The solid complex $Zn(CF_3)Br \cdot 2DMF$ as an alternative reagent for the preparation of both, trifluoromethyl and pentafluoroethyl copper, $CuCF_3$ and CuC_2F_5

Mikhail M. Kremlev [a,*], Wieland Tyrra [b,**], Aleksej I. Mushta [a], Dieter Naumann [b], Yurii L. Yagupolskii [a]

[a] Institute of Organic Chemistry, National Academy of Sciences of the Ukraine, Murmanskaya St. 5, UA-02094 Kiev, Ukraine
[b] Institut für Anorganische Chemie, Universität zu Köln, Greinstr. 6, D-50939 Köln, Germany

A B S T R A C T

Trifluoromethylcopper and pentafluoroethylcopper are prepared conveniently via the reaction of the solid complex $Zn(CF_3)Br \cdot 2DMF$ with copper(I) bromide in N,N-dimethylformamide. The reactions of both copper species with 2,4-dinitrochlorobenzene, 4-iodonitrobenzene, 4-nitrobenzyl iodide, 4-bromobenzoic acid ethyl ester, 4-iodobenzoic acid ethyl ester, 2-iodopyridine and 2-iodopyrimidine have been studied. The structure of 2,4-dinitrotrifluoromethylbenzene has been elucidated.

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1. Introduction

The study and development of methods for the introduction of fluorinated moieties into organic molecules to change their properties by design is one of the challenges in synthetic chemistry. Fluorine-containing physiologically active substances and the methodologies making them easily accessible are of great interest with special respect to the introduction of perfluoroalkyl groups [1].

From the view point of trifluoromethylation of organic halides, it is a real task to invent how to generate efficiently and conveniently trifluoromethylcopper species. For example, Kobayashi et al. directly prepared it by the reaction of trifluoroiodomethane with activated copper in DMF [2] or HMPA [3]. Kondratenko et al. [4] generated trifluoromethylcopper using $Hg(CF_3)_2$ as a trifluoromethyl source by transmetallation to copper. Trifluoromethylcopper has also been prepared via in situ metathesis of trifluoromethylcadmium or -zinc reagents with copper(I) salts [5]. Trifluoromethylcadmium or -zinc species were synthesized by the reactions of difluorodihalomethanes with activated cadmium or zinc powder [6]. These authors noted that addition of HMPA (hexamethyl phosphoric acid triamide) is necessary to

stabilize this trifluoromethylcopper reagent; warming to room temperature shows no change with only a single ^{19}F NMR signal at -28 ppm. Subsequently, signals for CuC_2F_5 (-84.7 (CF_3); -113.7 ppm (CF_2)) became visible upon prolonged stirring at ambient temperature. The amount of CuC_2F_5 formed was quantitatively based on the assumption that 2 equiv. of $CuCF_3$ produce 1 equiv. of CuC_2F_5 [5].

Some publications [7–11] show that the formation of $CuCF_3$ can be achieved using the commercially available compound Me_3SiCF_3 either starting from copper alkoxides [8,9] or the system of heavier copper halides and an alkali fluoride [7,10,11].

Most methods employed use expensive or toxic reagents [CF_3I, Me_3SiCF_3, $Hg(CF_3)_2$] or required autoclaves.

Earlier the method of preparation of the complex $Zn(CF_3)Br \cdot 2L$ (L = DMF or CH_3CN) from bromotrifluoromethane and zinc dust in DMF or acetonitrile was developed [12]. In solution, this complex undergoes Schlenk-type equilibria between $Zn(CF_3)Br$, $Zn(CF_3)_2$ and $ZnBr_2$; the ratio of $Zn(CF_3)Br$ and $Zn(CF_3)_2$ is strongly solvent-dependent (^{19}F NMR). It was mentioned in one Ph.D. Thesis [13] that treatment of the complex $Zn(CF_3)Br \cdot 2DMF$ with copper(I) iodide led to the formation of $CuCF_3$ but no reactions of $CuCF_3$ prepared in such a manner were reported.

The main advantage of the complex $Zn(CF_3)Br \cdot 2L$ compared with that prepared in situ is that it can be stored in an inert atmosphere for a long period (about 6–12 months) in an ordinary refrigerator without noteworthy decomposition. Therefore, it is not necessary to prepare this compound freshly every time when it is needed. In contrast to the acetonitrile adduct [14],

* Corresponding author.
** Corresponding author. Tel.: +49 221 4703276; fax: +49 221 4703276.
E-mail addresses: kremlyov1@yandex.ru (M.M. Kremlev), tyrra@uni-koeln.de (W. Tyrra).

