N-Fluorobis[(perfluoroalkyl)sulfonyl]imides. Efficient reagents for the fluorination of 1,3-dicarbonyl derivatives

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Abstract

Fluorination of 1,3-dicarbonyl derivatives with *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides, $(CF_3SO_2)_2NF$ (**1**), results in the formation of 2-fluoro- or 2,2-difluoro-1,3-dicarbonyl analogs, depending on the reaction conditions. High yields are obtained for a variety of structural types. In the case of 1,3-dicarbonyl derivatives with low enol content, only the sodium enolates react with **1**. Thus **1** has been demonstrated to be perhaps the best fluorinating reagent for the fluorination of 1,3-dicarbonyl derivatives. All of the 2-fluoro-1,3-dicarbonyl products exist predominantly as keto tautomers.

Introduction

Due to the interesting biological, chemical and physical properties of organofluorine compounds, the fluorination of organic molecules has attracted much attention. Considerable effort has been made over the past two decades to search for new fluorinating reagents and methodology for selective fluorination [1]. Much of organofluorine chemistry, however, remains outside of the mainstream of synthetic methodology since many of the available reagents such as F_2, CF_3OF, $FClO_3$, XeF_2 are hazardous or expensive and require special equipment and experience to handle safely. In recent years, some interesting *N*-fluoro-compounds have been introduced as electrophilic fluorinating agents, which are easy to handle and are effective in converting metal enolates into α-fluorocarbonyl compounds. Among these *N*-fluoro-compounds are *N*-fluoro2-pyridone [2], *N*-fluoropyridinium triflate [3], *N*-fluoroquinuclidinium fluoride [4], *N*-fluorosulfoamide [5], optically active *N*-fluorosulfoamides [6], labeled *N*-fluorosulfonamides and lactams [7], *N*-fluoro-*o*-benzendisulfonimide [8], and *N*-fluorobis[(perfluoroalkyl)sulfonyl]imides [9], the last of which were first synthesized in our laboratory and have been shown to be some of the best of the available reagents for electrophilic aromatic fluorination. As part of a continuing study of this new class of fluorinating agents, we report herein the fluorination of 1,3-dicarbonyl derivatives [9c].

Fluorination of 1,3-dicarbonyl compounds or their metal enolates with perchloryl fluoride ($FClO_3$) [10] and CH_3CO_2F [11] resulted in the corre-

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sponding monofluoro- or difluoro-dicarbonyl derivatives in acceptable yields. The major disadvantages of these reagents are that possible explosive conditions can develop and that acetyl hypofluorite cannot fluorinate β-diketones. A few β-diketones have been prepared using XeF_2 in the presence of a catalyst to produce difluoro analogs and other products, but monofluoro-compounds could not be obtained in reasonable yields. [12] Some reactions of this type with some *N*-fluoro-compounds have been reported [2, 3a, 4, 5a, 6], but their activity is low and the yields are not very good. The alternative approaches to preparing α-fluoro-1,3-dicarbonyl compounds are the Reformatsky condensation of bromofluoroacetates with aldehyde, followed by oxidation [13], and the fluorination of trimethylsilyl ethers by dilute fluorine [14]. Thenappan and Burton employed (fluorocarbethoxymethylene)tri-n-butylphosphorane to react with acid chlorides and furnished a good method to produce monofluoro β-ketoesters [15]*. However, there is no single reagent which can be used to selectively produce both mono- and difluoro-β-dicarbonyl compounds.

Experimental

Infrared spectra were taken as neat films on a Perkin-Elmer 1430 spectrometer with a 7500 data system. ^1H and ^{19}F NMR spectra were obtained on a Bruker AC-200 instrument at 200.13 and 188.31 MHz, respectively. Chemical shifts are reported for $CDCl_3$ solutions in ppm positive downfield from internal TMS for ^1H NMR spectra and from internal $CFCl_3$ for ^{19}F NMR spectra. Mass spectra were measured with a Hewlett Packard 5985B GC/MS spectrometer; chemical ionization (CI) was with methane gas and electron impact (EI) at 70 eV. Column chromatography was performed on silica gel 60A (100–200 mesh). All 1,3-dicarbonyl compound starting materials were obtained from Aldrich Chemical Co. and used as received.

