SOME CONVERSIONS OF AMIDES

OF α-AMINOPERFLUOROCARBOXYLIC ACIDS UDC 542.91+547.298.1+547.466+546.16

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We have shown previously that the action of ammonia on perfluoroolefin oxides forms amides of α -amino- or α, α -diaminoperfluorocarboxylic acids, depending on the structure of the oxide [1, 2]. The present work was devoted to a study of some reactions of the amides obtained.

When hydrochloric acid acts on amides of α, α -diaminoperfluorocarboxylic acids (I), the gem-diamino grouping is readily converted (even at room temperature) into a gem-dihydroxy grouping, amides of α, α dihydroxyperfluorocarboxylic acids (II) being formed. Under more severe conditions, the amide function also undergoes hydrolysis, leading to α, α -dihydroxyperfluorocarboxylic acids (hydrates of α -oxoperfluorocarboxylic acids) (III). The latterare identical with the acids obtained by the hydrolysis of the perfluoroolefin oxides [1].

$$\begin{array}{cccc} & \mathrm{NH}_2 & \mathrm{OH} \\ \mathrm{R-C-CONH}_2 & \overset{H_{2O}}{\underset{\mathrm{H}_2\mathrm{CI}}{\overset{H_{2O}}{\overset{H_{2O}}{\overset{H_{2O}}{\overset{H_{1O}}{\overset{H_{2O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{1O}}{\overset{H_{$$

In contrast to the gem-diamino groupings in the amides (I), the α -amino group in the amide of α aminoperfluoroisobutyric acid (IV), obtained from perfluoroisobutylene oxide, is stable to hydrolysis. The action of hydrochloric acid at room temperature on the amide (IV) gives the hydrochloride which, on heating (150°C), decomposes into HCl and the initial amide. The low stability of the hydrochloride is explained by the fact that the basic properties of the amino group are weakened through the electron-attracting action of the amide and trifluoromethyl groups.

When α -aminoperfluoroisobutyramide is heated with hydrochloric acid the α -aminoperfluoroisobutyric acid formed as an intermediate undergoes decarboxylation instantaneously and hexafluoroisopropylamine (V) is obtained. The acid can be trapped only in the form of the sodium salt (VI), which is obtained by the saponification of the amide in the presence of alkali



We obtained the corresponding α -hydroxy acid (VII) by the hydrolysis of perfluoroisobutylene oxide



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The acylation of α -aminoperfluoroisobutyramide (IV) and α , α -diaminoperfluoropropionamide (Ia) led to the corresponding mono- and diacyl derivatives (VIII) and (IX)



The latter reaction shows the great stability of the gem-diamino grouping in amides of α , α -diamino-perfluorocarboxylic acids as compared with the geminal diamines known previously (see [3]).

EXPERIMENTAL

 α , α -Dihydroxyperfluoropropionamide (IIa). A solution of 0.5 g of the amide (Ia) in 2 ml of dilute HCl (1:1) was evaporated at room temperature. This gave 0.2 g (40% of theoretical) of the amide (IIa), mp 111-113°C (from ethanol-benzene). Found %: C 23.08; H 2.68; N 8.54; F 35.83. C₃H₄F₃NO₃. Calculated %: C 22.64; H 2.52; N 8.80; F 35.85. The amide (IIa) was also obtained by the action of aqueous ammonia on trifluoropyruvic ester.

 α , α -Dihydroxy- ω -hydroperfluorocaprylamide (IIb). At room temperature, 0.2 g of α , α -diamino- ω -hydroperfluorocaprylamide was treated with 2 ml of concentrated HCl. The amide dissolved, but a new precipitate formed immediately. After 4 h, the precipitate was filtered off, and washed with water. This gave 0.1 g (50% of theoretical) of the amide (IIb), mp 170-172°C (from aqueous ethanol). Found %: F 58.77; N 3.44. C₈H₅F₁₂NO₃. Calculated %: F 58.31; N 3.58.

 α , α -Dihydroxyperfluoropropionic Acid (IIIa). A mixture of 0.5 g of the amide (Ia) and 2 ml of dilute HCl (1:1) was boiled for 2 h, and then the solution was evaporated in the water bath. This gave 0.2 g (39%) of the acid (IIIa), mp 124-126°C (from dichloroethane). A mixture with an authenic sample [1] gave no depression of the melting point.

 α , α -Dihydroxy- ω -hydroperfluorocaprylic Acid (IIIb). A mixture of 4.8 g of ω hydroperfluorooctene oxide, 0.7 ml of water, 10 ml of ether, and 0.2 g of finely ground silica gel was heated in a steel tube in the boiling water bath for 4 h. After evaporation of the filtrate, 4 g (80%) of the acid (IIb) was obtained as a residue, mp 98-100°C (from dichloroethane). Found %: C 23.26; H 1.64; F 54.31. C₈H₄F₁₂O₄ · H₂O. Calculated %: C 23.41; H 1.46; F 55.60. Neutralization equivalent: found 420, calculated 410. IR spectrum: 1735 and 1785 cm⁻¹ (two CO groups).

A mixture of 0.6 g of α, α -diamino- ω -hydroperfluorocaprylamide and 8 ml of concentrated HCl was boiled for 2 h and evaporated to dryness. From the residue absolute ether extracted the acid (IIIb), yield 0.5 g (82.5%), mp 98-100° C (from dichloroethane). A mixture with the sample obtained in the preceding experiment gave no depression of the melting point.

