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SYNTHETIC METHODS OF CARBOXYAMIDES BY USING ISOCYANIDES

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ABSTRACT

The amide functional group is an important and ubiquitous in nature as well as synthetic organic chemicals. *N*-Aryl amides are valuable compounds that are widely present in pharmaceutically active compounds, agrochemicals, polymers, important organic functional materials and a vast number of naturally occurring and artificial molecules with biological activity [1]. In the present review gives overall scenario and opportunities amidation reactions.

Keywords: *Amidation, N-Arylation, Pharmaceutical, Catalysis.*

I. INTRODUCTION

Amide bond plays a major role in the elaboration and composition of biological systems as the backbone of proteins, i.e. to make peptide linkages in proteins. Amides are very important class of compounds in chemistry as well as in biology, which also found in the synthesis of advanced materials such as supported catalysts, fine chemicals, nylon, artificial silks, intensifiers of perfumes, colour pigments for inks, photographic products, hydrogels and biocompatible matrices for cell growth, indicators in chemical laboratories and as biological stains [2].

In past, few synthetic strategies have been developed for the preparation of amides, which can be achieved by the classical method for the synthesis of amides. It is the condensation reaction of carboxylic acids [3] or activated carboxylic acid derivatives (ester [4], acyl chloride [5], anhydride [6]) with amines or amine surrogates at high temperature and in presence of stoichiometric amount of catalyst, resulting in poor atom-efficiency and formation of a significant amount of chemical waste are major drawbacks of this approach. Subsequently other techniques also reported which includes Pd or Cu-catalyzed method using isonitrile with aryl halides or boronic acids. Some selected literature reports for amide synthesis by using isonitrile are as follows.

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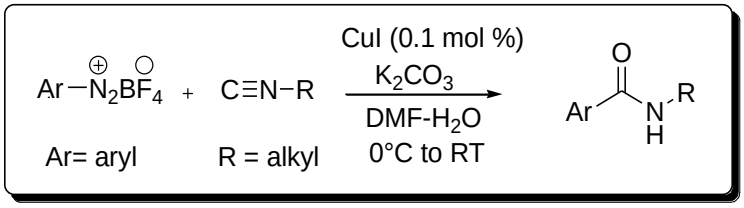
1) Y. Li *et al.* (2016) [7]

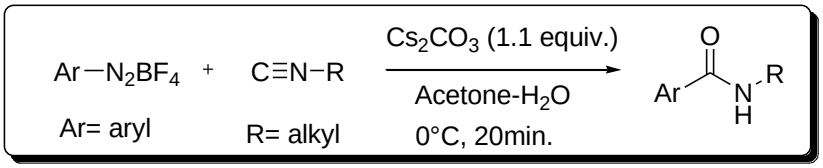
Y. Li *et al.* have reported the homogeneous copper catalysed cross-coupling reaction for preparation of arylcarboxyamides from aryl diazonium salts and isocyanides with moderate to good yield under mild conditions (**Scheme 1**).



Scheme 1

2) Z. Xia and Q. Zhu(2013) [8]

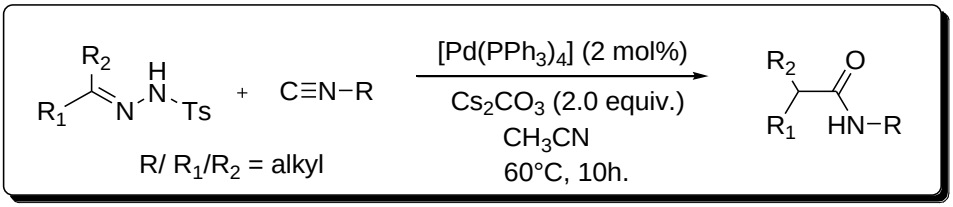
Z. Xia and Q. Zhu reported the transition metal and ligand free Cs_2CO_3 (1.1equiv.) as base catalysed amidation reaction using diazonium tetrafluoroborate and isocyanides in mixture of acetone and water under mild condition, through aryl radical intermediate initiated by base and solvent induced SET reductive dediazotisation of aryl diazonium tetrafluoroborate, provides good yields of carboxyamides (**Scheme 2**).



