A SIMPLE METHOD FOR PREPARING DIFLUORODIIODOMETHANE FROM DIFLUORO(FLUOROSULFONYL)ACETYL FLUORIDE

Ji-Chang XIAO, Jian-Xin DUAN, An-Rong LI, Yong GUO
and Qing-Yun CHEN[1,]*

Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, PR China;
e-mail: [1] chenqy@pub.sioc.ac.cn

Received May 14, 2002
Accepted June 21, 2002

Dedicated to the memory of Professor Miloš Hudlický.

Difluorodiiodomethane is prepared in 60% yield by the reaction of difluoro(fluorosulfonyl)acetyl fluoride with I_2/KI in the presence of a catalytic amount of SiO_2 in acetonitrile at 60–65 °C.

Keywords: Difluorodiiodomethane; Difluoro(fluorosulfonyl)acetyl fluoride; Silica gel; Iodine; Potassium iodide; Iodination.

Recently, the chemistry of difluorodiiodomethane (CF_2I_2, **1**) has been developed significantly since its synthesis was improved in our laboratory ten years ago. Like its photo- or dibenzoyl-peroxide-induced reactions with alkenes reported first by Dolbier *et al.*[1], **1**, as an difluoroiodomethyl radical source, can add to electron-rich olefins in the presence of $[PdCl_2(PPh_3)_2]$ [2], $[Pd(PPh_3)_4]$ [2], $Na_2S_2O_4$ [3], Fe [4] or unactivated Zn [4]. Lead tetraacetate[5] or high temperature (185 °C)[6] is even able to promote the addition reaction of **1** to poly- or perfluoroalkenes. Compound **1** was also shown to be a trifluoromethylating agent for aza-aromatic compounds and enamines when irradiated in DMF[7]. Different from CF_2Br_2, diethyl (difluoroiodomethyl)phosphonate could be readily obtained in nearly quantitative yield by simple treatment of **1** with triethyl phosphite in diethyl ether[8]. However, the desired vinyl iodides, $ICF_2CH{=}CIR$, derived from the addition reaction of **1** to alkynes, could not be obtained through the initiation with either $Pb(OAc)_4$ [5] or aqueous hydrogen peroxide in acetone[9]. Instead, non-fluorinated compounds, β-iodo-α,β-unsaturated carboxylic esters and acids were formed. Unlike other difluorocarbene precursors such as CF_2Cl_2 [10], CF_2Br_2 [10],

doi:10.1135/cccc20021320

CF_2BrCl[10], treatment of **1** with phenoxides in DMF at room temperature gave $ArOCF_2I$ only in 7–15% yields, the diphenyl carbonates being the major products, while with benzenethiolates afforded difluoromethylene derivatives ($ArSCF_2I$, $ArSCF_2SAr$ and $ArSCF_2H$) also in low yields[11].

In principle, **1** can be prepared by the addition of difluorocarbene to iodine. However, previous methods from various difluorocarbene precursors suffered from low yields (*ca* 20%)[12]. The fluorination of CI_4 with HgF_2 gives **1**, but the yields are unsatisfactory (27%)[1]. It was found that using methyl bromodifluoroacetate or potassium bromodifluoroacetate as difluorocarbene source, **1** can be obtained in 50–60% yield with KI/I_2 in the presence of a catalytic amount of CuI in DMF[13]. A higher yield (85%) of **1** was also reported on heating 1,2-epoxyhexafluoropropane with I_2 in autoclave at 185 °C[14].

In order to investigate further the reactions of **1**, it seems necessary to have a simpler way to synthesize **1**, because the starting materials of the above mentioned approaches are not readily available or a special equipment is needed. Fortunately, a synthetic method for **1** from difluoro(fluorosulfonyl)acetyl fluoride(FSO_2CF_2COF, **2**) was found to serve the purpose. Using **2**, **1** can be prepared on 100 g scale in a ordinary glassware. We present herein the results.

EXPERIMENTAL

Difluoro(fluorosulfonyl)acetyl fluoride was obtained from Engineering Research Center in Organic Synthesis, Chinese Academy of Sciences. Acetonitrile (CH_3CN) was dried over phosphorus pentoxide and freshly distilled prior to use. Potassium iodide (KI) was dried over a direct flame. Silica gel (SiO_2, 300–400 mesh) was baked in an oven at 120 °C for 6 h. ^{19}F NMR spectra (δ, ppm) were recorded on a Bruker AM-300 (282 MHz) spectrometer using $CFCl_3$ as external standard, upfield shifts being designated as negative. Mass spectra were taken on a Hewlett–Packard HP-5989A spectrometer.

