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Efficient Preparation of 3-Fluoropyrrole Derivatives

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Noble *N*-substituted-3-fluoropyrroles derivatives were prepared from new precursor *via* ring formation. The addition reaction of ethyl iododifluoroacetate to vinyl trimethylsilane under the Cu(0) catalyst resulted in the formation of ethyl-2,2-difluoro-4-iodo-4-(trimethylsilyl)butanolate, which reacted with diisobutylaluminium hydride at −30 °C to yield 2,2-diflouro-4-iodo-4-(trimethylsilyl)butanal. Finally, a series of *N*-substituted-3-fluoropyrrole derivatives were synthesized by the reaction of 2,2-diflouro-4-iodo-4-(trimethylsilyl)butanal with NH_4OH or primary amines followed by reaction with KF solution.

Key Words: 2,2-Difluoro-4-iodo-4-(trimethylsilyl)butanal, β-Fluoropyrrole, 3,3-Difluoro-5-(trimethylsilyl) pyrrolidin-2-ol, Diisobutylaluminum hydride (DIBAH)

Introduction

Pyrrole derivatives constitute an important heterocyclic system in organic chemistry.[1] They are not only ubiquitous in biochemical, biological, and pharmaceutical structures and functions,[2] but also employed widely as building blocks in industrial chemistry.[1] There has been growing interest in selectively fluorinated pyrrole compounds because fluorine atoms tune the physicochemical properties of reagents, either electronically or sterically.[3-6]

Fluorinated pyrroles have been reported to have unique biological properties and have contributed as important building blocks in the preparation of several potent agrochemicals and pharmaceuticals.[7] Although selective fluorination of several classes of organic compounds can be performed, it remains a challenge to selectively fluorinate five-member heteroaromatic compounds.[8] Moreover, unlike the case for 3-chloro[9] or 3-bromo-1*H* pyrrole,[10] a convenient synthesis method for 3-fluoro-1*H* pyrrole has not been established.

Previously, efforts were made in this regard, using the following synthetic methods. 3-Fluoropyrroles have been synthesized by thermally or photochemically induced ring contraction of 2-azido-3,3-difluorocyclobutenes in the presence of nucleophilic arenes,[11] or *via* bromine-lithium exchange of 3-bromo-1-(triisopropylsilyl) pyrroles followed by treatment with *N*-fluorobenzenesulfonimide[12] and by the treatment of the corresponding lithio derivatives with *N*-fluorodibenzenesulfonamide. Leory *et al*.[14] prepared 3-fluoropyrrole derivatives as a precursor for the synthesis of porphyrins of the type *β*-F*n*TPP (*n* = 0, 2, 4, 6, 8). It was noted that instability and separation difficulty were the major hindrances to successful synthesis of 3-fluoropyrroles. In addition, harsh reaction conditions such as those of flash thermolysis at 300 °C and decarboxylation at 180 °C were blamed for the instability of 3-fluoropyrroles,[4] Nevertheless, impure samples of this compound obtained by the desilylation of 3-fluoro-1-(triisopropylsilyl)pyrrole were found to be stable at room temperature,[14] indicating the need for mild reaction conditions for successful synthesis.

Similarly, functionalized *N*-unsubstituted 3-fluoropyrrole moieties were prepared using various synthetic procedures.[15-18] Furthermore, 4-methyl-3-fluoropyrrole-2,5-dicarboxylic acid was synthesized through a multistep sequence involving fluorination and a modified Schiemann reaction.[19] 3-Fluoro-2,5-disubstiuted pyrroles have been produced in high yields by the reaction of ammonium hydroxide with α,α-difluoro-*γ*-(electron withdrawing group)-substituted ketones.[20] More recently, Surmont *et al*.[21] synthesized 5-alkoxymethyl-2-aryl-3-fluoro-1*H*-pyrroles and 2-aryl-3-fluoro-1*H*-pyrrole-5-carbaldehydes from the corresponding 2-aryl-5-(bromomethyl)-1-pyrrolines *via* electrophilic *α*,*α*-difluorination of the imino bond, using Selectfluor (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2.2.2]-octane bis-tetrafluoroborate) and subsequent aromatization by dehydrofluorination.

