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## SHORT COMMUNICATIONS

# Activity of 3-Hydrazino-1,2,4-triazines in Reaction with *N,N*-Dimethylcarbamoyl Bromide

**L. M. Mironovich[a] and M. A. Ivanov[b]**

[a]*Sumy State University, Sumy, Russia*
[b]*Engelgardt Institute of Molecular Biology, Russian Academy of Sciences, Moscow, 119991 Russia*
*e-mail: ivanovma73@mail.ru*

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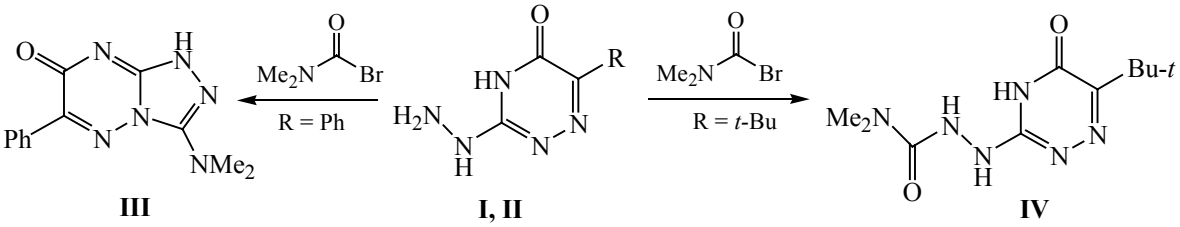
The synthesis of new derivatives of 1,2,4-triazines is interesting both from the theoretical and practical viewpoint due to the wide range of the biological activity of compounds from the 1,2,4-triazine series [1]. Published description exists of the preparation of fused systems underlain by the substituted 3-hydrazino-1,2,4-triazines treated with various acylating agents. It was established that the heterocyclization of compounds under consideration proceeded at the $N^2$ atom of the triazine ring providing the derivatives of [1,2,4]triazolo[4,3-*b*][1,2,4]-triazine and not [1,2,4]triazolo[4,3-*c*][1,2,4]triazine [1, 2].

We carried out the acylation of 3-hydrazinotriazines with *N,N*-dimethylcarbamoyl bromide aiming at the preparation of new derivatives and bicyclic systems of the 1,2,4-triazine series.

The selected objects of the study were 3-hydrazino-6-R-4,5-dihydro-1,2,4-triazin-5-ones **I, II** obtained by treating with hydrazine 3-thioxo-6-*R*-2,3,4,5-tetranydro-1,2,4-triazin-5-ones in alcohol by procedures [3] [(**I**), mp 222–223°C] and [4] [(**II**), mp 270–271°C].

Depending on the nature of the substituent in the position *6* of initial compounds **I** and **II** the acylation with the *N,N*-dimethylcarbamoyl bromide led to the formation of compounds of different chemical nature: 3-dimethylamino-6-phenyl-1,7-dihydro[1,2,4]triazolo[4,3-*b*][1,2,4] triazin-7-one (**III**) and $N^1$-dimethyl-aminocarbonyl-*N*-(6-*tert*-butyl-3-hydrazino-4,5-dihydro-1,2,4-triazin-5-one) (**IV**). The difference in the acylation products is presumably due to the high solubility of compound **II**. But more probably the course of the reaction is affected by dissimilar electron density distribution in initial compounds **I** and **II**. The structure of products obtained was derived from the combined data of the elemental analysis, IR, $^1$H NMR, and mass spectra. The IR spectrum of compound **IV** contains a characteristic absorption band of the carbonyl group of the *N,N*-dimethylcarbamoyl residue at 1710 cm$^{-1}$ lacking in the spectra of compounds **I**–**III**.

**3-Dimethylamino-6-phenyl-1,7-dihydro[1,2,4]-triazolo[4,3-*b*][1,2,4]triazin-7-one (III).** To a dispersion of 0.203 g (1 mmol) of 4,5-dihydro-1,2,4-triazin-5-one **I**




**III** **I, II** **IV**

R = Ph (**I**), *t*-Bu (**II**).

in 10 ml of DMF was added at stirring 0.22 g (1.5 mmol) of *N,N*-dimethylcarbamoyl bromide. The mixture was stirred at 70–80°C over 4.5–5 h. On cooling the reaction mixture was filtered and diluted with distilled water (1 : 3), the separated precipitate was filtered off, dried in air, and recrystallized from 2-propanol. Yield 0.2 g (78%), white crystals, mp 245–246°C (*i*-PrOH). IR spectrum, ν, $cm^{-1}$: 3156, 3064, 2988, 2920, 1680, 1580, 1564, 1520, 1444, 1328, 1312, 1260, 1252, 1156, 1076, 996, 892, 816, 788, 756, 700, 684, 564. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.51 s (6H, Me), 7.40–7.90 m (5H, Ph), 13.20 s (1H, NH). Found, %: C 56.3; H 4.7; N 32.8. $C_{12}H_{12}N_6O$. Calculated, %: C 56.24; H 4.72; N 32.79.

***N*$^1$-Dimethylaminocarbonyl-N-(6-*tert*-butyl-3-hydrazino-4,5-dihydro-1,2,4-triazin-5-one) (IV).** In 20 ml of DMF was dissolved 0.91 g (5 mmol) of 4,5-dihydro-1,2,4-triazin-5-one **II** and at stirring was added 1.05 g (7 mmol) of *N,N*-dimethylcarbamoyl bromide. The mixture was stirred at 45–50°C over 3.5–4 h. On cooling the precipitate was filtered off and recrystallized from ethanol. Yield 0.85 g (67%), yellow crystals, t.decomp. 268–269°C (EtOH). IR spectrum, ν, $cm^{-1}$: 3158, 3060, 2920, 1710, 1680, 1610, 1580, 1565, 1515, 1435, 1328, 1310, 1263, 1250, 1156, 1015, 995, 892, 816, 788, 700, 684, 564. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 1.29 s (9H, *t*-Bu), 1.52 s (6H, Me), 13.2 s (1H, NH). Mass spectrum, *m/z*: 255 $[M]^+$, 205, 192, 186, 185, 171, 170, 143, 138, 115, 111, 110, 103, 86, 84, 83, 82, 69, 68, 67, 64, 59, 57, 56, 55, 53, 43, 42, 41. Found, %: C 47.2; H 7.1; N 33.1. $C_{10}H_{18}N_6O_2$. Calculated, %: C 47.24; H 7.13; N 33.05.

IR spectra were recorded on a spectrophotometer UR-10 from pellets with KBr. $^1$H NMR spectra were registered on a spectrometer Varian Mercury VX-200 (200 MHz) in DMSO-$d_6$, internal reference HMDS. The mass spectrum was taken on a mass spectrometer MS-1302. The purity of compounds obtained was checked by TLC on Silufol UV-254 plates, eluent ethyl acetate–chloroform–acetone, 1 : 3 : 1.

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