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A Convenient Synthesis of 2-Fluoro- and 2-Chloromalonic Esters Mediated by Hypervalent Iodine

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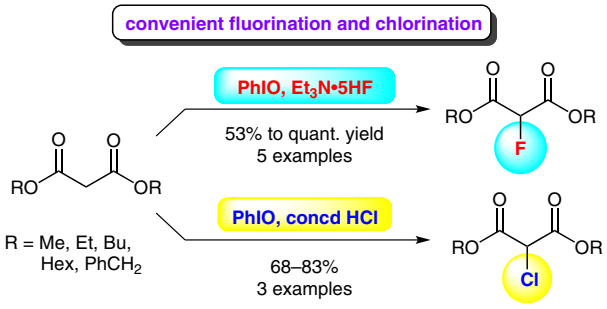

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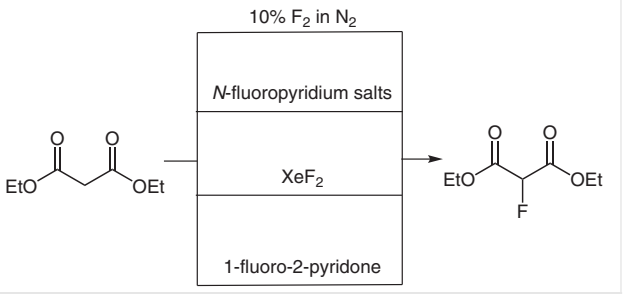
Abstract Direct fluorination of malonic esters with a reagent system of iodosylbenzene and $Et_3N{\cdot}5HF$ gave the corresponding 2-fluoromalonic esters in good to high yields. Direct chlorination using iodosylbenzene and hydrochloric acid also provided the 2-chloromalonates in high yields.

Key words 2-fluoromalonic esters, 2-chloromalonic esters, hydrogen fluoride, hydrochloric acid, iodosylbenzene

Monofluoromalonate derivatives are very attractive compounds because they are used as synthetic intermediates for pharmaceuticals and agricultural chemicals containing fluorine atoms. Very recently, Harsanyi and Sandford emphasized the importance of 2-fluoromalonic acid derivatives, reviewing that they are very versatile building blocks for introducing fluorine atoms into various aliphatic and heterocyclic compounds.[1] In spite of recognizing that monofluoromalonic esters are important for synthesis of fluorine-containing pharmaceuticals, the fluorination reaction of malonic esters is limited to some methods, as shown in Scheme 1. The fluorination reaction of malonic esters reported so far uses highly electrophilic fluorinating agents such as fluorine gas,[2] *N*-fluoropyridinium salts,[3] xenon difluoride,[4] and 1-fluoro-2-pyridone.[5] However, fluorine gas is highly toxic and explosive, and special cautions are required for the fluorination reactions. In addition, the fluorination reactions under basic conditions give difluorinated malonic esters as the major product.[6] Although *N*-fluoropyridinium salts,[7] xenon difluoride,[8] and 1-fluoro-2-pyridone[5] are useful fluorinating reagents, they are expensive. Since these fluorinating agents are prepared using fluorine gas, use of dangerous fluorine gas is inevitably needed. Therefore, the development of convenient and effective methods for preparing 2-fluoromalonic esters is still an important and challenging subject.



Scheme 1 Reported methods for preparing diethyl 2-fluoromalonate from diethyl malonate

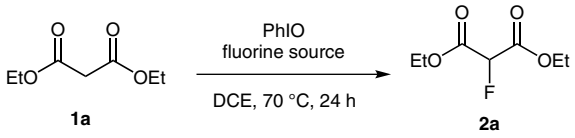
Although stepwise basic alcoholysis of hexafluoropropene[9] and fluorination of silyl ketene acetals[10] have been reported as the alternative method of the direct fluorination, they are not efficient due to the multistep processes involved. Conveniently, 2-fluoromalonic esters can be prepared from the corresponding 2-chloromalonic esters by exchanging chlorine and fluorine using HF reagents.[11]

The convenient fluorination reactions of carbonyl compounds mediated by hypervalent iodine compounds have been recently studied.[12] Since enols of the ketones generated in situ are fluorinated in these reactions, it is important for these reactions whether enolization of the carbonyl compound takes place easily. Generally the degree of enolization increases as the p*K* value decreases.[13] Therefore, it is expected that the degree of enolization decreases in the order: 1,3-diketones > β-keto esters > malonic esters. Judging from this result, the malonic ester is considered to show the lowest reactivity to the fluorination reaction among them.