Synthesis of 3-fluoropyrroles using any of the above methods has advantages, but at the same time, there are disadvantages such as it being expensive or difficult to handle some of the fluorinating agents, harsh reaction conditions, low or moderate yields of products, and multiple-step procedures. In this work, we report a mild, efficient, and convenient method for the synthesis of unbranched *N*-substituted 3-fluoropyrroles as well as a method for the synthesis of 3-fluoro-1*H*-pyrrole from 2,2-difluoro-4-iodo-4-(trimethylsilyl)butanal.

Experimental Section

General. ^1H, ^{13}C, and ^{19}F-nuclear magnetic resonance (NMR) spectra were recorded using Jeol JNM-ECP (500 MHz) and Bruker AC-300 (300 MHz) spectrometers and $CDCl_3$ solutions. Chemical shifts are expressed in parts per million (ppm) downfield from the internal standard, tetramethylsilane. ^{19}F-NMR spectra were referenced relative to an internal $CFCl_3$. High-resolution mass spectroscopy (HRMS) and mass spectroscopy (MS) spectra were obtained at 70 eV in electron impact mode using a Shimadzu GC 17A-QP5000.

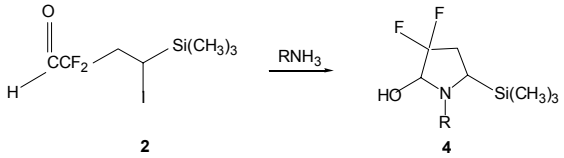
Ethyl-2,2-difluoro-4-iodo-4-(trimethylsilyl)butanoate (1): Iodofluoroacetate (1.25 g, 5.0 mmol) vinyl trimethylsilane (1.0 g, 10 mmol) and powder of activated copper (0.9 mg, 0.25 mmol) were added to acetonitrile (20 mL) dried over P_2O_5 in a round-bottom flask. The reaction mixture was stirred at 65 °C for 15 hr. The reaction was quenched by the addition of water and extraction was conducted with methylene chloride (10 mL × 3). The combined organic extracts were washed with water, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. Flash chromatography on silica gel 60 F_{25-4} using hexane/ethylacetate (3 : 1) afforded **1** (1.56 g, 91%) as a liquid. ^{1}H-NMR ($CDCl_3$) δ −0.18 (s, 9H), 1.38 (t, J = 7.1 Hz, 3H), 2.60 (m, 2H), 3.11 (t, J = 6.6 Hz, 1H), 4.36 (q, J = 7.1 Hz , 2H). ^{13}C-NMR ($CDCl_3$) δ −2.40, 4.41 (t, J = 4.2 Hz), 13.94, 39.15 (t, J = 24.2 Hz), 63.19, 115.74 (t, J = 252.6 Hz), 163.77 (t, J = 31.9 Hz). ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ −108.6 (dt, J = 73.0, 17.2 Hz), −102.3 (ddd, J = 261, 14.6, 12.2 Hz). Fourier-transform infrared spectroscopy (FT-IR) (CCl_4) 1095 (s), 1191 (s), 1254 (s), 1761 (s), 1774 (s), 2960 (m) cm^{-1}. Gas Chromatography-Mass Spectrometry (GC-MS) (*m*/*z*, relative intensity) 73 (78.0), 77 (53.7), 84 (25.7), 103 (100), 185 (5.5), 350 (M^+, 2.3). HRMS (EI) *m*/*z* observed: 350.00092. Calculated for $C_9H_{17}O_2F_2ISi$: 350.00107.

