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Studies on sulfinatodehalogenation: the addition reaction of halocarbons with olefins initiated by sodium dithionite

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Abstract

Halocarbons such as carbon tetrachloride, CCl_3Br, CF_3CCl_3, $BrCF_2CF_2Br$, $BrCF_2CFClBr$ and CF_2Br_2, reacted with olefins in the presence of the sulfinatodehalogenation reagent sodium dithionite under mild conditions to give the corresponding adducts. In the case of F113, $CFCl_2CF_2CFCl_2$ and CF_3Cl_3, the polyfluoroalkylation product resulted. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Halocarbons; Sodium dithionite; Addition reaction

1. Introduction

Since the sulfinatodehalogenation reaction was discovered in 1981 [1], the reaction has been extensively studied in our laboratory [2]. It was found that polyfluoroalkyl iodides and bromides reacted with sulfinatodehalogenation reagents, such as sodium dithionite, Rongalite and sodium bisulfite, to give the corresponding polyfluoroalkane-sulfinates [3]. In the presence of these reagents, the iodides and bromides reacted with olefins and alkynes to give 1:1 adducts [4]. The reaction is a good and practical method to generate polyfluoroalkyl radicals in the synthesis of fluorine-containing substances [5]. As a part of the research, here we wish to present the results of the reaction of halocarbons with olefins initiated by sodium dithionite under mild conditions.

In aqueous acetonitrile solution (the volume ratio of $CH_3CN{:}H_2O = 3{:}1$), halocarbons, such as CCl_4, CCl_3Br, CBr_4, CF_2Br_2, CF_2BrCF_2Br and $CF_2BrCFClBr$, reacted with 1-octene to give the corresponding adducts in moderate yields. Some oligomer was detected in the case of carbon tetrachloride. The addition reaction of CCl_4, CCl_3Br, CBr_4, $BrCF_2CF_2Br$ and $CF_2BrCFClBr$ with alkenes usually takes place at room temperature. In the case of CF_2Br_2, the reaction can happen even with cooling by ice.

$$CCl_3Br + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{1}}{CCl_3CH_2CHBrC_6H_{13}}$$

$$CCl_4 + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{2}}{CCl_3CH_2CHClC_6H_{13}}$$

$$CBr_4 + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{3}}{CBr_3CH_2CHBrC_6H_{13}}$$

$$\begin{aligned}&BrCF_2CF_2Br + CH_2{=}CHC_6H_{13}\\ &\quad\rightarrow \underset{\mathbf{4}}{BrCF_2CF_2CH_2CHBrC_6H_{13}}\end{aligned}$$

$$\begin{aligned}&BrCF_2CFClBr + CH_2{=}CHC_6H_{13}\\ &\quad\rightarrow \underset{\mathbf{5}}{BrCF_2CFClCH_2CHBrC_6H_{13}}\end{aligned}$$

$$CF_2Br_2 + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{6}}{BrCF_2CH_2CHBrC_6H_{13}}$$

In the case of CF_3CCl_3, $CF_2ClCFCl_2$ and $CFCl_2CF_2CFCl_2$, the polyfluoroalkylation product was formed instead of the 1:1 adduct. The reaction should be carried out at 40–45°C, if at room temperature, no adduct can be detected. The double polyfluoroalkylation product did not form in the reaction of $CFCl_2CF_2CFCl_2$, even with excess alkenes. The product was different from the other halocarbons possibly due to the high carbon–chlorine bond energy in these compounds [6]. A similar result was reported in the reaction of 1,1,2-triclorol-1,2,2-trifluoroethane (F113) with alkenes initiated by a redox system through an SET mechanism [7]. However, the mechanism was not clear.

$$CF_3CCl_3 + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{7}}{CF_3CCl_2C_8H_{17}}$$

$$CFCl_2CF_2Cl + CH_2{=}CHC_4H_9 \rightarrow \underset{\mathbf{8}}{ClCF_2CFClC_6H_{13}}$$

