NEW METHOD FOR THE SYNTHESIS OF QUINDOLINES ON THE BASIS OF 1,5-DIKETONES OF THE INDOLINONE SERIES

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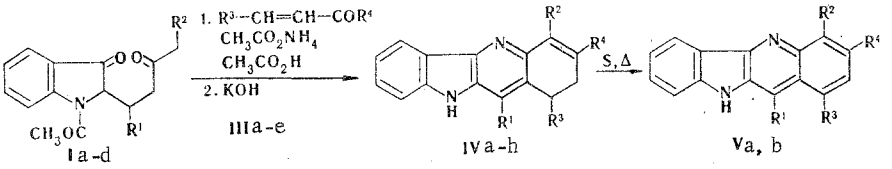
Quindoline is included in the composition of the alkaloid cryptolepine, which is of interest in a biogenetic respect [1]. We have found a new method for the synthesis of quindolines that differs favorably from the known methods [3] in that it makes it possible to obtain 3,4-benzo-δ-carbolines (10H-quindolines) with alkyl and aryl substituents in the quinoline part of the molecule. The starting compounds for this method are 1,5-diketones Ia-d (with the melting points given in parentheses): Ia (123-125°C), Ib (118-119°C), Ic (127-128°C), and Id (94-96°C). These diketones were obtained by the Michael reaction from 1-acetylindolin-3-one (II) and α,β-unsaturated ketones [3].



Ia $R^1=C_6H_5$, $R^2=H$, b $R^1=p$-Cl—C_6H_4, $R^2=H$; c $R^1=C_6H_5$, $R^2=CH_3$; d $R^1=CH_3$, $R^2=H$; IIIa,d,e $R^3=C_6H_5$; b $R^3=p$-Cl—C_6H_4; c $R^3=CH_3$; IIIa-c $R^4=CH_3$; d $R^4=C_2H_5$; e $R^4=C_6H_5$; IVa $R^1=R^3=C_6H_5$, $R^2=H$, $R^4=CH_3$; b $R^1=C_6H_5$, $R^2=H$, $R^3=p$-Cl—C_6H_4, $R^4=CH_3$; c $R^1=p$-Cl—C_6H_4, $R^2=H$, $R^3=C_6H_5$, $R^4=CH_3$; d $R^1=R^3=R^4=C_6H_5$, $R^2=H$; e $R^1=R^3=C_6H_5$, $R^2=CH_3$, $R^4=C_2H_5$; f $R^1=R^3=R^4=CH_3$, $R^2=H$; g $R^1=R^4=CH_3$, $R^2=H$, $R^3=C_6H_5$; h $R^1=R^3=p$-Cl—C_6H_4, $R^2=H$, $R^4=CH_3$

When 1,5-diketones Ia-d are heated with α,β-unsaturated ketones IIIa-e in acetic acid in the presence of ammonium acetate, they are converted in 53-83% yields to 1,2-dihydro-10H-quindolines (IVa-h): IVa (290-291°C), IVb (298-299°C), IVc (295-296°C), IVd (253-255°C), IVe (218-222°C), IVf (146-149°C), IVg (>260°C, dec.), and IVh (276-278°C). The acetyl protective group is removed by treatment of the reaction mixture with 10% KOH. Dihydroquindolines IVa, h can also be obtained in one step from indolinone II and α,β-unsaturated ketones IIIa, b in a ratio of 1:3 by heating in acetic acid in the presence of ammonium acetate.

The long-wave absorption bands in the UV spectra of the dihydroquindolines are shifted bathochromically as compared with the spectra of the corresponding δ-carbolines.

1,2-Dihydroquindolines IVa, h are readily dehydrogenated to give quindolines Va, b in high yields by heating with sulfur for 1.5-2 h: Va (341-342°C) and Vb (>308°C, dec.).

The results of elementary analysis were in agreement with the calculated values. The mass spectra and PMR spectra confirmed the proposed structures.

LITERATURE CITED

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