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N-Polyfluoro(trimethylsilyl)ethyl azole derivatives

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Abstract

A facile synthetic route to *N*-polyfluoro(trimethylsilyl)ethyl azole derivatives was developed starting from *N*-bromo(chloro)polyfluoroethyl-substituted azoles. The silanes thus obtained were reacted with various electrophiles in the presence of the fluoride ion to yield the corresponding fluorinated carbinols, ketones, carboxylic acids, and methyl dithiocarboxylates as well as *N*-pentafluoroethylbenzimidazole.

Keywords: *N*-Polyfluoro(trimethylsilyl)ethylazoles; C-nucleophiles; *N*-Pentafluoroethylbenzimidazole

1. Introduction

(Trifluoromethyl)trimethylsilane obtained for the first time by Ruppert et al. [1] is an efficient reagent in fluoroorganic chemistry. Its chemical behaviour was thoroughly studied by Prakash and Yudin [2]. Fluorinated silanes are similar to the Grignard reagents in their reactivity being, at the same time, synthetically convenient and stable to long-term storage, in contrast to extremely labile perfluoroalkylmagnesium and -lithium compounds.

Aza-heterocycles bearing fluorinated groups at the nitrogen atom, although little studied as yet, have already found agricultural applications, e.g., as herbicides (Sulfentrazone [3] and Carfentrazone [4]). The introduction of 2-bromoperfluoroethyl group to the heterocycle's nitrogen atom was done at first on 4-dimethylaminopyridine [5]. Recently, we have synthesized the N-CF_2CF_2Br [6] and N-CF_2CFCl_2 [7] substituted azole derivatives. Substitution of a trimethylsilyl group for the terminal halogen atom offers wide possibilities for functionalization of the polyfluorinated residue bound to the nitrogen atom of the heterocycle.

The imidazole and benzimidazole derivatives containing a CF_2SiMe_3 group at the nitrogen atom were described previously and their reactions with benzaldehyde and cyclohexanone were reported [8]. The corresponding secondary alcohols were obtained in the presence of tetramethylammonium fluoride [8]. Trimethylsilyl derivatives have been synthesized by treatment of appropriate bromodifluoromethyl-substituted compounds with tris(diethylamino)phosphine in methylene chloride. A serious drawback of the method is that the target silane is difficult to separate completely from unreacted tris(diethylamino)phosphine, particularly if the boiling points of the two substances are close enough. Moreover, tris(diethylamino)phosphine is a toxic reagent. The alternative route to obtain *N*-difluoro(trimethylsilyl)methyl derivatives of azoles was using Al powder in *N*-methylpyrrolydone [8,9].

A convenient synthetic access to difluoro(trimethylsilyl)-methyl-substituted acetylenes has been recently suggested which implies the reaction of the corresponding bromodifluoromethyl derivatives with trimethylchlorosilane and magnesium [10–12]. We have taken advantage of this approach to synthesize azoles containing a tetrafluoro(trimethylsilyl)ethyl group at the nitrogen atom. The heterocycles under study, including imidazole, benzimidazole, pyrazole, and 3,5-dimethylpyrazole, have been chosen among those most widespread in biologically active materials.

2. Results and discussion

The 2-bromotetrafluoroethyl (**1a–d**) and 2,2-dichlorotrifluoroethyl (**2a–d**) derivatives of the heterocycles concerned were synthesized by the procedures previously reported by us [6,7]; compound **1d** was obtained for the first time.

2-Bromotetrafluoroethyl derivatives react with magnesium and trimethylchlorosilane in anhydrous THF at 30–35 °C with a

