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Short communication

New approach to 3,3-difluoroallyl alcohol

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ABSTRACT

A new difluoroalkene with a triethylsilyl group, 4,4-difluoro-3-(triethylsilyl)- but-3-en-1-ol (**1**), was synthesized as a new building block for 1,1-difluoro-1-alkenes. Treatment of **1** with sodium hydride in the presence of a catalytic amount of *p*-methoxyphenol induced Si–Csp^2 bond dissociation. Subsequent addition of an aldehyde to the reactive intermediate afforded 3,3-difluoroallyl alcohol (**9**). The reaction was accelerated by added *p*-methoxyphenol.

1. Introduction

Fluorinated olefins have attracted much attention, especially for use in medicinal chemistry as bioisosteres [1]. Particularly notable are compounds with an *exo*-difluoromethylene moiety that can act as chemically stable bioisosteres of an aldehyde or ketone, being inherently reactive electrophiles [2,1c,1d]. Many studies on the bioisosteric propensity of *exo*-difluoromethylene-containing sugars and related compounds have been reported [3,1c]. For *exo*-difluoromethylene unit construction, ketones were shown to react with CF_2 carbene from sodium chlorodifluoroacetate [4]. This reaction and its variants are the method of choice with appropriate substrates. On the other hand, a variety of building blocks have been developed for a convenient access to 2,2-difluoroalkenes. In 1981, the first preparation of 2,2-difluorovinyllithium from gaseous 1,1-difluoroethene accelerated the search for such building blocks [5,6]. We considered that 1,1-difluorovinyl-2-triethylsilyl compound, **1**, could generate a 2,2-difluorovinyl anion species on treatment with sodium hydride through intramolecular bond dissociation of Si–Csp^2 bond. The resulting 2,2-difluorovinyl anion could react with aldehydes to generate a 3,3-difluoroallyl alcohol scaffold with a tethered hydroxyethyl chain capable of delivering a variety of substructures. Herein, we wish to report a new pathway to 3,3-difluoroallyl alcohols that are amenable to a variety of synthetic transformations (Fig. 1).

2. Result and discussion

Preparation of **1**, from 2,2,2-trifluoroethanol, **4**, was possible in the moderate yields appropriate for gram-scale synthesis. Treatment of **4** with excess LDA induced retro Brook rearrangement to give silyl ketone **5** [7]. Subsequently, the α,β-unsaturated ester **6** was constructed by Horner–Wadsworth–Emmons olefination of **5** [8]. The terminal hydrogen on difluorocarbon in **6** was sufficiently acidic that deprotonation with LDA to dienolate anion followed by acidification gave **7**. Addition of TMSCl to trap the LDA-generated dienolate increased the yield of **7**. Reduction of the ester group of **7** produced **1** that was the precursor required for further transformations (Scheme 1).

Commonly, dissociation of Si–Csp^2 bond is effected by treatment with a fluoride or oxide anion [9]. In the case of **1**, the Si–Csp^2 bond could be dissociated by the intramolecular assistance of alkoxide ion through 5 membered ring formation like intermediate **2** [10]. We explored the possibility of the Si–Csp^2 bond dissociation by conducting the reaction of **1** with NaH in several classes of solvents. Difluorovinyl anion generated was quenched by the addition of an aldehyde to afford a 3,3-difluoroallyl alcohol.

The results are summarized in Table 1. THF and CH_2Cl_2 were inferior solvents for the reaction. Meanwhile, DMF and DMPU were viable solvents for generation of adduct **9a**. Interestingly, the presence of small portions of water in the solvent increased the yield of **9a** around 30% along with a considerable amount of **10** (entry 8, Table 1). The result prompted us to investigate the effect of an additional hydroxide ion on this reaction system.