General procedure for fluorination

Into a solution of the 1,3-dicarbonyl compound starting material (**2**) in an appropriate solvent under N_2 at 22 °C, was added dropwise a solution of *N*-fluorobis[(trifluoromethyl)}sulfonimide (**1**) dissolved in the solvent during a period of 10–20 min with stirring. Reactions were followed by ^{19}F and ^1H NMR spectra methods. After the reaction appeared to be complete, the mixture was diluted with CH_2Cl_2, rinsed with aq. $NaHCO_3$ and saturated aqueous sodium chloride, and then dried over Na_2SO_4. The crude product was purified by chromatography on a silica gel column using CH_2Cl_2 as the eluent.

*3-Fluoro-3-methyl-2,4-pentanedione (**3a**)*

This was prepared from 3-methyl-2,4-pentanedione (**2a**) (0.23 g, 2.0 mmol) and **1** (0.6 g, 2.0 mmol) in 4 ml CH_2Cl_2. ^1H NMR δ:1.63 (3H,

*After this work was completed, *N*-fluoro sultam (**5f**) was reported to be able to selectively transfer enolates into mono- and difluorinated carbonyl compounds.

d, $J=21.3$ Hz, $CF-CH_3$); 2.27 (3H, s, CH_3); 2.29 (3H, s, CH_3). ^{19}F NMR δ: −157.83 (q, $J=21.1$ Hz, CF). MS *M/e* (EI): 133 (54.5, M+1); 90 (45.8, $M-CH_2CO$; 43 (100, CH_3CO). IR cm^{-1}: 1725 (C=O); 1709 (C=O).

*Ethyl 2-fluoro-2-methyl acetoacetate (**3b**) [16]*

This was prepared from ethyl 2-methyl acetoacetate (**2b**) (0.29 g, 2.0 mmol) and 1 (0.60 g, 2.0 mmol) in 4 ml CH_2Cl_2. ^1H NMR δ:1.31 (3H, t, $J=7.1$ Hz), CH_3); 1.69 (3H, d, $J=22.1$ Hz, $CF-CH_3$); 2.33 (3H, $J=4.6$ Hz, $COCH_3$); 4.28 (2H, q, $J=7.1$ Hz, OCH_2). ^{19}F NMR δ: −157.58 (q–q, $J=22.1$, 4.6 Hz, CF). MS *m/e* (EI):120 (3.4, $M-CH_2CO$); 92 (8.4, $FCO_2C_2H_5$); 43 (100, $COCH_3$). MS *m/e* (CI): 163 (100, M+1); 135 (6.8, $M-C_2H_4+1$); 120 (10.3, $M-CH_2CO$). IR cm^{-1}:1750; 1738 (CO_2R); 1724 (C=O).

*Ethyl 1-fluoro-2-oxocyclopentanecarboxylate (**3c**) [11]*

This was prepared from ethyl 2-oxocyclopentanecarboxylate (**2c**) (0.31 g, 2.0 mmol) and **1** (0.60 g, 2.0 mmol) in 8 ml CH_2Cl_2. ^1H NMR C_6D_6 δ:0.88 (3H, t, $J=7.1$ Hz, CH_3); 1.4–1.6 (2H, m, CH_2); 1.7–2.3 (4H, m, $2CH_2$); 3.87 (2H, q, $J=7.1$ Hz, OCH_2). ^{19}F NMR C_6D_6 δ: −163.8 (t, $J=20.6$ Hz, CF).

*Ethyl 2-fluoro acetoacetate (**3e**) [11, 14]*

This was prepared from ethyl acetoacetate (**2e**) (0.24 g, 1.5 mmol) and **1** (0.68 g, 2.3 mmol) in 10 ml CH_2Cl_2 and 3 ml H_2O and purified by chromatography using CH_2Cl_2–AcOEt (70:30) as the eluent. ^1H NMR δ:1.34 (3H, t, $J=7.1$ Hz, CH_3); 2.36 (3H, d, $J=4.0$ Hz, $COCH_3$); 4.32 (2H, q, $J=7.1$ Hz, OCH_2); 5.21 (1H, d, $J=49.3$ Hz, CHF). ^{19}F NMR δ: −193.72 (d–q, $J=49.6$ and 3.8 Hz, CFH for keto tautomer); −166.72 (s, CF for enol tautomer). MS *m/e* (EI): 149 (100, M+1); 121 (16.4, $M-C_2H_4+1$); 103 (94.8, $M-OC_2H_5$); 43 (93.7, $COCH_3$). IR cm^{-1}:1762; 1735 (CO_2R); 1726 (C=O).