Zn(CF$_3$)Br·2DMF exhibits significantly lower reactivity and only the reactions with iodine chloride [12] and some inorganic compounds [14] are documented.

2. Results and discussion

2.1. Formation of CuCF$_3$ and CuC$_2$F$_5$

The addition of copper(I) bromide to a solution of Zn(CF$_3$)Br·2DMF in molar ratio of 1:1 in DMF led to the formation of exclusively one trifluoromethylcopper species within 3 h at ambient temperature.

$$Zn(CF_3)Br \cdot 2DMF + CuBr \xrightarrow[DMF]{3\,h,\,rt} CuCF_3 + ZnBr_2 + 2DMF$$
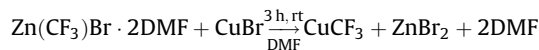
stirring for 4 h at +50 °C (alternatively 12 h at ambient temperature), CuC$_2$F$_5$ was the only species detected in the ^{19}F NMR spectrum.

$$2Zn(CF_3) \cdot 2DMF + 4CuBr \xrightarrow[DMF]{4\,h,\,50\,°C} CuC_2F_5 + 2ZnBr_2 + 4DMF$$
$$+ CuF_2(?) + \ldots$$
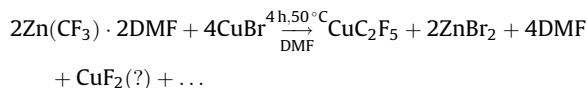
### 2.2. Reactions of CuCF$_3$ and CuC$_2$F$_5$ with aryl halides

Trifluoromethylcopper reacts with activated aryl chlorides and iodides to give the corresponding trifluoromethylated compounds **1–4** in good yields.
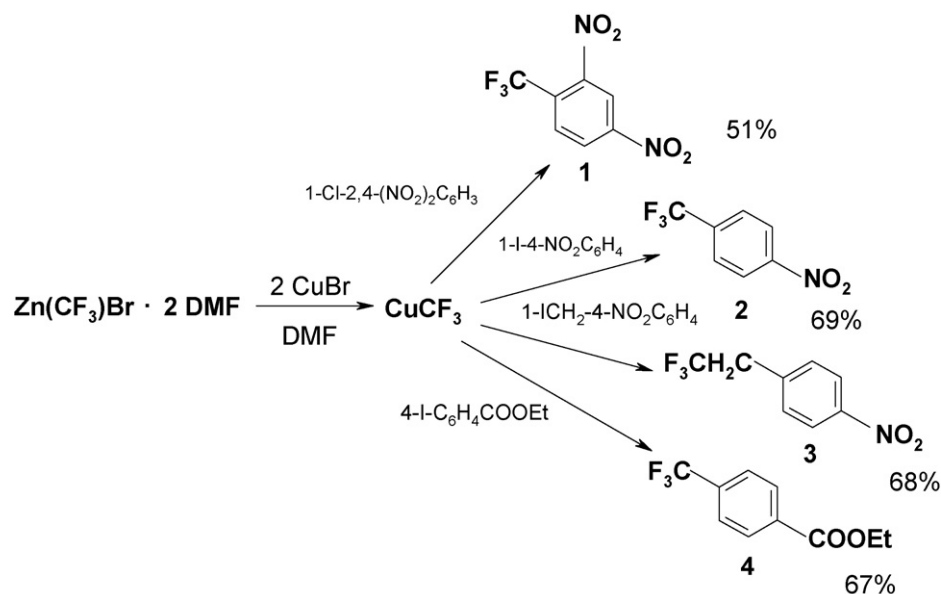
The signal of the CF$_3$-group occurs in the ^{19}F NMR spectrum at −32 ppm. Within the next 5 h, this "CuCF$_3$" derivative is completely converted into Cu[Cu^{III}(CF$_3$)$_4$] [15].
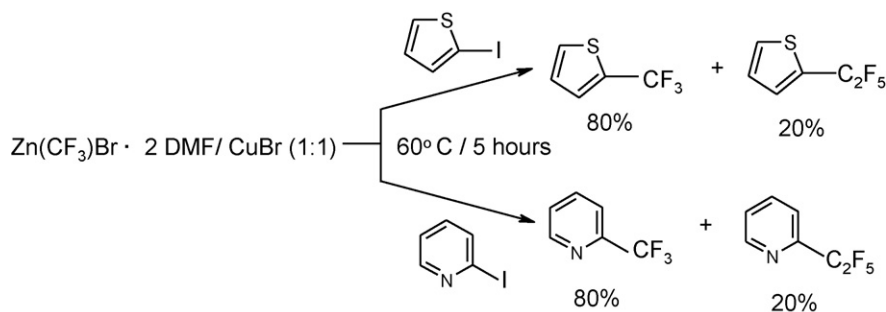
Addition of copper(I) bromide to a solution of Zn(CF$_3$)Br·2DMF in a molar ratio of 2:1 in DMF at ambient temperature after 20 min allowed the detection of both CuCF$_3$ (−32.0 ppm) and Cu[Cu(CF$_3$)$_2$] (−28.4 ppm) together with a small quantity of Cu[Cu^{III}(CF$_3$)$_4$] (−35.1 ppm) in the ^{19}F NMR spectrum. In accordance with the observations described [5], signals for CuC$_2$F$_5$ at −85.0 ppm (CF$_3$) and −113.9 ppm (CF$_2$) were detected which intensified upon prolonging the reaction time and rising the temperature to +50 °C. After

