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α-N-Acyliminium Ion - 2-Bromoalkene Cyclizations.

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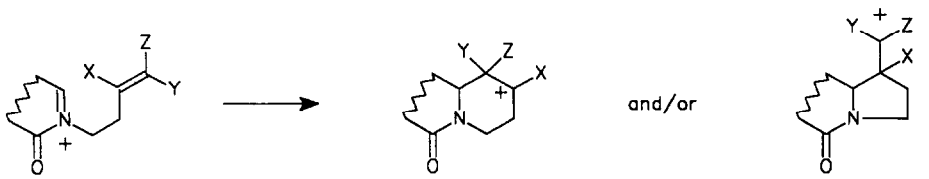
Abstract: *The cyclization of α-N-acyliminium ions generated from ethoxylactams* ***1-3*** *using trifluoroacetic acid, trifluoromethanesulfonic acid and anhydrous HF affords ketones, bromoalkenes and geminal bromofluoro compounds, respectively A non concerted process explains these results which demonstrate the high reactivity of the intermediate bromocarbenium ions with different nucleophiles The unexpected fluorination observed in HF is also observed with simple alkenes which give mixtures of epimeric fluoro derivatives*

INTRODUCTION

The use of α-N-acyliminium ions as intermediates for the construction of various heterocycles has been widely studied and particularly by Speckamp and Hiemstra starting from cyclic imides such as succinimide or glutarimide [1] The structures obtained after endo or exo type cyclization with π-nucleophiles are related to the important alkaloïds of the indolizidine and quinolizidine type [2] More recent developments are focused on acyl (or alkoxycarbonyl)-iminium ion cyclizations leading to oxazinones,[3] piperidines[4,5] or to cyclic aminoacids[6] starting from an acyclic precursor or to α-amino ketones starting from cyclic ones [3]



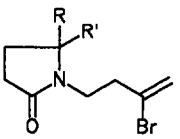
X,Y,Z= H, alkyl, SR, CH_2SiR_3

On the other hand 2-haloalkenes (mainly Cl) have been introduced as nucleophiles in carbocyclic cyclizations by Lansbury two decades ago [7] The deactivation of the electronically biased double bond

towards protonation allowed the reactions to be run in 85% H_2SO_4 at 20°C or at reflux in formic acid to give, usually after work-up, ketones We have recently used such nucleophiles in acid catalyzed cyclizations leading to chiral bicyclic ketones from (-)-carvone and shown that bromoalkenes are obtained when the reactions are run in CF_3COOH or HF while bromofluoro derivatives are formed in HF-Py [8] These results prompted us to study acyliminium cyclizations with such nucleophiles under different acidic conditions in order to get more information on the reactivity of the intermediate halocarbenium ion

PREPARATION OF ETHOXYLACTAMS

Compounds **1-3** are obtained in high yield by the method of Speckamp[9] from the cyclic N-alkyl imides **4-6** which are readily available from succinimide, glutarimide and phtalimide, respectively, and 3-bromo-1-tosyloxy-3-butene using solid PTC (K_2CO_3, 1% 18-Crown-6, toluene or benzene, reflux) [10]



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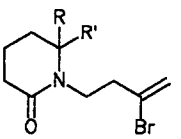

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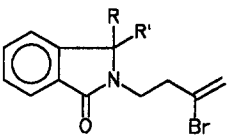


3 R=OEt, R'=H

4 5 6 R,R'=O

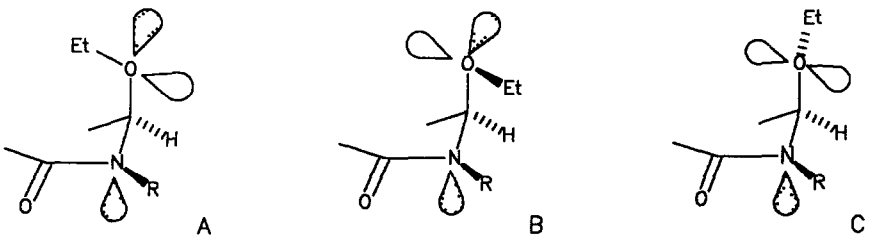
The structures of **1-3** are in agreement with their ^1H NMR spectra (see Table I)

