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(*E*)-Trimethyl(perfluoroprop-1-enyl)silane As a Reagent to Transfer Perfluoroprop-1-enyl Group to Ketones and Aldehydes Catalyzed by Fluoride

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ABSTRACT: Analogous to trifluoromethyltrimethylsilane (Ruppert's reagent) (*E*)-trimethyl(perfluoroprop-1-enyl)silane (**1**), prepared by deprotonation of (*Z*)-1,2,3,3,3-pentafluoroprop-1-ene (**2a**) at −78 °C in the presence of chlorotrimethylsilane, was shown to transfer the perfluoroprop-1-enyl group to a number of electrophiles containing carbonyl group in the presence of catalytic amount of fluoride anion. The perfluoroprop-1-enyl group was transferred to formaldehyde, acetaldehyde, benzaldehyde, acetone, trifluoroacetophenone resulting in formation of corresponding TMS-ethers of secondary and tertiary alcohols containing *Z*-$CF_3CF{=}CF-$ fragment. With some substrates such as hexafluoroacetone, formaldehyde, and trifluoroacetophenone, substituted 5-membered dioxolane products of the reaction can be obtained, depending on the reaction conditions and the source of fluoride catalyst.

INTRODUCTION

When a perfluoroalkyl group is introduced into an organic compound, physical, chemical, and biological properties of the new compound are remarkably changed due to high electronegativity of fluorine (4.0 on Pauling's electronegativity scale) combined with the strength of C−F bond. Straightforward and reliable procedures for the introduction of the perfluoroalkyl groups are of a great value. Perfluoroalkyl silicon compounds of the general formula R_FSiR_3 (R = alkyl) have become particularly popular in both organic and organometallic synthesis. The most used reagent for a broad variety of trifluoromethylation reactions is CF_3SiMe_3, which is often referred to as the Ruppert-Prakash reagent. The original report by Ruppert et al.[1] on the synthesis of CF_3SiMe_3 in 1984 was followed by demonstration of clean transfer of trifluoromethyl group to carbonyl compounds.[2] Many literature examples report using the Ruppert-Prakash reagent in synthesis as a method for trifluoromethylation.[3−6]

In contrast, the use of fluorinated vinylsilanes has been limited to very few examples. Thus, the transfer of a trifluorovinyl group from trifluorovinyltrimethylsilane to benzaldehyde promoted by fluoride ion was reported by the Yagupolskii group[7] (Scheme 1). Later this group reported analogous transfer of trifluorovinyl group to aromatic ketones.[8]

Recently Burton reported fluoride ion catalyzed highly stereoselective nucleophilic addition of the difluoroiodovinyl group to aromatic aldehydes using E-(1,2-difluoro-2-iodovinyl)-trialkylsilane reagent[9] (Scheme 2).

However, transfer of a pentafluoropropenyl group to electrophiles using a corresponding silane has not been described. Here we report the use of *E*-$CF_3CF{=}CFSi(CH_3)_3$ (**1**) as a reagent to transfer a pentafluoropropenyl group to electrophiles such as aldehydes and ketones. In majority of cases the product of the transfer is a siloxane that can be converted to the corresponding alcohol by hydrolysis. Also unexpected double addition of some substrates to the pentafluoropropenyl anion were observed which resulted in formation of novel fluorinated derivatives containing 1,3-dioxolane ring.

RESULTS AND DISCUSSION

The synthesis of *Z*-$CF_3CF{=}CFSi(CH_3)_3$ as a pure isomer was claimed by Tarrant.[10] In this paper it was reported that 1:1 mixture of E- and Z-isomers of $CF_3CF{=}CFH$ can be deprotonated at low temperature and converted into *Z*-$CF_3CF{=}CFSi(CH_3)_3$ in 90% yield after treatment with chlorotrimethylsilane. This claim was later addressed by the Burton group demonstrating that the mixture of E- and Z-isomers of $CF_3CF{=}CFH$ lithiated with *n*-BuLi at −78 °C and subsequently quenched with Me_3SiCl affords a corresponding mixture of E- and *Z*-$CF_3CF{=}CFSi(CH_3)_3$ rather than pure Z-isomer.[11] It should also be pointed out that the synthesis of a mixture of E- and Z-isomers of $CF_3CF{=}CFSi(CH_3)_3$ by using bis(trimethylsilyl)mercury reagent was reported by Haszeldine.[12] However, synthesis of the pure *E*-$CF_3CF{=}CFSi(CH_3)_3$ (**1**) as well as transfer of pentafluoropropenyl group to electrophiles using these silanes have not been reported.

In all three mentioned reports a mixture of Z-$CF_3CF{=}CFH$ (**2a**) and *E*-$CF_3CF{=}CFH$ (**2b**) was used as a starting material. In order to prepare pure *E*-$CF_3CF{=}CFSi(CH_3)_3$ (**1**) we decided to use pure **2a** which can be obtained using thermal isomerization of 1:1 mixture of **2a** and **2b** prepared by sequential addition of hydrogen to double bond of hexafluoropropylene followed by dehydrofluorination.[13] The mixture of **2a** and **2b** was isomerized at elevated temperature

