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*Preliminary Communication*

# An Unusual Formation of 5-Phenyltetrazole in Reaction of Phenylacetylene with Dimethylammonium Azide

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Phenylacetylene reacts with dimethylammonium azide to give a mixture of 4-phenyl-1,2,3-triazole and 5-phenyltetrazole. Formation of 5-phenyltetrazole could be explained by 1,3-cycloaddition of azide to benzonitrile formed by decomposition of 4-phenyl-1,2,3-triazole.

*Key words:* azidation, 4-phenyl-1,2,3-triazole, ring-expansion, 5-phenyltetrazole

It is known that ammonium azides are both effective and convenient azidation agents, which are widely used in the syntheses of tetrazoles in media of aprotic dipolar solvents.[1–3] However, until the present time, information about using these reagents for the synthesis of the 1,2,3-triazoles has been absent. In this case, alkali metal azides as well as trimethylsilyzide are the best known azidation agents.[4,5]

Here, we have considered the 1,3-dipolar cycloaddition reaction of dimethylammonium azide to phenylacetylene in DMF solution. We have applied the typical conditions for azidation reaction of acetylenes or nitriles in aprotic dipolar solvents: stirring at 120 °C for 10 hours with 1,2 molar excess amount of azidation agent.[1–5] After mixing the reaction mass with cold water and double treating with ether, the aqueous layer was acidified by HCl to pH 3. The precipitate contained two compounds (TLC), which were separated by efficient crystallization from ethylacetate and ethanol and iden-

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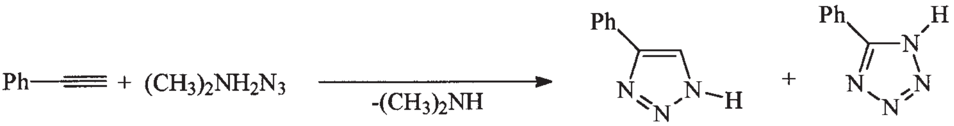
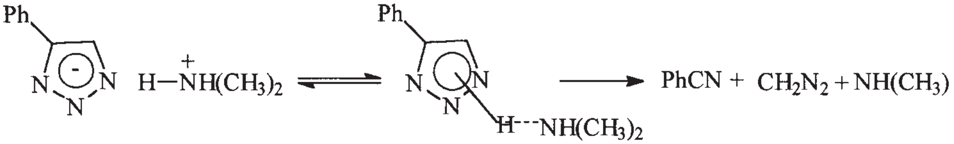


Scheme 1.



Scheme 2.

tified as 4-phenyl-1,2,3-triazole and 5-phenyltetrazole (yields 6 and 10%, respectively, Scheme 1). The organic layer contained unreacted phenylacetylene (NMR) and gum substance. Melting points, elemental analysis and NMR spectra of the heterocyclic compounds obtained agree with the known or calculated data.[4,6] Both products melt without depression with the previously known 4-phenyl-1,2,3-triazole and 5-phenyltetrazole obtained by independent methods.[3,5]

The unusual formation of 5-phenyltetrazole may be a result of the 1,3-cycloaddition of the azide to benzonitrile, which forms under the reaction conditions as the product of 4-phenyl-1,2,3-triazole ring expansion. Thus, in the first stage, dimethylammonium azide adds to phenylacetylene to give dimethylammonium 4-phenyl-1,2,3-triazolate in equilibrium with hydrogen-bonded complex of triazole and dimethylamine (Scheme 2).

Then, this complex may partially decompose to benzonitrile, diazomethane and dimethylamine.[7] This cleavage mechanism of triazole ring with the formation of nitriles and the corresponding diazomethyl derivatives is already well-known.[8] However, in the case of using silylazides or alkalimetal azides as azidation agents in primarily the same conditions,[4,5] such decomposition of phenyl-1,2,3-triazoles was not observed before. Obviously, the specificity of the studied reaction is due to the formation of the hydrogen-bonded complex of 1,2,3-triazole with amine, which increases greatly the lability of the triazole cycle.

We have calculated the enthalpies of the formation of the complexes of dimethylamine with 4-phenyl-1*H*-1,2,3-triazole, 4-phenyl-2*H*-1,2,3-triazole, and 5-phenyl-1*H*-1,2,3-triazole in the gas phase using the semiempirical AMI method.[9] In all three cases of the different prototropic tautomeric forms of triazole, we have obtained a practically equl value of the hydrogen bonding energy in these complexes, which consists of 3.2 kcal/mol and agrees with the known data on ammonium complexes of unsubstituted azoles.[10] These results show a relative stability of the complexes and do not contradict the above proposed hypothesis.

A more detailed study of the mechanism of the considered reaction will be performed.

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## SAŽETAK

### Neuobičajeno nastajanje 5-feniltetrazola u reakciji fenilacetilena s dimetilamonijevim azidom

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Fenilacetilen reagira s dimetilamonijevim azidom pri čemu nastaje smjesa 4-fenil-1,2,3-triazola i 5-feniltetrazola. Nastajanje 5-feniltetrazola može se objasniti 1,3-cikloadicijom azida na benzonitrile koji nastaju raspadom 4-fenil-1,2,3-triazola.