Table I: Characteristic ^1H NMR data (δ in ppm and J in Hz) of ethoxylactams **1-3.**

Compound	δ N-C<u>H</u>OEt	δ -NC<u>H</u>$_A$	δ -O-C<u>H</u>$_2$-CH$_3$	δ -NC<u>H</u>$_B$
1	4 99 d (J= 9)	3 50 m	3 50 m	3 50 m
2	4 64 s	3 76 dt (J= 14, 5 5)	3 56 m	3 41 dt (J= 14 7)
3	5 91 s	3 95 dt (J= 13 5, 6)	3 93 and 3 17 2dq (J= 14, 7 4)	3 61 dt (J=14, 7)

The highly deshielded signal observed for -C<u>H</u>OEt (confirming the axial orientation of the ethoxy group) and the -N-C<u>H</u>$_2$- signals with different chemical shifts due to hindered rotation and hence selective

deshielding by the amide carbonyl, have already been noticed [1] Interestingly the two methylene protons of the ethoxy group appear also different, especially in the case of the phtalimide derivative **3** ($\Delta\delta$= 0 76 ppm) This can be explained by an exo anomeric effect[12] which rules out **C** among the 3 possible rotamers **A**, **B** and **C** For **1** and **2** rotamer **B** is probably more stable than **A** where a steric repulsion does exist with at least one ring proton This does not hold for **3**, for which **A** may be preferred and hence the large difference observed for the methylene protons can then arise from aromatic ring anisotropy



CYCLIZATION OF ETHOXYLACTAMS

Three different acids have been studied CF_3COOH (H_0= -5), HF (H_0= -10) and CF_3SO_3H (H_0= -15) The results described below for each acid used are for isolated compounds (except **9**) after total conversion of starting material and flash chromatography over silica Apart from the reported compounds no other products were present in significant amounts

Trifluoroacetic acid.

Compounds **1-3** afford, after treatment with CF_3COOH (50 eq) for 16-24h at 20°C, ketones **7** (47%), **9**, and **11** (69%), with variable amounts (10-20%) of bromoalkenes **8a,b** from **1**, and **12a,b** from **3** Ketone **9** is the only detectable product in the reaction of **2**, however this material is chromatographically unstable (as already pointed out by Speckamp[11]) and no yield for pure compound can be given (about 50-60% of crude material) The use of 5 eq of CF_3COOH in dichloromethane or in acetic acid does not alter the relative amount of bromoalkenes

Triflic acid.

Only bromoalkenes are obtained by using 4 eq of triflic acid in dichloromethane at 20°C (overnight) **8a,b** (48 5%) from **1**, **10a,b** (36%) from **2**, and **12a,b** (79%) from **3** In each case an unseparable mixture of two alkenes is formed in an **a/b** ratio of about 4 to 1 as judged by the signals of the olefinic protons in ^{1}H NMR (except for **8** where both signals are superposed) or by HPLC For all series the minor isomer **b** is characterized by a higher deshielding of the ring junction proton with respect to the major isomer **a** and by an inverse effect for the -N-CH_2- signal in the case of isomer **a** in agreement with the allylic position of these protons Furthermore the olefinic proton for **12b** is more deshielded by the aromatic ring (δ 6 40 ppm) than for **12a** (δ 6 23 ppm) while the reverse is observed for **10b** (δ 5 89 ppm) and **10a** (δ 6 03 ppm)

Hydrofluoric acid.

All reactions carried out in anhydrous HF at 0°C (3h) give fluoro derivatives **13** (35% from **1**), **14a,b** (unseparable mixture, 27% from **2**), and **15** (76% from **3**). ^{1}H and ^{13}C characteristic signals are given in Table II

