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A NOVEL 1,3-SHIFT INDUCED BY FLUOROALKYL GROUPS IN ACETYLENIC THIOLESTERS

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SUMMARY

A novel 1,3-shift of a methylthio group induced by a fluoroalkyl group in acetylenic thiolesters occured when methyl fluoroacetylenic thiolesters were treated with aqueous sodium hydroxide in a heterogeneous system.

INTRODUCTION

In a previous paper [1] we found a convenient synthesis of perfluoro- and polyfluoroacetylenic thiolesters which would be expected to be good dipolarophiles and dienophiles and useful species for the synthesis of fluorinated heterocyclic compounds [2]. Further, perfluoro- and polyfluoroacetylenic thiolesters could undergo an unprecedented novel rearrangement in which the methylthio group would migrate to the β-carbon.

This paper is the 46th report on the studies of the application of elemento-organic compounds of the fifth and sixth groups in organic syntheses.

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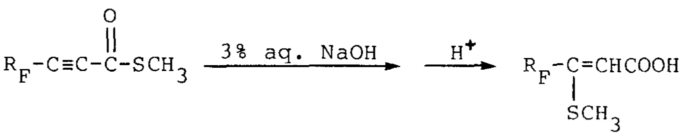
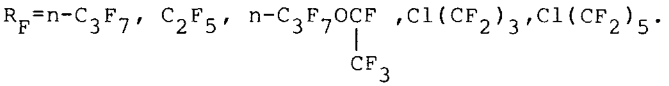
RESULTS AND DISCUSSION

In this paper we would like to report our investigation on this unprecedented novel rearrangement, a kind of 1,3-shift, in which the methylthio species, induced by fluoroalkyl group in acetylenic thiolesters, migrated to the β-carbon.



$$R_F\text{-}C{\equiv}C\text{-}\overset{\overset{O}{\|}}{C}\text{-}SCH_3 \xrightarrow{3\%\ aq.\ NaOH} \xrightarrow{H^+} R_F\text{-}\underset{\underset{SCH_3}{|}}{C}{=}CHCOOH$$

1 **2**



$$R_F{=}n\text{-}C_3F_7,\ C_2F_5,\ n\text{-}C_3F_7O\underset{\underset{CF_3}{|}}{C}F\ ,Cl(CF_2)_3,Cl(CF_2)_5.$$

It is of interest to note that treatment of methyl fluoroacetylenic thiolesters (**1**) with aqueous sodium hydroxide (3%) followed by acidification, afforded β-methylthiofluoroalkenyl carboxylic acids (**2**) in excellent yields. A novel 1,3-shift of methylthio group in heterogeneous system has occurred.

The stereochemical studies showed that this novel rearrangement was highly stereoselective and the Z-isomer predominated to the extent of above 90% in all cases.

The results are summarized in Table 1.

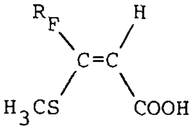
TABLE 1

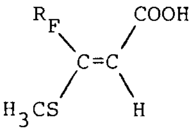
The Yields and the Stereochemistry of the Rearrangement

Compound	R_F	m.p. (°C)	Z:E	Yield (%)
2a	$n\text{-}C_3F_7$	36-38	90:10	96
2b	C_2F_5	69-71	92:8	97
2c	$n\text{-}C_3F_7OCF(CF_3)$	101/0.3*	96:4	94
2d	$Cl(CF_2)_3$	54-55	97:3	94
2e	$Cl(CF_2)_5$	67-68	93:7	92

* bp/mmHg

The configuration of the products can be ascertained from ^1H NMR data by comparison with those reported previously [3].


Z-isomer

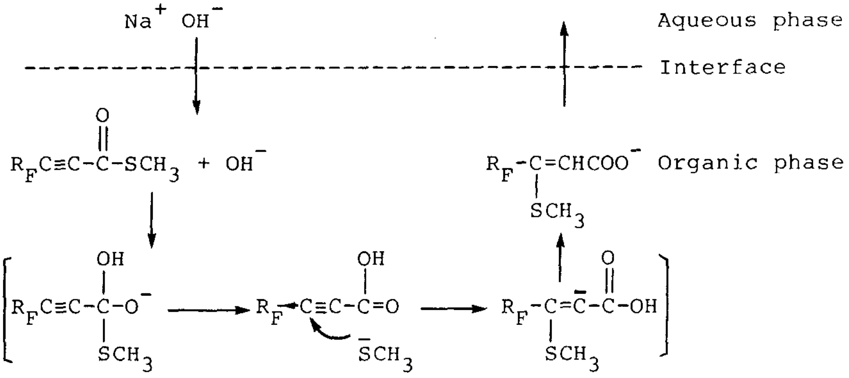

E-isomer

We suggest that when the vinyl proton is cis with respect to the fluoroalkyl group, the chemical shift is shifted downfield (for **2a**-Z, 6.60 ppm), while when it is trans with respect to the fluoroalkyl group, it is shifted upfield (for **2a**-E, 5.70 ppm).

The characteristic features of the present rearrangement are:

1. The 1,3-shift only occurred in the presence of the fluoroalkyl group which induced this shift.
2. The 1,3-shift only occurred by stirring a heterogeneous mixture of organic substrates with aqueous sodium hydroxide solution for several hours at 0°C, while in homogeneous ethanolic sodium hydroxide no 1,3-shift occurred.