The reaction of trifluoromethylcopper with inactivated aryl halides is accompanied by the competitive conversion of trifluoromethylcopper into pentafluoroethylcopper. As the result a mixture of trifluoromethyl- and pentafluoroethyl compounds is obtained. For example, the reaction of trifluoromethylcopper prepared by this method with 2-iodothiophene led to a mixture of 60% 2-trifluoromethylthiophene and 40% 2-pentafluoroethylthiophene. Treatment of trifluoromethylcopper with 2-iodopyridine at 80 °C for 6 h gave a mixture of 2-trifluoromethylpyridine and 2-pentafluoroethylpyridine in a 93% and 7% ratio. The maintenance of trifluoromethyl- and pentafluoroethyl derivatives were determined by ^{19}F NMR spectroscopy in both the mixtures.
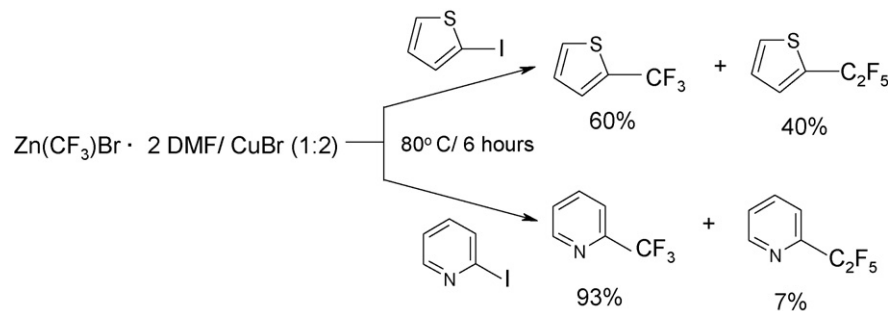
If a 1:1 molar ratio of Zn(CF$_3$)Br·2DMF and CuBr is chosen, the reactions with 2-iodothiophene or 2-iodopyridine at 60 °C for 5 h gave mixtures of the trifluoromethyl and pentafluoroethyl derivatives in 80:20 ratios in both cases determined by ^{19}F NMR spectroscopy.

Again, a selective conversion of trifluoromethylcopper into pentafluoroethylcopper is achieved by stirring of a 1:2 (CF$_3$ZnBr·2DMF/CuBr) reaction mixture either at ambient temperature for 12 h or at 50 °C for 4 h. The reagent prepared in such a manner may be used for the selective transfer of pentafluoroethyl groups to aryl halides.

