ELSEVIER

Journal of Fluorine Chemistry 81 (1997) 99-101

JOURNAL OF FLUORINE CHEMISTRY

Iron and zinc-induced electron-transfer reaction of difluorodiiodomethane with alkenes [1]

An-Rong Li, Qing-Yun Chen *

Shanghai Instituent of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, People's Republic of China

Received 26 November 1995; accepted 29 June 1996

Abstract

Treatment of difluorodiiodomethane with electron-rich or electron-deficient alkenes in the presence of zinc or iron results in the formation of difluoroiodomethylated products. An electron-transfer mechanism is proposed.

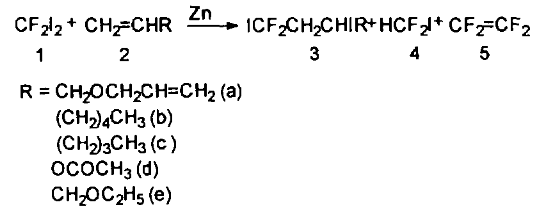
Keywords: Difluorodiiodomethane; Alkenes; Addition reaction; Difluoroiodomethylated compounds; Single-electron transfer; Metal

1. Introduction

The addition reaction of perfluoroalkyl iodides, R_fI, with alkenes is one of the most important procedures to synthesize commercial fluorocarbon intermediates and products [1]. However, the simple analogue, difluorodiiodomethane **1**, has been much less developed, probably because this reagent was difficult to prepare [2]. The only report on compound **1** was involved with its photo-or benzoyl-peroxide induced reactions with alkenes [3]. After our finding of a simple, good approach to prepare **1** [4], we were attracted to investigate its properties as a difluorocarbene or difluoroiodomethyl radical source. Very recently, we also found that **1** can be used as a trifluoromethylating agent for aza-aromatic compounds and enamines [5] when irradiated in DMF. Herein, we report its reaction with alkenes in the presence of zinc or iron powder.

2. Results and discussion

Under a nitrogen atmosphere, adding difluorodiiodomethane **1** to a mixture of alkenes **2** and zinc powder (**1**:**2**:Zn = 1:3:1) at 0 °C then 40–50 °C for 1–2 h gave the adducts **3** with a small amount of HCF_2I and $CF_2{=}CF_2$ (see Scheme 1). The results are listed in Table 1.



$$\underset{1}{CF_2I_2} + \underset{2}{CH_2{=}CHR} \xrightarrow{Zn} \underset{3}{ICF_2CH_2CHIR} + \underset{4}{HCF_2I} + \underset{5}{CF_2{=}CF_2}$$

$R = CH_2OCH_2CH{=}CH_2$ (a)
$(CH_2)_4CH_3$ (b)
$(CH_2)_3CH_3$ (c)
$OCOCH_3$ (d)
$CH_2OC_2H_5$ (e)

Scheme 1.

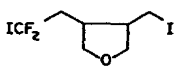
Table 1
Reaction of **1** with **2** in the presence of Zn at 0 °C then 40–50 °C for 1–2 h under N_2 [a]

Entry	**2**	Product	Yield (%) [b]
1	**2a**	**3a** [c]	73
2 [d]	**2a**	**3a**	0
3 [e]	**2a**	**3a**	0
4 [f]	**2a**	**3a**	20
5	**2b**	**3b**	70
6	**2c**	**3c**	68
7	**2d**	**3d**	72
8	**2e**	**3e**	64

[a] **1**:**2**:Zn = 1:3:1 (molar ratio). Zn was not activated by dilute HCl before use.

[b] Isolated yields based on **1** and **4** (5–7%), **5** (14–16%) were also observed.

[c] **3a**:



[d] 25 mol.% of p-dinitrobenzene (p-DNB) was added.

[e] 25 mol.% of di-tert-butylaminooxyl (t-Bu_2NO) was added.

[f] Without bubbling N_2.

The reaction was carried out in excess of **2**, which also served as a solvent. Neither polar or non-polar solvent, such as DMF, CH_3CN and n-hexane could be used in the reaction, otherwise, the yield decreased dramatically. For example,

---

* Corresponding author.

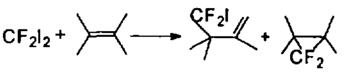
[1] Dedicated to Professor Wei-Yuang on the occasion of his 75th birthday.

