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AZIRIDINIMINIUM SALTS

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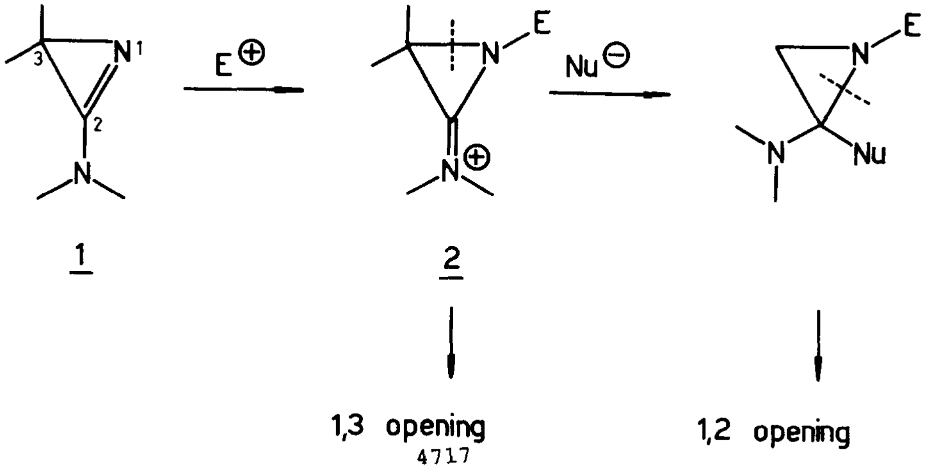
Summary : Stable aziridiniminium salts have been obtained from the reaction of 2-amino-1-azirines with trityl tetrafluoroborate or trimethylsilyl triflate. These new derivatives of α-lactams react with carbanions to give 2-amino-1-aziridines.

Previous studies [1,2] of our laboratory have resulted in the development of a practical method of synthesis of 2-amino-1-azirines 1 from tertiary amides. This new class of strained amidines was found to be extremely useful for the synthesis of a large number of heterocyclic structures[3].

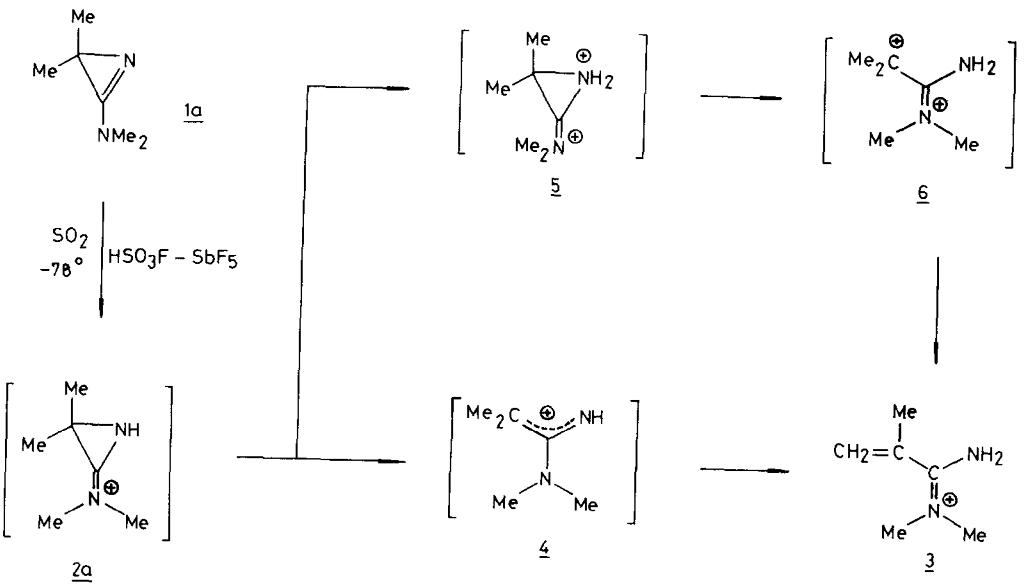
In general, 2-amino-1-azirines 1 undergo two types of selective ring opening by electrophiles. Aziridiniminium ions 2 are postulated as intermediates which, according to the substitution at C-3 and/or the nucleophilicity of the reaction medium, either undergo 1,3 ring opening or react with nucleophiles with subsequent 1,2 opening of the three-membered ring (Scheme 1).

Scheme 1



To date, however, intermediates 2 have not been isolated nor detected. Thus extraction of a pentane solution of 2a with a solution of HSO_3F-SbF_5 in SO_2 at -78° yielded instantaneously the rearranged amidinium salt 3 (Scheme 2).

