Chemistry of Heterocyclic Compounds, Vol. 37, No. 9, 2001

SYNTHESIS OF 8-*tert*-BUTYL-9-OXO-1,2,4-TRIAZOLO[4,5-*b*]-1,2,4-TRIAZOLO[3,4-*c*]-1,2,4-TRIAZINE

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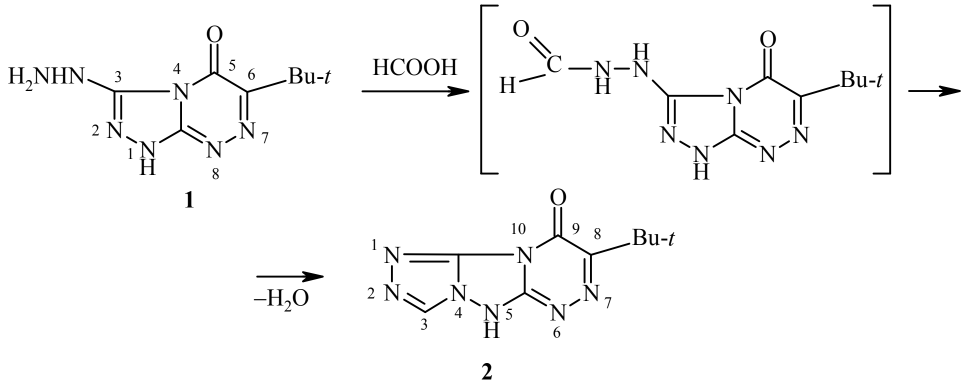
8-tert-Butyl-9-oxo-1,2,4-triazolo[4,5-b]-1,2,4-triazolo[3,4-c]-1,2,4-triazine has been synthesized by the interaction of 6-tert-butyl-3-hydrazino-1,2,4-triazolo[3,4-c]-1,2,4-triazin-5-one with formic acid. The conditions of carrying out the reaction are discussed. Spectral characteristics are given.

Keywords: 1,2,4-triazolo[4,5-*b*]-1,2,4-triazolo[3,4-*c*]-1,2,4-triazine, 1,2,4-triazolo[3,4-*c*]-1,2,4-triazine.

Condensed systems based on 1,2,4-triazines are of interest from the point of view of broadening the range of biologically active compounds. In the course of the synthesis of a triazolotriazine [1] by the condensation of hydrazine hydrate with 6-*tert*-butyl-4-(N,N-dimethylcarbamoyl)-5-oxo-3-thioxo-4,5-dihydro-1,2,4-triazine a compound was obtained containing a hydrazine group in the side chain, from which it was possible to obtain a whole series of new 1,2,4-triazine derivatives.

On boiling 6-*tert*-butyl-3-hydrazino-1,2,4-triazolo[3,4-*c*]-1,2,4-triazin-5-one (**1**) with an excess of formic acid in the absence of solvent 8-*tert*-butyl-9-oxo-1,2,4-triazolo[4,5-*b*]-1,2,4-triazolo[3,4-*c*]-1,2,4-triazine (**2**) was formed as a white crystalline substance insoluble in water. Its composition and structure were confirmed by data of elemental analysis, and IR and ^{1}H NMR spectroscopy.



Previously [2] we carried out the acylation of triazolohydrazine **1** with acetic anhydride and acetic acid, as a result of which triacetyl and diacetyl hydrazino derivatives of the triazine series were isolated. Formylation of **1** with formic acid led to the formation of the new condensed system. The general mechanism of acylation with acids [3] has been well studied and consists of nucleophilic addition of a hydrazine derivative at the

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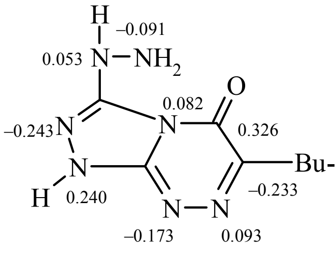
carbonyl group of the acylating agent with subsequent fission of the leaving group from the tetrahedral intermediate. A specific feature of the acylation of hydrazinotriazines is the possibility of tautomeric conversions and the recentering of the charge on the intermediate onto the triazine ring. This increases the stability of the intermediate and exerts an effect on the course of the reaction, enabling closure of a new ring at the nitrogen atoms of the heterocycle with the formation of condensed systems [4].

