1,2-Bis(dimethylphenylsilyl)tetrafluoroethane. Application to the Trifluorovinylation and Tetrafluoroethylenation of Carbonyl Compounds

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The reaction of 1,2-bis(dimethylphenylsilyl)tetrafluoroethane with a small excess of benzaldehyde in the presence of the promoter gave the trifluorovinylated product, 1,1,2-trifluoro-3-phenylpropen-3-ol, selectively. The tetrafluoroethylenated product, 2,2,3,3-tetrafluoro-1,4-diphenylbutane-1,4-diol, was also obtained in benzaldehyde solvent or at low temperatures.

Over recent years, much attention has been focused on (perfluoroalkyl)silanes such as (trifluoromethyl)trialkylsilanes, as a useful perfluoroalkylating reagent.[1,2] By using these reagents, the perfluoroalkyl groups can be introduced into carbonyl compounds[3-7] and organic halides[8] in the presence of the fluoride ion sources under the mild conditions. These methods have been extensively studied for the introduction of other fluorine-containing organic groups into carbonyl compounds, and (1,1-difluoroalkyl)silanes[9] and (trifluorovinyl)silanes[10] have been developed. Next, we became interested in the reactivity of α,ω-disilylperfluoroalkanes[11-14] and the interaction between their two silyl groups. One can easily expect that the longer perfluoroalkylene chain diminishes such interaction and two silyl moieties may react independently. Therefore, we chose disilyltetrafluoroethane as a candidate, where two silyl groups attach the adjacent carbon atoms. Fortunately, we have developed the preparation of 1,2-bis(dimethylphenylsilyl)tetrafluoroethane (**1**) by the nickel-catalyzed homocoupling reaction of (bromodifluoromethyl)-dimethylphenylsilane in the presence of Grignard reagent as a reductant.[14] In this paper, we wish to describe the trifluorovinylation and tetrafluoroethylenation of carbonyl compounds using 1,2-bis(dimethylphenylsilyl)tetrafluoroethane (**1**).

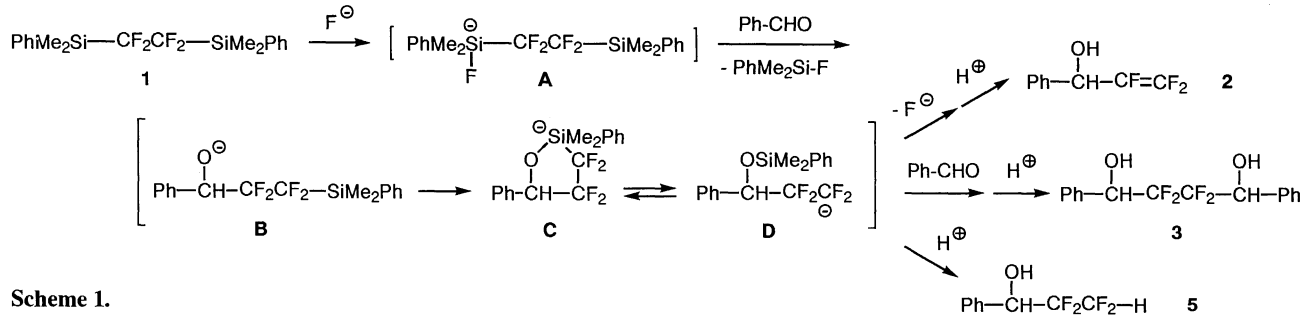
At first, the reaction of 1,2-bis(dimethylphenylsilyl)tetrafluoroethane (**1**) with a small excess (2.4 equiv.) of benzaldehyde was examined, where the formation of the tetrafluoroethylenated product, 2,2,3,3-tetrafluoro-1,4-diphenylbutane-1,4-diol (**3**), was expected. This reaction smoothly proceeded within 5 h at room temperature in the presence of 10 mol% of potassium fluoride (KF) as a promoter in DMF. Surprisingly, the trifluorovinylated compound, 1,1,2-trifluoro-3-phenylpropen-3-ol (**2**),[10] was obtained as a sole product, and the expected tetrafluoro-1,4-diol **3** was not detected in the reaction mixture (Entry 1 in Table 1). A corresponding amount of fluorodimethylphenylsilane was detected by ^{19}F-NMR and GLC analyses, and was much larger than that of employed KF. When a large excess (12.0 equiv.) of benzaldehyde was employed, the tetrafluoroethylenated product **3**[15] was obtained in addition to the trifluorovinylated **2**, though the reaction rate became remarkably slow (Entries 3 and 4 in Table 1). Interestingly, the reaction of **1** with 1.2 equivalents of benzaldehyde resulted in the predominant formation of **2**, in which not only tetrafluoroethylenated product **3** but also the silyltetrafluoroethylenated product, 3-(dimethylphenylsilyl)-2,2,3,3-tetrafluoro-1-phenylpropanol (**4**), were not detected at all (Entry 2 in Table 1).