2,2-Difluoro-4-iodo-4-(trimethylsilyl)butanal (2): Ethyl-2,2-difluoro-4-iodo-4-(trimethylsilyl)butanoate (**1**) (1.0 g, 2.86 mmol) was added to dried *n*-hexene (15 mL) in a 50 mL Erlenmeyer flask charged with nitrogen gas and cooled to −30 °C. Diisobutylaluminum hydride (5.72 mL,5.72 mmol) was then added dropwise while stirring. The reaction mixture was gradually warmed to room temperature and stirred at room temperature for 2 hr. The reaction mixture was quenched by the addition of 0.5 N HCl. The mixture was then extracted with methylene chloride (10 mL × 3). The combined organic extracts were washed with water then brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield the title compound **2** (0.77 g , 88%) as a colorless liquid; R_f = 0.72 (ethylacetate : *n*-hexane = 1 : 3). ^{1}H-NMR ($CDCl_3$) δ 0.17 (s, 9 H), 2.70 (m, 2H), 3.12-3.24 (m, 1H), 9.79 (s, CHO). ^{13}C-NMR ($CDCl_3$) δ −2.36, 4.93 (t, J = 20.78 Hz), 63.45 (t, J = 22.99 Hz), 120.57 (t, J = 245.70 Hz), 287.05. ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ −107.27 (ddd, J = 264.35, 17.03, 17.03 Hz, 1F), −105.08 (ddd, J = 264.35, 17.03, 17.03, 1F). FT-IR (CCl_3) 1215 (s), 1732 (s), 3020 (s) cm^{-1}. GC-MS (*m*/*z*, relative intensity) 53.05 (11.63), 59.05 (51.79), 68.05 (28.30), 73.10 (82.52), 77.10 (86.73), 81.0 (100), 167.0 (21.29), 189.0 (24.89), 242.0 (6.88), 306.0 (M^+, 2.08). HRMS (EI) *m*/*z* observed: 305.97452. Calculated for $C_7H_{13}OF_2ISi$: 305.97485.

3,3-Difluoro-5-(trimethylsilyl)pyrrolidin-2-ol (4a): 2,2-Difluoro-4-iodo-4-(trimethylsilyl)butanal (1.98 g, 6.50 mmol) and aqueous ammonium hydroxide solution (36.40 mL, 26.00 mmol) were added to acetonitrile (2 mL) in a round-bottom flask and stirred for 8 hr at room temperature. The reaction mixture was quenched by the addition of water and extracted with methylene chloride (10 mL × 3). The combined organic extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was chromatographed using an isocratic solvent system (*n*-hexane : ethyl acetate = 1 : 3) to yield **4a** (1.16 g, 95%) as a colorless liquid. ^{1}H-NMR ($CDCl_3$) δ 0.03 (s, 9H), 2.14 (m, 1H), 2.40 (m, 1H), 2.67 (m, 1H), 3.35 (s, NH), 3.35 (s, OH), 4.58 (t, J = 12.60 Hz, 1H). ^{19}F-NMR ($CDCl_3$) δ −93.91 (d, t, J_{FF} = 226.8 Hz, J_{HF} = 17.8 Hz), −98.54 (d, t, J_{FF} = 228.9 Hz, J_{HF} = 21.6 Hz), −109.10 (dd, J_{FF} = 226.3 Hz, J_{HF} = 5.1 Hz), −115.49 (dd, J_{FF} = 226.4 Hz, J_{HF} = 10.2 Hz). ^{13}C-NMR ($CDCl_3$) δ −2.34 (s), 39.49 (t, J = 22.15 Hz), 45.16 (s), 82.64 (t, J = 26.25 Hz), 132.88 (t, J = 254.70 Hz), −3.73(s). IR(CCl_4) 3475, 3435, 3055, 780 cm^{-1}. GC-MS (*m*/*e*, relative intensity) 196 (M^+, 25.80), 178 (1.22), 148 (1.31), 132 (20.58), 106 (8.37), 73 (100.00), 55 (7.20). HRMS (EI) *m*/*z* observed: 195.08825. Calculated for $C_7H_{15}NOF_2Si$: 195.08910.

