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THE INTERACTION OF ORGANOSILANES WITH TRIPHENYLMETHYL TETRAFLUOROBORATE

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Summary

Under mild conditions, Ph_3CBF_4 readily fluorinates the Si—H bond(s) of trialkylsilanes and dialkylsilanes. The use of this reagent in the successful fluorination of $HSiMe_2CH_2Fe(CO)_2Cp$ suggests that the reaction can be used to fluorinate silicon compounds that possibly would not survive more vigorous fluorination reactions. A convenient preparation of diorganofluorosilanes that have both hydrogen and fluorine bonded to silicon is described.

Introduction

As part of a study concerning the interaction of organosilanes with various reagents that are capable of hydride abstraction, we have observed that Ph_3CBF_4 readily fluorinates the Si—H bond of organosilanes at room temperature. If this reaction would parallel the mild halogenation of organosilanes by triphenylmethyl(trityl)-chloride, -bromide and -iodide [1], the observed fluorination would be of considerable value from a synthesis point of view in two respects. It would provide a method for fluorinating various silicon compounds that possibly would not survive other more standard fluorination reactions and it would offer a convenient synthesis of various diorganofluorosilanes that have both hydrogen and fluorine bonded to silicon. In this paper, we report the results of utilizing Ph_3CBF_4 as a mild fluorinating reagent in these two respects.

Results and discussion

Our results indicate that trialkylsilanes undergo quantitative reaction with solid Ph_3CBF_4 at room temperature to form the corresponding trialkylfluorosilane, BF_3, and Ph_3CH (eqn. 1). The reactions are particularly suited to vacuum

$$R_3SiH + Ph_3CBF_4 \rightarrow R_3SiF + Ph_3CH + BF_3 \quad (1)$$

R = Me, Et

line techniques on a preparative scale in that no solvent is required and the very volatile BF_3 (b.p. −101°) and non-volatile Ph_3CH by-products are easily separated from the moderately volatile fluorosilanes.

The course of the reaction is not surprising in view of an earlier observation by Corey and West that Ph_3SiH could be converted into Ph_3SiBr by its reaction with Ph_3CBBr_4 in dichloromethane (eqn. 2) [1]. These authors also found that in

$$Ph_3CBBr_4 + Ph_3SiH \rightarrow Ph_3SiBr + Ph_3CH + BBr_3 \quad (2)$$

appropriate solvents triphenylmethyl-chloride, -bromide, and -iodide also halogenate the Si—H bonds of Ph_3SiH, Ph_2SiH_2 (one or both Si—H bonds halogenated), Et_3SiH and $HSiCl_3$ smoothly at room temperature (eqn. 3). Our fluorination

$$\geqslant Si{-}H + Ph_3CX \rightarrow \geqslant Si{-}X + Ph_3CH \quad (3)$$

$(X = Cl, Br, I)$

results are different from the above in that a solvent was not required for the reaction and Ph_3CF did not appear to fluorinate organosilanes satisfactorily. Since the solid phase reaction utilizing the easily prepared (or purchased) Ph_3CBF_4 was so satisfactory from a synthesis point of view, we did not attempt to modify conditions or seek a suitable solvent for the possible fluorination utilizing Ph_3CF.

Although Me_3SiH and Et_3SiH are easily converted to the corresponding trialkylfluorosilane by this method, a particularly significant feature of the reaction is its ability to produce pure dialkylmonofluorosilanes by the interaction of equimolar amounts of Ph_3CBF_4 with dialkylsilanes (eqn. 4). In a previous

$$R_2SiH_2 + Ph_3CBF_4 \rightarrow R_2Si\begin{matrix} H \\ F \end{matrix} + Ph_3CH + BF_3 \quad (4)$$

R = Me, Et

publication, we pointed out the advantage of using organosilicon hydrides as precursors to these kinds of compounds [2]. However, until now the chief disadvantage of directly fluorinating silicon hydrides was the fact that more than one Si—H bond is fluorinated, invariably resulting in mixtures of fluorosilanes that are difficult to separate by conventional methods.

Although we were successful in the stepwise fluorination of dialkylsilanes by this method, we were not successful in partially fluorinating an organosilane that contained three Si—H bonds, viz. $EtSiH_3$. The rate of fluorinating this compound is much slower than it is with trialkyl or dialkylsilanes and during the longer reaction time required for fluorination, a mixture of ethylfluorosilanes resulted.

An example of utilizing Ph_3CBF_4 to introduce a silicon—fluorine bond into a silicon compound that possibly could not survive some of the more common procedures for producing such bonds [3] is found in the mild fluorination of $HSiMe_2CH_2Fe(CO)_2Cp$ by this reagent in methylene chloride (eqn. 5).

$$HSiMe_2CH_2Fe(CO)_2Cp + Ph_3CBF_4 \rightarrow FSiMe_2CH_2Fe(CO)_2Cp + Ph_3CH + BF_3 \quad (5)$$

A solvent was used in the reaction owing to the viscous nature of the hydrosilylmethyl complex. This silicon hydride derivative is not particularly stable thermally [4] and would most likely not survive a vigorous halogenation reaction.