Scheme 2

3) F. Zhou*et al.*(2011) [9]

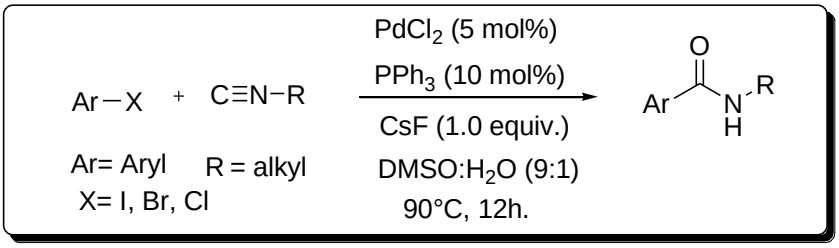
F. Zhou *et al.*have reported the new method for amidation reaction using *N*-tosylhydrazones with isocyanides via ketenimine intermediate in presence of $[Pd(PPh_3)_4]$ (2 mol%) homogeneous catalyst and Cs_2CO_3 (2.0 equiv.) as base in acetonitrile at 60°C for 10h, gave good yields (**Scheme 3**).



Scheme 3

4) H. Jiang *et al.*(2011) [10]

H. Jiang *et al.*have reported the synthesis of amide via $PdCl_2$ (5 mol%)/ PPh_3 (10mol%) as homogeneous catalysed C-C coupling of aryl halides with isocyanides in presence of CsF as base (1.0 equiv.) in DMSO:water (9:1 v/v) as solvent system at 90°C for 12h, provides good yields (**Scheme 4**).



Scheme 4

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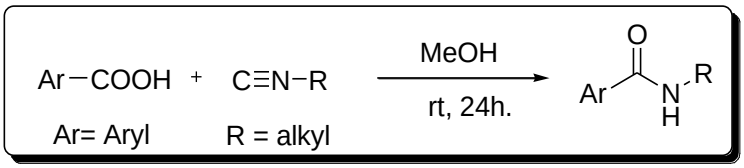
5) A. Shaabani *et al.* (2007) [11]

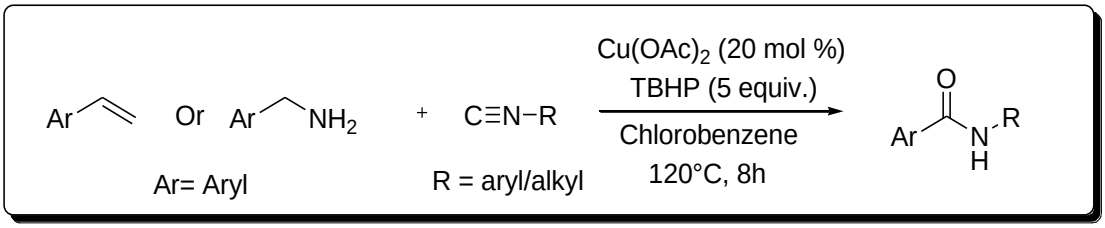
A. Shaabani *et al.*have developed the new method for the synthesis of arylcarboxyamides from carboxylic acids with isocyanides in methanol at ambient temperature to afford good yields (**Scheme 5**).