General procedure for synthesis of compounds (4b-4i): 2,2-Difluoro-4-iodo-4-(trimethylsilyl)butanal (10 mmol) and *n*-

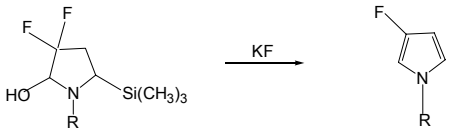
Table 1. Preparation of 3,3-difluoro-1-methyl-5-(trimethylsilyl) pyrrolidin-2-ol derivatives from 2,2-difluoro-4-iodo-4-(trimethylsilyl) butanal (**2**) and primary amines



2 **4**

Entry	Substrate	Reactants (R-NH_2)	Products	Yield (%)
1	2	H	**4a**	89
2	2	*n*-C_4H_9	**4b**	84
3	2	Cyclopentyl	**4c**	74
4	2	Cyclohexyl	**4d**	75
5	2	$CH_2C_6H_5$	**4e**	90
6	2	$CH_2CH_2C_6H_5$	**4f**	92
7	2	$CH_2C_6H_4$(*p*-OCH_3)	**4g**	91
8	2	4-Pyridine	**4h**	94
9	2	C_6H_5	**4i**	83

Table 2. Synthesis of *N*-substituted-3-fluoropyrrole derivatives from 3,3-difluoro-1-methyl-5-(trimethylsilyl)pyrrolidin-2-ol derivatives (**4**) and potassium fluoride



4 **5**

Entry	Reactants (R-NH_2)	Product	Yield (%)
1	H	**5a**	77
2	*n*-C_4H_9	**5b**	74
3	Cyclopentyl	**5c**	76
4	Cyclohexyl	**5d**	77
5	$CH_2C_6H_5$	**5e**	86
6	$CH_2CH_2C_6H_5$	**5f**	89
7	$CH_2C_6H_4$(*p*-OCH_3)	**5g**	85
8	4-Pyridine	**5h**	87
9	C_6H_5	**5i**	78

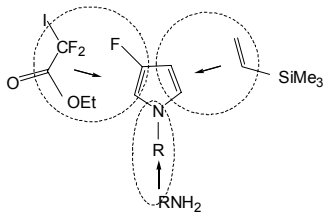
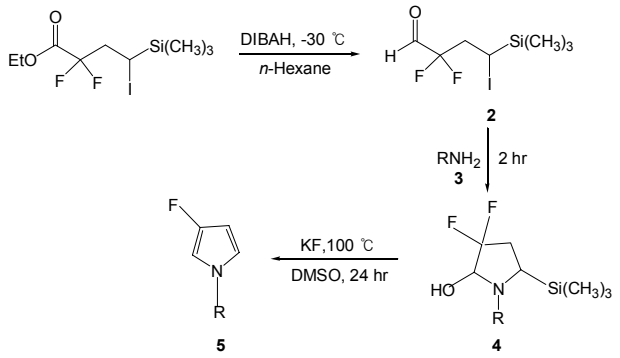
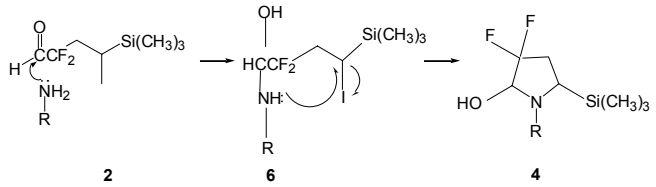


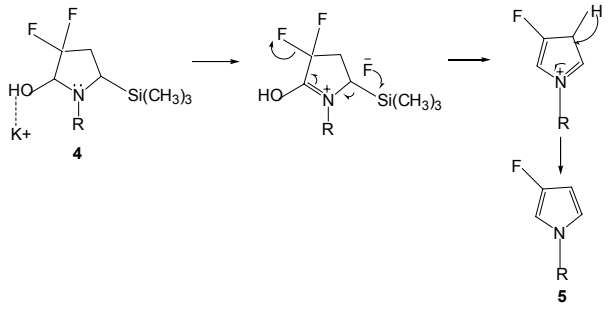
Figure 1. A design for the synthesis of *N*-substituted-3-fluoropyrroles.