PII S0022-1139(96)03510-5

when using CH_3CN as the solvent, the yield decreased to 10%, the main product was HCF_2I (32%) and $CF_2{=}CF_2$ (50%). Although catalytic amounts (10%) of Zn can induce the reaction with comparable yields, it takes a longer time (3–4 h) to complete the conversion; the optimum ratio of 1:Zn was 1:1.

Zinc powder used in the above reactions was not activated as usual by treating with dil. HCl acid before use. When using activated Zn, the reaction was strongly exothermic, and the main products were **4** (28%) and **5** (58%).

Zn can induce the reaction of **1** with 2,3-dimethyl-2-butene to afford the radical addition–elimination product and difluorocyclopropane derivative.



6 7

An attempt to react **1** with electron-deficient olefins, such as acrylonitrile or ethyl acrylate in the presence of Zn failed. However, it was found that iron powder is a more suitable initiator in the reaction not only for electron-rich but also for electron-deficient alkenes. The reaction conditions were rather mild and the yields were moderate to high (Scheme 2). The results are listed in Table 2.

The products obtained from electron-deficient alkenes were not direct adducts **3**, but further reduction products **8**.

$$\underset{1}{CF_2I_2} + \underset{2}{CH_2{=}CHR} \xrightarrow[50\text{-}60^oC]{Fe} \underset{3}{ICF_2CH_2CHIR} + \underset{4}{HCF_2I} + \underset{5}{CF_2{=}CF_2}$$

$R = CH_2OCH_2CH{=}CH_2$ (a)
$(CH_2)_4CH_3$ (b)
$(CH_2)_3CH_3$ (c)
$OCOCH_3$ (d)
$CH_2OC_2H_5$ (e)
CH_2OCOCH_3(f)

Scheme 2.

Table 2
Reaction of **1** with **2** in the presence of Fe at 50–60 °C (the molar ratio of **1**:**2**:Fe = 1:4:1)

Entry	2	*t* (h)	Product (%) [a]
1	**2a**	4	**3a** (78) [b]
2 [c]	**2a**	4	**3a** (0)
3 [d]	**2a**	4	**3a** (0)
4	**2b**	4	**3b** (72)
5	**2c**	4	**3c** (73)
6	**2d**	4	**3d** (70)
7	**2e**	4	**3e** (72)
8	**2f**	4	**3f** (76)
9	**2g**	5	**8g** (57)
10	**2h**	5	**8h** (60)

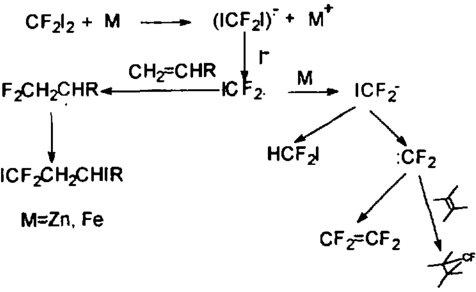
[a] Isolated yields based on **1** and **4** (5–7%), **5** (10–12%) were also observed.
[b] **3a**:

[c] 25 mol.% of p-dinitrobenzene (p-DNB) was added.
[d] 25 mol.% of di-tert-butylaminooxyl (t-Bu_2NO) was added.

$$\underset{1}{CF_2I_2} + \underset{2}{CH_2{=}CHR} \longrightarrow \underset{8}{ICF_2CH_2CH_2R} + \underset{4}{HCF_2I} + \underset{5}{CF_2{=}CF_2}$$

R = CN(g)
CO_2Me(h)

According to the widely accepted single electron transfer mechanism (SET) for the reaction of perfluoroalkyl iodides with alkenes in the presence of metals [6], it seems reasonable to assume a similar process operating in the present case. That the presence of oxygen and SET scavengers, *p*-dinitrobenzene (*p*-DNB) and di-tert-butylamino-oxyl significantly or completely suppressed the reaction (entries 2, 3, 4 in Table 1, and entries 2, 3 in Table 2) and that tetrahydrofuran derivatives were obtained from **1** and diallylether, strongly supports this suggestion. The mechanism may be described as follows:



Compound **1**, like perfluoroalkyl halides, accepts an electron from the metal to generate a radical anion, which dissociates to ICF_2. This species launches the addition onto alkenes or produces difluorocarbene after receiving another electron from the donor thus yielding all the compounds obtained. However, the different abilities of initiators between Zn and Fe, i.e. Fe can induce the addition reaction with both electron-rich and electron-deficient alkenes, while Zn only with electron-rich ones, is unclear. This problem is being investigated.

