# Facile conversion of perfluoroacyl fluorides into other acyl halides

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Nine perfluoroacyl fluorides underwent halogen exchange when treated with anhydrous lithium halides to give acyl chlorides, bromides and iodides in high yields. The temperature dependence of this reaction is described. In the reaction with perfluorodiacyl fluoride, the diacyl halides possessing different acyl halide-groups were also produced. Of the alkaline metal salts used halogen exchange was successful only with lithium salts because of the interaction between lithium and fluorine.

Although acyl iodides are more reactive acylating agents than acyl chlorides, they are rarely used in synthesis, the former being much more readily available and easier to handle. Nevertheless, there are some reactions which are successful only with acyl iodides.[1] There are several reports on the preparation of acyl iodides,[2] but few reports on perfluoroacyl iodides,[3] the synthesis of which is difficult by standard methods because of the electronegativity of the perfluoroalkyl group.

The difunctional nature of diacyl halides makes them important synthetic intermediates. Thus, perfluorodiacyl fluorides and chlorides are used to synthesize difunctional polyethers,[4] heterocyclic compounds[5] and macrocyclic ethers.[6] They have also been used for chelating fluoride and chloride ions[7] and as a ligand in cobalt chemistry.[8] Since the relative reactivity of perfluorodiacyl halides is in the decreasing order bromides > chlorides > fluorides,[9] perfluorodiacyl iodides should be the most reactive member of the series: however, until now, they had not been prepared in the absence of a suitably facile synthesis.

We here report a facile method for the synthesis of perfluoroacyl chlorides, bromides and iodides from an acyl fluoride, itself readily available by electrochemical fluorination[10] or oligomerization of hexafluoropropene oxide.[11] By the described method, products can be separated very easily from reactants by taking advantage of heterogeneous (solid/ liquid or solid/gas) reactions.

It is known that a strong interaction between lithium and fluorine[12] plays an important role in some reactions.[13] We found that halogen exchange of the acid fluorine of perfluoroacyl fluoride can be successfully achieved with lithium salts, while there is no reaction with other alkaline salts.

## Results and discussion

The results for the halogen exchange of perfluoro(morpholinoacetyl) fluoride 1-F, trifluoroacetyl fluoride 2-F and pentafluoropropionyl fluoride 3-F (Scheme 1) are summarized in Table 1. Halogen exchange is successful with lithium salts, although not with other alkaline metal salts (*e.g.* NaI and KI; runs 15, 16). It was also found that the reaction temperature was crucial for the optimization of halogen exchange. For example, the acyl chloride 1-Cl was formed from 1-F by treatment with LiCl at 120–300 °C (runs 1–4), although the reaction rate was very slow at 120 °C. Similarly, the acyl bromide 1-Br was formed by treatment of 1-F with LiBr at 120–250 °C (runs 5–7). At 300 °C, however, 1-Br decomposed into $R_F$Br as a result of decarbonylation (8% at 2.3 h and 46% at 7.8 h; runs 8, 9). The acyl iodide 1-I was obtained by treatment of 1-F in a similar fashion with LiI at 120 °C (run 13), but it decomposed completely into $R_F$I even at 200 °C (run 14).[14] Thus, the optimum temperatures for preparation of the corresponding
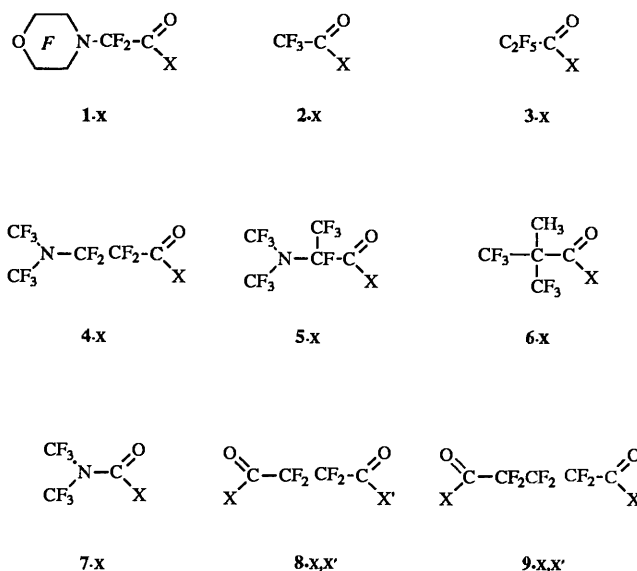


Scheme 1

acyl halides was 120 °C for iodides, 250 °C for bromides, and 300 °C for chlorides. This order is clearly correlated to the strength of carbon–halogen bond, that is, C–I < C–Br < C–Cl (Table 2).

