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SYNTHESIS OF 2-IMINO-3,4-DIHYDRO-2H-BENZOXA(THIA)ZOLO[3,2-*a*]-1,3,5-TRIAZIN-4-ONES(THIONES) BY REACTION OF BENZOXA(THIA)ZOLYL-2-GUANIDINES WITH TOSYL ISOCYANATE AND PHENYL ISOTHIOCYANATE

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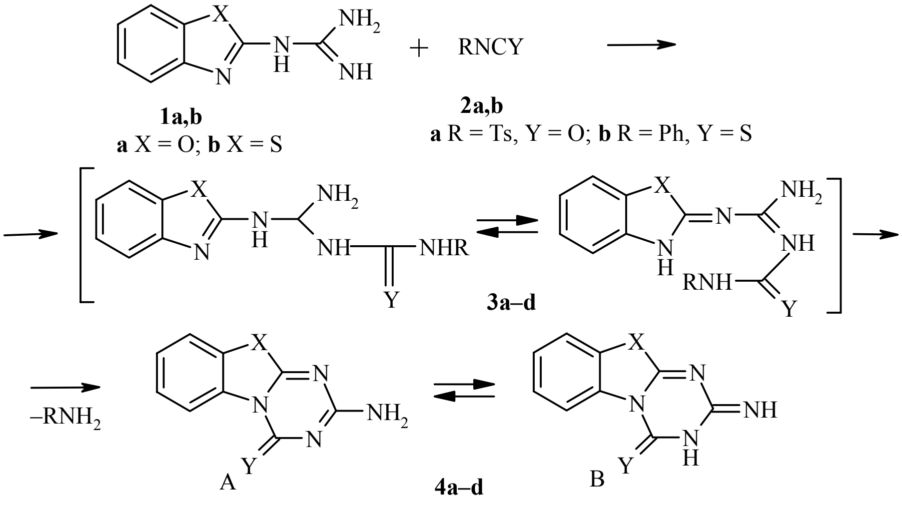
When benzoxa(thia)zolyl-2-guanidines **1a,b** react with tosyl isocyanate **2a** and phenyl isothiacyanate **2b**, instead of the expected addition products **3a-d,** we obtain 2-imino-3,4-dihydro-2H-benz[1,3]oxa(thia)zolo-[3,2-*a*]-1,3,5-triazin-4-ones(thiones) **4a-d**. Obviously, the ureas **3** are formed as intermediates in the first reaction step and then undergo ring closure to triazinones(thiones) **4a-d** with elimination of aniline or tosylamide.



1a,b
a X = O; **b** X = S

2a,b
a R = Ts, Y = O; **b** R = Ph, Y = S

3a–d

4a–d

4 a X = Y = O; **b** X = O, Y = S; **c** X = S, Y = O; **d** X = Y = S

The structure of compounds **4a-d** has been confirmed by ^{1}H NMR and mass spectroscopy. A typical feature of the ^{1}H NMR spectra of compounds **4a-d** is a downfield shift of the doublet signal from one of the *ortho* protons of the benzene ring, toward the 8-9 ppm region, due to the anisotropic effect of the adjacent Y

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atom. Compounds **4a-d** exist in the tautomeric imino form B; evidence in favor of this comes from the presence of two broadened singlets from NH protons in the ^{1}H NMR spectra. The aza analog of triazinethione **4b** (X = N, Y = S) was synthesized in [1] by reaction of benzimidazolyl-2-guanidine with carbon disulfide.

2-Imino-3,4-dihydro-2H-benzoxa(thia)zolo[3,2-*a*]1,3,5-triazin-4-ones(thiones) (4a-d). A mixture of compound **1** (15 mmol) with compound **2** (15 mmol) was heated in absolute dioxane (20 ml) at the boiling point for 4 h (**4a,c**) or 20 h (**4b**). In the case of thione **4d**, a mixture of guanidine **1b** (15 mmol) and isothiocyanate **2d** (30 mmol) in absolute pyridine (20 ml) was boiled. The precipitates were filtered off and recrystallized from DMF.

4a. Yield 72%; mp > 340°C. ^{1}H NMR spectrum (DMSO-d$_6$): 8.05 (1H, d, *J* = 8 Hz, Ar$_{ortho}$); 7.67; 7.64 (2H, 2 br. s, NH); 7.60-7.41 (3H, m, Ar). Mass spectrum: *m*/*z* = 202 [M]$^+$. Found, %: C 53.28; H 2.07; N 27.58. $C_9H_6N_4O_2$. Calculated, %: C 53.46; H 1.98; N 27.72.

4b. Yield 45%; mp 330°C. ^{1}H NMR spectrum (DMSO-d$_6$): 9.09 (1H, d, *J* = 8 Hz, Ar$_{ortho}$); 8.19, 7.81 (2H, 2 br. s, NH); 7.68-7.41 (3H, m, Ar). Mass spectrum: *m*/*z* = 218 [M]$^+$. Found, %: C 49.71; H 1.70; N 25.88. $C_9H_6N_4OS$. Calculated, %: C 49.54; H 1.83; N 25.69.

4c. Yield 63%; mp 335°C. ^{1}H NMR spectrum (DMSO-d$_6$): 8.65 (1H, d, *J* = 8 Hz, Ar$_{ortho}$); 7.58; 7.53 (2H, 2 br. s, NH); 7.91-7.41 (3H, m, Ar). Mass spectrum: *m*/*z* = 218 [M]$^+$. Found, %: C 49.41; H 1.99; N 25.55. $C_9H_6N_4OS$. Calculated, %: C 49.54; H 1.83; N 25.69.

4d. Yield 65%; mp 330°C. ^{1}H NMR spectrum (DMSO-d$_6$): 8.65 (1H, d, *J* = 8 Hz, Ar$_{ortho}$); 7.52; 7.59 (2H, 2 br. s, NH); 7.90-7.36 (3H, m, Ar). Mass spectrum: *m*/*z* = 234 [M]$^+$. Found, %: C 46.42; H 1.59; N 23.81. $C_9H_6N_4S_2$. Calculated, %: C 46.15; H 1.71; N 23.93.

REFERENCES

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