3. Experimental details

Boiling (melting) points are uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{19}F NMR spectra were determined on a Varian EM-360 spectrometer (60M) with TFA as external standard; ^1H NMR spectra were carried out on a FX-90Q (90M) instrument with TMS as reference. Mass spectra were obtained on a Finnigan GC-MS-4021 mass spectrometer. Silica gel (40 μm) was used for column chromatography.

3.1. General procedure for the reaction of difluorodiiodomethane with alkenes in the presence of zinc

Difluorodiiodomethane (5 mmol) was added dropwise with stirring to a mixture of unactivated zinc powder (5 mmol) and alkene (15 mmol) at 0 °C under nitrogen. After the addition was completed, the solution was warmed to 40–

50 °C and stirred for 1–2 h. Filtration and evaporation of the filtrate gave a residue which was purified by column chromatography on silica gel. Eluting with petroleum ether gave the product.

3-Iodomethyl-4-(2″-iodo-2″,2″-difluoroethyl)tetrahydrofurane (**3a**). m.p. 68–69 °C. Analysis: Calc. for $C_7H_{10}F_2I_2O$ (401.88): C, 20.90; H, 2.49%. Found: C, 20.80; H, 2.38%. MS *m/z* (rel. int.): 402 (M^+, 0.04); 275 (M^+–I, 43.10); 127 (69.00); 99 (100.0). IR (KCl) (cm^{-1}): 2850; 2700; 1425; 1240; 1210; 1175; 1045; 1015. ^1H NMR ($CDCl_3$) δ: 2.10–4.40 (10H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: −40.0 (2F, m) ppm.

1,3-Diiodo-1,1-difluorooctane (**3b**). HRMS calc. for $C_8H_{14}F_2I_2$ 401.9153. Found: 401.9149. MS *m/z* (rel. int.): 402 (M^+, 5.0); 127(I^+, 100.0). IR (film) (cm^{-1}): 2910; 1160; 1060; 895. ^1H NMR ($CDCl_3$) δ: 0.86 (3H, t, $J = 6$ Hz); 1.10–2.30 (8H, m); 2.70–3.40 (2H, m); 4.20 (1H, m) ppm. ^{19}F NMR ($CDCl_3$) δ: −42.2 (2F, m) ppm.

1,3-Diiodo-1,1-difluoroheptane (**3c**) [3]. MS *m/z* (rel. int.): 388 (M^+, 6.0); 133 (M^+–HI–I, 100.0). IR (film) (cm^{-1}): 2900; 1160; 1060; 900. ^1H NMR (CCl_4) δ: 1.00 (3H, t, $J = 6$ Hz); 1.20–2.20 (6H, m); 2.80–3.50 (2H, m); 4.30 (1H, m) ppm. ^{19}F NMR (CCl_4) δ: −41.30 (2F, m) ppm.

1,3-Diiodo-3,3-difluoropropyl acetate (**3d**). HRMS calc. for $C_5H_6F_2IO_2$ 262.9380. Found: 262.9341 (M^+–I). MS *m/z* (rel. int.): 391 ($M^+ + 1$, 13.70); 331 (40.90); 311 (21.10); 263 (19.44); 241 (29.16); 71 (29.39); 43 (100.0). IR (film) (cm^{-1}): 1740; 1365; 1220. ^1H NMR (CCl_4) δ: 2.0 (3H, s); 3.20–3.60 (2H, m); 6.80–7.00 (1H, m) ppm. ^{19}F NMR (CCl_4) δ: −40.0 (2F, m) ppm.

2,4-Diiodo-4, 4-difluorobutyl ethyl ether (**3e**). Analysis: Calc. for $C_6H_{10}F_2I_2O$ (389.88): C, 18.46; H, 2.56. % Found: C, 18.72; H, 2.60%. MS *m/z* (rel. int.): 391 ($M^+ + 1$, 0.24); 390 (M^+, 2.10); 345 (M^+–C_2H_5O, 11.20); 217 (M^+–HI–C_2H_5O, 100.0); 215 (75.29). IR (film) (cm^{-1}): 3000; 2900; 1100; 980. ^1H NMR ($CDCl_3$) δ: 1.20 (3H, t, $J = 6$ Hz); 2.80–3.23 (2H, m); 3.40–3.66 (4H, m); 4.23 (1H, m) ppm ^{19}F NMR ($CDCl_3$) δ: −42.60 (2F, m) ppm.

