to give HF, which then reacted with **3b** to give desilylation of the phenyl ring [25,26*].

Other approaches to equilibrating the isomers of **1** are mentioned here, since this was our initial goal. Treatment of **1b** with $LiAlH_4$ in refluxing ether or THF, or at room temperature in diglyme, for more than one week produced no significant isomerization. A similar observation was made for the isomers of **6** in refluxing ether. Silane **1b** was also treated with MeMgl in refluxing ether for one week without any significant isomerization or other reaction. Organosilicon hydrides undergo reversible reactions with transition metals under hetero- or homogeneous conditions as demonstrated by H–D exchange experiments [27,28]. These exchanges were shown to proceed with a high degree of, but not total, retention of configuration at silicon [28]. Treatment of **1b** with 5% Pd/C in benzene at 80 ° C caused a small amount of isomerization after two weeks, but decomposition was also detected. When a homogeneous metal complex, chloroplatinic acid / isopropyl alcohol (Speier's hydrosilation catalyst) [29 °], was employed in benzene at 80 ° C, a greater amount of isomerization was observed. Starting with pure **1b**, a 20/80 **1a**/**1b** isomer mixture was obtained after two weeks. Isomerization had apparently ceased at this point, but addition of fresh catalyst promoted further isomerization. However, equilibration of the isomers was not achieved, and a final isomer ratio of 30/70 **1a**/**1b** was measured.

The isomers of methoxysilane **2** were susceptible to isomerization in the presence of an acidic catalyst. When either pure isomer was kept in $CDCl_3$ at room temperature, slow isomerization occurred without decomposition. No such reaction occurred in purified $CDCl_3$ (distilled from phosphorus pentoxide) or in purified methanol at room temperature. A small amount of isomerization was observed when **2a** was heated at 75 ° C in purified CCl_4 over three weeks. Addition of catalytic amounts of benzoic acid to solutions of **2a** or **2b** in CCl_4 or purified $CDCl_3$ followed by heating at 80 ° C resulted in equilibration of the isomers. Importantly, the same equilibrium ratio of isomers was obtained as in the fluoride-induced equilibration reactions.

Mechanisms for the fluoride-induced isomerization reactions

As indicated in the introduction, one mechanism which can explain each of the isomerization reactions involves siliconate intermediates. Kinetic evidence supporting a mechanism is difficult to obtain due to the heterogeneous nature of the reaction medium. This mechanism involves, as a first step, reversible coordination of fluoride ion to give the siliconate intermediate. Approach of the fluoride ion can conceivably occur along an apical or equatorial path to give the trigonal bipyramidal intermediate with fluoride in the axial or equatorial position, respectively [30*]. Calculations by Deiters and Holmes [16*] suggest that axial approach is generally more favorable. The pentacoordinate intermediate can then undergo intramolecular ligand rearrangement about the Si center via pseudorotation [31].

Another possible mechanism involves formation of hexacoordinate silicate intermediates, which have been proposed for some racemization and substitution reactions of optically active halosilanes [3*]. This mechanism requires coordination of a second fluoride ion or a solvent molecule to the Si center. This has not been considered likely for reasons similar to those brought forth by Frye and coworkers in their studies of alcoholysis reactions of chlorosilanes [32]. However, recent studies by Corriu et al. suggest that pentacoordinated silicon species may in fact be more susceptible to nucleophilic attack than tetracoordinate silicon [33].

Any mechanism that involves bond scission of one of the original substituents from the tetravalent silicon is extremely unlikely. Such mechanisms were used to describe isomerizations of halosilanes [34], but the halides are good leaving groups. With the exception of the methoxy group in **2**, there are no good leaving groups in the silanes studies here. This is especially true for phenylsilane **3**. Bond cleavage in the case of **3** would generate a free carbanionic species which would readily attack the solvent under the reaction conditions. This was not observed; indeed, isomerizations of **3** were the cleanest examined.