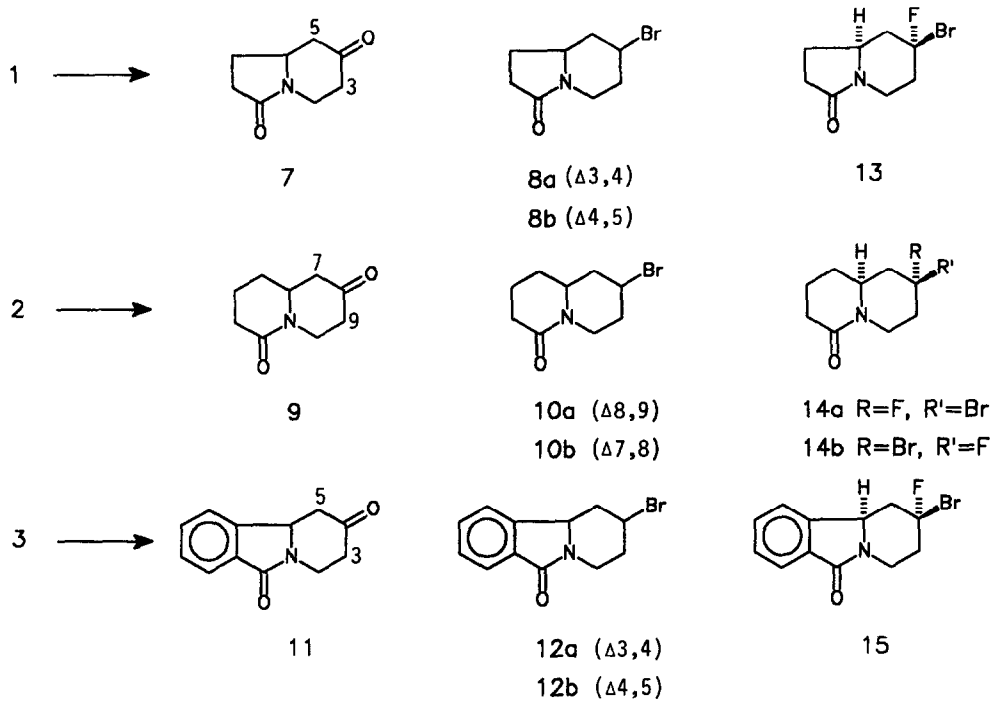
Table II: Characteristic ^{1}H and ^{13}C NMR data (δ in ppm and J in Hz) of compounds **13-15.**

Compounds	**13**	**14a**	**14b**	**15**
-NCH*	4 06 m	4 69 ddd (J= 13 5, 6, 2)	4 90 m	4 67 dd (J= 11 8, 3 8)
-NCH**	3.82	3 63	3.63	4 43
C(Br)-F	104.3 (C-4) d (J= 250)	104 6 (C-8) d (J= 250)	109 6 (C-8) d (J= 250)	104 0 (C-4) d (J= 252)
α C§	41 1 (C-3) d (J= 21) 49.3 (C-5) d (J= 21)	42 2 (C-9) d (J= 21) 49 9 (C-7) d (J= 21)	40 7 (C-9) d (J= 21) 48 9 (C-7) d (J= 21)	41 6 (C-3) d (J= 21 7) 47 5 (C-5) d (J= 20 3)
β C§§	36 8 (C-2) s 53 8 (C-6) s	39 1 (C-10) s 53 3 (C-6) s	39 4 (C-10) d (J= 11) 53 7 (C-6) d (J= 11)	36 1 (C-2) s 55 5 (C-6) s

^{1}H NMR * $N\text{-}CH_2$ proton in the plane of the amide carbonyl ** angular N-CH, m in all cases

^{13}C NMR § and §§ α and β with respect to the C(Br)-F

The signals of carbons bearing the geminal bromine and fluorine atoms appear between 104 and 110 ppm as large doublets (J= 250 Hz) The stereochemistry of **13** and **15** is proposed according to the lack of ^{3}J between the fluorine atom and the two corresponding ^{13}C which indicates the presence of an axial C-F bond [13] In the case of **14**, HPLC analysis shows that a 70/30 mixture of two isomers is present in agreement with the observation of a similar ratio between the two signals at 4 69 and 4 90 ppm for the N-CH protons deshielded by the amide carbonyl The major isomer **14a** may be assigned to the axial fluoro derivative due to the lack of $^{3}J_{C\text{-}F}$ as for **13** and **15**, and the minor one to the equatorial derivative since two $^{3}J_{C\text{-}F}$ of 11 Hz are observed for C-6 (δ 53 7 ppm) and C-10 (δ 39 4 ppm)