Experimental second-order kinetic constants of the reaction of perfluoro[3-($N,N$-dimethylamino)propionyl] fluoride 4-F and perfluoro[2-($N,N$-dimethylamino)propionyl] fluoride 5-F with an excess of lithium halides, calculated according to Eqn. (1), are summarized in Table 3.

$$d[R_FCOX]/dt = k_2[R_FCOF][LiX] \qquad (1)$$

The reaction of 4-F with lithium iodide proceeds easily, as did the reactions with lithium bromide and lithium chloride. The relative order of the reactivity in terms of the kind of halogen, iodide > bromide > chloride, corresponds to the relative lattice energies of LiX (LiI < LiBr < LiCl). Although the reactivity of 5-F was found to be 1/100–1/1000 of that of 4-F, the relative order of the reactivity in terms of the kind of halogen was found to be the same as that of 4-F. The difference between 4-F and 5-F in reactivity can be explained by assuming that an increase in the bulk of groups attached to the α-carbon atom sterically inhibits adsorption of the acyl fluorides onto the crystal surface and thus reducing the reaction rate of 5-F.

Results for the halogen exchange of 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propanoyl fluoride 6-F are summarized in Table 4. These reactions were very slow and it was difficult to

# Table 1 Syntheses of perfluoroacyl iodides, bromides and chlorides

| | R_FCOF | mmol | MX[a] X | mmol | $T/°C$ | $t/h$ | Products[b] (mmol) R_FCOF[c] | R_FCOX | R_FX |
|---|---|---|---|---|---|---|---|---|---|
| Run | | | | | | | | | |
| 1 | 1-F | 0.720 | Cl | 3.07 | 120 | 17.0 | 0.296 | 0.236 (45) | 0 |
| 2 | 1-F | 0.785 | Cl | 2.83 | 120 | 63.5 | <0.01 | 0.755 (96) | 0 |
| 3 | 1-F | 0.678 | Cl | 3.07 | 200 | 20.0 | <0.01 | 0.626 (92) | 0 |
| 4 | 1-F | 1.10 | Cl | 2.45 | 300 | 2.5 | <0.01 | 1.10 (100) | 0 |
| 5 | 1-F | 0.691 | Br | 2.99 | 120 | 17.0 | <0.01 | 0.672 (97) | 0 |
| 6 | 1-F | 1.01 | Br | 3.11 | 200 | 19.0 | 0.014 | 0.982 (97) | 0 |
| 7 | 1-F | 0.908 | Br | 2.69 | 250 | 6.0 | <0.01 | 0.854 (93) | 0 |
| 8 | 1-F | 1.16 | Br | 3.19 | 300 | 2.3 | 0.040 | 1.02 (88) | 0.090 (8) |
| 9 | 1-F | 1.30 | Br | 2.59 | 300 | 7.8 | 0.100 | 0.570 (44) | 0.600 (46) |
| 10 | 2-F | 0.67 | Br | 7.8 | 330 | 5.0 | <0.01 | 0.436 (65) | 0.208 (31) |
| 11 | 3-F | 0.614 | Br | 4.02 | 180 | 2.0 | 0.104 | 0.466 (76) | 0 |
| 12 | 3-F | 0.644 | Br | 3.18 | 250 | 2.0 | 0.135 | 0.586 (91) | 0 |
| 13 | 1-F | 0.688 | I | 2.91 | 120 | 17.0 | <0.01 | 0.623 (91) | 0 |
| 14 | 1-F | 0.804 | I | 3.20 | 200 | 5.0 | <0.01 | 0 | 0.471 (59)[d] |
| 15 | 1-F | 0.780 | I[e] | 3.47 | 200 | 15.5 | 0.756 | 0 | 0 |
| 16 | 1-F | 0.737 | I[f] | 2.91 | 200 | 67.0 | 0.704 | 0 | 0 |
| 17 | 2-F | 3.00 | I | 38.3 | 100 | 7.0 | <0.01 | 2.88 (96) | 0 |
| 18 | 2-F | 0.77 | I | 10.2 | 180 | 7.0 | <0.01 | 0.200 (26) | 0.562 (73) |
| 19 | 3-F | 0.843 | I | 3.06 | 120 | 2.0 | <0.01 | 0.846 (100) | 0 |
| 20 | 3-F | 0.819 | I | 3.03 | 180 | 2.0 | <0.01 | 0.287 (35) | 0.462 (52) |
| 21 | 3-F | 0.831 | I | 2.94 | 180 | 4.0 | <0.01 | 0.107 (13) | 0.615 (74) |

[a] Lithium salts were used unless otherwise noted. [b] The values in parenthesis are yields (%) based on acyl fluoride used. [c] Recovered acyl fluoride. [d] R_FH was also produced (0.166 mmol). [e] Sodium salt was used. [f] Potassium salt was used.

