# Difluoroiodomethane: Practical Synthesis and Reaction with Alkenes

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Difluorocarbene precusors **2**, $FSO_2CF_2COF$, $FSO_2CF_2CO_2H$, $FSO_2CF_2CO_2Me$ and $XCF_2CO_2M$ react with KI to give $HCF_2I$ **1** in high yields; a smooth reaction of **1** with alkenes or alkynes in the presence of $Na_2S_2O_4$ gives the difluoromethylated adducts in good yields.

In difluorocarbene chemistry, difluoromethanes, $HCF_2Cl$, $HCF_2Br$, $HCF_2I$ are important precusors.[1] However, iododifluoromethane, $HCF_2I$ **1**, has received little attention.[2–4] In comparison with $HCF_2Cl$ and $HCF_2Br$, reduced application of **1** may be ascribed to its availability. Previously, **1** was prepared inconveniently by fluorination of iodoform with $HgF^5$ or hydrolysis of bromodifloromethyltriphenyl phosphonium bromide $[Ph_3PCF_2Br]^+Br^-$ in the presence of an excess of NaI.[6]

We found that **1** can be obtained from the available difluorocarbene precusors **2**, *i.e.* $FSO_2CF_2CO_2H$,[7a] $FSO_2CF_2CO_2Me$,[7b] $BrCF_2CO_2K$, $ClCF_2CO_2K$, $BrCF_2CO_2H$, $ClCF_2CO_2H$, $FSO_2CF_2COF$ with potassium iodide. Treatment of **2** with KI under appropriate conditions gave **1**, see Table 1.†

$$\underset{\mathbf{2}}{XCF_2COY} + KI \longrightarrow \underset{\mathbf{1}}{HCF_2I} + CO_2 + KF \qquad (1)$$

| | |
|---|---|
| **2a** | $FSO_2CF_2COF$ |
| **b** | $FSO_2CF_2CO_2H$ |
| **c** | $FSO_2CF_2CO_2Me$ |
| **d** | $BrCF_2CO_2K$ |
| **e** | $ClCF_2COOK$ |
| **f** | $BrCF_2CO_2H$ |
| **g** | $ClCF_2CO_2H$ |

**Table 1** Reaction of **2** with potassium iodide (KI : **2** = 2 : 1)

| Entry | **2** | Solvent | Time/ h | Temp./ °C | Yield (%)[a] |
|---|---|---|---|---|---|
| 1 | **a**[b] | MeCN[c] | 0.5 | 30–40 | 80 |
| 2 | **b** | MeCN[c] | 5 | 40 | 80 |
| 3[d] | **c** | $Bu^nOH$ | 5 | 60 | 73 |
| 4[e] | **d** | DMF[c] | 6 | 80 | 74 |
| 5[e] | **e** | DMF[c] | 6 | 80 | 75 |
| 6[e] | **f** | DMF[c] | 6 | 80 | 77 |
| 7[e] | **g** | DMF[c] | 7 | 90 | 70 |

[a] Isolated yields based on **2**, besides **1**, $CO_2$, $SO_2$ (for **2a**, **2b** and **2c**) were identifed by GC-MS. [b] $NaHCO_3$ : KI : **2a** = 1 : 2 : 1. [c] Containing a trace of water. [d] $Bu^nOCF_2H$, a difluorocarbene insertion product, was also obtained in 5% yield (determined by $^{19}F$ NMR spectroscopy) based on **2**. [e] CuI was added, KI : CuI : **2** = 2 : 1 : 1.

Similar to those reported previously,[8] the mechanism of the formation of **1** is that the difluorocarbene generated from these precusors combines with the iodide ion to give $ICF_2^-$, which is captured by a proton donor, *e.g.* HI, $H_2O$ or $Bu^nOH$ to afford the final product **1**.

There was no record on the reaction of **1** with ordinary alkenes or alkynes except the photochemical reaction of **1** with ethylenes.[2] It was found better to use Huang's sulfinatodehalogenation method[9] to synthesize the difluoromethylated products from alkenes or alkynes under very mild conditions. Treatment of **1** with alkenes **3** in the presence of sodium dithionite in aqueous MeCN at room temp. for 6–15 h gave the adducts **4** in good yields, eqn. (2).†

$$\underset{\mathbf{1}}{HCF_2I} + \underset{\mathbf{3}}{R^1CH{=}CHR^2} \xrightarrow[\text{room temp.}]{Na_2S_2O_4\text{–}NaHCO_3,\ MeCN\text{–}H_2O,} \underset{\mathbf{4}}{HCF_2CH_2CHIR} \qquad (2)$$