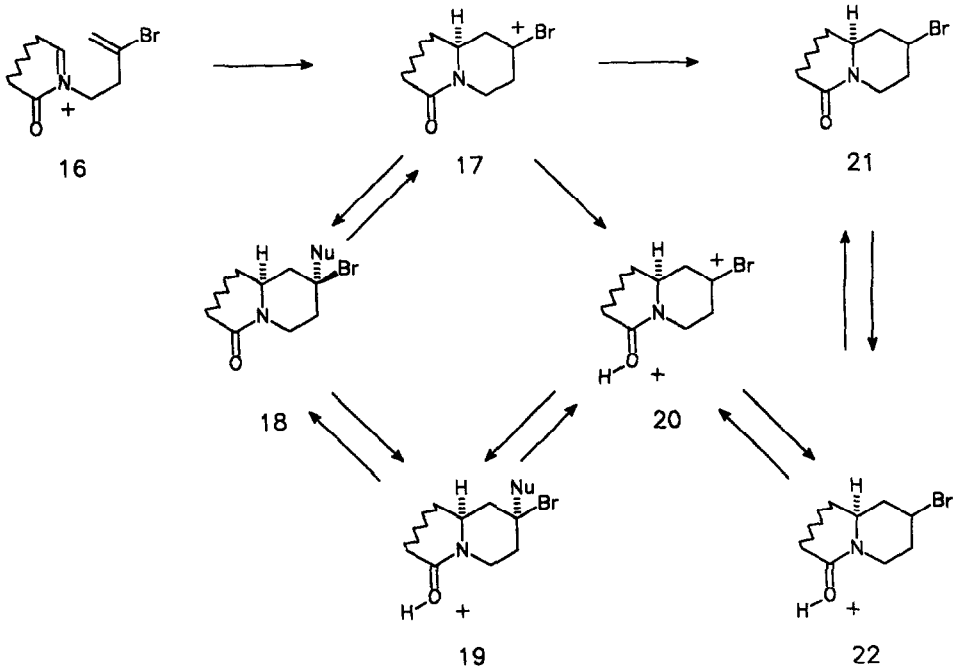


DISCUSSION

The results obtained in the cyclization of ethoxylactams **1-3** show a great influence of the acid promotor on product composition and, compared to the cyclizations carried out on terpenoids, unexpected formation of ketones and bromofluoroderivatives is observed respectively in trifluoroacetic acid and in hydrofluoric acid, respectively (instead of bromoalkenes as observed previously) These cyclizations proceed from acyliminium ion **16** to the intermediate bromocarbenium ion **17** The latter may either react with a nucleophile to give **18** which is then protonated to **19** (alternatively **19** may also be obtained by amide protonation followed by nucleophilic attack on **20**), or may be deprotonated to **21**, and then protonated to **22** (alternatively obtained from **20**) Since we have already shown that bromoalkenes are not protonated in CF_3COOH and HF,[8] the formation of **21** (and **22**) must be irreversible (imides **4-6** are stable in presence of these two acids) The product compositions obtained here imply an unexpectedly high reactivity of **17** (or **20**) towards CF_3COO^- (giving intermediate bromotrifluoroacetates which are hydrolyzed to ketones) and F^- Subsequent solvolysis of such compounds under these conditions may be prevented by the protonation of the amide group In presence of the more acidic CF_3SO_3H such a process leading ultimately to bromoalkenes is possible as shown by the complete conversion of the fluoro derivative **15** to **12a,b** under the conditions used for cyclization of **3** (the intermediate formation of bromotriflates cannot be ruled out on the basis of similar reactivity of bromoalkynes under these conditions) [14]

The fluorination observed in HF affords the more stable axial isomer exclusively in the succinimide and phtalimide series and an 80/20 mixture in favor of this isomer in the glutarimide series In the latter case

such a selectivity may be explained by the occurrence of a major stepwise cyclization process instead of a reversible addition of F^- To underline the effect of the bromine atom, simple alkenes **23-25** were then treated with HF In the succinimide and phtalimide series, 50/50 (as judged by HPLC and/or ^1H NMR) mixtures of two epimeric fluoro derivatives **26a,b** (29%) and **28a,b** (75%) are isolated, while in the