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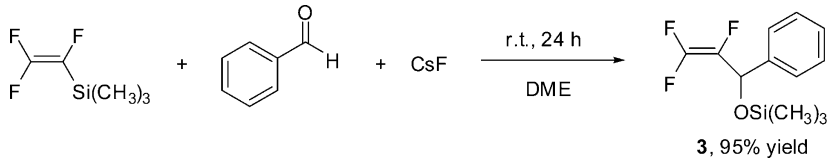
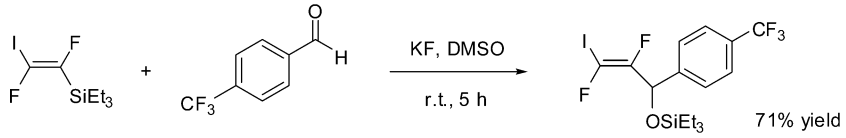
Scheme 1. Fluoride promoted trifluorovinyl addition to benzaldehyde



3, 95% yield

Scheme 2. Fluoride-promoted difluoroiodovinyl addition to substituted benzaldehyde



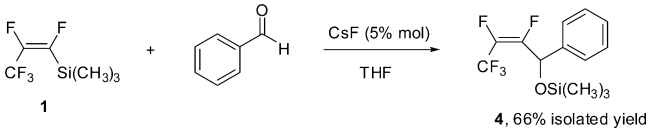
71% yield

over a catalyst to obtain the thermodynamically stable isomer **2a** with 95+% purity.[14] After that **2a** was further purified to 99+ % level by distillation.

When attempting the synthesis of **1** by first generating anion $CF_3CF{=}CF^-$ by deprotonation of **2a** using either *n*-BuLi or LDA at −78 °C in THF or ether solvent, only decomposition products were observed by NMR analysis, after quick darkening of the reaction mixture within minutes even at −78 °C. We found that changing addition order of the reagents has a significant effect on the process and the best approach was to add chlorotrimethylsilane (TMS-Cl) to LDA solution at −78 °C in ether followed by addition of **2a**. With this order of addition **1** was formed in satisfactory yield (77%), presumably due to the fact that anion $CF_3CF{=}CF^-$ was trapped by TMS-Cl as soon as it was forming. After addition of **2a** to the reaction mixture, the light yellow reaction solution was allowed to warm up to room temperature, filtered to remove LiCl, and compound **1** was isolated by distillation. Ether is preferred as a solvent over THF due to a lower boiling point which makes the isolation of **1** (boiling point is 94 °C) easier.

With silane **1** in hand we set out to study its reactions with electrophiles containing a carbonyl group. After equimolar amounts of benzaldehyde and **1** were combined in anhydrous THF at room temperature in the presence of 5 mol % of CsF and the reaction mixture was agitated at ambient temperature for 3 h (Scheme 3), we were pleased to find that all the starting

Scheme 3. Fluoride-catalyzed pentafluoropropenyl addition to benzaldehyde



4, 66% isolated yield

material **1** was gone and an expected product **4** was observed by ^{19}F NMR analysis along with a small amount of **2a** which presumably formed due to a reaction of **1** with adventitious moisture in reaction mixture and with small amount of fluorotrimethylsilane (TMS-F). Both **2a** and TMS-F along with THF are easily distilled off to afford crude product **4**. Pure **4** (>99%) was obtained as a colorless liquid by vacuum distillation in 66% isolated yield. As compared to the synthesis of **3** (Scheme 1), our improvements include using catalytic CsF (5 mol %) as well as shortening reaction time to just 3 h even in the less polar THF instead of DME. These differences indicate that the pentafluoropropenyl group of **1** is more readily transferred to benzaldehyde than trifluorovinyl group of $CF_2{=}CFSiMe_3$ under the same conditions.

In order to study the scope of the reaction, other carbonyl-containing substrates were tested as electrophiles in the reaction with **1**. The substrates along with yields of corresponding products (siloxanes or alcohols) are shown in Table 1, and the details of synthesis are described in the Experimental Section section. Compound **5** was isolated by distillation as colorless liquid with a boiling point 30 °C at 0.12 mmHg. Compound **9** was isolated by sublimation under vacuum as white crystalline solid. It should be pointed out that only one isomer was identified by ^1H and ^{19}F NMR analyses which indicated that the nucleophilic attack of the fluorinated anion occurs selectively from one side of the carbonyl double bond. The crystal structure of **9** shown in Figure 1 reveals the exo-isomer which suggests that the nucleophilic attack at the carbonyl group occurs from the less sterically hindered position. Also, contrary to all other products, compound **9** is isolated as alcohol, rather than a trimethylsilyl ether. Presumably due to the steric hindrance, the TMS-ether hydrolyzes to the alcohol rapidly upon an aqueous workup.

Compounds **6**−**8** were not isolated due to the small scale for these reactions, but instead the reaction mixtures were characterized by NMR analysis. Reaction of acetone with **1** at room temperature afforded a mixture of **2a** and **8** in a ratio 4:1, however, when reaction was carried out at −30 °C the ratio changed to 1:1. Presumably enolizable substrates may afford low yields of the desired addition product due to their facile deprotonation by the fluorinated anion to give **2a** and enolate tautomer. The GC/MS analysis of the reaction mixture detected small amounts of two side products that originated from the corresponding enolate, $CH_3C(O)CH_2C(CH_3)_2OSi(CH_3)_3$ and $CH_3C(O)CH{=}C(CH_3)_2$. Also a reaction of **1** with 1,1,1-trifluoroacetone produced mostly **2a** along with a complex mixture of species containing CF_3 group according to ^{19}F NMR analysis, while no addition product was observed in this case.

In order to prepare compound **7**, potassium fluoride had to be used as a catalyst, while catalysis with cesium fluoride affords a different type of product which is described later in the paper. This reaction was much slower than previously described CsF catalyzed reactions, so it took 15 days at room temperature to complete conversion of **1** into **7**. A very significant portion of **1** is lost to the common side product, **2a** (about 40%), due to inevitable presence of moisture in paraformaldehyde.

