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# Synthesis of Mono- and Difluoroacetyltrialkylsilanes and the Corresponding Enol Silyl Ethers

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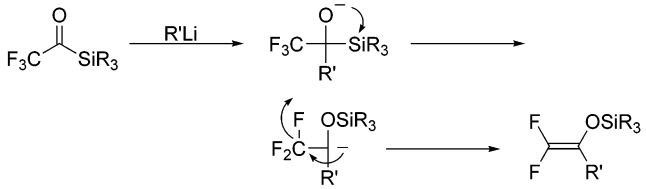
A variety of mono- and difluoroacetylsilanes and the corresponding silyl enol ethers were prepared from trifluoroethanol and chlorotrialkylsilanes in the presence of LDA through retro-Brook rearrangement. Sterically demanding silyl groups, especially those bound to oxygen, resulted in higher yields of difluoroacetylsilanes. The yields of difluoroacetylsilanes were also dramatically affected by the method of the termination of the reaction. Difluorohaloacetylsilanes were prepared from the corresponding difluoroethenyl silyl ethers with electrophilic halogenating reagents in good yields. A $\gamma$-fluorinated $\beta$-diketone **9a** was prepared from monofluoroacetyltriisopropylsilane by nucleophilic acylation with methyl trifluoroacetate.

## Introduction

Acylsilanes, recognized as synthetic equivalents of aldehydes due to the facile scission of the carbon−silicon bonds, have been studied extensively for more than 30 years.[1] The Brook rearrangement,[2] a unique transformation of acylsilanes that involves 1,2-silyl group migration from the carbonyl carbon atom to the adjacent oxygen atom, has been utilized for the synthesis of versatile building blocks[3] and complex natural products.[4] The incorporation of fluorine atoms into acylsilanes offers a new route to impart the unexpected and often unique properties that result from fluorination. For example, the reactions of fluorinated acylsilanes with organometallic reagents such as Grignard or lithium reagents resulted in the formation of fluorinated enol silyl ethers via Brook rearrangement and subsequent defluorination (Scheme 1).[5] The reactions of nonfluorinated acylsilanes with trifluoromethyltrimethylsilane have been reported to form enol silyl ethers by a similar mechanism.[6]

Electrophilic reactions of fluoroacylsilanes[5,7−9] and intramolecular rearrangements of enol ethers have been reported, as well as several interesting synthetic applications.[10] The utility of nucleophilic reactions typical of enolizable carbonyl compounds, such as the Reformatsky reaction or the aldol condensation, for carbon−carbon bond formation at the α carbon atom of acylsilanes has been restricted because of the difficulty in the formation of enolates of fluoroacylsilanes. In addition, synthetic methods for the preparation of fluorinated acylsilanes have been limited.[5a,8,11,12]

**SCHEME 1. Formation of Enol Silyl Ether via Brook Rearrangement and Defluorination**




The preparation of simple mono- and difluoroacetylsilanes and the corresponding enol silyl ethers, capable of forming substituted acylsilanes on reaction with either

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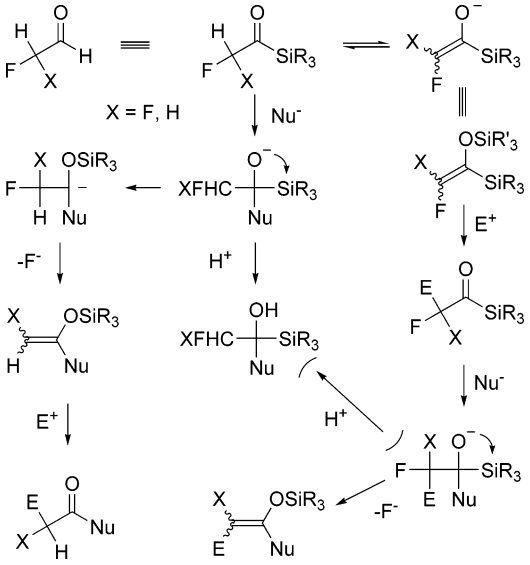
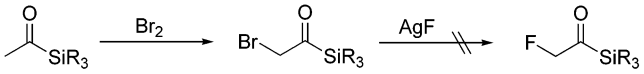
**SCHEME 2. Enolizable Fluoroacetylsilane Derivatives Allowing Electrophilic Modification on the α-Carbon Atom**



