Chemistry

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Abstract

Full Text

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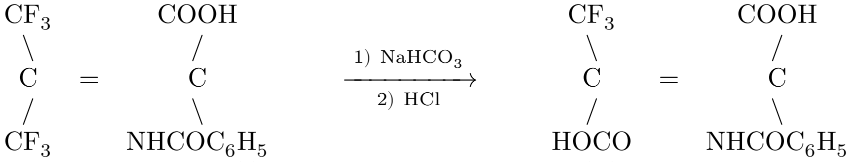
On the Mobility of Fluorine Atoms in Derivatives of Benzamidohexafluorodimethylacrylic Acid

The fluorine atoms of the trifluoromethyl group, which are usually not prone to heterolytic cleavage, acquire the capacity for such cleavage if the C—F bonds are conjugated with a carbon-carbon double bond (^{1}).

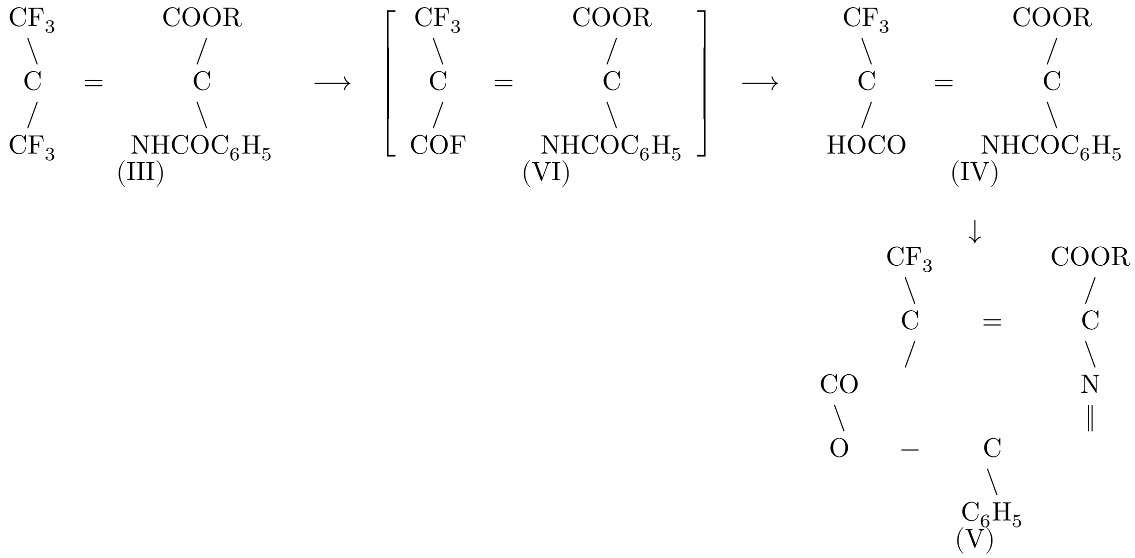
The fluorine atoms of the trifluoromethyl group in α-benzamidohexafluorodimethylacrylic acid and its derivatives, obtained from 2-phenyl-4-hexafluoroisopropylideneoxazolone-5 (^{2}), as it turned out, are saponified with unusual ease. α-Benzamidohexafluorodimethylacrylic acid (I), on reacting with a saturated solution of sodium bicarbonate at room temperature, is converted into the salt of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (II)



$$(CF_3)_2C=C(COOH)NHCOC_6H_5 \xrightarrow[2)\ HCl]{1)\ NaHCO_3} (CF_3)(HOCO)C=C(COOH)NHCOC_6H_5$$

(I) (II)

The esters of α-benzamidohexafluorodimethylacrylic acid (III) behave similarly; however, in this case, in addition to the acid esters of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (IV), 2-phenyl-4-carbalkoxy-5-trifluoromethyl-1,3-oxazin-6-ones (V) are also obtained, probably as a result of cyclization of the intermediately formed fluoroanhydrides (VI). These oxazine derivatives were also obtained by dehydration of the acid esters (IV) with the aid of ketene

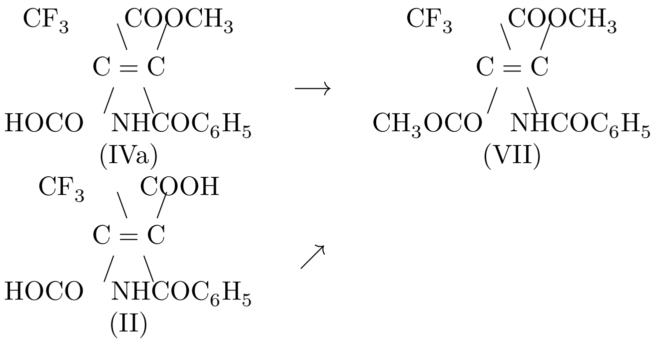


(III) (VI) (IV) (V)