After being dried for several days over P_2O_5 at 60°C, the acid (IIIb) was converted into α -oxo- ω -hydroperfluorocaprylic acid, mp 71-76°C. Found %: C 25.70; H 0.60; F 60.84. $C_8H_2F_{12}O_3$. Calculated %: C 25.67; H 0.53; F 60.96. Neutralization equivalent: found 379, calculated 374.

 α -Aminoperfluoroisobutylamide Hydrochloride. A mixture of 1 g of α -aminoperfluoroisobutylamide (IV) and 2 ml of concentrated HCl was evaporated at room temperature and the residue was reprecipitated with ether from ethanolic solution. This gave 0.7 g (60%) of the hydrochloride of the amide (IV) mp 145-150°C (decomp., remelting at 60-67°C). Found %: 46.08; N 11.53; Cl (ionic) 14.83. C₄H₄F₆N₂O \cdot HCl. Calculated %: F 46.25; N 11.36; Cl 14.43.

Sodium α -Aminoperfluoroisobutyrate (VI). A solution of 2.8 g of the amide (IV) and 0.6 g of NaOH in 4 ml of water was boiled for 1.5 h and evaporated to dryness in vacuum in the water bath, after which the residue was washed with absolute ether. This gave 1.85 g (60%) of the salt (VI). For analysis, the salt was recrystallized from aqueous ethanol. Found %: 5.64. C₄H₂F₆NNaO₂. Calculated %: N6.01. IR spectrum: 1670 cm⁻¹ (C = O); 3320, 3390, 3420 cm⁻¹ (N-H).

<u>Hexafluoroisopropylamine</u> (V). Eight milliliters of dilute HCl (3:1) was slowly added to 6 g of the salt (VI). After the evolution of CO_2 had ceased, the resulting solution was treated with a solution of 1.5 g of NaOH in 2 ml of water, the amine formed being distilled off simultaneously into a receiver containing solid KOH. This gave 2 g (46%) of the amine (V), bp 57°C. Literature data [4]: bp 57°C. When the amine (V) was treated with phenyl isocyanate, N-phenyl-N'-hexafluoroisopropylurea was obtained with mp 212°C (from aqueous ethanol). A mixture with an authentic sample [4] gave no depression of the melting point.

 α -Hydroxyperfluoroisobutyric Acid (VII). A mixture of 12 g of perfluoroisobutylene oxide, 3 ml of water, 8 ml of acetone, and 0.7 g of ground silica gel was heated in a steel tube in the boiling water bath for 12 h and filtered, the acetone was distilled off from the filtrate, and the residue was dried with MgSO₄ and distilled. This gave 4.6 g (39%) of the acid (VII), bp 150-153°C, mp 78-80°C. Neutralization equivalent: found 210, calculated 212. Aniline salt – mp 102°C (from benzene). A mixture with the salt obtained from an authentic sample of the acid [5] gave no depression of the melting point. Found %: N 4.88. C₅H₂F₆O₃ · C₆H₇N. Calculated %: N 4.59.

 $\frac{\alpha - A \operatorname{cetamidoperfluoroisobutyramide} (VIII).}{\alpha} A \operatorname{mixture of 4.2 g of the amide} (IV), 2 g of acetyl chloride, and 15 ml of absolute benzene was boiled for 2 h. This gave as a precipitate 4 g (80%) of the amide (VIII), mp 173-174°C (from acetonitrile). Found %: 28.49; H 2.52; F 45.88. C₆H₆F₆N₂O₂. Calculated %: C 28.57; H 2.38; F 45.24.$

 α , α - Dibenzamidoperfluoropropionamide (IX). A mixture of 1.5 g of the amide (Ia), 1.4 g of benzoyl chloride, and 5 ml of acetonitrile was heated at 60°C for 2 h. The hot solution was filtered, the filtrate was evaporated in vacuum at 50°C, and the residue was crystallized after repeated treatment with absolute ether. This gave 1 g (44%) of the adduct of the amide (IX) with one molecule of dioxane, mp 208-210°C (from dioxane). Found %: C 55.94; H 4.79; F 12.49; N 9.14. C₁₇H₁₄F₃N₃O₃ · C₄H₈O₂. Calculated %: C 55.63; H 4.86; F 12.59; N 9.27. IR spectrum: 1500, 1670, and 1750 cm⁻¹ (C = O)

CONCLUSIONS

1. The acid hydrolysis of amides of α -amino- and α, α -diaminoperfluorocarboxylic acids have been studied. In the diaminoamides, the gem-diamino grouping hydrolyses first and then (under more severe conditions) in the amide function, which leads to the formation of α, α -dihydroxyperfluorocarboxylic acids (hydrates of α -oxoperfluorocarboxylic acids). In the hydrolysis of α -aminoperfluoroisobutyramide, the unstable α -aminoperfluoroisobutyric acid is formed which immediately undergoes decarboxylation to form hexafluoroisopropylamine.

2. α -Hydroxyperfluoroisobutyric and α -oxo- ω -hydroperfluorocaprylic acids have been obtained by the hydration of perfluoroisobutylene oxide and ω -hydroperfluorooctene oxide, respectively.

3. The acylation of α -aminoperfluorobutyramide and α , α -diaminoperfluoropropionamide has given the corresponding mono- and bis (acylamino) amides.

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