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PERACID OXIDATION OF AN IMMONIUM FLUOROBORATE
A NEW EXAMPLE OF OXAZIRIDINIUM SALT.

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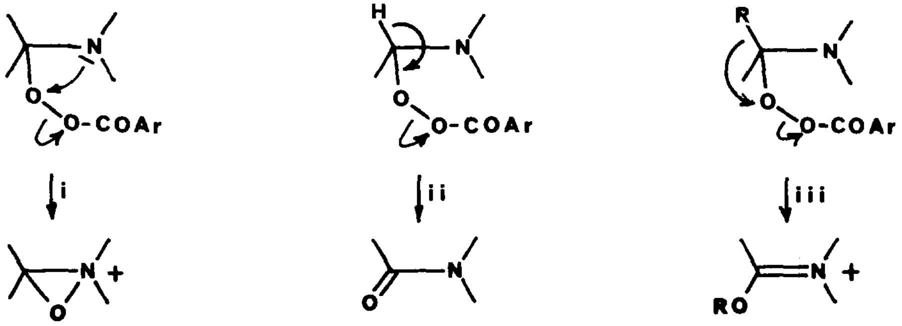
Summary : The second oxaziridinium salt described so far has been prepared by alkylation of an oxaziridine and by oxygenation of an immonium salt. This confirms that this function is indeed accessible, though very reactive.

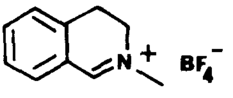
The occurrence of an oxaziridinium salt has been established for the first and only time in 1976, in connection with the part this new function plays in the peracid oxidation of a steroidal pyrrolinic immonium salt[1]. Two other paths for the action of a peracid on an immonium salt were previously known : the formation of an amide from an azetinic immonium[2], and a Baeyer-Villiger-like oxygen insertion for an immonium included in an aromatic ring[3]. These reactions were thought to result from the addition of the peracid on the immonium, giving a perester which reacted further according to different routes (scheme 1).



Scheme 1

A more comprehensive investigation will be needed to estimate the role of the various orienting factors in these reactions. Nevertheless, with the description of just one example of an oxaziridinium salt, a function which shows some potentialities as an oxygen-transfer reagent, it was of some interest to look for another substrate for this function, more available than the steroidal pyrrolinium salt formely studied and from which some information might be obtained on the relative importance of the three possible paths described in scheme 1.

The N-methyl isoquinolinium salt 1 has been chosen, although the presence of a benzylic hydrogen and the conjugation of the immonium with an aromatic nucleus should favor a reaction according to paths ii or iii of scheme 1.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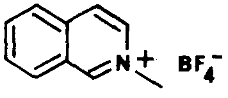
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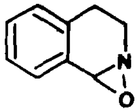
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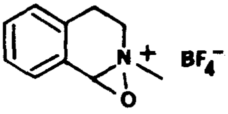
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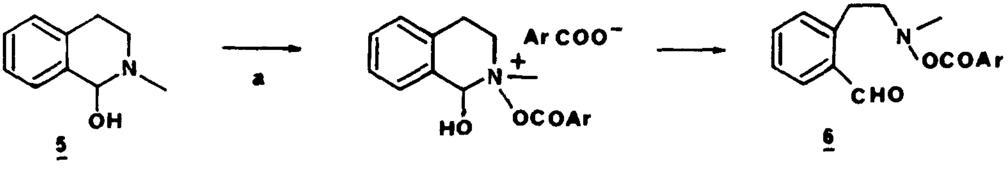
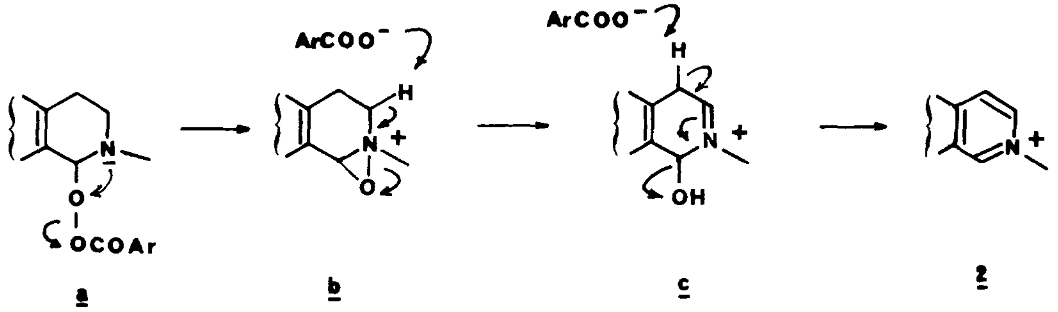
In methylene chloride, p-nitroperbenzoic acid does not react with N-methyl 3,4-dihydroisoquinolinium fluoroborate 1 [4]. In the presence of one equivalent of sodium hydrogen carbonate, a reaction takes place leading to a mixture of N-methyl isoquinolinium fluoroborate 2 (58%)[5], N-p-nitrobenzoyloxy-N-methyl-2-(o-formyl-phenyl)-ethylamine 6 (19%)[6] and starting material 1 (23%)[7]. With 0.1 equivalent of solid sodium hydrogen carbonate in methylene chloride, the peracid reacts also but gives the oxaziridinium fluoroborate 4 and p-nitrobenzoic acid ; only traces of the salts 1 and 2 are then formed and product 6 is not observed. The oxaziridinium salt 4[8] is also obtained by reaction between the oxaziridine 3[9] and trimethyloxonium fluoroborate. On the other hand, the seco-aldehyde 6 is also obtained by reaction between the pseudobase 5[10] and p-nitrobenzoyl peroxide (56%).