*2-Fluoro-1-phenyl-1,3-butanedione (**3f**) [14]*

This was prepared from benzoylacetone (**2f**) (0.24 g, 1.5 mmol) and **1** (0.60 g, 2.0 mmol) in 10 ml CH_2Cl_2 and 3 ml H_2O. ^1H NMR δ:2.31–2.33 (3H, m, CH_3 for keto and enol tautomers); 5.95 (0.72H, d, $J=50.0$ Hz, CHF); 7.44–7.62 (3H, m, Ar H); 7.93–8.03 (2H, m, Ar H); 11.15 (s, OH for enol tautomer). ^{19}F NMR δ: −190.06 (0.79F, d–d, J=49.9 and 3.5 Hz, CFH for keto tautomer); −170.53 (0.21F, s, CF for enol tautomer). MS *m/e* (EI): 180 (21.0, M); 179 (22.7, M−1); 105 (100, C_6H_5CO); 77 (62.1, C_6H_5); 43 (17.5, $COCH_3$). MS *m/e* (CI): 361 (51.6, 2M+1); 285 (100, $2M-CH_3COCFH$); 181 (73.8, M+1); 180 (31.4, M); 179 (7.0, M−1); 105 (75.5, C_6H_5CO). IR cm^{-1}:1728 (C=O); 1687 (C=O); 1593 (Ar C=C).

*Ethyl 2-fluoro-3-phenyl-3-oxo-propanate (**3g**) [13]*

This was prepared from ethyl benzoyl acetate (**2g**) (0.29 g, 1.5 mmol) and **1** (0.68 g, 2.3 mmol) in 10 ml CH_2Cl_2 and 3 ml H_2O. ^1H NMR δ:1.25

(3H, t, J = 7.1 Hz, CH_3); 4.30 (2H, q, J = 7.1 Hz, OCH_2); 5.89 (1H, d, J = 48.8 Hz, CHF). ^{19}F NMR δ: −190.95 (d, J = 49.1 Hz, CFH). MS *m/e* (EI): 211 (3.7, M+1); 105 (100, C_6H_5CO); 77 (11.6, C_6H_5). MS *m/e* (CI): 211 (100, M+1); 105 (48.9, C_6H_5CO). IR cm^{-1}:1759 (CO_2R); 1687 (C=O); 1593 (Ar C=C).

*Dimethyl 2-fluoro malonate (**3h**) [11]*

This was prepared from dimethyl sodium malonate, which was formed by adding 0.11 g (4.6 mmol) of powdered NaH to 0.35 g (2.65 mmol) of dimethyl malonate (**2h**) in 6 ml of dry THF followed by filtration of excess NaH, and **1** (0.85 g, 2.84 mmol) in THF under N_2 at −50 °C up to room temperature. ^{1}H NMR δ:3.86 (6H, s, $2OCH_3$); 5.32 (1H, d, J = 48.0 Hz, CHF). ^{19}F NMR δ: − 195.73 (d, J = 47.8 Hz, CFH). MS *m/e* (EI): 119 (25.4, M − OCH_3); 106 (39.8, $CFH(CO)_2O$); 101 (20.6, M − F − OMe + 1); 91 (34.6, M − CO_2CH_3); 63 (67.7, FCO_2); 61 (56.3, $CFHCO_2H$); 60 (43.9, $CFHCO_2$); 59 (100, CO_2CH_3). MS *m/e* (CI): 301 (3.1, 2M+1); 283 (10.9, 2M − CH_3 − 1); 256 (7.4, 2M − OCH_3 − CH_3 + 1); 241 (24.2, 2M − CO_2CH_3); 183 (7.6, 2M − $2CO_2CH_3$ + 1); 165 (100, M+15); 151 (22.9, M+1); 133 (90.7, $CH_2(CO_2CH_3)_2$ + 1); 106 (10.9, $CFH(CO)_2O$). IR cm^{-1}: 1750 (CO_2R).

