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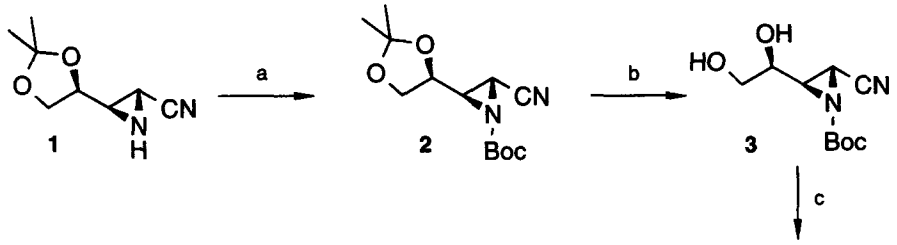
Synthesis of *tert*-Butyl (2*R*,3*R*)-2-cyano-3-formyl-aziridine-1-carboxylate - A New Potential Building Block for Amino Alcohols and Polyamines[1]

Klaus Jähnisch

Institut für Angewandte Chemie Berlin-Adlershof e.V., Rudower Chaussee 5, D-12484 Berlin, Germany

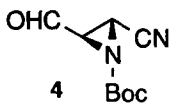
Abstract: The cyano dihydroxyethyl aziridine **3** was obtained by acid catalyzed hydrolysis of the acetonide protected aziridine **2**. Subsequent transformation by glycol cleavage yielded *tert*-butyl (2*R*,3*R*)-2-cyano-3-formyl-aziridine-1-carboxylate (**4**). Copyright © 1996 Elsevier Science Ltd

Whereas formylaziridines are of importance as building blocks[2-4], formylaziridine carboxylic acid derivatives are yet unknown. We here report the synthesis of the first example of this class of compounds. We used enantiomerically pure 1H-aziridine carboxylic acid derivatives which we recently prepared by asymmetric Michael-type addition of ammonia to chiral α-bromoacrylonitriles[5].



1 2 3

a) Boc_2O, DMAP, CH_2Cl_2, 84 %; b) Amberlyst 15 (H^+ form), MeOH, 48 h, 86 %
c) $NaIO_4$, CH_2Cl_2/H_2O, 88 %



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Starting material is (2*R*,3*R*,4*S*)-3-(2,2-dimethyl-1,3-dioxolan-4-yl)-aziridine-2-carbonitrile (**1**) which is transformed in the first step to the protected compound **2** by reaction with Boc anhydride in the presence of dimethylaminopyridine. Selective hydrolysis of the acetonide is achieved by acid catalysis using the ion exchange re-

sin Amberlyst 15 (H^+ form). Finally glycol cleavage of **3** with sodium metaperiodate in CH_2Cl_2/H_2O gave *tert*-butyl (2*R*,3*R*)-2-cyano-3-formyl-aziridine-1-carboxylate (**4**) in high yield.[6]

Acknowledgement.

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References and Notes

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6. Procedure: *tert*-Butyl 2-cyano-3-[1,2-dihydroxy-(1*S*)-ethyl]-(2*R*,3*R*)-aziridine-1-carboxylate (**3**): **2** (60 mg, 0.22 mmol) was dissolved in 2 ml of methanol. 44 mg Amberlyst 15 (H^+ form) was added and the mixture was stirred for 48 h at r.t.. After filtration, the solvent was removed under reduced pressure. The residue was chromatgraphed by HPLC. Yield: 44 mg (86 %) oil - $[\alpha]_D^{20}$ = + 26.4 (c = 1, $CHCl_3$) - ^1H NMR ($CDCl_3$, TMS): δ = 1.57 (s, 9 H, CH_3), 2.48 (2 H, OH), 3.03 (m, 1 H, 3-H), 3.07 (d, 1 H, 2-H, J = 3.0 Hz), 3.8 - 3.9 (m, 3 H, CH_2-O, CH-O) - ^{13}C NMR ($CDCl_3$). 23.9 (C-2), 28.0 (CH_3), 45.2 (C-3), 64.7 (CH_2-O), 68.2 (CH-O), 84.6 (*tert*-C), 115.3 (CN), 158.4 (N-C=O).
tert-Butyl (2*R*,3*R*)-2-cyano-3-formyl-aziridine-1-carboxylate (**4**): A solution of sodium metaperiodate (68 mg, 0.32 mmol) in 0.3 ml of H_2O was added dropwise with stirring to a solution of **3** (37 mg, 0.16 mmol) in 1.5 ml CH_2Cl_2. The stirring was continued for 1 h at r.t. and sodium sulfate was added. After filtration the residue was washed with CH_2Cl_2 (2 x 0.5 ml) and the solvent was removed in vacuo. Yield: 28 mg (88 %) pale yellow oil - $[\alpha]_D^{20}$ = + 4.2 (c = 1, $CHCl_3$) - ^1H NMR ($CDCl_3$, TMS): δ = 1.5 (s, 9 H, CH_3), 3.31 (d, 1 H, 2-H, J = 2.4 Hz), 3.64 (m, 1 H, 3-H), 9.43 (1H, dd, CHO, $J_{CHO\text{-}CHCN}$ = 2.9 Hz) - ^{13}C NMR ($CDCl_3$): 27.1 (C-2), 27.7 (CH_3), 44.4 (C-3), 85.0 (*tert*-C), 114.1 (CN), 155.6 (N-C=O), 191.8 (CH=O).

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