for 1 h. The mixture was stirred for an additional hour at 0°C and for 1 hr without cooling. The organic layer was separated, the residue was extracted with ether (2×10 mL). The combined extracts were dried with Na_2SO_4 and concentrated to yield a red oil, which was passed through a chromatographic column packed with silica gel, using a benzene—MeCN (3:1) mixture as the eluent. The yield of compound **5** was 114 mg (19 %).

3-[(1*S*)-Camphor-10-sulfonylamino]-2,2,5,5-tetramethylpyrrolidine-1-oxyl (7). To a stirred solution of **6** (157 mg, 1 mmol) and Et_3N (0.1 mL) in 3 mL of 1,2-dimethoxyethane, a solution of (1*S*)-(+)-camphor-10-sulfonyl chloride (300 mg, 1.2 mmol) in 2 mL of 1,2-dimethoxyethane was added dropwise over 10 min. After 15 min the starting **6** was no longer detected by TLC in the reaction mixture. The precipitated $Et_3N \cdot HCl$ was separated, the solvent was evaporated, and the residue was passed through a column of silica gel using a benzene—EtOAc mixture (1:1) as the eluent, to give 280 mg of **7** (75 %).

Resolution of the two diastereomers of compound 5. The separation was monitored by HPLC under the conditions described above, with 60 vol. % MeOH as the eluent. Diastereomers **5a** and **5b** had retention volumes of 1250 μL and 1700 μL, respectively.

66 mg of **5** was dissolved with a gentle heating in 2.2 mL of pure MeCN. The solution was left in a refrigerator for 3 days to deposit the crystals that were separated from the mother liquor, washed twice with 0.5 mL of cold MeCN, and dried to give 21.5 mg of a crystalline solid, with the **5b**:**5a** ratio of 10 : 1. Repeated crystallization of the enriched mixture from 0.8 mL of MeCN yielded 9.3 mg of crystals as elongated prisms, containing 98.4 % of **5b**, mp 240—243°C (dec.). These crystals were used for the X-ray structural analysis.

For the sake of better recovery of **5b**, the first mother liquor (2.2 mL) was concentrated by one half and left to stand in a refrigerator for 2 days. The precipitated crystals were separated, and the residue was evaporated to dryness and crystallized from 0.4 mL of EtOAc to produce 10.4 mg of pink crystals in the shape of cubic prisms, mp 222—226°C (dec.). The content of **5a** in this specimen was 95.3 %.

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Interaction of 1-*tert*-perfluorobutyl-3,3-di(perfluoromethyl)-2-aziridinone with weak nucleophiles

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The title perfluoro-α-lactam (**1**) was found to react with N,N-dimethylformamide to give initially a betaine (**2**) which undergoes ring enlargement to produce the isomeric 2-dimethylamino-3,4,4-tri(perfluoroalkyl)substituted 5-oxazolidone (**3**). Related betaines were also obtained on reaction of **1** with pyridine, quinoline, benzalaniline, and *p*-dimethylaminobenzaldehyde.

Key words: perfluoro-α-lactam, addition of weak bases; betaines, isomerization; 5-oxazolidone, tri(perfluoroalkyl)substituted.

α-Lactams are known to react with N,N-dimethylformamide (DMF) only on prolonged contact at ~20°C or under irradiation; the reaction leads to the corresponding 4-oxazolidones which result from the cleavage of the N—alkyl bond.[1,2] Contrary to this, we have found that the perfluoro-α-lactam (**1**) reacts exothermically

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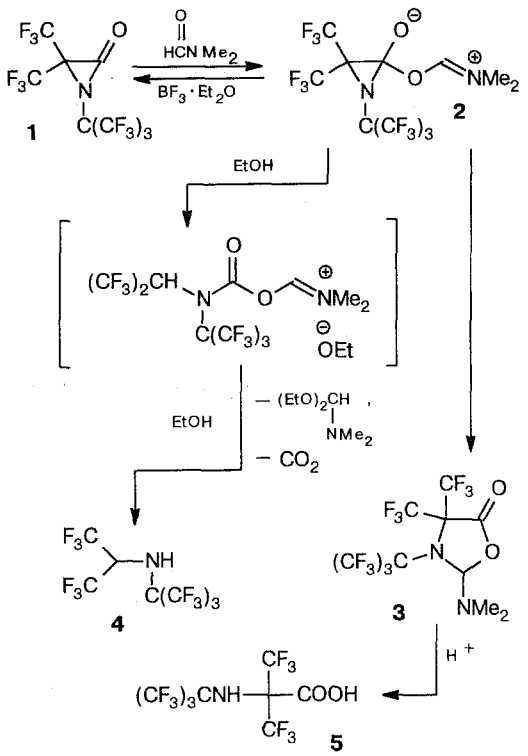
Scheme 1



