

CHAPTER- II

Synthesis of Nitriles from Aldehydes and Hydroxylamine hydrochloride on silica-gel

CHAPTER- II

SECTION-A

II . A. A brief review on nitriles, synthesis and its applications

II . A.1. Nitrile

A nitrile is an organic compound which has a $-CN$ functional group. Prefix cyano- is used interchangeably with the term nitrile in industrial literature. Organic compounds containing multiple $-CN$ groups are known as cyanocarbons. Inorganic compounds containing $-CN$ group are not called nitriles, rather cyanides. In spite of the same origin of cyanides and nitriles from cyanide salts, nitriles are generally non toxic. Nitriles include many useful compounds. Milrinone (**fig. II .A.1.**), marketed as Primacor, is a nitrile, acts as phosphodiesterase inhibitor used for treating heart failure .¹

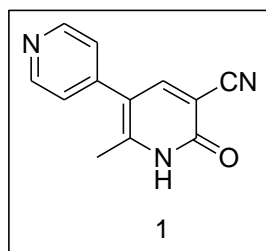


Fig. II .A.1. Milrinone

Methyl cyanoacrylate is a nitrile containing compound, used in super glue and nitrile rubber, a polymer used in laboratory and medical gloves. Nitrile rubber is resistant to fuels and oils, therefore it is used as automotive and other seals. It is also used in the nuclear industry as a protective gloves. Nitrile butadiene rubber is used to make footwear, moulded goods, sponges, sealants and floor mats.

II .A.2. Natural occurrence of organo nitriles

Nitriles occur naturally in a diverse set of plant and animal sources. Certain seeds and fruit stones, e.g., apricots, apples and peaches, contains cyanides. Cyanides usually bound to sugar molecules to form cyanogenic glycosides² in plants. Nitriles are commonly encountered in fruit pits, especially almonds, and cabbage, cauliflower, during cooking, release nitriles through

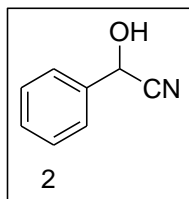


Fig. II .A.2. Mandelonitrile

hydrolysis. Mandelonitrile (**fig. II .A.2.**), a cyanohydrin produced by ingesting almond or some other fruit pits, releases hydrogen cyanide, which is responsible for toxicity of cyanogenic glycosides.³

II .A.3. Structure of nitriles

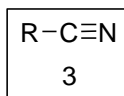


Fig. II .A.3. Structure of nitrile

The geometry of N-C-C is linear in nitriles, which is the characteristic of sp hybridization of the triply bonded carbon. The C-N distance is short (1.16 Å⁰), consistent with a triple bond. Nitriles are polar, as indicated by high dipole moments.

II .A.4. Discovery of organo nitriles

The first compound of nitriles, the nitrile of formic acid, hydrogen cyanide was first prepared by C.W. Scheele in 1782. In 1811, J.L. Gay-Lussac prepared the very toxic and volatile pure acid. In 1832, the nitrile of benzoic acid, benzonitrile, was synthesized by Friedrich Wöhler and Justus Von Liebig, but the yield was poor and due to this reason, physical or chemical properties was not determined. Theophile-Jules Pelouze synthesized propionitrile in 1834, that was believed to be an ether of propionic alcohol and hydrocyanic acid. In 1844, Hermann Fehling prepared benzonitrile by heating ammonium benzoate in a method yielding sufficient quantity for chemical research. Fehling determined the structure of nitrile by comparing the structure of already known synthesis of hydrogen cyanide from heating ammonium formate to his result. He introduced the name “nitrile ” for this group of compound.

II .A.5. Biological importance of nitriles

Nitriles are a class of compounds having important pharmaceutical and biological role. More than 30 nitrile-containing pharmaceuticals are used for medicinal purpose with more than 20 additional nitrile-containing pharmaceutical leads in clinical development. Vildagliptin (4) , an aminonitrile, is used as an antidiabetic drug, where nitrile bearing carbon is not fully substituted.⁴ Pericyazine (5) is an antipsychotic drug, believed to act on several receptors in brain. It is widely used to minimize withdrawal symptoms after drug addiction.⁵ Ripivirine (6) is the most potent anti-HIV agent out of many entravirine analogs.⁶ Drug anastrozole (7) under trade name Arimidex, marketed by Astra-Zeneca, is used as a drug of choice for treating oestrogen dependent breast cancer.⁷