Analysis of the results of quantum chemical calculations carried out with the semiempirical variant PM-3 with the HYPER 5.01 program showed that the molecule of compound **1** is polar and its dipole moment is 2.188 D. Closure of the new condensed system polarizes the molecule of compound **2** still more. Its dipole moment is 4.018 D. The distribution of charges on the atoms of compounds **1** and **2** is shown in the molecular diagrams. From the calculations the total energy of the molecule of compound **1** is equal to 2577.3 eV, and of compound **2** 2456.3 eV; enthalpies were 69.35 (**1**), and 204.208 (**2**) kcal.



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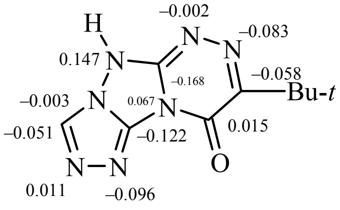

2

Probably, formic acid initially formylates the hydrazino group of compound **1** with the formation of 6-*tert*-butyl-3-formylhydrazino-1,2,4-triazolo[3,4-*c*]-1,2,4-triazin-5-one, which was not isolated from the reaction mixture due to its high reactivity. Further heating of the formyl derivative leads to elimination of water and ring closure at the nitrogen atom in position 2 of the triazole ring.

The distribution of electron density in the molecule of the initial triazolotriazine **1** shows that in reality $N_{(2)}$ of the triazole ring has increased electron density and closure of the new ring is quite possible. A proton singlet appears at 1.90 ppm in the ^{1}H NMR spectrum of compound **2** belonging to the =C–H group of the triazole ring, and the group of weak broadened signals at 8.42, 6.70. and 4.50 ppm, assigned to protons of the hydrazine group in compound **1**, disappears. In connection with the increased electron density at $N_{(2)}$ of the triazole ring of compound **1** formylation may also occur at it, however due to its lower basicity in comparison with the basicity of the amino nitrogen atom of the hydrazine residue this is not very likely. Formylation at $N_{(1)}$ of the triazole ring does not occur due to the localization on it of a significant positive charge, which was confirmed by data of NMR spectroscopy. A singlet for the $N_{(5)}H$ proton of the triazole ring was present at 9.01 ppm in the ^{1}H NMR spectrum of compound **2**, but was located at 12.04 ppm in the initial compound. Characteristic absorption bands were present in the IR spectrum of compound **2** for the carbonyl group of the triazine ring at 1590 cm^{-1} which were displaced to longer wavelengths compared with compound **1** (1660 cm^{-1}).

EXPERIMENTAL

The IR spectrum was taken on a Specord M 80 instrument in a KBr disk, the ^{1}H NMR spectrum was recorded on a WP 100 SY (80 MHz) spectrometer in DMSO-d$_6$, internal standard was HMDS. The purity of the product was checked by TLC (Silufol UV 254, chloroform–acetone, 3 : 1).

The starting material **1** was obtained as described in [1].

8-*tert*-Butyl-9-oxo-1,2,4-triazolo[4,5-*b*]-1,2,4-triazolo[3,4-*c*]-1,2,4-triazine (2). Compound **1** (2.23 g, 10 mmol) in formic acid (10 ml) was boiled for 5 h. The reaction mixture was left overnight, then filtered. Distilled water at a ratio of 2:1 was added to the filtrate. The precipitated solid was filtered off, dried in the air, and recrystallized from isopropyl alcohol. White crystals (2 g, 86%) of mp 212-213°C were isolated. IR spectrum, ν, cm^{-1}: 1590 (C=O), 1125, 1085, 1060, 1005 (heterocycle). ^1H NMR spectrum, δ, ppm: 9.01 (1H, s, NH); 1.90 (2H, s, CH); 1.35 (9H, s, *t*-Bu). Found, %: C 46.10; H 4.60; N 42.20. $C_9H_{11}N_7O$. Calculated, %: C 46.36; H 4.75; N 42.04.

RERERENCES

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