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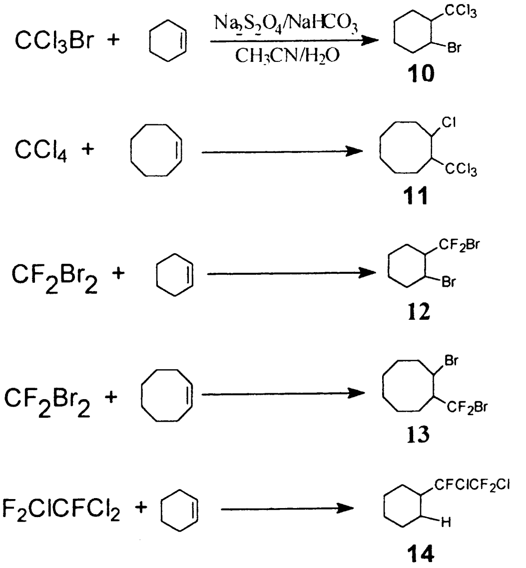
$$CFCl_2CF_2CFCl_2 + CH_2{=}CHC_6H_{13} \rightarrow \underset{\mathbf{9}}{CFCl_2CF_2CFClC_8H_{17}}$$

Under similar conditions, CCl_4, CCl_3Br, etc., reacted with disubstituted olefins, such as cyclohexene and cyclooctene, to give the corresponding addition products, the ratio of the *cis*- and *trans*-isomer in **12** was 1:1 as estimated by ^{19}F NMR. The polyfluoroalkylation product **14** was formed from the reaction of $CF_2ClCFCl_2$ (F113) with cyclohexene [8].



The addition reaction of CCl_4 and CCl_3Br with ethyl 3,3-dimethyl-4-pentenoate (**15**) initiated by sodium dithionite gave the 1:1 adducts **16** and **17** in good yields under mild conditions, respectively. CF_2Br_2 reacted with diethyl allylmalonate (**18**) to give **19**. Adducts **16**, **17** and **19** are intermediates for a number of pyrethroid syntheses [9].

$$CCl_4 + \underset{\mathbf{15}}{CH_2{=}CHC(CH_3)_2CH_2CO_2Et} \xrightarrow[CH_3CN/H_2O]{Na_2S_2O_4/NaHCO_3} \underset{\mathbf{16}}{CCl_3CH_2CHClC(CH_3)_2CH_2CO_2Et}$$

$$CCl_3Br + CH_2{=}CHC(CH_3)_2CH_2CO_2Et \rightarrow \underset{\mathbf{17}}{CCl_3CH_2CHBrC(CH_3)_2CH_2CO_2Et}$$

$$CF_2Br_2 + \underset{\mathbf{18}}{CH_2{=}CHCH_2CH(CO_2Et)_2} \rightarrow \underset{\mathbf{19}}{BrCF_2CH_2CHBrCH_2CH(CO_2Et)_2}$$

2. Experimental

All boiling and melting points were uncorrected. IR spectra were recorded on an IR-440 spectrometer using film or potassium bromide pellets. ^{19}F NMR spectra were recorded on 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 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 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 mass spectrometer and Finnigan-8430 for high resolution mass spectra (HRMS). The elemental analysis group of Shanghai Institute of Organic Chemistry obtained the elemental analysis data. Column chromatography was performed by using silica gel H with petroleum ether and ethyl acetate as the eluent.

3. Typical procedure

3.1. The addition reaction of halocarbons with olefins

Bromotrichloromethane (4.0 g, 20 mmol), 1-octane (3.4 g, 30 mmol), sodium dithionite (7.4 g, 40 mmol), sodium hydrogencarbonate (3.7 g, 40 mmol), acetonitrile (60 ml) and water (20 ml) were stirred at room temperature for several hours. Then 100 ml of water was added. The mixture was extracted with ether (3 × 25 ml). The combined organic layer was washed with saturated brine solution, dried over sodium sulfate. After removal of ether, the residue was distilled or purified over silica gel to give the pure product **1** in 64% yield. Bp 120°C/3 mmHg; δ_H (neat): 0.8–2.2 (13H, m, C_6H_{13}), 3.30 (2H, m, CH_2CCl_3), 4.4 (1H, m, CHBr) ppm; *m/z* (%): 121 ($M^+ - CCl_3Br$, 100), 55 (77.36), 69 (60.03), 157 (48.65), 43 (50.89), 115 (45.70), 109 (43.45), 93 (42.63) [10].