## Table 2 Bonding energy of the C–X bond of trifluoroacetyl halides

| | Bonding energy ($10^{-18}$ J) | | |
|---|---|---|---|
| Method | X = Cl | X = Br | X = I |
| PM3 | −1.73 | −1.36 | −1.22 |
| AM1 | −1.93 | −1.80 | −1.65 |

## Table 3 Kinetic constants of halogen exchange reaction[a]

| Acyl fluoride | LiX | $k_2'/\text{mol}^{-1}\,\text{min}^{-1}$ | $k_2^{rel}$ |
|---|---|---|---|
| 4-F | LiI | $5.99 \times 10^{-3}$ | (1) |
| 4-F | LiBr | $2.72 \times 10^{-3}$ | 0.45[b] |
| 4-F | LiCl | $1.77 \times 10^{-3}$ | 0.30[b] |
| 5-F | LiI | $6.54 \times 10^{-5}$ | (1) |
| 5-F | LiBr | $3.07 \times 10^{-6}$ | 0.047[c] |
| 5-F | LiCl | $1.93 \times 10^{-6}$ | 0.030[c] |

[a] At 100 ± 2 °C. [b] Relative rate constant to that of the reaction of 4-F + LiI. [c] Relative rate constant to that of the reaction of 5-F + LiI.

stop further reaction to produce the alkyl halide R_FX; e.g., R_FI was produced even for a 46% conversion, and no acyl iodide 6-I was found at a conversion of 93%. The halogen exchange of bis(trifluoromethyl)carbamic fluoride 7-F with lithium chloride and lithium bromide proceeded slower than that of 6-F; that is, the yield of 7-Cl (at 200 °C; 22 days) was 37% and that of 7-Br (at 200 °C; 13 days) was 43%. With lithium iodide no reaction occurred; that is, 7-F was recovered at 120 °C (20 h) and 150 °C (8 days) and the carbonized product was found at 200 °C (25 days).

Halogen exchange can be applied to the syntheses of diacyl halides. The results of the reaction of diacyl difluorides 8-F,F and 9-F,F with lithium halides are summarized in Table 5. The diacyl dihalides 8-I,I, 8-Br,Br, 8-Cl,Cl and 9-Br,Br† were produced by the reaction of 8-F,F or 9-F,F with an excess of

† Diacyl diiodide 9-I,I could not be isolated because of its very high boiling point.

lithium halides in good yields (96, 88, 80 and 67, respectively). One acyl fluoride-group of the diacyl fluoride can be converted into acyl halide by using ca. 0.5 equiv. of lithium halides successfully; the yields of tetrafluorobutanedioyl fluoride iodide 8-F,I, tetrafluorobutanedioyl bromide fluoride 8-F,Br and tetrafluorobutanedioyl chloride fluoride 8-F,Cl were 55, 56 and 71%, respectively.

Previously, tetrafluorobutanedioyl fluoride iodide was the only example of a diacyl halide possessing two different acyl halide groups.[16] With our method, the formation of any combination of halides of the two acyl halide groups can be easily achieved by using a mixture of lithium halides (Scheme 2); e.g. the reaction of 8-F,F (2.63 mmol) with a mixture of lithium bromide (4.03 mmol) and lithium iodide (2.61 mmol) produced tetrafluorobutanedioyl bromide iodide 8-Br,I (49.0%) and the reaction of 8-F,F (3.54 mmol) with a mixture of lithium chloride (3.30 mmol) and lithium iodide (2.69 mmol) produced tetrafluorobutanedioyl chloride iodide 8-Cl,I (40.5%). This reaction can provide a new perfluoroacylating reagent possessing two reactive site with different reactivity (iodide > bromide > chloride > fluoride).

Since use of < 1 equiv. of lithium halide gave rise to 8-I,I : 8-F,I : 8-F,F or 8-Br,Br : 8-F,Br : 8-F,F in the ratio 1:2:1, and further addition of lithium halide converted residual acyl fluoride, it is considered that the two acyl fluoride groups of 8-F,F react independently with lithium halide (Scheme 3).

The decarbonylation of one acyl halide group of diacyl halide possessing a different acyl halide group can be achieved by taking account of the decomposition temperature of the acyl halide; that is, 200 °C for iodide and 300 °C for bromide (Scheme 2). By this method, perfluoro-3-iodopropanoyl bromide, perfluoro-3-iodopropanoyl chloride and perfluoro-3-iodopropanoyl fluoride can be synthesized from the corresponding diacyl halide 8-X,X' at 230 °C, and perfluoro-3-bromopropanoyl chloride and perfluoro-3-bromopropanoyl fluoride can be synthesized at 350 °C.