**SCHEME 3**



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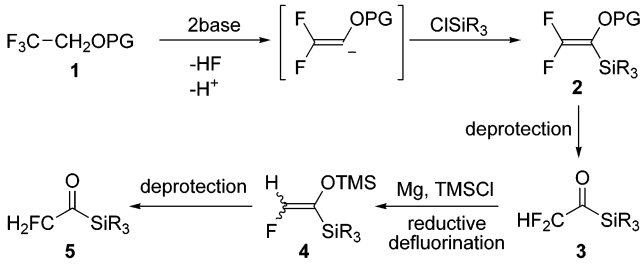


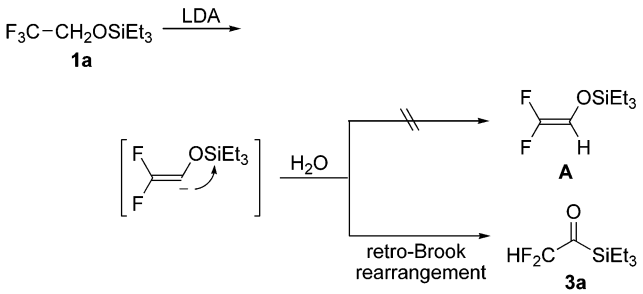
electrophiles or nucleophiles, would facilitate the exploration of the utility of fluorinated acylsilanes in synthetic transformations. These compounds will also be useful tools in the study of the chemistry of fluorinated organosilicon compounds (Scheme 2).

## Results and Discussion

Having failed in our initial attempts to prepare monofluoroacetyltrialkylsilanes from brominated acetyltrialkylsilanes by a halogen-exchange reaction (Scheme 3), we turned to the reactions of difluorovinyl anions to construct the desired fluoroacetylsilanes.

Difluorovinyl anions, generated from protected trifluoroethanol derivatives **1** by treatment with a strong base such as LDA (Scheme 4), have been described.[13] The reaction of protected difluorovinyl anion with trialkylchlorosilanes, followed by deprotection of the resulting enol ethers **2**, was therefore proposed as a route to the desired difluoroacetylsilanes **3**. Reductive defluorination[14] of **3** followed by the hydrolysis of **4** might then form monofluoroacetylsilanes **5**.

**SCHEME 5**



**SCHEME 6**

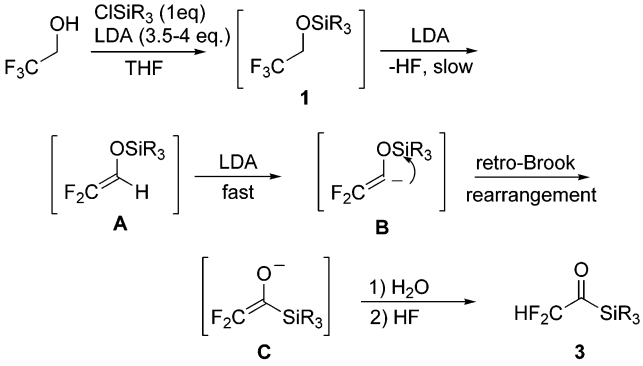


**TABLE 1. Preparation of Difluoroacetyltrialkylsilanes 3**

| **3** | $SiR_3$ | yield/ % | conditions |
|---|---|---|---|
| **3a** | $SiEt_3$ (TES) | 60 | 0 °C, 3 h or −20 °C, overnight |
| **3b** | Si(*i*-Pr)$_3$ (TIPS) | 63 | 0 °C, 1.5 d then rt, 1 d, with HMPA |
| **3c** | Si(*t*-Bu)$Ph_2$ (TBDPS) | 74 | 0 °C, 4 h then rt, overnight, with HMPA |
| **3d** | Si(*t*-Bu)$Me_2$ (TBDMS) | 13 | −20 °C, overnight with HMPA |
| **3e** | $SiMe_3$ (TMS) | 0 | −15 °C, overnight |
| **3f** | $SiPh_3$ (TPS) | 0 | −15 °C, overnight |
| **3f** | $SiPh_3$ (TPS) | 18 | acidic workup/controlled hydrolysis[a] |

In a model reaction, the triethylsilyl ether of trifluoroethanol **1a** was prepared and treated with LDA and then $H_2O$. However, difluoroacetyltriethylsilane **3a** was found instead of the anticipated difluorovinyl silyl ether **A**. It was postulated that **3a** was formed directly by retro-Brook rearrangement (Scheme 5).