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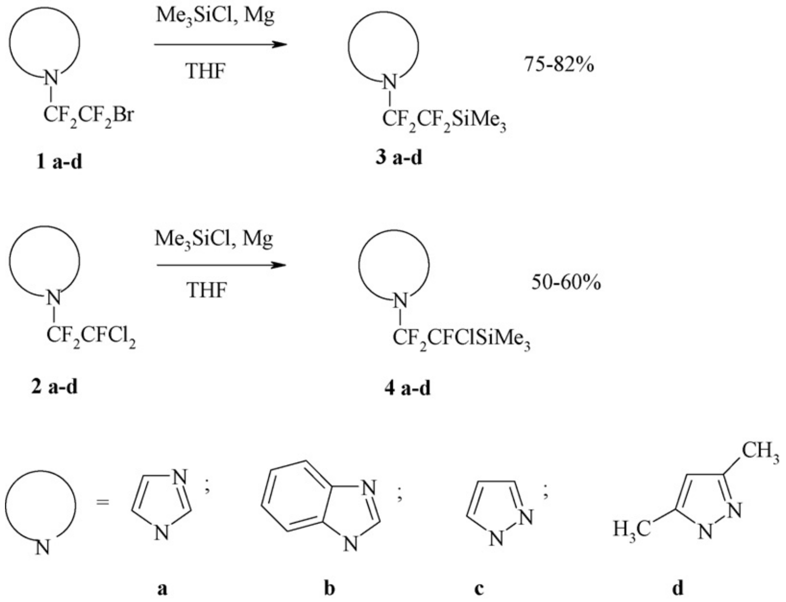
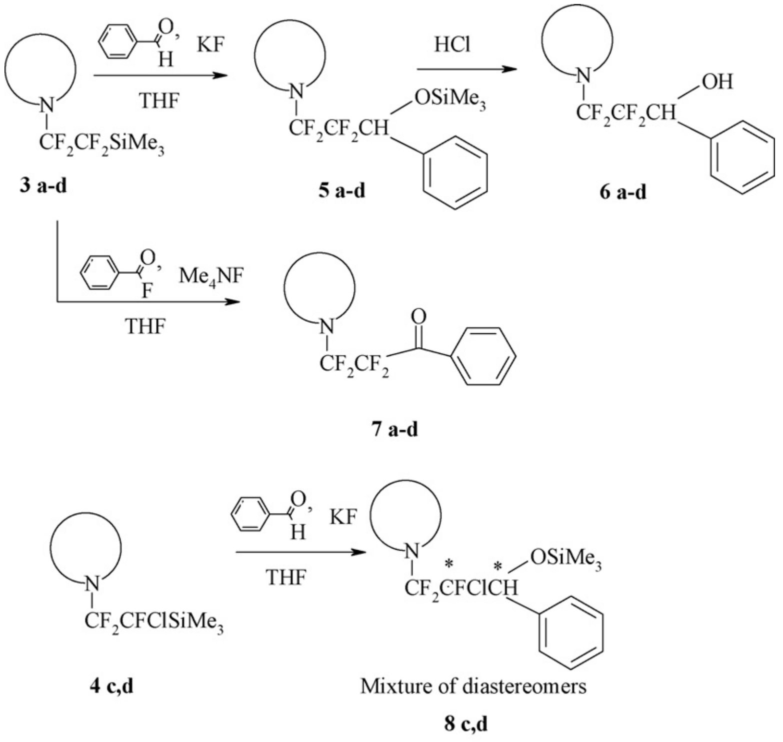


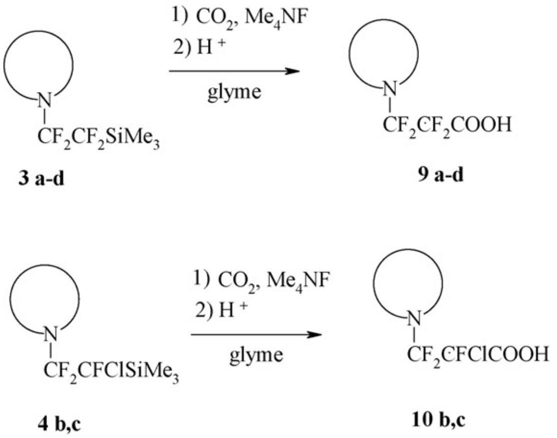
Scheme 1.

significant exothermic effect (Scheme 1). The synthesis is almost entirely free of side reactions and hence furnishes (2-hetaryltetrafluoroethyl)trimethylsilanes **3a–d** in high yields (75–82%). Compounds **2a–d** react analogously at the same temperature with a much smaller heat release. Only one of two chlorine atoms is substituted by the trimethylsilyl group to give (1-chloro-2-hetaryltrifluoroethyl)trimethylsilanes **4a–d**. The yields of the target products are somewhat lower (50–60%) due to the side reaction, viz., abstraction of two halogen atoms, which results in the unsaturated 2-chloro-1,2-difluoroethenyl residue at the nitrogen atom. Silanes **4a–d** are easy to purify by distillation, as they have much higher boiling points than the side products with the unsaturated fluorinated N-substituent.

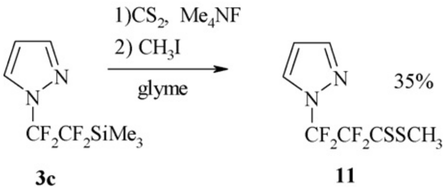
The silanes obtained were reacted with benzaldehyde in the presence of catalytic amounts of the fluoride ion (Scheme 2). As a source of fluoride ions, we used potassium fluoride, instead of



Scheme 2.



Scheme 3.

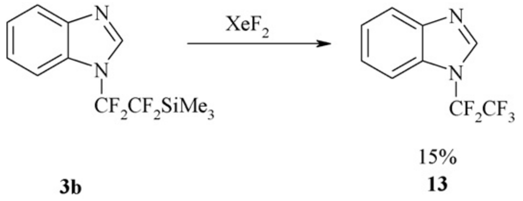


Scheme 4.

tetramethylammonium fluoride suggested formerly [7]. Compounds **3a–d** were thus converted at room temperature into the corresponding trimethylsilyl ethers of 2-hetaryltetrafluoroethyl(phenyl)carbinols **5a–d**, which were hydrolyzed to the carbinols **6a–d**. By interaction of compounds **3a–d** with benzoyl fluoride in the similar conditions, 2-hetaryltetrafluoroethyl(phenyl)ketones **7a–d** were obtained.

