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A CONVENIENT SYNTHESIS OF

2-ALKYL-3-FLUORO-3-POLYFLUOROALKYL-2-PROPENALS

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SUMMARY

The synthesis and identification of 2-alkyl-3-fluoro-3-polyfluoroalkyl-2-propenals are described.

INTRODUCTION

The common methods for the synthesis of polyfluoroalkanal are by the reduction of corresponding acids and derivatives [1,2] or by the oxidation of corresponding alcohol.[3] Both suffer from the disadvantage of low yields. In our previous communication,[4] we reported a Pd catalyzed reaction of polyfluoroalkyl iodides with tertiary amines to give enamines (1) in almost 100% conversion and 45-50% yields. Now we report a convenient and general method for the synthesis of 2-alkyl-3-fluoro-3-polyfluoroalkyl-2-propenals from the corresponding enamines.

RESULTS AND DISCUSSION

We found that β -alkyl- β -polyfluoroalkylenamines can be readily hydrolyzed with 2M HCl at 40°C for 30 min to produce 2-alkyl-2-polyfluoroalkylacetaldehydes (2) in 80-90% yield, which on treating with silica gel afforded 2-alkyl-3-fluoro-3-polyfluoroalkyl-2-propenals (3) quantitatively. The reaction scheme is shown in Table 1.

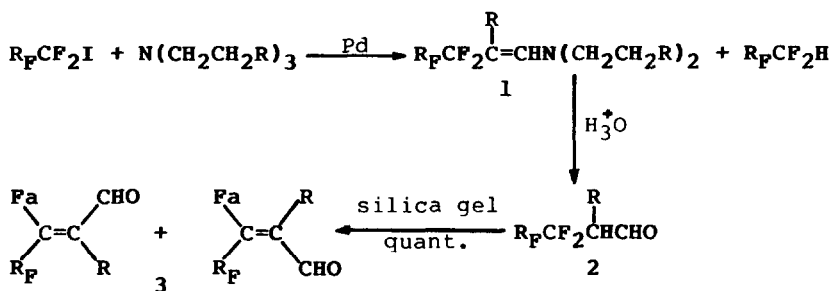


Table 1

Synthesis of Compound 3

R_F	R	Yield ^a of 3 (%)	B.p. of 3 ^b (°C/torr)	Molecular Formula	3(Z):3(E) ^c	
a	$Cl(CF_2)_3$	CH_3	38.5	50/40	$C_7H_4ClF_7O$ (272.5)	54:46
b	$Cl(CF_2)_5$	CH_3	45	62-64/25	$C_9H_4ClF_{11}O$ (372.5)	43:57
c	$Cl(CF_2)_3$	C_2H_5	41	56-60/40	$C_8H_6ClF_7O$ (286.5)	31:69
d	$Cl(CF_2)_5$	C_2H_5	43	75/25	$C_{10}H_6ClF_{11}O$ (386.5)	32:68

^a based on iodide

^b mixture of Z and E

^c determined by capillary chromatography

It is noteworthy that the **Z** and **E** isomers of the unsaturated aldehyde have not been identified previously.[5] By means of the lanthanide induced shift technique we identified the **Z** and **E** isomers of **3** satisfactorily. Based upon the principle of LIS [6,7] on addition of europium reagent, the chemical shift of **Fa** in the **Z** isomer shifts downfield more than **Fa** in the **E** isomer. The reagent used is tris[2,2-dimethyl-6,9-di(trifluoromethyl)-7,10-dioxa-6,8,8,9,11,11,12,12,13,13,13-undecafluoro-tridecane-3,5-dione]europium. The downfield shift in the two isomers reached 1.8 ppm (**Z**>**E**)