In order to demonstrate that the TMS-ethers can be easily hydrolyzed to the corresponding alcohols, compound **4** was

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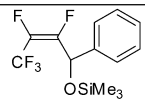
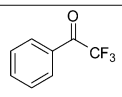
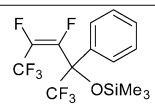
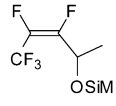
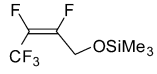
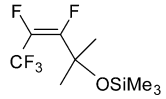
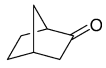
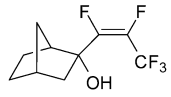
Table 1. Substrates and products of fluoride promoted reactions of 1 with aldehydes and ketones

Entry	Substrate	Catalyst	Product	Product Identifier	Yield, %
1		CsF		**4**	66
2		CsF		**5**	48
3		CsF		**6**	~50[a]
4	paraformaldehyde	KF		**7**	45[a]
5		CsF		**8**	28[ab]
6		CsF		**9**	45
7		CsF	-		-

[a]Yield determined by ^{19}F NMR integration, [b]Yield of the reaction carried out at −30 °C

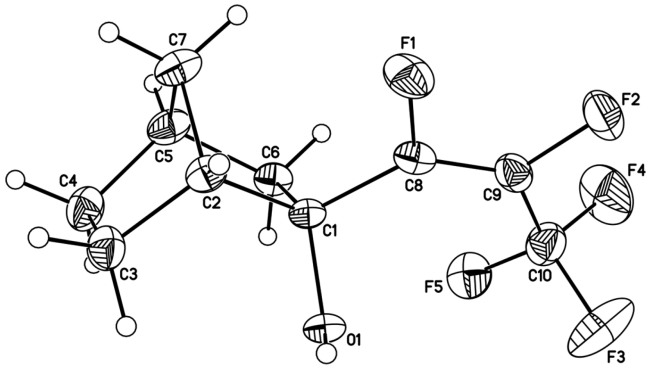
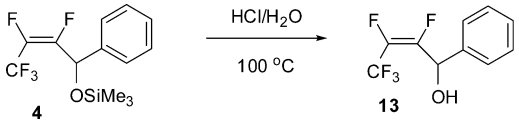


Figure 1. Crystal structure of **9** with thermal ellipsoids drawn to the 30% probability level.

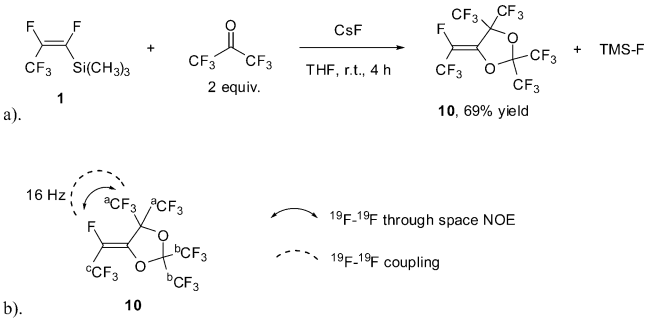
treated by 1 M aqueous solution of HCl at elevated temperature. At 50 °C no reaction was detected, while at 100 °C an essentially complete conversion to alcohol **13** was observed (Scheme 4). Most likely analogous hydrolysis can be done for TMS-ethers **5**−**8** to obtain corresponding alcohols, however, these reactions were not attempted in this study.

An unexpected result was observed when **1** was reacted with hexafluoroacetone (HFA) in the presence of CsF in THF. Along with unreacted **1** was observed a new fluorinated compound that had only one vinylic fluorine according to ^{19}F NMR. The analysis by GC/MS showed that the molecular weight of the new material is 444 g/mol which is consistent with the structure **10** (Scheme 5). Formation of **10** probably is a result of adding a second HFA equivalent to the initial 1:1

Scheme 4. Hydrolysis of TMS-ether 4 to secondary alcohol 13



Scheme 5. (a) Fluoride-promoted reaction of 1 with 2 equiv of HFA to afford 10; (b) $^{19}F-^{19}F$ through-space NOE interactions and coupling in 10



adduct followed by nucleophilic intramolecular cyclization giving a 5-membered ring after the loss of fluoride ion and reestablishing the double bond. In fact the product of a single addition is not observed even in a small amount. When 2 equiv of HFA are added, a full conversion of **1** to **10** was observed while reaction mixture remained almost colorless throughout the reaction. The pure product was obtained by distillation in

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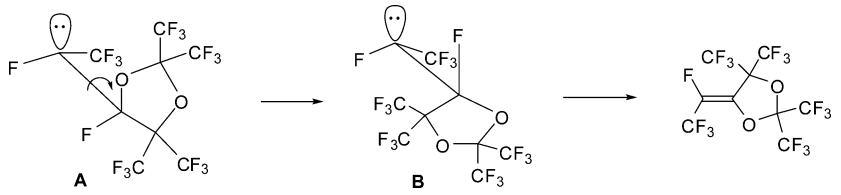
Scheme 6. Proposed rationale for the stereochemistry of 10



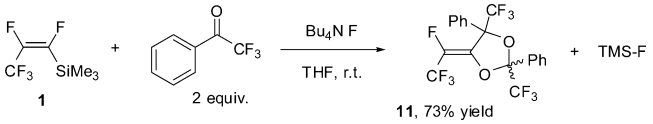
69% isolated yield. An interesting detail about this reaction is that due to limited solubility, **10** forms a separate liquid phase.

