**AZIDE-TETRAZOLE EQUILIBRIUM IN PYRIDO[3,2-*d*]PYRIMIDINES**

**AZĪDA-TETRAZOLA LĪDZSVARS PIRIDO[3,2-*d*]PIRIMIDĪNOS**

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Heterocycles with an azido-azomethine structural entity are interesting due to their intrinsic dynamic azide-tetrazole tautomeric equilibrium in the solution phase [1] alongside rich azide functional group chemistry [2].

Herein, a method for the synthesis of 5-substituted tetrazolo[1,5-*a*]pyrido[2,3‑*e*] pyrimidines from 2,4-diazidopyrido[3,2-*d*]pyrimidine in SNAr reactions with *N*-, *O*-, and *S*‑ nucleophiles is presented [3]. The tetrazolo[1,5-*a*]pyrimidine derivatives can be regarded as 2‑azidopyrimidines due to present azide-tetrazole valance tautomerism and functionalized in copper(I)-catalyzed azide-alkyne dipolar cycloaddition (CuAAC) and Staudinger reactions.

Equilibrium constants and thermodynamic values were determined using variable temperature 1H NMR and were found to be ΔG298 = −3.33 to −7.52 (kJ/mol), ΔH = −19.92 to −48.02 (kJ/mol) and ΔS= −43.74 to −143.27 (J/mol·K). The negative Gibbs free energy values assert tetrazole as the major tautomeric form in solutions. Furthermore, the key starting material 2,4-diazidopyrido[3,2-*d*]pyrimidine shows a high degree of tautomerization in different solvents presenting up to 7 tautomeric forms.



**Scheme 1.**  Azide-tetrazole equilibrium guided SNAr reaction of azidopyrimidines.

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