Scheme 1. Synthesis of 1-substituted-3-fluoropyrrole derivatives from ethyl-2,2-difluoro-4-iodo-(trimethylsilyl)butanoate



Scheme 2. Proposed mechanism for the synthesis of 3,3-difluoro-*N*-substituted-5-(trimethylsilyl)pyrrolidin-2-ol derivatives from 2,2-difluoro-4-iodo-4-(trimethylsilyl)butanal (**2**)



Scheme 3. Proposed mechanism for the synthesis of 3-fluoropyrrole derivatives from 3,3-difluoro-*N*-substituted-5-(trimethylsilyl)pyrrolidin-2-ol (**4**). Conversion of **4** into **5** would occur *via* desilylation and aromatization in Scheme 2 and 3. When **4** was isolated and allowed to react with KF, the reaction finished within 18 hr.

butylamine (30 mmol) were added to acetonitrile (10 mL) in a round-bottom flask and stirred for 8 hr at room temperature. The reaction mixture was quenched by the addition of 1% acetic acid solution, washed with water, and extracted with methylene chloride (10 mL × 3). The combined organic extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Separation of the resulting residue by column chromatography on silica gel (ethyl acetate/*n*-hexane) afforded compound **4** (74 ~ 94%) as a colorless liquid.

3-Fluoro-1*H*-pyrrole (5a): 3,3-Difluoro-5-(trimethylsilyl) pyrrolidein-2-ol (1.2 g, 4.41 mmol) and potassium fluoride (0.31 g, 5.33 mmol) were added to dimethyl sulfoxide (DMSO) (15 mL) in a round-bottom flask. The reaction mixture was stirred for 15 hr at 100 °C. The reaction mixture was quenched by the addition of water and the aqueous solution was extracted with diethyl ether (10 mL × 3). The combined organic extracts were washed with water and dried over anhydrous magnesium sulfate. The residue was vacuum-distilled fractionally into a set of U-traps at several trapping temperatures. The apparatus for the vacuum fractionation is the same as that adopted in conventional borane/carborane chemistry. Residual impurities were removed by distillation at −40 °C under 5 mmHg pressure to give the title compound **5a** (0.32 g, 77%). ^{1}H-NMR ($CDCl_3$, TMS) δ 5.94 (q, J = 2.5 Hz, 1H), 6.51 (m, 2H), 7.72 (s, N-H). ^{13}C-NMR ($CDCl_3$) δ 97.28 (d, J = 17.7 Hz), 101.85 (d, J = 30.7 Hz), 117.46 (d, J = 6.9 Hz), 155.34 (d, J = 237.8 Hz). ^{19}F-NMR($CDCl_3$,$CFCl_3$) δ −172.32 (s). HRMS (EI) *m*/*z* observed: 85.03265. Calculated for C_4H_4NF: 85.03278.

General procedure for synthesis of compounds (5b-5i): 1-*n*-Butyl-3,3-difluoro-5-(trimethylsilyl)pyrrolidein-2-ol (4.8 mmol) and potassium fluoride (9.8 mmol) were added to DMSO (15 mL) in a round-bottom flask. The reaction mixture was stirred for 15 hr at 100 °C. It was then quenched by the addition of water and extracted with diethyl ether (10 mL × 3). The combined organic extracts were first washed with water and then with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography on silica gel, using diethyl ether/*n*-hexane (1 : 4), afforded **5b** (74 ~ 89%) as a liquid.

