

Cyclocondensation of Nitromalonaldehyde Sodium Salt with Substituted 1-Amino-3-butanones

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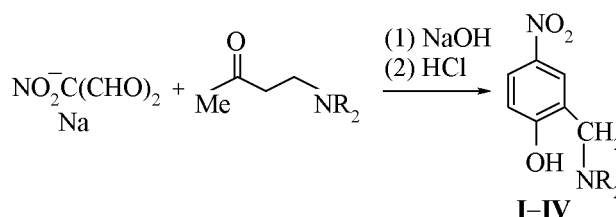
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Abstract—Cyclocondensation of nitromalonaldehyde sodium salt with substituted 1-amino-3-butanones afforded 2-dimethyl-, diethylaminomethyl-4-nitrophenols and 2-piperidyl-, morpholylomethyl-4-nitrophenols.

At present N-substituted 2-aminomethyl-4-nitrophenols are synthesized either by Mannich reaction from *p*-nitrophenol, formaldehyde, and an appropriate amine [1–5] or by condensation of *p*-nitrophenol with amina [6, 7]. Yet a method is known for preparation of 2- and 2,6-substituted *p*-nitrophenols by cyclocondensation of nitromalonaldehyde sodium salt with aliphatic ketones [8].

We carried out a reaction between nitromalonaldehyde sodium salt and N-substituted 1-amino-3-butanones that in the aqueous alcohol in the presence of bases gave rise to substituted 2-aminomethyl-4-nitrophenols **I–IV** in 15–30% yield.

Physical characteristics of compounds **I–IV** are given in the table. In the electronic spectra of compounds **I–IV** in 0.1 N NaOH an absorption peak is present at λ 410 nm identical to the peak of *p*-nitrophenol in 0.1 N NaOH.



R = Me (**I**); R = Et (**II**); NR_2 = piperidyl (**III**);
 NR_2 = morpholyl (**IV**).

In the IR spectra of compounds **I–IV** appear absorption bands at $3400\text{--}3300\text{ cm}^{-1}$ of O–H stretching vibrations and at $1300\text{--}1280\text{ cm}^{-1}$ of C–O stretching vibrations in agreement with the published data on compound **I** [9]. The absorption bands at $1527\text{--}1510\text{ cm}^{-1}$ correspond to symmetrical stretching vibrations of N–O bonds. Melting point of compounds **I** and **II** are consistent with the literature data.

Yields, melting points, and spectral characteristics of substituted 2-(aminomethyl)-4-nitrophenols **I–IV**

Compound	Yield, %	UV spectrum (0.1 N NaOH), λ_{max} , nm (ϵ)	IR spectrum (KBr), ν , cm^{-1}	mp, °C (publ. mp, °C)
2-(Dimethylaminomethyl)-4-nitrophenol (I)	20	410 (22500)	3300–3400 br (OH), 1510 s (N–O), 1283 s (C–O)	168 (168–170 [5])
2-(Diethylaminomethyl)-4-nitrophenol (II)	15	410 (25000)	3300–3400 br (OH), 1516 s (N–O), 1292 m (C–O)	128 (127–128 [7])
2-(Piperidylomethyl)-4-nitrophenol (III)	30	410 (17000)	3400–3500 br (OH), 1515 s (N–O), 1280 s (C–O)	139–141
2-(Morpholylomethyl)-4-nitrophenol (IV)	15	410 (11200)	3200–3400 br (OH), 1527 s (N–O), 1281 s (C–O)	125

[†] Deceased.

EXPERIMENTAL

Electronic spectra were recorded on SF-26 instrument at cell thickness 1 cm and concentration 0.5×10^{-4} mol l⁻¹ in the region 200–400 nm. IR spectra were measured on Impact-400 instrument. 1-Diethyl-amino-3-butanone, 1-dimethylamino-3-butanone, 1-morpholy-3-butanone, and 1-piperidyl-3-butanone were prepared along procedures [10–12] respectively.

General procedure for preparation of 2-amino-methyl-4-nitrophenols I-IV. To a mixture of 0.00827 mol of 1-amino-3-butanone, 0.00719 mol of nitromalonaldehyde sodium salt, 6.6 ml of ethanol, and 9.4 ml of water was added 0.02 mol of NaOH as 20% water solution. The reaction mixture was maintained at room temperature for 3 days and then neutralized with 19% HCl and extracted with ethyl ether (2 × 30 ml). On evaporating the ether the oily residue was crystallized from ethanol. Spectral characteristics, melting points, and yields of compounds synthesized are listed in the table.

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