Scheme 5

6) P. Sharma and N. Jain (2018) [12]

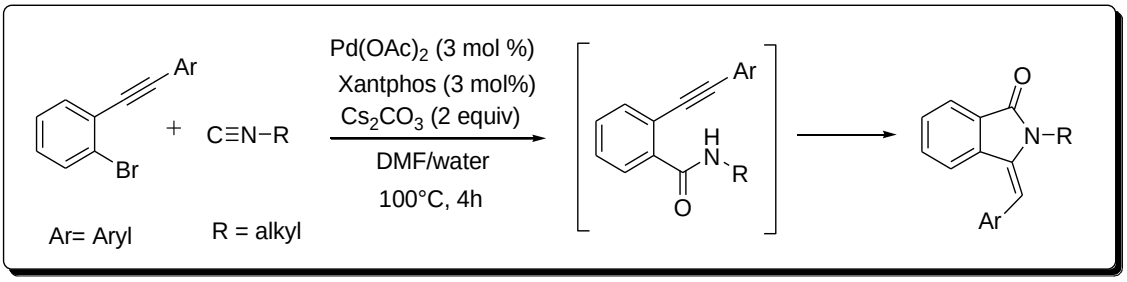
P. Sharma and N. Jain reports new method for the synthesis of *N*-aryl/alkyl substituted amides from Isocyanides coupling with styrene or benzyl amine in presence of $Cu(OAc)_2$ (20mol%) as catalyst and TBHP (5 equiv.) as oxidant in chlorobenzene at 120°C for 8h. TBHP serves as a promoter and oxygen source. Both the pathway are believed to proceed through an initial oxidative C-C bond cleavage of styrene or benzyl amine. In this method styrene or benzyl amine are used as aryl surrogate of carboxylate group (**Scheme 6**).



Scheme 6

7) R. S. Pathare *et al.* (2016) [13]

R. S. Pathare *et al*. have reports the use of isocyanide as an amide surrogate for the synthesis and isoindolin-1-one derivatives (**Scheme 7**). They exploited to generate 2-alkynylbenzamide in situ from 2-haloarylalkyens with isocyanides in presence of $Pd(OAc)_2$ (3 mol %) as catalyst, Xantphos as ligand (3mol%) with base Cs_2CO_3 (2equiv.) in DMF/H_2O at 100°C for 4h.



Scheme 7

8) X. He *et al.* (2017) [14]

X. He *et al.*have developed the new strategy for the synthesis of 2-hydroxy-6-oxocyclohex-1-ene carboxamides through a $Rh_2(OAc)_4$ (5mol%) catalyzed C-C-bond forming amidation reaction of cyclic 2-diazo-1,3-diketones with isonitrile in presence of water (3 equiv.) in acetone at 60°C for 6h gives 62-74% yield (**Scheme 8**).

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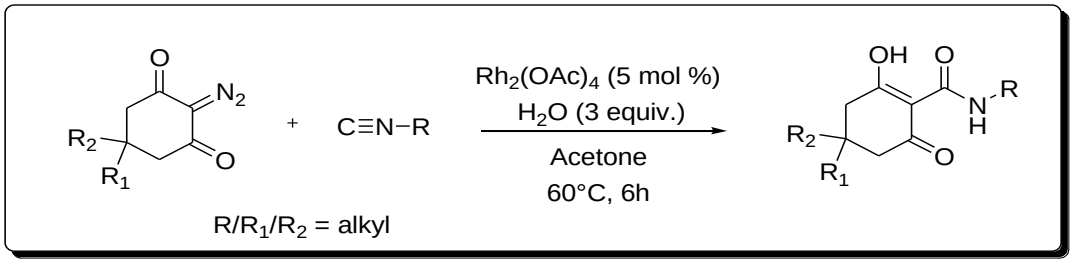
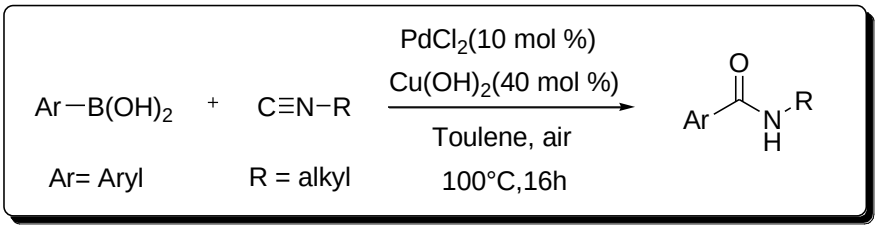