In the previous fluorination reaction with the reagent prepared from iodosylbenzene and hydrofluoric acid, 1,3-dicarbonyl compounds and β-keto esters gave the fluorinated products in good yields, but this fluorination reaction could not be applied to monocarbonyl compounds such as acetophenone.[12a,b] After screening the fluorine sources, triethylamine·hydrogen fluoride complexes (Et_3N·nHF) showed higher reactivity than hydrofluoric acid and enabled the fluorination of acetophenone derivatives in the presence of iodosylbenzene.[12c] Encouraged by this finding, we decided to extend this reaction to malonic esters because the p*K* values are lower than those of acetophenones.[13] In this paper, we want to report for the first time the hypervalent iodine-mediated fluorination of malonic esters.

At the beginning, the reaction of diethyl malonate (**1a**) was conducted in order to find the optimal conditions for the fluorination. The results are given in Table 1. The fluorination of **1a** was carried out using 55% hydrofluoric acid as a fluorine source in the presence of iodosylbenzene (PhIO) in 1,2-dichloroethane (DCE) at 70 °C for 24 hours, in analogy with the reaction of 1,3-diketones or β-keto esters.[12a,b] However, the desired diethyl 2-fluoromalonate (**2a**) was formed only in 25% yield (Table 1, entry 1). Increasing the amount of PhIO to 2.5 equivalents did not improve the yield (entry 2). Although the fluorine source was replaced by Et_3N·3HF instead of 55% hydrofluoric acid, the yield of **2a** was decreased (entries 3 and 4). The use of Et_3N·5HF in the fluorination improved the yield of **2a** to 41% (entry 5). Increasing the amount of PhIO to 2 equivalents drastically enhanced the yield of **2a** (80%) (entry 6). Finally, the use of 2.5 equivalents of PhIO resulted in quantitative formation of **2a** (entry 7). The reaction using pyridine·HF complex decreased the yield of **2a** (entry 8). Furthermore, we examined a 10 mmol-scale reaction. When the reaction using 10 mmol of **1a** was conducted at 70 °C for 48 hours, **2a** was isolated in 56% yield by column chromatography on silica gel (entry 9).

Table 1 Optimization of Fluorination of Diethyl Malonate[a]



1a **2a**

Entry	PhIO (mmol)	Fluorine source (mmol)	Yield (%)[b]
1	1.2	55% aq HF (20 mmol HF)	25
2	2.5	55% aq HF (20 mmol HF)	24
3	1.2	Et_3N·3HF (6.67 mmol)	9
4	2	Et_3N·3HF (6.67 mmol)	11
5	1.2	Et_3N·5HF (4 mmol)	41
6	2	Et_3N·5HF (4 mmol)	81
7	2.5	Et_3N·5HF (4 mmol)	100 (85)
8	2.5	pyridine·$(HF)_x$ (20 mmol HF)	49
9[c]	25	Et_3N·5HF (40 mmol)	(56)

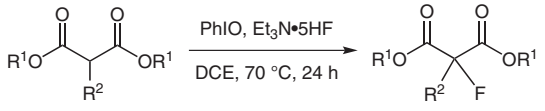
[a] Conditions: **1a** (1 mmol), PhIO, a fluorine source (20 equiv HF), DCE (2 mL), 70 °C, 24 h.
[b] Yields were determined by ^{1}H NMR spectroscopy using an internal standard. Isolated yield is given in parenthesis.
[c] The reaction was conducted using **1a** (10 mmol) and DCE (20 mL) for 48 h.

