REACTION OF 1,1,2-TRIFLUORO-2-CHLOROETHYLDIETHYLAMINE WITH FLUOROCARBOXYLIC ACIDS

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1,1,2-Trifluoro-2-chloroethyldiethylamine (I) is widely used to replace the CO group of benzaldehydes [1] and the OH group of various unsubstituted alcohols [2-4] by the F atom. Similarly, the alcohols CH_3COOH and CH_3COOK react quite easily with (I) to give acetyl fluoride [2]. At the same time, the polyfluorinated alcohols give only the intermediate compounds, namely the products of replacing the α-F atoms in (I) by the corresponding polyfluoroalkoxyl group [5].

In the present paper it was established that fluorinated carboxylic acids when reacted with (I) easily exchange the OH group for F to give the corresponding polyfluoroacyl fluorides in over 75% yield.

$$R_FCOOH + CHClFCF_2NEt_2 \xrightarrow[-HF]{} R_FCOF + CHFClCONEt_2$$

$$R_F = CF_3(II), CF_2H(III), O_2NCF_2(IV), CF_3OCF_2(V), ClCF_2CF_2(VI), C_3F_7(VII), C_4F_9(VIII), (CF_3)_2CH(IX), C_6F_{13}(X)$$

In the case of the lower fluorocarboxylic acids the reaction is accompanied by a substantial exothermic effect, while in order to obtain perfluoroenanthyl fluoride it is necessary to heat the reaction mixture, which is apparently associated with the effect of steric factors. The reaction is run with the simultaneous distillation of the formed polyfluoroacyl fluoride, and depending on its aggregate state, into either a trap or a receiver containing fused KF in order to bind the liberated HF. Redistillation gives the pure polyfluoroacyl fluoride. It is interesting to mention that under analogous conditions we obtained as a final result from perfluorobenzoic acid not perfluorobenzoyl fluoride, but instead pentafluorobenzene (XI). This unexpected result can apparently be explained by the reaction of perfluorobenzoyl fluoride with the potassium bifluoride, formed by the binding of HF with KF, in the step of distilling the product from the KF-containing mixture.

$$C_6F_5COOH \xrightarrow[-CHFClCONEt_2]{CHFClCF_2NEt_2} [C_6F_5COF + HF \cdot KF] \xrightarrow[[-COF_2]]{t} \underset{(XI)}{C_6F_5H}$$

It was postulated that the salts of polyfluorocarboxylic acids, the same as CH_3COOK [2], will react more vigorously with (I) than the free acids. However, on the example of the K salt of α-monohydroperfluoroisobutyric acid it was established that the salts of fluorocarboxylic acids react with (I) only when heated, and here the yield of the acid fluoride drops substantially.

$$(CF_3)_2CHCOOK + CHFClCF_2NEt_2 \xrightarrow[-KF]{} (CF_3)_2CHCOF + CHFClCONEt_2$$

As a result, it may be assumed that nucleophilic replacement of the α-F atom in (I) by an acyl moiety occurs in the first step of the reaction of fluorocarboxylic acids with (I). Protonation of the N atom apparently facilitates decomposition of the intermediate adduct to the corresponding acyl fluoride and fluorochloroacetic acid diethylamide.

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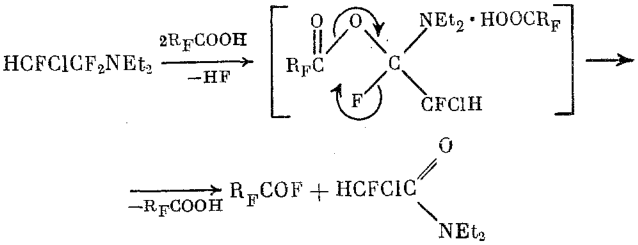
TABLE 1

Compound	Chemical shift, ppm						J,Hz
	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	
$\overset{1}{C}F_2\overset{2}{H}\overset{3}{C}OF$ (III)	51,26d.d	6,12t	−98,62 t	–	–	–	$J_{1,2}$=52,5, $J_{1,3}$=10,2
$\overset{1}{C}F_3O\overset{2}{C}F_2\overset{3}{C}OF$ (V)	−21,13 t	1,91d.q	−90,70 t	–	–	–	$J_{1,2}$=8,5, $J_{2,3}$=2,2
$Cl\overset{1}{C}F_2\overset{2}{C}F_2\overset{3}{C}OF$ (VI)	−6,38 d.t	39,65 d.t	−102,66 t.t	–	–	–	$J_{1,2}$=4,5, $J_{1,3}$=8,5, $J_{2,3}$=5,9
$\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}OF$ (VII)	4,57 t.t	51,35 d.q	43,42 d.q	−100,94 t.t	–	–	$J_{1,2}$=1,1, $J_{1,3}$=8,5, $J_{3,4}$=9,0, $J_{2,4}$=6,2
$\overset{1}{C}F_3\overset{2}{C}F_2\overset{3}{C}F_2\overset{4}{C}F_2\overset{5}{C}OF$ (VIII)	4,89 t.t	49,37 m	46,80 m	41,70 m	−100,66t	–	$J_{1,2}$=2,2, $J_{1,3}$=9,6, $J_{4,5}$=7,8
$(\overset{1}{C}F_3)_2C\overset{2}{H}\overset{3}{C}OF$ (IX)	−11,29 d.d	4,23 d. sept	−126,41 d. sept	–	–	–	$J_{1,2}$=7,3, $J_{1,3}$=9,0, $J_{2,3}$=2,1
$\overset{1}{C}F_3\overset{2}{C}F_2(\overset{3}{C}F_2)_2\overset{4}{C}F_2\overset{5}{C}F_2\overset{6}{C}OF$ (X)	5,35 m	50,08 m	46,67 m	45,96 m	42,41 m	−99,82 m	