1-*n*-Butyl-3-fluoropyrrole (5b): ^{1}H-NMR ($CDCl_3$) δ 6.38 (m, 1H), 6.33 (m, 1H), 5.84 (t, J = 2.3 Hz, 1H), 3.84 (m, 2H), 1.69 (m, 2H), 1.29 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ^{13}C-NMR ($CDCl_3$) δ 151.79 (d, J = 236.9 Hz), 117.35 (d, J = 5.8 Hz), 103.69 (d, J = 26.9 Hz), 95.80 (d, J = 17.3 Hz), 50.17 (s), 33.37 (s), 19.86 (s), 13.66 (s). ^{19}F-NMR ($CDCl_3$, $CFCl_3$) δ −166.26 (s, 1F). IR (KBr): 2959, 2928, 2872, 1456, 1385, 1122, 619 cm^{-1}. GC-MS (*m*/*z*, relative intensity) 141 (M^+, 40.64), 99 (100.0), 98 (79.4), 85 (25.34), 71 (13.64), 57 (17.66), 51 (32.45), 41 (42.15). HRMS (EI) *m*/*z* observed: 141.09522. Calculated for $C_8H_{12}NF$: 141.09538.

Results and Discussion

The starting materials for unbranched *N*-substituted-3-fluoropyrroles were designed as illustrated in Figure 1. The detailed syntheses for target compounds are as follows. Ethyl bromodifluoroacetate, Zn, I_2, and $HgCl_2$ were reacted in triglyme solution to give ethyl iododifluoroacetate with 64% yield *via* the Reformatsky reaction. It is problematic to remove the solvent using this method unless the scale of the reaction is

large enough. In acetonitrile, however, we found that the use of only Zn and I_2 at 0 °C was sufficient to prepare ethyl iododifluoroacetate with 92% yield. The addition reaction of ethyl iododifluoroacetate to vinyl trimethylsilane under a Cu (0) catalyst resulted in the formation of ethyl-2,2-difluoro-4-iodo-4-(trimethylsilyl)butanoate (**1**) with 91% yield. Compound **1** was reduced by diisobutylaluminium hydride to afford 2,2-difluoro-4-iodo-4-(trimethylsilyl)butanal (**2**) at −30 °C. When compound **2** was reacted with excess aqueous NH_4OH (more than 8 mol) at room temperature, compound **5** formed very slowly (over 72 hr), as monitored by either ^{19}F-NMR or thin-layer chromatography. In this case, the yield was not more than 30% (Scheme 1). However, when compound **2** reacted with three equivalences of NH_4OH and primary amines, compound **4** instead of **5** formed quantitatively (Scheme 2). 3,3-Difluoro-1-methyl-5-(trimethylsilyl) pyrrolidin-2-ol derivatives were isolated by flash column chromatography. In our reaction scheme, it was expected that the addition of ammonia or primary amines to (**2**) would form 2,2-difluoro-4-iodo-1-(alkylamino)-4-(trimethylsilyl)butan-1-ol (**6**) *via* a nucleophilic addition reaction. In turn, a ring closure reaction would occur intramolecularly *via* the nucleophilic attack of the amino group on the carbon with iodine to give 3,3-difluoro-5-(trimethylsilyl) pyrrolidin-2-ol (**4**). The results of reaction are summarized in Table 1. A possible reaction mechanism is suggested on basis of the isolated molecules and reaction stoichiometry, as illustrated in Scheme 2. Compound **4** was then reacted with KF in DMSO at 100 °C for 15 hr to give compound **5** (Table 2). The desilylation of compound **4** was conducted using KF. The results showed that it was more effective (yield 10% greater) than tetrabutylammonium fluoride.

Conclusions

In conclusion, unbranched *N*-substituted-3-fluoropyrroles as well as 3-fluoro-1*H*-pyrrole were prepared conveniently and efficiently from 2,2-diflouro-4-iodo-4-(trimethylsilyl)butanal. We believe that these compounds would be useful in pyrrole-based macrocycle chemistry. In addition, we successfully prepared *N*-phenyl-3-fluoropyrrole (**5j**), which is of importance because the arylation of heterocyclic nitrogen has been a long-standing problem and drawn much attention in both pharmaceutical and industrial applications.

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