During the course of exploring the generality of the formation of **3**, it was found that silyl trifluoroethyl ethers **1** prepared in situ could be used without purification (Scheme 6) in this transformation. In every case, the intermediate difluorovinyl silyl ether **A** was not detected, implying that the rate-determining step is dehydrofluorination or, in the case of especially bulky silyl groups, the formation of the silyl trifluoroethyl ether (Table 1).

The triethylsilyl derivative **3a** was obtained in 60% yield in the absence of HMPA; however, **3b** and **3c**, which

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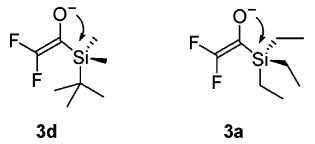
**SCHEME 7**




contain larger silyl groups, were obtained in better yields at elevated temperatures employing HMPA. On the other hand, the much less hindered TMS derivative **3e** and the relatively labile triphenylsilyl derivative **3f** formed little to none of the desired product in the crude mixture. The products were not isolable by the same protocol used for **3a**−**c**.

The low yield of **3d** was unexpected since the TBDMS group is, in general, a more stable and hindered protecting group in comparison with the TES group. The reason for this low yield is not clear, although it may be a consequence of the diminished steric demand of the geminal dimethyl groups of TBDMS relative to the ethyl groups of TES (Scheme 7). This effect may be especially significant in the Brook rearrangement, which leads to the hydrolytically unstable enol silyl ether **A** (Scheme 6). This is in contrast to the thermal stability of the corresponding copper $\beta$-diketonate complexes where TBDMS derivatives exhibit greater stability suggesting that decomposition in that case is dependent upon backside attack on silicon.[15]

During the preparation of **3**, it was found that the workup procedure profoundly affected the yields of isolated product. The best results were obtained when the reaction mixtures were quenched with water or weakly basic solutions such as aqueous sodium bicarbonate at room temperature (Figure 1).

In the case of TIPS (spectrum 2), the $^{19}$F NMR spectrum of the crude organic phase, obtained after quenching with water, resulted in predominant formation of a doublet at −127 ppm (**3b**), while this resonance was nearly undetectable in the case of TPS (spectrum 1).

On the other hand, workup with an acidic solution gave quite different results. It was postulated that acidic solutions, miscible with the reaction mixtures at low temperatures, would effectively protonate the enolate and result in improved yields. However, quenching with a 5:1 mixture of methanol and concentrated hydrochloric acid at −78 °C or with acetic acid at room temperature resulted in two sets of doublets in the fluorine NMR spectra for both the TIPS and TPS cases (spectra 3 and 4). From the similar chemical shifts for the corresponding silyl ethers ($\delta$ −96 and $\delta$ −115 ppm for TIPS derivative **2b** and $\delta$ −89 and $\delta$ −108 ppm for TPS derivative **2g**, respectively) and the lack of additional H−F coupling known to be associated with intermediate **A** (Scheme 6), the products generated by the acidic workup possess 2,2-difluoro-1-trialkylsilylvinyl moieties.

Attempted purification of the unexpected products failed, as these products underwent facile decomposition even in pentane at −78 °C. The relatively simple NMR spectra of the crude isolates suggest the intermediacy of

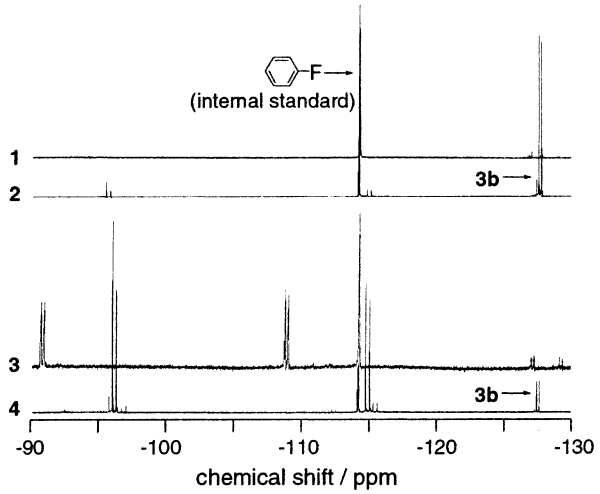



**FIGURE 1.** Effects of workup procedure on $^{19}$F NMR spectrum: spectra 1 and 2, quenched with $H_2O$ at rt; spectra 3 and 4, quenched with 2 M HCl in MeOH−$H_2O$ (5:1) at −78 °C; spectra 1 and 3, triphenylsilyl (TPS); spectra 2 and 4, triisopropylsilyl (TIPS).