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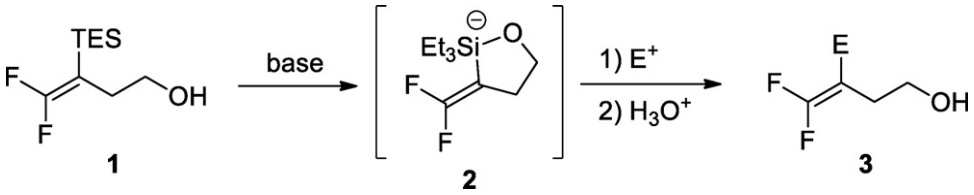
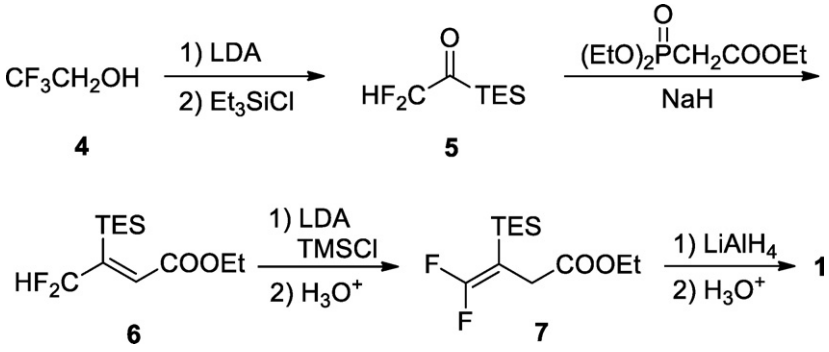
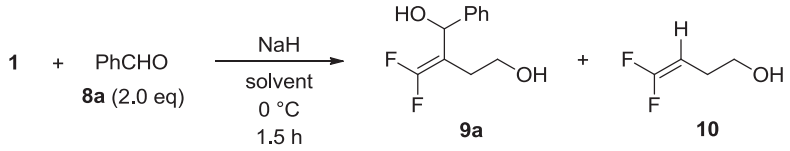


Fig. 1. Si–Csp^2 bond dissociation strategy through intramolecular assistance of alkoxide ion.



Scheme 1. Synthesis of **1**.

Table 1
Intramolecular Si–Csp^2 bond dissociation reaction and subsequent trapping of the generated carbanion.



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Entry	Solvent	Temp. (°C)	Time (h)	Yield (%) **9a**[a]	Yield (%) **10**[a]
1[b]	THF	0 to rt	12	nr	
2[c]		0 to rt	12	nr	
3[b]	CH_2Cl_2	0 to rt	12	nr	
4[c]		0 to rt	12	nr	
5[b]	DMF	0 to rt	12	11	7
6[c]		0	1.5	36	20
7[b]	DMPU	0 to rt	12	8	23
8[c]		0	1.5	30	60

[a] Isolated yield.
[b] Anhydrous solvent was used.
[c] Solvent was used without dehydration.

Table 2
Acceleration effect of oxide anion on the reaction.

Entry	Additive (equiv)	NaH (equiv)[a]	Solvent	Yield (%) **9a**[b]	Yield (%) **10**[b]
1	H_2O (1.0)	2.5	DMF	33	55
2	H_2O (0.25)	1.75		35	35
3	H_2O (1.0)	2.5	DMPU	39	57
4	H_2O (0.25)	1.75		71	16
5	EtOH (0.25)	1.75		59	15
6	CF_3CH_2OH (0.25)	1.75		74	9
7	*p*-MeO–C_6H_4OH (0.25)	1.75		76	5
8	PhOH (0.25)	1.75		66	10
9	*p*-NO_2–C_6H_4OH (0.25)	1.75		64	11

[a] Same amount of NaH with additive was added extra for the generation of corresponding oxide anion in the reaction media.
[b] Isolated yield.

Addition of an equimolar amount of hydroxide ion improved the reaction slightly in both solvents (entries 1 and 3 in Table 2), while a catalytic amount of hydroxide ion accelerated the reaction markedly to yield a 71% of **9a** with suppression of the generation of **10** (entry 4). On the basis of these findings, a search for more suitable additives was conducted (see Table 2). *p*-Methoxyphenoxide ion was the most expedient additive producing an optimal yield of **9a** with formation of **10** notably suppressed (entry 7) (Table 3).

To determine the optimal condition, the influence of the alkoxide counter cation was also investigated. Neither potassium nor lithium hydride, was more effective than sodium hydride, with both cations retarding the reaction by comparison.

Subsequently, the scope and limitation of the reaction with several aromatic and aliphatic aldehydes under the optimized conditions were explored. The reaction with the more electron-rich *p*-anisaldehyde proceeded in only 56% yield (entry 3, Table 4),

Table 3
Effect of counter cation on the reaction.

Entry	Base	Temp. (°C)	Time (h)	Yield (%) **9a**[a]
1	NaH	0	1.5	76
2	KH	0	1.5	37
3	LiH	0 to rt	24	57

[a] Isolated yield.