TABLE 2

Compound	Yield, %	M. p., °C	d_{20}^{4}	Found, %			Empirical formula	Calculated, %		
				C	H (Cl) [N]	F		C	H (Cl) [N]	F
(II)*	80,2	-60÷-58	–	21,33	–	64,98	C_2F_4O	20,69	–	65,52
(III)	76,2	2–4	–	24,07	1,26	57,70	C_2HF_3O	24,49	1,02	58,16
(IV) †	75,6	15–17	–	16,69	[9,41]	39,04	$C_2F_3NO_3$	16,22	[9,46]	38,51
(V)	88,5	5–7	–	20,02	–	61,96	$C_3F_6O_2$	19,78	–	62,64
(VI)	82,7	21–24	–	19,69	(18,82)	52,11	C_3ClF_5O	19,73	(19,45)	52,05
(VII)	86,5	7–9	–	22,29	–	70,81	C_4F_8O	22,22	–	70,37
(VIII)	85,3	32	1,601	22,84	–	71,53	$C_5F_{10}O$	22,56	–	71,43
(IX)	83,8	31–32	1,508	23,98	0,57	67,52	C_4HF_7O	24,24	0,51	67,17
(X)	69,6	85–87	1,683	23,19	–	72,80	$C_7F_{14}O$	22,95	–	72,68
(XI) ‡	53,1	85–86	1,526	42,67	0,86	55,99	C_6HF_5	42,85	0,60	56,54

* Cf. [7].
† Cf. [8].
‡ Cf. [9].



This postulation is possibly substantiated by the substantially greater activity displayed by (I) toward fluorocarboxylic acids than toward their salts.

EXPERIMENTAL

The PMR and ^{19}F NMR spectra were taken on a Hitachi R-20 instrument (60 and 56.45 MHz) from HMDS and CF_3COOH (Table 1).

Typical Experiment. With stirring, 0.1 mole of the fluorocarboxylic acid was added dropwise to 0.12 mole of 1,1,2-trifluoro-2-chloroethyldiethylamine and the formed acid fluoride, depending on its aggregate state, was collected either in a receiver, cooled to 0°C, or a trap (−78°C), containing 0.12 mole of fused KF. To complete the reaction the reaction mass was gradually heated up to 100°C. The liberated acid fluoride was fractionally distilled from the employed receiver. Acid fluorides (II)-(IX) were obtained by this typical experiment. The residual reaction mass was treated with water, dried over $MgSO_4$, and after fractional distillation we obtained fluorochloroacetic acid diethylamide in 76-89%, bp 55°C (1 mm) d_D^{20} 1.164, n_D^{20} 1.4502 (cf. [6]).

Perfluoroenanthyl Fluoride (X). A mixture of 20 g (0.0549 mole) of perfluoroenanthic acid and 12.5 (0.0661) mole of 1,1,2-trifluoro-2-chloroethyldiethylamine (I) was gradually heated up to 110-120°C with the simultaneous distillation of the formed volatile products into a receiver containing 4 g (0.069 mole) of fused KF, from which (X) was isolated by fractional distillation.

Pentafluorobenzene (XI). With stirring and cooling, 24 g (0.127 mole) of (I) was added in drops to 21.2 g (0.1 mole) of perfluorobenzoic acid. The reaction mass was gradually heated up to 130°C and the distilled products (~19 g) were collected in a cooled receiver containing 8 g (0.138 mole) of fused KF, from which (XI), spectrally and chromatographically identical with an authentic specimen, was isolated by fractional distillation.

The yields, properties, and elemental analysis data of the synthesized compounds are given in Table 2.

CONCLUSIONS

The corresponding acyl fluorides are formed as the result of reacting 1,1,2-trifluoro-2-chloroethyldiethylamine with fluorocarboxylic acids.

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