Likewise, compounds **4c**,**d** containing the $CF_2CFClSiMe_3$ moiety with an asymmetric carbon atom easily enter into this reaction to produce an inseparable 1:1 diastereomeric mixture of trimethylsilyl ethers of 1-chloro-2-hetaryltrifluoroethyl(phenyl)carbinols **8c**,**d**.

Silanes **3a–d** and **4a–c** react with carbon dioxide in glyme at −80 to −30 °C under presence of an equimolar quantity of tetramethylammonium fluoride (Scheme 3). (In this case, potassium fluoride is ineffective as a catalyst, in contrast to the reaction with benzaldehyde.) The resulting carboxylic acids, **9a–d** and **10b,c**, obtained in 60–65% yields appear as stable and readily crystallizable substances which can be involved in further conversions.



Scheme 6.

Unlike carboxylic acids **9** and **10**, their dithio analogues produced by the reaction of silanes **3** and **4** with carbon disulfide are unstable compounds. Treatment of silane **3c** with carbon disulfide and tetramethylammonium fluoride followed by methylation with methyl iodide at −10 to 0 °C affords the corresponding methyl dithiocarboxylate **10** in about 35% yield (Scheme 4). It appears as a stable red liquid distilling without decomposition. At lower temperatures (−50 to −70 °C), the reaction with carbon disulfide does not go to completion.

Silane **3c**, when reacted with an activated halogenoarene, such as *p*-iodonitrobenzene, in the presence of copper salts (as in Ref. [13]) produces compound **12** (Scheme 5).

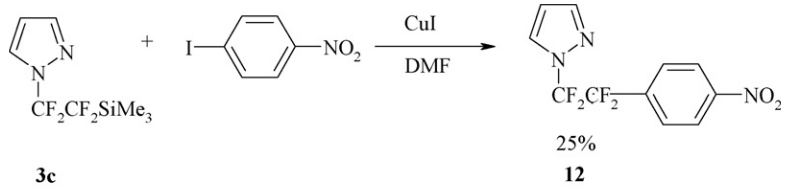
It was of interest to ascertain whether perfluorinated N-substituents could result from the substitution of a fluorine atom for the trimethylsilyl group in the silanes synthesized. Previously we used the fluoride anion to generate a nucleophilic N-hetaryltetrafluoroethyl anion reacting with electrophiles. To convert the $CF_2CF_2SiMe_3$ group into a C_2F_5 radical, it is expedient to involve a positivated fluorine atom. We have chosen xenon difluoride as an electrophilic fluorinating agent. Even bearing a highly electron-acceptor polyfluorinated group at the nitrogen atom, azoles remain reactive towards halogenating agents, the substitution normally proceeding at the heterocyclic ring. On the contrary, the reaction with benzimidazole leads to N-pentafluoroethyl derivative **13**, though obtained in a low yield and mixed with side-reaction products (Scheme 6).

To conclude, we have obtained a number of novel synthons derived from various azoles which contain the tetrafluoro(trimethylsilyl)ethyl and chlorotrifluoro(trimethylsilyl)ethyl groups at the nitrogen atom. On this basis, synthetic routes have been found to fluorinated heterocyclic carbinols, ketones, carboxylic acids, and methyl dithiocarboxylates as well as to *N*-pentafluoroethyl benzimidazole.

3. Experimental

3.1. General

Boiling and melting points are uncorrected. ^1H NMR-spectra were recorded in $CDCl_3$ on a Varian VXR-300



Scheme 5.

(300 MHz) using TMS as an internal standard. ^{19}F NMR-spectra were recorded in $CDCl_3$ on a Varian VXR-200 (188 MHz) using CCl_3F as an internal standard. IR spectra were recorded on UR-20 spectrophotometer. All reactions were carried out under argon. THF and glyme were freshly distilled from sodium benzophenone ketyl, immediately prior to use. DMF were distilled from BaO after previous fractionalisation.

*3.2. 1-(2-Bromotetrafluoroetyl)-3,5-dimethylpyrazole **1d***

The compound was obtained by the procedure given in Ref. [6].

Yield 82%; bp 72–74 °C (15 Torr); ^{19}F NMR δ −95.95 (s, 2F), −62.82 (s, 2F). ^{1}H NMR δ 2.21 (s, 3H), 2.35 (s, 3H), 5.95 (s, 1H). Anal. Calcd. for $C_7H_7BrF_4N_2$: C, 30.57; H, 2.57; Br, 29.05. Found: C, 30.85; H, 2.77; Br, 28.66.