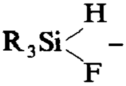
New reactions of fluoride-activated silyl hydrides

In our preliminary communication [2], we reported a fluorination reaction of silane **1** in carbon tetrachloride in the presence of CsF. Isomerization of **1** was not observed during this reaction. This reaction was investigated further since it provided a new means for synthesizing silyl fluorides from silyl hydrides [35]. When a mixture of **1** (isomer mixture) and a slight excess of CsF and CCl_4 in DMF was heated at 50 ° C in a ^1H NMR tube (5 mm), a slow fluorination occurred over three days which produced the isomers of fluorosilane **4** as the only silicon-containing product. Chloroform was the other product, evident from the absorption at 7.2 ppm in the ^1H NMR spectrum. This fluorination was examined in more detail with triphenylsilane (**7**) (eq. 2). Both the solvent and metal fluoride were varied, and the

$$\underset{\mathbf{7}}{Ph_3SiH} + MF + CCl_4 \xrightarrow[r.t.]{solvent} Ph_3SiF + CHCl_3 + MCl \qquad (2)$$

progress of the reaction was monitored by following the attenuation of the Si–H absorbance in the ^1H NMR spectra. With CsF in either DMF or MeCN, complete fluorination occured within 5 min to give the silyl fluoride in nearly quantitative yields. When KF in DMF was used, complete reaction required 1.5 h. LiF in DMF or CsF in benzene gave no reaction after one day. When triethylsilane was treated with CsF in DMF under the same conditions, ca. 1h was necessary for complete reaction.

The mechanism for fluorination undoubtedly involves the siliconate intermediate 8, which possesses significant hydridic character. This is the same intermediate



$$R_3Si\genfrac{}{}{0pt}{}{\diagup H}{\diagdown F}\ ^{-}$$

8

proposed for other reactions of silyl hydrides activated by fluoride ion [14]; the fluorination reaction provides evidence for the intermediacy of the siliconate in the isomerization reactions.

Intermediate **8** must also be involved in the side-reactions with DMF mentioned earlier. The first attempted racemization of **5** was performed by heating it with a mixture of CsF in DMF at 60 °C for 12 h, since an extremely facile racemization was not expected. Analysis of the resultant product mixture indicated complete conversion of **5** to a disiloxane as evident from the IR spectrum, which showed strong Si–O–Si absorption and the absence of the Si–H absorption. The odor of a free amine indicated the nature of the other reaction product. This reaction was explored further with silane **7**. When **7** was stirred with CsF in DMF at room temperature, a white solid precipitated from the reaction mixture. Nitrogen was passed through the reaction system and the effluent gases were collected in a −77 °C cold trap, since trimethylamine was an anticipated product. Instead, bis(dimethylamino)methane (**9**) (eq. 3) was isolated; ^1H and ^{13}C NMR spectra and the IR spectrum were identical with authentic **9**. The solid product was collected by

$$7 + CsF + DMF \xrightarrow{r.t.} \underset{\mathbf{9}}{(Me_2N)_2CH_2} + \underset{\mathbf{10}}{Ph_3SiOSiPh_3} \qquad (3)$$

filtration to give a 97% yield of hexaphenyldisiloxane (**10**). This result confirms the suspected reaction between activated silyl hydrides and DMF mentioned in a previous report [36]. It is further noted that the reagent combination $Ph_3SiH/CsF/$ DMF is analogous to similar hydride transfer combinations described in the literature; both pentavalent [37] and hexavalent [38] anions have been invoked in the fluoride catalyzed reduction of aldehydes and ketones with various hydrosilanes.

Reactions with two other amides were carried out in order to obtain additional information on this reaction type. When *N*-methylformanilide was treated with CsF and **7** in MeCN at room temperature, disiloxane **10** was formed and *N*-methylaniline was observed in ca. 40% yield by GC. Spectroscopic and GC analyses were conducted to confirm C–N bond cleavage had occurred; comparisons with authentic *N*-methylaniline and *N,N*-dimethylaniline clearly showed the monomethyl aniline to be the product. The closest precedent for this chemistry is the study of the reactions of chlorosilanes with DMF at 150 °C; the reaction of Ph_3SiCl with DMF was reported to give dimethylamine hydrochloride, carbon monoxide, and hexaphenyldisiloxane (**10**) [39]. In the other reaction, benzamide was treated with

CsF and **7** in MeCN at 40 °C. Benzonitrile was collected by distillation in 70% yield; siloxane **10** was also isolated. In contrast to these observations, Benkeser et al. found that reaction of benzamide with Cl_3SiH/Pr_3N gave no recognizable products, whereas, reaction of *N,N*-dimethylbenzamide with Cl_3SiH/Pr_3N gave α-(*N,N*-dimethylamino)benzyltrichlorosilane [40]. Clearly, the reaction of amides with silanes is dependent on the reagents and reaction conditions.

