Chemistry of Heterocyclic Compounds, Vol. 41, No. 7, 2005

PHOTOCONVERSIONS OF 1-ACETYL-2,2,4-TRIMETHYL-[2H]-DIHYDROQUINOLINE

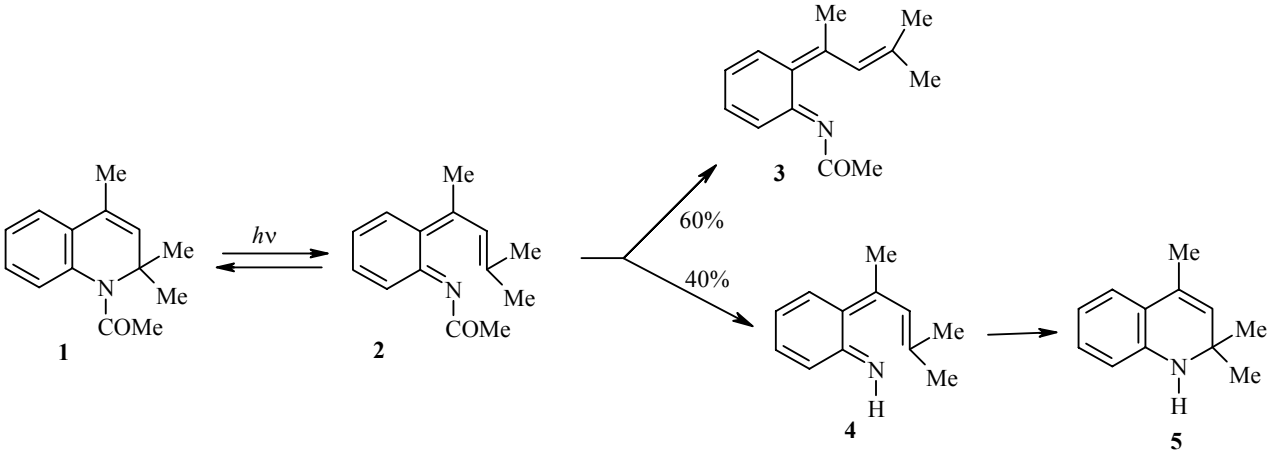
B. S. Lukyanov, M. B. Lukyanova, and N. V. Volbushko

Keywords: dihydroquinoline, photoreaction product, photochromism.

The photochromic properties of [2H]-dihydroquinolines, observed earlier at -196°C [1], have not yet been studied in detail. We have observed that when a solution of 1-acetyl-2,2,4-trimethyl-[2H]-dihydroquinoline (**1**) [2] in dioxane is exposed to light with λ_{max} 313 nm at room temperature, its photocoloration occurs with formation of a stable photoinduced form. To monitor the course of the process, we withdrew test samples from the solution and recorded their absorption spectra (Specord M-40). Irradiation was stopped within 12 h, after the optical density of the absorption band for the photoinduced form (λ_{max} 420 nm) stopped increasing and the absorption band at λ_{max} 310 nm of the starting compound **1** disappeared. The photoreaction product was successfully separated chromatographically into 2 fractions, which were identified by IR and ^{1}H NMR spectroscopy.

The ^{1}H NMR spectrum was taken on a Varian Unity-300 (300 MHz), internal standard TMS.

The first fraction, a colored (λ_{max} 420 nm) solid (mp 146-147°C), was identified as the open form 1-acetyl-2,2,4-trimethyl-[2H]-dihydroquinoline (N-acetylacetone anil) **3**. In the IR spectrum (Specord IR-75), there is an absorption band at 1670 cm^{-1} for the stretching vibrations of the C=O group of the N-acetyl moiety (ν_{CO} 1682 cm^{-1} for the closed form **1**). ^{1}H NMR spectrum, δ, ppm: 1.20 (6H, s, $C(CH_3)_2$); 1.90 (3H, s, CH_3); 2.25 (N–CO–CH_3); 5.10 (1H, s, arom.); 6.45-7.05 (4H, m, C_6H_4).



Scientific Research Institute of Physical and Organic Chemistry, Rostov State University, Rostov-on-Don 344090, Russia; e-mail: bluk@ipoc.rsu.ru. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1103-1105, July, 2005. Original article submitted March 13, 2005.

 0009-3122/05/4107-0936©2005 Springer Science+Business Media, Inc.

The second fraction, a colorless oil, was identified as 2,2,4-trimethyl-[2H]-dihydroquinoline (acetone anil) (**5**) and contains an absorption band at 3375 cm^{-1}, which coincides with the band for the stretching vibration of the NH group in the IR spectrum of acetone anil [3]. The ^1H NMR spectrum also matches the ^1H NMR spectrum of acetone anil [3], δ, ppm: 1.10 (6H, s, $C(CH_3)_2$); 1.83 (3H, s, CH_3); 3.60 (1H, s, NH); 5.05 (1H, s, arom.); 6.05-6.9 (4H, m, C_6H_4).

Thus we may have the following scheme for conversions of 1-acetyl-2,2,4-trimethyl-[2H]-dihydroquinoline (**1**) when it is exposed to light with λ_{max} 313 nm in dioxane at room temperature:

This work was carried out with the financial support of the Russian Foundation for Fundamental Research (grant 04-03-32485) and grant NSh-945.2003.3.

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