16 17 21 18 20 19 22

23 n=1 26a,b

24 n=2 27a,b

25 28a,b

a R=F, R'=H

b R=H, R'=F

glutarimide series the equatorial epimer **27b** is predominant (**a/b**· 21/79, 38% isolated yield) The structures of **27a,b** are in agreement with the observation of a more intense C-6 signal as a doublet (J= 12 Hz) at 53 9 ppm for **27b** compared to the smaller singlet observed at 50 7 for **27a** These results indicate that the cyclizations seem to proceed at least partly by a concerted process and to a higher extent in the glutarimide series, for which the corresponding α-N-acyliminium ion has been shown to be relatively less stable than from the other, five membered, ethoxylactams.

In conclusion, cyclizations of N-acyliminium ions with 2-bromoalkenes afford different products (ketones, bromoalkenes, geminal bromofluoro derivatives) depending on the acid used, arising from the unexpected reactivity of the intermediate bromocarbenium ion toward nucleophiles. Such type of cyclizations may be applied to other electronically biased alkenes or alkynes and to other α-N-acyl (or alkoxycarbonyl) iminium ions

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EXPERIMENTAL

Melting points were determined on a Tottoli Buchi 510 melting point apparatus and are uncorrected ^1H and ^{13}C NMR were recorded on a Brücker WP200SY, using $CDCl_3$ as a solvent and TMS as an internal standard Mass spectra were obtained on an INCOS 500 (Finnigan) spectrometer and IR spectra were recorded on a Beckman Acculab 2 or 4250 HRMS were obtained from the "Service Central de Microanalyses" (CNRS, Lyon) Separations and purifications were carried out by flash chromatography over Matrex silica (0 02-0 0045 mm) or column chromatography over Merck Kieselgel 60 silica (0 063-0 2 mm) or by preparative TLC using silica gel coated plates ($60F_{254}$, 1 mm) Extraction as usual means double extraction with a solvent such as dichloromethane or diethyl ether, followed by washing with water, brine, drying over sodium sulfate and evaporation in vacuo (rotavapor) of volatiles

General procedure for reduction of imides 4-6 to ethoxylactams 1-3:

The reductions of imides **4-6** are carried out between -10°C and -15°C in anhydrous ethanol (0.1 M) by slow addition of $NaBH_4$ (5 molar eq) After stirring for 15 min , 5-10 drops of a 1M solution of sulfuric acid in ethanol are added every 15 min (total volume added about 3 mL per mmole of imide) until completion of the reduction (2-5 hrs) The reaction mixture is then diluted with water and extracted as usual with dichloromethane

1 oil (95 6%) ^1H NMR δ 1 25 (t, 3H, J= 9 Hz), 3 50 (m, 4H), 4 99 (d, 1H, J= 6 Hz), 5.47 (s, 1H) and 5 66 (s, 1H) IR 1685, 1410, 1260 and 890 cm^{-1}

2 oil (90%) ^1H NMR δ 1 25 (t, 3H, J= 7 Hz), 2 84 (dt, 1H, J= 14 and 7 Hz), 3 41 (m, 1H), 3 56 (qd, 2H, J= 7 Hz), 3 76 (m, 1H), 4 64 (s, 1H), 5 44 (s, 1H) and 5 63 (s, 1H) ppm. IR 1640, 1460, 1435, 1415, 1170 and 1070 cm^{-1}

3 oil (92%) ^{1}H NMR δ 1 16 (t, 3H, J= 7Hz), 2 80 (m, 1H), 2.93 (m, 1H), 3 04 (m, 1H), 3 17 (m, 1H), 3 61 (m, 1H), 3 95 (m, 1H), 5 46 (d, 1H, J= 1 5 Hz), 5.67 (s, 1H), 5 91 (s, 1H), 7.55 (m, 3H) and 7 81 (d, 1H, J= 6 5 Hz) ppm IR. 1700, 1630, 1420, 1270, 1165, 1105, 1070 and 895 cm^{-1}

Cyclizations in trifluoroacetic acid:

To the ethoxylactams **1-3** is added trifluoroacetic acid (50 mol eq) and the resulting solution is stirred at 20°C for 16-24 hrs and then poured into an aqueous sodium bicarbonate solution and extracted as usual Purification is then done by chromatography.

