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O-Fluoromethyl Carboxylates and *O*-Fluoromethyl Carbamates

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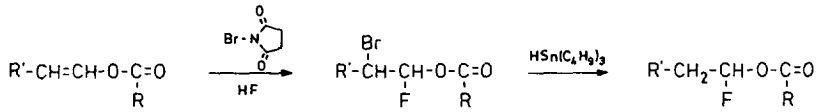
Abstract : The fluoride catalyzed reaction between acyl fluorides and monomeric formaldehyde affords fluoromethyl carboxylates in acceptable yields. - Fluoromethyl fluoroformate, readily accessible from the corresponding dichloro compound, condenses with amines to give fluoromethyl carbamates.

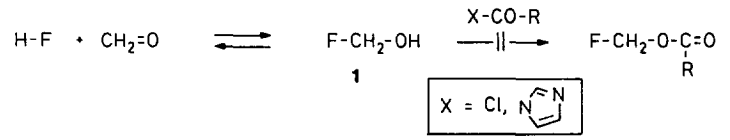
Recently we have described a convenient route leading to 1-fluoroalkyl carboxylates [1]. The protocol consists of two stages : simultaneous treatment of an 1-alkenyl carboxylate ("enester") [2] with *N*-bromosuccinimide and triethylamine-tris(hydrogenfluoride) and radical type debromination of the resulting 2-bromo-1-fluoroalkyl carboxylate using tributyltin hydride.



For obvious reasons, this method is not suited for the preparation of fluoromethyl carboxylates. On the other hand, this class of compounds deserves particular attention as it may provide potential inhibitors [3] of esterases and lipases. Fluoromethyl carboxylates are so far only accessible, with poor yields, through a complicated procedure, the key step of which consists of a silver fluoride [4] or silver tetrafluoroborate [5] promoted halogen exchange in chloromethyl carboxylates [6].

We wondered whether it would not be possible to accomplish an ester formation between fluoromethanol and either carboxylic acids or acyl halides under acidic conditions. According to a literature claim [7], fluoromethanol can be prepared by the reduction of ethyl fluoroacetate with lithium aluminum hydride. However, despite many attempts to repeat this procedure we were unable to isolate anything else but paraformaldehyde and hydrogen fluoride containing ethanol. As a rough thermochemical evaluation [8] reveals, the reaction between formaldehyde and hydrogen fluoride to give fluoromethanol should be only slightly exothermal ($\Delta H°$ hardly exceeding 5 kcal/mol). Thus, the positive entropy term will inevitably overcompensate the enthalpy gain at ordinary or slightly elevated temperatures. Actually, fluoromethanol was reported to decompose rapidly at room temperature, mainly to afford di(fluoromethyl) ether [9], but to be formed when gaseous formaldehyde is condensed into a solution of hydrogen fluoride cooled to -75 °C [10]. We have improved the latter method by employing a solution [11] of formaldehyde in tetrahydrofuran and generating the anhydrous

hydrogen fluoride *in situ* from *N*-(2-chloro-1,1,2-trifluoroethyl)diethylamine ("Yarovenko-Raksha reagent") [12] and *tert*-butyl alcohol. However, all our efforts to accomplish an *O*-acylation of fluoromethanol (**1**), either using acyl chlorides in the presence of boron trifluoride or acyl imidazolides [13], remained unsuccessful.



Thus, the esterification had to be carried out under basic conditions. Unlike trifluoromethanolate [14], pentafluoroethanolate [15] and other polyfluorinated alcoholates [16] which can be spectroscopically detected, fluoromethanolate should exothermally [17] decompose to give formaldehyde and fluoride ion. On the other hand, there was a chance to intercept the alcoholate, if it existed in stationary, though minute concentrations in equilibrium with its components. When potassium fluoride and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6") were added to a solution of formaldehyde and an acyl fluoride **2** in tetrahydrofuran, the corresponding fluoromethyl carboxylates **3** was produced indeed (see Table 1).

