Brief Communications

Synthesis of *N*-alkylamides of 3-fluoroalkylaziridine-2-carboxylic acids

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The *N*-alkylamides of 3-fluoroalkylaziridine-2-carboxylic acids have been prepared for the first time by the interaction of ethyl β-fluoroalkyl-α,β-dibromocarboxylates with primary amines.

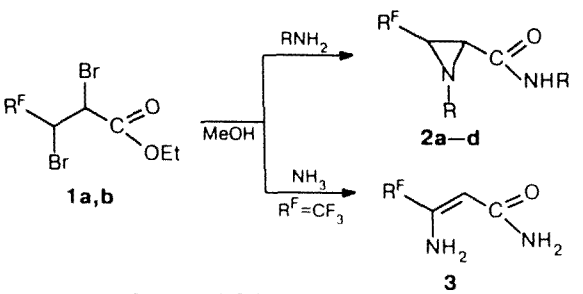
Key words: esters of α,β-dibromo-β-fluoroalkylcarboxylic acids, *N*-alkylamides of 3-fluoroalkylaziridine-2-carboxylic acids.

Esters of α-bromo-α,β-unsaturated carboxylic acids containing no fluorine react with primary amines to give aziridine-2-carboxylic acids.[1] We found that during the interaction of ethyl α,β-dibromo-β-fluoroalkylcarboxylates (**1**)* with primary amines (Scheme 1), closure of an aziridine ring is accompanied by amidation to give previously unknown 2-fluoroalkylaziridine-3-carboxamides **2** (Tables 1 and 2). This is explained by the fact that the reactivity of the ethoxycarbonyl group substantially increases due to the effect of the electron-withdrawing polyfluoroalkyl substituent.

Obviously, the first step of this reaction involves dehydrobromination of α,β-dibrominated ester **1** to the α-bromo-α,β-unsaturated ester, by analogy with β-fluoroalkyl-α,β-dibromoketones.[3]

The reaction of α,β-dibrominated ester **1a** with NH_3 does not lead to the expected aziridine **2**. Instead, a complex mixture of products is formed; the main component of this mixture, the amide of 3-amino-4,4,4-trifluorobut-2-enoic acid (**3**), was identified by comparing the ^1H NMR spectrum of the mixture with that of an authentic sample[4] of **3** (a singlet at 5.05 ppm (CH) and two broadened signals at 3.0 and 6.2 ppm (2 NH_2)). Esters of aziridinecarboxylic acids containing no fluorine were formed as mixtures of *cis*- and *trans*-isomers.[1] Compounds **2** were obtained as a single isomer, whose

Scheme 1



R^F = CF_3 (**1a**, **2a–c**); $H(CF_2)_2$ (**1b**, **2d**), R = Me (**2a,d**); C_6H_{13} (**2b**); $PhCH_2$ (**2c**).

* Prepared by a known procedure;[2] characteristics of previously unknown ester **1b** are given in the Experimental section.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2795–2796, November, 1996.

1066-5285/96/4511-2654 $15.00

Table 1. 3-Perfluoroalkylaziridine-2-carboxamides

Compound	R^F	R	M.p. /°C	Molecular formula	Found / Calculated (%)				Yield (%)
					C	H	F	N	
2a	CF_3	Me	74.0—74.5	$C_6H_9F_3N_2O$	39.62 39.56	5.41 4.98	31.67 31.29	15.19 15.38	69.8
2b	CF_3	C_6H_{13}	48.0—48.3	$C_{16}H_{29}F_3N_2O$	59.50 59.60	9.14 9.07	17.65 17.68	8.65 8.69	65.1
2c	CF_3	$PhCH_2$	127.0—128.0	$C_{18}H_{17}F_3N_2O$	63.99 64.66	5.35 5.12	17.64 17.07	8.47 8.38	71.3
2d	$H(CF_2)_2$	Me	70.0—71.0	$C_7H_{10}F_4N_2O$	39.07 39.26	4.70 4.71	35.04 35.48	12.77 13.08	73.2

Table 2. Spectral characteristics of 3-perfluoroalkylaziridine-2-carboxamides

Compound	R^F	R	IR spectrum, ν/cm^{-1}		^1H NMR spectrum ($CDCl_3$, δ, *J*/Hz)
			C=O	N—H	
2a	CF_3	Me	1640	3280	2.63 (s, 3 H, MeN); 2.68—2.75 (m, 2 H, H_α+H_β); 2.85 (d, 3 H, MeNH, *J* = 4.0); 6.80—7.10 (br. s, 1 H, NH)
2b	CF_3	C_6H_{13}	1620	3280	0.83—0.94 (m, 6 H, 2 Me); 1.18—1.53 (m, 16 H, 2 C_4H_8); 2.51—2.94 (m, 4 H, 2 CH_2); 3.17—3.36 (m, 2 H, H_α+H_β); 7.01 (br. s, 1 H, NH)
2c	CF_3	$PhCH_2$	1630	3280	2.75 (br. s, 1 H, NH); 3.17 (m, 2 H, H_α+H_β); 4.02 (s, 2 H, NCH_2Ph); 4.39 (d, 3 H, $NHCH_2$, *J* = 5.0); 7.00—7.37 (m, 10 H, 2 Ph)
2d	$H(CF_2)_2$	Me	1675	2970	2.60 (s, 3 H, MeN); 2.65—2.84 (m, 5 H, H_α+H_β+MeNH); 5.84 (tt, 1 H, HCF_2); 7.63 (br. s, 1 H, NH)

configuration could not be determined, since the signals of the ring protons in the ^1H NMR spectra overlap.

Experimental

IR spectra were recorded on a Specord 75 IR spectrophotometer. ^1H NMR spectra were recorded on a Tesla BS-567A spectrometer (100 MHz) using tetramethylsilane as the internal standard.

Ethyl 2,3-dibromo-4,4,5,5-tetrafluorovalerate (1b) (two diastereomers), b.p. 92—93 °C (8 Torr). IR (Nujol), ν/cm^{-1}: 1745 (C=O). ^1H NMR ($CDCl_3$), δ: 1.30 and 1.32 (t, 3 H, Me, *J* = 7.04 and 7.28 Hz); 4.28 and 4.29 (q, 2 H, CH_2); 4.50—5.00 (m, 2 H, H_α+H_β); 5.61—5.89 (tm, 1 H, HCF_2).

General procedure for the preparation of amides 2. Amine (4 mol. equivalents) was added portionwise ($MeNH_2$ was bubbled through) to a solution of α,β-dibromo-ester **1** in MeOH, which was shaken at intervals. The mixture was kept for 24 h at ~20 °C, and diluted with a fivefold volume of H_2O. The product was extracted with $CHCl_3$, and the extracts were dried with $MgSO_4$ and filtered through a silica layer. The solvent was evaporated, and the residue was recrystallized from hexane.

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Received July 13, 1995;
in revised form May 13, 1996