With the optimal conditions of fluorination reaction of diethyl malonate having been determined, the reaction of other malonate esters was then examined to explore the scope of the substrate in this fluorination reaction. The fluorination reaction of other malonate esters such as dimethyl malonate (**1b**), dibutyl malonate (**1c**), dihexyl malonate (**1d**), and dibenzyl malonate (**1e**) was conducted and the results are given in Table 2. When these malonate esters were subjected to the fluorination reaction under the same conditions, the 2-fluoromalonates **2** were formed in 53–85% yields. These results suggest that other malonate esters also undergo the fluorination reaction efficiently. However, in the case of a substituted malonate ester, the present fluorination reaction suffered from steric effect. Actually, the fluorination of diethyl 2-methylmalonate (**1f**) decreased the yield of the fluorinated product **2f** to 18%. The fluorination of other substrates such as ethyl malonate monoamide, ethyl cyanoacetate, and ethyl phenylsulfonylacetate was attempted, but the fluorinated product was formed only in a low yield.

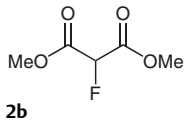
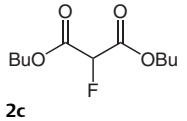
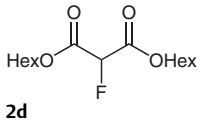
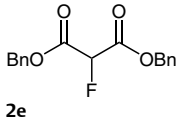
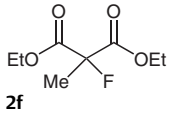
The fluorination of malonic esters promoted by hypervalent iodine is considered to proceed with a mechanism similar to the proposed one previously in the fluorination of 1,3-dicarbonyl compounds.[12a,b] In this fluorination reaction, iodosylbenzene is transformed into difluoroiodobenzene in the presence of HF. Since the reaction is conducted under acidic conditions, the enolization of malonic esters is considered to be easier than that under neutral conditions. Therefore, HF is not only essential for generation of $PhIF_2$, but also promotes the enolization of malonic esters. The enols of malonic esters react with difluoroiodobenzene to give the corresponding 2-fluoromalonic esters **2**. Under the present reaction conditions, monofluorinated malonic esters **2** were selectively formed. The ^{19}F NMR of the reaction mixture obtained from the reaction of **1a** showed a tiny peak at –112.4 ppm, which might be assignable to diethyl 2,2-difluoromalonate.[10] However, the integral was only 3% as compared with that of **2a**. Probably, the yield is 1–2% at most, even if diethyl difluoromalonate had formed.

As an alternative method for direct fluorination, 2-fluoromalonic esters were prepared from 2-chloromalonic esters using HF reagents in high yields.[11] Therefore, it is important to study the synthesis of 2-chloromalonic esters since the chlorination using hypervalent iodine reagents has not been applied to malonic esters.[14] Thus, a convenient

Table 2 Fluorination of Malonic Esters[a]

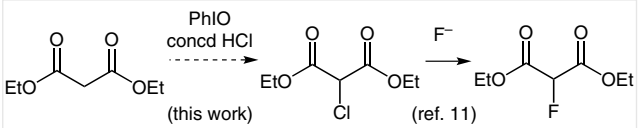


1 **2**

Entry	R^1	R^2	Product **2**	Yield (%)[b]
1	Me	H	 **2b**	53 (45)
2	Bu	H	 **2c**	85 (74)
3	Hex	H	 **2d**	61 (51)
4	Bn	H	 **2e**	58 (33)
5	Et	Me	 **2f**	18

[a] Conditions: **1** (1 mmol), PhIO (2.5 mmol), Et_3N·5HF (4 mmol), DCE (2 mL), 70 °C, 24 h.
[b] Yields were determined by ^1H NMR spectroscopy using an internal standard. Values in parentheses refer to the isolated yields.

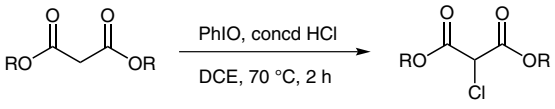
chlorination of malonic esters was explored with PhIO and a commercially available hydrochloric acid, as shown in Scheme 2.