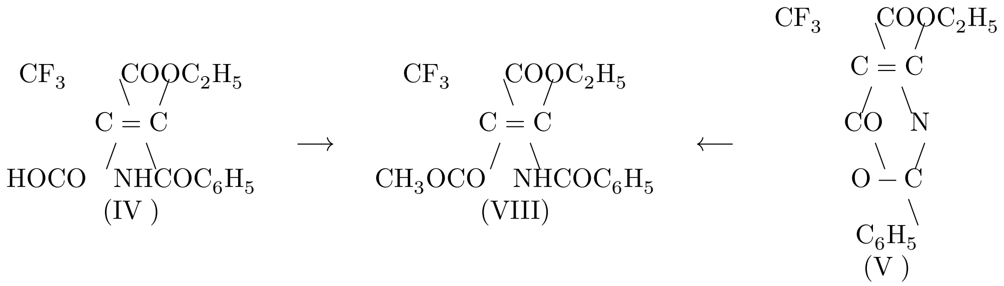
a) $R = CH_3$,
b) $R = C_2H_5$.

Similar six-membered analogs of oxazolones, which are internal cyclic anhydrides of β-benzamido acids, are known. Thus, dehydration of β-benzamidocrotonic acid under the action of acetic anhydride gave 2-phenyl-4-methyl-1,3-oxazinon-6 (3).

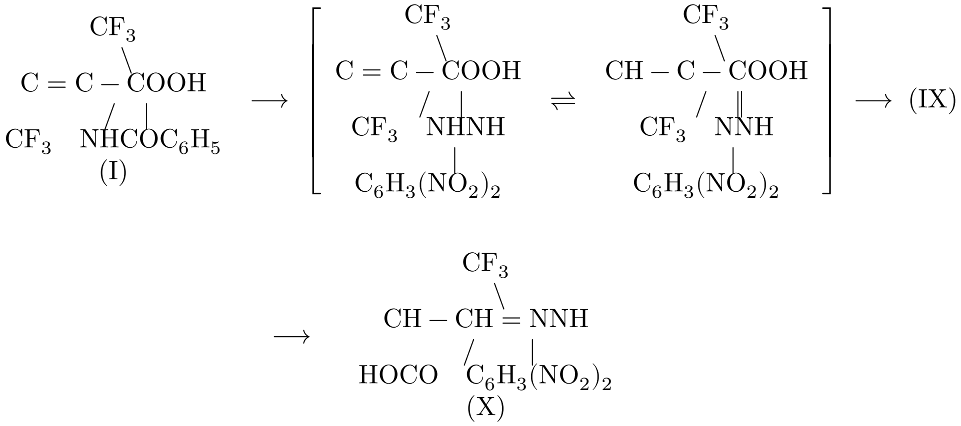
On reaction of the acid esters of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid with diazomethane, the corresponding full esters (VII and VIII) were obtained. Dimethyl ester VII is also formed on methylation of dicarboxylic acid II with diazomethane, and methyl ethyl ester VIII by the reaction of 2-phenyl-4-carbethoxy-5-trifluoromethyl-1,3-oxazinon-6 (V) with methyl alcohol in the presence of triethylamine:



(IVa) (VII) (II)


(IV) → (VIII) ← (V)

Examples demonstrating the ease of saponification of trifluoromethyl groups in α-benzamidohexafluorodimethylacrylic acid and its derivatives are not exhausted by reactions in alkaline medium. Thus, in an attempt to obtain a derivative of substituted pyruvic acid (IX) from acid I by boiling it with an hydrochloric-acid solution of 2,4-dinitrophenylhydrazine, as a result of decarboxylation and saponification of one of the trifluoromethyl groups, the 2,4-dinitrophenylhydrazone of the semialdehyde of α-trifluoromethylmalonic acid (X) was isolated:


(I) → (IX) → (X)

The exceptional ease of saponification of the trifluoromethyl groups in α-benzamidohexafluorodimethylacrylic acid and its derivatives is evidently explained by conjugation of the C–F bonds not only with the carbon-carbon double bond but also with the unshared electron pair of the nitrogen atom; these compounds may be regarded as vinylogs of acylated trifluoromethylamines

$$F_3C\text{–}C(=C(CF_3)\text{–}C(=C)(COOR)\text{–}NHCOC_6H_5) \qquad F_3C\text{–}NHCOC_6H_5$$

The high mobility of fluorine atoms in compounds of the latter type is well known. As an example one may cite the saponification of perfluoroalkylated ureas to ureas of perfluorocarboxylic acids, with loss of two fluorine atoms (4):

$$C_2F_5CF_2NHCONHR \rightarrow C_2F_5CONHCONHR$$

Experimental Part

1-Benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (II). A solution of 2 g of α-benzamidohexafluorodimethylacrylic acid (I) in 50 ml of saturated sodium bicarbonate solution was kept at room temperature for several days, then acidified with dilute hydrochloric acid. A precipitate of II separated; yield 1.07 g (58% of theory), m.p. 167–168° (with decomposition) (from dichloroethane).