*Diethyl 2-fluoro-2-phenyl malonate (**3i**) [4]*

This was prepared from diethyl sodium phenylmalonate, which was formed by adding 0.08 g (3.3 mmol) of powdered NaH to 0.35 g (1.5 mmol) of diethyl phenyl malonate (**2i**) in dry THF, and **1** (0.45 g, 1.5 mmol) at −78 °C up to room temperature. ^{1}H NMR δ:1.31 (3H, t, J = 7.1 Hz, CH_3); 4.32 (2H, q, J = 7.1 Hz, OCH_2); 7.39–7.42 (3H, m, Ar H); 7.57–7.62 (2H, m, Ar H). ^{19}F NMR δ: −161.45 (s, CF). MS *m/e* (EI): 255 (2.2, M+1); 254 (8.1, M); 236 (17.9, $C_6H_5CH(CO_2C_2H_5)_2$); 181 (62.8, M − $CO_2C_2H_5$); 125 (100, $CF(CO_2H)_2$), 105 (29.7, $CF(CO)_2O$) MS *m/e* (CI): 237 (100, $C_6H_5CH(CO_2C_2H_5)_2$ + 1). IR cm^{-1}: 1742 (CO_2R).

*Ethyl 2-fluoro-3-(4'-nitrophenyl)-3-oxo-propanoate (**3j**)*

This was prepared from ethyl 4-nitrobenzoylacetate (**2j**) (0.36 g, 1.5 mmol) and **1** (0.68 g, 2.3 mmol) in 10 ml CH_2Cl_2 and 3 ml H_2O. ^{1}H NMR δ:1.29 (3H, t, J = 7.1 Hz, CH_3); 4.67 (2H, q, J = 7.1 Hz, OCH_2); 5.99 (1H, d, J = 48.5 Hz, CHF); 8.25, 8.36 (AB-type, $J(AB)$ = 8.6 *Hz, Ar H*). ^{19}F NMR δ: −191.33 (d, J = 48.6 Hz, CFH for keto tautomer); −171.29 (s, CF for enol tautomer). MS *m/e* (EI): 150 (100, $NO_2C_6H_4CO$); 104 (20.5, $CFHCO_2C_2H_5$ − 1); 76 (12.4, C_6H_4). MS *m/e* (CI): 256 (100, M+1); 238 (14.4, $NO_2C_6H_4COCH_2CO_2C_2H_5$ + 1); 228 (14.2, M − C_2H_5 + 1); 150 (44.8, $NO_2C_6H_4CO$). IR cm^{-1}: 1756 (CO_2R); 1705 (C=O); 1599 (Ar C=C).

*Ethyl 2-fluoro-4-methyl-3-oxo-pentanoate (**3k**)*

This was prepared from ethyl isobutyrylacetate (**2k**) (0.24 g, 1.5 mmol) and **1** (0.60 g, 2.0 mmol) in 10 ml CH_2Cl_2 and 3 ml H_2O. ^{1}H NMR δ:1.15 (6H, dd, J = 6.9 and 1.1 Hz, $2CH_3$); 1.33 (3H, t, J = 7.1 Hz, CH_3); 3.13 (1H,

hept–d, $J=6.9$ and 3.2 Hz, CH); 4.32 (2H, q, $J=7.1$ Hz, OCH_2); 5.28 (1H, d, $J=49.2$ Hz, CHF). ^{19}F NMR δ: −196.23 (d, $J=49.3$ Hz, CFH). MS *m/e* (EI): 177 (33.5, M+1); 129 (27.3, M−F−C_2H_4); 78 (31.7, $CFHCO_2H+1$); 71 (93.7, $(CH_3)_2CHCO$); 43 (100, $(CH_3)_2CH$); 41 (32.1, C_3H_5). MS *m/e* (CI): 177 (63.4, M+1); 159 (41.1, $(CH_3)_2CHCOCH_2CO_2C_2H_5+1$); 131 (28.8, M−$OC_2H_5$); 129 (100, M−F−$C_2H_4$). IR cm^{-1}: 1753 (CO_2R); 1725 (C=O).

*3,3-Difluoro-2,4-pentanedione (**4d**) [12]*

This was prepared from 2,4-pentanedione (**2d**) (1.5 g, 1.5 mmol) and **1** (0.90 g, 3.0 mmol) in 4 ml CH_2Cl_2. ^1H NMR δ: 2.39 (t, $J=1.2$ Hz, $COCH_3$). ^{19}F NMR δ: −115.38 (s, CF_2). IR cm^{-1}: 1738 (C=O).