*3.3. (2-Hetaryltetrafluoroethyl)trimethylsilanes **3a–d**, and (1-chloro-2-hetaryltrifluoroethyl)trimethylsilanes **4a–d**: general procedure*

In a three-neck flask, magnesium (0.36 g, 0.015 mol) was activated with iodine vapour in a stream of argon. After cooling the system to room temperature, Me_3SiCl (4.35 g, 0.04 mol) in freshly distilled THF (10 ml) was added. A solution of compound **1** or **2** (0.01 mol) in THF (10 ml) was slowly added through a dropping funnel with a pressure equalizer and the mixture was stirred with a magnetic stirrer at the temperature not above 35 °C until an exothermic reaction occurred. After that, the stirring was continued for 1 h at 30–35 °C. Excess trimethylchlorosilane and a part of THF (30–40%) were removed by evaporation in vacuo. Hexane and water were added to the residue; the organic layer was separated, washed with water (3 × 50 ml), and dried with $MgSO_4$. Hexane was evaporated on a rotary evaporator and the residue was distilled in vacuo.

(**3a**) Yield 72%; bp 83–85 °C (15 Torr); ^{19}F NMR δ −127.94 (s, 2F), −91.62 (s, 2F). ^{1}H NMR δ 0.27 (s, 9H), 7.13 (m, 2H), 7.79 (s, 1H). Anal. Calcd for $C_8H_{12}F_4N_2Si$: C, 39.99; H, 5.03; Si, 11.69. Found: C, 39.95; H, 4.97; Si, 11.66.

(**3b**) Yield 67%; bp 110–115 °C (0.5 Torr); ^{19}NMR δ −126.79 (s, 2F), −91.20 (s, 2F). ^{1}H NMR δ 0.33 (s, 9H), 7.35 (m, 2H), 7.57 (m, 1H), 7.82 (m, 1H), 8.08 (s, 1H). Anal. Calcd. for $C_{12}H_{14}F_4N_2Si$: C, 49.64; H, 4.86; Si, 9.67. Found: C, 49.61; H, 4.78; Si, 9.65.

(**3c**) Yield 80%; bp 72–74 °C (20 Torr); ^{19}F NMR δ −127.88 (s, 2F), −94.99 (s, 2F). ^{1}H NMR δ 0.25 (s, 9H), 6.43 (dd, 1H, J = 2 Hz), 7.71 (d, 1H, J = 2 Hz), 7.77 (d, 1H, J = 2 Hz). Anal. Calcd. for $C_8H_{12}F_4N_2Si$: C, 39.99; H, 5.03; Si, 11.69. Found: C, 39.80; H, 5.15; Si, 11.70.

(**3d**) Yield 65%; bp 97–98 °C (15 Torr); ^{19}F NMR δ −126.10 (s, 2F), −92.82 (s, 2F). ^{1}H NMR δ 0.25 (s, 9H), 2.21 (s, 3H), 2.35 (s, 3H), 5.92 (s, 1H). Anal. Calcd. for $C_{10}H_{16}F_4N_2Si$: C, 44.76; H, 6.01; Si, 10.47. Found: C, 44.82; H, 5.98; Si, 10.54.

(**4a**) Yield 54%; bp 37–38 °C (0.5 Torr); ^{19}F NMR δ −149.97 (s, 1F), −90.09 (d, 1F, J = 220 Hz), −81.86 (d, 1F, J = 220 Hz). ^{1}H NMR δ 0.31 (s, 9H), 7.11 (d, 1H, J = 2 Hz), 7.17 (d, 1H, J = 2 Hz), 7.78 (s, 1H). Anal. Calcd. for $C_8H_{12}ClF_3N_2Si$: C, 37.43; H, 4.71; Si, 10.94. Found: C, 37.51; H, 4.79; Si, 10.70.

(**4b**) Yield 53%; bp 103–105 °C (0.03 Torr), mp 65–66 °C; ^{19}F NMR δ −148.70 (s, 1F), −88.99 (d, 1F, J = 220 Hz), −81.94 (d, 1F, J = 220 Hz). ^{1}H NMR δ 0.38 (s, 9H), 7.35 (m, 2H), 7.59 (m, 1H), 7.81 (m, 1H), 8.11 (s, 1H). Anal. Calcd. for $C_{12}H_{14}ClF_3N_2Si$: C, 46.98; H, 4.60; Si, 9.15. Found: C, 46.85; H, 4.55; Si, 9.09.

(**4c**) Yield 56%; bp 27–28 °C (0.5 Torr); ^{19}F NMR δ −148.30 (s, 1F), −89.43 (d, 1F, J = 214 Hz), −87.54 (d, 1F, J = 214 Hz). ^{1}H NMR δ 0.28 (s, 9H), 6.41 (s, 1H), 7.69 (d, 1H, J = 1.5 Hz), 7.78 (d, 1H, J = 1.5 Hz). Anal. Calcd. for $C_8H_{12}ClF_3N_2Si$: C, 37.43; H, 4.71; Si, 10.94. Found: C, 37.40; H, 4.56; Si, 11.00.

(**4d**) Yield 70%; bp 42–44 °C (0.5 Torr); ^{19}F NMR δ −146.46 (s, 1F), −92.61 (d, 1F, J = 200 Hz), −81.94 (d, 1F, J = 200 Hz). ^{1}H NMR δ 0.28 (s, 9H), 2.21 (s, 3H), 2.38 (s, 3H), 5.91 (s, 1H). Anal. Calcd. for $C_{10}H_{16}ClF_3N_2Si$: C, 42.23; H, 5.62; Si, 9.84. Found: C, 42.48; H, 5.86; Si, 9.63.