Another interesting feature of this process is the orientation of the substituents around the double bond in the product. The six fluorine atoms of two $^{a}CF_3$ groups on the carbon atom adjacent to the double bond are coupled to the only fluorine substituent on the double bond with a very significant coupling constant of 16 Hz and are not coupled at all to the $^{c}CF_3$ group on the double bond (Scheme 5b). That suggests a through-space coupling and orientation on the same side of the double bond for the single fluorine and $C(^{a}CF_3)_2$ group. This orientation was confirmed by the ^{19}F NOESY NMR experiment. As expected, the strongest interaction was observed between vinylic fluorine and $^{c}CF_3$. There was also interaction between vinylic fluorine and group $C(^{a}CF_3)_2$, while there was no interaction between $^{c}CF_3$ and $C(^{a}CF_3)_2$ or $C(^{b}CF_3)_2$ groups. These observations are consistent with the structure **10**. Such orientation is opposite to the expected orientation derived from the fluorinated anion intermediate. However, the explanation can be found in the proposed transition state shown in Scheme 6. The intermediate alkoxy anion can attack the double bond either from the top or from the bottom. The intermediate formed by attack from the top shown in Scheme 6 has a freedom to rotate around the bond that used to be the double bond and to relieve the strain of having two bulky substituents on the same side. The $C(CF_3)_2$ substituent moves away from the CF_3 group on the opposite side of the former double bond, but also in such a staggered orientation so that the electron pair of the anion is in a periplanar position to the fluorine that is about to leave (intermediate B). Thus, when the double bound is reestablished, the orientation of compound **10** is obtained. When the attack by alkoxy anion occurs from the bottom, the rotation takes the $C(CF_3)_2$ substituent into an antiperiplanar position to CF_3 group, and the departure of fluoride occurs also from an antiperiplanar position to the anion electron pair, resulting again in compound **10**.

When tetrabutylammonium fluoride was substituted for cesium fluoride in the reaction of **1** with 2 equiv of 2,2,2-trifluoro-1-phenylethanone in THF, a new 60:40 product mixture was observed instead of the expected product **5**. The two products have analogous sets of peaks in ^{19}F NMR spectrum with three CF_3 groups and with only one vinylic fluorine just like compound **10**. In addition, the GC/MS analysis suggested that both new products have molecular weight 460 g/mol, which is consistent with the dioxolane structure **11** (Scheme 7). These two species were not observed when the same reaction was done with catalytic CsF (entry 2, Table 1).

In order to elucidate the exact orientation of substituents in the two new species, the ^{19}F NOESY NMR and the ^{1}H HOESY NMR experiments were performed on the product mixture. Observed interactions and couplings can only be consistent with the structures shown in Figure 2. In the major isomer **11a** (60%) the vinylic fluorine has a strong through-space NOE

Scheme 7. Synthesis of 11 by the reaction of 1 with 2 equiv of 2,2,2-trifluoroacetophenone catalyzed by tetrabutylammonium fluoride; compound 11 is a mixture of two stereoisomers



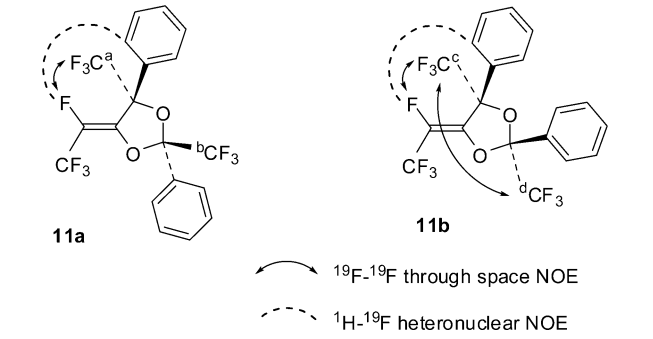


Figure 2. Through-space NOE interactions in **11a–b**.

interaction with the $^{a}CF_3$ group and a coupling constant $^{5}J_{FF}$ = 16.7 Hz; also it has a heteronuclear NOE with two protons in the ortho-position of the phenyl ring. On the other hand the $^{b}CF_3$ group has no interactions with any other fluorine atoms in the molecule which indicates that it can be on the $-CPhCF_3-$ group between two oxygen atoms, pointed away from the double bond, and on the opposite side of the plane of dioxolane ring from the $^{a}CF_3$ group. Thus, just as in compound **10** the bulky group, which in this case is the $-CPhCF_3-$ group, rotates away from the CF_3 group on the double bond into a trans-position, and cis to the smaller vinylic fluorine atom. In the minor isomer **11b** (40%) the vinylic fluorine has the same interactions with the $^{c}CF_3$ group and protons in ortho-position indicating the same orientation around the double bond as in isomer **11a**, but there is also significant interaction between $^{c}CF_3$ and $^{d}CF_3$ groups ($^{6}J_{FF}$ = 3.9 Hz), suggesting that they are located on the same side of the plane of the dioxolane ring. From the thermodynamic point of view it also makes sense that the major isomer would have the two bulkier phenyl groups on the opposite sides of the ring to alleviate the steric hindrance.

As we can see, the reaction of **1** with various electrophiles can give either TMS–ether as a product, or it can go further and give a product of double addition with a substituted dioxolane ring. An important conclusion can be made from the synthesis of **11** using tetrabutylammonium fluoride as a catalyst. Apparently, whether the TMS–ether or dioxolane derivative is formed depends not only on the nature of the substrate, but also on the catalyst. Thus, for the same substrate, 2,2,2-trifluoro-1-phenylethanone, both TMS–ether and dioxolane derivative can be prepared, depending on the catalyst. In fact,

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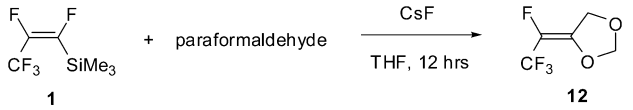
while the reaction of **1** with paraformaldehyde in the presence of KF as a catalyst gave the TMS−ether **7**, the analogous reaction catalyzed by cesium fluoride afforded clean, cyclic product **12** (Scheme 8). It was identified by the single vinylic fluorine in the ^{19}F NMR spectrum with the chemical shift at −167.2 ppm.