a symmetric material such as **D** formed by the condensation of enolate **C** with adventitiously formed **3** as shown in Scheme 8. Treatment of the TPS derivative of compound **D** with iodine in a 5:1 mixture of methanol and concentrated hydrochloric acid yielded a difluoroiodoacetylsilane derivative **7f**. Furthermore, controlled hydrolysis of the TPS derivative of compound **D** gave the crystalline difluoroacetylsilane **3f** in 18% yield. The molecular structure of **3f** was determined and confirmed its formulation. The most notable structural feature of **3f** is the strikingly long Si−C(carbonyl) bond length (1.947(3) Å), as compared to the Si−C(phenyl) bond lengths (1.865(2), 1.858(2), 1.865(2) Å). Such a difference has been previously observed for the parent compound, $MeC(O)SiPh_3$;[15] the longer former bond probably is a result of the juxtaposition of the electropositive Si and carbonyl C atoms.

It was also possible to trap enolate intermediate **C** with chlorotrialkylsilanes to form the enol silyl ether **2**. In all cases, the products were obtained in good yields, even with the TMS, TPS and TBDMS derivatives that previously had not given satisfactory results in the preparation of the corresponding ketone derivatives **3** (Scheme 9, Table 2).

Interestingly, the initial *O*-silylation leads to formation of *C*-silylated **2** after the retro-Brook rearrangement, while the addition of a second equivalent of silylating agent results in *O*-silylation. This process generally occurs without interchange of the silyl groups to give predominantly the expected products; however, in the cases of runs 1−4 and 7, small amounts of disilylated products were formed, such as **2e,** with both silyl groups TMS. Two regioisomers **2f** and **2g** were isolated in two cases (runs 6 and 7), respectively. The molecular structure of each isomer, as well as that of **2h**, was obtained. The structures contained no unusual bonding parameters and were in accordance with the proposed formulations. These results clearly establish that the intermediates exist in the enolate form **C** rather than the siloxyvinyl anion form **B**.

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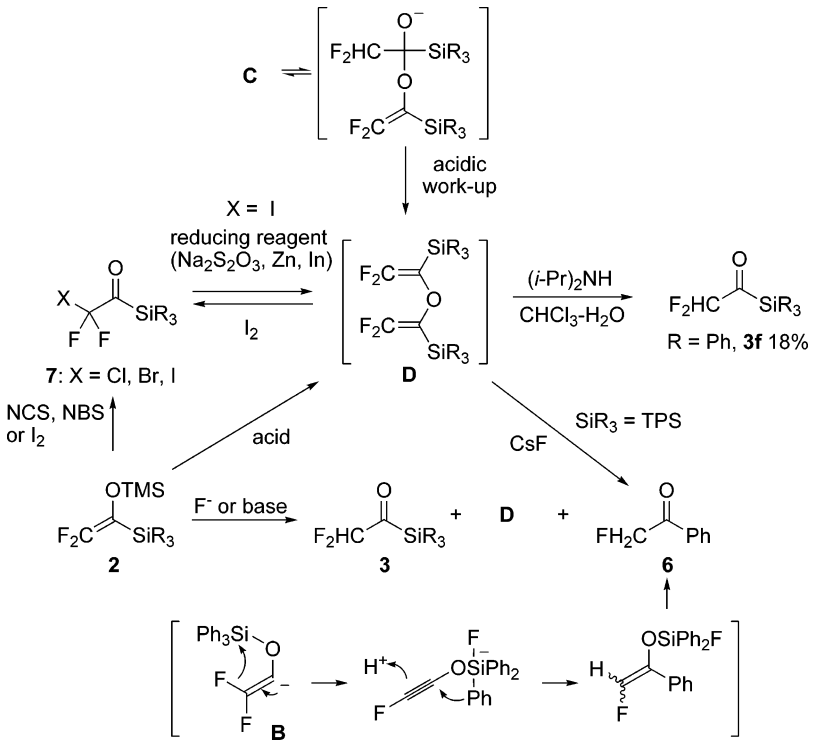
**SCHEME 8**