*3.4. Trimethylsilyl ethers of 2-hetaryltetrafluoroethyl(phenyl)carbinols **5a–d** and diastereomeric mixture of trimethylsilyl ethers of 1-chloro-2-hetaryltrifluoroethyl(phenyl)carbinols **8c,d**: general procedure*

In an inert atmosphere, a solution of compound **3** or **4** (0.004 mol) in anhydrous THF (7 ml) was mixed with a solution of benzaldehyde (0.48 g, 0.0045 mol) in anhydrous THF (7 ml). KF or Me_4NF (30–40 mg, 3.2×10^{-5} to 4.3×10^{-5} mol) were added to the stirred mixture. After stirring for 4–5 h at room temperature, the mixture was allowed to stand overnight. Then it was poured into water (30–40 ml) and the product was extracted with pentane or hexane (2 × 25 ml). The organic extracts were washed with water (3 × 50 ml) and dried with $MgSO_4$. After evaporating the solvent, the residue was distilled in vacuo.

(**5a**) Yield 72%; bp 93–95 °C (0.5 Torr); ^{19}F NMR δ −127.76 (dm, 1F, J = 280 Hz), −116.74 (d, 1F, J = 280 Hz), −94.06 (d, 1F, J = 225 Hz), −91.73 (dm, 1F, J = 225 Hz). ^{1}H NMR δ 0.03 (s, 9H), 5.05 (dd, 1H, J = 3 Hz), 7.10 (d, 2H, J = 2 Hz), 7.35 (m, 5H), 7.77 (s, 1H). Anal. Calcd. for $C_{15}H_{18}F_4N_2OSi$: C, 52.01; H, 5.24; Si, 8.11. Found: C, 52.18; H, 5.15; Si, 8.23.

(**5b**) Yield 54%; bp 129–131 °C (0.2 Torr), mp 53–54 °C, ^{19}F NMR δ −125.47 (dm, 1F, J = 280 Hz), −114.59 (d, 1F, J = 280 Hz), −93.65 (d, 1F, J = 225 Hz), −90.70 (dm, 1F, J = 225 Hz). ^{1}H NMR δ 0.03 (s, 9H), 5.15 (dd, 1H, J = 3 Hz), 7.36 (m, 7H), 7.58 (d, 1H, J = 2 Hz), 7.76 (m, 1H), 8.04 (s, 1H). Anal. Calcd. for $C_{19}H_{20}F_4N_2OSi$: C, 57.56; H, 5.09; Si, 7.08. Found: C, 57.61; H, 5.14; Si, 7.15.

(**5c**) Yield 60%; mp 23–25 °C; ^{19}F NMR δ −128.60 (dm, 1F, J = 280 Hz), −117.33 (d, 1F, J = 280 Hz), −94.22 (s, 2F,). ^{1}H NMR δ 0.03 (s, 9H), 5.21 (dd, 1H, J = 2 Hz), 6.44 (s, 1H), 7.38 (m, 5H), 7.75 (d, 1H), 7.79 (d, 1H). Anal. Calcd. for $C_{15}H_{18}F_4N_2OSi$: C, 52.01; H, 5.24; Si, 8.11. Found: C, 52.07; H, 5.32; Si, 8.05.

(**5d**) Yield 73%; bp 98–100 °C (0.5 Torr); ^{19}F NMR δ −125.35 (dm, 1F, J = 250 Hz), −114.94 (d, 1F, J = 250 Hz), −90.05 (d, 1F, J = 225 Hz), −89.14 (dd, 1F, J = 225 Hz). ^{1}H NMR δ 0.01 (s, 9H), 2.25 (s, 3H), 2.35 (s, 3H), 5.51 (dd, 1H, J = 2 Hz), 5.94 (s, 1H), 7.38 (m, 5H). Anal. Calcd. for $C_{17}H_{22}F_4N_2OSi$: C, 54.53; H, 5.92; Si, 7.50. Found: C, 54.41; H, 6.12; Si, 7.41.

(**8c**) Yield 64%; bp 102–104 °C (0.5 Torr); ^{19}F NMR δ −134.31 (m, 1F), −123.94 (m, 1F), −89.47 (dd, 2F, J = 225 Hz), −87.47 (dd, 2F, J = 210 Hz). ^{1}H NMR δ 0.02, 0.04 (s,s, 9H), 5.35, 5.45 (d,d, 1H, J = 2 Hz), 6.50 (m, 1H), 7.41 (m, 5H), 7.82–7.90 (m, 2H). Anal. Calcd. for $C_{15}H_{18}ClF_3N_2OSi$: C, 49.65; H, 5.00; Si, 7.74. Found: C, 49.53; H, 4.95; Si, 7.95.