The reaction of 4-iodonitrobenzene, 4-bromobenzoic acid ethyl ester, 2-iodopyridine and 2-iodopyrimidine with penta-fluoroethylcopper gave the corresponding pentafluoroethyl derivatives 5–8. It has to be mentioned, that CuCF$_3$ did not give a considerable amount of CF$_3$ and C$_2$F$_5$ derivatives (about 2–4%, 19F NMR reaction control) in reactions with aromatics containing electron releasing groups such as methyl or methoxy. The question why no significant amounts of CuC$_3$F$_7$ are formed will be subject of future investigations.
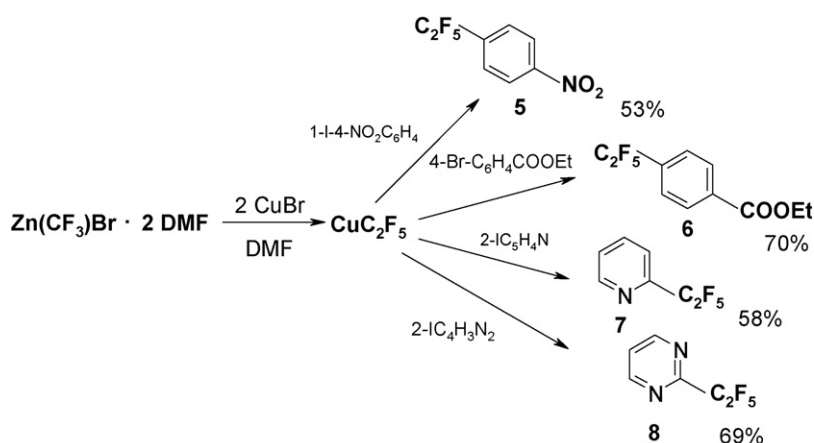
The perfluoroalkyl group transfer might be formulated as an addition–elimination mechanism involving copper(III) species as intermediates taking into account that CuR$_f$ [15,16] as well as CuR [17] derivatives are easily oxidized even at low temperature. However, alternative routes are also conceivable.

Alkaline hydrolysis of the esters 4, 6 followed by acidification allowed the synthesis of the corresponding benzoic acids 9, 10.

R$_f$ = CF$_3$ (4), C$_2$F$_5$ (6)   R$_f$ = CF$_3$ (9), C$_2$F$_5$ (10)
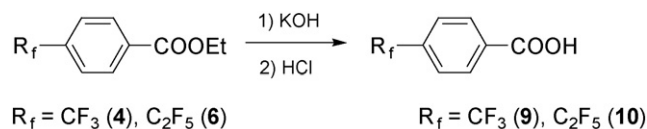
2.3. Solid-state structure of 2,4-dinitrotrifluoromethylbenzene (1)

Compound 1 crystallizes in the monoclinic space group *P*2$_1$/*c* (no. 14) with 4 molecules per unit cell. Its bond length and angles do not exhibit any peculiarities in comparison with the related structure of 2,4-dinitrochlorobenzene [18]. The molecule is quasi-

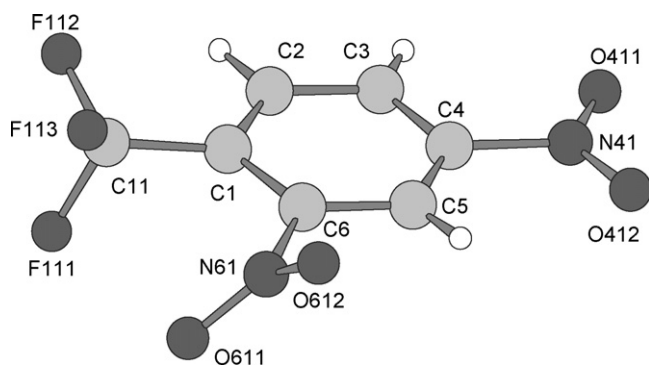**Fig. 1.** Molecular structure of 1. Selected bond lengths [Å] and angles [°] (with estimated standard deviations in parentheses): C1-C11 1.513(6); C11-F111 1.320(5); C11-F112 1.32(1); C11-F113 1.336(5); C4-N41 1.490(6); N41-O411 1.217(9); N41-O412 1.22(1); C6-N61 1.47(1); N61-O611 1.223(5); N61-O612 1.215(4); O411-N41-O412 125.4(3); O611-N61-O612 125.3(2); C5-C6-N61-O612 45.0(3); C1-C6-N61-O611 46.7(3).

planar with one NO_2 group (4-position) lying in the plane, while the other is twisted by approximately 45° out of the plane (Fig. 1). Selected bond lengths and angles are listed in the caption of Fig. 1.