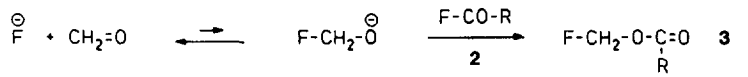
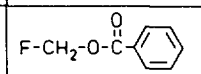
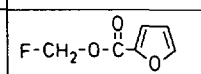
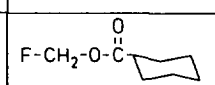
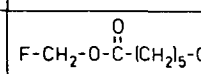
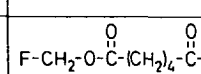
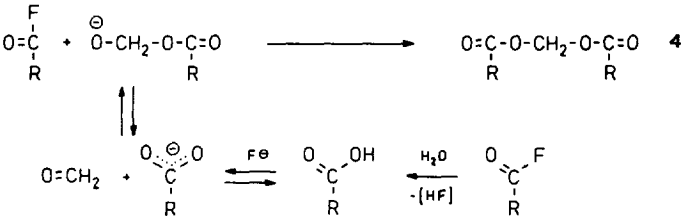


Table 1. Fluoromethyl carboxylates **3** prepared from acyl fluorides **2** and formaldehyde (using potassium fluoride as the catalyst).

cpd.nr.	product	yield
3a		42%
3b		52%
3c		50%
3d		49%
3e		51%

Virtually quantitative yields of *O*-fluoromethyl carboxylates **3a** and **3b** (98% and 97% isolated) were obtained when potassium fluoride was replaced by a catalytic amount of tris(diethylamino)sulfonium difluorotrimethylsilicate [18] ("TASF"). On the other hand, the same source of fluoride ions was found to cause extensive autocondensation of *enolisable* acyl fluorides and consequently only trace amounts of the *O*-fluoromethyl esters **3c**, **3d** and **3e** were produced.

As Table 1 reveals, the use of potassium fluoride consistently leads to moderate yields, the latter falling in the range of 50%. This is mainly due to a side reaction affording methylene dicarboxylates (formaldehyde acylals) **4** as by-products in varying amounts (20 - 40% yield with respect to the acylating agent). Obviously we had been unable to completely remove the water contained in the commercial grade potassium fluoride, a very hygroscopic material. Hydrolysis partially converts the acyl fluorides to the corresponding carboxylic acids which then combins with formaldehyde and unconsumed acyl fluoride to give the acylals **4**.



An independent entry into the series of *O*-(fluoromethyl) esters was attempted by treating fluoromethyl fluoroformate **5** with organomagnesium, organolithium or organocopper reagents. In all cases complex product mixtures resulted which contained only little if any of the desired fluoromethyl carboxylates **3**. In contrast, smooth reaction occurred with a variety of amines leading to *O*-(fluoromethyl) carbamates **6** (see Table 2).

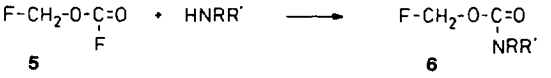
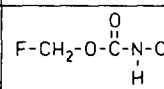
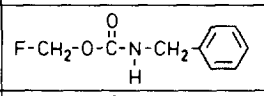
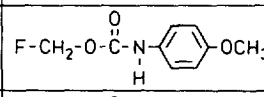
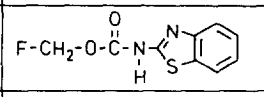
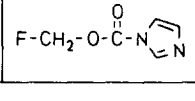


Table 2. *O*-(Fluoromethyl) carbamates **6** from fluoromethyl fluoroformate (**5**) and amines.

cpd.nr.	product	yield
6a		64%
6b		73%
6c		48%
6d		32%
6e		35%

Fluoromethyl fluoroformate (**5**) has previously been identified as one of the products formed upon oxidation of carbonyl difluoride with dimethylsulfoxide [19]. The compound can be prepared far more conveniently and with high yield by treatment of the commercially available chloromethyl chloroformate with potassium fluoride in the presence of the macrocyclic polyether 1,4,7,10,13,16-hexaoxacyclooctadecane.

EXPERIMENTAL PART

1. Generalities

For standard laboratory practice, techniques and abbreviations see related articles, *e.g.* ref. [20]. - ^{1}H- and ^{19}F-nmr spectra were recorded of $CDCl_3$ solutions at 250 and, respectively, 188 MHz unless otherwise stated.

2. Acyl Fluorides

Benzoyl fluoride was purchased from Aldrich Co. Furoyl fluoride [21], cyclohexanecarbonyl fluoride [22], heptanoyl fluoride [23] and adipoyl fluoride [24] were prepared according to literature procedures.

3. Fluoromethyl Carboxylates

General procedure : A stream of gaseous formaldehyde [11] (from 3.75 g, 125 mmol paraformaldehyde) and nitrogen was bubbled during 4 h into a vigorously stirred suspension of potassium fluoride (5.81 g, 100 mmol) in anhydrous tetrahydrofuran (50 mL) containing the acyl fluoride **6** (50 mmol) and 1,4,7,10,13,16-hexaoxacyclooctadecane ("18-crown-6", 2.0 g, 7.5 mmol). After centrifugation, the supernatant solution was decanted and evaporated; the residue was distilled.