with DMF to give a crystalline betaine (**2**), stable at 0—5°C. Within a few days, betaine **2** isomerizes in an ethereal solution to a 5-oxazolidone (**3**) due to the rupture of the N—acyl bond. Similar isomerization takes place on storing the solid **2** at ~20°C; however, in this case it is accompanied by the formation of two destruction products, perfluoroisopropylisocyanate and monohydroperfluoroisobutane. The action of BF_3 etherate upon **2** leads to the starting **1**; this suggests that the three-membered ring is retained in the reactions. Reaction of **2** with EtOH gives mainly an amine (**4**), whereas **1** reacts with EtOH to give a complex mixture of unidentified products (^{19}F NMR data). Formation of **3** and **4** (cf.[3]) supports our assumption that lactam **1** is attacked by the oxygen atom of DMF (Scheme 1).

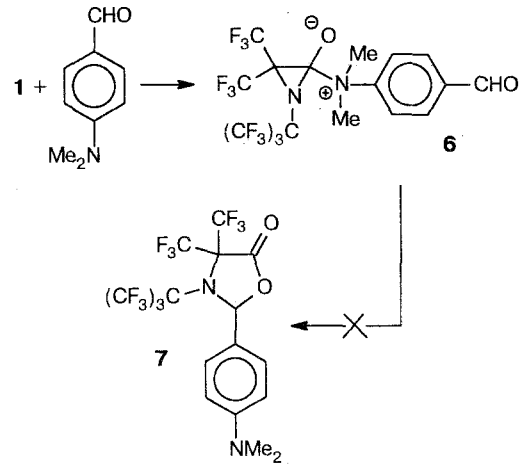
The structure of **3** is confirmed by spectral data and by its hydrolysis to the respective perfluoro-α-aminoacid (**5**).

p-Dimethylaminobenzaldehyde also reacts with **1** to form a betaine (**6**). However, betaine **6** did not rearrange to the anticipated cycloadduct (**7**) even on prolonged heating at 100°C. This difference in the behavior of **2** and **6** can be explained by the fact that **1** is attacked by the oxygen atom of DMF (cf.[4]), while *p*-dimethylaminobenzaldehyde attacks this lactam via its nitrogen atom (Scheme 2).

Benzalaniline reacts with **1** similarly to *p*-dimethylaminobenzaldehyde. Again, no cycloadduct is formed in this case but a stable betaine (**8a**) (cf.[5]).

Recently it has been found[6] that tetrakis(trifluoromethyl)allene and its heteroanalogs form stable betaines

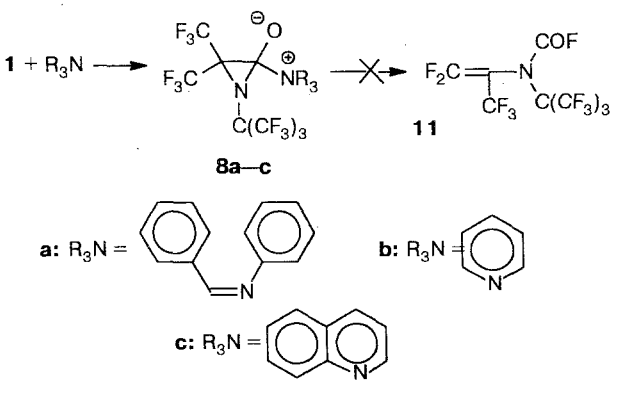
Scheme 2



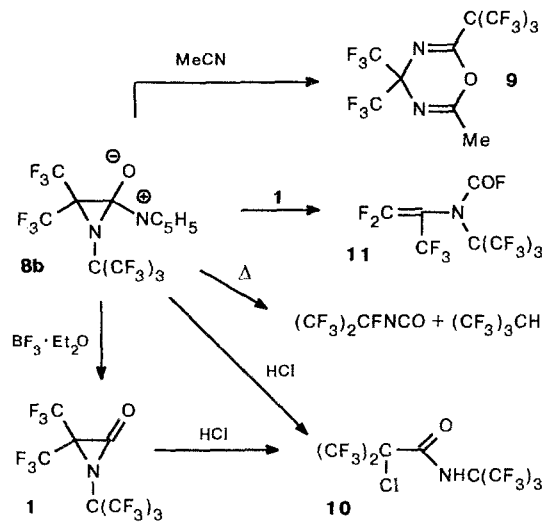
with 4-dimethylaminopyridine (DMAP) due to the attack of the cumulene electrophilic center by the ring nitrogen atom. We found that **1** reacts with DMAP to give a mixture of unidentified products. However, the less basic pyridine and quinoline enter this reaction to give the corresponding betaines (**8b,c**) in good yields (Scheme 3).

