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Study of Buchwald-Hartwig reaction with catalysts based on monovalent copper

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Abstract

Many natural substances and drugs includes *N*-aryl-substituted heterocycles. These substances can be synthesized in various conditions, one of which is the amination of Buchwald-Hartwig. In this reaction formation of N-substituted anilines was observed as the resalt of the interaction between aryl halides and tin amides in palladium catalysis condition. It was discovered by Buchwald and Hartwig in 1994. In 1996, toxic amides of tin and P(*o*-Tol)$_3$ were replaced by amines and chelating diphosphines. Due to high yields and good reproducibility, Buchwald-Hartwig amination is the attractive method for producing aromatic amines. Currently, this amination is carried out with triphenylphosphine palladium complexes. The main drawback of these catalysts is the high cost and toxicity. In this regard, work is underway to replace these catalysts on copper containing. Currently using complexes of monovalent copper with the following chelating agents: diamines, amino acids, 1,10-phenanthroline, diols.

In this work, we studied the reaction of C-N cross-combination using a catalytic system based on a complex of monovalent copper and 1-ethylbenzimidazole. The efficiency of this catalytic system is compared with the copper – L proline system described in the literature. It is shown that the use of copper – 1-ethyl-benzimidazole system can reduce the synthesis time from forty hours to twelve. It is established that the presence of the acceptor substituent in the substrate increase the yield of the product in the Buchwald-Hartwig reaction. Indole was used as a substrate. Arylation was carried out by iodobenzene, *o*-iodotoluene and *p*-iodnitrobenzen.

References

[1] A.V. Syromolotov, A.A. Kimyashov, and S.V. Sukhorukov. Synthesis of 5-(methyl-5'indolyl-3')-indolyl-3-acetic acid. *Butlerov Communications.* **2018**. Vol.54. No.6. P.69-73. DOI: 10.37952/ROI-jbc-01/18-54-6-69
[2] A.V. Syromolotov, A.A. Kimyashov, and D.R. Khafizova. Synthesis of *N*-substituted 1-piperazinoalkylindoles. *Butlerov Communications.* **2018**. Vol.54. No.4. P.94-98. DOI: 10.37952/ROI-jbc-01/18-54-4-94
[3] E.S. Selezneva, and Z.P. Belousova. Concerning the study of genotoxicity effect of indole derivatives on *Allium cepa. Butlerov Communications.* **2016**. Vol.47. No.7. P.21-25. DOI: 10.37952/ROI-jbc-01/16-47-7-21
[4] I.V. Mikhura, A.A. Formanovsky, M.M. Rumyantseva, and G.A. Borisova. *N*-Ethylamide 3-indolcarboxylic acid derivatives. *Butlerov Communications.* **2016**. Vol.46. No.6. P.71-73. DOI: 10.37952/ROI-jbc-01/16-46-6-71
[5] A.S. Guram. Palladium-Catalyzed Aromatic Aminations with in situ Generated Aminostannanes. *J. Am. Chem. Soc.* **1994**. Vol.116. P.7901-7902.
[6] J.P. Wolfe. An improved catalyst system for aromatic carbon-nitrogen bond formation: The possible involvement of bis(phosphine) palladium complexes as key intermediates. *J. Am. Chem. Soc.* **1996**. Vol.118. P.7215-7216.
[7] Ma. Dawei, Cai. L. Qian. Proline promoted Ullmann-type coupling reactions of aryl iodides with indoles, pyrroles, imidazoles or pyrazoles. *Synlett.* **2004**. Vol.1. P.128-130