7 mp 54-55°C (47%), mp_{Litt} [11] 53-57°C ^{1}H NMR δ 3.00 (m, 1H, H-2ax), 3 86 (m, 1H, H-6) and 4 46 (m, 1H, H-2eq) ppm ^{13}C NMR δ 206.2 (C-4), 173 7 (C-9), 56 4 (C-6), 48 5 (C-2), 39 8 (C-5), 38.0 (C-3), 29 6 (C-8), 24 9 (C-7) ppm IR 1710, 1690, 1420, 1260, 1160 and 895 cm^{-1}

9· oil, Litt[11] oil (50-60% crude). ^{1}H NMR· δ 2 94 (m, 1H, H-10ax), 3 70 (m, 1H, H-6ax) and 4.91 (dt, 1H, J= 12 5 and 4 5 Hz, H-10eq) ppm ^{13}C NMR δ 206.9 (C-8), 169.5 (C-2), 55.0 (C-6), 48 2 (C-10), 41 0 (C-7), 40.6 (C-9), 32.7 (C-3), 29 7 (C-5) and 18.9 (C-4) ppm IR· 1725, 1645, 1470, 1450, 1420, 1340 and 1250 cm^{-1}

11 oil (69%) ^{1}H NMR. δ 2 26 (dd, 1H, J= 13 8 and 1 4 Hz, H-8ax), 2 56 (m, 2H, H-8eq and H-6eq), 3 02 (dd, 1H, J= 13 4 and 4 1 Hz, H-6ax), 3 44 (m, 1H, H-5ax), 4 73 (m, 2H, H-9 and H-5eq), 7 44 (d, 1H, J= 7 Hz, H-10), 7 56 (m, 2H, H-11 and H-12) and 7 88 (d, 1H, J= 6 7 Hz, H-13) ppm ^{13}C NMR· δ 205 5 (C-7), 166 3 (C-2), 144 3 (C-4), 131 9, 131.6, 128.8, 124.1 and 121 7 (C-Ar), 57 7 (C-5), 46.2 (C-9), 39 6 (C-6) and 37 3 (C-8) ppm IR 1720, 1690, 1420, 1270 and 890 cm-1. MS (EI) 201 (M)

Cyclizations using triflic acid:

To a 0.25M solution of ethoxylactams **1-3** in anhydrous dichloromethane is added trifluoromethanesulfonic acid (4 eq) The reaction mixture is stirred for 15-17 hrs at 20°C and then poured into a saturated sodium bicarbonate solution and extracted as usual Chromatography using 2% MeOH in CH_2Cl_2 affords the mixture of bromoalkenes

8a,b oil (48 5%) ^{1}H NMR: δ 1 75 (m, 1H, H-5ax), 2 95 (dt, 0 75H, J=11 9 and 5 4 Hz, H-5a), 3 52 (d, 0 75H, J= 18 3 Hz, H-2axa), 3 81 (m, 0 75H, H-6a), 4 27 (m, 1H, H-6b and H-2eqa) and 6 07 (s, 1H, H-3a and H-5b) ppm ^{13}C δ 173 8 (C-9), 172 9 (C-9), 129 3, 124 6, 112 0 and 117 7 (C-alkene), 56 5 (C-6), 54 1 (C-6), 41 9 (C-2), 41.4 (C-2), 37 5 and 34 3 (C-5a and C-3b), 31 0 (C-8), 29 5 (C-8), 25 4 (C-7) and 24 6 (C-7) ppm IR 1685, 1600, 1440, 1420 and 905 cm^{-1} MS (EI) 217 and 215 (M) HRMS calcd for $C_8H_{10}{}^{79}BrNO$· 214 9946 Found 214 9943