Betaines **8a** and **8c** are stable crystalline products, undergoing no change on prolonged heating at 100°C. Betaine **8b** is an oil which we were unable to distill since it decomposed on heating to give mainly perfluoroisopropylisocyanate and monohydroperfluoroisobutane. On treatment with BF_3, etherate betaines **8b,c** partially decompose to the starting **1**, which suggests that the three-membered ring is retained in these compounds. Despite this fact, the adduct **8b**, in contrast to **1**, does not enter the cycloaddition reactions. Thus, **8b** reacts with diphenylnitrone to give decomposition products,[7] while the reaction of **8b** with acetonitrile yields, along with decomposition products, an oxadiazine (**9**). The latter is the product of addition to an isomer of **1**, hexafluoroacetone perfluoropivaloylimine (cf.[8]), rather than to the α-lactam itself. A decrease in the reactivity

Scheme 3



Scheme 4



of **1** upon betainization is also observed in the reaction with hydrogen chloride. Whereas **1** reacts with HCl within 8 h to give α-chlorohexafluoroisobutyramide (**10**) (Scheme 4), in the case of **8b** the reaction is not complete even in 50 h.

If a catalytic amount of pyridine is used for the reaction with **1** instead of an equimolar amount, then the betaine **8b** formed in the reaction causes, in analogy to tertiary amines,[9] slow isomerization of the α-lactam to carbamoyl fluoride (**11**).

Thus, unlike non-fluorinated α-lactams the perfluoro-α-lactam **1** reacts with weak nucleophiles to give betaines, the reactivity of which is quite different from that of the starting α-lactam despite the retention of the three-membered ring.

Experimental

The ^{19}F NMR spectra were recorded using Perkin-Elmer R-32 (84.6 MHz) and Bruker WP-200 SY (200 MHz for ^1H and 188.3 Hz for ^{19}F) spectrometers with TMS and CF_3COOH as external standards. IR spectra were recorded using a UR-20 instrument.

Interaction of α-lactam (1) with DMF. ***a***. To a stirred solution of **1** (7 g in 5 mL of abs. ether) abs. DMF (1.25 g) was added dropwise with cooling. The mixture was kept for 1 h at 0°C and for 0.5 h at ~20°C, and then cooled to −78°C. The precipitated product was collected by filtering to give 4.6 g (56 %) of 1-perfluoro(*tert*-butyl)-2-(N,N-dimethyliminio)-methylenoxy-3,3-bis(trifluoromethyl)azyridine-2-olate (**2**), mp 52—54°C (from hexane). Found (%): C 27.12; H 1.84; F 59.25. $C_{11}H_7F_{15}N_2O_2$. Calculated (%): C 27.27; H 1.44; F 58.88. IR spectrum, ν (cm^{-1}): 1830. ^{19}F NMR spectrum (ether), δ: −4.7 (dec, CF_3); −15.5 (dec, CF_3); −16.1 (g, $(CF_3)_3C$, J_{F-F} = 8.5 Hz).

The filtrate was kept for 6 days and then distilled to give 2-dimethylamino-3-perfluoro(*tert*-butyl)-4,4-bis(trifluoromethyl)-5-oxazolidone (**3**), bp 73—75°C (7 Torr). Yield 2.1 g (25.5 %). Found (%): C 27.27; H 1.42; F 58.83. $C_{11}H_7F_{15}N_2O_2$. Calculated (%): C 27.27; H 1.44; F 58.88. IR spectrum, ν (cm^{-1}): 1740, 1790. ^1H NMR spectrum, δ: 2.7 (s, CH_3); 6.4 (s, CH). ^{19}F NMR spectrum, δ: −2.9 (s, $(CF_3)_2C$); −11.3 (br.s, $(CF_3)_3C$).

b. To a stirred solution of **1** (1.2 g in 2 mL of abs. ether) 0.22 g of abs. DMF was added dropwise with cooling. The mixture was kept at ~20°C and distilled 6 days later to afford 0.8 g (56.5 %) of oxazolidone **3**, bp 73—75°C (7 Torr).

c. Betaine **2** isomerizes in 6 days at ~20°C in ether to the 5-oxazolidone **3** (^{19}F NMR data).