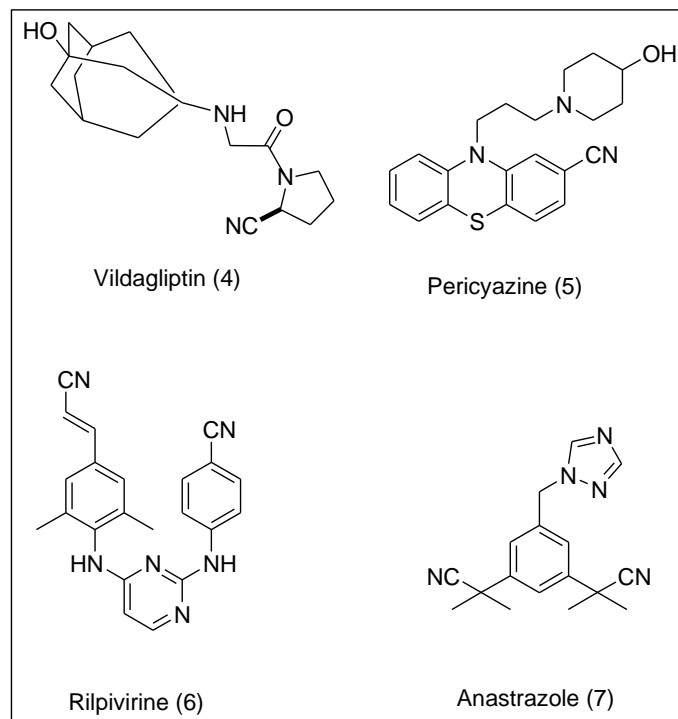
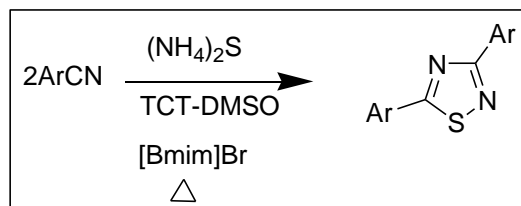


Fig. II .A.4. Some biologically important nitrile drugs

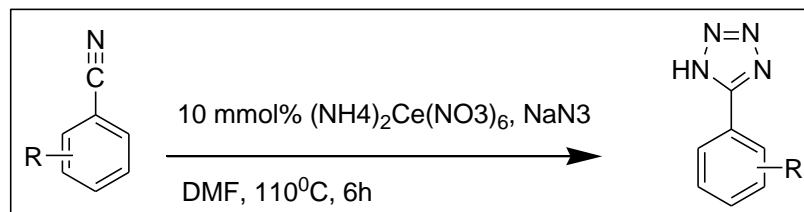
II .A.6. Application of nitriles in organic synthesis

Nitriles are important precursor for the synthesis of several nitrogen containing heterocyclic compounds, such as AgNO_3 catalyzed synthesis of 5-substituted-1H-tetrazole via [3+2] cycloaddition from the reaction of nitriles with sodium azide.⁸ Synthesis of 2-substituted pyrrolidines from nitriles.⁹ Synthesis of 3, 5-diaryl-1, 2, 4-thiadiazoles from aryl nitriles in 1-butyl-3-methylimidazolium bromide promoted by $(\text{NH}_4)_2\text{S}^{10}$ (**Scheme. II .A.1**), Substituted pyridine derivatives are synthesized from two different alkynes and a nitrile using zirconocene and nickel complexes by Tamotsu Takahashi et.al.¹¹ One-pot synthesis of pyrimidine derivatives.¹²

$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ catalyzed synthesis of 5-substituted -1H- tetrazoles from nitriles¹³
(Scheme. II .A.2.)

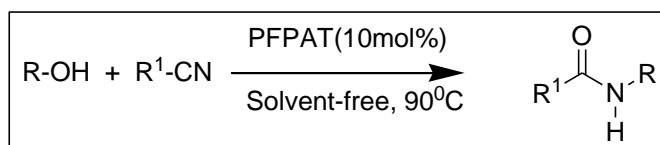


Scheme. II .A.1. Synthesis of 3, 5-diaryl-1, 2, 4-thiadiazoles from aryl nitriles



