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The addition of F113 and $CFCl_2CF_2CFCl_2$ to alkenes promoted by sodium dithionite

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Abstract

The addition of F113 and $CFCl_2CF_2CFCl_2$ to alkenes promoted by sodium dithionite occurs to give the corresponding fluoroalkylation products in moderate yields. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: F113; $CFCl_2CF_2CFCl_2$; Sodium dithionite; Fluoroalkylation

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1. Introduction

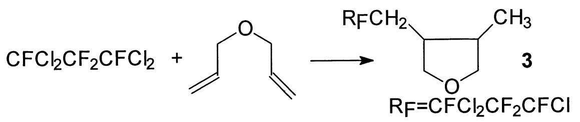
Polyfluoroalkylation initiated by sulfinatodehalogenation reagents, such as sodium dithionite, Rongalite, sodium bisulfite was studied in our laboratory in recent years [1,2]. Polyfluoroalkyl halides containing groups, such as CF_2I, CF_2Br, CCl_3, could undergo the polyfluoroalkylation reaction in the presence of the sulfinato-dehalogenation reagents [3–7]. Due to the high chemical stability of F113, there have been only a few reports on its reaction [8,9]. Herein we wish to present the addition reaction of F113 and $CFCl_2CF_2CFCl_2$ with alkenes initiated by sodium dithionite.

In aqueous acetonitrile solution, F113 reacted with alkenes and 1-hexyne at 40–50°C for 12 h to give the corresponding polyfluoro-alkylation products in moderate yields. For example,

$$CF_2ClCFCl_2 + CH_2{=}CH(CH_2)_3CH_3 \rightarrow \underset{\mathbf{1}}{CF_2ClCFCl(CH_2)_5CH_3}$$

$$CF_2ClCFCl_2 + CH{\equiv}C(CH_2)_3CH_3 \rightarrow \underset{\mathbf{2}\,(E/Z)}{CF_2ClCFClCH{=}CH(CH_2)_3CH_3}$$

Under similar conditions, $CFCl_2CF_2CFCl_2$ reacted with diallyl ether to give the corresponding addition-cyclization product, a tetrahydrofuran derivative **3** as the major product. Further results are summarized in Table 1.



The reaction was considered to proceed through polyfluoroalkyl radical intermediate. Only the hydropolyfluoroalkylation product was formed apparently due to the high bond energy of carbon–chlorine bond. Thus

$$CF_2ClCFCl_2 + SO_2^{\bullet-} \rightarrow CF_2ClCFCl^{\bullet} + SO_2 + Cl^-$$

$$CF_2ClCFCl^{\bullet} + CH_2{=}CHR \rightarrow CF_2ClCFClCH_2CHR^{\bullet}$$

$$\xrightarrow{\text{H abstraction}} CF_2ClCFClCH_2CH_2R$$

2. Experimental

All boiling and melting points were uncorrected. IR spectra were recorded on IR-440 spectrometer using film or potassium bromide pellet. ^{19}F NMR spectra were recorded on a Varian EM-360L (56.4 MHz) or FX-90Q (84.6 MHz) spectrometers in carbon tetrachloride, $CDCl_3$ or d_6-acetone using TFA as external standard. Chemical

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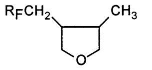
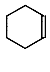
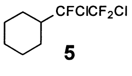
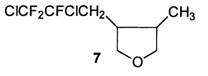
Table 1
The adducts of F113, $CFCl_2CF_2CFCl_2$ with alkenes

Entry	Halide	Alkene	Adduct	Yield(%)
1	$CF_2ClCFCl_2$	$C_4H_9CH=CH_2$	$CF_2ClCFClC_6H_{13}$ 1	56
2	$CF_2ClCFCl_2$	$CH\equiv CC_4H_9$	$CF_2ClCFClCH=CHC_4H_9$ 2 (E/Z)	50
3	$CFCl_2CF_2CFCl_2$	Diallyl ether	 3	49
4	$CFCl_2CF_2CFCl_2$	$C_6H_{13}CH=CH_2$	$R_FC_8H_{17}$ 4	46
5	$CF_2ClCFCl_2$		 5	50
6	$CFCl_2CF_2Cl$	$CH_2=CHCH_2OH$	$CF_2ClCFCl(CH_2)_3OH$ 6	48
7	$CFCl_2CF_2Cl$	Diallyl ether	 7	55