2,3,3-Trimethyl-4-iodo-4, 4-difluoro-1-butene (**6**) [3]. MS *m/z* (rel. int.): 261 ($M^+ + 1$, 1.0); 83 (100.0). ^1H NMR ($CDCl_3$) δ: 1.42 (6H, s); 1.90 (3H, m); 5.10, 5.02 (2H, br) ppm. ^{19}F NMR ($CDCl_3$) δ: −35.60 (2F, m) ppm.

1,1-Difluoro-2, 2, 3, 3-tetramethyl-cyclopropane (**7**) [3]. ^1H NMR ($CDCl_3$) δ: 1.40 (12H, s) ppm. ^{19}F NMR ($CDCl_3$) δ: 72.0 (2F, s) ppm.

3.2. General procedure for the iron-initiated reaction of difluorodiiodomethane with alkenes

Under nitrogen atmosphere, the mixture of difluorodiiodomethane (5 mmol), iron powder (5 mmol) and alkenes (20 mmol) was allowed to react at 50–60 °C for 4–5 h. Filtration and evoporation of the filtrate gave a residue which was purified by column chromatography on silica gel to give **3** or **8**.

2,4-Diiodo-4,4-difluorobutyl acetate (**3f**). Analysis: Calc. for $C_6H_8F_2I_2O_2$ (403.86): C, 17.82; H, 1.98%. Found: C, 18.06; H, 1.93%. MS m/z (rel. int.): 405 ($M^+ + 1$, 2.0); 217 (100.0); 43 (81.0). IR (film) (cm^{-1}): 1740; 1380; 1360; 1220; 1040. ^1H NMR ($CDCl_3$) δ: 2.0 (3H, s); 3.0–3.50 (2H, m); 4.20 (3H, m) ppm. ^{19}F NMR ($CDCl_3$): δ: −41.0 (2F, m) ppm.

4-Iodo-4,4-difluoro-butyronitrile (**8g**). HRMS calc. for $C_4H_4F_2IN$: 230.9357. Found: 230.9366. MS *m/z* (rel. int.): 232 ($M^+ + 1$, 28.0); 127 (10.0); 104 (100.0). IR (film) (cm^{-1}): 2950; 2250; 1430; 1100. ^1H NMR ($CDCl_3$) δ: 2.70–3.20 (4H, m) ppm. ^{19}F NMR ($CDCl_3$): δ: −38.0 (2F, m) ppm.

Methyl 4-iodo-4,4-difluorobutanoate (**8h**). HRMS calc. for $C_5H_7F_2O_2$: 137.0414 (M^+–I). Found: 137.0392. MS *m/z* (rel. int.): 233 (23.17); 137 (100.0); 117 (26.54); 105 (16.50); 89 (44.94); 77 (53.32). IR (film) (cm^{-1}): 2950; 1740; 1640; 1440; 1340; 1260; 1140. ^1H NMR ($CDCl_3$) δ: 2.5–3.00 (4H, m); 3.63 (3H, s) ppm. ^{19}F NMR ($CDCl_3$): δ: −39.0 (2F, m) ppm.

Acknowledgements

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

References

[1] M. Hudlicky, *Chemistry of Organofluorine Compounds*, 2nd edn., Ellis Horwood, Chichester, UK, 1976.

[2] W. Mahler, *Inorg. Chem.*, *2* (1963) 230; R.A. Mitsch, *J. Heterocycl. Chem.*, *1* (1964) 233; H.S. Kesling and D.J. Burton, *Tetrahedron Lett.*, *39* (1975) 3358; G.A. Wheaton and D.J. Burton, *J. Org. Chem.*, *43* (1978) 2643.

[3] S. Elsheimer, W.R. Dolbier and M. Murla, *J. Org. Chem.*, *49* (1984) 205.

[4] D.-B. Su, J.-X. Duan and Q.-Y. Chen, *J. Chem. Soc., Chem. Commun.*, (1992) 807.

[5] Q.-Y. Chen and Z.-T. Li, *J. Chem. Soc., Perkin Trans. 1*, (1992) 1443.

[6] Q.-Y. Chen, Z.-Y. Yang, C.-X. Zhao and Z.-M. Qiu, *J. Chem. Soc., Perkin Trans. 1*, (1988) 563, and references cited therein.