**3**:**a**:$R^1 = H$, $R^2 = Bu^n$; **b**:$R^1 = H$, $R^2 = n\text{-}C_5H_{11}$; **c**:$R^1 = H$, $R^2 = MeCO_2CH_2CH_2\text{–}$; **d**:$R^1 = H$, $R^2 = CH_2{=}CHCH_2OCH_2\text{–}$**e**:$R^1 = R^2 = \text{–}(CH_2)_2\text{–}$

Similarly, alkynes **5** reacted with **1** gave alkenes **6**, eqn. (3). All the results are listed in Table 2.

$$\underset{\mathbf{1}}{HCF_2I} + \underset{\mathbf{5}}{HC{\equiv}CR} \xrightarrow[\text{room temp.}]{Na_2S_2O_4\text{–}NaHCO_3,\ MeCN\text{–}H_2O,} \underset{\mathbf{6}\,(E/Z)}{HCF_2CH{=}CIR} \qquad (3)$$

**5**:**a**: $R = Bu^n$; **b**: $R = Ph$

**Table 2** Results of **1** with alkenes **3** and alkynes **5**[a]

| Entry | **3** or **5** | Time/h | Yield (%)[b] | E:Z[c] |
|---|---|---|---|---|
| 1 | **3a** | 14 | 86 | |
| 2 | **3b** | 15 | 70 | |
| 3 | **3c** | 6.5 | 60 | |
| 4 | **3d** | 12 | 69[d] | |
| 5 | **3e** | 12 | 50 | 1:3 |
| 6[e] | **5a** | 6 | 64 | 1:2 |
| 7 | **5b** | 6 | 60 | 1:3 |

[a] All the reactions were carried out in MeCN–$H_2O$ (1 : 1.2 v/v) at room temp., **1**:**3** or **5**:$Na_2S_2O_4$:$NaHCO_3$ = 1:1:2:2. [b] Isolated yields based on **1**. The structures of all products were identifed by elemental analyses, IR, $^{19}F$ NMR, $^1H$ NMR and mass spectroscopy. [c] Determined by $^{19}F$ NMR spectroscopy. [d] **4a**, $HCF_2CH_2\overline{CHCH_2OCH_2C}HCH_2I$. [e] Reaction temp. 40°C.

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## Footnote

† *Typical procedure* for the preparation of **1** and **4**: For **1**: KI (93 g, 0.6 mol) and MeCN (250 ml) were placed in a 500 ml three-necked round-bottomed flask equipped with thermometer and magnetic stirrer. When the mixture was heated to 40°C, **2b** (53 g, 0.3 mol in 20 ml MeCN) was added dropwise during 2 h. Then the reaction temp. was raised to 60°C and heated for another 2 h. On completion **1** was distilled out and collected in a trap cooled to −78°C and further purification through trap to trap distillation gave 42 g of pure **1** (80%): bp 21–23°C (20°C),[10] $^{19}F$ NMR $\delta_F$: ($CFCl_3$) −68 (d, *J* 56 Hz), $\delta_H$: 8.1, MS *m*/*z* 178 ($M^+$, 100), 51 ($M^+ - I$, 25), 127 ($I^+$, 64).

Preparation of **4b**: Hept-1-ene (0.98 g, 10 mmol), $Na_2S_2O_4$ (3.48 g, 20 mmol), $NaHCO_3$ (1.68 g, 20 mmol), 6 ml MeCN, 7 ml $H_2O$ and **1** (1.78 g, 10 mmol) were placed in a 100 ml two-necked flask equipped with magnetic stirrer and thermometer. After stirring at room temp. for 15 h, the reaction mixture was treated with 20 ml water, the aqueous layer was extracted with diethyl ether (3 × 20 ml). After usual work-up **4b** (1.93 g, 70%) was obtained, bp 88–90°C $^{19}F$ NMR

$\delta_F$: −117 (m), $\delta_H$: 5.97 (dddd, *J* 54.9, 54.3, 6.42, 3.05 Hz, 1H), 4.05 (m, 1H), 2.3–0.8 (13H); MS *m*/*z*: 149 ($M^+ - I$, 18), 127 ($I^+$, 10), 65 ($HCF_2 - CH_2^+$, 12), 57 ($C_4H_9^+$, 100), IR: ν/cm$^{-1}$ 1480–1380, 1480–1380, 1180–1080.

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