## Experimental

### Reagents
All the nitrogen-containing perfluoroacyl fluorides used were synthesized by electrochemical fluorination of the correspond-
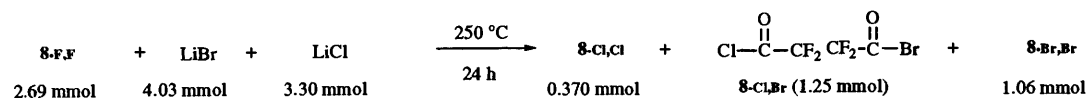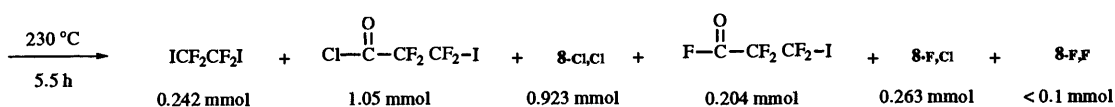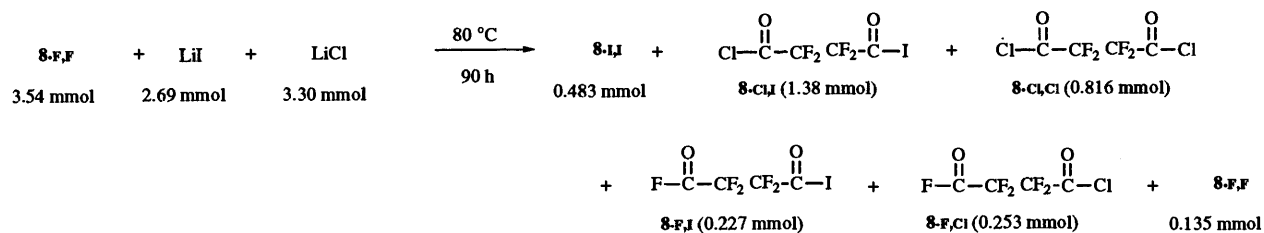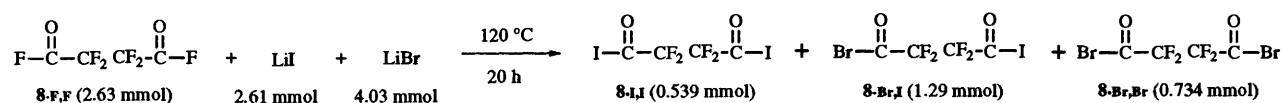
Table 4   Halogen exchange reaction of 3,3,3-trifluoro-2-methyl-2-(trifluoromethyl)propanoyl fluoride 6-F

| 6-F (mmol) | LiX | | | | Conversion (%) | Yield (%) | |
|---|---|---|---|---|---|---|---|
| | X | mmol | $T/°C$ | $t/h$ | | $R_FCOX$ | $R_FX$ |
| 0.986 | I | 3.12 | 120 | 2.0 | 9 | 0 | 0 |
| 0.819 | I | 3.07 | 120 | 16.0 | 26 | 24 | 0 |
| 0.966 | I | 3.28 | 120 | 23.0 | 46 | 57 | 19 |
| 1.12 | I | 3.07 | 120 | 214.0 | 93 | 0 | 78 |
| 1.04 | Br | 3.09 | 250 | 2.0 | 37 | 19 | 4 |
| 0.982 | Br | 3.02 | 250 | 22.0 | 81 | 44 | 6 |

Table 5   The reaction of diacyl fluoride with lithium halides

| | Diacyl fluoride | Lithium halide | | | | Conversion (%) | Yield (%) | |
|---|---|---|---|---|---|---|---|---|
| | mmol | X | mmol | $T/°C$ | $t/h$ | | $F,X^a$ | $X,X^b$ |
| 8-F,F | 2.98 | I | 7.26 | 120 | 3.5 | 100 | <1 | 96 |
| 8-F,F | 4.53 | I | 3.09 | 120 | 5.0 | 66 | 55 | 7 |
| 8-F,F | 3.12 | Br | 8.01 | 250 | 5.0 | 100 | 1 | 88 |
| 8-F,F | 2.96 | Br | 2.43 | 250 | 5.0 | 75 | 56 | 19 |
| 8-F,F | 2.88 | Cl | 12.3 | 330 | 5.0 | 100 | 8 | 80 |
| 8-F,F | 2.48 | Cl | 2.38 | 330 | 5.0 | 78 | 71 | 25 |
| 9-F,F | 8.08 | Br | 27.8 | 250 | 6.5 | 100 | <1 | 67 |

$^a$ The yield of 8-F,X or 9-F,X.   $^b$ The yield of 8-X,X or 9-X,X.



Scheme 2

$$\text{8-F,F} \xrightarrow[\text{120 °C, 12 h}]{\text{LiI (2.30 mmol)}} \text{8-I,I} + \text{8-F,I} + \text{8-F,F}$$
2.41 mmol

$$21 \quad : \quad 46 \quad : \quad 33$$

$$\xrightarrow[\text{120 °C, 20 h}]{\text{LiBr (2.60 mmol)}} \text{8-I,I} + \text{8-Br,I} + \text{8-Br,Br}$$

$$26 \quad : \quad 46 \quad : \quad 28$$

$$\text{8-F,F} \xrightarrow[\text{250 °C, 17 h}]{\text{LiBr (5.50 mmol)}} \text{8-Br,Br} + \text{8-F,Br} + \text{8-F,F}$$
5.27 mmol

$$20 \quad : \quad 53 \quad : \quad 27$$

$$\xrightarrow[\text{250 °C, 71 h}]{\text{LiCl (6.51 mmol)}} \text{8-Br,Br} + \text{8-Cl,Br} + \text{8-Cl,Cl}$$