*Ethyl 2,2-difluoro acetoacetate (**4e**) [10b]*

This was prepared from **2e** (0.20 g, 1.5 mmol) and **1** (0.90 g, 3.0 mmol) in 4 ml CH_2Cl_2. ^1H NMR δ:1.36 (3H, t, $J=7.1$ Hz, CH_3); 2.41 (3H, t, $J=1.5$ Hz, $COCH_3$); 4.38 (2H, q, $J=7.1$ Hz, OCH_2). ^{19}F NMR δ: −114.20 (s, CF_2). MS *m/e* (CI): 167 (100, M+1); 149 (17.7, $CH_3COCFHCO_2C_2H_5+1$); 139 (29.4, M−C_2H_5+1); 121 (5.5, $CH_3COCH_2CO_2C_2H_5+1$). IR cm^{-1}: 1763 (CO_2R); 1738 (C=O).

*2,2-Difluoro-1-phenyl-1,3-butanedione (**4f**)*

This was prepared from **2f** (0.20 g, 1.23 mmol) and **1** (0.74 g, 2.47 mmol) in 10 ml CH_2Cl_2. ^1H NMR C_6D_6 δ:1.83 (3H, m, CH_3); 6.8–7.1 (3H, m, Ar H); 7.9–8.0 (2H, m, Ar H). ^{19}F NMR C_6D_6 δ: −108.9 (m, $J=1.4$ Hz, CF_2).

*Ethyl 2,2-difluoro-3-phenyl-3-oxo-propanoate (**4g**) [13]*

This was prepared from **2g** (0.37 g, 1.9 mmol) and **1** (1.2 g, 4.0 mmol) in 10 ml CH_2Cl_2. ^1H NMR C_6D_6 δ:0.75 (3H, t, $J=7.1$ Hz, CH_3); 3.84 (2H, q, $J=7.1$ Hz, OCH_2); 6.91–7.07 (3H, m, Ar H); 7.98–8.03 (2H, m, Ar H). ^{19}F NMR C_6D_6 δ: −107.38 (s, CF_2). MS *m/e* (EI): 201 (34.9, M−C_2H_5+1); 151 (66.2, M−C_6H_5CO); 135 (100, M−F−$CO_2C_2H_5$−1). MS *m/e* (CI): 229 (100, M+1); 211 (50.5, $C_6H_5COCFHCO_2C_2H_5+1$); 105 (97.9, C_6H_5CO). IR cm^{-1}: 1768 (CO_2R); 1708 (C=O); 1594 (Ar C=C).

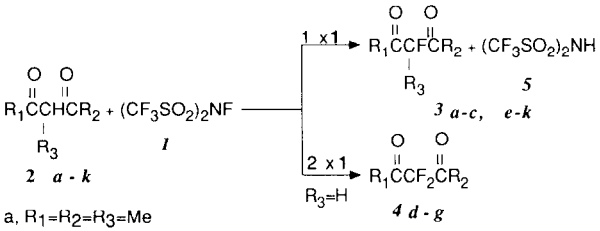
*Reaction of ethyl sodium acetoacetate with **1**. Preparation of ethyl 3-trifluoromethanesulfonyloxy-2-crotonate (**7**)*

A solution of ethyl sodium acetoacetate in dry THF [prepared by adding 0.08 g (3.3 mmol) of powdered NaH to **2e** (0. 20 g, 1.5 mmol) in 5 ml THF, followed by filtration of excess NaH] was added under N_2 to a stirred solution of **1** in 2 ml THF at −50 °C. After 1 h, the mixture was diluted with diethyl ether, washed with aq. $NaHCO_3$ and sat. brine, and then dried over Na_2SO_4. The crude product was purified by column silica gel chromatography using CH_2Cl_2 as the eluent, and 0.15 g colorless liquid was identified as **7**. ^1H NMR δ:1.30 (3H, t, $J=7.1$ Hz, CH_3); 2.17 (3H, s, CH_3); 5.24 (2H, 1, $J=7.1$ Hz, OCH_2); 5.76 (1H, pent, $J=0.9$ Hz, C=CH). ^{19}F

NMR δ: −75.17 (s, CF_3). MS *m/e* (EI): 263 (5.4, M+1); 262 (3.8, M); 87 (40.2, $CH_2CO_2C_2H_5$); 85 (88.8, CH_3COCH_2CO); 69 (100, CF_3); 43 (44.9, CH_3CO). MS *m/e* (CI): 263 (100, M+1); 217 (48.9, M−OC_2H_5). IR cm^{-1}: 1725, 1686 (RO−C=C−CO_2R'); 1424 (SO_2).

