CONVERSION OF CINCHONINE INTO IPECACUANHA ALKALOIDS THROUGH CINCHOLOIPON ETHYL ESTER

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The synthesis of l-emetine from natural cinchonine is described. It was undertaken as the vehicle for synthetic efforts toward general ipecacuanha alkaloid and analogous alkaloid preparations through cincholoipon ethyl ester where the later reaction steps could take advantage of high stereoselectivity due to the two asymmetric centers at the 3- and 4-positions.

A TOTAL SYNTHESIS OF dl-DIHYDRODEOXYEPIALLOCERNUINE SOME FINDINGS ON THE HOFMANN-LOEFFLER TYPE OF REACTION

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Cernuine is an alkaloid isolated from Lycopodium Cernuum L. The present work constitutes a total synthesis of the entitled compound, whose final step was effected by photocyclization of the Hofmann-Loeffler type in the absence of any strong acid. N-acetylisopelletierine was refluxed with $Et_3O^+BF_4^-$ in methylene chloride to afford the corresponding iminoether, which was heated with t-BuOK in t-BuOH, and the product was hydrogenated to give 2-methyl-4-quinolizidone.

The foregoing product was condensed with α-picolyl lithium to furnish 2-methyl-4-(2-picolidene)-quinolizidone, which was successively hydrogenated to afford piperidylmethylquinolizidine, whose N-chloro derivative was irradiated with a 300 W high pressure mercury lamp in ether in the absence of strong acid to readily afford dl-dihydrodeoxyepiallocernuine as the free base with no base treatment. The features of the present photocyclization are remarkably different from those of the known Hofmann-Loeffler reaction. Several compounds of 1,3-diaza six-membered ring system were prepared by the present procedure.

The mechanism of the present photoreaction will be discussed.