Table 4
Scope and limitation of the reaction.[a]

Entry	**8**	RCHO	**9**	Yield (%)[b]
1	**8a**	Ph-	**9a**	76
2[c]	**8a**		**9a**	42
3	**8b**	*p*-MeO–C_6H_4–	**9b**	56
4	**8c**	*p*-CF_3–C_6H_4–	**9c**	31
5	**8d**	2-Pyridyl	**9d**	35
6	**8e**	Isopropyl	**9e**	nd
7[c]	**8e**		**9e**	23
8[c]	**8f**	Cyclohexyl	**9f**	51

[a] Reaction was conducted with *p*-methoxyphenol (0.25 equiv) and NaH (1.75 equiv).
[b] Isolated yield.
[c] Reaction was conducted with *p*-methoxyphenol (0.25 equiv) and NaH (0.30 equiv).

a yield lower than that of benzaldehyde. The chemical yield of the reaction was also reduced with the electron deficient aromatic aldehydes *p*-trifluoromethylbenzaldehyde and 2-pyridinecarboxaldehyde (entries 4 and 5). With aliphatic aldehydes bearing an α-hydrogen, aldol condensation predominated. The desired product was not obtained. The difficulties encountered with aliphatic aldehydes could be ameliorated slightly by reducing the amount of NaH (entry 7). Application of this approach to cyclohexanecarbaldehyde which was susceptible to aldol condensation in the basic media led to formation of **9f** of 51%.

3. Conclusion

In summary, a new difluorovinyl anion source **1** was prepared from readily available 2,2,2-trifluoroethanol. Reaction of **1** with NaH in the presence of an aldehyde afforded **9**. The reaction was accelerated by the addition of a catalytic amount of *p*-methoxyphenoxide with the generation of **10** suppressed. Although the reaction proceeded in moderate yield, the structural features of **9** that allow diverse synthetic transformations are fascinating. The mechanistic studies required for a more complete understanding of this reaction are currently under investigation.

4. Experimental

4.1. General

^{1}H NMR and ^{13}C NMR spectra were recorded on JNM-GX400 and JEOL-ECA-600SN spectrometers. ^{19}F NMR spectrum was recorded on Hitachi FT-NMR R-90H spectrometer. Chemical shifts of ^{1}H NMR and ^{13}C NMR are reported in ppm from tetramethylsilane (TMS) as an internal standard. Chemical shifts of ^{19}F NMR are reported in ppm from ethyl α,α,α-trifluorotoluene as an internal standard. Mass spectra were obtained on JEOL JMS-700T spectrometer. Melting points were measured on Yanagimoto micro melting point apparatus MP-S3.

4.2. Synthesis of ethyl 4,4-difluoro-3-(triethylsilyl)but-3-enoate (7)

Under an argon atmosphere, *n*-butyllithium (9.4 mL, 1.60 M in hexane, 15.0 mmol) was added slowly to a solution of diisopropylamine (2,1 mL, 15.0 mmol) in THF (50 mL) at 0 °C and the mixture was stirred for 30 min. To the mixture was added solution of **6** (3.6 g, 13.6 mmol) in THF (10 mL) over 30 min. After stirring for further 30 min at 0 °C, TMSCl (1.92 mL, 15.0 mmol) was added slowly into the reaction mixture and whole was stirred for 1 h at room temperature. The reaction mixture was poured into ice-cold aqueous 10% HCl, extracted with Et_2O and organic layer was dried over anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, EtOAc:hexane = 5:95) to give **7** (3.24 g, 90%). **7**: A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.67 (q, J = 8.0 Hz, 6H), 0.95 (t, J = 8.0 Hz, 9H), 1.26 (t, J = 7.1 Hz, 3H), 2.98 (t, J = 0.4 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 2.9 (dd, J = 1.7, 1.6 Hz), 7.1, 14.1, 31.2 (dd, J = 8.1, 5.1 Hz), 60.8, 73.9 (dd, J = 35.4, 5.3 Hz), 157.3 (dd, J = 306.3, 282.6 Hz), 171.1 (dd, J = 3.9, 2.6 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −7.8 (d, J = 31.0 Hz, 1F), −15.4 (d, J = 31.0 Hz, 1F); IR (neat) ν_{max} 2964, 1742 cm^{-1}; MS m/z = 235 (M^+−29).