Results and discussion

Reactions of β-diketones and β-ketoesters with *N*-fluorobis[(trifluoromethyl)sulfonyl]imide (**1**) in dichloromethane at 22 °C proceed smoothly to give α-fluoro-products. Thus α-monofluoro-compounds could be obtained in good yields via the reaction of α-monosubstituted β-diketones and β-keto esters (entries 1–3 in Table 1, and α,α-difluoro-compounds (**4**) were formed when unsubstituted substrates **2** (R_3=H) reacted with 2 equiv. **1** (entries 4–7 in Table 1), while a mixture of mono- and difluoro-compounds was obtained in the reaction with an equimolar amount of **1**. Malonate esters failed to react under the same conditions.



a, R_1=R_2=R_3=Me
b, R_1=R_3=Me, R_2=OEt
c, R_1,R_3=$(CH_2)_3$, R_2=OEt
d, R_1=R_2=Me, R_3=H
e, R_1=Me, R_2=OEt, R_3=H
f, R_1=C_6H_5, R_2=Me, R_3=H
g, R_1=C_6H_5, R_2=OEt, R_3=H
h, R_1=R_2=OMe, R_3=H
i, R_1=R_2=OEt, R_3=C_6H_5
j, R_1=p-$NO_2C_6H_4$, R_2=OEt, R_3=H
k, R_1=$(Me)_2CH$, R_2=OEt, R_3=H

It is thought that electrophilic addition of **1** to the enol tautomers of dicarbonyl compounds accounts for product formation. Therefore β-diketones and β-keto esters, which contain significant amounts of the enol tautomer at equilibrium, react readily with **1**. For β-diesters, the contribution of the enol form is small and thus no reaction takes place between the substrate and the *N*-fluoro-compound. The monofluoro-compounds **3** (R_3=H) can be enolized in the presence of acid or base and react further with the *N*-fluoro-compound to form difluoro-derivatives.

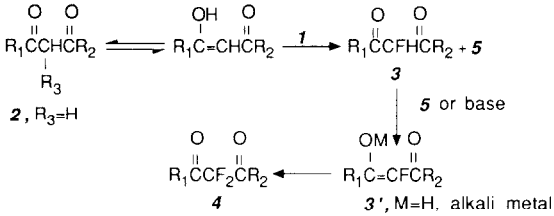
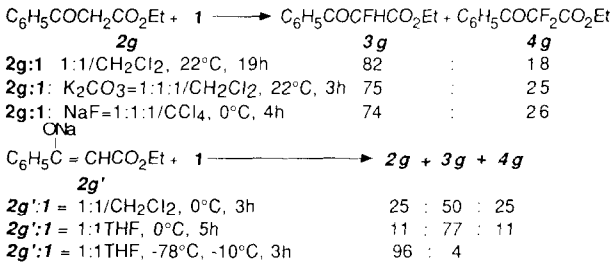


TABLE 1

Reaction of 1,3-dicarbonyl derivatives with $(CF_3SO_2)_2NF$ at 22 °C

Entry	Substrate	Mol% **1**	Solvent	Time (h)	Product	Yield (%)[a]
1	**2a**	100	CH_2Cl_2	7	**3a**	91
2	**2b**	100	CH_2Cl_2	7	**3b**	83
3	**2c**	100	CH_2Cl_2	4	**3c**	100
4	**2d**	200	CH_2Cl_2	3	**4d**	54
5	**2e**	200	CH_2Cl_2	20	**4e**	80
6	**2f**	200	CH_2Cl_2	24	**4f**	90
7	**2g**	200	CH_2Cl_2	24	**4g**	96
8	**2h**[b]	100	THF	5	**3h**	78
9	**2i**[b]	100	THF	3	**3i**	92
10	**2e**	150	CH_2Cl_2–H_2O	8	**3e**	86
11	**2f**	130	CH_2Cl_2–H_2O	11	**3f**	93
12	**2g**	150	CH_2Cl_2–H_2O	11	**3g**	86
13	**2j**	150	CH_2Cl_2–H_2O	10	**3j**	94
14	**2k**	130	CH_2Cl_2–H_2O	14	**3k**	91