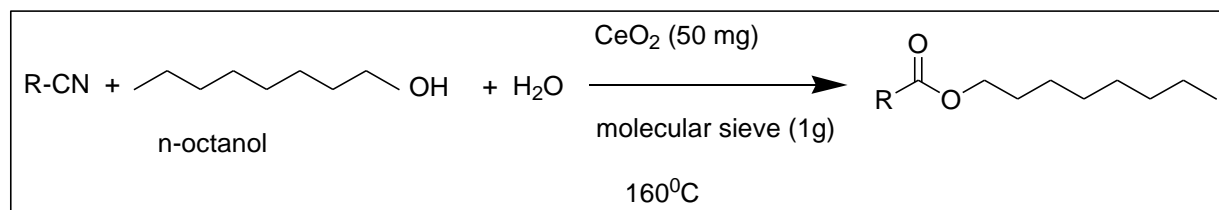
Scheme. II .A.2. Reaction of benzonitrile with sodium azide in DMF

Nitriles are also important for functional group transformation from nitriles to another groups and in the synthesis of many important reagents. e.g. synthesis of amides from nitriles via the Ritter reaction¹⁴ **(Scheme. II .A.3),**



Scheme. II .A.3. Synthesis of amides from nitriles

Masazumi Tamura et.al. synthesized esters from nitriles from the reaction of CeO₂ catalyzed reaction of nitriles with alcohol,¹⁵ (**Scheme. II .A.4**)

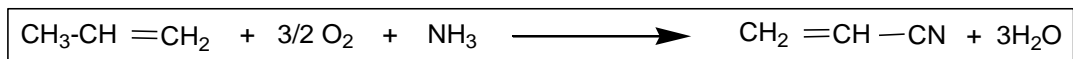


Scheme. II .A.4. Synthesis of esters from nitriles

II .A.7. Classical method for the synthesis of nitriles

II .A.7.1. Ammoxidation

In ammoxidation reaction, a hydrocarbon is partially oxidized in presence of ammonia. Large scale preparation of acrylonitrile is achieved by this process. A side product, acetonitrile is formed during the production of acrylonitrile. Several nitriles are produced by ammoxidation. This process is catalyzed by metal oxides and proceed through imine.¹⁶

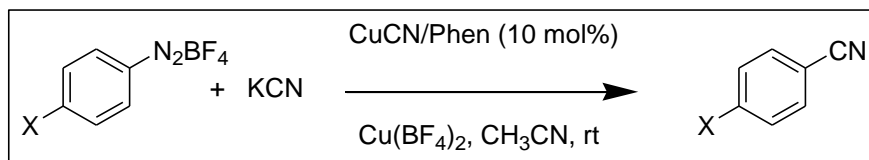


Scheme. II .A.5. Synthesis of acrylonitrile from propene

II .A.7.2. Sandmeyer reaction

Aromatic nitriles are often prepared from aniline via diazonium compounds. In this reaction, diazonium salt reacts with cuprous cyanide to produce aryl nitrile. Cu(I)/Cu(II) catalyzed synthesis of aryl nitriles from aryl diazonium salts by KCN was reported by I.P. Beletskaya

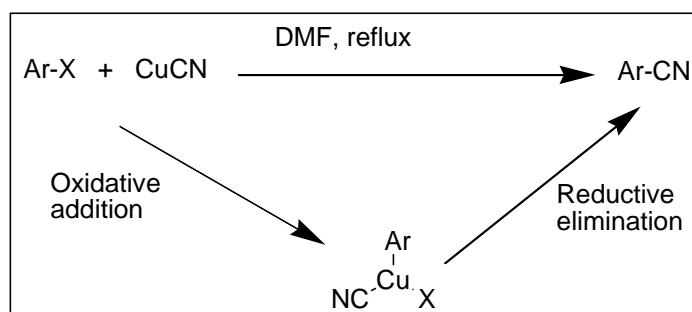
et.al.¹⁷(**Scheme. II .A.6.**). Since inorganic cyanides are used in Sandmeyer reaction, the toxicity of reagent makes Sandmeyer reaction less acceptable for nitrile preparation.



Scheme. II .A.6. Synthesis of nitrile from aryl diazonium salt and KCN by Cu catalyst

II .A.7.3. Rosenmund- Von Braun reaction

Preparation of aryl nitriles by nucleophilic substitution of aryl halides with excess copper (I) cyanide in polar and high-boiling solvents such as, nitrobenzene, DMF and pyridine at reflux condition is known as Rosenmund- Von Braun reaction.¹⁸ The mechanism involves the formation of Cu(III) entity by oxidative addition of aryl halide followed by reductive elimination give rise to the formation of product (**Scheme. II .A.7.**)



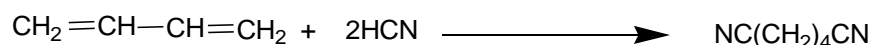
Scheme. II .A.7. Synthesis of nitrile from aryl halide and CuCN

Aryl bromides requires drastic conditions(150-280) in this reaction, which is not suitable for sensitive compounds. Besides this, there is few limitation of Rosenmund-Von Braun reaction, e.g. copper(I) cyanide used in this reaction is not easily separable from the product nitrile, the polar, high-boiling solvent, high temperature and excess amount of copper cyanide, which makes waste disposal problem, makes Rosenmund-Von Braun reaction less applicable.