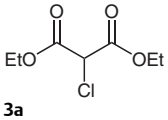
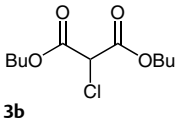
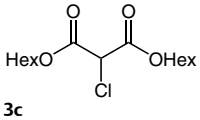
Scheme 2 Chlorination of diethyl malonate for diethyl 2-fluoromalonate

Using the optimized conditions obtained by the fluorination reaction, the reaction of **1a** with concentrated hydrochloric acid was examined. When the reaction of **1a** with concentrated HCl was conducted in the presence of PhIO at 70 °C for two hours, diethyl 2-chloromalonate (**3a**) was obtained in 68% isolated yield (Table 3, entry 1). Increasing the reaction time to 24 hours decreased the yield to 50% (entry 2). Similarly, the chlorination reaction of **1b** and **1c** gave the corresponding 2-chloromalonates **3b** and **3c** in 83 and 80% isolated yield, respectively (entries 3 and 4). Thus, the present chlorination method was helpful in supplying the starting materials for the alternative fluorination method using the chloride exchange.

Table 3 Chlorination of Malonic Esters[a]



1 **3**

Entry	R	Product **3**	Yield (%)[b]
1 2[c]	Et	 **3a**	68 50
3	Bu	 **3b**	83
4	Hex	 **3c**	80

[a] Conditions: **1** (0.5 mmol), PhIO (1.25 mmol), concd HCl (5 mmol), DCE (7.5 mL), 70 °C, 2 h.
[b] Isolated yields.
[c] The reaction was conducted for 24 h.

In summary, we have demonstrated that malonic esters could be efficiently fluorinated with a convenient fluorinating reagent composed of PhIO and Et_3N·5HF to form the corresponding 2-fluoromalonic esters. This method has been applied to the chlorination reaction because 2-chloromalonic esters are useful as the starting materials for the alternative fluorination reaction. Due to increasing the importance of fluoromalonic esters as a building block, this convenient procedure is useful in synthesis of pharmaceuticals and agricultural chemicals containing fluorine atoms.

All solvents and starting materials were used during the research work as received without further purification unless otherwise indicated. ^1H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{19}F NMR (376 MHz) were recorded on an Agilent 400-MR NMR spectrometer in $CDCl_3$ solution. The chemical shifts for ^{19}F NMR were determined using hexafluorobenzene as an internal standard. High-resolution mass spectra were measured by the Analytical Center, Institute for Materials Chemistry and Engineering, Kyushu University. Column chromatographic separation was carried out using Silica Gel 60, spherical (Kanto Chemical Co.). Pre-coated plates (silica gel 60 F254, Merck) were used for TLC examination.

Fluorination of Malonic Esters 1; General Procedure

PhIO (550 mg, 2.5 mmol), $Et_3N{\cdot}5HF$ (800 mg, 4 mmol), and DCE (1 mL) were placed in a Teflon test tube. After stirring at r.t. for 15 min, the appropriate malonic ester **1** (1 mmol) and DCE (1 mL) were added. The test tube was sealed with a septum rubber and heated at 70 °C for 24 h with stirring. The reaction mixture was neutralized with aq $NaHCO_3$ and the product was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The product was purified by column chromatography on silica gel with hexane–CH_2Cl_2 as eluent.

Diethyl 2-Fluoromalonate (2a)[2a]

Yield: 151 mg (85%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, *J* = 7 Hz, 6 H, CH_3), 4.33 (q, *J* = 7 Hz, 4 H, CH_2), 5.28 (d, *J* = 48 Hz, 1 H, CHF).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 62.6, 85.2 (d, *J* = 195 Hz), 163.9 (d, *J* = 24 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –195.19 (d, *J* = 48 Hz).

Dimethyl 2-Fluoromalonate (2b)[15]

Yield: 67.5 mg (45%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 6 H, CH_3), 5.34 (d, *J* = 49 Hz, 1 H, CHF).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 53.3, 85.0 (d, *J* = 196 Hz), 164.2 (d, *J* = 24 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –195.47 (d, *J* = 49 Hz).