Experimental

General comments

The preparations of the bicyclic compounds used here have been described in previous reports; the pertinent NMR spectral data and GC characteristics of these compounds, and the instrumentation used were reported [17,18] therein. Optical rotations were measured using a Perkin–Elmer Model 141 polarimeter in 1-ml cells of 1-dm path-length with irradiation using the sodium D-line. All reactions were run in glassware or 5 mm NMR tubes which were oven dried at ≥ 115 °C for at least 12 h before use; reactions were performed under a nitrogen atmosphere.

All solvents were fractionally distilled under nitrogen in dried glassware and stored under nitrogen; transfers were made using standard syringe techniques. DMF was shaken with KOH pellets and distilled from CaH_2 under reduced pressure, ca. 10 mm. MeCN was stirred over CaH_2 overnight, pressure filtered under nitrogen, and distilled from phosphorus pentoxide. DMF and MeCN were used within three weeks of distillation. Benzene, ether, and THF were distilled from Na/K/benzophenone; ether and THF were used directly after distillation. Methanol was distilled from magnesium methoxide. Carbon tetrachloride and chloroform were distilled from phosphorus pentoxide.

CsF, KF, LiF, BaF_2, CaF_2, and KCN were dried in vacuo over phosphorus pentoxide at 140–180 °C for at least 12 h. The best results with CsF were obtained after drying at 140 °C for 36–48 h. AgF was dried in vacuo at room temperature over phosphorus pentoxide for 24 h. All weighings and transfers of salts were performed in a glove box or glove bags using phosphorus pentoxide as a desiccant. CsF (99.999%) was obtained from Cerac, Inc., of Milwaukee, Wl; other salts were obtained from Aldrich Chemical Co. of Milwaukee, Wl. Tetrabutylammonium fluoride/THF solution and bis(dimethylamino)methane were obtained from Aldrich. 18-crown-6 ether was dried by treatment with $MgSO_4$ in dichloromethane solution, followed by pressure filtration under nitrogen and removal of the solvent under reduced pressure: the solid was further dried over phosphorus pentoxide under reduced pressure (ca. 75 mm), and subsequent transfers were made in a glove bag.

General procedure for reactions in ^1H NMR tubes

A pre-weighed (to 0.1 mg) 5-mm ^1H NMR tube was taken into a glove bag and the solid was added. After reweighing, the tube was taken back into the glove bag where 0.4–0.6 ml of the solvent was added via a 1-ml syringe. In reactions using 18-crown-6, the crown ether was added prior to solvent addition, and the tube reweighed. The tube was capped with a rubber septum and taken to the analytical balance. The silane was added using a syringe; normally, 50–100 mg was used. The tube was shaken and an initial ^1H NMR spectrum was recorded. If heating were required, the NMR tube was flame sealed. Final reaction mixtures were analyzed by GC; these mixtures were then pressure filtered through a sintered-glass frit into a 10-mm NMR tube, rinsing with $CDCl_3$, and analyzed by ^{13}C NMR spectroscopy. Isomerizations of silanorbornane **6** are described in additional detail in ref. 18.

Racemization reactions of 5

Silane **5** prepared by the procedure of Sommer et al. [19] had $[\alpha]_D$ 30° (*c* 0.03 in cyclohexane). Portions of **5** (0.300 g, 0.60 mmol) were added to 15-ml roundbottom flasks which contained magnetically stirred mixtures of CsF (0.05 g, 0.3 mmol) in 8 ml of the desired solvent. After stirring for a specified period of time at room temperature, each reaction mixture was poured onto 20 ml of 5% sodium bicarbonate solution overlaid with 20 ml of ether. The organic layer was washed three times with 20-ml portions of water, dried (Na_2SO_4), and the volatiles were removed on the rotary evaporator. The separate residues were weighed and portions were taken up in cyclohexane and diluted to 5.00 ml in volumetric flasks. After the optical rotations were measured, each solution was evaporated and the residues were analyzed by ^{13}C NMR and IR spectroscopy.

Four reactions were carried out in DMF; reaction times were 15, 30, 60, and 90 min. The silane was isolated from each reaction in high recovery; $[\alpha]_D$ 0° (*c* 0.03 in cyclohexane) for each recovered product. In the latter two reactions, new peaks in the ^{13}C NMR spectra showed the presence of a side product; the IR spectra showed a new absorption at 1030 cm^{-1} (s, broad) indicative of a siloxane. One reaction was performed in MeCN for 9 h. Analysis showed $[\alpha]_D$ 0° and no side products were observed. A control reaction was carried out in which **5** was stirred in DMF at 60°C for 12 h. Workup and analysis showed $[\alpha]_D$ 30° and no side products were observed.

