OXIDATION REACTIONS OF BICYCLIC PYRROLE DERIVATIVES

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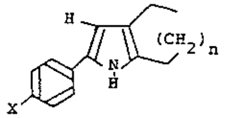
The $NaIO_4$ oxidation and the photosensitized oxygenation of bicyclic pyrrole derivatives were studied, and chemical properties of hydroperoxides obtained by the photooxygenation were explored.

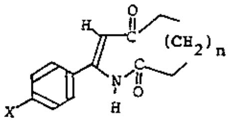
The oxidation of 2-substituted bicyclic pyrrole derivatives 1a-g with $NaIO_4$ in aqueous methanol at -5 °C gave 8-11 membered cyclic ketolactams 2a-g in good yields. In these reactions, the double bond involved in the ring fusion was regioselectively oxidized.

Irradiation of 1a-f in methanol at -50 – 0 °C in the presence of methylene blue (MB) under a continuous stream of O_2 with a 300 W halogen lamp gave hydroperoxides 3a-f in quantitative yields. The mechanistic study suggested that $^1O_2$ is an active species for this photooxygenation. The selectivity in this photoreaction was extremely high.

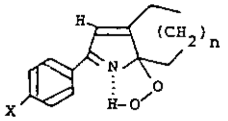
The reduction of 3a-f with PPh_3 in Et_2O or Me_2S in MeOH afforded alcohols 4a-f in quantitative yields. The pyrolysis of 4a-d at 180 °C for 3 min under argon atmosphere gave spirolactams 5a-d in high yields (80-90%) via a 1,5-sigmatropic rearrangement. However, the pyrolysis of 4e-f under similar conditions afforded bicyclic compounds with an olefinic double bond 6e-f in 30-40% yields. The reaction of 3a with $FeSO_4$ in a 2N H_2SO_4 aqueous solution or with $Fe_3(CO)_{12}$ in benzene yielded spirolactam 5a in 80-90% yields.



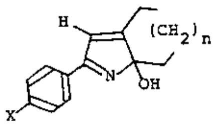
1a-g



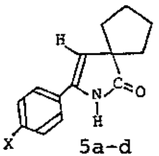
2a-g



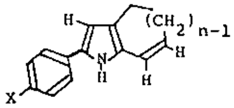
3a-f



4a-f



5a-d



6e-f

a; n=2, X=H　b; n=2, $X=CH_3$　c; n=2, X=Cl　d; n=2, X=Br
e; n=3, X=H　f; n=4, X=H　g; n=1, X=H