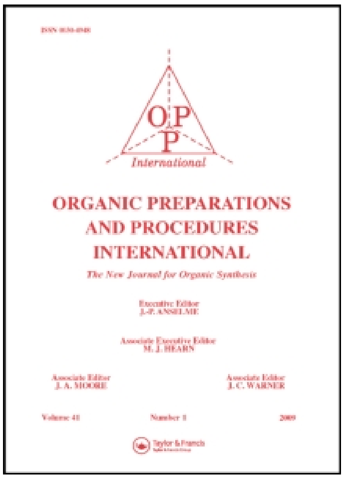

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DDQ DEHYDROGENATION OF DIHYDRODICTAMNINE

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DDQ DEHYDROGENATION OF DIHYDRODICTAMNINE

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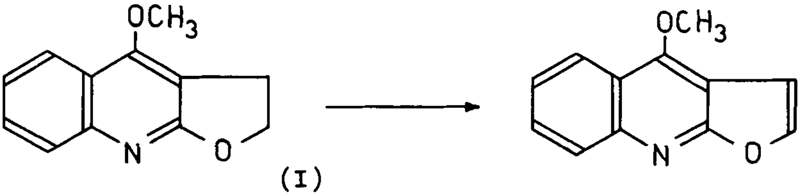
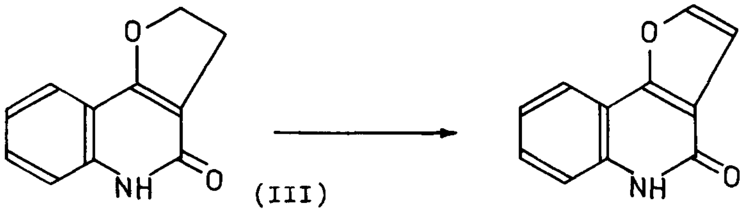
The dehydrogenation of the dihydrofuran ring is the final step in many classical syntheses[1-3] of furoquinoline alkaloids, whose simplest homolog is dictamnine (II). This goal was firstly achieved[1] by refluxing a diphenylether solution of a dihydrofuroquinoline derivative in the presence of 10% palladium-charcoal, but the yield was reported as very poor (5%). Better results were obtained by N-bromosuccinimide bromination and treatment of the crude intermediate with diethylaniline[1] or with collidine[2,3]: many furoquinoline alkaloids or their derivatives were prepared[1-9] in yields ranging from 60% to 70%.

We report the use of 2,3-dichloro-5,6-dicyanoquinone (DDQ) as a new reagent in the dehydrogenation step of the synthesis of dictamnine. DDQ had been already reported[10] to be effective in the transformation of dihydrobenzofuran derivatives into benzofuran products. When tested on dihydrodictamnine (I), DDQ gave a nearly quantitative yield of dictamnine (II) after 36 hr. refluxing in dioxane solution.

No dehydrogenation occurred when the reaction was carried on in benzene, or in acetonitrile or in methanol solution, even in the presence of catalytic amounts of acetic acid.


(I) (II)

In our hands, Cooke and Haynes's synthesis[2] of dihydrodictamnine (I) gave as a by-product also a small amount of the angular derivative (III) described by Grundon[11]. DDQ dehydrogenation of (III) to (IV) in dioxane solution was completed after only 6 hr.: it is interesting to remark that Grundon[11] obtained (IV) in good yield (58%) by dehydrogenation of (III) in diphenylether solution in the presence of 10% palladium-charcoal.


(III) (IV)

Angular dihydrofuroderivatives, therefore, seem to dehydrogenate more easily than linear derivatives.

Experimental

Dictamnine (II).

A solution of dihydrodictamnine[2] (I)(200 mg) and DDQ (400 mg) in anhydrous dioxane (100 ml) was refluxed for 36 hr. After evaporation of the solvent in vacuum, the residue was taken up many times with ether: the ethereal solution was washed with 10% Na_2CO_3, then with water, dried and evaporated. The white residue (190 mg) is dictamnine, single spot on TLC plate (eluent $CHCl_3$-AcOEt 4:1 on silica gel GF_{254} Merck, R_f 0.80) as no trace of dihydrodictamnine (R_f 0.50) is detectable: m.p. 132°-133° after one crystallization (from petrol ether 40°-70°). Lit. m.p. 132°[1,3], 132°-133°[12], 134°-135°[13]. Spectral data are identical with those reported (UV[1,14], IR[14], NMR[15], MS[16]) for dictamnine.

1,2-Dihydro-2-oxo-furano(3',2'-3,4)quinoline (IV).

1,2,4',5'-Tetrahydro-2-oxo-furano(3',2'-3,4)quinoline (III), m.p. 280-282°,[11] was isolated as a by-product (yield 5%)[17] in the PPA cyclisation[2] of 3-β-hydroxyethyl-4-methoxy-2-quinolone to dihydrodictamnine. A solution of (III)(10 mg) and DDQ (20 mg) in dioxane (5 ml) was refluxed for 6 hr. After the treatment described above for dictamnine, the dehydrogenated product (IV)(8 mg) was crystallized, m.p. 247-249°, lit. m.p. 249-250°.[11] The UV spectrum is identical with that previously reported.[11]

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17. The raw product obtained from PPA cyclisation[2] was boiled with petrol ether (b.p. 40-50°), in which (III) is sparingly soluble while dihydrodictamnine is easily dissolved; product (III) was recrystallized from ethanol.

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