General procedure for the fluorination of triphenylsilane

Triphenylsilane **7** (1.1 mmol) was added to a magnetically stirred mixture of the alkalimetal fluoride (1.5 mmol) and CCl_4 (2.0 mmol) in 3 ml of DMF or MeCN. The reaction was monitored by following the disappearance of the Si–H absorption in the ^1H NMR spectrum. After completion of the reaction, the reaction mixture was poured onto 20 ml of 5% sodium bicarbonate overlaid with 20 ml CH_2Cl_2. The layers were separated and the aqueous layer was extracted once with 20 ml of CH_2Cl_2. The combined organic fractions were washed successively with 20 ml of water, 20 ml of 10% H_2SO_4, and three 20-ml portions of water. After drying with Na_2SO_4, the solvent was removed on the rotary evaporator to give 100% of crude fluorotriphenylsilane. The crude product sometimes contained traces of hexaphenyldisiloxane (**10**) as indicated in the ^{13}C NMR spectra. The fluorosilane was dissolved in methanol and recrystallized by the dropwise addition of water: m.p. 59–61°C; (lit. [41] 62–63°C); ^{13}C NMR ($CDCl_3$): δ 134.6 (J 1.8 Hz), 131.1 (J 17.1 Hz), 130.4, 127.7; ^{19}F NMR ($CDCl_3$): δ −170.1 ($CFCl_3$ ref. std.)

Reaction of 7 with DMF in the presence of CsF

Silane **7** (5.2 g, 20 mmol) and CsF (1.0 g, 7.0 mmol) in 30 ml of DMF were magnetically stirred at room temperature for 14 h. The reaction flask was purged with nitrogen and the effluent gases were passed through a cold trap cooled in dry ice/acetone. The white solid formed during the reaction was collected by suction filtration; this was washed with water and dried to give 5.2 g (97%) of siloxane **10**. A portion of this was recrystallized from boiling hexane (ca. 0.1 g per 25 ml): m.p. 227–228 °C (lit. [42] 226 °C); ^{13}C NMR ($CDCl_3$): δ 135.0, 134.8, 129.4, 127.3. A clear, colorless liquid with a strong amine odor was collected in the cold trap; this was taken up in benzene-d_6. The ^{1}H and ^{13}C NMR spectral data were identical with those of authentic **9**.

Reaction of 7 with N-methylformanilide in the presence of CsF

Silane **7** (2.1 g, 8.0 mmol), *N*-methylformanilide (0.25 ml, 0.28 g, 2.0 mmol, previously purified by fractional distillation), and CsF (0.61 g, 4.0 mmol) in 10 ml of MeCN were magnetically stirred at room temperature for 2 days. A reaction was monitored by observing the disappearance of the Si–H and N–Me absorptions in the ^{1}H NMR spectral assays. A white precipitate was formed during the reaction; this was separated by suction filtration to give 1.78 g of **10**. An additional 0.78 g of **10** crystallized from the filtrate. ^{13}C NMR and melting point analyses (ca. 224 °C) confirmed these solids to be siloxane **10**. The filtrate was evaporated and passed through a short column of silica gel (ca. 3 g) eluting with ether. Evaporation of the ether gave 0.3 g of light brown viscous mass; NMR analyses showed the presence of siloxane **10**, *N*-methylaniline, and a small amount of *N*-methylformanilide. The *N*-methylaniline was collected by preparative GC using a 6′ × 1/4″ 5% QF-1 column at 120 °C and 60 ml/min flow rate. GC characteristics on two columns (6′ × 1/8″ 3% SE-30 and 10% Carbowax 20M) and the ^{1}H and ^{13}C NMR and IR spectral properties were identical with authentic *N*-methylaniline.

Reaction of 7 with benzamide in the presence of CsF

Silane **7** (1.1 g, 4.0 mmol), benzamide (0.12 g, 1.0 mmol), and CsF (0.30 g, 2.0 mmol) in 7 ml of acetonitrile were stirred at 40 °C for 4 days. Siloxane **10** (1.0 g) was separated by pressure filtration through a sintered-glass frit. The filtrate was first concentrated by simple distillation and then under reduced pressure (ca. 10 mm). The residue was bulb-to-bulb distilled at 0.4 mm and a pot temperature of 25–75 °C to give 0.069 g (70%) of benzonitrile as a clear, colorless, odorous liquid. ^{1}H and ^{13}C NMR and IR spectral analyses of the product were identical with authentic benzonitrile.