3. Experimental

Schlenk techniques were used throughout all manipulations. Purifications were carried out in ambient atmosphere. NMR spectra of compounds isolated were recorded on a Bruker Avance II 300 (^{1}H, 300.1 MHz; ^{19}F, 282.4 MHz; ^{13}C, 75.4 MHz) spectrometer in CDCl$_3$ solutions unless quoted. External standards were used in all cases (^{1}H, [13]C: Me$_4$Si; [19]F: CCl$_3$F). Chemical shifts (δ) are given in ppm; couplings (J) in Hz. Assignment of NMR signals was carried out using 1D (^{1}H, ^{19}F, [13]C{^{1}H}, ^{13}C{^{19}F})and 2D (COSY, HSQC, HMBC) NMR techniques. Visible melting points were determined using a Stuart melting point apparatus SMP10. The solid complex Zn(CF$_3$)Br·2DMF was prepared from bromotrifluoromethane and zinc powder in DMF [12]. Copper(I) bromide was freshly prepared from copper sulphate, potassium bromide and sulphur dioxide or Na$_2$SO$_3$ in distilled water prior to use following Ref. [19].

3.1.1. Preparation of copper(I) bromide

A mixture of 101.2 g (0.45 mol) of CuBr$_2$ and 500 ml of water was stirred for 20 min at ambient temperature; then 28.9 g (0.45 mol) of copper powder was added. The reaction mixture was stirred for 1 h at ambient temperature, afterwards for 2 h at 50–60 °C before a solution of 1 g of Na$_2$SO$_3$ in 15 ml of water was added. The reaction mixture was stirred at 50–60 °C for another hour. The reaction mixture was cooled to ambient temperature; the precipitate was filtered off, washed with water, methanol, diethyl ether and dried under reduced pressure at 60 °C for 2 h. The yield was 121.0 g (93%) of colourless to very pale blue CuBr.

All compounds are characterized by melting or boiling points, elemental analyses and NMR spectroscopic data. For known compounds, only melting or boiling points as well as ^{1}H and ^{19}F NMR data are listed, while values of elemental analyses are omitted.

3.1.2. Crystal structure determination

Compound **1** forms single crystals which were sealed in glass capillaries and the suitability was checked with the help of an IP-diffractometer (STOE IPDS I). The same device was used to collect the reflection data of the respective best specimen using graphite-monochromated Mo-K$_\alpha$ radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. The programs used in this work are Stoe's X-Area [20], including X-RED [21] and X-Shape [22] for data reduction and numerical absorption correction, and SIR-92 [23] and SHELXL-97 [24] for structure solution and refinement. All hydrogen atoms were placed in idealized positions and constrained to ride on their parent atom.

3.2. Reactions of trifluoromethylcopper with organic substrates

To a well stirred mixture of Zn(CF$_3$)Br·2DMF (3.6 g, 10 mmol) in 20 ml DMF freshly prepared copper(I) bromide (2.88 g, 20 mmol) was added at room temperature. After stirring for 3 h, the formation of CuCF$_3$ was complete. The corresponding halogen containing derivative (10 mmol) was added and the reaction mixture was stirred for 8 h at 85–90 °C. The reaction was terminated after signals of CuCF$_3$ were no longer detected in the ^{19}F NMR spectra. The mixture was poured into 15% aqueous ammonia (100 ml) and the organic layer was extracted with diethyl ether. The ether extract was washed with water, dried over MgSO$_4$ and the solvent was evaporated on a water bath. The remainder was distilled under reduced pressure or crystallized.

3.2.1. 2,4-Dinitrotrifluoromethylbenzene (1)

Yellow crystals. Yield 1.20 g (51%), m.p. 47–48 °C (pentane), lit. m.p. 48 °C [4]. ^{19}F NMR: δ −60.7 (s, CF$_3$); ^{1}H NMR: δ 7.80 (m, 1H, phenyl), 8.40 (m, 1H, phenyl), 8.70 (m, 1H, phenyl) [25].

X-ray crystal structure analysis of **1**: C$_7$H$_3$F$_3$N$_2$O$_4$ (FW = 236.11), monoclinic, $P2_1/c$ (no. 14), a = 7.327(1) Å, b = 10.060(2) Å, c = 13.799(2) Å, β = 117.12(1) Å, V = 905.3(3) Å^3, Z = 4, $D_{calc.}$ = 1.732 g cm^{-3}, T = 293(2) K. The final R factor was 0.0348 (Rw = 0.0925 for all data) for 2013 reflections with $I > 2\sigma(I)$. Crystallographic data for the structure have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-736284. 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).

