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REACTION OF PERFLUORO-2-AZAPROPENE WITH CARBOXYLIC ACIDS

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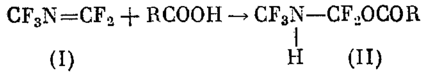
In a previous communication [1] it was shown that perfluoro-2-azapropene (I) is more electrophilic than perfluoroisobutylene. It seemed of interest to study the reaction of (I) with carboxylic acids.

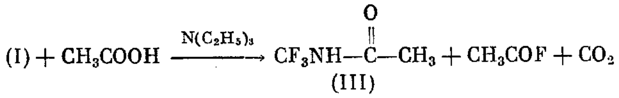
As it proved, in contrast to perfluoroisobutylene [2], (I) reacts easily, without nucleophilic assistance, with carboxylic acids. In the case of weak acids (acetic, benzoic) the reaction proceeds in ether solution at low temperature (0 to −20°C). Less nucleophilic strong carboxylic acids (trifluoro- and trichloroacetic, perfluorobutyric) react without a solvent at room temperature. The addition products, the (trifluoromethylamino)difluoromethyl esters of the corresponding acids (IIa-e), are formed in all cases:



$$\underset{\text{(I)}}{CF_3N{=}CF_2} + RCOOH \rightarrow \underset{\text{(II)}}{CF_3\underset{H}{\underset{|}{N}}{-}CF_2OCOR} \qquad (1)$$

$R = CH_3$ (a), C_6H_5 (b), CCl_3 (c), CF_3 (d), C_3F_7 (e)

The structure of the (II) esters was confirmed by the ^{19}F NMR and IR spectral data. The ^{19}F NMR spectra displayed two multiplets at −17.3 to −21.5 and −19.6 to −22.5 ppm from the difluoromethyl and trifluoromethyl groups, respectively, with a 2:3 ratio of the integral intensities. The multiplet structure of the signals is evidently due to the additional splitting of the nuclei of the fluorine atoms on the proton of the NH group. Actually, the addition of D_2O to the sample transforms the multiplet structure to a triplet from the CF_3 group and a quartet from the CF_2 group. The IR spectra of all of the obtained compounds have a band in the 3300 cm^{-1} region (NH). The (II) esters are heat unstable and, depending on the acyl radical, decompose in two directions. Whereas the esters of weak acids (IIa, b) when heated decompose to the corresponding acyl fluoride and trifluoromethylcarbamoyl fluoride,* the derivatives of strong acids decompose to the starting compounds. It is interesting that in the presence of catalytic amounts of triethylamine the reaction product of (I) with AcOH is not the ester (II), but rather a mixture of acetyl fluoride and N-trifluoromethylacetamide (III):



$$\text{(I)} + CH_3COOH \xrightarrow{N(C_2H_5)_3} \underset{\text{(III)}}{CF_3NH{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + CH_3COF + CO_2 \qquad (2)$$

Apparently, the initially formed addition product (II) is decomposed to acetyl fluoride and trifluoromethylcarbamoyl fluoride. The latter in the presence of triethylamine forms the mixed anhydride of trifluoromethylcarbamic and acetic acids (IV), the decarboxylation of which leads to amine (III):

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*The reaction of (I) with AcOH, followed by treatment of the trifluoromethylcarbamoyl fluoride with KF, is a convenient method for the synthesis of trifluoromethyl isocyanate.

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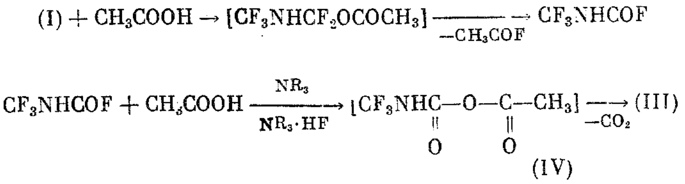


$$(I) + CH_3COOH \rightarrow [CF_3NHCF_2OCOCH_3] \xrightarrow[-CH_3COF]{} CF_3NHCOF$$

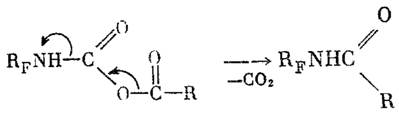
$$CF_3NHCOF + CH_3COOH \xrightarrow[NR_3\cdot HF]{NR_3} \underset{(IV)}{[CF_3NH\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_3]} \xrightarrow[-CO_2]{} (III) \qquad (3)$$

We experimentally confirmed the ability of trifluoromethylcarbamoyl fluoride to react with AcOH in the presence of triethylamine to give N-trifluoromethylamide (III).