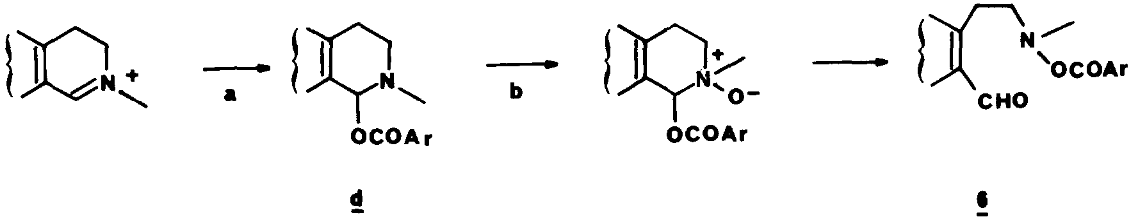
Ar = $p\,NO_2C_6H_5$-

a p-nitrobenzoyl peroxide

The oxaziridinium salt 4 could come from the perester a, itself resulting from the addition of the peracid anion to the immonium salt 1. From the oxaziridinium salt, a known rearrangement into the immonium-carbinol c^1, catalyzed by the p-nitrobenzoate anion, would yield 2, with elimination of a molecule of water.



The competitive formation of the ester d may account for the formation of product 6, an oxygen being transfered on the nitrogen of the intermediate d by either the peracid or the oxaziridinium salt. The role of an oxaziridinium salt as oxygen transfer agent has been previously demonstrated[1] ; furthermore a mixture of the pseudobase 5, p-nitrobenzoic acid and the oxaziridinium salt 4, in stoichiometric amounts, does indeed produce derivative 6, in accordance with this hypothesis.



a ArCOO$^-$, b peracid or oxaziridinium salt 4

The termination of the reaction at the oxaziridinium stage 4, as well as the absence of seco-aldehyde 6 in the products, when the reaction is conducted in the presence of a substoichiometric amount of sodium hydrogen carbonate, corroborate this hypothesis. In this case the p-nitrobenzoate anion released reacts as a base and catalyzes the formation of the perester a. Thus the p-nitrobenzoate anion is no longer available to induce the b → c elimination and the formation of the ester d.

In conclusion :

- although the isoquinolinium substrate is prone to react according to paths ii or iii of scheme 1, the intermediate perester a gives only the oxaziridinium 4. Consequently path i seems the preferential one if specific factors do not come into play. As already suggested[1], reaction according to iii can follow another path than the Baeyer-Villiger-like one when the immonium is included in an aromatic ring ;

- The necessity of a basic catalysis has been shown, as well as the occurrence of autocatalysis after initiation with a base ;
- The concurrent oxygenation of the ester of a pseudobase formed in the presence of a stoechiometric amount of base is suppressed when the reaction is autocatalyzed ;
- Finally, preparation of the new, more easily available, oxaziridinium salt 4 will facilitate further investigation of this neglected function.

Bibliography and notes

1 MILLIET, P. ; PICOT, A. ; LUSINCHI, X., Tetrahedron Letters, 1976, 1573 and 1577. Tetrahedron 1981, 31, 4201.

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3 a) ISHII, H. ; ISHIKAWA, T. ; LU, S.T. ; CHEN, I.S., J. Chem. Soc. Perkin Trans. I, 1984, 1769. b) MURUGESAN, N. ; SHAMMA, M., Tetrahedron Letters, 1979, 4521.

4 Obtained by reaction of trimethyloxonium fluoroborate and 3,4-dihydroisoquinoline. NMR ($CDCl_3$, CF_3COOH-δ) : 3.8 s (N-methyl) ; 8.72 s (H-1).

5 NMR ($CDCl_3$, CF_3COOH-δ) : 4.52 s (N-methyl) ; 9.43 s (H-1)

6 For $C_{17}H_{16}N_2O_5$ = 328, MS (FAB) : 329 (M + 1) ; (EI) : 209 (p-$NO_2C_6H_4$-CO-O-N-(CH_3)=CH_2). IR : 2720 (H-C=O), 1770 (ester), 1700cm^{-1} (C=O). NMR ($CDCl_3$, δ) : 2.95 s (3H, N-methyl) ; 3.30 m (4H, methylene H) ; 7.40, 7.80 m (4 aromatic H) ; 8.25 m (4H, $pNO_2C_6H_4$) ; 10.15 s (1H, H-C=O).

7 The insoluble sodium p-nitrobenzoate is eliminated by filtration, the solvent is evaporated, and the derivative 5 is dissolved in chloroform. The insoluble fraction (immonium salts 1 and 2) is dissolved in a mixture of deuteriochloroform and trifluoroacetic acid (3:1) and identified by NMR. The percentages of 1, 2 and 6 are measured on the NMR spectra of the crude mixture in DMSO d_6.

8 Mp 89-90° ; $C_{10}H_{12}NOBF_4$ = 249. MS (FAB) : 162 (M-BF_4). NMR ($CDCl_3$, CF_3COOH, δ) : 3.85 s (N-methyl) ; 6.05 s (H-1).

9 OGATA, Y. ; SAWAKI, Y., J. Amer. Chem. Soc., 1973, 75, 4692.

10 Obtained by stirring salt 1 in dichloromethane with an aqueous solution of NaOH. NMR ($CDCl_3$, δ) : 2.20 s (N-methyl), 4.60 s (H-1).

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