**SCHEME 9**

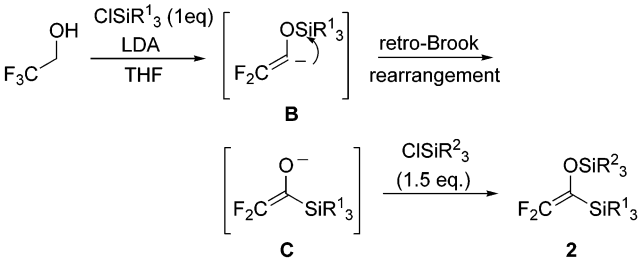



**TABLE 2. Preparation of 2,2-Difluoro-1-trialkylsilylenol Trialkylsilyl Ethers 2**

| run | 2 | $SiR^1_3$ | $SiR^2_3$ | yield/% |
|---|---|---|---|---|
| 1 | **2a** | TES | TMS | 80 |
| 2 | **2b** | TIPS | TMS | 69 |
| 3 | **2c** | TBDPS | TMS | 71 |
| 4 | **2d** | TBDMS | TMS | 65 |
| 5 | **2e** | TMS | TMS | 62 |
| 6 | **2f** | TMS | TPS | 68 |
| 7 | **2g** | TPS | TMS | 67 |
| 8 | **2h** | TPS | TPS | 43 |

No general method for the hydrolytic deprotection of the *O*-silyl groups of **2** to form **3** (Scheme 8) has led to satisfactory results. Under basic conditions, the results were the same as those found on quenching with water; for example, the TIPS derivative **2b** exclusively formed the corresponding difluoroketone **3b**. The TBDMS and TMS derivatives **2d** and **2e** gave mixtures of the corresponding ketone **3** and unknown products with the same $^{19}F$ resonances previously attributed to **D**. The TPS derivative **2g** formed a trace of **3f** along with significant amounts of monofluoroacetophenone **6,** probably generated by an anion-promoted 1,3-phenyl rearrangement of the Brook-rearranged intermediate **B**. Under acidic conditions, the $^{19}F$ resonances corresponding to **D** disappeared over time.

**TABLE 3. Preparation of Difluorohaloacetylsilanes 7**

| **2** | 7 | $SiR_3$ | reagent | *T*/°C | reaction time | X | yield/ % |
|---|---|---|---|---|---|---|---|
| **2b** | **7a** | TIPS | NCS (5 equiv) | rt | 3 d | Cl | 81 |
| | **7b** | | NBS (2 equiv) | 0 °C | 30 min | Br | 85 |
| | **7c** | | $I_2$ (2 equiv) | 0 °C | 30 min | I | 76 |
| **2f** | **7d** | TPS | NCS (5 equiv) | rt | 4 d | Cl | 32 |
| | **7d** | | NCS (10 equiv) | rt | 2 d | Cl | 75 |
| | **7e** | | NBS (2 equiv) | 0 °C | 30 min | Br | 70 |
| | **7f** | | $I_2$ (2 equiv) | 0 °C | 30 min | I | 53 |

Next, since **2** was found to react with halogenating reagents, the corresponding α-difluorohalo derivatives **7** were prepared by treating **2** with electrophilic halogenating reagents (Scheme 8, Table 3).

The reaction of **2b** and **2f** with electrophilic halogenation reagents *N*-chlorosuccinimide, *N*-bromosuccinimide, and iodine formed the corresponding difluorohaloacetylsilanes **7a**−**f**, respectively, in good yields. Chlorination reactions with *N*-chlorosuccinimide did require longer reaction times and higher reaction temperatures compared to bromination and iodination. Chlorination of TPS derivative **2f** with 10 equiv of *N*-chlorosuccinimide gave a satisfactory yield in shorter reaction times. However, when the excess of chlorinating agent was decreased to 5 equiv of *N*-chlorosuccinimide, there was an increase in reaction time, as well as an increase in byproduct formation resulting in lower yields. The molecular structure of **7f** was determined; the Si−C(carbonyl) bond length (1.950(5) Å) again was found to be significantly longer than the Si−C(phenyl) bond lengths (1.870(5), 1.863(5), 1.861(5) Å), just as in **3f**.