Scheme 8. Fluoride-promoted reaction of 1 with paraformaldehyde to afford 12



An attempt was made to prepare a dioxolane derivative with benzaldehyde as a substrate using tetrabutylammonium fluoride. The starting material **1** had reacted, and a complex mixture was obtained. Although no product could be isolated from that mixture, after partial purification by column chromatography on silica gel with ethyl acetate, a small amount of the two isomers of dioxolane derivative were observed in the ^{19}F NMR spectrum along with unidentified materials. The two isomers had signals for vinylic fluorine atoms with a signature chemical shift of −161.9 and −164.8 ppm. It was difficult to fully characterize these two isomers due to very low yield (about 5%), but clearly the reaction took a different path compared to the reaction catalyzed by cesium fluoride. It can be noticed that a catalyst with tighter pairing of fluoride with countercation favors formation of TMS−ether, while a catalyst with less coordinated fluoride is more likely to produce a dioxolane derivative for the same substrate (Table 2).

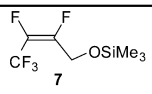
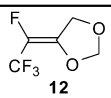
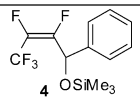
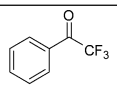
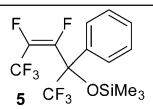
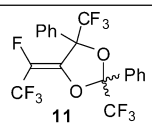
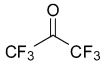
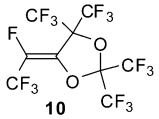
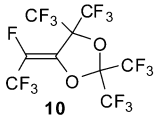
CONCLUSION

The results reported here show that compound **1** serves as a convenient reagent to transfer the Z-$CF_3CF{=}CF-$ group to aldehydes and ketones under ambient conditions. Two outcomes of the reaction are possible, depending on the nature of a substrate and a catalyst. In the first one the reaction stops at a single addition of a substrate to the fluorinated anion to afford a TMS−ether with retention of the stereochemistry around the double bond. In the second outcome, a double addition of a substrate occurs to afford 5-membered dioxolane products with the orientation around the double bond that is opposite to the expected orientation derived from **1**, due to the steric factors.

EXPERIMENTAL SECTION

All reactions were performed in dried glassware, under an atmosphere of nitrogen. ^1H and ^{19}F NMR spectra were recorded on a Bruker DRX-500 spectrometer. ^1H NMR spectra were referenced to the protio impurity in the solvent. ^{19}F NMR spectra were referenced to external $CFCl_3$ (0.00 ppm). GC and GC/MS analyses were carried out on an HP-6890 instrument, using an HP-1 capillary column and either TCD (GC) or mass-selective (GS/MS) detectors, respectively. Anhydrous THF and ether were purchased from Aldrich and used without further purification. KF and CsF (Aldrich) were dried at 150−180 °C under dynamic vacuum for 4−6 h and then were stored and handled inside a drybox. Pure **2a** was obtained using thermal isomerization of a 1:1 mixture of **2a** and **2b** prepared by sequential addition of hydrogen to the double bond of hexafluoropropylene followed by dehydrofluorination.[13] The mixture of **2a** and **2b** was isomerized at elevated temperature over a catalyst to obtain the thermodynamically stable isomer

Table 2

Entry	Substrate	KF	CsF	$Bu_4N F$
1	paraformaldehyde	 **7** TMS-ether	 **12** cyclic	-
2		-	 **4** TMS-ether	$FSiMe_3$ complex mix
3		-	 **5** TMS-ether	 **11** cyclic
4		 **10** cyclic	 **10** cyclic	-

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2a with 95+% purity.[14] After that **2a** was further purified to 99+ % level by distillation.

Crystallography. X-ray data for **9** were collected at −100 °C using a Bruker 1K CCD system equipped with a sealed-tube molybdenum source and a graphite monochromator. The structures were solved and refined using the Shelxtl[15] software package, refinement by full-matrix least-squares on F^2, scattering factors from International Tables, Vol. C, Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (including structure factors) for this structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC #990931. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Preparation of (*E*)-Trimethyl(perfluoroprop-1-enyl)-silane (1). To the 500 mL flask was added anhydrous ether (120 mL) and cooled to −78 °C on dry ice/acetone bath. Then 2.0 M *n*-BuLi in pentane (100 mL, 0.20 mol) was added followed by slow addition of diisopropylamine (28.3 mL, 20.3 g, 0.20 mol). The resultant mixture was allowed to warm up to 0 °C while stirring for 30 min. Then the mixture was cooled down to −78 °C again, chlorotrimethylsilane (21.7 g, 25.3 mL, 0.20 mol) was slowly added, and (*Z*)-1,2,3,3,3-pentafluoroprop-1-ene (26.5 g, 0.20 mol) was slowly bubbled through the agitated reaction mixture. After that the reaction mixture was allowed to warm up to room temperature and stirred for 1 h, and the resultant mixture was filtered and washed with 0.5 M aqueous solution of HCl (2 × 250 mL). Then the organic phase was dried over $MgSO_4$, and the product was isolated by distillation as colorless liquid (31.5 g, 77% yield, bp 94 °C).

