Practical Synthesis of *N*-Substituted Cyanamides as N-C-N Building Blocks for Heterocycle Synthesis

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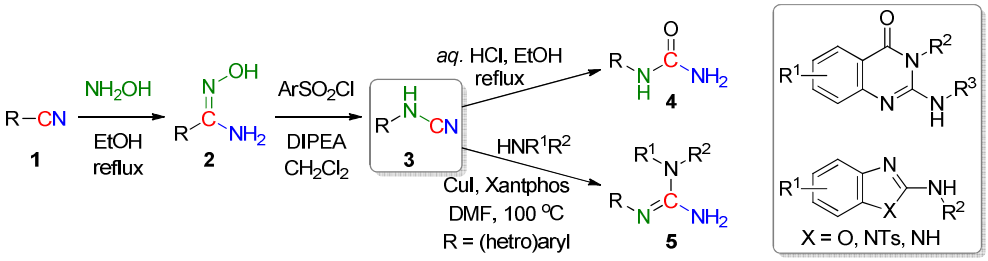
A variety of carboxamidoximes (**2**), prepared from carbonitriles with NH_2OH, could react with benzenesulfonyl chlorides (TsCl or *o*-NsCl) and DIPEA to form *N*-substituted cyanamides (**3**) in very good yields. The benzenesulfonyl chlorides promoted Tiemann rearrangement of carboxamidoximes (**2**) is readily amenable for the synthesis of a wide variety of cyanamide derivatives in multi-gram scales from carbonitriles.[1] Acidic hydrolysis of the *N*-substituted cyanamides (**3**) afforded the corresponding *N*-monosubstituted ureas (**4**) in good yields. The preparation of the *N*-monosubstituted ureas (**4**) could also be accomplished in a one-pot fashion effectively from carbonitriles (**2**) with comparable yields.[2] *N*-Alkyl-*N'*-arylguanidines (**5**) could be obtained from the reaction of *N*-arylcyanamides (**3**) with various primary and secondary alkylamines, under the catalysis of CuI and Xantphos in DMF. This methodology provides a direct access to versatile *N*,*N'*-disubstituted guanidine derivatives (**5**) from previously described *N*-arylcyanamides (**3**).[3] The application of *N*-substituted cyanamides (**3**) toward the synthesis of various heterocycles, including benzimidazoles, benzoxazoles, and quinazolinones, has also been demonstrated.



References

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