4.3. Synthesis of 4,4-difluoro-3-(triethylsilyl)but-3-en-1-ol (1)

Under an argon atmosphere, a solution of **7** (2.65 g, 10.0 mmol) in Et_2O (10 mL) was added slowly to a suspension of $LiAlH_4$ (507 mg, 13.2 mmol) in Et_2O (100 mL) at 0 °C. After stirring for 30 min at room temperature, the reaction mixture was poured into ice-cold aqueous 10% HCl, extracted with Et_2O and organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residue was purified by column chromatography (SiO_2, EtOAc:hexane = 20:80) to give **1** (1.82 g, 82%). **1**: A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.67 (q, J = 8.0 Hz, 6H), 0.95 (t, J = 8.0 Hz, 9H), 1.42 (bs, 1H), 2.25 (tt, J = 7.2, 1.2 Hz, 2H), 3.60 (t, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 3.1 (dd, J = 1.7, 1.6 Hz), 7.2, 29.0 (dd, J = 6.7, 3.5 Hz), 62.2 (dd, J = 3.4, 2.5 Hz), 75.4 (dd, J = 30.0, 5.4 Hz), 156.8 (dd, J = 305.6, 281.6 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −8.7 (d, J = 36.0 Hz, 1F), −12.5 (d, J = 36.0 Hz, 1F); IR (neat) ν_{max} 3336, 2960, 1690, 1468, 1420, 1228, 1050, 720 cm^{-1}; MS m/z = 193 (M^+−29).

4.4. Typical procedure for the synthesis of 9

Under an argon atmosphere, *p*-methoxyphenol (19 mg, 0.15 mmol) was added into a suspension of NaH (60% dispersion in mineral oil, 50.4 mg, 1.05 mmol) in DMPU (2.4 mL). To the suspension, a solution of **1** (133.3 mg, 0.6 mmol) and benzaldehyde (151 μL, 1.2 mmol) was added in DMPU (0.6 mL) over 1 h at a temperature of ice cooling. After stirring for 30 min, the reaction mixture was poured into saturated aqueous solution of $NaHCO_3$, extracted with Et_2O and organic layer was dried with anhydrous $MgSO_4$. After evaporation of the solvent, the residue was separated by column chromatography to give **9**.

2-(Difluoromethylene)-1-phenylbutane-1,4-diol (9a): A colorless solid; Mp = 73.0–74.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.85–1.95 (m, 1H), 2.21–2.29 (m, 1H), 3.53 (td, J = 10.4, 3.6 Hz, 1H), 3.60 (bs, 1H), 3.64–3.70 (m, 1H), 4.84 (bs, 1H), 5.64–5.66 (m, 1H), 7.23–7.37 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.6, 61.2, 67.9 (dd, J = 3.5, 2.3 Hz), 91.6 (dd, J = 13.9, 13.8 Hz), 125.4, 127.3, 128.3, 141.6, 154.8 (dd, J = 289, 289 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −29.2 to −30.8 (m, 2F); IR (KBr) ν_{max} 3300, 2948, 1742 cm^{-1}; MS m/z = 214 (M^+); HRMS m/z M^+ calcd. for $C_{11}H_{12}F_2O_2$: 214.081; found: 214.080.

2-(Difluoromethylene)-1-(4-methoxyphenyl)butane-1,4-diol (9b): A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.88–1.99 (m, 1H), 2.22–2.30 (m, 1H), 3.54 (td, J = 10.0, 3.2 Hz, 1H), 3.60 (bs, 1H), 3.65–3.72 (m, 1H), 3.80 (s, 3H), 4.52 (bs, 1H), 5.62 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.25 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.6, 55.3, 61.4 (dd, J = 3.3, 1.6 Hz), 67.7 (dd, J = 5.0, 2.5 Hz), 91.7

(dd, J = 13.3, 13.3 Hz), 113.7, 126.6, 133.7 (dd, J = 5.0, 2.5 Hz), 154.6 (dd, J = 298, 298 Hz), 158.8; ^{19}F NMR (90 MHz, $CDCl_3$) δ: −28.7 to −30.1 (m, 2F); IR (neat) ν_{max} 3344, 2936, 1742, 1622, 1416, 1330, 1164, 860 cm^{-1}; MS m/z = 244 (M^+); HRMS m/z M^+ calcd. for $C_{12}H_{14}F_2O_3$: 244.091; found: 244.092.