3.2.2. 1-Nitro-4-trifluoromethylbenzene (2)

Colourless crystals. Yield 1.32 g (69%), m.p. 39–40 °C (pentane), lit. m.p. 40–41 °C [4]. ^{19}F NMR: δ −63.6 (s, CF$_3$); ^{1}H NMR: δ 7.83 ("d", 2H, H-3,5, J_{HH} = 8.4 Hz), 8.35 ("d", 2H, H-2,6, J_{HH} = 8.4 Hz) [26].

3.2.3. 1-Nitro-4-(2,2,2-trifluoroethyl)benzene (3)

Colourless crystals. Yield 1.40 g (68%), m.p. 63–65 °C (pentane), lit. m.p. 65 °C [4]. ^{19}F NMR: δ −65.3 (t, CF$_3$, J_{FH} = 10.7 Hz); ^{1}H NMR: δ 3.50 (q, 2H, CH$_2$, J_{HF} = 10.7 Hz), 7.50 ("d", 2H, H-3,5, J_{HH} = 8.7 Hz), 8.20 ("d", 2H, H-2,6, J_{HH} = 8.7 Hz) [27].

3.2.4. 4-Trifluoromethylbenzoic acid ethyl ester (4)

Colourless liquid. Yield 1.46 g (67%), b.p. 90–92 °C (10 mm Hg). lit. b.p. 78–80 °C (5.0 Torr) [28]. ^{19}F NMR: δ −63.62 (s, CF$_3$); ^{1}H NMR: δ 1.40 (t, 3H, CH$_3$, J_{HH} = 7.2 Hz), 4.38 (q, 2H, CH$_2$, J_{HH} = 7.2 Hz), 7.58 ("d", 2H, H-3,5, J_{HH} = 9.0 Hz), 7.90 ("d", 2H, H-2,6, J_{HH} = 9.0 Hz) [26].

3.3. Preparation of pentafluoroethylcopper and its reaction with organic substrates

To a well stirred mixture of Zn(CF$_3$)Br·2DMF (3.60 g, 10 mmol) in 20 ml DMF freshly prepared copper(I) bromide (2.88 g, 20 mmol) was added at room temperature. After stirring for 30 min, the formation of CuCF$_3$ was complete and the reaction mixture was heated under stirring at 50 °C for 4 h, until the formation of CuC$_2$F$_5$ was complete. The corresponding halogen containing derivative (5 mmol) was added and the reaction mixture was stirred for 8 h at 85–90 °C. The reaction was terminated after signals of CuC$_2$F$_5$ were no longer detected in the ^{19}F NMR spectra. The mixture was poured into 15% aqueous ammonia (100 ml) and the organic layer was extracted with diethyl ether. The ether extract was washed with water, dried over MgSO$_4$ and the solvent was evaporated. The remainder was distilled under reduced pressure or crystallized.

3.3.1. 1-Nitro-4-pentafluoroethylbenzene (5)

Yellow liquid. Yield 0.63 g (53%), b.p. 43 °C (9.4 × 10^{-2} mbar), lit. b.p. 50 °C (0.4 mm Hg) [29]. ^{19}F NMR: δ −85.0 (s, 3F, CF$_3$), −115.9 (s, 2F, CF$_2$); ^{1}H NMR: δ 7.83 ("d", 2H, H-3,5, J_{HH} = 9.0 Hz), 8.39 ("d", 2H, H-2,6, J_{HH} = 9.0 Hz) [30].

3.3.2. 4-Pentafluoroethylbenzoic acid ethyl ester (6)

Colourless liquid. Yield 0.94 g (70%), b.p. 105–107 °C (10 mm Hg) [7]. ^{19}F NMR: δ −85.2 (s, 3F, CF$_3$), −115.9 (s, 2F, CF$_2$); ^{1}H NMR: δ 1.40 (t, 3H, CH$_3$, J_{HH} = 7.2 Hz), 4.38 (q, 2H, CH$_2$,

J_{HH} = 7.2 Hz), 7.55 ("d", 2H, H-3,5, J_{HH} = 9.0 Hz), 7.88 ("d", 2H, H-2,6, J_{HH} = 9.0 Hz).