MS: *m*/*z*, 204 (M^+), 189 ($-CH_3$), 93, 89, 81, 77, 73, 69 (CF_3).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 0.30 (s, 9H, $Si(CH_3)_3$).

^{19}F NMR ($CDCl_3$, 470.23 MHz, 25 °C) δ −67.58 (dddectet, $^3J_{FF}$ = 13.5 Hz, $^4J_{FF}$ = 6.5 Hz, $^6J_{FH}$ = 0.8 Hz, 3F, CF_3), −137.66 (dqdectet, $^3J_{FF}$ = 11.1 Hz, $^4J_{FF}$ = 6.5 Hz, $^4J_{FH}$ = 1.1 Hz, 1F, CF), −142.13 (qd, $^3J_{FF}$ = 13.5 Hz, $^3J_{FF}$ = 11.1 Hz, 1F, $CFCF_3$).

^{13}C NMR ($CDCl_3$, 125.68 MHz, 25 °C) δ −2.31 (s, 3C, $Si(CH_3)_3$), 119.44 (qdd, $^1J_{CF}$ = 270 Hz, $^2J_{CF}$ = 37.5 Hz, $^3J_{CF}$ = 11 Hz, 1C, CF_3), 145.21 (dqd, $^1J_{CF}$ = 271 Hz, $^2J_{CF}$ = 40 Hz, $^2J_{CF}$ = 21 Hz, 1C $CFCF_3$), 158.56 (ddq, $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 6.5 Hz, $^3J_{CF}$ = 3 Hz, 1C, CFSi).

Preparation of (*Z*)-Trimethyl(2,3,4,4,4-pentafluoro-1-phenylbut-2-enyloxy)silane (4). To the 100 mL Schlenk flask were added cesium fluoride (350 mg, 2.3 mmol) anhydrous THF (40 mL), benzaldehyde (4.5 g, 42 mmol), and *E*-$CF_3CF{=}CFSi(CH_3)_3$ (9.2 g, 45 mmol). The resultant mixture was stirred for 3 h at room temperature. The product was isolated by vacuum distillation as colorless liquid (8.6 g, 66% yield, bp 43 °C/0.25 mmHg).

MS: *m*/*z*, 310 (M^+), 295 ($-CH_3$), 241 ($-CF_3$), 217, 201, 171, 151, 77 (Ph), 73 (TMS).

^{1}H NMR ($CDCl_3$, 401.13 MHz, 25 °C) δ 0.19 (s, 9H, $Si(CH_3)_3$), 5.70 (d, $^3J_{FH}$ = 26.7 Hz, 1H, CH), 7.34−7.46 (m, 5H, C_6H_5).

^{19}F NMR ($CDCl_3$, 377.44 MHz, 25 °C) δ −65.02 (dd, $^3J_{FF}$ = 12.0 Hz, $^4J_{FF}$ = 8.8 Hz, 3F, CF_3), −137.56 (dqd, $^3J_{FH}$ = 26.7 Hz, $^4J_{FF}$ = 8.8 Hz, $^3J_{FF}$ = 4.5 Hz, 1F, $CFCH$), −157.06 (qdd, $^3J_{FF}$ = 12.0 Hz, $^3J_{FF}$ = 4.5 Hz, $^4J_{FH}$ = 1.8 Hz, 1F, CF).

Preparation of (*Z*)-Trimethyl(1,1,1,3,4,5,5,5-octafluoro-2-phenylpent-3-en-2-yloxy)silane (5). To the 100 mL Schlenk flask were added cesium fluoride (350 mg, 2.3 mmol), anhydrous THF (40 mL), trifluoroacetophenone (5.7 g, 33 mmol), and last was added *E*-$CF_3CF{=}CFSi(CH_3)_3$ (7.4 g, 36 mmol). The mixture was stirred for 3 h at room temperature and the resultant solution was filtered. The product was isolated by vacuum distillation as colorless liquid (5.9 g, 48% yield, bp 30 °C/0.12 mmHg).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 0.06 (s, 9H, $Si(CH_3)_3$), 7.44−7.64 (m, 5H, C_6H_5).

^{19}F NMR (C_6D_6, 470.2 MHz, 25 °C) δ −61.95 (m, 3F, CCF_3), −72.69 (dm, *J* = 12. Hz, 3F, $CFCF_3$), −121.96 (m, 1F), −146.26 (m, 1F).

Hydrolysis of (*Z*)-Trimethyl(2,3,4,4,4-pentafluoro-1-phenylbut-2-enyloxy)silane (3) to the Corresponding Alcohol (*Z*)-2,3,4,4,4-Pentafluoro-1-phenylbut-2-en-1-ol (13). To the 50 mL flask were added (3.0 g, 9.7 mmol) and 1.0 M HCl solution (20 mL). The resultant biphasic mixture was heated at 50 °C for 30 min. No change was detected by ^{19}F NMR analysis. The temperature was raised to 100 °C, and stirring continued for 1 h. A full conversion into the product was observed. The organic phase was separated, solvent removed, and the product obtained as colorless liquid (2.1 g, 90% yield).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 5.71 (br d, $^3J_{FH}$ = 26.9 Hz, 1H, CH), 7.38−7.45 (5H, C_6H_5).

