

SHORT
COMMUNICATIONS

Zeolites in the Synthesis of 1-Alkyl-2-oxonicotinitriles

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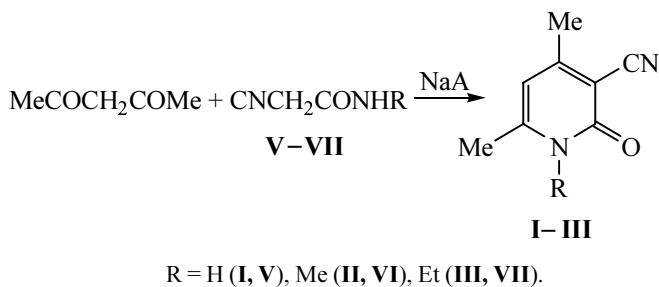
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Cyclocondensations of acetylacetone with cyanoacetamide or *N*-alkylcyanoacetamides in the presence of NaA zeolite afford 4,6-dimethyl-2-oxonicotinonitrile or 1-alkyl-4,6-dimethyl-2-oxonicotinonitriles respectively. The condensation of 3-hydroxyiminopenta-2,4-dione with cyanoacetamide in the presence of NaA zeolite furnished 4,6-dimethyl-5-nitroso-2-oxonicotinonitrile.

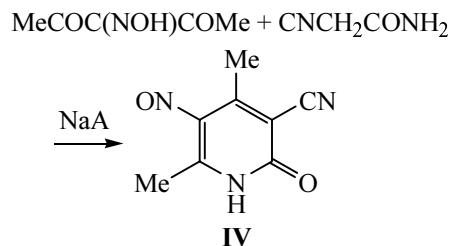
2-Oxonicotinonitriles exhibit vasodilating effect [1] and immunosuppressive activity [2]. They are constituents of plant growth regulators, herbicides, and defoliants for they are modulators of chlorophyll biosynthesis in plants [3].

2-Oxonicotinonitriles **I–IV** are commonly prepared by the cyclocondensation of cyanoacetamide or its *N*-alkyl derivatives with acetylacetone [4] or 3-hydroxyiminopenta-2,4-dione [5]. The reaction is carried out either in a buffer solution at pH 9.1 [6] or in the presence of catalysts. As catalysts were applied potassium carbonate [6], secondary and tertiary amines [4–7], and lipase from *Candida cylindracea* [8].

We suggested to use as catalyst in this reaction the NaA zeolite for zeolites were known to catalyse the aldol condensation of acetone [9]. It actually proved that acetylacetone entered into cyclocondensation with the cyanoacetamide (**V**) and *N*-alkylcyanoacetamides **VI** and **VII** in the presence of NaA zeolite. The reaction gave rise to 1-alkyl-4,6-dimethyl-2-oxonicotinonitriles **I–III**.



The reaction of 3-hydroxyiminopenta-2,4-dione with cyanoacetamide in the presence of NaA zeolite furnished 4,6-dimethyl-5-nitroso-2-oxonicotinonitrile (**IV**).



The condensation of acetylacetone with cyanoacetamide or its *N*-alkyl derivatives always occurred with a quantitative yield.

4,6-Dimethyl-2-oxonicotinonitriles I–III. General preparation procedure. A mixture of 2.79 g of NaA zeolite, 0.006 mol of cyanoacetamide **V–VII**, 0.774 g (0.007 mol) of acetylacetone, and 9 ml of methanol was heated at reflux for the period indicated in the table. The zeolite was removed by filtering the hot reaction mixture. On cooling the separated precipitate of 2-oxonicotinonitrile **I–III** was filtered off. The melting points of compounds **I–III** coincided with the published data.

4,6-Dimethyl-5-nitroso-2-oxonicotinonitrile (IV). A mixture of 0.0547 g of freshly calcined NaA zeolite, 0.0084 g (0.1 mmol) of cyanoacetamide, 0.0129 g

Reaction time, yields, and melting points of alkyl-2-oxonicotinonitriles **I–III**

Compd. no.	Boiling time, h	Yield, %	mp, °C
I	4	95	289 [10]
II	5	67	202–203 [11]
III	5.5	56	163–165 [4]

(0.1 mmol) of 3-hydroxyiminopenta-2,4-dione, and 9 ml of methanol was kept at 23°C for 20 h. Then the reaction mixture was diluted with water to a precise volume of 10 ml, an aliquot of 0.5 ml was charged into a volumetric flask of 25 ml, diluted to 25 ml with 0.1 N NaOH solution, and electronic spectrum of the solution obtained was measured. The conversion was determined from the optical density at the wavelength in the region 600–700 nm using the known value of ϵ equal to 3925 for 4,6-dimethyl-5-nitroso-2-oxonicotinonitrile prepared along procedure [5]. The conversion was 66%.

Electronic spectra were measured on SF-26 instrument at the cell thickness 1 cm and at concentration 5×10^{-5} mol l⁻¹ in the region 200–400 nm and at concentration 10^{-2} mol l⁻¹ in the region 600–800 nm. The zeolite NaA was calcined for 3 h at 300–350°C.

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