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PHOTOCHEMICAL OXIDATIVE DEHYDROGENATION OF CYCLIC ENAMINO DIKETONES OF THE 8-AZASTEROID SERIES

A. A. Akhrem, V. Z. Kurbako, O. V. Gulyakevich,
V. N. Pshenichnyi, V. A. Khripach, and N. I. Garbuz

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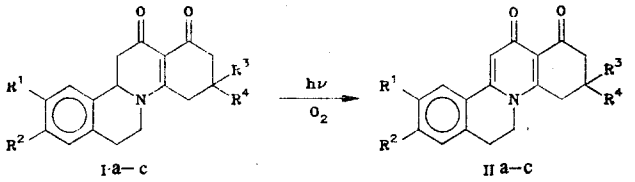
We have previously found [1, 2] that tetracyclic enamino diketones of the 8-azasteroid series (Ia-c) are dehydrogenated under the influence of chloranil or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, as well as catalytically over palladium, to give γ-pyridones IIa-c. These products were also obtained by condensation of dihydroisoquinoline N-oxides with 2-acetylcycloalkane-1,3-diones [1].



I a-c II a-c

I, II a $R^1=R^2=R^3=R^4=H$; b $R^1=R^2=H$, $R^3=R^4=CH_3$; c $R^1=R^2=CH_3O$, $R^3=R^4=CH_3$

We have shown for the first time that the dehydrogenation of enamino dicarbonyl compounds Ia-c can be realized photochemically by irradiation of alcohol solutions of Ia-c in a quartz reactor with the light of a DRSh-1000 UV lamp at room temperature and while passing oxygen and air through the reaction mixture. The reaction in an oxygen atmosphere takes place in 2.5-4 h, as compared with 15-20 h in an air atmosphere. The yields of tetracyclic γ-pyridones IIa-c, obtained as a result of normal workup, range from 60% to 80%. The structures of the isolated IIa-c were confirmed by the IR, UV, and PMR spectra and were in agreement with the data in [1, 2].

It should be noted that virtually no dehydrogenation occurs in the case of irradiation in an argon atmosphere and in an oxygen atmosphere without irradiation.

The observed photochemical oxidative dehydrogenation is of considerable interest in connection with the problem of the preparation of new biologically active substances of the 8-azasteroid series that are characterized by valuable pharmacological properties [3] and may find application in the synthesis of some alkaloids and other nitrogen-containing rings.

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