Found, %: C 47.65; 47.04; H 2.70; 2.87; F 19.03; 19.65
$C_{12}H_8F_3O_5N$. Calculated, %: C 47.53; H 2.66; F 18.80;

Acid methyl ester of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (IVa) and 2-phenyl-4-carbomethoxy-5-trifluoromethyl-1,3-oxazin-6-one (Va). 2.7 g of methyl ester of α-benzamidohexafluorodimethylacrylic acid (IIIa) was treated with an excess of saturated sodium bicarbonate solution at room temperature for 3 days, with thorough trituration from time to time. The precipitate was filtered off and recrystallized from heptane. 0.15 g of Va was obtained (6.3% of theory), m.p. 157–158.5°.

Found, %: C 51.85; 52.27; H 2.63; 2.80; F 19.18; 19.35; N 4.47; 4.69
$C_{13}H_8F_3O_4N$. Calculated, %: C 52.18; H 2.69; F 19.05; N 4.68

On acidification of the bicarbonate filtrate, 0.5 g of IVa was isolated (20% of theory), m.p. 146–148° (with decomposition) (from toluene).

Found, %: C 49.60; 49.67; H 3.01; 3.37; F 17.37; 18.35; N 4.53; 4.74
$C_{13}H_{10}F_3O_5N$. Calculated, %: C 49.22; H 3.18; F 17.97; N 4.42.

IVa, on treatment with ketene in ethereal solution, is converted into Va.

Acid ethyl ester of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (IVb) and 2-phenyl-4-carbethoxy-5-trifluoromethyl-1,3-oxazin-6-one (Vb). IVb and Vb were obtained from ethyl ester of

α-benzamidohexafluorodimethylacrylic acid (IIIb) analogously to the methyl esters. Yield of IVb 6.9% of theory, m.p. 131–132° (with decomposition) (from a mixture of benzene with heptane).

Found, %:	C 50.35;	H 3.68;	F 16.37;	N 4.34
$C_{14}H_{12}F_3O_5N$. Calculated, %:	C 50.76;	H 3.65;	F 17.21;	N 4.23

Yield of Vb 36.4% of theory, m.p. 148.5–150° (from heptane).

Found, %:	C 54.04; 54.24;	H 3.33; 3.39;	F 18.71; 18.53
$C_{14}H_{10}F_3O_4N$. Calculated, %:	C 53.68;	H 3.22;	F 18.20

Dimethyl ester of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (VII). VII was obtained in the usual manner by treating 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (II), or its methyl ester (IVa), with an equivalent amount of diazomethane in ethereal solution. M.p. 109–111° (from hexane).

$C_{14}H_{12}F_3O_5N$.	Found %:	C	50.94; 50.90;	H	3.76; 3.80;	F	16.65; 17.15
	Calculated %:	C	50.76;	H	3.65;	F	17.21

Methyl ethyl ester of 1-benzamido-2-trifluoromethylethylene-1,2-dicarboxylic acid (VIII). A solution of 0.4 g of 2-phenyl-4-carbethoxy-5-trifluoromethyl-1,3-oxazinone-6 (V), 0.09 g of methanol, and 3 drops of triethylamine in 20 ml of benzene was kept at room temperature for several days. After removal of the solvent, the precipitate was washed with sodium bicarbonate solution and with water. Obtained: 0.4 g (91% of theory) of VIII, m.p. 107–107.5° (from heptane).

$C_{15}H_{14}F_3O_5N$.	Found %:	C	52.28; 52.32;	H	4.00; 4.07;	F	17.43; 16.89
	Calculated %:	C	52.16;	H	4.09;	F	16.50

VIII was also obtained from IV by treatment with diazomethane in ethereal solution.

2,4-Dinitrophenylhydrazone of the half-aldehyde of α-trifluoromethylmalonic acid (X). 0.5 g of α-benzamidohexafluorodimethylacrylic acid (I) was boiled with an excess of hydrochloric acid solution of 2,4-dinitrophenylhydrazine for 1 hour. The precipitate was filtered off and recrystallized from dichloroethane. Obtained: 0.34 g (66% of theory) of X, m.p. 200–201°.

$C_{10}H_7F_3O_6N_4$. Found %: C 35.62; H 1.86; F 18.21; N 16.74
Calculated %: C 35.71; H 2.08; F 16.96; N 16.66

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Note: Figure translations are in progress. See original paper for figures.