(**8d**) Yield 25%; bp 110–112 °C (0.1 Torr); ^{19}F NMR δ −132.66 (m, 1F), −124.59 (m, 1F), −86.90 (dd, 1F, J = 225 Hz), −84.75 (dd, 1F, J = 210 Hz) −84.42 (d, 1F, J = 210 Hz), −82.34 (dd, 1F, J = 225 Hz).

^{1}H NMR δ 0.02–0.04 (s,s, 9H), 2.26 (s, 3H), 2.35, 2.38 (s,s, 3H), 5.56, 5.63 (s,s 1H), 5.93, 5.95 (s,s 1H), 7.36–7.91 (m, 5H). Anal. Calcd. for $C_{17}H_{22}ClF_3N_2OSi$: C, 52.23; H, 5.67; Si, 7.18. Found: C, 52.30; H, 5.65; Si, 7.12.

3.5. 2-Hetaryltetrafluoroethyl(phenyl)carbinols ***6a–d****: general procedure*

Compounds **5a–d** (0.0035 mol) and concentrated HCl (5 ml) were mixed in a flask. The stirred mixture was boiled for 0.5 h. After alkalizing the solution to pH 8–9, the product was extracted with methylene chloride (3 × 20 ml), dried with $MgSO_4$, and recrystallized from hexane on cooling with liquid nitrogen.

(**6a**) Yield 70%; mp 91–92 °C; ^{19}F NMR δ −129.12 (dd, 1F, J = 280 Hz), −118.01 (d, 1F, J = 280 Hz), −94.07 (d, 2F,). ^{1}H NMR δ 4.82 (br.s, 1H), 4.94 (dd, 1H, J = 3 Hz), 6.97 (s, 1H), 7.16 (s, 1H), 7.38–7.45 (m, 5H), 7.71 (s, 1H). Anal. Calcd. for $C_{12}H_{10}F_4N_2O$: C, 52.56; H, 3.68; N, 10.22. Found: C, 52.52; H, 3.75; N, 10.31.

(**6b**) Yield 72%; mp 133–134 °C; ^{19}F NMR δ −150.59 (dm, 1F, J = 280 Hz), −139.69 (dm, 1F, J = 280 Hz), −118.75 (dm, 1F, J = 225 Hz), −116.30 (dm, 1F, J = 225 Hz). ^{1}H NMR δ 4.87 (br.s, 1H), 4.95 (dd, 1H, J = 3 Hz), 7.39 (m, 8H), 7.59 (d, 1H, J = 2 Hz), 8.08 (s, 1H). Anal. Calcd. for $C_{16}H_{12}F_4N_2O$: C, 59.26; H, 3.73; N, 8.64. Found: C, 59.33; H, 3.68; N, 8.74.

(**6c**) Yield 90%; mp 80–81 °C; ^{19}F NMR δ −130.44 (dm, 1F, J = 280 Hz), −115.82 (dd, 1F, J = 280 Hz), −98.22 (dd, 1F, J = 225 Hz), −93.16 (dd, 1F, J = 225 Hz). ^{1}H NMR δ 4.84 (br.s, 1H), 5.01 (dd, 1H, J = 3 Hz), 6.53 (s, 1H), 7.41–7.55 (m, 5H), 7.83 (d, 1H, J = 2 Hz), 7.91 (s, 1H, J = 2 Hz). Anal. Calcd. for $C_{12}H_{10}F_4N_2O$: C, 52.56; H, 3.68; N, 10.22. Found: C, 52.72; H, 3.52; N, 10.14.

(**6d**) Yield 70%; mp 55–56 °C; ^{19}F NMR δ −128.40 (dm, 1F, J = 260 Hz), −113.95 (dd, 1F, J = 260 Hz), −94.68 (dd, 1F, J = 210 Hz), −89.56 (dd, 1F, J = 210 Hz). ^{1}H NMR δ 2.27 (s, 3H), 2.41 (s, 3H), 4.91 (dd, 1H J = 3 Hz), 6.03 (s, 1H), 7.41 (m, 5H). Anal. Calcd for $C_{14}H_{14}F_4N_2O$: C, 55.63; H, 4.67; N, 9.27. Found: C, 55.62; H, 4.58; N, 9.30.

3.6. 2-Hetaryltetrafluorethyl(phenyl)ketones ***7a–d****: general procedure*

In an inert atmosphere, a solution of compound **3a–d** (0.004 mol) in anhydrous THF (7 ml) was mixed with a solution of benzoyl fluoride (0.56g, 0.0045 mol) in anhydrous THF (7 ml). Me_4NF (30–40 mg, 3.2×10^{-5} to 4.3×10^{-5} mol) were added to the stirred mixture. After stirring for 4–5 h at room temperature, the mixture was allowed to stand overnight. After evaporating the solvent in vacuo, the residue was distilled in vacuo.

(**7a**) Yield 70%; bp 108–110 °C (0.5 Torr); ^{19}F NMR δ −114.10 (s, 2F), −92.77 (s, 2F). ^{1}H NMR δ 7.20 (s, 1H), 7.62–7.70 (m, 3H), 7.82–7.87 (m, 1H), 8.03–8.05 (m, 2H), 8.30 (s, 1H). IR spectra: 1705 cm^{-1} (C=O). Anal. Calcd. for $C_{12}H_8F_4N_2O$: C, 52.95; H, 2.96; N, 10.29. Found: 53.12; H, 3.08; N, 10.36.

