Features of the of deoxygenation of derivatives of 1-(1-nitroaliheteryl)-1*H*-azoles with trivalent phosphorus compounds

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Abstract

Nitro compounds play a huge role in everyday human life and in organic synthesis. The importance of nitro compounds has been growing every year since Mitscherlich first synthesized nitrobenzene in 1837. Historically nitro compounds are important precursors for aza dyes and explosives. Until now the importance of nitro compounds has not changed in the manufacture of dyes and energy-rich materials. Also nitro compounds have proved to be valuable reagents for the synthesis of complex molecules. The versatility of nitro compounds in organic synthesis is largely due to their availability and ease of transformation into various functional groups.

Reduction takes an important place in the nitro compounds chemistry. Cleavage of the N–O bond is the main result of the reduction of aromatic and aliphatic nitro compounds. Phosphorus (III) compounds such as trialkyl- triarylphosphines and trialkylphosphites are the most famous and widespread reducing agents. Deoxygenation of nitroaromatic compounds in the presence of organic compounds of trivalent phosphorus leads to the formation of a wide range of nitrogen-containing heterocycles. The direction and depth of this reaction in the aliphatic series depends on the structure of the initial nitroalkane and the properties of the reducing agent. To date several methods are known for the deoxygenation of primary and secondary nitroalkanes with trivalent phosphorus compounds leading to the formation of nitriles, amines and oxime derivatives. Information on the reactivity of tertiary nitro compounds under similar conditions remains insufficient.

The main goal of the present work was study of the interaction of derivatives of 1-(1-nitroalkyl)-1*H*-azoles with phosphorus (III) compounds.

The main tasks were:

1. Obtaining nitro-containing alicyclic heterocycles
2. Study of the deoxygenation reaction of nitro-containing alicyclic heterocycles

Scientific novelty: For the first time using the example of 3-nitro-3-azolyl-substituted azetidines and 5-nitro-5-azolyl-substituted-1,3-dioxanes, it has been shown that the interaction of nitro-containing aligeterocycles with phosphorus (III) compounds makes it possible to obtain new nitrogen-containing heterocyclic systems. A method for the synthesis of substituted 1-(2,5-dihydro-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles from 3-nitro-3-triazolyl-substituted azetidines is proposed. A new method for the synthesis of 1-(1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles was proposed which consists in the oxidation of 1-(2,5-dihydro-1*H*-imidazol-4-yl)-1*H*-1,2,3-triazoles. First proposed one-step and two-step methods for the preparation of 4-azolyl-substituted-1*H*-imidazoles from 1-(1-*tert*-butyl-3-nitroazetidin-3-yl)-4-phenyl-1*H*-1,2,3-triazole and 1-(1-*tert*-butyl-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole. A method was developed for the synthesis of 6-heteryl-substituted 4,7-dihydro-1,3,5-dioxazepines by deoxygenation of the corresponding 5-nitro-5-azolyl-substituted-1,3-dioxanes.

Theoretical and practical significance of the work consists in the study of the regularities of the interaction of nitroaligheterocycles with trivalent phosphorus compounds. As a result methods were developed for the synthesis of new heterocyclic systems containing in their structure, along with the azole fragment, 4,7-dihydro-1,3,5-dioxazepine and 2,5-dihydro-1*H*-imidazole rings. Based on the reactions of 3-nitro-3-azolyl-substituted azetidines and 5-nitro-5-azolyl-substituted-1,3-dioxanes, 5-nitro-5-azolyl-substituted hexahydropyrimidines and 5-nitro-5-azolyl-substituted tetrahydrooxazines with triethyl phosphite the applicability of the deoxygenation reaction essentially depends on the structure of the saturated nitroheterocycle. It was shown high prospects of 1-(1-(*tert*-butyl)-2,5-dihydro-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole and 6-(1*H*-benzo[d][1,2,3]triazol-1-yl)-2,2-dimethyl-4,7-dihydro-1,3,5-dioxazepine to obtain functionalized 1*H*-imidazoles and 4,7-dihydro-1,3,5-dioxazepines. It was found that among the compounds obtained 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(trimethylsilyl)-1*H*-1,2,3-triazole, 1-(1-(*tert* -butyl)-1*H*-imidazol-4-yl)-4-phenyl-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(2-fluorophenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(2-chlorophenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(3-chlorophenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(2,4-dichlorophenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-

1*H*-imidazol-4-yl)-4-(4-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-1*H*-imidazol-4-yl)-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole, 1-(1-(*tert*-butyl)-3-nitroazetidin-3-yl)-4-(2,4-dichlorophenyl)-1*H*-1,2,3-triazole and 1-(1-(*tert*-butyl) -2,5-dihydro-1*H*-imidazol-4-yl)-4-(2,4-dichlorophenyl)-1*H*-1,2,3-triazole have fungicidal activity against three types of fungi - *Rhizoctonia solani*, *Venturia inaequalis*, *Bipolaris sorokiniana.*

Defense provisions:

1. The preparation method of 2,5-dihydro-1*H*-imidazoles
2. The preparation method of 4,7-dihydro-1,3,5-dioxazepines
3. One-step and two-step methods of obtaining 4-azolyl-substituted-1*H*-imidazoles