[a]Isolated yield after purification as described in Experimental section.
[b]*Sodium enolate was used.*

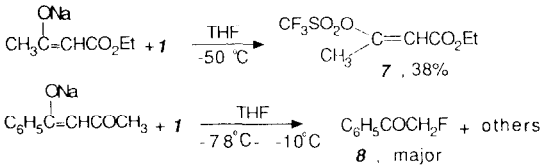


Scheme 1.

In an attempt to neutralize the strong acid $(CF_3SO_2)_2NH$ (**5**) formed in these reactions [17], the initial choice was to use a suspension of potassium carbonate or sodium fluoride in the reaction mixture. But the results showed that the difluoro-derivatives increased in the presence of base (Scheme 1). Next, the dicarbonyl compounds were converted into the sodium enolates. Thus, the sodium enolate of **2g** (**2g'**) reacted with **1** in CH_2Cl_2 or THF and produced a mixture of the monofluoro- and difluoro-derivatives and **2g**. Obviously, the enolate **2g'** is a strong base and this can enolize the monofluoro-analog **3g** to **3g'**, converting **2g'** back to **2g**. When a solution of the sodium enolate of **2g** in THF, however, was added into **1** at a rate sufficient to maintain the reaction mixture under almost neutral conditions and at low temperature, the reaction was highly selective and the monofluoro-analog **3g** was obtained (Scheme 1).

Unfortunately, this procedure could not be extended to other 1,3-dicarbonyl compounds. When the sodium enolate of ethyl acetoacetate (**2c'**)

was treated with **1**, only a 38% yield of the enol triflate **7** was formed. When the sodium enolate of acetylacetone (**2d'**) was brought to contact with **1**, neither the mono- nor difluoro-derivative were observed and the starting materials could not be detected in the complicated reaction mixture. When the sodium enolate of benzoylacetone (**2f'**) reacted with **1**, the fluoro acetophenone (**8**) was detected as the main product, together with the monofluoro-, difluoro- and trifluoro-compounds. These results implied that some Lewis bases may react in a complicated manner with the *N*-fluoro-compound, which is similar to some reactions of CF_3OF [18]. However, the sodium enolate of malonate esters react cleanly with **1** and produce monofluoro-derivatives in good yield (entry 8 and 9 in Table 1.



Finally, it was found that the reaction of β-diketones and β-keto esters with **1** could be stopped at the monofluorination stage to give the desired product **3** (R_3 = H) in good yield (entries 10–14 in Table 1 when CH_2Cl_2–H_2O was used as the solvent. In this case, the *N*-fluoro-compound **1** should be used in slight excess. Considering that the strong acid $(CF_3SO_2)_2NH$ (**5**) is highly water-soluble, it is obvious that **5** was rapidly partitioned into H_2O as formed and thereby removed from the reaction system (CH_2Cl_2 solution). Hence, the enolization of the monofluoro-compound and the subsequent fluorination to the difluoro-compound ar greatly reduced.

All of the monofluoro 1,3-dicarbonyl products **3** (R_3 = H, i.e. **3e–3h, 3j** and **3k**) exist predominantly as the keto tautomers [14]. ^{19}F NMR spectroscopy showed that **3e** and **3j** contain about 4% of the enol tautomer at equilibrium in chloroform solution and 21% of **3f** enolizes in chloroform and benzene, while no detectable (NMR) enol tautomers were observed for **3g**, **3h** and **3k**. The fluorine atom in the α-position of the β-dicarbonyl compounds decreases the enolization, compared to the parent unfluorinated compounds [19]. This is in accord with previous observations that a group with electron-donating abilities destabilizes the enolic form [14, 20]. As is well known, fluorine is not only a very good inductive electron-withdrawing group, but it also has a strong mesomeric effect, tending to return electron density to the unsaturated systems via a nonbonding electron pair [21].

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