$$25 \quad : \quad 48 \quad : \quad 27$$
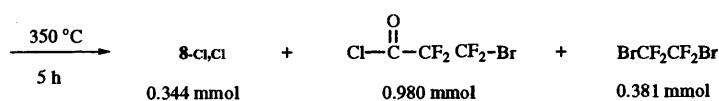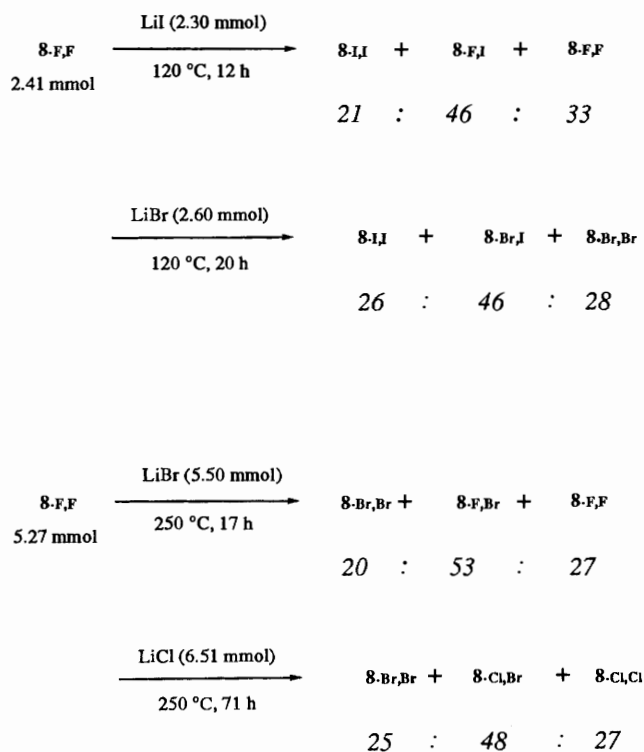
**Scheme 3**

ing methyl alkylamino-substituted carboxylates [10] and fractionally distilled with a dry sodium fluoride. Anhydrous lithium halides (Aldrich) were handled under a dry nitrogen atmosphere and further dried by heating *in vacuo* before use. Trifluoroacetyl fluoride (PCR), pentafluoropropionyl fluoride (PCR) and 3,3,5,5,5-pentafluoro-4-(trifluoromethyl)-2-oxapentane (Daikin) were used as received.

### General procedures

A conventional vacuum system, consisting of a Pyrex glass vacuum line equipped with a Heise Bourdon tube, was used to handle gases and volatile liquids. Standard PVT techniques or direct weighing were used to quantitative starting materials or products. Fractional condensation (trap-to-trap distillation) or gas chromatography was used for the purification of products. Analytical GLC work was carried out with a Gasukuro LL-75 modified gas chromatograph using 3-mm diameter stainless-steel columns packed with 25% Kel-F 90 on Chromosorb PAW. The carrier gas was helium in all cases. IR spectra were recorded on a Hitachi EPI-G3 spectrometer with a 7-cm glass cell equipped with KBr windows. $^1$H and $^{19}$F NMR spectra were obtained on a Hitachi R-90H spectrometer using CDCl$_3$ as a solvent. Chemical shifts for $^1$H and $^{19}$F NMR spectra were reported with respect to Me$_4$Si and CFCl$_3$, respectively. $J$ Values were given in Hz.

**Perfluoro(morpholinoacetyl) fluoride 1-F.** The acyl fluoride 1-F was synthesized by electrochemical fluorination of methyl morpholinoacetate, and fractionally distilled with a dry sodium fluoride (bp 74.5–76.0 °C); $\delta_F$(84.68 MHz; CDCl$_3$) 14.3 [1 F, CF$_2$C(=O)F], −85.9 [6 F,‡ OCF$_2$CF$_2$N and CF$_2$C(=O)F] and −91.9 (4 F, OCF$_2$CF$_2$N).

**Perfluoro(morpholinoacetyl) iodide 1-I.** A mixture of lithium iodide (0.39 g, 2.91 mmol) and 1-F (0.688 mmol) was heated at 120 °C for 17 h in a 30 cm$^3$ stainless steel reactor to give 1-I (91%); $\delta_F$(84.68 MHz; CDCl$_3$) −85.6 (4 F, OCF$_2$CF$_2$N), −86.1 {2 F, CF$_2$C(=O)I} and −91.1 (4 F, OCF$_2$CF$_2$N).

**Perfluoro(morpholinoacetyl) bromide 1-Br.** A mixture of lithium bromide (0.26 g, 2.99 mmol) and 1-F (0.691 mmol) was heated at 120 °C for 17 h in a 30 cm$^3$ stainless steel reactor to

give 1-Br (97%); $\delta_F$(84.68 MHz; CDCl$_3$) −85.2 [2 F, CF$_2$C(=O)Br], −85.7 (4 F, OCF$_2$CF$_2$N) and −91.4 (4 F, OCF$_2$CF$_2$N).

**Perfluoro(morpholinoacetyl) chloride 1-Cl.** A mixture of lithium chloride (0.12 g, 2.83 mmol) and 1-F (0.785 mmol) was heated at 120 °C for 63.5 h in a 30 cm$^3$ stainless steel reactor to give 1-Cl (96%); $\delta_F$(84.68 MHz; CDCl$_3$) −85.5 [2 F, CF$_2$C(=O)Cl], −85.7 (4 F, OCF$_2$CF$_2$N) and −91.5 (4 F, OCF$_2$CF$_2$N).

