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Isomerization of a perfluoro-α-lactam

D.P. Del'tsova* and N.P. Gambaryan

A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117813 Moscow (Russian Federation)

Abstract

Prolonged heating of the perfluoro-α-lactam $(CF_3)_2C(CO)(NC(CF_3)_3)$ (I) at 110–150 °C gives a mixture of isocyanate $(CF_3)_3C-C(CF_3)_2NCO$ (V) (as the main product), acylimine $(CF_3)_2C=N-C(O)C(CF_3)_3$ (III), $(CF_3)_3C-C(CF_3)_3$ (VI) and other products. A radical mechanism is proposed for the reaction.

Introduction

α-Lactams are known to isomerize at 40–60 °C into iminolactones, which decompose to give carbonyl compounds and isonitriles [1, 2]. The formation of methacrylic acid amide, noted previously [3], is caused by the presence of impurities in the starting α-lactam [2]. These isomerizations are connected with the C−N bond opening of the α-lactam ring.

The perfluoro-α-lactam **I** undergoes quite different conversions. Through the action of nucleophiles (CsF, R_3N), α-lactam **I** isomerizes with cleavage of the C−C bond in its ring even at room temperature. The intermediate anion **II** is stabilized by migration either of the anion $(CF_3)_3C$ from the N atom or of the fluoride anion from the trifluoromethyl group to a carbonyl group, resulting in the acylimine **III** [4] or the carbomoyl fluoride **IV** [5], respectively (Scheme 1).

Results and discussion

In spite of its high thermal stability, the perfluoro-α-lactam **I** isomerizes under prolonged heating at 110–150 °C with cleavage of its ring C−C bond and migration of the $(CF_3)_3C$ group from an N atom to the carbon atoms. This isomerization gives a mixture of the isocyanate **V** (the main product), acylimine **III**, perfluoro-2,2,3,3-tetrakis(trifluoromethyl)butane (**VI**) and unidentified reaction products. The product ratio is virtually independent of the temperature. Increasing the temperature to 150–160 °C causes a significant decrease in the thermolysis time accompanied by a negligible increase in isocyanate yield (from 50 to 55%), while the yield of acylamine **III** remains unchanged (16–17%).

The formation of compound **VI** (the product of the dimerization of $(CF_3)_3C$ radicals [6]) is confirmed by the NMR spectra of the mixture (−20.4 ppm (s, d) [cf. ref. 7]), thus supporting the radical nature of the reaction. Hence we may assume that under thermolytic conditions, α-lactam **I** decomposes to form the cyclic radical **VII** and a perfluoro-t-butyl radical (Scheme 2).

Attack by the $(CF_3)_3C$ radical (cf. ref. 8) at a carbonyl O-atom of α-lactam **I** provides the main reaction route. The resulting radical **VIII** eliminates the $(CF_3)_3C$ radical from the nitrogen atom to give the azirine **IX**; the latter isomerizes into isocyanate **V** under the reaction conditions. (Isomerization of methoxyazirine into the isocyanate has been reported previously [9]). Recombination of a perfluoro-t-butyl radical with radical **X** (the latter being formed as a result of the isomerization of the cyclic radical **VII**) gives acylamine **III**.

Attempts to separate the isomers by distillation after thermolysis failed because of their high volatilities and the closeness of their boiling points. Isocyanate **V** was isolated by preparative GLC methods. The structure of product **V** was confirmed by spectral means (IR, MS, ^{19}F NMR). Its reaction with ethanol leads to an addition product, uretane **XI**, which slowly eliminates $(CF_3)_3CH$ in the presence of ethanol to give uretane **XII**. Acylamine **III** was isolated from the mixture as oxadiazine **XIII** [10], the product of a 1,4-cycloaddition to PhCN.