Interaction of betaine 2 with BF_3 Et_2O. To a solution of betaine **2** (3.7 g) in 7 mL of abs. ether, BF_3 Et_2O (1.6 g, in 3 mL of abs. ether) was added with stirring. The mixture was left at ~20°C for 2 days. The volatile products were removed *in vacuo* using a trap (−78°C) and the lower layer was separated at −78°C and distilled to give 0.9 g (29 %) of **1**, bp 100—103°C.

Interaction of betaine 2 with ethanol. A mixture of **2** (2.5 g) with abs. ethanol (1 mL) was stirred at ~20°C until dissolution, and diluted with water. The lower layer was separated, dried with $MgSO_4$, and distilled to give 1.1 g (47.5 %) of perfluoro(*tert*-butyl)-α-hydrohexafluoroisopropylamine (**4**), bp 94—95°C. A specimen intended for analysis was distilled over conc. H_2SO_4. Found (%): C 21.77; H 0.63; F 73.85. $C_7H_2F_{15}N$. Calculated (%): C 21.81; H 0.51; F 74.02. IR spectrum, ν (cm^{-1}): 3460 (NH). ^1H NMR spectrum (acetone-d_6), δ: 3 (br.d, NH); 5.3 (dh, CH; J_{H-F} = 4.9 Hz, J_{H-H} = 9 Hz). ^{19}F NMR spectrum (acetone-d_6), δ: −6.7 (dec, $(CF_3)_2C$); −8.8 (h, $(CF_3)_3C$, J_{F-F} = 2.8 Hz).

Hydrolysis of oxazolidone 3. To 1.3 g of oxazolidone **3** conc. H_2SO_4 (1.5 mL) was added with cooling. The mixture was kept for 30 min at ~20°C, diluted with water, and extracted with ether. The solvent was distilled off to leave 0.7 g (62 %) of acid **5**, mp 108—110°C (sublimation), which was identical to the known[5] specimen.

Betaines 6,8a,b,c. ***a***. *p*-Dimethylaminobenzaldehyde (0.73 g) was added to a solution of **1** (2 g in 5 mL of abs. ether). After 16 h at ~20°C, the ether was distilled off and hexane was added to the residue. 1.7 g (63 %) of **6** was obtained as a precipitate, mp 94—96°C (from hexane). Found (%): C 36.70; H 2.09; F 50.74. $C_{17}H_{11}F_{15}N_2O_2$. Calculated (%): C 36.42; H 1.96; F 50.89. IR spectrum, ν (cm^{-1}): 1620, 1820. ^{19}F NMR spectrum (CCl_4), δ: −8.1 (dec, CF_3); −16.8 (dec, CF_3); −17.4 (h, $(CF_3)_3C$, J_{F-F} = 8.3 Hz).

b. A mixture of **1** (2 g) and benzaldehyde (0.86 g) in 5 mL of abs. ether was left at ~20°C for 48 h. The solvent was distilled off, hexane was added to the residue, and the mixture was cooled to −78°C to deposit 1.6 g (56 %) of **8a**, mp 65—67°C (from aqueous alcohol). Found (%): C 42.48; H 1.84; F 48.14; N 4.77. $C_{21}H_{11}F_{15}N_2O$. Calculated (%): C 42.57; H 1.85; F 48.10; N 4.73. IR spectrum, ν (cm^{-1}): 1780. ^{19}F NMR spectrum (CCl_4), δ: −5.3 (dec, CF_3); −18.4 (h, $(CF_3)_3C$); −19.8 (dec, CF_3, J_{F-F} = 8.4 Hz).

c. To a stirred solution of **1** (0.5 g) in 1 mL of abs. ether abs. pyridine (0.1 g) was added with cooling, and the mixture was agitated for 10—15 min at 20°C. Then the ether was distilled off to give 0.55 g (91 %) of **8b**. IR spectrum, ν (cm^{-1}): 1790. ^{19}F NMR spectrum, δ: −11.1 (dec, CF_3); −13.1 (dec, CF_3); −17.5 (h, $(CF_3)_3C$; J_{F-F} = 8.4 Hz).