**Pentafluoropropanoyl halide 3-X.** $\delta_F$(84.68 MHz; CDCl$_3$) for 3-I; −80.9 (3 F, CF$_3$), −114.5 (2 F, CF$_2$): for 3-Br; −81.6 (3 F, CF$_3$) and −115.3 (2 F, CF$_2$).

**Perfluoro[3-(*N,N*-dimethylamino)propanoyl] fluoride 4-F.** The acyl fluoride 4-F was synthesized by electrochemical fluorination of methyl 3-(*N,N*-dimethylamino)propanoate, and fractionally distilled with a dry sodium fluoride (bp 67–74 °C); $\delta_F$(84.68 MHz; CDCl$_3$) 25.4 [1 F, CF$_2$C(=O)F], −52.9 (6 F, CF$_3$), −92.0 [2 F, CF$_2$CF$_2$C(=O)F] and −117.6 [2 F, CF$_2$CF$_2$C(=O)F].

**Perfluoro[3-(*N,N*-dimethylamino)propanoyl] iodide 4-I.** A mixture of lithium iodide (0.42 g, 2.80 mmol) and 4-F (1.59 mmol) was heated at 120 °C for 3 h in a 30 cm$^3$ stainless steel reactor to give 4-I (77%); $\delta_F$(84.68 MHz; CDCl$_3$) −52.7 (6 F, CF$_3$), −90.0 [2 F, CF$_2$CF$_2$C(=O)I] and −110.0 [2 F, CF$_2$-CF$_2$C(=O)I].

**Perfluoro[3-(*N,N*-dimethylamino)propanoyl] bromide 4-Br.** A mixture of lithium bromide (0.26 g, 2.99 mmol) and 4-F (1.59 mmol) was heated at 120 °C for 3 h in a 30 cm$^3$ stainless steel reactor to give 4-Br (76%); $\delta_F$(84.68 MHz; CDCl$_3$) −52.8 (6 F, CF$_3$), −90.4 [2 F, CF$_2$CF$_2$C(=O)Br] and −111.1 [2 F, CF$_2$CF$_2$C(=O)Br].

**Perfluoro[3-(*N,N*-dimethylamino)propanoyl]chloride 4-Cl.** A mixture of lithium chloride (0.12 g, 2.83 mmol) and 4-F (1.58 mmol) was heated at 120 °C for 3 h in a 30 cm$^3$ stainless steel reactor to give 4-Cl (34%); $\delta_F$(84.68 MHz; CDCl$_3$) −52.8 (6 F, CF$_3$), −90.6 [2 F, CF$_2$CF$_2$C(=O)Cl] and −112.8 [2 F, CF$_2$CF$_2$C(=O)Cl].

**3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propanoyl fluoride 6-F.** The acyl fluoride 6-F was synthesized from 3,3,5,5,5-pentafluoro-4-(trifluoromethyl)-2-oxapentane,[17] and fractionally distilled (bp 46–48 °C); $\delta_H$(90 MHz; CDCl$_3$) 1.79 (s); $\delta_F$(84.68 MHz; CDCl$_3$) 40.8 [1 F, sept, $J$ 9.93, C(=O)F] and −69.9 (6 F, d, $J$ 9.93, CF$_3$).

**3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propanoyl iodide 6-I.** A mixture of lithium iodide (0.439 g, 3.28 mmol) and 6-F (0.97 mmol) was heated at 120 °C for 23 h in a 30 cm$^3$ stainless steel reactor to give 6-I (57% based on consumed 6-F); $\delta_H$(90 MHz; CDCl$_3$) 1.76 (s); $\delta_F$(84.68 MHz; CDCl$_3$) −67.6 (s).

**3,3,3-Trifluoro-2-methyl-2-(trifluoromethyl)propanoyl bromide 6-Br.** A mixture of lithium bromide (0.262 g, 3.02 mmol) and 6-F (0.98 mmol) was heated at 250 °C for 22 h in a 30 cm$^3$ stainless steel reactor to give 6-Br (44% based on consumed 6-F); $\delta_H$(90 MHz; CDCl$_3$) 1.86 (s); $\delta_F$(84.68 MHz; CDCl$_3$) −68.3 (s).

**Bis(trifluoromethyl)carbamic fluoride 7-F.** The acyl fluoride 7-F was synthesized by electrochemical fluorination of *N,N*-dimethylformamide, and isolated in a trap cooled to −97.5 °C after having passed one at −38.5 °C; $\nu_{max}$(gas)/cm$^{-1}$ 1883s (C=O), 1372vs, 1348w, 1314vs, 1233vs, 1181w, 1031w, 996s, 754w, 729w and 708w; $\delta_F$(84.68 MHz; CDCl$_3$) 5.5 [1 F, sept, $J$ 17.37, C(=O)F] and −56.0 (6 F, d, $J$ 17.37, CF$_3$).