(**7b**) Yield 72%; mp 61–62 °C; ^{19}F NMR δ −114.00 (s, 2F), −95.29 (s, 2F). ^{1}H NMR δ 7.34–7.37 (m, 2H), 7.48–7.53 (m, 2H), 7.61–7.64 (m, 2H), 7.80–7.83 (m, 1H), 8.02–8.05 (m, 2H), 8.18 (s, 1H). IR spectra: 1700 cm^{-1} (C=O) Anal. Calcd. for $C_{16}H_{10}F_4N_2O$: C, 59.63; H, 3.13; N, 8.69. Found: C, 59.52; H, 3.20; N, 8.57.

(**7c**) Yield 69%; bp 90–95 °C (0.5 Torr); ^{19}F NMR δ −114.51 (s, 2F), −92.13 (s, 2F). ^{1}H NMR δ 6.45 (m, 1H), 7.47–7.52 (m, 2H), 7.64 (m, 2H), 7.89 (m, 1H), 8.02 (m, 2H). IR spectra: 1695 cm^{-1} (C=O). Anal. Calcd. for $C_{12}H_8F_4N_2O$: C, 52.95; H, 2.96; N, 10.29. Found: C, 52.88; H, 2.98; N, 10.09.

(**7d**) Yield 70%; mp 62–64 °C, bp 115–117 °C (0.5 Torr); ^{19}F NMR δ −114.00 (s, 2F), −90.19 (s, 2F). ^{1}H NMR δ 1.98 (s, 3H), 2.43 (s, 3H), 5.91 (s, 1H), 7.48–7.62 (m, 3H), 7.99–8.02 (m, 2H). IR spectra: 1710 cm^{-1} (C=O). Anal. Calcd. for $C_{14}H_{12}F_4N_2O$: C, 56.00; H, 4.03; N, 9.33. Found: C, 56.10; H, 3.90; N, 9.60.

3.7. 2-Hetaryltetrafluoroethyl-1-carboxylic acids ***9a–d*** *and 2-hetaryl-1-chlorotrifluoroethyl-1-carboxylic acids* ***10b,c***

A solution of compound **3** or **4** (0.005 mol) in anhydrous glyme (15 ml) was placed into a flask annealed in a stream of argon. Then the system was cooled to −90 to −80 °C and excess CO_2 (2–3 g) was condensed in it after passing through a tube filled with P_2O_5. Then Me_4NF (0.55 g, 0.006 mol) was poured into the stirred mixture and the stirring was continued for 0.5 h at −35 to −40 °C and for 1 h at room temperature. Glyme was evaporated in vacuo; ether (30 ml) and 1% HCl (10 ml) were added to the residue. The mixture was placed into a separating funnel and the aqueous layer was separated. Ether was evaporated at atmospheric pressure adding benzene to remove the dissolved water. The residue was recrystallized from hexane with a small amount of SiO_2 added (to remove a little of unknown polymeric material).

(**9a**) Yield 55%; mp 216–217 °C; ^{19}F NMR δ −118.06 (s, 2F), −94.05 (s, 2F). ^{1}H NMR δ 7.43 (s, 1H), 7.79 (s, 1H), 8.76 (s, 1H), 11.87 (br.s, 1H). Anal. Calcd. for $C_6H_4F_4N_2O_2$: C, 33.98; H, 1.90; N, 13.21. Found: C, 33.85; H, 1.93; N, 13.33.

(**9b**) Yield 66%; mp 150–152 °C; ^{19}F NMR δ −121.66 (s, 2F), −97.50 (s, 2F). ^{1}H NMR δ 7.15 (m, 2H), 7.36–7.38 (m, 1H), 7.55–7.56 (m, 1H), 7.96 (s, 1H), 11.47 (br.s, 1H). Anal. Calcd. for $C_{10}H_6F_4N_2O_2$: C, 45.82; H, 2.31; N, 10.69. Found: C, 45.69; H, 2.55; N, 10.71.

(**9c**) Yield 62%; mp 126–127 °C; ^{19}F NMR δ −120.08 (s, 2F), −95.60 (s, 2F). ^{1}H NMR δ 6.17 (s, 1H), 7.38 (s, 1H), 7.58 (s, 1H), 13.48 (br.s, 1H). Anal. Calcd. for $C_6H_4F_4N_2O_2$: C, 33.98; H, 1.90; N, 13.21. Found: C, 33.99; H, 2.04; N, 13.16.

(**9d**) Yield 59%; mp 110–112 °C; ^{19}F NMR δ −117.69 (s, 2F), −92.85 (s, 2F). ^{1}H NMR δ 2.27 (d, 3H), 2.45 (d, 3H), 6.07 (s, 1H), 13.14 (br.s, 1H). Anal. Calcd. for $C_8H_8F_4N_2O_2$: C, 40.01; H, 3.36; N, 11.67. Found: C, 39.80; H, 3.32; N, 11.82.