A catalytic amount of triethylamine is sufficient to accomplish this reaction, since the (I) present in the reaction medium is capable of regenerating it from the hydrofluoride:

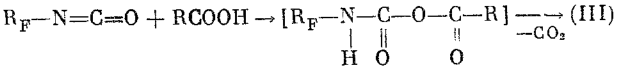
$$(I) + (C_2H_5)_3N\cdot HF \rightleftarrows (CF_3)_2\overset{\ominus}{N}(C_2H_5)_3\overset{\oplus}{N}H \rightleftarrows (CF_3)_2NH + (C_2H_5)_3N \qquad (4)$$

The decomposition of the mixed anhydrides of trifluoromethylcarbamic and alkylcarboxylic acids can be compared to the Borodin–Hunsdiecker reaction:



(5)

Proof that the formed mixed anhydride (IV) is unstable is the fact that the reaction of the trifluoromethyl and α-monohydrohexafluoroisopropyl isocyanates with carboxylic acids (autoclave, 24 h) also leads to N-trifluoromethylamides:



$$R_F-N=C=O + RCOOH \rightarrow [R_F-\underset{\underset{H}{|}}{N}-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R] \xrightarrow[-CO_2]{} (III) \qquad (6)$$

$R_F = CF_3$, $R = CH_3$ (a); $R_F = CF_3$, $R = CF_3$ (b); $R_F = (CF_3)_2CH$, $R = CH_3$ (c);
$R_F = (CF_3)_2CH$, $R = H$ (d)

The proposed schemes (3)-(6) make it possible to explain the formation of N-trifluoromethylamides when carboxylic acids are reacted with (I) and NaF (1:2) [3].

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were taken on a Perkin–Elmer R-20 instrument (56.46 MHz). The chemical shifts are given in parts per million (using CF_3COOH and HMDS as the standards).

Acetate (IIa). To a stirred solution of 10.2 g of (I) in 30 ml of abs. ether at −70° was added 3 g of anhydrous AcOH, the temperature of the mixture was brought up to 20°, and the mixture was stirred for another hour and then vacuum-distilled. We obtained 6.0 g (62.8%) of (IIa), bp 42-43° (75 mm); n_D^{20} 1.3191. Found: C 24.93; H 2.98; N 7.41; F 49.23%. $C_4H_4F_5NO_2$. Calculated: C 24.88; H 2.09; N 7.25; F 49.19%. ^{19}F NMR spectrum: −20.8 m (CF_2); −22.0 m (CF_3).

Benzoate (IIb). Obtained the same as (IIa). ^{19}F NMR spectrum: −21.5 m (CF_2); −22.5 m (CF_3).

Trichloroacetate (IIc). A steel test tube, containing 6.7 g of (I) and 8.0 g of CCl_3-COOH, was kept for 24 h and then the mixture was vacuum-distilled to give 7.1 g (40%) of (IIc), bp 51-52° (23 mm); n_D^{20} 1.3818. Found: C 16.89; H 0.63; N 4.86; F 31.20%. $C_4HF_5NO_2Cl_3$. Calculated: C 16.21; H 0.34; N 4.73; F 32.05%. ^{19}F NMR spectrum: −18.3 m (CF_2); −21.7 m (CF_3).

Trifluoroacetate (IId). Obtained the same as (IIc). Yield 45.5%, bp 61-62°; $n_D^{20} < 1.3$. Found: C 19.56; H 0.46; N 5.82%. $C_4HF_8NO_2$. Calculated: C 19.4; H 0.41; N 5.67%. ^{19}F NMR spectrum: −17.3 m (CF_2); −19.6 m (CF_3).

Perfluorobutyrate (IIe). Obtained the same as (IIc). ^{19}F NMR spectrum: −17.3 m (CF_2); −19.7 m (CF_3).