Some qualitative experiments were carried out concerning the interaction of Ph_3CBF_4 with the substituted hydrosilanes, $MeSiHCl_2$ and $(HSiMe_2)_2O$. In the attempted fluorination of $MeSiHCl_2$, substitution occurred at the Si—Cl bond rather than at the Si—H bond (eqn. 6). The mixed chloro-fluoro derivative

$$MeSiHCl_2 + Ph_3CBF_4 \rightarrow MeSiHClF + Ph_3CCl + BF_3 \quad (6)$$

in eqn. 6 was not isolated, but under the conditions of the reaction it presumably underwent disproportionation to form $MeSiHCl_2$ and $MeSiHF_2$. The major volatile product in the reaction of Ph_3CBF_4 with $(HSiMe_2)_2O$ (1/1 mole ratio) was Me_2SiHF. Fluorination of the Si—H bond did occur, as evidenced by the isolation of a small amount of $(FSiMe_2)_2O$, but the BF_3 generated in the fluorination undoubtedly cleaved the starting siloxane producing the Me_2SiHF (eqn. 7) [5].

$$3\,(HSiMe_2)_2O + 2\,BF_3 \rightarrow 6\,Me_2SiHF + B_2O_3 \quad (7)$$

Experimental

Apparatus and techniques

All preparations and purifications of air sensitive compounds were carried out in nitrogen or in vacuo by using standard dry-box or vacuum line techniques [6]. Equipment employed has been described in previous publications [7]. Unless otherwise stated, each reaction was carried out in a 100 ml round-bottomed flask that could be attached to the vacuum line via a 4 mm stopcock and ground glass joint. NMR spectra were obtained in $DCCl_3$ (~ 20% concentrations), using TMS and/or cyclohexane as internal standards.

Materials

Dimethylsilane and $EtSiH_3$ were prepared by a standard $LiAlH_4$ reduction of the corresponding chloride in di-n-butyl ether [8]. Diethylsilane, Et_3SiH, Me_3SiH, $MeSiHCl_2$ and $(HSiMe_2)_2O$ were obtained from commercial sources and purified on the vacuum line. The purity of each of the above silicon compounds was checked by spectroscopic analyses. Triphenylmethyl tetrafluoroborate was prepared by adding fluoroboric acid dropwise to a solution of Ph_3COH in propionic anhydride [9]. The material was recrystallized from methylene chloride and ether and stored in a brown bottle in a desiccator*. Triphenylmethyl fluoride and KBF_4 were obtained from commercial sources and used as received.

The synthesis of $HSiMe_2CH_2Fe(CO)_2Cp$ is described in a separate publication [10].

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* Triphenylmethyl tetrafluoroborate purchased from Cationic Reagents, Inc. was also found to be satisfactory for the fluorination reactions described in this work.

TABLE 1

CONDITIONS AND PRODUCTS FOR THE REACTION OF TRIPHENYLMETHYL TETRAFLUOROBORATE WITH SOME ORGANOSILANES[a]

Organosilane	Quantity (mmol)	Ph_3CBF_4 (mmol)	Reaction time (h)	Organofluorosilane isolated	Quantity (mmol)	Yield (%)
Me_3SiH[b]	1.9	2.4	0.5	Me_3SiF	1.9	100
Et_3SiH	2.1	2.6	1.5	Et_3SiF	2.1	100
Me_2SiH_2	2.0	2.5	0.5	Me_2SiHF	2.0	100
Me_2SiH_2	2.0	4.4	8	Me_2SiF_2	1.9	95
Et_2SiH_2	2.0	2.4	1.5	Et_2SiHF[c]	2.0	100

[a] All reactions were carried out at room temperature. [b] In a separate experiment, Me_3SiH was condensed into a side arm attached to the reaction vessel so that the Me_3SiH vapor could interact with the solid Ph_3CBF_4. After 30 min, a spectral analysis revealed that about 70% of the Me_3SiH had been converted into Me_3SiF. Because of the incomplete reaction under these conditions, in all subsequent experiments, the organosilane was condensed directly into the vessel containing the Ph_3CBF_4. [c] The ^1H NMR spectrum of pure Et_2SiHF in the Si—H region consists of a doublet of 5 line (1/4/6/4/1) patterns centered at τ 5.37 (J(HCSiH) 2.4 Hz, J(HCSiF) 51.3 Hz). In a separate experiment where the reactants were allowed to react for 30 min at 0°, incomplete conversion was noted by the appearance of a quintet representing the Si—H signal of unreacted Et_2SiH_2 at τ 6.35 in the NMR spectrum of the −134° fraction. Since it is very difficult to separate Et_2SiH_2 from Et_2SiHF on the vacuum line, it is important to note that the sample's NMR spectrum is a very sensitive check to determine if any of the starting organosilanes is present.

