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## SHORT COMMUNICATIONS

*Dedicated to the Correspondiny Member of the Russian Academy of Sciences B. V. Gidaspov on occasion of his 60th anniversary*

# 3*H*-Pyrido[6,7-*b*]-1,3,4-triazepines from 5-Aryltetrazoles

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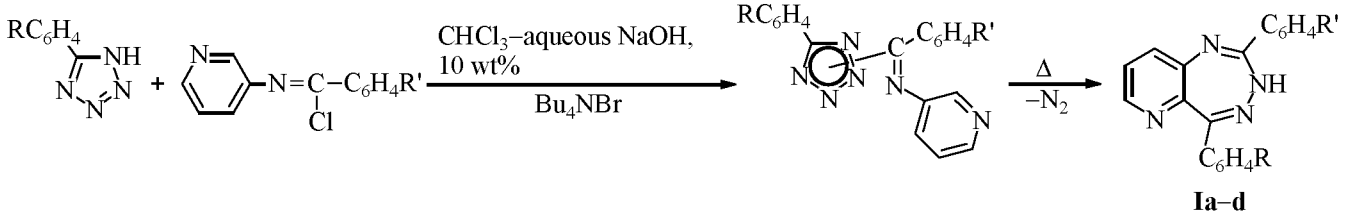
The study of thermal transformation of *N*-imidoyltetrazoles generated under conditions of phase-transfer catalysis from 5-substituted tetrazoles and *N*-arylbenzimidoyl chlorides resulted in development of a new preparation method for previously unavailable 3*H*-1,3,4-benzotriazepines [1–7].

We have shown by numerous examples that the method is of general character and can be used for building up complex heterocyclic systems including several triazepine rings [5, 6]. However up till now remained unclear whether this approach is suitable for triazepines synthesis with triazepine ring fused not to a benzene but to pyridine ring.

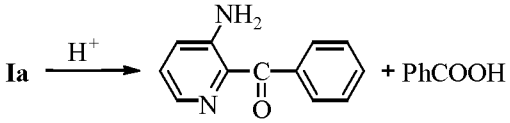
We report below on the new data showing the possibility to prepare by this procedure triazepines fused with a puridine ring. We found that thermolysis of *N*-imidoyltetrazoles obtained under conditions of the phase-transfer catalysis from 5-aryltetrazoles and *N*-(*m*-pyridyl)benzimidoyl chloride gave rise to previously unknown 3*H*-pyrido[6,7-*b*]-1,3,4-triazepines.



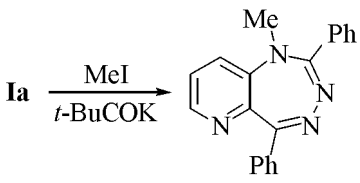

**Ia–d**

R = R' = H (**a**), R = 4-Br, R' = H (**b**), R = 4-Cl, R' = H (**c**), R = H, R = 4-Me (**d**).

3*H*-Pyrido[6,7-*b*]-1,3,4-triazepines (**Ia–d**), as also 3*H*-1,3,4-benzotriazepines [2, 5], are stable against bases but are easily hydrolyzed in water solutions of mineral acids.




At treatment of reagent **Ia** with methyl iodide in the presence of potassium *tert*-butylate arises the corresponding N-methyl derivative.




**2,5-Diphenyl-3*H*-pyrido[6,7-*b*]-1,3,4-triazepine (Ia).** To a mixture of 0.01 mol of 5-phenyltetrazole, 0.001 mol of tetrabutylammonium bromide, 10 ml of 10% water solution of NaOH, and 30 ml of chloroform was added at 20°C while stirring within 30 min 0.01 mol of *N*-(*m*-pyridyl)benzimidolyl chloride in 10 ml of chloroform. The reaction mixture was stirred for 4 h at 20°C, the phases were separated, the organic layer was washed with 1% water solution of NaOH, with water (2–10 ml), and dried with magnesium sulfate. The chloroform was removed in a vacuum, to the solid residue was added 20 ml of toluene, and it was heated for 3 h to 110°C. Then the toluene was removed in a vacuum, the residue was recrystallized from acetonitrile. Yield 1.35 g (57%). After additional purification by column chromatography on silica gel (eluent carbon tetra-

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chloride–ethyl acetate, 3:2) mp 205–208°C. IR spectrum, cm–1: 926, 984, 1001, 1026, 1055, 1076, 1121, 1167.