Dibutyl 2-Fluoromalonate (2c)[16]

Yield: 173 mg (74%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7 Hz, 6 H, CH_3), 1.35–1.42 (m, 4 H, CH_2), 1.64–1.71 (m, 4 H, CH_2), 4.28 (dt, *J* = 4, 6 Hz, 4 H, CH_2), 5.29 (d, *J* = 48 Hz, 1 H, CHF).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 18.8, 30.3, 66.4, 85.2 (d, *J* = 195 Hz), 164.0 (d, *J* = 24 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –195.48 (d, *J* = 48 Hz).

Dihexyl 2-Fluoromalonate (2d)

Yield: 148 mg (51%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (t, *J* = 7 Hz, 6 H, CH_3), 1.31–1.38 (m, 12 H, CH_2), 1.65–1.72 (m, 4 H, CH_2), 4.26 (dt, *J* = 4, 7 Hz, 4 H, CH_2), 5.28 (d, *J* = 48 Hz, 1 H, CHF).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 22.4, 25.2, 28.2, 31.2, 66.6, 85.2 (d, *J* = 195 Hz), 164.0 (d, *J* = 24 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –195.14 (d, *J* = 48 Hz).

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{28}FO_4$: 291.1972; found: 291.1972.

Dibenzyl 2-Fluoromalonate (2e)[17]

Yield: 100 mg (33%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.24 (s, 4 H, CH_2), 5.36 (d, *J* = 48 Hz, 1 H, CHF), 7.29–7.35 (m, 10 H, 2 × C_6H_5).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 68.2, 85.2 (d, *J* = 196 Hz), 128.4, 128.65, 128.7, 134.2, 163.6 (d, *J* = 24 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –195.32 (d, *J* = 48 Hz).

Diethyl 2-Fluoro-2-methylmalonate (2f)[10]

Yield: 18%; colorless oil. This compound could not be isolated purely and the yield was determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.31 (t, *J* = 7 Hz, 6 H, 2 × CH_2CH_3), 1.76 (d, *J* = 22 Hz, 3 H, CH_3), 4.27 (q, *J* = 7 Hz, 4 H, 2 × CH_2).

^{19}F NMR (376 MHz, $CDCl_3$): δ = –157.53 (d, *J* = 22 Hz).

Chlorination of Malonic Esters 1; General Procedure

PhIO (275 mg, 1.25 mmol) and DCE (1.5 mL) were placed in a 15 mL test tube. After adding concd HCl (5 mmol), additional DCE (2 mL) was introduced. After stirring at r.t. for 15 min, the appropriate malonic ester **1** (0.5 mmol) and DCE (4 mL) were added. The test tube was sealed with a septum rubber and heated at 70 °C for 2 h with stirring. The reaction mixture was neutralized with aq $NaHCO_3$ and the product was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (20 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The product was purified by column chromatography on silica gel with hexane–CH_2Cl_2 as eluent.

Diethyl 2-Chloromalonate (3a)[18]

Yield: 66.2 mg (68%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (t, *J* = 7 Hz, 6 H, CH_3), 4.31 (q, *J* = 7 Hz, 4 H, CH_2), 4.85 (s, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.8, 55.4, 63.1, 164.5.

Dibutyl 2-Chloromalonate (3b)

Yield: 104 mg (83%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7 Hz, 6 H, 2 × CH_3), 1.36–1.42 (m, 4 H, 2 × CH_2), 1.63–1.70 (m, 4 H, 2 × CH_2), 4.22–4.26 (m, 4 H, 2 × CH_2), 4.85 (s, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.5, 18.9, 30.3, 55.5, 66.9, 164.6.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{20}ClO_4$: 251.1050; found: 251.1050.

Dihexyl 2-Chloromalonate (3c)

Yield: 123 mg (80%); colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (t, *J* = 7 Hz, 6 H, 2 × CH_3), 1.31–1.37 (m, 12 H, 6 × CH_2), 1.64–1.71 (m, 4 H, 2 × CH_2), 4.23 (t, *J* = 7 Hz, 4 H, 2 × CH_2), 4.85 (s, 1 H, CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.4, 25.2, 28.2, 31.2, 55.5, 67.2, 164.5.

HRMS (FAB): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{28}ClO_4$: 307.1676; found: 307.1674.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378747.

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