II .A.7.4. Hydrocyanation

Hydrocyanation¹⁹ is an industrial process for the synthesis of nitriles from the reaction of hydrogen cyanide and alkenes. The process requires homogeneous catalyst. Transition-metal catalyzed addition of hydrogen cyanide across double or triple bonds occur in a Markownicov or anti-Markownicov fashion providing saturated or vinyl nitriles. Generally nickel(0) and palladium(0) complexes are used as a catalyst for hydrocyanation. Nickel-catalyzed hydrocyanation for the production of adiponitrile (1, 4-dicyanobutane) is a precursor of nylon-6,6 from 1, 3-butadiene

(**Scheme. II .A.8.**)

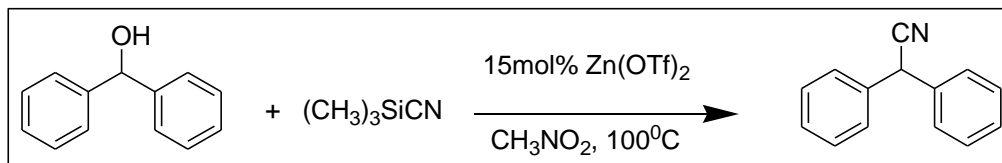


Scheme. II .A.8. Synthesis of adiponitrile from 1, 3-butadiene

II .A.8. Modern methods for the synthesis of nitriles from different functional groups

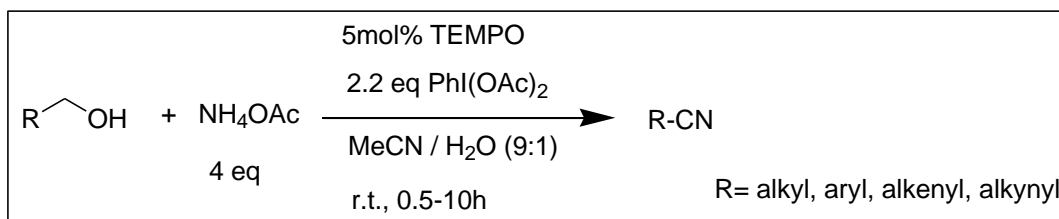
II .A.8.1. Synthesis of nitriles from alcohols

P. Theerthagiri and A. Lalitha synthesized α -aryl nitriles from benzylic alcohols directly by $\text{Zn}(\text{OTf})_2$ as catalyst²⁰ (Scheme. II .A.9). But this process involves increase in one carbon atom.



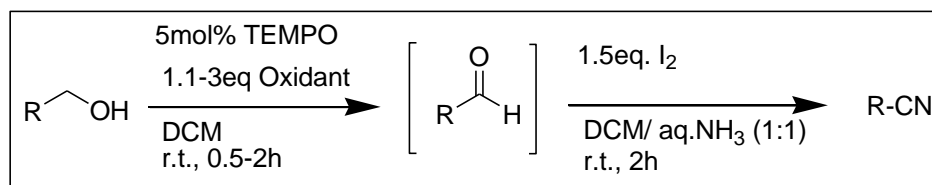
Scheme. II .A.9. Synthesis of benzylic alcohol to α -nitrile

J.M.Vatele explored a direct transformation²¹ of a wide range of aliphatic, heteroaromatic, benzylic, allylic and propargyl alcohols to nitriles with 2,2,6,6-tetramethyl piperidine-1-oxyl (TEMPO), iodosobenzene diacetate and ammonium acetate, used as a nitrogen source. The reaction proceeds through an oxidation-imination-aldehyde oxidation sequence in situ. High chemoselectivity of ammoxidation of primary alcohols in presence of secondary alcohols was also achieved (**Scheme. II .A.10.**).



