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# Fluorination of some fluorine-containing oxo esters by sulfur tetrafluoride

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**Abstract**

Treatment of fluorine-containing oxo esters with $SF_4$ resulted in concomitant fluorination of keto groups and dehydrofluorination to give unsaturated esters in high yields.

*Keywords:* Oxo esters; Keto acids; Sulfur tetrafluoride; Reduction; Dehydrofluorination; Unsaturated esters

## 1. Introduction

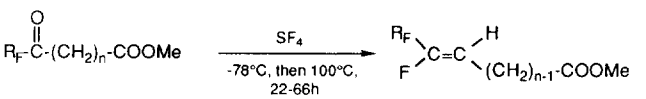
The goal of the present work was to remove the keto group adjacent to a perfluoroalkyl chain in some highly fluorinated oxo esters [1]. Attempted reduction to the methylene group using classical [2] or modified [3,4] Wolf–Kishner procedure or Huang-Minlon reaction [5,6] failed. Since, it has been described in the literature that the Clemmensen reaction [7] or a specific reduction promoted by zinc or amalgam [8] in many cases give no reaction with oxo acids, or hydrolysis of the ester function occurs, these reactions were not attempted.

## 2. Results and discussion

On the other hand, it is well known that sulfur tetrafluoride is a remarkably effective reagent for the replacement of a carbonyl oxygen atom by two fluorines [9–11]. The reactions with keto acids (esters) usually proceed selectively by converting the keto group into a difluoromethylene group while the ester function remains unchanged.

Therefore, we attempted the conversion of keto groups in oxo esters **1a,b** by treating them with sulfur tetrafluoride. However, concomitant fluorination and dehydrofluorination reactions occurred to give unsaturated esters **2a,b** as the only products and in high yield (see Scheme 1).

The reactions proceeded with high stereoselectivity such that *Z* isomers were obtained exclusively. The assignment of the configuration of compounds **2a,b** has been based on the magnitude of the coupling constants, $^3J_{H-F} = 33.4$–$33.6$ Hz ($\delta_H = 5.6$ ppm; $\delta_F = -132$ ppm), typical of a *trans* hydrogen-to-fluorine coupling [12].




**1***a,b* **2***a,b*

(**a**): $R_F = C_7F_{15}$, $n = 4$
(**b**): $R_F = C_7F_{15}$, $n = 5$

Scheme 1.

However, the detailed mechanism of dehydrofluorination is not clear at the present stage.

## 3. Experimental details

$^1$H NMR spectra were recorded in $CDCl_3$ on a Varian 200 MHz spectrometer using $(CH_3)_4Si$ (TMS) as internal standard. $^{19}$F NMR were recorded in $CDCl_3$ on a Varian 200 MHz spectrometer using $CFCl_3$ as internal standard. IR spectra were performed on a Perkin-Elmer (FT-IR Paragon 1000 spectrometer) and mass spectra were run on a Nermag R 10-10 C mass spectrometer.

Oxo esters **1a,b** were prepared according to the literature procedure [1].

### 3.1. General procedure

In a typical experiment, oxo ester **1** (0.01 mol) was placed in a 100 ml stainless steel autoclave, the autoclave was cooled to −78 °C by immersion in an acetone Dry Ice bath, evacu-

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ated to ca. 2 Torr and then sulfur tetrafluoride (ca. 9 g) was condensed in it. The autoclave was placed in a rocking muffle furnace and heated at 100 °C for 22 h or 60 h. After cooling to ambient temperature, the gases generated ($SOF_2$, $SF_4$, HF) were slowly released and the remaining brown liquid washed out with methylene chloride (30 ml). Dry sodium fluoride (2–3 g) was added and the solution left overnight (removal of HF). Evaporation of the solvent under atmospheric pressure (water bath) left a brown oily residue which was purified by column chromatography on silica gel (230–400 mesh) using n-hexane/chloroform (10:4) as eluent to give **2** in 78% yield and >96% purity.

Analytical data are given below.

Methyl 6-fluoro-6-*F*-heptyl-hexen-5(*Z*)-oate (**2a**): IR (film) ($cm^{-1}$): 1100–1300; 1742. $^1H$ NMR ($CDCl_3$/TMS) δ: 1.79 (q, $J$=7.3 Hz, 2H, $CH_2$); 2.33 (t, $J$=7.3 Hz, 4H, $2CH_2$); 3.68 (s, 3H, $CH_3$); 5.60 (dt, $^3J_{HF}$=33.4 Hz, $^4J_{HF}$=7.8 Hz, 1H, CH=) ppm. $^{19}F$ NMR ($CDCl_3$/$CFCl_3$) δ: −81.4 (t, $J$=9.65 Hz, 3F, $CF_3$); −118.0 (m, 2F, $CF_2$); −122.6 (m, 4F, $2CF_2$); −123.4 (m, 2F, $CF_2$); −123.6 (m, 2F, $CF_2$); −126.7 (m, 2F, $CF_2$); −132.0 (m, 1F, $CF$=) ppm. MS (70 eV) $m/z$: 514 ($M^+$); 74 (100%); 59; 69; 87; 119; 121; 131; 483. Analysis for $C_{14}H_{10}F_{16}O_2$ (514.20): Calc.: C, 32.70; H, 1.96; F, 59.11%. Found: C, 32.82; H, 2.03; F, 59.34%.

Methyl 7-fluoro-7-*F*-heptyl-hepten-6(*Z*)-oate (**2b**): IR (film) ($cm^{-1}$): 1100–1300; 1742. $^1H$ NMR ($CDCl_3$/TMS) δ: 1.5 (m, 2H, $CH_2$); 1.65 (m, 2H, $CH_2$); 2.25 (m, 2H, $CH_2$); 2.33 (t, 2H, $CH_2$); 3.67 (s, 3H, $CH_3$); 5.59 (dt, $^3J_{HF}$=33.6 Hz, $^4J_{HF}$=7.8 Hz, 1H, $CH$=) ppm. $^{19}F$ NMR ($CDCl_3$/$CFCl_3$) δ: −81.0 (t, $J$=9.6 Hz, 3F, $CF_3$); −117.9 (m, 2F, $CF_2$); −122.5 (m, 4F, $2CF_2$); −123.3 (m, 2F, $CF_2$); −123.5 (m, 2F, $CF_2$); −126.6 (m, 2F, $CF_2$); −132.5 (m, 1F, $CF$=) ppm. MS (70 eV) $m/z$: 528 ($M^+$); 74 (100%); 59; 69; 87; 119; 121; 131; 434; 497. Analysis for $C_{15}H_{12}F_{16}O_2$ (528.23): Calc.: C, 34.11; H, 2.29; F, 57.55%. Found: C, 34.28; H, 2.35; F, 57.68%.

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