We have thus established some new rearrangements of the perfluoro-α-lactam **I** into its linear isomers **III**,

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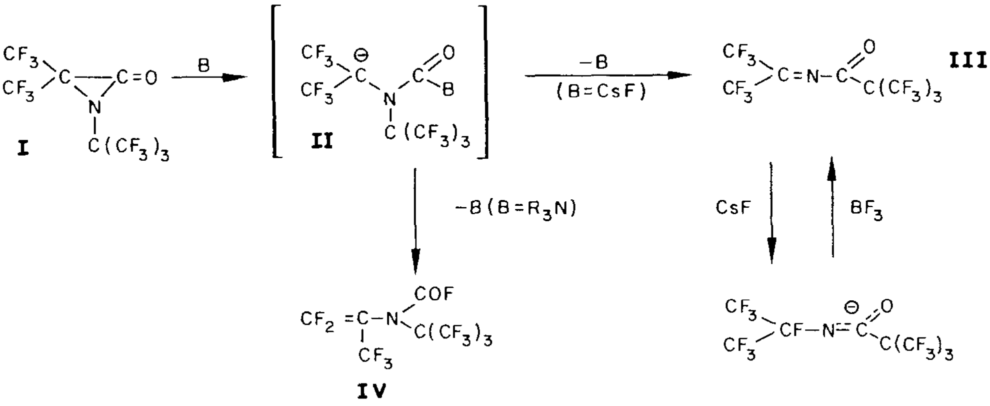
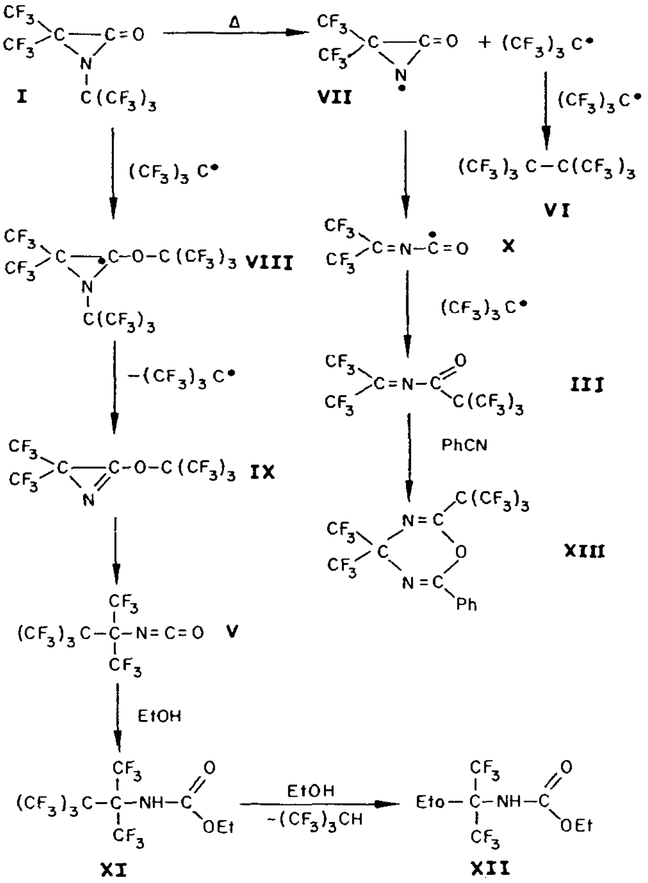
*To whom all correspondence should be addressed.



Scheme 1.



Scheme 2.

IV and V that have no analogues in non-fluorinated compounds.

Experimental

^{1}H and ^{19}F NMR spectra were recorded using a Bruker WP-200S (200.0 and 188.3 MHz) spectrometer with TMS and CF_3COOH as external standards. Chemical shifts are quoted in parts per million. IR spectra were obtained with a UR-20 spectrometer. Mass spectra (70 eV) were recorded with a VG7070E instrument; *m/z*, intensity (%) are given. Preparative GLC separation was conducted on a Carlo Erba chromatograph using a column packed with 20% FS-1265 on Chromosorb N.