2: Yield 65%; bp 110°C/3 mmHg; δ_H (neat): 0.7–2.1 (13H, m, C_6H_{13}), 3.20 (2H, m, CH_2CCl_3), 4.2 (1H, m, CHCl) ppm [10].

3: Yield 68%; δ_H (neat): 0.7–3.2 (15H, m, other hydrogen atoms), 4.3 (1H, m, CHBr) ppm [10].

4: Yield 65%; bp 84°C/1 mmHg; δ_H (neat): 0.8–2.2 (13H, m, C_6H_{13}), 2.7 (2H, m, CH_2CF_2), 4.2 (1H, m, CHBr) ppm; δ_F (neat): 64.8 (s, 2F, CF_2Br), 109.8 (m, 2F, CF_2) ppm [10].

5: Yield 70%; bp 95°C/1 mmHg; δ_H (neat): 0.7–2.2 (13H, m, C_6H_{13}), 2.2–3.2 (2H, m, CH_2CFCl), 4.4 (1H, m, CHBr) ppm; δ_F (neat): 60.5 (s, 2F. CF_2Br), 117.0 (m, 1F, CFCl) ppm [10].

10: Yield 50%; δ_H (neat): 4.5 (1H, m, CHBr), 1.5–2.6 (9H, m, C_6H_9) ppm [12].

11: Yield 57%; bp 58–60°C/1 mmHg; δ_H (neat): 4.30 (1H, m, CHCl), 1.42–2.67 (13H, m, C_8H_{13}) ppm; *m/z* (%): 109 ($M^+ - CCl_4$, 100.0), 191 ($M^+ - Cl_2$, 19.43), 67 (41.34), 119 (34.39), 155 (31.71), 157 (16.50), 81 (16.06), 69 (18.32). Anal.: $C_9H_{14}Cl_4$ (MW 264); calc.: C 40.91, H 5.30; found: C 40.89, H 5.41%.

16: Yield 70%; bp 118–120°C/1 mmHg; υ_{max}: 1730, 1180, 1130, 1090, 975, 800, 685 cm^{-1}; δ_H (CCl_4): 4.37 (dd, 1H, CHCl), 4.07 (q, 2H, CO_2CH_2), 3.40–2.85 (m, 2H,

CH_2CCl_3), 2.60–2.20 (m, 2H, CH_2), 1.27 (t, 3H, CH_2CH_3), 1.22 (s, 3H, CH_3), 1.10 (s, 3H, CH_3) ppm [13].

17: Yield 80%; υ_{max}: 1730, 1225, 1220, 1150, 1030, 960, 805, 710 cm^{-1}; δ_H (CCl_4): 4.49 (dd, 1H, CHBr), 4.08 (q, 2H, CO_2CH_2), 3.40–3.15 (m, 2H, CH_2CCl_3), 2.60 (d, 1H, CH_2), 2.23 (d, 1H, CH_2), 1.23 (m, 6H, $2CH_3$), 1.13 (s, 3H, CH_3) ppm [13].

3.2. The addition reaction of dibromodifluoromethane with olefins

The mixture of dibromodifluoromethane (2.10 g, 10 mmol), 1-octene (1.68 g, 15 mmol), sodium dithionite (3.69 g, 18 mmol), sodium hydrogencarbonate (1.40 g, 16 mmol), acetonitrile (6 ml) and water (2 ml) was stirred at 0–5°C for 4 h. Dibromodifluoromethane was converted completely as shown by ^{19}F NMR. The mixture was extracted with ether (3 × 20 ml). The ethereal layer separated was dried over anhydrous magnesium sulfate. After evaporation of the solvent, the resultant liquid could be distilled or chromatographed on a silica gel column using petroleum ether as eluent to give the adduct **6** (2.83 g, 88% yield). Bp 50°C/1 mmHg; δ_H (neat): 4.30 (1H, m, CHBr), 3.0 (2H, m, CH_2CF_2Br), 0.9–2.10 (13H, m, other hydrogen atoms) ppm; δ_F ($CDCl_3$): 41.8 (2F, m, CF_2Br) ppm [11].