Table 2Spectroscopic and Analytic Data for Compound **3**

IR(neat) ^a (cm ⁻¹)	¹ H NMR(CDCl ₃ /TMS) ^b (ppm)	¹⁹ F NMR(CDCl ₃ /CFCl ₃ ext) ^c (ppm)	Analysis Found(Calc.)
3a 1695(C=O)	Z : 1.76(q,3H,J _{HF} =3.6Hz)	Z : 67.4(t,2F,J=11.2Hz)	C 31.01(30.88)
1663(C=C)	10.24(s,1H)	114.3(m,2F)	H 1.60(1.47)
1300-1100 (C-F)	E : 1.82(dt,3H,J _{HF} =4.9Hz J _{HF} =2.2Hz)	120.6(m,2F)	Cl 13.32(13.05)
	10.00(s,1H)	125.6(m,1F)	F 48.56(48.90)
		E : 67.4(t,2F,J=11.2Hz)	
		106.3(m,1F)	
		110.2(q,2F,J=12Hz)	
		120.6(m,2F)	
3b 1695(C=O)	Z : 1.90(q,3H,J _{HF} =3.4Hz)	Z : 67.2(t,2F,J=13Hz)	C 29.02(28.99)
1665(C=C)	10.24(s,1H)	115(m,2F)	H 1.08(1.07)
1300-1100 (C-F)	E : 1.97(dt,3H,J _{HF} =4.8Hz J _{HF} =2.3Hz)	119.6(m,2F)	Cl 9.48(9.53)
	10.00(s,1H)	120.6(m,2F)	F 56.57(56.11)
		122.5(m,2F)	
		125.8(m,1F)	
		E : 67.2(t,2F,J=13Hz)	
		106.0(m,1F)	
		110.8(q,2F,J=11.5Hz)	
		119.6(m,2F)	
		120.6(m,2F)	
		122.5(m,2F)	

(continued)

Table 2 (cont.)

3c	1695(C=O)	Z: 1.04 (t, 3H, J=7.5Hz)	Z: 66.5 (t, 2F, J=11.2Hz)	C 33.35 (33.51)
	1660(C=C)	2.37 (m, 2H)	113.4 (m, 2F)	H 2.04 (2.10)
	1300-1100	10.28 (S, 1H)	120.0 (m, 2F)	Cl 12.15 (12.39)
	(C-F)	E: 1.06 (t, 3H, J=7.5Hz)	125.1 (m, 1F)	F 46.56 (46.42)
		2.48 (m, 2H)	E: 66.5 (t, 2F, J=11.2Hz)	
		10.03 (S, 1H)	107.4 (m, 1F)	
			109.2 (q, 2F, J=11.2Hz)	
			120.0 (m, 2F)	
3d	1695(C=O)	Z: 1.05 (t, 3H, J=7.5Hz)	Z: 66.8 (t, 2F, J=13.3Hz)	C 31.39 (31.10)
	1660(C=C)	2.38 (m, 2H)	114.3 (m, 2F)	H 1.67 (1.55)
	1300-1100	10.21 (S, 1H)	118.7 (m, 2F)	Cl 8.84 (9.18)
	(C-F)	E: 1.07 (t, 3H, J=7.5Hz)	119.7 (m, 2F)	F 54.02 (54.08)
		2.48 (m, 2H)	121.6 (m, 2F)	
		9.97 (S, 1H)	125.8 (m, 1F)	
			E: 66.8 (t, 2F, J=13.3Hz)	
			108.0 (m, 1F)	
			110.1 (q, 2F, J=11.2Hz)	
			118.7 (m, 2F)	
			119.1 (m, 2F)	
			121.6 (m, 2F)	

^a Recorded on a Shimadzu IR-440 spectrometer.

^b Recorded on a Varian XL-200 spectrometer.

^c Recorded on a Jeol FX-90Q spectrometer.

EXPERIMENTAL

2-Methyl-3-fluoro-6-chloro-4, 4, 5, 5, 6, 6-hexafluoro-2-hexenal 3a; Typical Procedure: To 10 ml n-hexane 725 mg (2 mmol) were added Cl(CF₂)₄I, 572 mg (4 mmol) N(C₃H_{7-n})₃ and 115 mg (0.1 mmol) Pd(PPh₃)₄. The reaction mixture was heated under N₂ at 50°C for 30 min with stirring (the conversion of iodide was 100%). After removal of solvent, excess N(C₃H_{7-n})₃

and solid, the residue was hydrolyzed with 2M HCl at 40°C for 30 min, and the solution was extracted with ether and worked up to give 275 mg (47% based on iodide) of **2a**. To a solution of 175 mg (0.6 mmol) **2a** in 5 ml petroleum ether, 1 g silica gel was added, the system was stirred at 40°C for 5 h. After removal of silica gel and solvent, 163 mg of **3a** was obtained. Distillation gave pure product.

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