Reaction of (I) with Acetic Acid under Pressure. A steel test tube, containing 6.7 g of (I) and 3 g of anhydrous AcOH, was kept for 24 h. Vacuum-distillation gave 2 g of acetyl fluoride, bp 22°, and 5.6 g (86%) of trifluoromethylcarbamoyl fluoride, bp 44° (80 mm). The ^{19}F NMR spectrum was identical with the spectrum of an authentic specimen.

Reaction of (I) with Benzoic Acid under Pressure. In a similar manner, from 6.1 g of benzoic acid and 6.7 g of (I) we obtained 4.9 g of benzoyl fluoride, bp 157°, and 4.6 g (74%) of trifluoromethylcarbamoyl fluoride, bp 43-44° (80 mm).

Thermal Decomposition of Esters (IIa) and (IIb). When (IIa) and (IIb) were kept on the steam bath for 2 h we obtained trifluoromethylcarbamoyl fluoride, bp 44° (80 mm) (the ^{19}F NMR spectrum was identical with the spectrum of an authentic specimen), and respectively acetyl fluoride, bp 18-20°, and benzoyl fluoride, bp 157°.

Thermal Decomposition of Esters (IIc), (IId), and (IIe). Similar to the preceding, when (IIc), (IId), and (IIe) were heated we obtained (I), bp −28 to −33° (the ^{19}F NMR spectrum was identical with the spectrum of an authentic specimen), and the corresponding acids.

Reaction of (I) with Acetic Acid in the Presence of Triethylamine. A mixture of 10 g of anhydrous AcOH, 25 g of (I), and several drops of Et_3N was kept in an autoclave for 7 h. After distilling off the acetyl fluoride and bis(trifluoromethyl)amine (the ^{19}F NMR spectra were identical with the spectra of authentic specimens) the residue was sublimed to give 8 g (38%) of N-trifluoromethylacetamide, mp 84°. Found: N 45.22; N 11.10%. $C_3H_4F_3NO$. Calculated: F 44.92; N 11.0%. ^{19}F NMR spectrum: −22.2 d (CF_3C).

Amide (IIIa). An autoclave, containing 3 g of anhydrous AcOH and 7 g of trifluoromethyl isocyanate, was shaken for 5 h. The obtained amide (IIIa) was sublimed in vacuo (4.3 g, 67%), mp 83-84°. Found: F 45.41; N 10.64%. $C_3H_4F_3NO$. Calculated: F 44.92; N 11.0%.

Amide (IIIb). Obtained in a similar manner in 53% yield, mp 40-41°; bp 98-100°; mass spectrum (m/e): 181 (M^+, C_3HNOF_6), 112 ($M - CF_3C_2HF_2NO$), 84 ($M - C_2F_2NO$, CHF_3), 97 ($M - CHF_3O$). ^{19}F NMR spectrum: −22.12 (CF_3) −21.01 (CF_3C).

Amide (IIIc). Obtained in a similar manner in 96.3% yield, mp 153°. Found: F 54.97; N 7.10%. $C_5H_5F_6NO$. Calculated: F 54.54; N 6.76%. Mass spectrum (m/e): 209 (M^+, $C_5H_5F_6NO$), 194 ($M - CH_3$, $C_4H_2F_6NO$), 124 ($M - C_2H_4F_3$, $C_3HNO_2F_2$). ^{19}F NMR spectrum: −21.33 (CF_3C). ^1H NMR spectrum: 6.82 m (NH); 5.11 m (CH).

Amide (IIId). Obtained in a similar manner in 94.4% yield, mp 71°. Found: F 59.02; N 6.89%. $C_4H_3F_6NO$. Calculated: F 58.48; N 7.18%. Mass spectrum (m/e): 195 (M^+ $C_4H_3F_6NO$), 126 ($M - CF_3$, $C_3H_3F_3NO$).

CONCLUSIONS

1. The reaction of perfluoro-2-azapropene with carboxylic acids gave the (trifluoromethylamino)difluoromethyl esters of the corresponding acids. The latter are heat unstable and, depending on the acyl radical, decompose either to the starting compounds or to the acyl fluoride and trifluoromethylcarbamoyl fluoride.

2. N-Trifluoromethylacetamide was obtained when perfluoro-2-azapropene is reacted with acetic acid in the presence of triethylamine.

3. The reaction of trifluoromethyl and α-monohydrohexafluoroisopropyl isocyanates with carboxylic acids gave the corresponding carboxamides.

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