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$NiCl_2$/Al-promoted addition of per(poly)fluoroalkyl iodides to per(poly)fluoroalkyl-substituted ethenes

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Abstract

In the presence of $NiCl_2 \cdot 6H_2O$/Al the addition of per(poly)fluoroalkyl iodides to per(poly)fluoroalkyl-substituted ethenes proceeds smoothly, giving the corresponding addition–elimination products in moderate yield.

Keywords: Nickel chloride/aluminum-promoted addition; Per(poly)fluoroalkyl iodides; Per(poly)fluoroalkyl-substituted ethenes

1. Introduction

Numerous works have been reported on the introduction of per(poly)fluoroalkyl groups into organic molecules via either radical or carbanion routes by reduction (electrochemically or with metals or metal complexes), photolysis or thermolysis of perfluoroalkyl halides [1]. Electron-rich carbon–carbon multiple bonds have been used extensively as acceptors for this purpose. In recent years, reports on the addition of electrophilic perfluoroalkyl radicals to electron-deficient alkenes such as acrylates, acrylonitriles, etc. have appeared [2]. However, works concerning the addition of the perfluoroalkyl radical $R_F\cdot$ to perfluoroalkyl-substituted alkenes, a type of electron-deficient alkene, are few [3]. Preliminary work demonstrated that a redox system such as Co^{III}/Zn or Cr^{III}/Fe, although sufficiently effective to initiate the addition of $R_F\cdot$ to electron-deficient alkenes such as acrylates etc. [2], failed in this case. Hence, the search for more effective initiators has been the subject of much interest. Herein we report the results of a study of the $NiCl_2 \cdot 6H_2O$/Al bimetal redox couple promoted addition of R_FI to $R_FCH{=}CH_2$. Such a redox system has been used effectively in organic chemistry [4].

2. Results and discussion

Perfluoroalkyl-substituted ethenes reacted with R_FI in CH_3CN in the presence of 20 mol% $NiCl_2 \cdot 6H_2O$ and 2 equiv. of Al when maintained at 25–30 °C for ca. 12 h giving **3** in 45%–60% yield. ^1H and ^{19}F NMR spectroscopy, MS and elemental analytical data on the products were consistent with the assigned structures.

$$\underset{(1)}{R_FI} + \underset{(2)}{CH_2{=}CHCF_2R_F'} \longrightarrow \underset{(3)}{R_FCH_2CH{=}CFR_F'} + R_FH$$

The results obtained are summarized in Table 1.

Experiments showed that solvents played an important role in this reaction. If solvents like DMF, EtOH, etc. were used instead of CH_3CN, only the product of the reduction of **1** (R_FH) was found. If an aprotic solvent like THF was used instead of CH_3CN, no reaction occurred at all. Initiators like $NiCl_2 \cdot 6H_2O$/Zn gave complicated products. If $NiCl_2 \cdot 6H_2O$/Fe was used instead of $NiCl_2 \cdot 6H_2O$/Al, no reaction took place.

Parallel experiments showed that aluminum powder, aluminum/nickel alloy or $NiCl_2 \cdot 6H_2O$ alone did not initiate this reaction. $NiCl_2 \cdot 6H_2O$/Al readily initiated the addition of perfluoroalkyl iodides to 1-hexene, an electron-rich alkene, as well as to ethyl acrylate, an electron-deficient alkene. This fact might imply that the low-valent nickel species formed in situ is the real initiator and the reaction might proceed through an SET mechanism.

In conclusion, the $NiCl_2 \cdot 6H_2O$/Al bimetal redox couple was found to be an effective promotor for the addition of R_FI to $R_FCH{=}CH_2$, giving addition–elimination products in moderate yield.

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Table 1
Addition of R_FI to fluoroalkyl-substituted ethenes [a]

Run No.	R_FI (**1**)	$CH_2{=}CHCF_2R_F'$ (**2**)	Product **3** (Yield)
1	ClC_4F_8I	$CH_2{=}CHCF_2C_3F_6Cl$	$ClC_4F_8CH_2CH{=}CFC_3F_6Cl$ (**3a**) (55%)
2	ClC_4F_8I	$CH_2{=}CHCF_2C_5F_{10}Cl$	$ClC_4F_8CH_2CH{=}CFC_5F_{10}Cl$ (**3b**) (58%)
3	$ClC_6F_{12}I$	$CH_2{=}CHCF_2C_3F_7$	$ClC_6F_{12}CH_2CH{=}CFC_3F_7$ (**3c**) (45%)
4	$ClC_6F_{12}I$	$CH_2{=}CHCF_2C_3F_6Cl$	$ClC_6F_{12}CH_2CH{=}CFC_3F_6Cl$ (**3d**) (56%)
5	$ClC_6F_{12}I$	$CH_2{=}CHCF_2C_5F_{10}Cl$	$ClC_6F_{12}CH_2CH{=}CFC_5F_{10}Cl$ (**3e**) (60%)
6	$ClC_8F_{16}I$	$CH_2{=}CHCF_2C_3F_7$	$ClC_8F_{16}CH_2CH{=}CFC_3F_7$ (**3f**) (50%)
7	$ClC_8F_{16}I$	$CH_2{=}CHCF_2C_3F_6Cl$	$ClC_8F_{16}CH_2CH{=}CFC_3F_6Cl$ (**3g**) (55%)
8	$ClC_8F_{16}I$	$CH_2{=}CHCF_2C_5F_{10}Cl$	$ClC_8F_{16}CH_2CH{=}CFC_5F_{10}Cl$ (**3h**) (59%)