Scheme. II .A.10. Direct synthesis of nitriles from alcohols by TEMPO

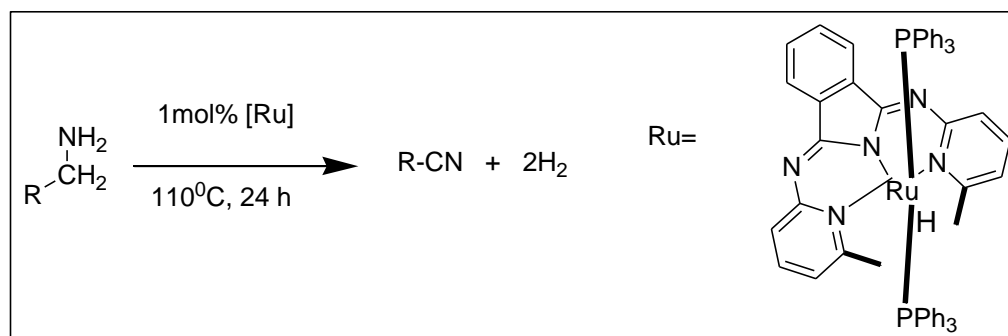
H. Shimojo et.al.²² synthesized nitriles very efficiently from various alcohol at room temperature. The reaction was catalyzed by tert-butyl hypochlorite, diiodine, or 1, 3-diiodo-5, 5-dimethylhydantoin (DIH) in the presence of TEMPO and then treated with diiodine and aqueous ammonia. The reaction mixture was extracted with chloroform and solvent was removed later. The yield and purity of nitrile was excellent (**Scheme. II .A.11.**)



Scheme. II .A.11. Synthesis of nitriles from alcohols by DIH

II .A.8.2. Synthesis of nitriles from primary amine

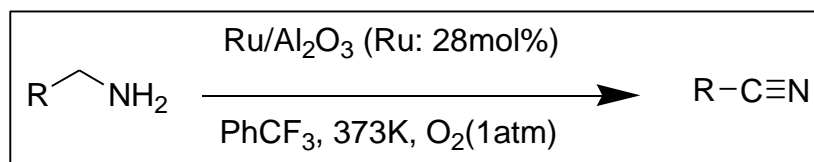
K. N.T.Tseng et. al.²³ explored oxidant-free transformation of primary amines to nitriles. The reaction involves chemoselective dehydrogenation of primary and secondary amines to the corresponding nitriles and imines by an amide-derived NNN-Ru(II) hydride complex catalyzed reaction, which is oxidant-free and acceptorless. The reaction is accompanied with liberation of dihydrogen. The reaction is oxidizable functional group tolerant and only primary amines ($-\text{CH}_2\text{NH}_2$) is susceptible to this reaction in presence of amines without α -CH hydrogens. (**Scheme. II .A.12.**)



Scheme. II .A.12. Synthesis of oxidant-free nitriles from primary amines

Noritaka Mizuno et.al.²⁴ synthesized nitriles from primary amines by direct oxidation of amines. They used heterogeneous catalyst Ru/ Al_2O_3 (1.4 wt % of Ru) for the oxidation of amines (activated

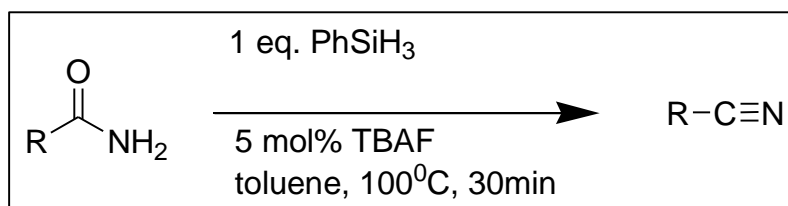
as well as non-activated amines) into the corresponding nitriles with air or 1 atm dioxygen in trifluoro toluene as solvent. (**Scheme. II .A.13.**)



Scheme. II .A.13. Oxidative transformation of primary amine to nitriles by Ru/Al₂O₃ catalyst

II .A.8.3. Synthesis of nitriles from amides

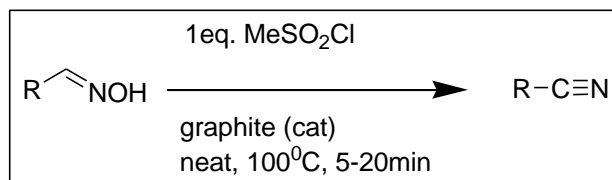
S. Zhou et.al.²⁵ introduced a convenient protocol for the synthesis of nitriles by catalytic dehydration of aromatic and aliphatic amides using silanes in presence of fluoride (catalytic amount). This protocol allows synthesis of the wide range of aromatic and aliphatic nitriles under mild condition with high selectivity (**Scheme. II .A.14.**)



