

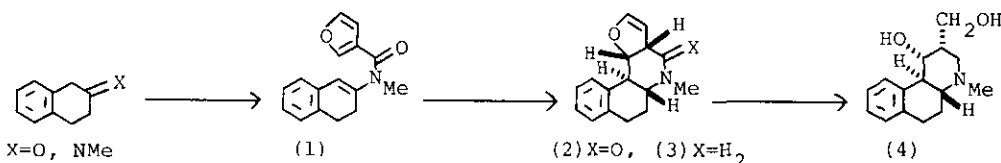
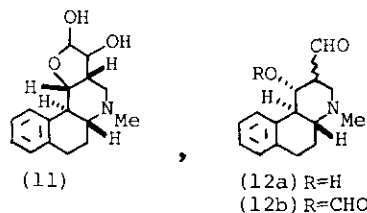
SYNTHESES OF DESPYRROLE ANALOGS OF ERGOLINE GROUP OF ALKALOIDS

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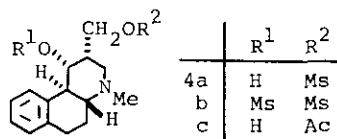
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Reductive photocyclization of the enamide (1), prepared from 2-tetraloneimine by acylation with 3-furoyl chloride, yielded the lactam (2) in good yield, which was used as a common starting compound for the syntheses of various despyrrole analogs of alkaloids such as lysergic acid (5), isolysergic acid (6), isolysergol (7), isofumigaclavine (8), lysergene (9), and isolysergine (10), thus established a general synthetic route to respective natural alkaloids.

(1) Conversion of the Amine (3) into Respective Ergoline Analogs (5,6,7,8)

The amine (3), obtained by LiAlH_4 reduction of (2), afforded upon OsO_4 treatment the glycols (11) which were subjected to periodate cleavage to give the hydroxyaldehyde (12a) under alkaline and its O-formate (12b) under acidic conditions, of which the former was further

oxidized with $\text{CrO}_3\text{-H}_2\text{SO}_4$ in MeOH followed by dehydration to give lysergic acids (5 and 6), while the latter (12b) afforded isolysergol (7) by NaBH_4 reduction. Wolff-Kishner reduction of (12a) afforded isofumigaclavine (8).

(2) Conversion of the Diol (4) into Respective Ergoline Analogs (7,8,9,10)

The diol (4), prepared from (2) by ozonolysis and LiAlH_4 reduction, was mesylated to give the mono- or dimesylate (4a,b) depending on the temperature. Dimesylate (4b) underwent double elimination by base to

give lysergene (9) while the monomesylate (4a) afforded isolysergine (10) upon LiAlH_4 reduction followed by elimination via mesylate. Protection of the methylol group by acetylation at 0°C (4c) furnished the synthesis of isolysergol (7).