This new type of reaction is somewhat like a phase-transfer reaction, but takes place in the absence of any added phase-transfer catalyst. In a heterogeneous system, hydroxide ion transfer occurs at the interface and reacts with organic substrate, followed by solution of the sodium salt of 1,3-shift product as shown in the following scheme. The driving force which led to the 1,3-shift is the positive charge of the acetylenic carbon linked to the fluoroalkyl group caused by the inductive effect of the fluoroalkyl group and conjugative effect of carboxylic group.



Further study on the mechanism of this rearrangement is being pursued.

EXPERIMENTAL

All melting points and boiling points were uncorrected. Infrared spectra of solid products were obtained as KCl disks and liquid products as films on a Shimadzu IR-440 Spectrometer. NMR spectra (chemical shifts in ppm from internal TMS for ^{1}H NMR and from external TFA for ^{19}F NMR positive for upfield shifts) were obtained on a EM-360 Spectrometer at 60 MHz. Mass spectra were obtained on a Finnigan GC-MS 4021 Mass Spectrometer.

General procedure for inducing a 1,3-shift in fluoroacetylenic thiolester

Methyl fluoroacetylenic thiolester (2 mmol) and precooled (0°C) 3% aqueous sodium hydroxide solution (8-10 ml)were placed in a flask.The reaction mixture was maintained at 0°C with stirring until it becomes homogeneous. After standing overnight in a refrigerator, the reaction mixture was cooled to 0°C, washed with petroleum ether (30-60°C) and acidifed with concentrated hydrochloric acid. The product was separated and the aqueous layer was extracted with petroleum ether. After evaporation of petroleum ether another portion of product was obtained. The ratios of Z- and E-isomer were estimated from the ^{1}H NMR spectra of the crude products which were then recrystallized from petroleum ether (30-60°C) to give pure Z-isomer.

2a: 96% yield; m.p. 36-38°C; IR(KCl): 1700(s),1580(s) cm^{-1}; ^{1}H NMR(CDCl$_3$): δ 2.50(Z)+2.37(E)(s,3H);6.60(Z)+5.70(E)(s,1H);10.76(s,1H); ^{19}F NMR(CDCl$_3$):δ2.0(t,3F,J=11Hz);29.6(q,2F,J=11Hz);46.8(br.s,2F)ppm; MS m/e: 286(M$^+$),269(M$^+$-OH),69(CF$_3$$^+$). Analysis: Calcd for $C_7H_5F_7O_2S$: C,29.38, H,1.76; Found: C,29.27, H,1.78.

2b: 97% yield; m.p. 69-71°C; IR(KCl): 1680(s),1580(s) cm^{-1}; ^{1}H NMR(CDCl$_3$): δ 2.58(Z)+2.48(E)(s,3H);6.68(Z)+5.83(E)(S,1H);10.75(s,1H); ^{19}F NMR(CDCl$_3$):δ4.5(br.s,3F);32.0(br.s,2F)ppm; MS m/e: 236(M$^+$),219(M$^+$-OH),69(CF$_3$$^+$). Analysis: Calcd for $C_6H_5F_5O_2S$: C,30.52, H,2.13; Found: C,30.45, H,1.87.

2c: 94% yield;b.p.101°C/0.3mmHg IR(KCl): 1710(s),1600(s) cm^{-1}; ^{1}H NMR(CDCl$_3$): δ 2.36(Z)+2.27(E)(S,3H);6.47(Z)+5.65(E)(s,1H);10.55(s,1H); ^{19}F NMR(CDCl$_3$):δ4.8(t,3F,J=4Hz);5.8(d,3F,J=4Hz);6.0(AB,2F);47.8-48.8(m,1F);52.3(br.s,2F)ppm; MS m/e:402(M$^+$),385(M$^+$-OH),69(CF$_3$$^+$). Analysis: Calcd for $C_9H_5F_{11}O_3S$: C,26.88, H,1.25, Found: C,26.53, H,1.24.

2d: 94% yield; m.p. 54-55°C IR(KCl): 1630(s),1570(s) cm^{-1}; ^{1}H NMR(CDCl$_3$): δ 2.30(Z)+2.20(E)(s,3H);6.28(Z)+5.63(E)(s,1H);11.53(s,1H); ^{19}F NMR(CDCl$_3$):δ-11.5(t,2F,J=14Hz);27.5(t,2F,J=14Hz);40.3-40.7(m,2F)ppm; MS m/e: 302(M$^+$),285(M$^+$-OH),69(CF$_3$$^+$). Analysis: Calcd for $C_7H_5ClF_6O_2S$: C,27.78, H,1.67, Found: C,27.85, H,1.67.

2e: 92% yield; m.p. 67-68°C IR(KCl): 1650(s),1550(s) cm^{-1}; ^1H NMR($CDCl_3$): δ 2.45(Z)+2.25(E)(S,3H);6.48(Z)+5.70(E)(s,1H);10.23(s,1H); ^{19}F NMR($CDCl_3$):δ-10.7(t, 2F,J=10Hz);27.6-28.6(m,2F);41.0-43.1(m,6F)ppm;MS m/e: 402(M^+),385(M^+-OH),69(CF_3^+). Analysis: Calcd for $C_9H_5ClF_{10}O_2S$: C,26.85, H,1.25, Found: C,26.64, H,1.52.

ACKNOWLEDGEMENT

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