Scheme. II .A.14. Synthesis of nitriles from amides using silanes

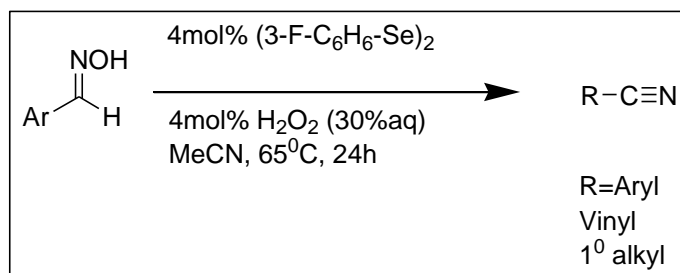
II .A.8.4. Synthesis of nitriles from oximes

H.Shargi et.al.²⁶ synthesized nitriles from oximes by heating with MeSO₂Cl, catalyzed by graphite under neat reaction condition at short time (**Scheme. II .A.15.**)



Scheme. II .A.15. Synthesis of nitriles from oximes under neat condition

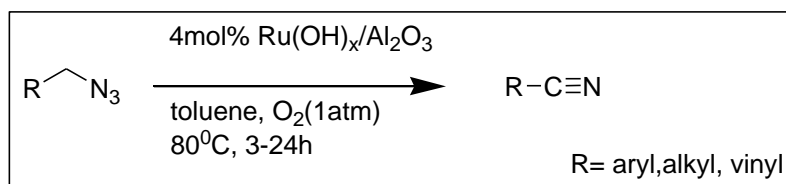
L.Yu.et.al.²⁷ synthesized nitriles by dehydration of aldoximes by Areneselenenic acids (ArSeOH), which is readily formed from diaryl diselenides and H₂O₂ by oxidation in situ. The catalyst is efficient and recyclable (**Scheme. II .A.16.**)



Scheme. II .A.16. Synthesis of nitriles from oximes

II .A.8.5. Synthesis of nitriles from azides

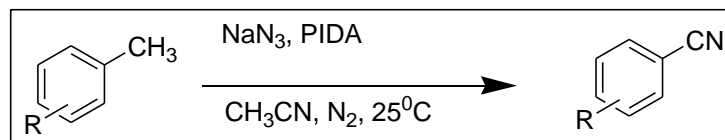
In this methodology, nitriles are prepared from various primary azides, e.g. benzylic, aliphatic, allylic azides by an easily prepared and supported ruthenium hydroxide, Ru(OH)_x/Al₂O₃ catalyst into the corresponding nitriles in excellent yields. (**Scheme. II .A.17.**)²⁸



Scheme. II .A.17. Synthesis of nitriles from azides by Ru(OH)_x/Al₂O₃ catalyst

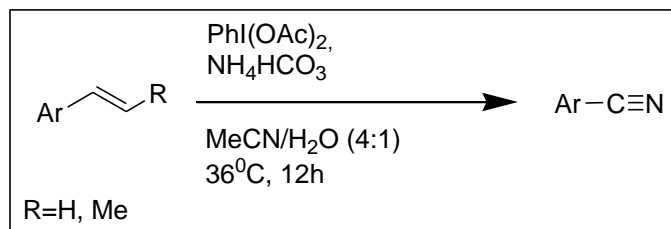
II .A.8.6. Synthesis of nitriles from alkenes, alkynes, methyl arenes and benzyl or allyl halides

The direct transformation of alkenes, alkynes, methyl arenes, allyl or benzyl halides are well known in literature. But elongation of one carbon atom takes place in parent compound in these cases. Ning Jiao et.al.²⁹ reported direct transformation of methyl arenes to aryl nitriles at ambient temperature. In this reaction, they used NaN₃, PIDA, CuSO₄, 5H₂O in acetonitrile at room temperature (**Scheme. II .A.18.**)



