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# FORMATION OF 2-PYRIDONE IN THE PROCESS OF THE ENAMINE REARRANGEMENT OF PYRIMIDINIUM SALTS

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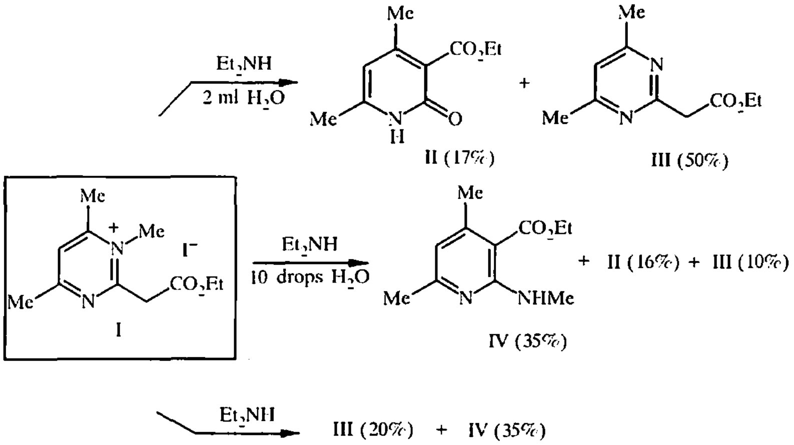
While continuing the investigation of the enamine rearrangement of pyrimidine iodomethylates into 2-methylaminopyridines occurring in alcoholic solution of methylamine [1,2], we discovered that heating 2-(ethoxycarbonylmethyl)-1,4,6-trimethylpyrimidinium iodide (I) for 20 h in a sealed ampoule at 100°C with aqueous alcoholic solution of diethylamine gave a mixture of ethyl ester of 4,6-dimethyl-2-oxo-1,2-dihydronicotinic acid II and its demethylation product, pyrimidine III. The same reaction in alcoholic diethylamine with small quantity of water added (only a few drops) led mainly to the rearrangement product, viz. 4,6-dimethyl-2-methylaminonicotinic acid ethyl ester IV (35%), although in this case we isolated pyridone II and pyrimidine III. Finally, under anhydrous conditions in alcohol solution of diethylamine, as already reported recently in [3], the reaction proceeds with the formation of compound III (20%) and IV (35%).



Pyridone II was also isolated in 20% yield by the reaction of salt I with *tert*-butylamine (10 drops of water were added to the reaction mixture).

Apparently, smooth incomplete hydrolysis of the enamine group occurs at the stage of converting the open form V. The resulting enol VI is then converted into compound II. Nicotinate IV is obtained on cyclization of the intermediate V.

We have therefore discovered a new conversion of pyrimidinium salts and have found a method of obtaining 2-oxo-1,2-dihydronicotinic acids.

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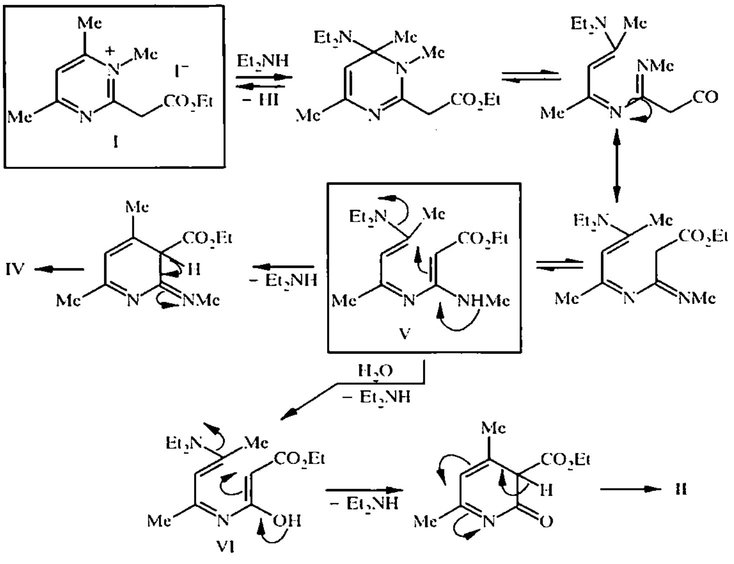

The $^1$H NMR spectra were obtained on a Varian Mercury 300 spectrometer in the Center for the Investigation of Molecular Structure of the Armenian National Academy of Sciences (program US CRDF RESC 17-5).

## EXPERIMENTAL

**Compounds III and IV** were identical with samples obtained previously in [2] according to chromatographic data and $^1$H NMR spectra.

**Compound II**: mp 134-135°C, $R_f$ 0.54 (benzene–acetone, 1 : 2). $^1$H NMR spectrum ($CDCl_3$): 1.38 (3H, t, $J$ = 7.2 Hz, $OCH_2\underline{CH_3}$); 2.24 [3H, s, 4(6)-$CH_3$]; 2.31 [3H, s, 6(4)-$CH_3$]; 4.39 (2H, q, $J$ = 7.2 Hz, $OCH_2CH_3$); 5.94 ppm (1H, s, 5-H). $^{13}$C NMR ($CDCl_3$): 14.26 ($CH_3$); 18.97 ($CH_3$); 20.09 ($CH_3$); 61.05 ($OCH_2$); 109.0 ($C_{(5)}$); 120.05($C_{(3)}$); 146.8 ($C_{(6)}$); 152.2 ($C_{(4)}$); 162.8 ($C_{(2)}$); 166.74 ppm (C=O). Mass spectrum, $m/z$ ($I_{rel}$, %): 195 (84, $M^+$), 151 (12), 150 (95), 149 (78), 123 (70); 122 (13), 121 (100), 95 (7), 94 (21), 93 (17), 92 (8), 77 (13), 53 (26), 52 (10), 43 (37), 42 (36), 41 (44). Found, %: C 61.75; H 6.84; N 7.03. $C_{10}H_{13}NO_3$. Calculated, %: C 61.53; H 6.71; N 7.17.

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