Scheme 8

9) F. Lu*et al.* (2017) [15]

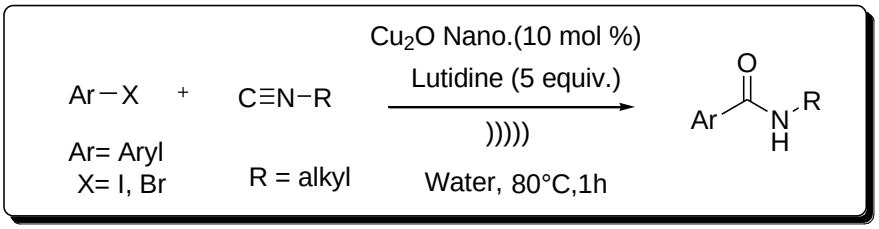
F Lu *et al.* have reports an alternative oxidative cross coupling C-C bond forming strategy for the synthesis of amides by using arylboronic acid couples with isocyanides in presence of $PdCl_2$ (10mol%) and $Cu(OH)_2$ (40mol%) without base in toulene at 100°C under air for 16h obtained in good yields (**Scheme 9**).



Scheme 9

10) S. Sarkar *et al.* (2015) [16]

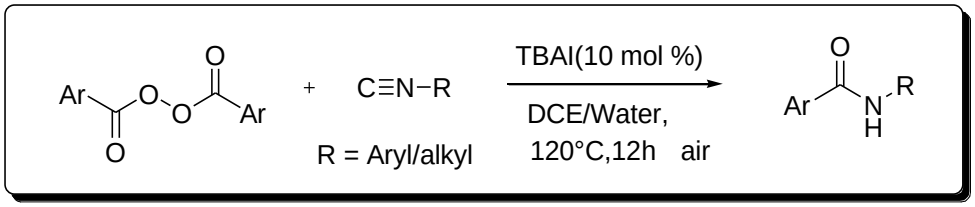
S. Sarkar *et al.*reported an ultrasound assisted Cu_2O nano catalysed C-C bond forming amidation reaction by using aryl halide coupled with isocyanide in presence of a Lutidine (5 equiv) as a base in aqueous medium under sonication at 80°C for 1h in aerobic condition to obtained good yields (**Scheme 10**).



Scheme 10

11) M. Chen *et al.* (2017) [17]

M. Chen *et al.*developed the TBAI (10 mol%) catalysed synthesis of aryl carboxyamides from acyl peroxide and isocyanides in DCE/H_2O at 120°C for 12h under aerobic condition to obtained good yields. In this study, an oxygen-centered radical addition between arylcarboxy radicals and isocyanides; finally of carbon dioxide affords to byproduct via an intramolecular rearrangement (**Scheme 11**).



Scheme 11

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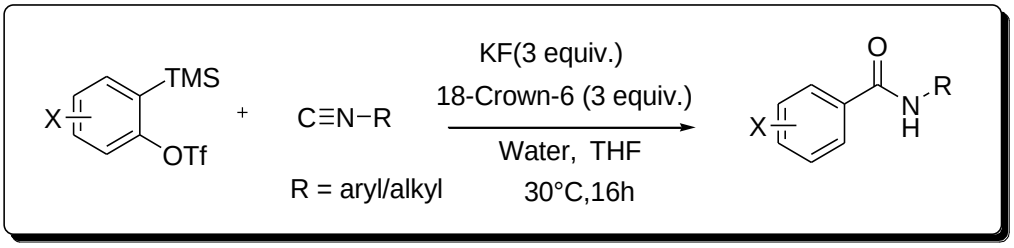
12) A. T. Biju *et al.* (2014) [18]