Thermolysis of the α-lactam I

α-Lactam **I** [11] (10.0 g) was heated in a sealed ampoule for 60 h at 150 °C and the resulting mixture distilled. A mixture (9.1 g, b.p. 98–105 °C), containing 55% isocyanate **V** and 17% acylimine **III** was obtained. Perfluoro-α-t-butylisopropyl-isocyanate (**V**) was isolated from the above mixture by preparative GLC methods, b.p. 121 °C, m.p. 74–76 °C. Analysis: Found: C, 23.21; F, 69.56; N, 3.40%. $C_8F_{15}NO$ requires: C, 23.35; F, 69.34; N, 3.40%. IR (ν, cm^{-1}): 2300 (NCO). MS: 342 (20) $(M-CF_3)^+$; 323 (1.36) $(M-CF_3-F)^+$; 254 (6.45) $(M-2CF_3-F)^+$; 226 (1.49) $(M-2CF_3-COF)^+$; 204 (4.35) $(M-3CF_3)^+$; 193 (3.31) $(M-2CF_3-2F-NCO)^+$; 192 (67.53) $(M-C_4F_9)^+$; 181(2.11) $(C_4F_7)^+$; 173 (0.61) $(C_3F_5NCO)^+$; 143 (1.91) $(C_4F_5)^+$; 142 (32.09) $(C_2F_4NCO)^+$; 138 (0.62) $(C_2F_6)^+$; 131 (0.68) $(C_3F_5)^+$; 123 (0.96) $(C_2F_3NCO)^+$; 112 (0.60) $(C_3F_4)^+$; 100 (0.62) $(C_2F_4)^+$; 93 (2.72) $(C_3F_3)^+$; 92 (15.61) $(CF_2NCO)^+$; 76 (1.44) $(CF_2CN)^+$; 69 (100) $(CF_3)^+$; 54 (1.47) $(CNCO)^+$; 50 (2.62) $(CF_2)^+$; 47 (4.03) $(COF)^+$; 31 (2.27) $(CF)^+$. ^{19}F NMR (ether) δ: −11.9 (dec, $(CF_3)_2C$); −18.2 (h, $(CF_3)_3C$, $J(F-F)=12.2$ Hz) ppm.

Under similar conditions at 100–110 °C for 310 h, α-lactam **I** gave a mixture containing 50% isocyanate **V** and 17% acylimine **III** (^{19}F NMR data).

Reaction of isocyanate V with alcohol

To a solution consisting of 0.9 g isocyanate **V** in 2 ml anhydrous ether, 0.1 g anhydrous ethanol was added under cooling and stirring. After 30 min stirring, the ether was removed by distillation. *N*-Perfluoro-α-t-butylisopropyl-*O*-ethyluretane (**XI**) (0.9 g, 90%) was obtained, m.p. 36–38 °C (sublimation). Analysis: Found: C, 26.18; H, 1.32; F, 62.40%. $C_{10}H_6F_{15}NO_2$ requires: C, 26.25; H, 1.31; F, 62.36%. IR (ν, cm^{-1}): 1550, 1790 (C=O); 3450 (NH). ^1H NMR (CCl_4) δ: 1.1 (t, CH_3); 4.0 (q, CH_2); 5.1 (br s, NH, $J(CH_3-CH_2) = 7.6$ Hz ppm. ^{19}F NMR (CCl_4) δ: -16.1 (dec, $(CF_3)_2C$); -19.4 (h, $(CF_3)_3C$, $J(F-F) = 12$ Hz) ppm.

After standing in excess ethanol for 40 d at 20 °C, uretane **XI** decomposed to give uretane **XII** [4] and $(CF_3)_3CH$ (^{19}F NMR data).

Reaction of the mixture of thermolysis products with PhCN

To the mixture of thermolysis products (3.0 g), an excess of anhydrous PhCN was added and the mixture heated for 20 h at 95 °C. Unreacted products were removed *in vacuo* (2–3 mmHg) into a trap (-78 °C) and the residue distilled. Oxadiazine **XIII** (0.5 g), m.p. 59–61 °C (hexane), was isolated from the fraction with b.p. 80–95 °C/5 mmHg and identified by comparison with an authentic sample [10].

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