The reductions of the iododifluoro derivatives **7c** and **7f** were attempted in an effort to prepare the difluoro-

**SCHEME 10**

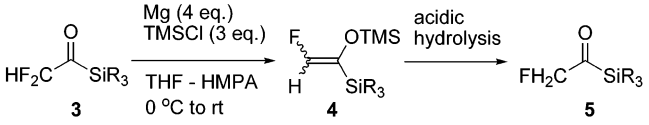
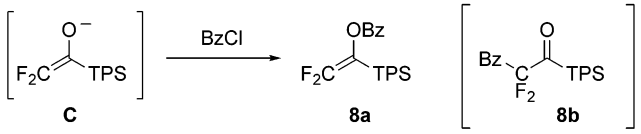



**TABLE 4. Preparation of Monofluoroacetylsilane Derivatives 4 and 5**

| 3 | $SiR_3$ | 4 | yield of 4/% | 5 | yield of 5/% |
|---|---|---|---|---|---|
| **3a** | TES | **4a** | 74 | **5a** | 75 |
| **3b** | TIPS | **4b** | 76 | **5b** | 82 |
| **3c** | TBDPS | | | **5c** | 69 |
| **3d** | TBDMS | **4d** | 69 | **5d** | 85 |
| **3f** | TPS | | | **5f** | 68 |

**SCHEME 11**



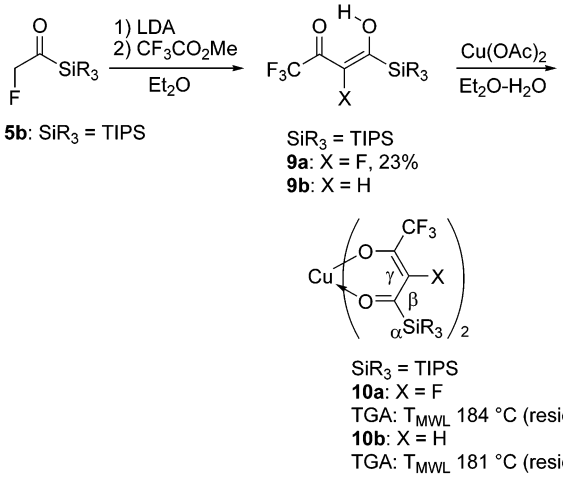

ketones **3**; however, only $^{19}F$ resonances corresponding to compound **D** were observed in both cases. For the TPS derivative **7f**, the product of reduction (**D**) was treated additionally with cesium fluoride and found to form monofluoroacetophenone **6** (Scheme 8).

Several difluoroacetylsilanes **3** were reduced to the corresponding monofluoro derivatives **4** and **5** by reductive defluorination with magnesium in the presence of TMSCl. The addition of HMPA apparently prevents passivation of the magnesium surface. The monofluoroenol trimethylsilyl ethers **4** and the corresponding hydrolysis products, monofluoroacetylsilanes **5**, were prepared in good yields (Scheme 10, Table 4). In the case of monofluoroenol ethers **4**, the hydrolysis was successful in contrast to the attempted hydrolyses of difluoroenol ethers **2**. The structure of monofluoroacetylsilane **5f** was confirmed by single-crystal X-ray diffraction methods; in this case, the asymmetric unit contained two crystallographically independent molecules. Like **3f** and **7f**, the Si−C(carbonyl) bond lengths (1.948(4) Å avg) in the two independent molecules of **5f** were significantly longer than the Si−C(phenyl) bonds (1.870(4) Å avg).

In preliminary findings, attempts to trap the enolate **C** of difluoroacetylsilanes **3** with alkyl halides such as allyl bromide or benzyl bromide, or benzaldehyde, were unsuccessful. The reaction of the enolate **C** of the TPS derivative with benzoyl chloride gave solely the *O*-benzoylated product **8a** instead of the expected *C*-benzoylated product **8b** (Scheme 11), presumably due to the low nucleophilicity of the α-carbon atom and the relatively high polarity of the solvent system.

The structure of **8a** was confirmed by X-ray diffraction methods; bond lengths and angles were within normal ranges. On the contrary, the Claisen condensation of monofluoroacetylsilane **5b** and methyl trifluoroacetate gave the expected γ-fluorinated β-diketone **9a,** along with a small amount of the reduced product **9b** (Scheme 12). Subsequently, copper complex **10a** was prepared by standard methods.[16] The volatility of **10a,** as assessed by thermogravimetric analysis (TGA), was compared to that of **10b**, which lacks a γ-fluorine atom. The results

**SCHEME 12**




revealed that the introduction of a fluorine atom at the γ-position resulted in little change in the temperature of maximum rate of weight loss ($T_{MWL}$; Scheme 12).[16]

## Summary

A variety of mono- and difluoroacetylsilanes and the corresponding silyl enol ethers were prepared from trifluoroethanol and chlorotrialkylsilanes in the presence of LDA through retro-Brook rearrangement. Sterically hindering silyl groups, especially those bound to oxygen, resulted in higher yields of difluoroacetylsilanes. The yields of difluoroacetylsilanes were also drastically affected by the method of the termination of the reaction with acidic conditions seemingly solely and unexpectedly forming dimerized−dehydrated unstable products that could be successfully hydrolyzed to give a difluoroacetylsilane in the case of the triphenylsilyl derivative.

