CYCLOCONDENSATION OF (BENZIMIDAZOL-2-YL)CYANAMIDE WITH ACETYLACETONE IN THE PRESENCE OF NICKEL ACETYLACETONATE

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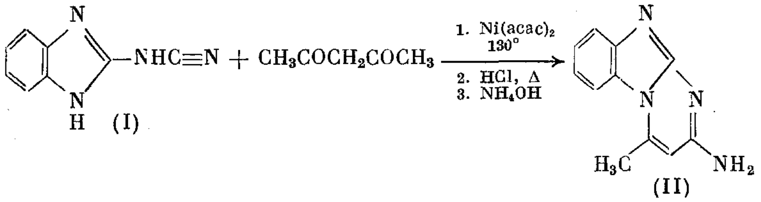
We have found that (benzimidazol-2-yl)cyanamide (I) and acetylacetone (acacH) in the presence of Ni(acac)$_2$ undergo cyclocondensation with the formation of the pyrimido[1,2-a] benzimidazole system.



(1)

The fusion of the pyrimidine ring to the benzimidazole system is likely facilitated by the activation of the C≡N group in (I) due to Ni(acac)$_2$, without which the reaction does not proceed. (For example, β-diketonates of transition metals have been found to catalyze the reaction of β-diketones with dicyanogen [1].)

A mixture of 1.00 g (I), 2.44 g Ni(acac)$_2$ and 8 ml acacH was stirred under argon at 130°C for 30 min. The excess acacH was distilled off. The residue was heated at reflux with concentrated hydrochloric acid for 2.5 h and treated with aq. NH_3. The precipitate was filtered off and washed with aq. NH_3 and acetonitrile to give 1.02 g (80%) 2-amino-4-methylpyrimido[1,2-a]benzimidazole (II), mp 319-320°C (dec., from acetonitrile). IR spectrum in KBr pellet (ν, cm^{-1}): 3430, 3300 (NH), 3200-2500 (NH, CH), 1665, 1640 (C=N). PMR spectrum in DMSO-d_6 (δ, ppm): 7.86 d (1H, H^9), 7.51 d (1H, H^6), 7.27 t (1H, H^8), 7.20 br. s (2H, NH_2). 7.09 t (1H, H^7), 6.13 s (1H, H^3), 2.82 s (3H, CH_3). Mass spectrum: 198 M^+.

N(exo)-acetyl-(II) (III) is isolated if the reaction mixture is treated with aqueous ammonia without heating at reflux in hydrochloric acid. Reaction (1) apparently involves the intermediate formation of 3-acetyl-(II) with subsequent 1,3-(C → N) migration of the acetyl group. The yield of (III) was 81%, mp 324-325°C (dec., from acetonitrile). IR spectrum in KBr pellet (ν, cm^{-1}): 1710 (C=O). PMR spectrum in DMSO-d_6 (δ, ppm): 11.5 s (1H, NH), 8.13 d (1H, H^9), 7.75 d (1H, H^6), 7.73 s (1H, H^3), 7.48 t (1H, H^8), 7.30 t (1H, H^7), 3.02 s (3H, CH_3), 2.13 s (3H, CH_3CO). A doublet is found for C^3 at 105.73 ppm in the ^{13}C NMR spectrum in CD_3CO_2H (J_{C^3-H} = 181 Hz). Mass spectrum: 240 M^+. Correct elemental analyses were obtained for (II) and (III).

Product (III) were also obtained by the acylation of (II) with acetic anhydride.

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