^{19}F NMR ($CDCl_3$, 470.23 MHz, 25 °C) δ −65.39 (dd, $^3J_{FF}$ = 11.7 Hz, $^4J_{FF}$ = 8.7 Hz, 3F, $CFCF_3$), −139.09 (dqd, $^3J_{FH}$ = 26.9 Hz, $^4J_{FF}$ = 8.7 Hz, $^3J_{FF}$ = 4.1 Hz, 1F, $CFCCH$), −155.15 (qdd, $^3J_{FF}$ = 11.7 Hz, $^3J_{FF}$ = 4.1 Hz, $^4J_{FH}$ = 1.6 Hz, 1F, CF_3CF).

Preparation of (Z)-Trimethyl(3,4,5,5,5-pentafluoro-pent-3-en-2-yloxy)silane (6). To the 50 mL Schlenk flask were added cesium fluoride (200 mg, 1.3 mmol), anhydrous THF (15 mL), acetaldehyde (0.43 g, 9.8 mmol), and *E*-$CF_3CF{=}CFSi(CH_3)_3$ (2.0 g, 9.8 mmol). The resultant mixture was stirred for 6 h at room temperature. The product was observed by NMR analysis in the reaction mixture (50% yield based on integration in ^{19}F NMR spectrum).

^{19}F NMR (377.44 MHz, 25 °C) δ −66.34 (dd, $^3J_{FF}$ = 12.0 Hz, $^4J_{FF}$ = 8.6 Hz, 3F, CF_3), −139.32 (dqd, $^3J_{FH}$ = 26.3 Hz, $^4J_{FF}$ = 8.6 Hz, $^3J_{FF}$ = 4.0 Hz, 1F, $CFCH$), −160.37 (qd, $^3J_{FF}$ = 12.0 Hz, $^3J_{FF}$ = 4.0 Hz, 1F, CF).

Preparation of (*Z*)-Trimethyl(2,3,4,4,4-pentafluoro-but-2-enyloxy)silane (7). To the 100 mL Schlenk flask were added paraformaldehyde (1.3 g, 43 mmol), potassium fluoride (200 mg, 3.4 mmol) anhydrous THF (20 mL), and *E*-$CF_3CF{=}CFSi(CH_3)_3$ (3.8 g, 18 mmol). The resultant mixture was stirred for 15 days at room temperature. The product was observed by NMR analysis in the reaction mixture (45% yield based on integration in ^{19}F NMR spectrum).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 0.16 (s, 9H, $Si(CH_3)_3$), 4.37 (ddq, $^3J_{FH}$ = 23.9 Hz, $^4J_{FH}$ = 3.4 Hz, $^5J_{FH}$ = 1.4 Hz, 2H, CH_2).

^{19}F NMR ($CDCl_3$, 470.24 MHz, 25 °C) δ −66.48 (ddt, $^3J_{FF}$ = 12.0 Hz, $^4J_{FF}$ = 8.6 Hz, $^5J_{FH}$ = 1.4 Hz, 3F, CF_3), −127.24 (tqd, $^3J_{FH}$ = 23.9 Hz, $^4J_{FF}$ = 8.6 Hz, $^3J_{FF}$ = 3.5 Hz, 1F, $CFCH_2$), −155.53 (qdt, $^3J_{FF}$ = 12.0 Hz, $^3J_{FF}$ = 3.5 Hz, $^4J_{FH}$ = 3.4, 1F, CF).

Preparation of (*Z*)-Trimethyl(3,4,5,5,5-pentafluoro-2-methylpent-3-en-2-yloxy)silane (8). To the 100-mL Schlenk flask were added CsF (200 mg, 1.3 mmol), anhydrous THF (10 mL) and the mixture was cooled to −30 °C. Then dry acetone (0.44 g, 7.6 mmol) was added followed by addition of *E*-$CF_3CF{=}CFSi(CH_3)_3$ (1.5 g, 7.4 mmol) and the mixture was stirred for 3 hours at −30 °C. The product was observed by

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NMR and GC analyses in the reaction mixture (28% yield based on ^{19}F NMR and GC integration).

^{1}H NMR ($CDCl_3$, 400 MHz, 21 °C) δ 0.16 (s, 9H, $Si(CH_3)_3$), 1.51 (dd, J_{FH} = 2.4 Hz, J_{FH} = 0.9 Hz, 6H, $2CH_3$).

^{19}F NMR (377.44 MHz, 25 °C) δ −61.65 (dd, $^{3}J_{FF}$ = 9.8 Hz, $^{4}J_{FF}$ = 7.8 Hz, 3F, $CFCF_3$), −126.9 (qm, $^{4}J_{FF}$ = 9.8 Hz, 1F, $CFCCH$), −157.4 (qm, $^{3}J_{FF}$ = 7.8 Hz, 1F, CF_3CF).

Preparation of (*Z*)-2-(Perfluoroprop-1-enyl)bicyclo-[2.2.1]heptan-2-ol (9). To the 100 mL Schlenk were added cesium fluoride (400 mg, 2.6 mmol), norcamphor (3.5 g, 32 mmol), anhydrous THF (30 mL), and *E*-$CF_3CF{=}CFSi(CH_3)_3$ (8 g, 39 mmol). The resultant mixture was stirred for 16 h at room temperature. After that the mixture was washed with a 0.5 M aqueous solution of HCl (50 mL), and THF solvent was removed to vacuum. The product was isolated by sublimation as off-white crystalline material (3.4 g, 44% yield).

MS: *m*/*z*, 224 (MH^+, −F), 222 (−HF), 196, 178, 160,159, 131, 109, 68, 67.

^{1}H NMR ($CDCl_3$, 499.75 MHz, 21 °C) δ 1.33−1.50 (4H), 1.60−1.68 (2H), 1.97 (m, 1H), 2.01 (br s, 1H, OH), 2.25 (m, 1H), 2.32 (m, 1H), 2.60 (m, 1H).