Scheme 2

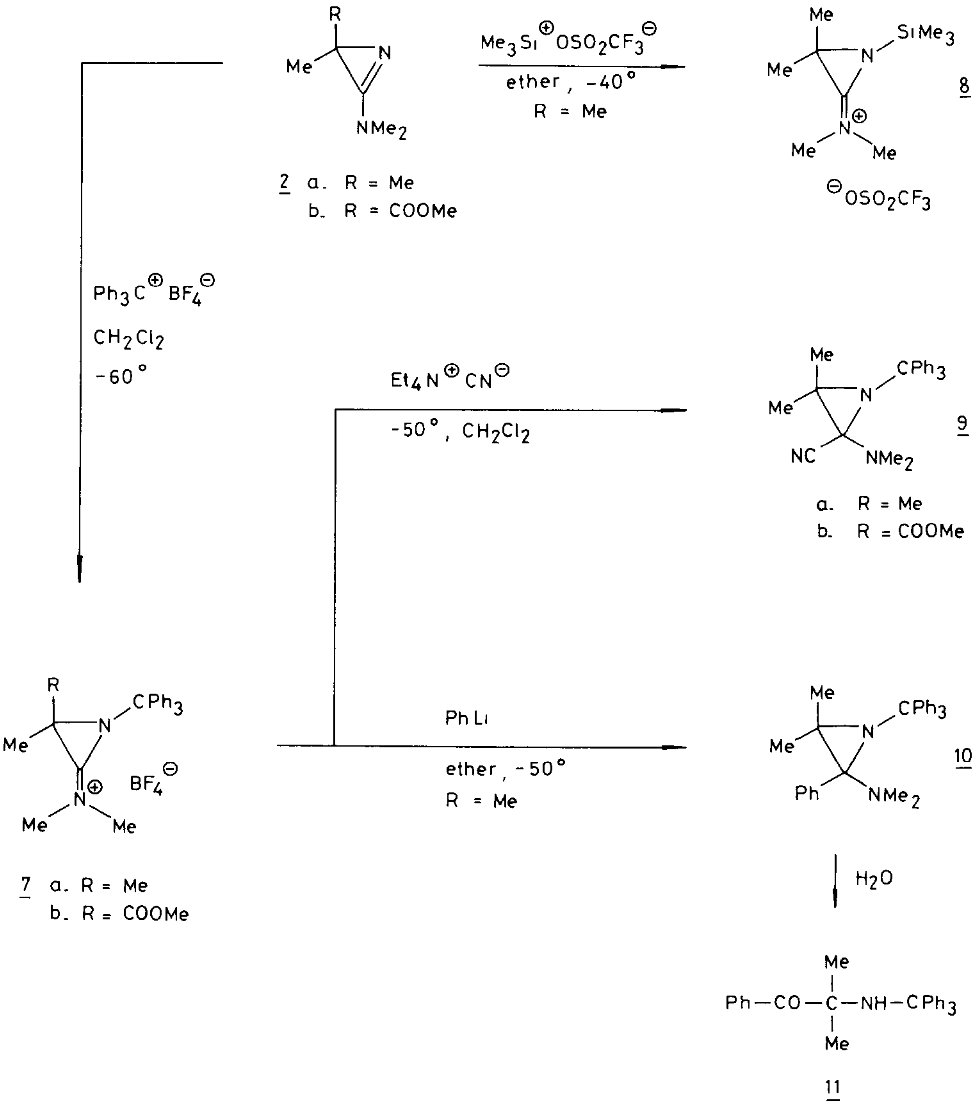


This result was rather unexpected since (a) the corresponding carbocyclic system (cyclopropaniminium cation) had been found[4] to be stable under these conditions; (b) theoretical calculations[5] predicted that the presence of electron-donating groups on the central carbon atom of an allylic cation should destabilize this open form with respect to the cyclic ion. This should be a fortiori true for the heterocyclic ion 2a since the highly stabilizing amidinium resonance is lost in going from 2a to the aza-allylic ion 4. A possible explanation for the facile rearrangement of 2a could rest upon the possibility of forming a dication 5 under these extremely acidic conditions. This very unstable species could lose energy by cleavage of the N-C_3 bond to give 6 and, after deprotonation, the observed product 3.

The use of bulkier electrophiles would be expected to suppress the formation of dications. Indeed, addition of 1a-b into solutions of trityl tetrafluoroborate in CH_2Cl_2 at -60° yielded quantitatively the crystalline aziridiniminium salts 7a-b (Scheme 3). At 20°, under argon atmosphere, crystals of 7b remained unchanged for several weeks. Compound 7a was less stable under comparable conditions but could be easily isolated and characterized.

Similarly, 1a was reacted with trimethylsilyl triflate in ether at -40° to give a crystalline solid 8.

Scheme 3



All new compounds showed spectral properties in agreement with the proposed structures. Typically 7a gave the following data :

ir (CH_2Cl_2) : $1850 cm^{-1}$, ^1H NMR ($CDCl_3$, δ) : 1.58[s, 6H, $C(CH_3)_2$], 2.46 and 3.36[2s, 6H, $C=\overset{+}{N}(CH_3)_2$], 6.8-7.4[m, 15H, $C(C_6H_5)_3$]; ^{13}C NMR ($CDCl_3$, -20°, δ) 21.2[$C(\underline{C}H_3)_2$], 39.2 and 42.1[$C=\overset{+}{N}(\underline{C}H_3)_2$], 54.8[$\underline{C}(CH_3)_2$], 78.8[$\underline{C}Ph_3$], 127.6, 128.6 and 140.3[$\underline{C}$ arom], 149.6[$\underline{C}=\overset{+}{N}(CH_3)_2$].

Treatment of 2a-b with tetraethylammonium cyanide in CH_2Cl_2 at -50° yielded the stable 2-amino-1-aziridines[6] 9a (77%, m.p. 132.5-133.5°) and 9b (83%, m.p. 188.5-189.5°). The resistance of 9a-b toward heterolytic cleavage obviously resulted from the presence of the cyano groups which would destabilize a positive charge at C-2. Indeed, the reaction of 2a with phenyllithium at -50° gave 10 which could be analyzed spectroscopically but was found to decompose on standing overnight at room temperature. Hydrolysis of 10 gave the amino-ketone 11 (61% from 2a, m.p. 132-133°).

Thus, it is now possible to prepare stable 2-amino-1-azirininiminium salts by reacting the readily available 2-amino-1-azirines with bulky electrophiles. This should further enhance the synthetic potential of 2-amino-1-azirines *as equivalents of α-lactams.*

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