Difluorohaloacetylsilanes were prepared from the corresponding difluoroethenyl silyl ethers with electrophilic halogenating reagents in good yields. A γ-fluorinated β-diketone **9a** was prepared from monofluoroacetyltriisopropylsilane by nucleophilic acylation with methyl trifluoroacetate. The homoleptic Cu(II) complex **10a** of the corresponding γ-fluorinated β-diketonate anion was prepared, and the effect of γ-fluorination on the volatility of the copper complex was investigated. The introduction of a γ-fluorine atom had little or no effect on volatility.

## Experimental Section

**Synthesis of Difluoroacetyltrialkylsilanes 3: General Procedure.** To a round-bottom flask (flame-dried, three-neck with a septum cap, 500 mL) under an inert atmosphere, containing THF (50 mL), trifluoroethanol (5.00 g, 50 mmol), the appropriate chlorotrialkylsilane (50 mmol), and HMPA (5 mL) as required for hindered chlorotrialkylsilanes (Table 1) in a dry ice bath, was added dropwise a solution of LDA (175 mmol, 3.5 equiv, in 100 mL of THF). After the addition was complete, the solution was stirred at an elevated temperature for the requisite time (Table 1) and then was injected into slowly stirring $H_2O$ (500 mL) in a 1000-mL flask at rt via syringe. After being stirred for 10 min, 5 M aqueous HF (100 mL) was added, and the solution was vigorously stirred for 30 min at rt to allow the conversion of the silanol to the

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corresponding fluorosilane. Pentane, for low-boiling products **3a** and **3d**, or hexane (50 mL) was added, and the organic phase was separated, washed with aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. After removal of the drying agent, the solvent was evaporated under gentle vacuum (important for low-boiling products **3a** and **3d**). The residue was subjected to distillation or silica gel column chromatography to afford the product.

**Preparation of Difluoroacetyltriphenylsilane 3f by the Controlled Hydrolysis of the Dimerized Intermediate D.** To a flame-dried 100-mL Schlenk flask equipped with a large stirring bar and an Ar inlet was added $Ph_3SiCl$ (2.95 g, 10.0 mmol); the atmosphere in the flask was then displaced with Ar using a vacuum manifold. THF (10 mL), $CF_3CH_2OH$ (1.00 g, 10.0 mmol), and diisopropylamine (1.41 mL, 10.0 mmol) were added; the mixture was allowed to react with vigorous stirring for 10 min and then chilled in a dry ice bath. A solution of LDA (38 mmol in 20 mL of THF) was then slowly transferred to the $Ph_3SiOCH_2CF_3$ solution with vigorous stirring. The temperature of the reaction mixture was raised to −10 °C, and stirring was continued overnight. To a 200-mL Erlenmeyer flask with a stirring bar were added concentrated HCl (10 mL) and MeOH (50 mL); this solution was chilled in a dry ice bath, followed by injection of the reaction mixture into the solution. Pentane was added, and the organic layer was separated, quickly washed with ice-cold $H_2O$, and put into a 200 mL-round-bottom flask on ice. The solvent was removed at ice temperature using a vacuum pump and a dry ice-cold trap. To the residual solid were added $CHCl_3$, aq $NaHCO_3$, and diisopropylamine (0.2 mL), and the mixture was stirred on ice for 3.5 h. The organic phase was separated, washed with aqueous citric acid solution and $H_2O$, respectively, and then dried over anhydrous $Na_2SO_4$. After the removal of the drying agent by filtration, the solvent was evaporated and the residue was purified by silica gel column chromatography (0−20% $CH_2Cl_2$ in hexane) to give the fluorescent solid **3f** in 18% yield. The product was kept cold in the dark.

**Synthesis of 2,2-Difluorovinyl-1-trialkylsilylenol Trialkylsilyl Ethers 2: General Procedure.** Each of the 2,2-difluorovinylsilylenolate intermediates **C** (Scheme 9) was prepared by the same method as for the preparation of the corresponding **3** (Table 1). To the enolate solution, 1.2−1.5 equiv of an appropriate chlorotrialkylsilane (Table 2) was added, and then the reaction was allowed to stir for 4 h for TMS derivatives or overnight for TPS derivatives. Hexane and $H_2O$ were added to the resulting solution, and the organic layer was separated, washed with two portions of $H_2O$, and dried over anhydrous $Na_2SO_4$. After the removal of the drying agent, the solvent was evaporated in vacuo and the residue was subjected to distillation or silica gel column chromatography to afford the product.