Procedure

The fluorination was found to be most successful when the organosilane was condensed from a suitable tube on the vacuum line directly into the vessel containing Ph_3CBF_4. In most cases, a slight excess of the tetrafluoroborate salt was required to bring about quantitative conversions. The reaction vessel was allowed to warm slowly from −196° to room temperature and was then removed from the vacuum line for occasional shaking to expose most of the salt to the silane. One method for monitoring the course of the reaction was through the disappearance of the bright yellow color of the Ph_3CBF_4 and the appearance of the off-white Ph_3CH. The necessary reaction time could often be determined just by visual inspection of the solid in the reaction flask.

In most of the successful fluorinations, the products could be quantitatively separated by allowing them to distill through a trap maintained at −134° into a trap maintained at −196°. The fluorosilane condenses in the −134° trap and the BF_3, identified by its infrared spectrum [11], condenses in the −196° trap. The solid Ph_3CH, identified by comparing both its infrared and proton NMR spectra with spectra obtained for an authentic sample of Ph_3CH, remains in the reaction flask.

The identity and purity of the fluorosilane obtained was confirmed by one or more of the following methods: infrared spectroscopy, ^1H NMR spectroscopy, and gas phase molecular weight measurements. Infrared spectra obtained were compared either with spectra in the literature, Me_3SiF [12], Me_2SiF_2 [13], or authentic samples of material available in our laboratory.

Details for five of the fluorination reactions carried out in the above manner are summarized in Table 1.

Other Reactions

Ph_3CBF_4 and $HSiMe_2CH_2Fe(CO)_2Cp$. A solution of $HSiMe_2CH_2Fe(CO)_2Cp$ (6.8 mmol) in 25 ml of deoxygenated CH_2Cl_2 was cooled to 0° in a 100 ml round-bottomed flask under nitrogen. A CH_2Cl_2 solution (15 ml) of Ph_3CBF_4 (6.8 mmol) was added dropwise from a pressure equalizing addition funnel over a period of 30 min. During the addition, the reaction mixture was maintained at 0° and a gas presumed to be BF_3 was evolved. The reaction was allowed to continue for an additional hour while most of the CH_2Cl_2 was removed by a stream of nitrogen gas. The residue was eluted on an acid washed alumina column with 5/95 ether/pentane and the large yellow band which appeared was collected. After removal of the solvent, both the NMR and infrared spectra indicated that the sample was a mixture of $FSiMe_2CH_2Fe(CO)_2Cp$ and Ph_3CH which was not appreciably separated by the chromatographic technique. Since it was not easy to separate the fluoro derivative from Ph_3CH, a yield was not determined. However, the reaction appeared to be nearly quantitative based on the fact that $FSiMe_2CH_2Fe(CO)_2Cp$ and Ph_3CH were the only major components observed in the product mixture.

A small sample of the compound was purified by first removing a large amount of the Ph_3CH by crystallizing it from pentane at −78°. Pentane was removed and the remaining product was distilled on the vacuum line, R.T. ~ −196°. In a very slow distillation, pure $FSiMe_2CH_2Fe(CO)_2Cp$ collected in the −196° trap. The purity of the material was confirmed by its analysis* (found: C, 45.2; H, 4.9. $C_{10}H_{13}FFeO_2Si$ calcd.: C, 44.8; H, 4.9%), mass measurement (M^+ found: 268.0018, calcd.: 268.0018), and proton NMR spectrum (τ 9.76 (d) CH_3, $J(H_3CSiF)$ 7.0 Hz; τ 10.46 (d) CH_2, $J(CH_2SiF)$ 8.7 Hz; τ 5.21 Cp).

Ph_3CBF_4 and $MeSiHCl_2$. Ph_3CBF_4 (2.7 mmol) and $MeSiHCl_2$ (2.3 mmol) were allowed to react for 3 h at room temperature and fractionated as previously described in the general procedure. The −134° fraction appeared to be a mixture of $MeSiHCl_2$, $MeSiHF_2$ and a third component, possibly MeSiHClF. The −196° fraction was BF_3. The contents of the −134° fraction were returned to the reaction vessel and allowed to react for an additional 16 h A second fractionation yielded a mixture of $MeSiHCl_2$ and $MeSiHF_2$ in the −134° trap. Since very little BF_3 was generated during this additional 16 h reaction, it appears that MeSiHFCl was produced initially and then underwent disproportion (eqn. 8). Examination of the solid residue remaining in the reaction vessel

$$2MeSiHClF \rightarrow MeSiHCl_2 + MeSiHF_2 \qquad (8)$$

showed that it was Ph_3CCl by comparing both its infrared and proton NMR spectra with corresponding spectra of an authentic sample of Ph_3CCl. No indication of the formation of Ph_3CH was observed in this experiment, and all of the Ph_3CBF_4 had apparently reacted. The stoichiometry for the reaction was not determined owing to the difficulty in fractionating the reaction products. However, these preliminary results do indicate that only the Si—Cl bond of $MeSiHCl_2$ was attacked by Ph_3CBF_4, leaving the Si—H bond unchanged.

