

THE REACTIONS OF 6-(*tert*-BUTYL)- 3-HYDRAZINO-1,2,4-TRIAZIN-5(2H)-ONE WITH CARBONYL COMPOUNDS

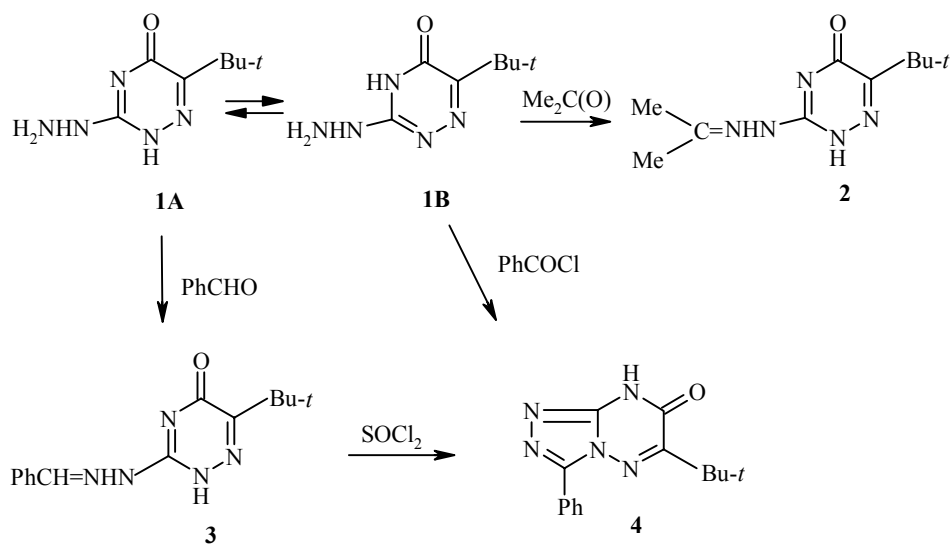
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The reaction of 6-(*tert*-butyl)-3-hydrazino-1,2,4-triazin-5(2H)-one with acetone and benzaldehyde yields the corresponding hydrazones. In the presence of thionyl chloride the benzaldehyde hydrazone is converted to 3-(*tert*-butyl)-6-phenyl-1,2,4-triazolo[4,3-*b*]-1,2,4-triazin-2(1H)-one and this can also be formed via the acylation of the starting hydrazinotriazinone using benzoyl chloride.

Keywords: 6-(*tert*-butyl)-3-hydrazino-1,2,4-triazin-5(2H)-one hydrazones, 3-(*tert*-butyl)-6-phenyl-1,2,4-triazolo[4,3-*b*]-1,2,4-triazin-2(1H)-one.

We have previously studied the reaction of carbonyl compounds (acids, anhydrides and acid halides) with substituted 5- and 6-hydrazino-1,2,4-triazines and shown that monoacylhydrazido-1,2,4-triazines are formed under usual acylation conditions. The possibility of heterocyclization at the N atoms of the triazine ring to give bicyclic systems does not occur [1, 2].

In this work we have examined the reaction of acetone, benzaldehyde, and benzoyl chloride with 6-(*tert*-butyl)-3-hydrazino-1,2,4-triazin-5(2H)-one (**1**) which had been synthesized from hydrazine hydrate and 6-(*tert*-butyl)-1,2,4-triazin-3(2H)-thion-5(4H)-one using a known method [3].



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A short reflux of the hydrazine **1** with excess acetone or refluxing for 5 h with benzaldehyde in alcohol gave the [2H-6-(*tert*-butyl)-5-oxo-1,2,4-triazin-3-yl] hydrazones **2** and **3** respectively.

Refluxing compound **3** with excess thionyl chloride gives 3-(*tert*-butyl)-6-phenyl-1,2,4-triazolo[4,3-*b*]-1,2,4-triazin-2(1H)-one (**4**). The latter proved identical to the product of the reaction of compound **1** with benzoyl chloride (IR spectrum, ¹H NMR data, absence of a depression in melting point for a mixed sample).