($R_F=CFCl_2CF_2CFCl$)

shifts in ppm were positive for upfield shifts ($\delta_{CFCl_3}=\delta_{TFA}+76.8$ ppm). ^1H NMR spectra were recorded on an EM-360A (60 MHz) spectrometer in carbon tetrachloride, $CDCl_3$ or d_6-acetone using TMS as external or internal standard, or obtained on a FX-90Q (90 MHz), Varian XL-200 (200 MHz) or Bruker AC-300 (300 MHz) spectrometers in $CDCl_3$ or d_6-acetone. MS spectra were obtained on a Finnigan GC-MS-4021 spectrometer and a Finnigan-8430 for high resolution mass spectra (HRMS). Elemental analysis data were obtained by the elemental analysis group of Shanghai Institute of Organic Chemistry. The column chromatography was performed by using silica gel H with petroleum ether and ethyl acetate as the eluent.

3. Typical procedure:

The mixture of F113 (3.75 g, 20 mmol), 1-hexene (0.84 g, 10 mmoL), sodium dithionite (4 g), sodium bicarbonate (2 g), acetonitrile (30 ml) and water (10 ml) was stirred at 40–45°C for 20 h. 60 ml water was added to dissolve the solid. The mixture was extracted by ether. The combined organic layer was washed with saturated aqueous sodium chloride solution, and dried over anhydrous sodium sulfate. After removal of the organic solvent, the crude product was purified over silica gel to give the adduct **1** in yield of 56% [9].

(1): δ_H (CCl_4): 0.90 (3H, t, CH_3), 2.30(2H, m, CH_2CFCl), 1.30–2.20 (8H, m, other hydrogen atoms) ppm. δ_F (CCl_4): 66.8 (2F, s, CF_2Cl), 118.8 (1F, m, CFCl) ppm.

(2): δ_H (CCl_4): 0.90 (3H, t, CH_3), 1.35 (4H, m, $2\times CH_2$), 2.30 (2H, m, CH_2), 5.60, 6.40 (2H, m, CH=CH)ppm. δ_F (CCl_4): 66.8 (2F,s, CF_2Cl), 118.4, 121.2 (*E/Z*, 1F, m, CFCl) ppm [9].

(3): δ_H ($CDCl_3$): 0.90 (3H, t, CH_3), 4.0 (m), 3.50 (m), 1.70–2.90 (m) ppm. δ_F (CCl_4): 65.8 (1F, s, $CFCl_2$), 109.8 (2F, s, CF_2), 114.8 (1F, m, CFCl) ppm. *m/z* (%): 321 (2.34), 320 (1.19), 319 (8.26), 318 (2.32), 317 (11.24), 316 (M^+, 1.79), 288 (7.82), 286(7.96),99 (6.74), 90 (16.36), 69 (100), 55 (17.99).

(4): δ_H (CCl_4): 0.90 (3H, t, CH_3), 2.30 (2H, m, CH_2CFCl), 1.30–2.20 (12H, m, other hydrogen atoms) ppm. δ_F (CCl_4): 66.8 (1F, s, $CFCl_2$), 109.8 (2F, s, CF_2), 114.8 (1F, m, CFCl) ppm. *m/z* (%): 311 (2.66), 330(M^+), 287 (7.45), 211 (21.71), 141 (11.14), 111 (15.34), 97 (20.66), 85 (49.48), 71 (65.11), 69 (32.84), 57 (100), 43 (70.05). *Anal.* Calc. for $C_{11}H_{17}Cl_3F_4$ (MW 331.5) C 39.82 H 5.13 F 22.93. Found: C 40.00 H 5.42 F 23.10

(5): δ_H (CCl_4): 3.50 (1H, m, CHCFCl), 1.20–2.50 (10H, m, other hydrogen atoms) ppm. δ_F (CCl_4): 61.8 (2F, s, CF_2Cl), 116.8 (1F, m, CFCl) ppm [9].

(6): δ_H (CCl_4): 1.90 (2H, m, CH_2), 2.30 (2H, m, CH_2CFCl), 3.55 (2H, t, CH_2OH), 3.90 (1H, s, OH) ppm. δF (CCl_4): 65.8 (2F, s, CF_2Cl), 119.0 (1F, m, CFCl) ppm [9].

(7): δ_H (CCl_4): 1.33 (3H, m, CH_3), 2.30–3.0 (4H, m), 3.70 (2H, m, CH_2), 4.20 (2H, m, CH_2) ppm. δ_F (CCl_4): 66.6 (2F, s, CF_2Cl), 118.8 (1F, m, CFCl) ppm [9].

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