Acknowledgements

This work was supported in part from NATO Grant No. RG206.80 and the Marquette University Committee on Research C.B thanks the Society of Sigma Xi for a grant in support of this project, and the A.J. Schmitt foundation for a Fellowship (1980–1981), Mr. Dave Kube for technical assistance, and Ms. Marjorie Glembin for help with the preparation of compound **5**.

References

1 Taken from the Ph.D. Dissertation of C. Blankenship, Marquette University, Feb. 1982. Portions of this work were also presented at the XV Organosilicon Symposium, Durham, NC, USA, March 1981, and at the 38th Southeastern Regional ACS Meeting, Louisville, KY, USA, Nov. 1986.
2 S.E. Cremer and C. Blankenship, Tetrahedron Lett., 21 (1980) 3979.

3 Corriu and Guerin have compiled the most extensive recent reviews in the area of nucleophilic substitutions at silicon, including nucleophile-induced isomerizations and racemizations: (a) R.J.P.l Corriu and C. Guerin, J. Organomet. Chem., 198 (1980) 231; (b) R.J.P. Corriu and C. Guerin, Adv. Organomet. Chem., 20 (1982) 265; (c) R.J.P. Corriu; C. Guerin and J.J.E. Moreau, Topics in Stereochem., 15 (1984) 43.

4 (a) L.H. Sommer, Stereochemistry, Mechanism, and Silicon; McGraw-Hill: New York, 1965; (b) L.H. Sommer, D.L. Bauman, J. Am. Chem. Soc., 91 (1969) 7045; (c) L.H. Sommer, Intra-Sci. Chem. Reports, 7 (1973) 1.

5 For isomerizations of cyclic organosilicon halides, see: (a) K. Tamao; M. Ishikawa and M. Kumada, J. Chem. Soc., Chem. Comm., 73 (1969); (b) F.K. Cartledge, B.G. McKinnie and J.M. Wolcott, J. Organomet. Chem., 118 (1976) 7; (c) J. Dubac, P. Mazerolles, M. Joly, F.K. Cartledge and J.M. Wolcott, ibid., 154 (1978) 203.

6 In our initial communication, brief, qualitative reference to the isomerization and equilibration of the isomers of 1,2-dimethyl-1-silacyclobutane induced by cyanide ion was made: B.G. McKinnie, N.S. Bhacca, F.K. Cartledge, and J. Fayssoux, J. Org. Chem., 41 (1976) 1534. Further information concerning these cyanide-induced isomerizations are provided in the Ph.D. Dissertations of B.G. McKinnie and J.M. Wolcott, Louisiana State University, 1975. Of particular interest was the observation that tetrabutylammonium fluoride did not bring about any isomerization of 1,2-dimethyl-2-silacyclopentane in CDCl$_3$ after six days at room temperature. Slow isomerization of this silacyclopentane was observed by treatment with KCN in 95% DMF/H$_2$O (J.M. Wolcott, Ph.D. Dissertation, p. 68–69). We are extremely grateful to Dr. Frank Cartledge of Louisiana State University for sharing this information with us.

7 The racemization of optically-active silane **5** with or without hydride exchange has been observed by treatment with lithium aluminum hydride or sodium trimethoxyborohydride under specific conditions: G.A. Parker, Ph.D. Dissertation, Pennsylvania State University, 1964. We are grateful to Dr. Cecil Frye of Dow Corning Corporation for providing this information.

8 The term "siliconate" is useful for distinguishing pentacoordinate silicon species (10-Si-5) from hexacoordinate silicon species, or " silicates" (12-Si-6), following the usage of Martin, et al., J. Org. Chem., 46 (1981) 1049.

9 The subject of penta- and hexacoordinate silicon compounds was recently covered in an excellent review: S.N. Tandura; M.G. Voronkov and N.V. Alekseev, Topics in Current Chem., 131 (1986) 99.