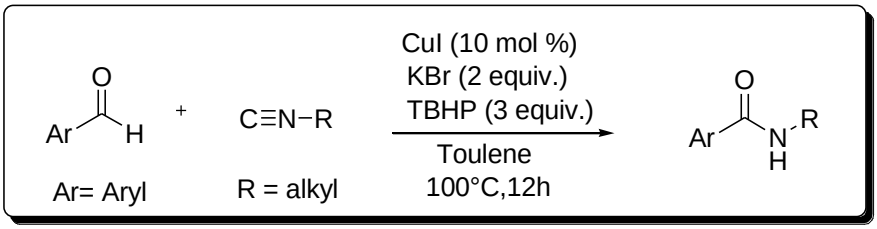
A.T. Biju *et al.*have reported the transition metal free C-C bond forming amidation reaction involving arynes and isocyanide with H_2O in presence of KF (3.0 equiv) as base and 18-crown-6 ether (3.0 equiv) in THF at 30°C for 16h resulted in the formation of aromatic amides in moderate to good yields (**Scheme 12**).



Scheme 12

13) J-Q. Liu *et al.*(2017) [19]

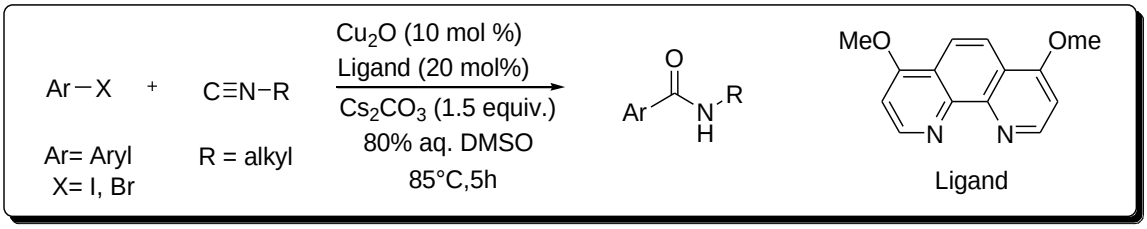
J-Q. Liu *et al.* reports a copper catalysed oxidative amidation via C-N coupling reaction of aromatic aldehyde as acid surrogate with isocyanide. The isocyano group acted as an N1 synthon rather than exhibiting the carbene-like reactivity (**Scheme 13**).



Scheme 13

14) I. Yavari *et al.* (2014) [20]

I. Yavari *et al.*have developed a Cu_2O (10 mol%) catalysed C-C cross coupling amidation reaction between aryl halide and isonitrile in presence of 4,7-dimethoxy-1,10-phenantroline (20 mol%) as ligand with Cs_2CO_3 (1.5 equiv.) in aqueous DMSO at 85°C for 5h under argon atmosphere gave the moderate to good yields (**Scheme 14**).



Scheme 14

15) B. M. Bhanageand B. J. Khairnar (2014) [21]

B. M. Bhanage and B. J. Khairnar developed a PS-Pd-NHC (1mol%) catalysed C-C cross coupling reaction between aryl halide and isonitrile in the presence of base CsF (1.0 equiv.) in DMSO/H_2O at 90°C for 9h gave the good yields of corresponding amides (**Scheme 15**).

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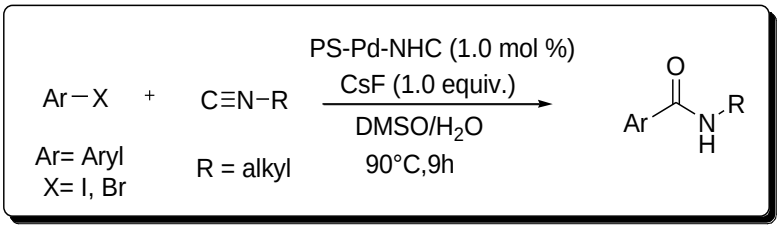

Scheme 15

II. CONCLUSION

In this review was emphasized the chemistry, which deals with synthetic applications of amide products and various methods from it could be synthesized and used as precursor in organic synthesis.

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