^{19}F NMR ($CDCl_3$, 470.24 MHz, 21 °C) δ −64.00 (dd, $^{3}J_{FF}$ = 10.3 Hz, $^{4}J_{FF}$ = 8.7 Hz, 3F, CF_3), −121.22 (qm, $^{4}J_{FF}$ = 8.7 Hz, 1F, CF), −155.86 (q, $^{3}J_{FF}$ = 10.3 Hz, 1F, $CFCF_3$).

Preparation of (*E*)-5-(Perfluoroethylidene)-2,2,4,4-tetrakis(trifluoromethyl)-1,3-dioxolane (10). To the 250 mL flask equipped with dry ice condenser were added cesium fluoride (1 g, 6.6 mmol), anhydrous THF (20 mL) and the mixture was cooled to 0 °C. Then hexafluoroacetone (20 g, 0.12 mol) was bubbled through the solution followed by addition of *E*-$CF_3CF{=}CFSi(CH_3)_3$ (10 g, 0.049 mol). The resultant reaction mixture was stirred for 4 h at room temperature. The mixture was transferred to a separatory funnel, and the bottom phase was separated. It was washed with 1 M aqueous solution of HCl (2 × 30 mL) and dried over $MgSO_4$ (anh), and the product was obtained as colorless liquid (15 g, 69% yield, bp 100 °C).

MS: *m*/*z*, 444 (M^+), 425 (−F), 375 (−CF_3), 325 (−CF_2CF_3), 259, 159, 97, 69 (CF_3).

^{19}F NMR ($CDCl_3$, 470.23 MHz, 25 °C) δ −68.69 (d, $^{3}J_{FF}$ = 10.1 Hz, 3F, CF_3), −72.23 (dseptet, $^{5}J_{FH}$ = 16.0 Hz, $^{6}J_{FF}$ = 5.1 Hz, 6F, $2CF_3$), −78.59 (septet, $^{6}J_{FF}$ = 5.1 Hz, 6F, $2CF_3$), −156.69 (septetq, $^{5}J_{FF}$ = 16.0 Hz, $^{3}J_{FF}$ = 10.1 Hz, 1F, CF).

Preparation of (*E*)-5-(Perfluoroethylidene)-2,4-diphenyl-2,4-bis(trifluoromethyl)-1,3-dioxolane (11). To the 100 mL Schlenk flask were added tetrabutylammonium fluoride monohydrate (500 mg, 1.8 mmol), anhydrous THF (20 mL), trifluoroacetophenone (14 g, 80 mmol), and last was added *E*-$CF_3CF{=}CFSi(CH_3)_3$ (6.9 g, 34 mmol). The mixture was stirred at room temperature for 16 h, and the resultant solution was filtered. The product was isolated by vacuum distillation as pale-yellow liquid (11.4 g, 73% yield, bp 73 °C/0.075 mmHg).

MS: *m*/*z*, 441 (−F), 391 (−CF_3), 286, 258, 217, 189, 169, 105, 77.

^{1}H NMR ($CDCl_3$, 400.55 MHz, 21 °C) δ 7.10−7.62 (overlapping peaks for aromatic protons of both isomers).

Major isomer. ^{19}F NMR ($CDCl_3$, 376.89 MHz, 21 °C) δ −67.72 (d, $^{3}J_{FF}$ = 10.9 Hz, 3F, $CFCF_3$), −74.18 (d, $^{5}J_{FF}$ = 16.7 Hz, 3F, CF_3), −81.91 (s, 3F, CF_3), −164.31 (qq, $^{3}J_{FF}$ = 16.7 Hz, $^{3}J_{FF}$ = 10.9 Hz, 1F, CF).

Minor isomer. ^{19}F NMR ($CDCl_3$, 376.89 MHz, 21 °C) δ −67.68 (d, $^{3}J_{FF}$ = 10.9 Hz, 3F, $CFCF_3$), −73.86 (dq, $^{5}J_{FF}$ = 21 Hz, $^{6}J_{FF}$ = 3.8 Hz, 3F, CF_3), −82.66 (q, $^{6}J_{FF}$ = 3.8 Hz, 3F, CF_3), −164.72 (qq, $^{5}J_{FF}$ = 21 Hz, $^{3}J_{FF}$ = 10.9 Hz, 1F, CF).

Preparation of (*E*)-4-(perfluoroethylidene)-1,3-dioxolane (12). To the 100 mL Schlenk flask were added paraformaldehyde (2.0 g, 67 mmol), cesium fluoride (200 mg, 1.3 mmol) anhydrous THF (15 mL), and *E*-$CF_3CF{=}CFSi(CH_3)_3$ (5.3 g, 26 mmol) and the resultant mixture was stirred for 20 h at room temperature. After that the mixture was washed with a 1.0 M aqueous solution of HCl (20 mL). The product was isolated by distillation as colorless liquid (1.1 g, 25% yield).

^{1}H NMR ($CDCl_3$, 500 MHz, 25 °C) δ 4.68 (dq, $^{4}J_{FH}$ = 3.4, $^{5}J_{FH}$ = 2.8, 2H, CH_2), 5.34 (s, 2H, OCH_2O).

^{19}F NMR ($CDCl_3$, 470.2 MHz, 25 °C) δ −68.14 (dt, $^{3}J_{FF}$ = 14.8 Hz, $^{5}J_{FH}$ = 2.8 Hz, 3F, CF_3), −167.21 (qt, $^{3}J_{FF}$ = 14.8 Hz, $^{4}J_{FH}$ = 3.4, 1F, CF).

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Notes

The authors declare no competing financial interest.

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