[a] All reactions were performed at 25–30 °C for ca. 12 h under N_2. Molar ratio of $R_FI/NiCl_2 \cdot 6H_2O/$**2** = 1:0.2:2 or 1:0.2:5.

3. Experimental details

All boiling points are uncorrected. IR spectra were recorded on an IR-440 Shimadzu spectrometer, ^{19}F NMR spectra on a Varian-360L (56.4 MHz) spectrometer in $CDCl_3$ using CF_3COOH as external standard, the values being positive for an upfield shift. ^1H NMR spectra were recorded on a Varian-360L (60 MHz) spectrometer in $CDCl_3$. Mass spectra were obtained on a Finnigan GC-MS-4021 spectrometer.

3.1. Preparation of compounds 3: typical procedure

$ClC_6F_{12}I$ (10 mmol) was added dropwise to a stirred mixture consisting of 2 mmol of $NiCl_2 \cdot 6H_2O$, 20 mmol of Al powder, 15 mmol of **2** and 20 ml of CH_3CN maintained at 25–30 °C. After stirring for 12 h, dilute hydrochloric acid was added and the solution extracted with Et_2O (3 × 10 ml). The combined organic extracts were washed with saturated $NaHCO_3$ solution, brine and dried (Na_2SO_4). Removal of the solvent and distillation gave **3** in 45%–60% yield.

Compound **3a**: B.p. 92–94 °C/10 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.80 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −8.60 (s, 4F, 2 × CF_2Cl); +36.2 (s, 2F, CF_2CH_2); +40.8 (s, 2F, $CF_2CF{=}C$); +43.2, 45.0, 45.8 (3 × s, 6F, $C_2F_4CF_2Cl$, CF_2CF_2Cl); +47.8 (br.s, 1F, CF=CH) ppm. MS (m/e): 478 (M^+, 11.56); 459 ($M^+ - F$, 3.81); 443 (($M^+ - Cl$, 7.18); 343 ($M^+ + 1 - C_2F_4Cl$, 100); 293 ($M^+ - C_3F_6Cl$, 12.26). Analysis: Calc. for $C_{10}H_3Cl_2F_{15}$: C, 25.05; H, 0.63; Cl, 14.82; F, 59.50%. Found: C, 24.93; H, 0.50; Cl, 14.74; F, 60.24%.

Compound **3b**: B.p. 110–112 °C/10 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.79 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −8.60 (s, 4F, 2 × CF_2Cl); +36.6 (s, 2F, CF_2CH_2); −401.6 (s, 2F, $CF_2CF{=}C$); +43.6, 44.6, 46.0 (3 × s, 10F, $C_3F_6CF_2Cl$, $C_2F_4CF_2Cl$); +48.1 (br.s, 1F, CF=CH) ppm. MS (m/e): 578 (M^+, 11.34); 559 ($M^+ - F$, 96.59); 534 ($M^+ - Cl$, 100). Analysis: Calc. for $C_{12}H_3Cl_2F_{19}$: C, 24.87; H, 0.52; Cl, 12.26; F, 62.35%. Found: C, 24.93; H, 0.50; Cl, 12.27; F, 62.38%.

Compound **3c**: B.p. 108–110 °C/20 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.80 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −8.70 (s, 2F, CF_2Cl); +4.50 (s, 3F, CF_3); +36.0 (s, 2F, CF_2CH_2); +42.3 (s, 2F, $CF_2CF{=}C$); +43.3, 44.3, 46.0 (3 × s, 8F, $C_4F_8CF_2Cl$); +48.0 (br.s, 1F, CF=CH); +50.7 (s, 2F, CF_2CF_3) ppm. MS (m/e): 562 (M^+, 1.39); 543 ($M^+ - F$, 3.65); 493 ($M^+ - CF_3$, 3.34); 443 ($M^+ + 1 - C_2F_5$, 100). Analysis: Calc. for $C_{12}H_3ClF_{20}$: C, 25.60; H, 0.53; F, 67.56%. Found: C, 25.02; H, 0.51; F, 66.47%.

