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LETTERS TO THE EDITOR

Reactions of Phenylpropynal *N-tert*-Butylimine with 4-Amino-3-mercapto-1,2,4-triazole Derivatives

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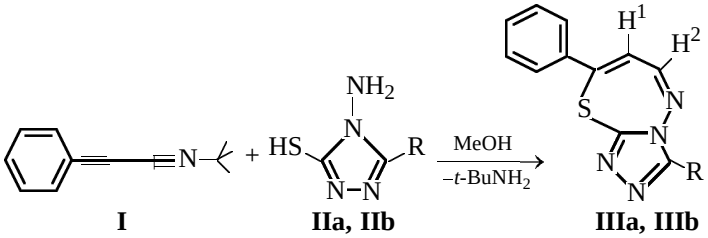
1-Aza-1,3-enynes (α,β-acetylenic aldimines) are widely used in the synthesis of five-membered heterocycles, including those containing functional substituents in the side chain. The synthesis is usually performed as 1,3-dipolar cycloaddition (reactions with nitrilimines [1], benzonitrile oxide [2], etc. [3]). Heterocycles could form in reactions of 1-aza-1,3-enynes with binucleophilic agents; however, such reactions were not studied previously. Our attempts to perform the reactions of 1-aza-1,3-enynes with *o*-aminophenol and *o*-aminothiophenol failed. However, in the reactions of phenylpropynal *N-tert*-butylimine with 4-amino-3-mercapto-1,2,4-triazoles we unexpectedly obtained crystalline substances in good yield. The IR spectra of these substances contain no bands assignable to the C≡C stretching vibrations, and the ^{1}H NMR spectra contain signals characteristic of the $C_{sp^2}H^1C_{sp^2}H^2$ fragment. These data suggest that the compounds have the thiadiazepine structure (**IIIa**, **IIIb**) and that the reaction of acetylenic aldimines with aminotriazoles can be suggested as an accessible general route to substituted thiadiazepines.



I **IIa, IIb** **IIIa, IIIb**

R = H (**a**), Me (**b**).

The related structures were prepared previously by reactions of acetylenic aldehydes with appropriate aminomercaptotriazoles [4]. However, the reactions were performed under more severe conditions (prolonged heating in ethanol under nitrogen). The reactions were accompanied by formation of by-products and tarring.

8-Phenyl-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazepine IIIa. To a solution of 0.01 mol of aldimine **I** in 20 ml of methanol, 0.01 mol of aminomercaptotriazole **IIa** was added with stirring in small portions over a period of several minutes. The reaction mixture slightly warmed up with little darkening. The reaction progress was monitored by TLC on Merck plates in the system ethyl acetate–petroleum ether, 1 : 1 by volume. The mixture was kept for 1 h at room temperature, after which the solvent was evaporated and the crystals were recrystallized from aqueous ethanol or toluene. Yield 65%, mp 189–192°C. ^{1}H NMR spectrum, δ, ppm: 6.78 d (1H, $^3J_{HH}$ 5.1 Hz), 7.46–7.49 m (3H), 7.81–7.84 m (2H), 8.05 d (1H, $^3J_{HH}$ 5.1 Hz), 8.69 s (1H).

3-Methyl-8-phenyl-1,3,4-triazolo[3,4-*b*][1,3,4]-thiadiazepine IIIb was prepared similarly. Yield 60%, mp 210–214°C. ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H), 6.74 d (1H, $^3J_{HH}$ 4.35 Hz), 7.46–7.49 m (3H), 7.80–7.84 m (2H), 8.01 d (1H, $^3J_{HH}$ 4.35 Hz).

The ^{1}H NMR spectra were recorded on a Varian

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XL-300 spectrometer with a working frequency of 300.13 MHz (^{1}H), solvent DMSO-d_6, with the residual solvent proton signal as internal reference.

Compounds **IIIa** and **IIIb** were prepared using analytically pure grade solvents and reagents.

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