Difluorodiiodomethane (**1**)

A solution of dry KI (0.8 mol, 132.8 g) and I_2 (0.8 mol, 203.2 g) in CH_3CN (600 ml) was placed in a 1 000 ml three-necked flask fitted with a dropping funnel, a water condenser connected to a dry ice condenser, a thermometer and a magnetic stirrer. To the solution dry silica gel (0.06 mol, 3.6 g) was added during stirring. After heating the content to 60–65 °C, compound **2** (1.1 mol, 198 g) was slowly added under vigorous stirring during 8 h for finishing the reaction. Then the mixture was kept for additional time until the ^{19}F NMR spectroscopy showed the end of the reaction (*ca* 2 h). Simple distillation gave a solution of **1** in CH_3CN which then was poured into H_2O (2 l). The oil was separated, washed with H_2O (5 × 50 ml) and dried over anhydrous Na_2SO_4. About 171 g (0.56 mol, 70%) of crude product **1** was obtained. Redistillation gave 148 g (0.49 mol, 61%); b.p. 101 °C. MS, *m/z*: 304 (8.6, M^+), 285 (1.1, CFI_2), 254 (100, I_2), 177 (30.3, CF_2I), 158 (1.4, CFI), 127 (75.7, I), 50 (2.3, CF_2). ^{19}F NMR ($CDCl_3$): 18.6 (s)[1].

RESULTS AND DISCUSSION

Difluoro(fluorosulfonyl)acetyl fluoride (**2**) is one of the starting materials for producing the commercial ion-exchange resin Nafion-H [15]. Compound **2** is readily available or can be prepared by the reaction of $CF_2=CF_2$ with SO_3[16]. In our laboratory, a variety of its derivatives, such as HCF_2SO_2R [(R = F, OC_6H_5, $OCH_2CF_2CF_2H$, OC_6F_5, HCF_2O, $N(CH_3)C_6H_5$)][17], $CH_3O_2CCF_2SO_2R$ (R = F, OC_6H_5, $HCF_2CF_2CF_2CF_2CHO$)[17], HCF_2SO_3H [18] and $FO_2SCF_2CO_2SiMe_3$ [19] were prepared as difluorocarbene precursors, which can generate CF_2: under neutral, alkaline or even strongly acidic conditions. Interestingly, **2** was recently found to be a difluorocarbene source, from which **1** could be synthesized in the presence of a catalytic amount of silica gel.

Slow dropwise addition of **2** to a stirred solution of I_2/KI in CH_3CN in the presence of 5–10 mole % of silica gel at 60–65 °C in several hours gave **1**, after usual work-up, in 60–70% yield.

$$\underset{\mathbf{2}}{FSO_2CF_2COF} + KI + I_2 \xrightarrow[\substack{SiO_2 \\ 60\text{–}65\ ^{\circ}C}]{CH_3CN} \underset{\mathbf{1}}{CF_2I_2}$$

The presence of SiO_2 is essential for the reaction; in its absence, the acid fluoride did not decompose. A 5 – 10 mole % of SiO_2 relative to I_2 is the optimum ratio. Using one equivalent or more results not only in dramatically decreasing yield but also in formation of an unidentified by-product (δ 42.8 ppm). In the absence of KI, the reaction did not occur. It was found that both the KI/I_2 ratio 1 : 1 and the concentration of I_3^- in CH_3CN 1.3–1.5 mol l^{-1} are necessary, otherwise the reaction is either too fast or too slow and the yields become lower. The results of the effect of the reactant ratios on the yield are listed in Table I.

The exact mechanism is not completely understood yet although the generation of CF_2 resulting from SiO_2 induced decomposition of **2** seems to be beyond doubt. Other silicon compounds, such as $Si(OEt)_4$, silicone and Al_2O_3 can also trigger the same reaction under similar conditions, but the yields are not better (32, 31 and 45%, respectively).

In conclusion, we have developed a new, simple method for the synthesis of difluorodiiodomethane from readily available difluoro(fluorosulfonyl)acetyl fluoride.

TABLE I
The effects of the reactant ratios on the yield of **1**

Entry	FSO_2CF_2COF	I_2	KI	SiO_2	Yield, %[a]
1	2	1	1	1.6	10
2	1.7	1.3	1.3	1	12
3	2.4	1	1	0	0
4	24	10	10	1	59
5	13	10	10	1	57
6	12	10	10	1	58
7	11	10	10	1	53
8	10	10	10	1	61
9	7	10	10	1	62[b]
10	20	10	5	1	0
11	11	10	0	1	0

[a] Isolated yield based on I_2; [b] isolated yield based on FSO_2CF_2COF.

We thank the National Science Foundation of China for financial support of this work.

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