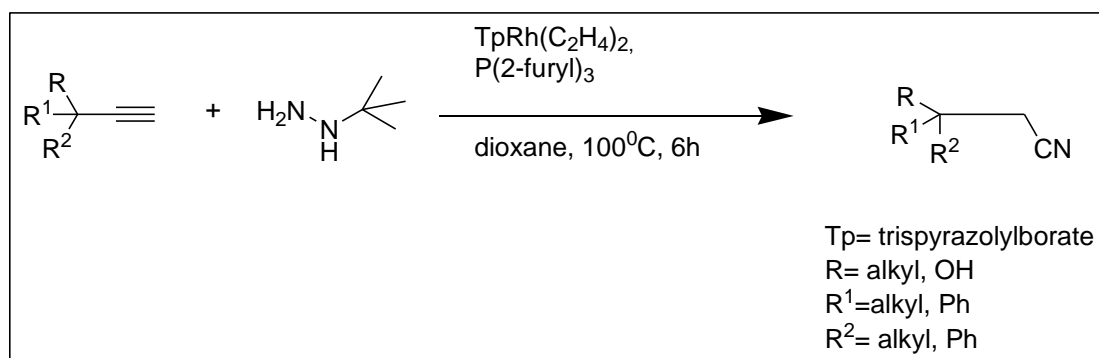
Scheme. II .A.18. Synthesis of aryl nitriles from methyl arenes

Synthesis of nitriles from alkenes by metal-free PhI(OAc)₂ mediated nitrogenation of alkenes is reported. The reaction proceeds through C=C bond cleavage where inorganic ammonia salt act as a nitrogen source. The reaction is mild which affords nitriles in excellent yield. (**Scheme. II .A.19.**)³⁰



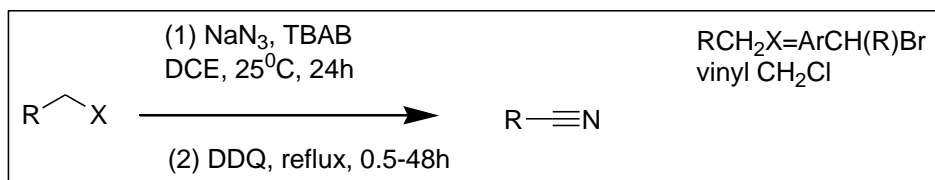
Scheme. II .A.19. Synthesis of nitriles from alkenes

Y.Fukumoto et.al.³¹ (2016) reported that the combination of $\text{TpRh}(\text{C}_2\text{H}_4)_2$ and $\text{P}(2\text{-furyl})_3$ catalyzes the reaction of tertiary alkyl-substituted alkynes with tert-butylhydrazine resulting in the formation of 3, 3, 3-trisubstituted propionitrile derivatives (**Scheme. II .A.20.**)



Scheme. II .A.20. Synthesis of nitriles from alkynes

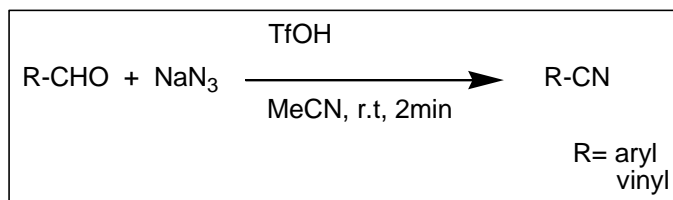
W.Zhou et.al.³² reported synthesis of aryl or alkenyl nitriles from allyl or benzyl halides by a tandem TBAB- catalyzed substitution followed by novel oxidative rearrangement. The mild reaction condition and broad reaction scope make this method useful in organic synthesis. (**Scheme. II .A.21.**)



Scheme. II .A.21. Synthesis of nitriles from allyl or benzyl halides

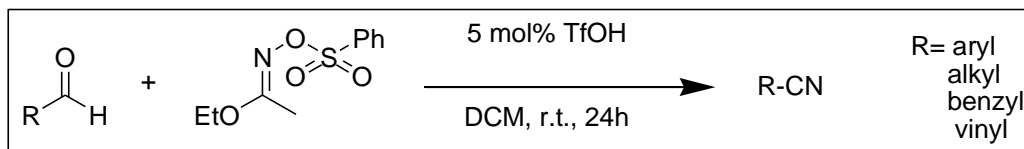
II .A.8.7. Synthesis of nitriles from aldehydes

B.V. Rokade et.al.³³ reported Schmidt reaction for the synthesis of nitriles from aldehydes with NaN_3 in near quantitative yield in presence of TfOH and the reaction shows several electron-donating as well as electron-withdrawing functional group tolerance. The reaction is nearly instantaneous (**Scheme. II .A.22.**)