**5-(4-Bromophenyl)-2-phenyl-3*H*-pyrido-[6,7-*b*]-1,3,4-triazepine (Ib).** Yield 17%. mp 221–222°CC. IR spectrum, cm–1: 935, 950, 990, 1020, 1035, 1075, 1120, 1170, 1180, 1230, 1270, 1290, 1325, 1390, 1450, 1475, 1495, 1565, 1600, 1635, 2865, 2935, 3085, 3335. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 7.3–8.4 m (12H arom) 9.5 s (1H, NH). Found, %: C 60.49; H 3.27; N 14.87. $C_{19}H_{13}BrN_4$. Calculated, %: C 60.48; H 3.45; N 14.85.

**2-Phenyl-5-(4-chlorophenyl)-3*H*-pyrido-[6,7-*b*]-1,3,4-triazepine (Ic).** Yield 31%. mp 204–208°C. IR spectrum, cm$^{-1}$: 925, 950, 990, 1010, 1020, 1035, 1060, 1080, 1095, 1120, 1170, 1185, 1240, 1275, 1295, 1330, 1400, 1450, 1475, 1495, 1560, 1585, 1605, 1640, 2865, 2935, 3085, 3350. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 7.3–8.4 m (12H arom), 9.0 s (1H, NH). Found, %: C 68.63; H 4.05; N 16.72. $C_{19}H_{13}ClN_4$. Calculated, %: C 68.57; H 3.91; N 16.84.

**2-(4-Tolyl)-5-phenyl-3*H*-pyrido[6,7-*b*]-1,3,4-triazepine (Id).** Yield 25%. mp 212–213°C. IR spectrum, cm$^{-1}$: 930, 950, 985, 1010, 1025, 1040, 1060, 1085, 1095, 1120, 1170, 1180, 1200, 1220, 1235, 1280, 1295, 1320, 1330, 1400, 1415, 1455, 1475, 1505, 1525, 1565, 1605, 1735, 2870, 2940, 3045, 3065, 3350. $^1$H NMR spectrum (DMSO-$d_6$), δ, ppm: 2.4 s (3H'$CH_3$), 7.2–8.2 m (12H arom), 9.4 s (1H, NH). Found, %: C 77.01; H 5.27; N 17.93. $C_{20}H_{16}N_4$. Calculated, %: C 76.92; H 5.13; N 17.95.

**Acid hydrolysis of 2,5-diphenyl-3*H*-pyrido-[6,7-*b*]-1,3,4-triazepinea (Ia).** A mixture of 1.2 mmol of triazepine **Ia**, 10 ml of 17% hydrochloric acid was heated for 2 h to 100°C, cooled to 5°C, the separated precipitate of benzoic acid was filtered off to obtain 0.058 g (40%) of benzoic acid, mp 123°C. To the filtrate was added 10% water solution of NaOH till pH 10–12, the separated precipitate was filtered off, washed with water (10 ml), and dried in air to obtain 0.212 g (89%) of 3-amino-2-benzylpyridine, mp 99–101°C (from hexane) [8].

**2,5-Dipheny-1-methylpyrido[6,7-*b*]-1,3,4-triazepine.** To a solution of 1.7 mmol of reagent **Ia** in 30 ml of anhydrous tetrahydrofuran was added 2 mmol of potassium *tert*-butylate. The reaction mixture was stirred for 30 min at 20°C, 2.5 mmol of methyl iodide was added thereto. The stirring was continued for 2 h at 20°C, 150 ml of water was added, and the separated precipitate was filtered off. Yield 0.334 g (63%), mp 198–200°C. IR spectrum, cm$^{-1}$: 920, 935, 950, 975, 990, 1010, 1025, 1045, 1060, 1080, 1090, 1140, 1165, 1180, 1190, 1240, 1260, 1280, 1315, 1330, 1440, 1450, 1475, 1495, 1550, 1580, 1595, 2835, 2870, 2930, 2960, 3005, 3035, 3070. $^1$H NMR spectrum (DMSO-*d*6), δ, ppm: 3.15 s (3H, $CH_3$), 7.39–8.45 m (13H arom). Found, %: C 77.09; H 5.25; N 17.80. $C_{20}H_{16}N_4$. Calculated, %: C 76.92; H 5.13; N 17.95.

IR spectra were recorded on spectrometer UR-20 from KBr pellets, $^1$H NMR spectra were registered on spectrometer Bruker AC-200. The purity and homogeneity of compounds obtained was tested by TLC on Silufol UV-254 plates, eluent mixture of carbon tetrachloride and ethyl acetate, 3:2. The study was carried out under financial support of the Ministry of Education of Russian Federation (Federal Program "Integratsiya", grant no. I 0667).

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