**Bis(trifluoromethyl)carbamic bromide 7-Br.** A mixture of lithium bromide (0.422 g, 4.86 mmol) and 7-F (0.139 g, 0.70 mmol) was heated at 200 °C for 13 days in a 30 cm$^3$ stainless steel reactor to give 7-Br (43%); $\nu_{max}$(gas)/cm$^{-1}$ 1796 (C=O); $\delta_F$(84.68 MHz; CDCl$_3$) −54.0 (s, CF$_3$).

**Bis(trifluoromethyl)carbamic chloride 7-Cl.** A mixture of lithium chloride (0.546 g, 12.9 mmol) and 7-F (0.177 g, 0.89 mmol) was heated at 200 °C for 22 days in a 30 cm$^3$ stainless steel reactor to give 7-Cl (37%); $\nu_{max}$(gas)/cm$^{-1}$ 1805 (C=O); $\delta_F$(84.68 MHz; CDCl$_3$) −54.6 (s, CF$_3$).

‡ The two signals, 4 F of OCF$_2$CF$_2$N and 2 F of CF$_2$C(=O)F, overlap.

**Tetrafluorobutanedioyl difluoride 8-F,F.** A mixture of sulfur tetrafluoride (30.03 mmol) and sodium tetrafluorobutanedioate (3.6 g, 15.38 mmol) was heated at 150 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-F,F** (2.35 g, 81%), isolated in a trap cooled to −78 °C; $\nu_{max}$(gas)/cm⁻¹ 1886vs (C=O), 1296s, 1234s, 1205s, 1132s, 1066s, 960s, 934w, 754w, 696w and 624w; $\delta_F$(84.68 MHz; CDCl₃) −119.1 [4 F, s, C$F_2$C(=O)F] and 25.3 [2 F, s, CF₂C(=O)$F$].

**Tetrafluorobutanedioyl diiodide 8-I,I.** A mixture of lithium iodide (0.972 g, 7.26 mmol) and **8-F,F** (0.578 g, 2.98 mmol) was heated at 120 °C for 3.5 h in a 30 cm³ stainless steel reactor to give **8-I,I** (96%); $\nu_{max}$(liq)/cm⁻¹ 1765vs (C=O), 1270s, 1149s and 724s; $\delta_F$(84.68 MHz; CDCl₃) −110.2 (s).

**Tetrafluorobutanedioyl fluoride iodide 8-F,I.** A mixture of lithium iodide (0.413 g, 3.09 mmol) and **8-F,F** (0.879 g, 4.53 mmol) was heated at 120 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-F,I** (55% based on consumed **8-F,F**); $\nu_{max}$(gas)/cm⁻¹ 1888s, 1853s, 1778s, 1295w, 1195s, 1115w and 1051s; $\delta_F$(84.68 MHz; CDCl₃) 24.6 [1 F, CF₂C(=O)$F$], −111.5 [2 F, IC(=O)CF₂] and −118.6 [2 F, C$F_2$C(=O)F].

**Tetrafluorobutanedioyl dibromide 8-Br,Br.** A mixture of lithium bromide (0.696 g, 8.01 mmol) and **8-F,F** (0.606 g, 3.12 mmol) was heated at 250 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-Br,Br** (88%); $\nu_{max}$(liq)/cm⁻¹ 1789vs (C=O), 1278s, 1218s, 1157vs, 863s and 746s; $\delta_F$(84.68 MHz; CDCl₃) −111.6 (s).

**Tetrafluorobutanedioyl bromide fluoride 8-F,Br.** A mixture of lithium bromide (0.211 g, 2.43 mmol) and **8-F,F** (0.575 g, 2.96 mmol) was heated at 250 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-F,Br** (56% based on consumed **8-F,F**); $\nu_{max}$(gas)/cm⁻¹ 1887s, 1852s, 1817s, 1791s, 1296s, 1192vs, 1116s, 1051s, 998w, 953w and 798s; $\delta_F$(84.68 MHz; CDCl₃) 24.8 [1 F, CF₂C(=O)$F$], −112.6 [2 F, BrC(=O)CF₂] and −118.5 [2 F, C$F_2$C(=O)F].

**Tetrafluorobutanedioyl dichloride 8-Cl,Cl.** A mixture of lithium chloride (0.522 g, 12.3 mmol) and **8-F,F** (0.558 g, 2.88 mmol) was heated at 330 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-Cl,Cl** (80%); $\nu_{max}$(gas)/cm⁻¹ 1799vs (C=O), 1233w, 1174s and 791vs; $\delta_F$(84.68 MHz; CDCl₃) −113.5(s).

**Tetrafluorobutanedioyl chloride fluoride 8-F,Cl.** A mixture of lithium chloride (0.101 g, 2.38 mmol) and **8-F,F** (0.482 g, 2.48 mmol) was heated at 330 °C for 5 h in a 30 cm³ stainless steel reactor to give **8-F,Cl** (71% based on consumed **8-F,F**); $\nu_{max}$(gas)/cm⁻¹ 1885vs, 1849s, 1796vs, 1296s, 1192vs, 1116vs, 1051vs, 1001s, 951w, 827vs and 716w; $\delta_F$(84.68 MHz; CDCl₃) 24.8 [1 F, CF₂C(=O)$F$], −114.3 [2 F, ClC(=O)CF₂] and −118.7 [2 F, C$F_2$C(=O)F].

