ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 5, pp. 971–972. © Pleiades Publishing, Ltd., 2007.
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LETTERS TO THE EDITOR

Aminolysis of 2-Amino-5-benzylidene-1,3-thiazol-4(5*H*)-one in Cyclic Amines: Recyclization to 2-Amino-5-benzylidene-1,5-dihydro-4*H*-imidazol-4-one Derivatives

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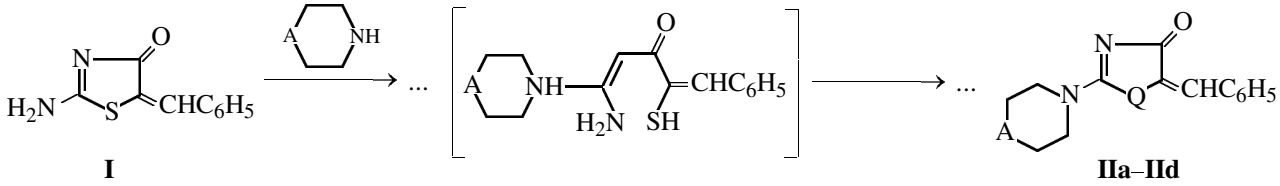
Received November 17, 2006

DOI: 10.1134/S1070363207050313

It is known [1] that the amino group in 2-amino-5-benzylidene-1,3-thiazol-4(5*H*)-one (5-benzylidene-pseudothiohydantoin, **I**) is replaced by phenylamino group by the action of aniline. We have found that aminolysis of compound **I** in piperidine or morpholine involves not only expected transamination to give 2-piperidino (**IIa**) or 2-morpholino derivative (**IIb**) of 5-benzylidene-1,3-thiazol-4(5*H*)-one but also replacement of the endocyclic sulfur atom by nitrogen with formation of 2-piperidino- or 2-morpholino-5-benzylidene-1,5-dihydro-4*H*-imidazol-4-one **IIc** or **IId**, respectively.



I **IIa–IId**

Q = S (**a, b**), NH (**c, d**); A = CH_2 (**a, c**), O (**b, d**).

The formation of compounds **IIa** and **IIb** is likely to occur without opening of the thiazole ring [2], while dihydroimidazole derivatives **IIc** and **IId** can be formed only as a result of recyclization of open-chain intermediate arising from opening of the thiazole ring at the C^2–S or C^5–S bond in a way similar to the reaction of **I** with hydroxide ion [3] or reactions of amines with 4,5-dihydrothiazol-2-amine [4, 5]. The structure of the alkaline hydrolysis [6], alcoholysis [2], and aminolysis products [7] of 2-amino-1,3-thiazol-4(5*H*)-one derivatives suggests that these reactions involve cleavage of the C^2–S bond.

2-Amino-5-benzylidene-1,3-thiazol-4(5*H*)-one (I) was synthesized by the procedure described in [8]. Aminolysis of 2-amino-5-benzylidene-1,3-thiazol-4(5*H*)-one (**I**) in piperidine. A mixture of 1.00 g of compound **I** and 9.57 g of piperidine was heated under reflux until it became homogeneous (about 10 min) and was then left to stand for 24 h at room temperature. The precipitate was filtered off, washed with petroleum ether–ethanol (10 : 1), and recrystallized from toluene to isolate 0.250 g (20%) of **5-benzylidene-2-piperidino-1,5-dihydro-4*H*-imidazol-4-one (IIc)** with mp 208–210°C (published data [9]: mp 198°C for the *Z* isomer). The filtrate was combined with the washings, and a solid separated from the solution in several days. The precipitate was filtered off and recrystallized first from toluene and then from ethanol. We thus isolated 0.253 g (19%) of **5-benzylidene-2-piperidino-1,3-thiazol-4(5*H*)-one (IIa)** with mp 202–204°C; published data: mp 202–204°C [10], 209–211°C [11].

Aminolysis of 2-amino-5-benzylidene-1,3-thiazol-4(5*H*)-one (I) in morpholine. A mixture of

2.00 g of compound **I** and 9.20 g of morpholine was heated under reflux until it became homogeneous (about 5 min) and was left to stand overnight at room temperature. The precipitate was filtered off, washed with petroleum etherethanol (1 : 1), and treated in succession with boiling acetone and propan-2-ol. After 2 days, a solid separated from the solution in propan-2-ol; it was filtered off and recrystallized from propan-2-ol. Yield of **5-benzilydene-2-morpholino-1,5-dihydro-4*H*-imidazol-4-one (IId)** 0.501 g (19.9%), mp 220–221°C; published data [9]: mp 232°C, *Z* isomer). The filtrate was combined with the washings; after 30 min, the precipitate was filtered off and recrystallized twice from toluene. Yield of **5-benzylidene-2-morpholino-1,3-thiazol-4(5*H*)-one (IIb)** 0.284 g (10.6%), mp 202–204°C; published data: mp 202–204°C [10], 203-204°C [11].

The purity of compounds **IIa**–**IId** was checked by TLC and elemental analysis, and their structure was confirmed by the IR and ^{1}H NMR spectra. The *m/z* values for the molecular ions in the mass spectra of **IIc** and **IId** coincided with the calculated values.

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