Chemistry of Heterocyclic Compounds, Vol. 43, No. 11, 2007

DIRECTION OF HYDROLYSIS OF ESTERS OF SOME PYRIMIDINE-5-CARBOXYLIC ACIDS

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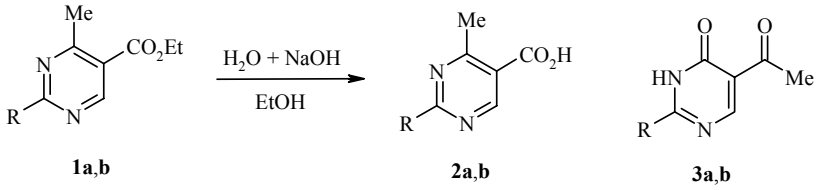
Keywords: pyrimidine-5-carboxylic acids, rearrangement.

Since the first report on the rearrangement of an ester of pyrimidine-5-carboxylic acid [1], this reaction has been repeatedly described. The alkaline hydrolysis of esters of pyrimidine-5-carboxylic acids **1** may proceed to give trivial products (pyrimidine-5-carboxylic acids **2**) [2, 3] or with rearrangement to give acetylpyrimidines **3** [4-6].



1a,**b** **2a**,**b** **3a**,**b**

1–3 **a** R = Me, **b** R = NH_2

Acids **2** or ketones **3** are formed under similar conditions, while the melting points and spectral characteristics of acid **2a** and ketone **3a** as well as of acid **2b** and ketone **3b** are extremely similar. Schenone et al. [2] demonstrated the structure of acids **2a**,**b** by their decarboxylation to the corresponding disubstituted pyrimidines. On the other hand, the evidence for the structure of ketones **3a**,**b** given by various workers [4-6] is not entirely convincing.

We carried out the hydrolysis of ester **1** under the conditions described by both groups of authors. When the hydrolysis was carried out in water as described by Schenone et al. [2], we obtained a compound with mp 150-152°C (154-155°C [2]). When the hydrolysis was carried out in ethanol as described by Danagulyan et al. [5], we obtained a compound with mp 148-150°C (146-148°C [5]). These two compounds proved identical with identical NMR spectra. The NMR spectra of a mixture of the two preparations contained one set of signals. The NMR spectra of our samples were similar to the spectra described in previous work [2, 5]. According to the ^{13}C NMR spectral data (δ, ppm: 24.7, 26.5, 122.1, 159.3, 167.1, 168.5, 169.9), this compound is acid **2a** rather than ketone **3a**. A signal for the carbonyl carbon atom in ketone **3a** would have been expected at 195-210 ppm. For example, the signal for the carbonyl carbon atom is found at 201.7 ppm in the ^{13}C NMR spectrum of 5-acetyl-4,6-dichloropyrimidine synthesized in our laboratory according to the procedure of Clark et al. [7].

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Decarboxylation of the compound obtained in the present work as described by Schenone et al. [2] gave 2,4-dimethylpyrimidine. Judging from the ^{13}C NMR spectrum for the compound given by Danagulyan et al. [5] (the signal for the carbonyl carbon atom is at 168 ppm), these authors also obtained acid **2a**, which was erroneously assigned the structure of ketone **3a**.

Analogously, we studied the hydrolysis of ester **1b** and obtained only acid **2b**, mp >300°C. ^{13}C NMR spectrum, δ, ppm: 25.1, 112.7, 162.1, 164.6 167.3, 170.7.

Thus, we may conclude that the rearrangement of esters of pyrimidine-5-carboxylic acids in basic medium is not general in nature and, at least in the two cases studied in our laboratory, does not occur.

The ^{1}H and ^{13}C NMR spectra were taken on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively, in DMSO-d_6 with residual signals as the internal standard at 2.50 ppm for DMSO-d_5 in the ^{1}H NMR spectra and 39.7 for DMSO-d_6 in the ^{13}C NMR spectra.

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