Compound **3d**: B.p. 106–108 °C/20 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.73 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.12 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −9.10 (s, 4F, 2 × CF_2Cl); +36.1 (s, 2F, CF_2CH_2); +40.7 (s, 2F, $CF_2CF{=}C$); +43.4, 44.7, 46.3 (3 × s, 10F, $C_3F_6CF_2Cl$, $C_2F_4CF_2Cl$); +47.3 (br.s, 1F, CF=CH) ppm. MS (m/e): 559 ($M^+ - F$, 8.15); 543 (M + Cl, 12.83); 443 ($M^+ + 1 - C_2F_4Cl$, 100). Analysis: Calc. for $C_{12}H_3Cl_2F_{19}$: C, 24.87; H, 0.52; F, 62.46%. Found: C, 24.05; H, 0.48; F, 62.22%.

Compound **3e**: B.p. 102–104 °C/10 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.76 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −8.7 (s, 4F, 2 × CF_2Cl); +36.0 (s, 2F, CF_2CH_2); +41.4 (s, 2F, $CF_2CF{=}C$); +43.7, 44.5, 46.4 (3 × s, 14F, $C_3F_6CF_2Cl$, $C_4F_8CF_2Cl$); +47.4 (br.s, 1F, CF=CH) ppm. MS (m/e): 659 ($M^+ - F$, 5.49); 643 ($M^+ - Cl$, 2.57); 543 ($M^+ - C_2F_4Cl$, 6.55); 444 ($M^+ + 1 - C_4F_8Cl$, 100). Analysis: Calc. for $C_{14}H_3Cl_2F_{23}$: C, 24.94; H, 0.44; Cl, 10.46; F, 64.36%. Found: C, 24.51; H, 0.39; Cl, 10.43; F, 63.81%.

Compound **3f**: B.p. 90–92 °C/10 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.80 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −8.80 (s, 2F, CF_2Cl); +3.0 (s, 3F, CF_3); +34.6 (s, 2F, CF_2CH_2); +41.3 (s, 2F, $CF_2CF{=}C$); +42.2, 43.4, 45.0 (3 × s, 12F, $C_6F_{12}CF_2Cl$); +46.4 (br.s, 1F, CF=CH); +49.6 (s, 2F, CF_2CF_3) ppm. MS (m/e): 662 (M^+, 0.62); 643 ($M^+ - F$, 8.46); 627 ($M^+ - Cl$, 1.09); 543 ($M^+ + 1 - C_2F_5$, 100). Analysis: Calc. for $C_{14}H_3ClF_{24}$: C, 25.36; H, 0.45; F, 68.83%. Found: C, 25.23; H, 0.42; F, 67.95%.

Compound **3g**: B.p. 103–105 °C/3 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.84 (dt, 1H, J=30, 8 Hz, CH=CF–); 3.15 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −9.3 (s, 4F, 2 × CF_2Cl); +36.7 (s, 2F, CF_2CH_2);

+40.0 (s, 2F, $CF_2CF{=}C$); +43.0, 44.2, 45.6 (3×s, 14F, $C_6F_{12}CF_2Cl$, CF_2CF_2Cl); +47.0 (br.s, 1F, $CF{=}CH$) ppm. MS (*m/e*): 659 ($M^+ - F$, 1.19); 643 ($M^+ - Cl$, 3.60); 623 ($M^+ - 1 - Cl$, 2.63); 543 ($M^+ + 1 - C_2F_4Cl$, 100). Analysis: Calc. for $C_{14}H_3Cl_2F_{23}$: C, 24.74; H, 0.44; Cl, 10.46; F, 64.36%. Found: C, 24.23; H, 0.31; Cl, 10.83; F, 63.82%.

Compound **3h**: B.p. 105–107 °C/10 mmHg. IR (cm^{-1}): 1720 (C=C). ^1H NMR δ: 5.80 (dt, 1H, J=30, 8 Hz, $CH{=}CF{-}$); 3.10 (td, 2H, J=18, 8 Hz, CH_2CF_2) ppm. ^{19}F NMR δ: −9.0 (s, 4F, 2×CF_2Cl); +35.2 (s, 2F, CF_2CH_2); +41.7 (s, 2F, $CF_2CF{=}C$); +42.8, 44.3, 45.7 (3×s, 18F, $C_6F_{12}CF_2Cl$, $C_3F_6CF_2Cl$); +47.1 (br.s, 1F, $CF{=}CH$) ppm. MS (*m/e*): 759 ($M^+ - F$, 4.26); 743 ($M^+ - Cl$, 1.96); 643 ($M^+ + 1 - C_2F_4Cl$, 12.87); 544 ($M^+ + 1 - C_4F_8Cl$, 100). Analysis: Calc. for $C_{16}H_3C_{12}F_{27}$: C, 24.65; H, 0.38; F, 65.94%. Found: C, 24.06; H, 0.40; F, 65.47%.

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