**Tetrafluorobutanedioyl bromide iodide 8-Br,I.** A mixture of lithium bromide (0.35 g, 4.03 mmol), lithium iodide (0.35 g, 2.61 mmol) and **8-F,F** (0.511 g, 2.63 mmol) was heated at 120 °C for 20 h in a 30 cm³ stainless steel reactor to give **8-Br,I** (49%); $\delta_F$(84.68 MHz; CDCl₃) −110.4 [2 F, t, $J$ 4.24, IC(=O)CF₂] and −111.4 [2 F, t, $J$ 4.24, –CF₂C(=O)Br].

**Tetrafluorobutanedioyl bromide chloride 8-Cl,Br.** A mixture of lithium chloride (0.14 g, 3.03 mmol), lithium bromide (0.35 g, 4.30 mmol) and **8-F,F** (0.522 g, 2.69 mmol) was heated at 250 °C for 24 h in a 30 cm³ stainless steel reactor to give **8-Cl,Br** (46%); $\nu_{max}$(gas)/cm⁻¹ 1848 (C=O), 1799vs (C=O), 1227, 1172s, 1048, 787 and 765s; $\delta_F$(84.68 MHz; CDCl₃) −111.8 [2 F, BrC(=O)CF₂] and −113.3 [2 F, CF₂C(=O)Cl].

**Tetrafluorobutanedioyl chloride iodide 8-Cl,I.** A mixture of lithium chloride (0.14 g, 3.3 mmol), lithium iodide (0.36 g, 2.7 mmol) and **8-F,F** (0.686 g, 3.54 mmol) was heated at 80 °C for 90 h in a 30 cm³ stainless steel reactor to give **8-Cl,I** (41% based on consumed **8-F,F**); $\nu_{max}$(gas)/cm⁻¹ 1852s (C=O), 1803s (C=O), 1298s, 1192s, 1172s, 1135vs and 1050s; $\delta_F$(84.68 MHz; CDCl₃) −110.6 [2 F, t, $J$ 3.72, IC(=O)CF₂] and −113.2 [2 F, t, $J$ 3.72, CF₂C(=O)Cl].

**Perfluoro-3-iodopropanoyl bromide.** $\nu_{max}$(gas)/cm⁻¹ 1807s

(C=O), 1176s and 1093vs; $\delta_F$(84.68 MHz; CDCl₃) −57.3 [2 F, IC$F_2$CF₂C(=O)Br] and −104.8 [2 F, ICF₂C$F_2$C(=O)Br].

**Perfluoro-3-iodopropanoyl chloride.** $\nu_{max}$(gas)/cm⁻¹ 1805s (C=O) and 1095vs; $\delta_F$(84.68 MHz; CDCl₃) −60.6 [2 F, IC$F_2$CF₂C(=O)Cl], −106.6 [2 F, ICF₂C$F_2$C(=O)Cl].

**Perfluoro-3-iodopropanoyl fluoride.** $\delta_F$(84.68 MHz; CDCl₃) −62.1 [2 F, IC$F_2$CF₂C(=O)F] and −118.8 [2 F, ICF₂-C$F_2$C(=O)F].

**Heptafluoropentanedioyl dibromride 9-Br,Br.** $\delta_F$(84.68 MHz; CDCl₃) −110.9 [4 F, s, CF₂C$F_2$C(=O)Br] and −120.6 [2 F, s, C$F_2$CF₂C(=O)Br].

### Kinetic method

A typical experimental procedure is as follows: a mixture of lithium iodide (1.00 g, 7.47 mmol) and **4-F** (1.93 mmol) was heated in a 20 cm³ Pyrex tube at 100 °C (for 5, 10, 15 and 20 min) and then quenched at −78 °C. The products were isolated by a vacuum transfer from unchanged lithium iodide and the lithium fluoride formed, and the conversion was determined by GLC analysis. The pseudo-second-order rate constant was calculated from the slop of the plot of mol/([LiI]₀ − [**4-F**]₀)ln{[**4-F**]₀([LiI]₀ − [**4-I**])/([**4-F**]₀ − [**4-I**])/[LiI]₀} vs. $t$/min. Because this reaction was carried out between solid LiX and liquid/gas acyl fluoride, their true concentrations was indeterminant. Thus, molar amounts were used instead of the concentrations. The pseudo-second-order rate constant itself has no significance, but the relative value is enough to discuss the relative reactivities.

### Molecular orbital calculations

Molecular orbital calculations were conducted by a MOPAC program,[15] and a CAChe system (Sony Tektronix) was also used. The bond energy of the carbonyl carbon to halogen bond was calculated using ENPART-keyword by PM3 and AM1 Hamiltonian.

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