**Preparation of 2-Fluorovinyl-1-trialkylsilylenol Trimethylsilyl Ethers 4 and Monofluoroacetyltrialkylsilanes 5.** To a stirred mixture of Mg (0.486 g, 20 mmol) and chlorotrimethylsilane (1.63 g, 15 mmol) in THF (40 mL) and HMPA (25 mL) was added a solution of difluoroacetyltrialkylsilane (5 mmol) in THF (10 mL) at 0 °C; after addition, stirring was continued at room temperature overnight. DMF also can be used as a solvent instead of THF−HMPA. Usually, the ratios of the resulting cis−trans isomers were close to 1:1, while one of the isomers was hydrolyzed faster than the other during the subsequent purification. Each of the 2-fluorovinyl-1-trialkylsilylenol trimethylsilyl ethers **4** was obtained by addition of hexane and aqueous $NaHCO_3$; then the organic phase was separated, washed with two portions of $H_2O$ to remove HMPA, and dried over anhydrous $Na_2SO_4$. After the removal of the drying agent, the solvent was evaporated in vacuo and the residue was subjected to distillation or silica gel column chromatography to afford the product **4**.

To obtain the corresponding monofluoroacetyltrialkylsilanes **5**, 2 M HCl was added to the reaction mixture, and the resulting solution was stirred for 3 h at rt (a condenser was attached) except **5b** that the solution was refluxed overnight to the complete hydrolysis with addition of methanol (10 mL). The organic layer was separated, washed with saturated $NaHCO_3$ solution, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The product was purified by silica gel column chromatography or distillation under reduced pressure.

**Preparation of Difluorohaloacetyltrialkylsilanes 7.** To a solution of an appropriate quantity of halogenating reagent (Table 3) in THF (5 mL) was added a difluoroenol silyl ether **2** (1 mmol) in 5 mL of THF at 0 °C. After the required period of time (Table 3), stirring at 0 °C or at r, the reaction was quenched with satd sodium thiosulfite solution and extracted with hexane. The organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated. The product was purified by silica gel column chromatography using hexane as an eluent.

**Preparation of $\gamma$-Fluorinated $\beta$-Diketone 9a and the Copper Complex 10a.** To a solution of LDA (2.4 mmol, 1.2 equiv, in 15 mL of $Et_2O$) at −78 °C was slowly added **3b** (0.437 g, 2.0 mmol), followed by stirring for 5 min. Methyl trifluoroacetate (0.24 mL, 2.4 mmol, 1.2 equiv) was added, and then the solution was brought up to −20 °C and allowed to stir overnight. The reaction was terminated by addition of aqueous $NH_4Cl$ and hexane, and the organic layer was separated, washed with $H_2O$, and dried over anhydrous $MgSO_4$. After the removal of the drying agent, the solvent was evaporated in vacuo, and the residue was subjected to silica gel column chromatography. Reduced **9b** was eluted by hexane, and then the product **9a** was eluted by 4% $CH_2Cl_2$ in hexane.

Copper complex **10a** was prepared by mixing **9a** with copper(II) acetate hydrate in $Et_2O-H_2O$ as described elsewhere.[15a] The resulting crude product was dried at 60 °C in vacuo and was recrystallized from methanol to provide crystals suitable for X-ray diffraction studies. The TGA measurements on **10a** were performed as previously reported.[15]

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**Supporting Information Available:** Experimental details and characterization data (including 300 MHz $^1H$ NMR chemical shifts, 75 MHz $^{13}C$ NMR chemical shifts, 282 MHz $^{19}F$ NMR chemical shifts, and elemental analyses) for **2a**−**h**, **3a**−**c**,**f**, **4a**,**b**,**d**, **5a**−**d**,**f**, **7a**−**f**, **8a**, and **9a**. $^1H$, $^{13}C$, and $^{19}F$ NMR spectra and chemical shifts for intermediate **D**. Experimental details for single-crystal X-ray structural determinations, thermal ellipsoid drawings, and X-ray crystallographic data in CIF format for **2f**−**h**, **3f**, **5f**, **7f**, **8a**, and **10a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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