10a,b oil (36%) ^{1}H NMR δ 3 42 (d, 0 75H, J= 18 Hz, H-10axa), 3 68 (m, 0 75H, H-6axa), 4 00 (m, 0 25H, H-6axb), 4 81 (s, 1H, H-10eq), 5 89 (s, 0 25H, H-7b) and 6 03 (s, 0 75H, H-9a) ppm ^{13}C δ 169 4 (C-2), 168 8 (C-2), 129 8, 125 5, 121 2, 117 5 (C-alkene), 56 8 (C-6), 53 7 (C-6), 43 9, 42 3, 35 0, 32 9, 32 4, 29 9, 29 7, 28 7, 19 7 (C-4) and 18 5 (C-4) ppm IR 1660, 1640, 1460, 1440, 1340, 1250, 1170, 1090, 1040, 1030, 1005, 910 and 830 cm-1 MS (EI) 231 and 229 (M) HRMS calcd for $C_9H_{12}{}^{79}BrNO$ 229 0102 Found 229 0103

12a,b oil (79%) ^{1}H NMR δ 2 44 (m, 0 75H, H-5eqa), 2 76 (m, 0 25H, H-3axb), 3 08 (dd, 0 75H, J= 12 6 and 4 Hz, H-5axa), 3 34 (dt, 0 25H, J= 16 6 and 5 1 Hz, H-3eqb), 3 85 (d, 0 75H, J= 11 4 hz, H-2axa), 4 13 (t,0 25H, J= 5 1 Hz, H-2axb), 4 13 (m, 2x0 75H, H-2eq and H-6axa), 5 04 (s, 0 25H, H-

6axb), 6 23 (s, H-3a), 6.40 (s, 0 25H, H-5b), 7.47 (m, 3H, H-arom) and 7.85 (d, J= 7 Hz, H-arom) ppm. ^{13}C NMR δ 166.8 (C-9), 144.7, 132.2, 132.0, 131 7, 128.7, 126 1, 125.0, 122 1, 121.9 and 116.8 (C-Ar), 59 1 (C-6b), 55 8 (C-6a), 41 0, 39 7 and 37 7 ppm IR: 1680, 1620 and 1400 cm^{-1}. MS (EI) 265 and 263 (M) HRMS calcd for $C_{12}H_{10}{}^{79}BrNO$ 264.9925 Found. 264 9924

Cyclizations in HF:

A 0.2M solution of ethoxylactams **1-3** or **23-25** in anhydrous HF is stirred for 3 hrs at 0°C The reaction mixture is then poured into a sat. sodium bicarbonate solution and extracted as usual The pure bromofluoro derivative is obtained after chromatography using 2% MeOH in CH_2Cl_2 as eluent

13 oil (35%) ^{1}H NMR. δ 40 6 (ddd, J= 13 8, 5 5 and 1 5 Hz, H-2eq) ^{13}C NMR δ 173 4 (C-9), 104.3 (d, J= 252 Hz, C-4), 53 8 (C-6), 49.3 (d, J= 21 Hz, C-5), 41 1 (d, J= 21 Hz, C-3), 36 8 (C-2), 29.7 (C-8) and 23.9 (C-7) ppm IR 1685, 1450, 1430, 1410, 860 and 840 cm^{-1} MS (EI): 237 and 235 (M) HRMS calcd for $C_8H_{11}{}^{79}BrFNO^{\cdot}$ 235.0008. Found 235 0008

14a,b oil (27%) ^{1}H NMR δ 3.63 (m, 1H, H-6), 4 69 (ddd, 0.7H, J= 13.5, 6 and 2 Hz, H-10eqa) and 4 90 (m, 0 3H, H-10eqb) ppm. ^{13}C NMR: **a.** δ 169.2 (C-2), 104.6 (d, J= 250 Hz, C-8), 53 3 (C-6), 49.9 (d, J= 21 Hz, C-7), 42.2 (d, J= 21 Hz, c-9), 39.1 (C-10), 32.8 (C-3), 29 2 (C-5) and 19.4 (C-4) ppm; **b:** δ 169 2 (C-2), 109.6 (d, J= 250 Hz, C-8), 53 7 (d, J= 11 Hz, C-6), 48.9 (d, J= 21 Hz, C-7), 40 7 (d, J= 21 Hz, C-9), 39 4 (d, J= 11 hz, C-10), 32 8 (C-3), 29 2 (C-5) and 19.4 (C-4) ppm IR 1640, 1465, 1440, 1410, 1340, 1240, 1160, 1110, 1090, 1020, 1010 and 860 cm^{-1} MS (EI). 251 and 249 (M). HRMS calcd. for $C_9H_{13}{}^{79}BrNO$. 249.0164 Found 249 0165