2-(Difluoromethylene)-1-(4-(trifluoromethyl)phenyl)butane-1,4-diol (9c): A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.79–1.90 (m, 1H), 2.29 (dq, J = 15.2, 3.2 Hz, 1H), 3.60 (td, J = 10.4, 3.6 Hz, 1H), 3.72–3.78 (m, 1H), 3.80 (bs, 2H), 5.69 (s, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.5, 61.3, 67.6 (dd, J = 4.9, 3.3 Hz), 91.2 (dd, J = 15.0, 14.1 Hz), 127.4 (q, J = 272 Hz), 125.3 (q, J = 4.2 Hz), 125.9, 129.5 (q, J = 32 Hz), 145.9, 154.9 (dd, J = 290, 290 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: 0.00 (s, 3F), −27.8 to −29.2 (m, 2F); IR (neat) ν_{max} 3388, 2940, 1742, 1622, 1416, 1330, 1172, 856 cm^{-1}; MS m/z = 282 (M^+); HRMS m/z M^+ calcd. for $C_{12}H_{11}F_5O_2$: 282.068; found: 282.069.

2-(Difluoromethylene)-1-(pyridin-2-yl)butane-1,4-diol (9d): A colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.79–1.89 (m, 1H), 2.31–2.39 (m, 1H), 3.51–3.65 (m, 2H), 3.70 (bs, 1H), 5.45 (bs, 1H), 5.59 (s, 1H), 7.27 (dd, J = 8.0, 4.8 Hz, 1H), 7.33 (d, J = 8.4 Hz, 1H), 7.75 (td, J = 8.0, 2.4 Hz, 1H), 8.55 (dd, J = 4.8, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 26.5 (d, J = 1.8 Hz), 61.0 (dd, J = 3.3, 1.7 Hz), 67.9 (dd, J = 5.8, 3.2 Hz), 90.5 (dd, J = 13.1, 12.3 Hz), 120.8, 122.8, 137.3, 147.9, 155.4 (dd, J = 288, 288 Hz), 158.8 (dd, J = 3.0, 2.5 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −27.0 (ddd, J = 42.6, 4.2, 2.3 Hz, 1F), −28.0 (dd, J = 42.6, 3.5 Hz, 1F); IR (neat) ν_{max} 3296, 2932, 1742, 1596, 1440, 1272, 1054, 752 cm^{-1}; MS: m/z = 215 (M^+); HRMS m/z M^+ calcd. for $C_{10}H_{11}F_2NO_2$: 215.076; found: 215.076.

3-(Difluoromethylene)-5-methylhexane-1,4-diol (9e): A colorless solid; Mp = 40.0–41.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.77 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 1.71–1.86 (m, 1H), 2.09–2.20 (m, 1H), 2.37–2.46 (m, 1H), 3.29 (bs, 2H), 3.59 (td, J = 10.4, 3.6 Hz, 1H), 3.75–3.82 (m, 1H), 3.97 (d, J = 9.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 18.4, 19.2, 32.1, 61.5–61.7 (m), 72.7–73.0 (m), 90.1 (dd, J = 14.3, 14.3 Hz), 154.5 (dd, J = 288, 288 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −28.2 to −28.5 (m, 2F); IR (KBr) ν_{max} 3340, 2972, 1742, 1468, 1266, 1212, 1026, 700 cm^{-1}; MS m/z = 180 (M^+); HRMS m/z M^+ calcd. for $C_8H_{14}F_2O_2$: 180.096; found: 180.096.

1-Cyclohexyl-2-(difluoromethylene)butane-1,4-diol (9f): A colorless solid; Mp = 107.0–108.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.76–0.89 (m, 1H), 0.92–1.05 (m, 1H), 1.09–1.31 (m, 3H), 1.42–1.55 (m, 2H), 1.63–1.83 (m, 3H), 2.04–2.20 (m, 2H), 2.37–2.46 (m, 1H), 3.07 (bs, 2H), 3.63 (td, J = 10.0, 2.8 Hz, 1H), 3.77–3.84 (m, 1H), 4.05–4.11 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 25.7, 25.8, 26.0 (d, J = 2.3 Hz), 26.3, 28.6, 29.6, 41.2 (t, J = 2.0 Hz), 61.7 (dd, J = 3.3, 2.5 Hz), 71.7 (d, J = 5.0 Hz), 89.8 (dd, J = 14.0, 14.0 Hz), 154.6 (dd, J = 288, 288 Hz); ^{19}F NMR (90 MHz, $CDCl_3$) δ: −28.0 to −29.2 (m, 2F); IR (KBr) ν_{max} 3332, 2928, 1740, 1450, 1266, 1212, 1024, 690 cm^{-1}; MS m/z = 220 (M^+); HRMS m/z M^+ calcd. for $C_{11}H_{18}F_2O_2$: 220.127; found: 220.128.

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