Table 1. Reaction of benzaldehyde with **1** in the presence of KF [a]

Entry	Ph-CHO /equiv.	KF /mol%	Time /h	Conversion of **1** /% [b]	Yield /% [b] **2**	**3**
1	2.4	10	5	100	60	nd
2	1.2	10	5	100	64	nd
3	12	10	24	86	56	18
4	12	50	2	100	62	23

[a] In all entries, 0.25 mmol of **1** and 1.3 ml of DMF (solvent) were used. Reactions were carried out at room temperature. [b] Conversions and yields (conversion yield) were determined by ^{19}F-NMR. Nd = not detected.

The results can be reasonably explained through Scheme 1. The initially formed active species (**A**) from **1** and fluoride ion nucleophilically attacks benzaldehyde to produce an alkoxide intermediate (**B**), which can easily isomerize to 3-siloxy-tetrafluoropropyl carbanion (**D**) *via* a pentacoordinate silicon intermediate (**C**). Of course, the possibility of the equilibrium between **C** and **D** cannot be excluded. The elimination of fluoride ion from the carbanion **D** affords the trifluorovinylated product **2**, and the nucleophilic attack of the carbanion **D** to benzaldehyde forms the tetrafluoroethylenated product **3**. It is noteworthy that the formation of 2,2,3,3-tetrafluoro-1-phenylpropanol (**5**), which may arise from the hydrolysis of **D** (or **C**), was frequently observed in the reaction mixture in the



Scheme 1.

Table 2. Reaction of benzaldehyde with **1** using various promoters and solvents [a]

Entry	Promoter	Solvent	Time /h	Conversion of **1** /% [b]	Yield /% [b] **2**	**3**
1	TBAF [c]	DMF	1	100	52	trace
2	CsF	DMF	2	100	64	10
3	KOMe	DMF	1	100	25	11
4	Et_3N	DMF	6 days	99	63	28
5	KF	DMSO	2	100	27	11
6	KF	HMPA	2	100	69	24
7	KF	Ph-CHO	24	0	-	-
8	TBAF [c]	Ph-CHO	5	100	27	31
9	KF-18C6 [d]	Ph-CHO	5	100	40	42

[a] In all entries, 0.25 mmol of **1**, 0.13 mmol of promoter, 3.0 mmol of Ph-CHO and 1.3 ml of solvent were used. In entries 7-9, 1.3 ml of Ph-CHO was used for substrate and solvent. Reactions were carried out at room temperature. [b] Conversions and yields (conversion yield) were determined by ^{19}F-NMR. [c] THF solution (1 mol dm^{-3}). [d] 18-Crown-6 (0.13 mmol) was used with KF.

yield of trace to 10%.