12: Yield 75%; $(E)/(Z) = 1.0$ (estimated by ^{19}F NMR); υ_{max}: 2800–3000 (C–H). 1460, 1300, 1200 (C–F) cm^{-1}; δ_H ($CDCl_3$): (*E*): 4.18 (1H, td, $J_{HH} = 9$ Hz, $J_{HH} = 4$ Hz, CHBr), (*Z*): 4.72 (1H, br, s, CHBr) $(E) + (Z)$: 1.0–2.6 (9H, m, other hydrogen atoms) ppm; δ_F ($CDCl_3$): (*E*): 41.23 (AB system), (*Z*): 48.50 (d, AB system), (m, 2F, CF_2Br) ppm; *m/z* (%): 294 (0.04), 292 (0.11), 290 (M^+, 0.04), 211 ($M^+ - Br$, 3.92), 131 ($M^+ - Br_2$, 100), 111 (27.06), 91 (12.07), 77 (29.84), 52 (53.93) [11].

13: Yield 80%; δ_H ($CDCl_3$): 4.50 (1H, m, CHBr), 1.0–2.6 (13H, m, other hydrogen atoms) ppm; δ_F ($CDCl_3$): 47.3 (m, 2F, CF_2Br) ppm; *m/z* (%): 240 ($M^+ - Br$, 5.05), 238 (6.36), 160 ($M^+ - Br_2$, 54.36), 159 (54.13), 138 (45.80), 117 (34.82), 116 (21.18), 77 (64.14), 44 (100). Anal.: $C_9H_{14}Br_2F_2$ (MW 320); calc.: C 33.75, H 4.38, F 11.88; found: C 34.16, H 4.24, F 12.20%.

19: Yield 80%; δ_H (CCl_4): 4.10 (5H, m, CHBr + CO_2CH_2), 3.50 (1H, m, CH), 2.90 (2H, m, CH_2CF_2Br), 2.20 (2H, m CH_2), 1.20 (6H, t, $2CH_3$) ppm; δ_F (CCl_4): 41.8 (2F, s, CF_2Br) ppm; *m/z* (%): 413 (1.73), 411 (3.43), 409 ($M^+ + 1$, 1.79), 329 ($M^+ - Br$, 9.78), 311 (9.77), 257 (17.07), 255 (18.59), 175 (39.00), 160 (100), 133 (25.89), 103 (17.10), 101 (20.93), 73 (18.15). Anal.: $C_{11}H_{16}Br_2F_2O_4$ (MW 410); calc.: C 32.20, H 3.90, F 9.27; found: C 32.46, H 3.50, F 9.60%.

3.3. The addition reaction of halocarbons with $CFCl_2$ group with alkenes

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. Then 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 **8** in yield of 56%. 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 [7].

7: Yield 72%; δ_H (neat): 2.50–2.1 (2H, m, CH_2CCl_2), 1.90–0.90 (15H, m, other hydrogen atoms) ppm; δ_F (neat): 79.8 (3F, s, CF_3) ppm; *m/z* (%): 267 (0.81), 266 (1.12), 265 (4.80), 264 (M^+, 4.36), 223 (17.15), 221 (26.49), 149 (13.81), 71 (16.96), 57 (100), 55 (20.03), 56 (15.46), 43 (45.45) [7].

9: Yield 70%; δ_H (CCl_4): 0.90 (3H, t, CH_3), 2.30 (2H, m, CH_2CFCl), 1.30–2.20 (10H, 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.: $C_{11}H_{17}Cl_3F_4$ (MW 331.5); calc.: C 39.82, H 5.13, F 22.93; found: C 40.00, H 5.42, F 23.10%.

14: Yield 50%; 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 [7]. Anal.: $C_8H_{11}Cl_2F_3$ (MW 235.08) calc.: C 40.87, H 4.72, F 24.24; found: C 40.90, H 4.68, F 24.32%.

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