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* Analysis performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

Ph_3CBF_4 and $(HSiMe_2)_2O$. Equimolar amounts (2.0 mmol) of each reactant were allowed to react for 15 min at room temperature. The products were distilled at ~ −96° ~ −120° ~ −196°. The −196° fraction was BF_3 (1.2 mmol), the −120° fraction was MeSiHF (2.2 mmol) and the −96° fraction was a mixture of components that appeared to be unstable during its manipulation in the vacuum line. The sample was allowed to distill through a −23° trap, and in a separate fractionation allowed to condense in a −73° trap. The small sample obtained in the −73° trap was $(FSiMe_2)_2O$ identified by its molecular weight (found: 113.6, calcd.: 114.1) and infrared spectrum [14]. The total quantity was not determined since the fluorinated siloxane was not easily fractionated from the other unidentified reaction products. The study of this reaction was not pursued in any greater detail because the method does not have utility as a means of selectively fluorinating the Si—H bond of the siloxane without cleaving the Si—O—Si linkage.

KBF_4 and Me_3SiH. Finely ground anhydrous KBF_4 (2.6 mmol) was combined with Me_3SiH (2.0 mmol) and allowed to react at room temperature for 3 h. The volatile fraction was removed and shown to be pure Me_3SiH (2.0 mmol) with no indication of any BF_3 in the sample.

Ph_3CF and Me_2SiH_2. Ph_3CF (2.1 mmol) and Me_2SiH_2 (2.1 mmol) were combined and allowed to react at room temperature for 1 h. The volatile material was removed and identified as being unreacted $(CH_3)_2SiH_2$ (2.1 mmol). Identical results were obtained when approximately 25 ml of CH_2Cl_2 was added as a solvent and the reaction was repeated.

Ph_3CBF_4 and $EtSiH_3$. Equimolar amounts of each reactant (2.0 mmol) were combined and allowed to react for 30 min at room temperature. An infrared spectrum of the mixture revealed that only a trace of BF_3 had formed and that very little reaction had taken place. A similar conclusion was reached after the reaction continued for an additional 2.5 h. The reaction was allowed to continue for an additional 21 h, at which time the products were distilled as described in the general procedure. The material in the −134° trap could not be separated into its components, but appeared to be a mixture of $EtSiH_3$, $EtSiH_2F$, and $EtSiHF_2$ from its infrared spectrum. The −196° trap contained BF_3 (1.9 mmol).

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References

1 J.Y. Corey and R. West, J. Amer. Chem. Soc., 85 (1963) 2430.
2 M.A. Finch, L.H. Marcus, C. Smirnoff, C.H. Van Dyke and N. Viswanathan, Syn. Inorg. Metal. Org. Chem., 1 (1971) 103.
3 C.H. Van Dyke, in A.G. MacDiarmid, (Ed.), Organometallic Compounds of the Group IV Elements, Vol. 2, Part I, Marcel Dekker, New York, 1972.

4 K.H. Pannell, J. Organometal. Chem., 21 (1970) P17.
5 H.J. Emeleus and M. Onyszchuk, J. Chem. Soc., (1958) 604.
6 D.F. Shriver, The Manipulation of Air-Sensitive Compounds, McGraw Hill, New York, N.Y. 1969.
7 E.W. Kifer and C.H. Van Dyke, Inorg. Chem., 11 (1972) 404, C.H. Van Dyke, E.W. Kifer and G.A. Gibbon, Inorg. Chem., 11 (1972) 408.
8 A.E. Finholt, A.C. Bond, Jr., K.E. Wilzbach and H.I. Schlesinger, J. Amer. Chem. Soc., 69 (1947) 2692.
9 H.J. Dauben, Jr., L.R. Honnen and K.M. Harmon, J. Org. Chem., 25 (1960) 1442.
10 J.E. Bulkowski, Doctoral Dissertation, Carnegie-Mellon Univ., 1974.
11 J. Vanderryn, J. Chem. Phys., 30 (1959) 331.
12 H. Kriegsmann, Z. Anorg. Allg. Chem., 294 (1958) 113.
13 H. Spangenberg and M. Pfeiffer, Z. Phys. Chem., 232 (1966) 343.
14 G. Englehardt and H. Kriegsmann, Z. Anorg. Allg. Chem., 328 (1964) 194.