EPOXIDATION WITH PYRIDINE-TRIFLUOROACETIC ANHYDRIDE-MOLECULAR OXYGEN AND MECHANISTIC ASPECTS

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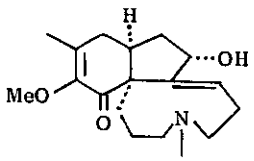
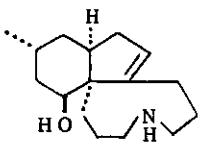
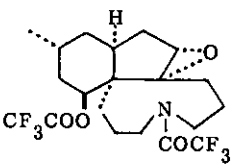
In connection with synthetic studies on Lycopodium alkaloid, lycophlegmarine (1), reaction of alcohol amine (2) with pyridine-trifluoroacetic anhydride (py-TFAA) overnight gave the epoxide (3) stereoselectively and was accelerated in an atmosphere of oxygen (O_2).



(1)

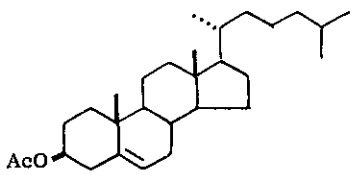


(2)

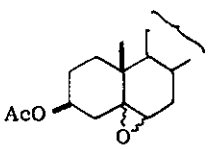


(3)

Next, oxidation of cholesteryl acetate (4) with py-TFAA-O_2 at 35° C for 4 hr gave the β-epoxide (5) (5.3%), α-epoxide (6) (7.8%), hydroxy trifluoroacetate (7) (65%), and bistrifluoroacetate (8) (11.5%). The result of reaction of (5) with py-TFAA indicated that (7) and (8) were formed from (5).

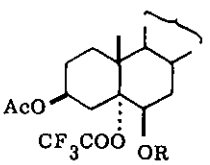


(4)



(5) β-epoxide

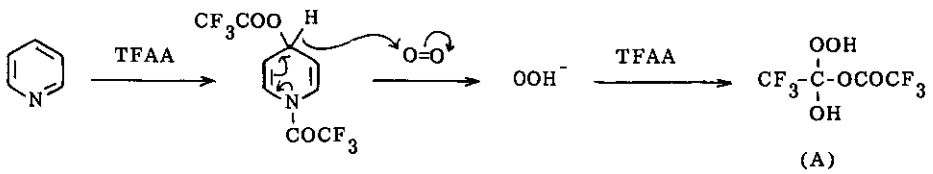
(6) α-epoxide



(7) R=H

(8) R=$COCF_3$

In order to investigate the mechanism (active species) of this reaction, epoxidation in pyridine derivatives such as picoline, lutidine, and collidine was examined. From the results, we propose the mechanism shown below as one possible mechanism, involving a hydroperoxide intermediate (A).



(A)