SYNTHESIS OF ENAMINE DERIVATIVES OF 3,4-DIHYDROISOQUINOLINE

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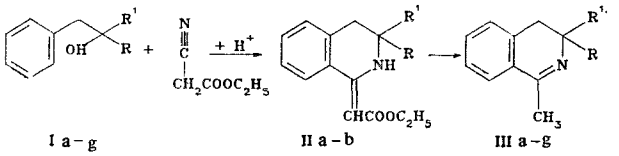
Continuing the study of the possibilities of the application of the Ritter reaction to the synthesis of the most inaccessible 3,3-dialkyl-3,4-dihydroisoquinolines, we used tertiary carbinols with an unactivated isocyclic ring (Ia-g) and ethyl cyanoacetate to obtain 3,3-dialkyl-3,4-dihydroisoquinolines containing a carbethoxymethylene group in position I (IIa,b) and 1-methyl-3,3-dialkyl-3,4-dihydroisoquinolines (IIa-g) with good yields [1, 2].



I a-g II a-b III a-g

I, III a R=R′=CH₃; b R=CH₃, R′=C₂H₅; c R=R′=C₂H₅; d R+R′=—(CH₂)₄—; e R+R′=—(CH₂)₅—; f R=CH₃, R′=(CH₂)₂N(CH₃)₂; g R=CH₃, R′=(CH₂)₂N(C₂H₅)₂; II a R=R′=CH₃; b R=CH₃, R′=C₂H₅

Depending on the time for carrying out the raction, compounds IIa and IIb (5-7 min) or IIIa-g (5 to 5 h 30 min) form with a 60-80% yield. The reaction takes place in a heterogeneous medium (benzene—sulfuric acid) at 75-78°C with equimolar amounts of the reactants (0.1 mole) in 50 ml of benzene and 40 ml of conc. H_2SO_4.

Compounds IIa and IIb exist in an enamine form, as is confirmed by the data from the PMR spectra of the bases and by reactions with various electrophiles, which take place exclusively at the α-carbon atom of the enaminocarbonyl system.

Compounds IIIa-g react with electrophiles in analogy to IIa and IIb; however, their PMR and IR spectra correspond to the azomethine (imine) form.

Compound IIa. PMR spectrum ($CDCl_3$): 1.20 (m, 9H), 2.66 (s, 2H), 4.00 (q, 2H), 4.99 (s, 1H), 7.18 (m, 4H), and 8.82 ppm (s, 1H). IR spectrum (in $CHCl_3$): 1610 (conjugated C=C), 1575 (C=C in benzene ring), 1650 (bound C=O), 1720 (free CO), 3030 (=C—H), 3275 cm^{-1} (bound N—H). Hydrochloride, mp 163-165°C. Compound IIIa. PMR spectrum ($CDCl_3$): 1.40 (s, 6H), 2.60 (s, 3H), 2.76 (s, 2H), 7.15 ppm (m, 4H). IR spectrum: 1580 (C=C in benzene ring), 1630 (C=N), 3030 cm^{-1} (=C—H). Hydrochloride, mp 175-176°C. Compound IIb: picrate, mp 93-95°C. Compound IIIb: salicylate, mp 85-87°C. Compound IIIc: salicylate, mp 72-73°C. Compound IIId: picrate, mp 166-167°C. Compound IIIe: salicylate, mp 168-160°C. Compound IIIf: bp 90-91°C (10 mm Hg). Compound IIIg: mp 92-93°C (10 mm Hg).

The data from the elemental analysis for C, H, N, and Cl for all the compounds obtained correspond to the calculated values.

LITERATURE CITED

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