Fluoromethyl benzoate (3a) : From benzoyl fluoride; 42%; mp 10 - 12 °C; bp 82 - 83 °C/10 mmHg; n_D^{20} 1.5001. - ^{1}H-NMR (360 MHz): δ 8.1 (2 H, m), 7.7 (1 H, m), 7.5 (2 H, m), 5.98 (2 H, d, *J* 50.5). - ^{19}F-NMR : δ -94.0 (t, *J* 50). - Analysis : calc. for $C_8H_7FO_2$ (154.14) C 62.34, H 4.58; found C 62.61, H 4.61%.

Fluoromethyl 2-furoate (3b) : From 2-furoyl fluoride; 52%; mp 33 - 36 °C; bp 75 - 76 °C/10 mmHg. - ^{1}H-NMR (360 MHz): δ 7.71 (1 H, dd, *J* 1.9, 1.0), 7.35 (1 H, dd, *J* 3.5, 1.0), 6.59 (1 H, dd, *J* 3.5, 1.9), 5.93 (2 H, d, *J* 51.0). - ^{19}F-NMR : δ -94.5 (t, *J* 51). - Analysis : calc. for $C_6H_5FO_3$ (144.10) C 50.01, H 3.50; found C 49.99, H 3.59%.

Fluoromethyl cyclohexanecarboxylate (3c) : From cyclohexanecarbonyl fluoride; 50%; bp 67 - 68 °C/ 10 mmHg; n_D^{20} 1.4313. - ^{1}H-NMR (360 MHz): δ 5.71 (2 H, d, *J* 51.3), 2.40 (1 H, tt, *J* 11.0, 3.5), 2.0 (2 H, m), 1.8 (2 H, m), 1.7 (1 H, m), 1.5 (2 H, m), 1.3 (3 H, m). - ^{19}F-NMR : δ -95.0 (t, *J* 51). - Analysis : calc. for $C_8H_{13}FO_2$ (160.19) C 59.98, H 8.18; found C 59.90, H 8.14%.

Fluoromethyl heptanoate (3d) : From heptanoyl fluoride; 49%; mp -50 to -48 °C; bp 64 - 65 °C/10 mmHg; n_D^{20} 1.4030. - ^{1}H-NMR (360 MHz): δ 5.72 (2 H, d, *J* 51.0), 2.43 (2 H, t, *J* 7.0), 1.69 (2 H, q, *J* 7.0), 1.3 (6 H, m), 0.91 (3 H, t, *J* 7.0). - ^{19}F-NMR : δ -95.0 (t, *J* 51). - Analysis : calc. for $C_8H_{15}FO_2$ (162.20) C 59.24, H 9.32; found C 59.34, H 9.32%.

Bis(fluoromethyl) adipoate (3e) : From adipoyl fluoride; 51%; mp 12 - 14 °C; bp 104 - 105 °C/10 mmHg. - ^{1}H-NMR (360 MHz): δ 5.70 (4 H, d, *J* 50.8), 2.4 (4 H, m), 1.7 (4 H, m). - ^{19}F-NMR : δ -95.3 (t, *J* 51). - Analysis : calc. for $C_8H_{12}F_2O_4$ (210.18) C 45.72, H 5.75; found C 45.78, H 5.68%.

Basically the same results, although somewhat lower yields were found when potassium fluoride was employed in only catalytic amounts (0.1 - 0.2 molar equivalents). - When gaseous formaldehyde was bubbled into a solution containing the acyl fluoride and 0.05 molar equivalents of tris(dimethylamino)sulfonium difluorotrimethylsilicate [18] (rather than 18-crown-6 and suspended potassium fluoride), esters **3a** and **3b** were obtained with 98% and 97% yield while only trace amounts of **3c**, **3d** and **3e** were isolated.

4. Acylals

Methylene dibenzoate [25] (**4**, R = C_6H_5) was isolated and purified by crystallization from ethanol: mp 101 - 102 °C. Methylene di-2-furancarboxylate (**4**, R = 2-C_4H_3O), methylene di(cyclohexanecarboxylate) (**4**, R = C_6H_{11}) and methylene diheptanoate [26] (**4**, R = C_6H_{13}) were identified by the characteristic singlet exhibited in the ^{1}H-nmr spectra around 6.3 ppm. Adipoyl fluoride appears to have given rise to a polymeric rather than cyclic acylal.