Next, we modified the reaction conditions in order to increase the yield of the tetrafluoroethylenated product **3**. The results obtained from the reactions using various promoters and solvents were shown in Table 2. The ionic promoters such as tetrabutylammonium fluoride (TBAF), cesium fluoride (CsF), and potassium methoxide brought the reactions to completion within a few hours, but the ratios of **3** *vs.* **2** in the products were not improved (Entries 1-3 in Table 2). It seemed that the yields of **3** decreased with increasing the basicity of the fluoride ions (basicity: KF < CsF < TBAF), then the promotion ability of amine was also investigated because we recently found that Lewis bases such as amines were applicable as promoters for the perfluoroalkylation of carbonyls with perfluoroalkylsilanes.[16] Triethylamine could promote the present reaction, but its activity was very weak and the product ratio was moderate (Entry 4 in Table 2). Though the reaction proceeded not only in DMF but also in DMSO or HMPA, no remarkable effect on the yield of **3** was observed (Entries 5 and 6 in Table 2). On the basis of the finding that the yield of **3** rose on using a large excess of benzaldehyde as a substrate, the reactions in benzaldehyde as a solvent were studied (Entries 7-9 in Table 2). The reaction in this solvent could not be promoted by KF but were allowed to proceed by the action of soluble promoters such as TBAF or KF-crown ether complex, and **3** was obtained as a main product together with **2** (Entries 8 and 9 in Table 2).

The results of the reactions at low temperatures were shown in Table 3. Although the reaction using KF hardly proceeded at -50 °C, the soluble promoters, CsF or KF-crown ether complex, were again effective, and the moderate yields of **3** were obtained in addition to **2** (Entries 3 and 4 in Table 3).

The reaction of **1** with acetophenone was also examined, where only trifluorovinylated **7** was obtained as a sole product in spite of using 12 equiv. of acetophenone. In this case, the starting **1** was consumed within 2 h at room temperature but the yield of **7** was much lower than that from benzaldehyde. This may be due to the lower reactivity of the intermediately formed **A** and **D** toward acetophenone.

Table 3. Reaction of benzaldehyde with **1** at low temperature [a]

Entry	Promoter	Conditions	Conversion of **1** /% [b]	Yield /% [b] **2**	**3**
1	KF	0 °C, 1 h	100	35	22
2	KF	-50 °C, 9 h	10	trace	trace
3	CsF	-50 °C, 10 h	100	40	41
4	KF-18C6 [c]	-40 °C, 5 h	100	44	32

[a] In all entries, 0.25 mmol of **1**, 0.13 mmol of promoter, 3.0 mmol of Ph-CHO and 1.3 ml of DMF (solvent) were used. [b] Conversions and yields (conversion yield) were determined by ^{19}F-NMR. [c] 18-Crown-6 (0.13 mmol) was used with KF.

In conclusion, new trifluorovinylation and tetrafluoroethylenation of carbonyl compounds with 1,2-disilyltetrafluoroethanes were achieved. This silane behaved as a trifluorovinylating reagent in the presence of a small amount of benzaldehyde, but tetrafluoroethylenated product was also obtained on using a large excess of the substrate. The yield of the tetrafluoroethylenated product was increased by carrying out the reaction in benzaldehyde solvent or the reaction at low temperature. It was revealed that this 1,2-disilyltetrafluoroethane could be used for both purposes of the trifluorovinylating reagent and the tetrafluoroethylenating reagent, by modulating the reaction conditions.

References and Notes

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15 2,2,3,3-tetrafluoro-1,4-diphenylbutane-1,4-diol (**3**: mixture of two diastereomers) ^{1}H-NMR (TMS, $CDCl_3$) δ= 1.86 (b, 2H), 5.11-5.26 (m, 2H), 7.34-7.51 (m, 10H). ^{19}F-NMR ($CFCl_3$, $CDCl_3$) δ= -130.85 to -129.10 (dm, J= 266 Hz, 1.1F), -128.46 to -126.82 (dm, J= 274 Hz, 0.9F), -117.75 to -116.13 (dm, J= 266 Hz, 1.1F), -117.20 to -115.64 (dm, J= 274 Hz, 0.9F).
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