The composition and structure of the synthesized compounds **2-4** were proved through the results of elemental analysis and from IR, mass spectroscopic, and ¹H NMR data (see Experimental). The structure of compound **4** as the product of cyclization of hydrazone **3** at the N₍₂₎ atom was confirmed since its characteristics (mp, IR and ¹H NMR data) do not agree with the characteristics for the known 1,2,4-triazolo[3,4-*c*]-1,2,4-triazine [4] which must be formed if cyclization is through the N₍₄₎ atom. It is known [5] that 3-hydrazino-1,2,4-triazine can exist in various tautomeric forms including the 3-hydrazino-1,2,4-triazin-5(2H)-one (**1A**) and 3-hydrazino-1,2,4-triazin-5(4H)-one (**1B**) in which the distribution of electron density on the ring nitrogen atoms is significantly different. In tautomer **1B** the electron density is higher on atom N₍₄₎ and in tautomer **1A** it is significantly greater on N₍₂₎. Evidently, when carrying out the reaction the starting triazine exists principally in the form **1A** and the ring closure occurs at the N₍₂₎ atom to form a substituted 1,2,4-triazolo[4,3-*b*]-1,2,4-triazine and not the 1,2,4-triazolo[3,4-*c*]-1,2,4-triazine.

EXPERIMENTAL

IR spectra were recorded on a Specord M-80 instrument for KBr tablets and ¹H NMR spectra on a WP-100-SY spectrometer (80 MHz) with DMSO-*d*₆ solvent and HMDS internal standard. Mass spectra were taken on an MC-1302 mass spectrometer with an electron ionization energy of 70 eV. The purity of the products was monitored using TLC on Silufol UV-254 plates in the system chloroform–acetone–benzene (1:3:1).

Acetone [6-(*tert*-Butyl)-5-oxo-2H-1,2,4-triazin-3-yl]hydrazone (2). A mixture of acetone (5 ml) and the hydrazine **1** (0.46 g, 25 mmol) was refluxed for 15 min. The reaction mixture was cooled and the precipitated product **2** was filtered off, dried in air, and purified by recrystallization from 2-propanol to give compound **2** (0.52 g, 93%) as white crystals; mp 201-202°C (tarring). IR spectrum, ν , cm⁻¹: 1600 (C=O), 1092, 1060, 1011 (heterocycle). ¹H NMR spectrum, δ , ppm: 1.28 (9H, s, *t*-Bu); 1.89 and 1.96 (6H, two s, 2 CH₃). Found, %: C 53.70; H 7.70; N 31.20. C₁₀H₁₇N₅O. Calculated, %: C 53.81; H 7.67; N 31.36.

Benzaldehyde [6-(*tert*-Butyl)-5-oxo-2H-1,2,4-triazin-3-yl]hydrazone (3). A mixture of compound **1** (0.92 g, 5 mmol) and freshly distilled benzaldehyde (0.53 g, 5 mmol) in 2-propanol (30 ml) was refluxed for 5 h. The reaction mixture was cooled and the precipitated product **3** was filtered off, dried in air, and purified by recrystallization from 2-propanol to give compound **3** (1.2 g, 88%) as white crystals; mp 231-232°C. ¹H NMR spectrum, δ , ppm: 7.59-7.92 (5H, m, Ph); 9.10 (1H, s, =CH); 1.38 (9H, s, *t*-Bu). Found, %: C 61.20; H 6.30; N 25.90. C₁₄H₁₇N₅O. Calculated, %: C 61.97; H 6.34; N 25.90.

3-(*tert*-Butyl)-6-phenyl-1,2,4-triazolo[4,3-*b*]-1,2,4-triazin-2(1H)-one (4). A. A mixture of compound **1** (0.37 g, 2 mmol) and freshly distilled benzoyl chloride (10 ml) was refluxed for 4.5-5 h and then held at room temperature for 16 h. The precipitated product **4** was filtered off, dried in air and purified by recrystallization from 2-propanol to give compound **4** (0.4 g, 74%) as white crystals; mp 248-249°C. IR spectrum, ν , cm⁻¹: 1714 (C=O), 1626, 1537, 1365 (C=N, C=C). ¹H NMR spectrum, δ , ppm: 1.34 (9H, s, *t*-Bu); 7.33-7.77 (5H, m, Ph). Mass spectrum, m/z : 269 [M]⁺, 254, 240, 226, 214, 199, 187, 173, 160, 146, 138, 129, 113, 104, 96, 77, 68, 57, 41. Found, %: C 62.30; H 5.70; N 26.50. C₁₄H₁₅N₅O. Calculated, %: C 62.44; H 5.62; N 26.00.

B. A mixture of compound **3** (0.67 g, 2.5 mmol) and freshly distilled thionyl chloride (5 ml) was held with stirring on a water bath for 3-3.5 h. The excess thionyl chloride was distilled off under vacuum. Distilled water was added to the reaction mixture (1:3) and the product was extracted with petroleum ether (60-80°C).

The filtrate was evaporated and the precipitate was purified by recrystallization from 2-propanol to give the product (0.39 g, 59%) as white crystals with mp 248-249°C which did not show a melting point depression when mixed with a sample of **4** prepared by method A.

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