5. *O*-(Fluoromethyl) Carbamates

Fluoromethyl fluoroformate (5) [19] : Under nitrogen atmosphere, a mixture of chloromethyl chloroformate (4.4 mL, 6.4 g, 50 mmol), potassium fluoride (11.6 g, 0.20 mol) and 1,4,7,10,13,16-hexaoxacyclooctadecane (4.0 g, 15 mmol) in acetonitrile or tetrahydrofuran (50 mL) was vigorously stirred for 12 h. The mixture was immediately used without isolation or purification. - ^{1}H-NMR : δ 5.69 (2 H, dd, *J* 49.5, 0.6). - ^{19}F-RMN : δ -95.6 (1 F, td, *J* 50, 4), 45.8 (1 F, dt, *J* 4, 0.5).

General procedure : At -15 °C, the amine (80 mmol) was added to a solution of fluoromethyl fluoroformate (50 mmol) in acetonitrile. After 15 min at -15 °C and 1 h at 25 °C, diethyl ether (100 mL) was added and the mixture was washed with water (3 × 200 mL), dried, filtered and concentrated. The residue was purified by distillation, chromatography or crystallization.

Fluoromethyl *N*-butylcarbamate (6a) : From butylamine; isolated by distillation; 64%; bp 70 - 71 °C/ 1 mmHg; n_D^{20} 1.4180. - ^{1}H-NMR : δ 5.66 (2 H, d, *J* 52.3), 5.1 (1 H, s, broad), 3.21 (2 H, q, *J* 7.0), 1.5 (2 H, m), 1.4 (2 H, m), 0.91 (3 H, t, *J* 7.0). - ^{19}F-NMR : δ -91.4 (t, *J* 52). - Analysis : calc. for $C_6H_{12}FNO_2$ (149.17) C 48.31, H 8.11; found C 48.35, H 8.10%.

Fluoromethyl *N*-benzylcarbamate (6b) : From benzylamine; isolated by chromatography on silica gel using a 1 : 1 (v/v) mixture of diethyl ether and pentane as the eluant; 73%; mp 36 - 37 °C. - ^{1}H-NMR : δ 7.3 (5 H, m), 6.71 (2 H, d, *J* 52.0), 5.3 (1 H, s, broad), 4.42 (2 H, d, *J* 6.0). - ^{19}F-NMR : δ -91.5 (t, *J* 51). - Analysis : calc. for $C_9H_{10}FNO_2$ (183.18) C 59.01, H 5.50; found C 59.38, H 5.75%.

Fluoromethyl *N*-(4-methoxyphenyl)carbamate (6c) : From *p*-methoxyaniline; isolated by chromatography on silica gel using a 4 : 1 (v/v) mixture of diethyl ether and pentane; 48%; mp 82 - 83 °C (from water). - ^{1}H-NMR : δ 7.31 (2 H, d, *J* 8.5), 7.1 (1 H, s, broad), 7.86 (2 H, d, *J* 51.5), 5.76 (2 H, d, *J* 51.5), 3.79 (3 H, s). - ^{19}F-NMR : δ -91.8 (t, *J* 50). - Analysis : calc. for $C_9H_{10}FNO_3$ (199.18) C 54.27, H 5.06; found C 54.34, H 5.09%.

Fluoromethyl 1*H*-imidazole-1-carbamate (6d) : From imidazole; isolated by distillation; 35%; mp 29 - 30 °C (from pentane); bp 64 - 65 °C/1 mmHg. - ^{1}H-NMR : δ 8.2 (1 H, s, broad), 7.46 (1 H, q, *J* 1.5), 7.11 (1 H, pent, *J* 1.5), 5.95 (2 H, dd, *J* 49.5, 1.8). - ^{19}F-NMR : δ -94.5 (t, *J* 49). - Analysis : calc. for $C_5H_5FN_2O_2$ (144.11) C 41.76, H 3.50; found C 41.70, H 4.05%.

Fluoromethyl *N*-(benzothiazol-2-yl)carbamate (6e) : From 2-aminobenzothiazole; isolated by crystallization; 32%; mp 288 - 290 °C (from 10% aqueous dimethylsulfoxide). - ^{1}H-NMR (DMSO-D_6) : δ 12.6 (1 H, s, broad), 8.98 (1 H, d, *J* 7.5), 7.71 (1 H, d, *J* 8.0), 7.43 (1 H, t, *J* 7.3), 7.29 (1 H, t, *J* 7.5), 5.90 (2 H, d, *J* 51.5). - ^{19}F-NMR (DMSO-D_6) : δ -93.8 (t, *J* 51). - Analysis : calc. for $C_9H_7FN_2O_2S$ (226.23) C 47.78, H 3.12; found C 47.70, H 3.25%.

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