Synthesis and Autoxidation of New Tetracyclic

9H.10H-Indolizino[1,2-b]indole-1-ones

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Abstract

The new tetracyclic 9H,10H-indolizino[1,2-b]indole-1-one derivatives (7a-d, 7ea, 7eb) have been synthesized by modified Fischer indole synthesis from the enol ether of 2,5-dihydroxy-7-methyl-6-cyano-indolizine (3) and arylhydrazines (4a-g). Attempted N-methylation of 7a-d produced a series of autoxidized products including 10-hydroperoxy-1-methoxyindolizino[1,2-b]indole (9a-d) as the major product accompanied with methylperoxides (10a-d and 11a-d) and 2-formyl-3-(pyridine-2-yl)indole (12a, 12c) derivatives as the minor products. A plausible mechanism of the autoxidation is postulated based on the isolation of some intermediates. The reaction is thought to proceed through azaenolate/enamine intermediates following a novel type of autoxidation.