15: mp 144-145°C (76 5%). ^{1}H NMR· δ 2 07 (dt, 1H, J= 36 and 12 Hz, H-5ax), 2 38 (dtd, 1H, J= 37.5, 13 5 and 6 Hz, H-3ax), 2 82 (m, 1H, H-2ax), 3 39 (m, 2H, H-3eq and H-5eq), 4 43 (dd, 1H, J= 13 8 and 5 1 Hz, H-2eq), 4 67 (dd, 1H, J= 11 8 and 3 8 Hz, H-6ax), 7 59 (m, 3H, H-Arom), and 7.91 (d, J= 6 7 Hz, H-Arom) ppm ^{13}C NMR δ 166 1 (C-9), 143 7 (C-7), 131 9 (C-8), 128 8, 124 3 and 121 7 (C-Ar), 104.0 (d, J= 252 Hz, C-4), 55 5 (C-2), 47 5 (d, J= 20 3 Hz, C-3), 41 6 (d, J= 22 Hz, C-5) and 36 1 (C-6) ppm IR 1690, 1470, 1420, 1290, 1260 and 890 cm^{-1} MS (EI) 285 and 283 (M) HRMS calcd. for $C_{12}H_{11}{}^{79}BrNO$ 283 0008 Found 283 0008

26a,b oil (29%) ^{1}H NMR δ 2 66 (t, 0.5H, J= 13 8 Hz, H-2ax), 3 02 (td, 0 5H, J= 16 and 3 2 Hz, H-2ax), 3 54 (m, 0 5H, H-6ax), 3 83 (m, 0 5H, H-6ax), 4 03 (dd, 0.5H, J= 13 and 6 Hz, H-2eq), 4 24 (m, 0 5H, H-2eq), 4 65 (dm, 0 5H, J= 47 9 Hz, H-4b) and 5 01 (d, 0 5H, J= 47 5 Hz, H-4a) ppm ^{13}C NMR δ 173 5 and 173 3 (C-9), 89 4 (d, J= 175 Hz) and 86 8 (d, J= 168 Hz) (C-4), 54 8 (d, J= 13Hz, C-6b) and 51 2 (C-6a) ppm (other signals not determined due to extensive overlaping) IR 1680, 1465, 1445, 1420 and 1310 cm^{-1} MS (CI, isobutane) 158 (M+1)

27a,b oil (38%) ^{1}H NMR δ 2 83 (td, 1H, J= 14 and 3 5 Hz, H-10ax) and 4 4-5 1 (m, 2H, H-8 and H-10eq) ppm ^{13}C NMR δ 169 3 and 169 2 (C-2), 89 5 (d, J= 174 Hz) and 86 9 (d, J= 170 Hz) (C-8), 53 9 (d, J= 12 Hz, C-7b) and 50 7 (C-7a) ppm (other signals complex) IR 1620, 1460, 1440, 1405, 1350, 1330, 1240, 1160, 1090 and 1015 cm^{-1} MS (CI, isobutane) 172 (M+1)

28a,b mp 97°C (75%) ^{1}H NMR δ 3 04 (td, 0 5H, J= 13 and 3 5 Hz, H-2ax), 3 35 (td, 0 5H, J= 13 and 3 5 Hz, H-2ax), 4 3-5 3 (m, 3H, H-2eq, H-4 and H-6), 7 5 (m, 3H, H-arom) and 7 86 (m, 1H, H-arom) ppm ^{13}C NMR δ 166 0 (C-9), 145 2 and 144 2 (C-7), 132 3 and 132 0 (C-8), 89 6 (d, J= 177 Hz, C-4), 86 6 (d, J= 171 Hz, C-4), 56 5 (d, J= 13 Hz, C-6b), 53 2 (C-6a), 37 7 (d, J= 20 Hz, C-5),

36.2 (C-2a), 36.1 (d, J= 20 Hz, C-3), 33.7 (d, J= 2 2 Hz, C-2b) ppm (other signals complex). IR: 1690, 1470, 1420, 1340, 1105, 1090 and 1050 cm^{-1} MS (CI, isobutane): 206 (M+1)

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