10 F. Klanberg and E.L. Muetterties, Inorg. Chem., 7 (1968) 155.

11 R. Damrauer and S.E. Danahey, Organometallics, 5 (1986) 1490.

12 J.J. Harland, J.S. Payne, R.O. Day and R.R. Holmes, Inorg. Chem., 26 (1987) 760.

13 G. Majetich, A. Casares, D. Chapman and M. Behnke, J. Org. Chem., 51 (1986) 1745.

14 R.J.P. Corriu, R. Perz and C. Reye, Tetrahedron, 39 (1983) 999.

15 J.L. Fry and M.A. McAdam, Tetrahedron Lett., 25 (1984) 5859.

16 J.A. Deiters and R.R. Holmes, J. Am. Chem. Soc., 109 (1987) 1686 and 1692. For a prior discussion of mechanisms involving pseudorotation of pentacoordinate intermediates, see I. Fleming in N. Jones (Ed.), Comprehensive Organic Chemistry, Vol. 3, Pergamon Press, Oxford, 1979, p. 554–561.

17 S.E. Cremer and C. Blankenship, Organometallics, 5 (1986) 1329.

18 S.E. Cremer and C. Blankenship, J. Org. Chem., 47 (1982) 1626.

19 L.H. Sommer; C.L. Frye; G.A. Parker and K.W. Michael, J. Am. Chem. Soc., 86 (1964) 3271.

20 R.J. Ouellette, J. Am. Chem. Soc., 96 (1974) 2421.

21 J. Boyer; R.J.P. Corriu; R. Perz and C. Reye, J. Organomet. Chem., 157 (1978) 153.

22 See ref. 6 for cases where KCN was used as an isomerizing agent.

23 H.H. Anderson, J. Am. Chem. Soc., 80 (1958) 5083.

24 D.A. Wynn, M.M. Roth and B.D. Pollard, Talanta, 31 (1984) 1036.

25 G. Fritz and D. Kummer, Z. Anorg. Allgem. Chem., 308 (1961) 105.

26 This suggestion was first made by Dr. Cecil Frye of Dow Corning Corp. Studies of the thermal decomposition of tetrabutylammonium fluoride indicate that HF_2^- is formed: R.K. Sharma and J.L. Fry, J. Org. Chem., 48 (1983) 2112.

27 J.W. Ryan and J.L. Speier, J. Am. Chem. soc., 86 (1964) 895.

28 L.H. Sommer; J.E. Lyons and H. Fujimoto, J. Am. Chem. Soc., 91 (1969) 7051.

29 R.A. Benkeser and J.J. Kang, J. Organomet. Chem., 185 (1980) C9. The identity of this catalyst was determined to be $H[(C_3H_6)PtCl_3]$ in isopropyl alcohol.

30 See discussions by Corriu et al., in ref. 3 for arguments favoring equatorial approach by a hard nucleophile to a silicon center.

31 (a) K. Mislow, Acc. Chem. Res., 3 (1970) 321; (b) R.R. Holmes, in S.J. Lippard (Ed.), Progress in Inorganic Chemistry, Vol. 32, J. Wiley & Sons, N.Y., 1984, p. 119–235.

32 H.K. Chu, M.D. Johnson and C.L. Frye, J. Organomet. Chem., 271 (1984) 327.

33 R.J.P. Corriu, C. Guerin; B.J.L. Henner and W.W.C. Man, Organometallics, 7 (1988) 237.

34 See ref. 3, 5b and: J. Chojnowski, M. Cypryk, J. Michalski and L. Wozniak, J. Organomet. Chem., 288 (1985) 275.

35 R.M. Pike and K.A. Koziski in D. Seyferth, A.G. Davies, E.O. Fischer, J.F. Normant and A.O. Reutov (Ed.), Organometallic Chemical Reviews, J. Organomet. Chem. Library, 9 Elsevier, Amsterdam, 1980; p. 41–152.

36 C. Chuit; R.J.P. Corriu, R. Perz and C. Reye, Synthesis, (1982) 891.

37 D. Yang and D.D. Tanner, J. Org. Chem., 51 (1986) 2267.

38 M. Fujita and T. Hiyama, Tetrahedron Lett., 28 (1987) 2263.

39 E.G. Rochow and K. Gingold, J. Am. Chem. Soc., 76 (1954) 4852.

40 R.A. Benkeser, G.S. Li and E.C. Mozdzen, J. Organomet. Chem., 178 (1979) 21.

41 L. Tsanjo, Acta Chem. Scand., 18 (1964) 465.

42 W.H. Daudt and J.F. Hyde, J. Am. Chem. Soc., 74 (1952) 386.