(**10b**) Yield 37%; mp 133–135 °C; ^{19}F NMR δ −125.50 (s, 1F), −91.06 (d, 1F, J = 220 Hz), −88.97 (d, 1F, J = 220 Hz). ^{1}H NMR δ 7.23 (s, 1H), 7.38 (m, 1H), 7.81 (m, 2H), 8.96 (s, 1H), 13.20 (br.s, 1H). Anal. Calcd. for $C_{10}H_6ClF_3N_2O_2$: C, 43.11; H, 2.17; Cl, 12.72. Found: C, 43.25; H, 2.15; Cl, 12.75.

(**10c**) Yield 45%; mp 113–114 °C; ^{19}F NMR δ −127.00 (s, 1F), −95.27 (d, 1F, J = 220 Hz), −91.10 (d, 1F, J = 220 Hz). ^{1}H NMR δ 6.55 (s, 1H), 7.88 (d, 1H), 7.94 (d, 1H), 13.17 (br.s, 1H). Anal. Calcd. for $C_6H_4ClF_3N_2O_2$: C, 31.53; H, 1.76; Cl, 15.51. Found: C, 31.72; H, 1.68; Cl, 15.33.

*3.8. 2-(1-Pyrazolyl)tetrafluoroethyl-1-methylditiocarboxylate **11***

In a flask annealed in a stream of argon, compound **3c** (0.96 g, 0.004 mol) and CS_2 (0.6 g, 0.008 mol) were mixed in anhydrous glyme (15 ml). The mixture was cooled to −20 °C and Me_4NF (0.46 g, 0.005 mol) was added in a stream of argon. After stirring at −10 to −15 °C for 5 min, CH_3I (0.5 ml, 1.1 g, 0.008 mol) was added, followed by stirring for another 0.5 h at room temperature and evaporating glyme. The residue was treated with water (20 ml) and the product was extracted with pentane (2 × 20 ml). The pentane solution was washed with water (3 × 20 ml) and dried with $MgSO_4$. Pentane was evaporated and the residue was distilled in vacuo. Yield 35%; bp 96–98 °C (10 Torr); ^{19}F NMR δ −104.87 (s, 2F), −96.32 (s, 2F). ^{1}H NMR δ 2.18 (s, 3H), 6.42 (m, 1H), 7.65 (d, 1H J = 2 Hz), 7.75 (d, 1H, J = 2 Hz). Anal. Calcd. for $C_7H_6F_4N_2S_2$: C, 32.56; H, 2.34; S, 24.83. Found: C, 32.36; H, 2.32; S, 24.58.

*3.9. 1-(1-Pyrazolyl)-2-(4-nitrophenyl)tetrafluoroethane **12***

4-Iodonitrobenzene (0.47 g, 0.0019 mol), CuI (0.48 g, 0.0025 mol), and a solution of compound **3c** (0.48 g, 0.002 mol) in anhydrous DMF (2 ml) were mixed in an annealed flask. After adding KF (0.002 mol) to the mixture, it was stirred for 1 h at 100–120 °C, poured into water, extracted with ether, and dried with $MgSO_4$. The solvent was evaporated and the product was isolated by column chromatography on silica gel (with a 1:1 mixture of methylene chloride and hexane used as an eluent). Yield 25%; mp 84–86 °C; ^{19}F NMR δ −112.91 (s, 2F), −98.56 (s, 2F). ^{1}H NMR δ 6.44 (s, 1H), 7.66–7.89 (m, 4H), 8.27 (d, 1H, J = 2 Hz), 8.30 (d, 1H, J = 2 Hz). Anal. Calcd. for $C_{11}H_7F_4N_3O_2$: C, 45.69; H, 2.44; N, 14.53. Found: C, 45.58; H, 2.52; N, 14.62.

*3.10. 1-Pentafluoroetylbezimidazole **13***

Xenon difluoride (1.86 g, 0.011 mol) was suspended in anhydrous methylene chloride (20 ml) at −30 °C in an inert dry atmosphere and compound **3b** (2.9 g, 0.01 mol) was slowly added to it. Gradual heating of the reaction mixture up to −5 °C resulted in an exothermic reaction with the release of xenon. The stirred mixture was cooled so that the temperature was not above 20 °C. The reaction flask was equipped with a reflux condenser and methylene chloride was evaporated in vacuo. The residue was fractioned and the most volatile product was collected. Yield 15%; bp 78–80 °C (20 Torr); ^{19}F NMR δ −98.98 (s, 2F), −85.22 (s, 3F). ^{1}H NMR δ 7.35 (m, 2H), 7.56 (m, 1H), 7.79 (m, 1H), 8.10 (s, 1H). Anal. Calcd. for $C_9H_5F_5N_2$: C, 45.78; H, 2.13; N, 11.86. Found: C, 45.71; H, 2.24; N, 11.78.

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