3.3.3. 2-Pentafluoroethylpyridine (7)

Colourless liquid. Yield 1.14 g (58%), b.p. 149–151 °C, lit. b.p. 152 °C [31]. ^{19}F NMR: δ −83.4 (t, CF$_3$, $^1J_{F,C}$ = 286 Hz, $^2J_{F,C}$ = 38 Hz, $^3J_{F,F}$ = 1.8 Hz), −117.5 (q, CF$_2$, $^1J_{F,C}$ = 255 Hz, $^2J_{F,C}$ = 37 Hz). ^{1}H NMR: δ 7.67 ("d", 1H, H-3); 7.85("t", 1H, H-4); 7.46 ("dd", 1H, H-5); 8.71 ("d", 1H, H-6). ^{13}C NMR: δ 119.0 (CF$_3$); 111.2 (CF$_2$); 147.8 (C-2, $^2J_{F,C}$ = 25 Hz); 121.9 (C-3, $^3J_{F,C}$ = 4 Hz); 137.2 (C-4); 126.3 (C-5); 149.9 (C-6).

3.3.4. 2-Pentafluoroethylpyrimidine(8)

Colourless liquid. Yield 1.20 g (69%), b.p. 44–46 °C (9.6 × 10^{-2} mbar). ^{19}F NMR: δ −82.6 (t, CF$_3$, $^1J_{F,C}$ = 287 Hz, $^2J_{F,C}$ = 37 Hz, $^3J_{F,F}$ = 1.8 Hz); −117.7 (q, CF$_2$, $^1J_{F,C}$ = 256 Hz, $^2J_{F,C}$ = 35 Hz, $^3J_{F,F}$ = 1.8 Hz); Lit. ^{19}F NMR: δ −80.4 (CF$_3$), −115.0 (CF$_2$) [25]; ^{1}H NMR, δ(ppm): 8.92 (d, 2H, H-4,6); 7.53(t,1H, H-5, $^3J_{H,H}$ 5 Hz). ^{13}C NMR: δ 118.8 (CF$_3$); 109.5 (CF$_2$); 157.0 (C-2); 123.1 (C-5); 157.9 (C-4,6). The compound contained 1% of the 2-trifluoromethyl- and 3% of the n-heptafluoropropyl-derivatives.

3.4. Hydrolysis of 4-perfluoroalkylbenzoic acid ethyl esters (4, 6)

A well stirred mixture of corresponding ester (4, 6) (1 mmol) and 45% aqueous KOH (3 ml) was heated at 115 °C for 1 h. The reaction mixture was poured into 30 ml of water and was acidified with hydrochloric acid to pH 4–5. The precipitate was filtered, washed with water, dried and crystallized.

3.4.1. 4-Trifluoromethylbenzoic acid (9)

Colourless crystals. Yield 0.17 g (90%), m.p. 219–221 °C (benzene), lit. m.p. 220–221 °C [32]. ^{19}F NMR: δ −61.3 (s, CF$_3$); ^{1}H NMR: δ 7.70 (d, 2H, H-3,5, J_{HH} = 8.4 Hz), 7.88 (d, 2H, H-2,6, J_{HH} = 8.4 Hz) [33].

3.4.2. 4-Pentafluoroethylbenzoic acid (10)

Colourless crystals. Yield 0.22 g (92%), m.p. 154–156 °C (benzene), lit. m.p. 155–156.5 °C [34]. ^{19}F NMR (DMSO-d$_6$): δ −84.0 (s, 3F, CF$_3$, $^1J_{F,C}$ = 287 Hz, $^2J_{F,C}$ = 39 Hz), −114.1 (s, 2F, CF$_2$, $^1J_{F,C}$ = 254 Hz, $^2J_{F,C}$ = 37 Hz); ^{1}H NMR (DMSO-d$_6$): δ 7.84 ("d", 2H, H-2,6, J_{HH} = 8.4 Hz), 8.16 ("d", 2H, H-3,5, J_{HH} = 8.4 Hz); ^{13}C NMR (DMSO-d$_6$): δ 119.0 (q, CF$_3$, $^1J_{F,C}$ = 287, $^2J_{F,C}$ = 39 Hz), 113.0 (q, CF$_2$, $^1J_{F,C}$ = 254, $^2J_{F,C}$ = 37 Hz), 135.3 (s, C-1), 130.5 (s, C-2,6), 127.2 (s,C-3,5, $^3J_{F,C}$ = 6 Hz), 131.2 (t, C-4, $^2J_{F,C}$ = 23 Hz), 166.6 (s, COOH).

Acknowledgements

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