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SHORT COMMUNICATIONS

Thiocarbamoylation of 1,3,3-Trimethyl-3,4-dihydroisoquinolines with Benzoyl Isothiocyanate

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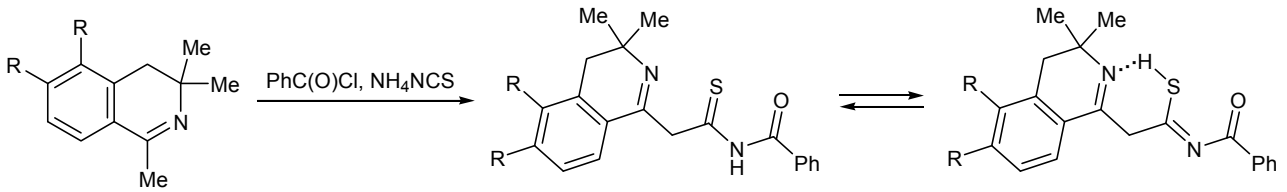
We previously studied reactions of enamines of the 3,3-dialkyl-1,2,3,4-tetrahydroisoquinoline series with phenyl isothiocyanate [1]. Reactions of these substrates with acyl isothiocyanates have not been reported so far. It is known that aroyl isothiocyanates can be generated *in situ* from the corresponding aroyl chloride and ammonium thiocyanate [2]. Aroyl isothiocyanates are more reactive electrophiles than aryl isothiocyanates, and enamines **1** and **2** [3, 4] reacted with benzoyl isothiocyanate in acetone at 20°C almost instantaneously with formation of compounds **3**, **4**.

Unlike enamino thioamides synthesized previously [1], compounds **3** and **4** in solution exist as imino tautomers. Their ^{1}H NMR spectra contained a singlet from protons in the exocyclic CH_2 group (δ 3.28 ppm) and two singlets at δ 9.96, 13.19 (**3**) and 9.51, 13.29 ppm (**4**) due to NH and SH protons of the two tautomers. Thioamide–iminothiol tautomerism is typical of thioamides [5]; it is favored by the presence of electron-withdrawing benzoyl group, which increases the acidity of the NH proton.

N-Benzoyl thioamides **3** and **4** attract interest as intermediate products and potential biologically active substances.

***N*-[2-(3,3-Dimethyl-3,4-dihydroisoquinolin-1-yl)-1-sulfanylideneethyl]benzamide (3).** A solution of 1.2 mL (10 mmol) of benzoyl chloride in 15 mL of acetone was added dropwise to a solution of 0.78 g (10 mmol) of ammonium thiocyanate in 30 mL of hot acetone, and the resulting suspension was added to a solution of 1.73 g (10 mmol) of enamine **1** in 15 mL of acetone. The mixture instantaneously turned yellow and was cooled to 20°C and diluted with 200 mL of ice water. An oily material separated and slowly crystallized on cooling to ~0°C. The precipitate was filtered off, dried, and recrystallized from propan-2-ol. Yield 2.09 g (62%), yellow crystals, mp 211–213°C. IR spectrum, ν, cm^{-1}: 3450 (NH, amide), 3275 (NH, chelate), 1675 (C=O), 1615 (C=N). ^{1}H NMR spectrum, δ, ppm: 1.33 s (6H, CH_3), 2.95 s (2H, 4-H), 3.28 s (2H, 1-CH_2), 7.33–7.91 m (9H, H_{arom}), 9.96 (0.5H, NH), 13.19 s (0.5H, SH). Found, %: C 71.18; H 5.78; N 8.42; S 9.35. $C_{20}H_{20}N_2OS$. Calculated, %: C 71.40; H 5.99; N 8.33; S 9.53.

***N*-[2-(2,2-Dimethyl-1,2-dihydrobenzo[*f*]isoquinolin-4-yl)-1-sulfanylideneethyl]benzamide (4)** was synthesized in a similar way from 2.23 g (10 mmol) of compound **2**. Yield 2.32 g (60%), yellow crystals,



1, **2** **3**, **4**

1, **3**, R = H; **2**, **4**, RR = benzo.

mp 151–153°C. IR spectrum, ν, cm^{-1}: 3450 (NH, amide), 3250 (NH, chelate), 1670 (C=O), 1620 (C=N). ^1H NMR spectrum, δ, ppm: 1.53 s (6H, CH_3), 3.05 s (2H, 1-H), 3.28 s (2H, 4-CH_2), 7.51–8.23 m (11H, H_{arom}), 9.51 (0.5H, NH), 13.29 s (0.5H, SH). Found, %: C 74.47; H 5.63; N 7.34; S 8.24. $C_{24}H_{22}N_2OS$. Calculated, %: C 74.58; H 5.74; N 7.25; S 8.30.

The ^1H NMR spectra were recorded on a Bruker-300 spectrometer (300 MHz) using DMSO-d_6 as solvent and HMDS as internal standard (δ 0.05 ppm). The IR spectra were measured on a Specord M-80 spectrometer from solutions in chloroform. The purity of the isolated compounds was checked by TLC on Silufol UV-254 plates using acetone–ethanol–chloroform (1 : 3 : 6) as eluent; spots were visualized under UV light or by treatment with iodine vapor.

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