d.To a stirred solution of **1** (1 g) in 2 mL of abs. ether 0.3 g of abs. quinoline was added with cooling, and the mixture was kept for 10—15 min at 20°C. The solvent was evaporated to leave 1.1 g (85 %) of **8c** as a precipitate, mp 98—100°C (from hexane). Found (%): C 37.83; H 1.30; F 52.79; N 5.18. $C_{17}H_7F_{15}N_2O$. Calculated (%): C 37.77; H 1.29; F 52.77; N 5.18. $C_{17}H_7F_{15}N_2O$. IR spectrum, ν (cm^{-1}): 1770. ^{19}F NMR

spectrum (ether), δ: −10 (dec, CF_3); −12.2 (dec, CF_3); −17.8 (h, $(CF_3)_3C$, J_{F-F} = 9.4 Hz).

Interaction of betaines 8b,c with BF_3 Et_2O. ***a***. A mixture of **8b** (0.65 g) with BF_3 Et_2O (0.5 g) was left at ~20°C for 3 h. The lower layer was separated and distilled to give 0.2 g of **1**, bp 101—103°C (identified by its ^{19}F NMR spectrum).

b. A mixture of **8c** (1 g) and BF_3 Et_2O (0.6 g) was heated for 15 h at 100°C in a sealed ampule, and the volatile products were removed *in vacuo* using a freezing trap (−78°C) and then redistilled. The yield of lactam **1** (bp 100—103°C) was 0.6 g.

Interaction of betaine 8b with CH_3CN. Compound **8b** reacts with CH_3CN (in excess) at ~20°C to give, in 16 h, a mixture of $(CF_3)_2C{=}CF_2$, $(CF_3)_3CH$, $(CF_3)_2CNCO$, and compound **9** identical to the previously obtained[8] oxadiazine (^{19}F NMR data).

N-*tert*-Perfluorobutyl-α-chlorohexafluoroisobutyramide (10). A flow of dry gaseous HCl was passed through a solution of **1** (1.7 g) in 5 mL of abs. ether until **1** disappeared (^{19}F NMR data). After 8 h the ether was removed by distillation, and the residue was distilled to give 1.3 g (60 %) of amide **10**, bp 78—79°C (100 Torr). Found (%): C 21.65; H 0.18; Cl 7.59; F 63.77. $C_8HClF_{15}NO$. Calculated (%): C 21.45; H 0.22; Cl 7.93; F 63.68. IR spectrum, ν (cm^{-1}): 1540, 1770 (C=O); 3430 (NH). ^{19}F NMR spectrum, δ: −6.4 (s, $(CF_3)_2C$); −7.3 (s, $(CF_3)_2C$).

Under similar conditions, passing dry HCl through a suspension of betaine **8b** in Et_2O (50 h) resulted in almost complete transformation of **8b** to amide **10** (^{19}F NMR data).

Interaction of α-lactam 1 with a catalytic amount of pyridine. Interaction of **1** with a catalytic amount of pyridine at 20°C for 7 days gives **8b** and carbamoylfluoride **11** (^{19}F NMR data).[9]

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Synthesis and fluorination of nitro-substituted thionocarbonates

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Thiocarbonylchloride reacts with β-nitroalcohols yielding symmetrical thionocarbonates. Transesterification of bis(2-fluoro-2,2-dinitroethyl)thioncarbonate affords alkyl 2-fluoro-2,2-dinitroethylthionocarbonates. Fluorination of these thionocarbonates yields the corresponding difluoroformals.

Key words: thionocarbonates, nitro-substituted, synthesis; fluorination; difluoroformals, β-nitro-substituted.

Nitro-substituted thionocarbonates having the general formula ROC(S)OR' (where R = R' = $CH_2CF_2NO_2$, $CH_2CF(NO_2)_2$, $CH_2C(NO_2)_3$, $CH_2C(NO_2)_2Me$, or R = $CH_2CF(NO_2)_2$, R' = CH_2CF_3, $CH_2C(NO_2)_2Me$)[1—3] have hitherto been obtained by the reaction of β-nitro alcohols with thiocarbonyl chloride in the presence of alkali[1] or with 1,1'-thionocarbonyl-di-1,2,4-triazole.[2,3] The authors of ref.[1] studied the interaction of thiocarbonyl chloride with nitro alcohols only for the case of 2-fluoro-2,2-dinitroethanol. The reaction with other nitro alcohols could not be reproduced under analogous conditions[2,3] due to the deformylation of

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