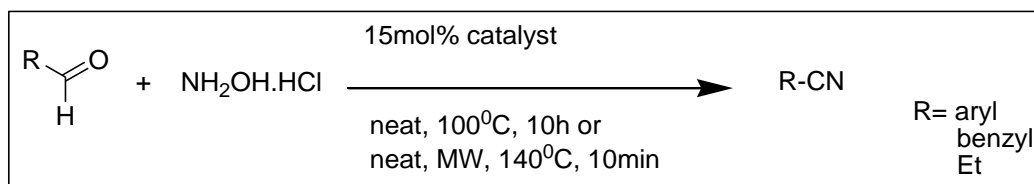
Scheme. II .A.22. Synthesis of nitriles from aldehydes by NaN_3

K. Hyodo et.al.³⁴ (2017) used an O-protected oxime rather than explosive O-protected hydroxylamine for the synthesis of nitriles with a safe Bronsted acid –catalyst via O-protected aldoximes through transoximation (**Scheme. II .A.23.**)



Scheme. II .A.23. Synthesis of nitriles from aldehydes through transoximation

U.B.Patil et.al.³⁵ (2013), Synthesized nitriles from aldehydes by an eutectic mixture of choline chloride and urea (1:2) mixture as an efficient and ecofriendly catalyst for this transformation under solvent-free condition. The reaction was carried out under neat and microwave irradiation. The yield was reported to be good to excellent (**Scheme. II .A.24.**)

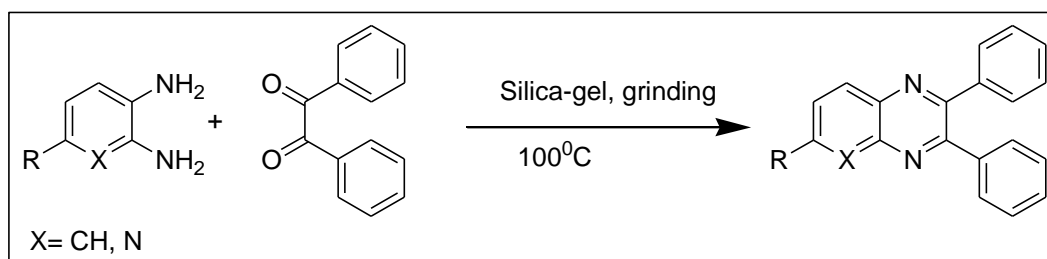


Scheme. II .A.24. Synthesis of nitriles from aldehydes by choline chloride and urea mixture (1:2)

II .A.9. Application of silica-gel in organic transformations

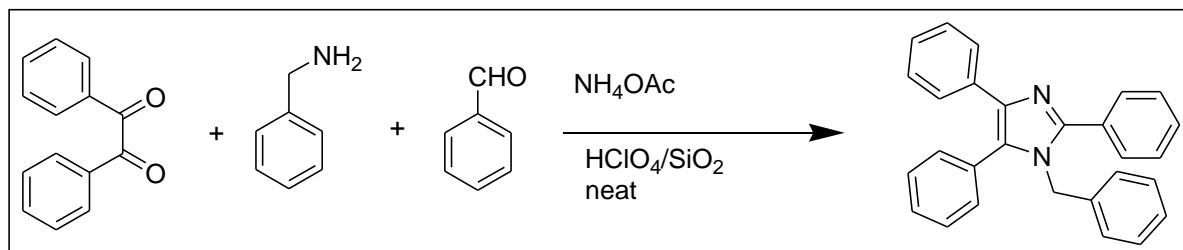
In recent days, solvent-free synthesis have attracted the attention of chemist because the process is environmentally benign. Silica-gel has been effectively used in organic synthesis not only as a simple medium but also as a mild acid catalyst or as an accelerator. It is easily separable from the reaction mixture because of its insolubility in organic solvents. Previously silica-gel has been widely used in many reactions such as – Selective allylation of aldehyde with tetrabutyltin,³⁶ Selective C-S bond formation, etc. Silica-gel supported catalysts such as SiO₂/FeCl₃; SiO₂/NaHSO₄; SiO₂/BF₃ and

$\text{SiO}_2/\text{H}_2\text{SO}_4$ ³⁷ have also been used widely in several organic transformation. It is less expensive, ecofriendly and easily available and can easily be separated from reaction mixture. G.C. Nandi et.al.³⁸ synthesized quinoxaline derivatives from 1, 2-diketones and 1, 2-diamines under solvent-free condition, catalyzed by silica-gel (**Scheme. II .A.25.**)



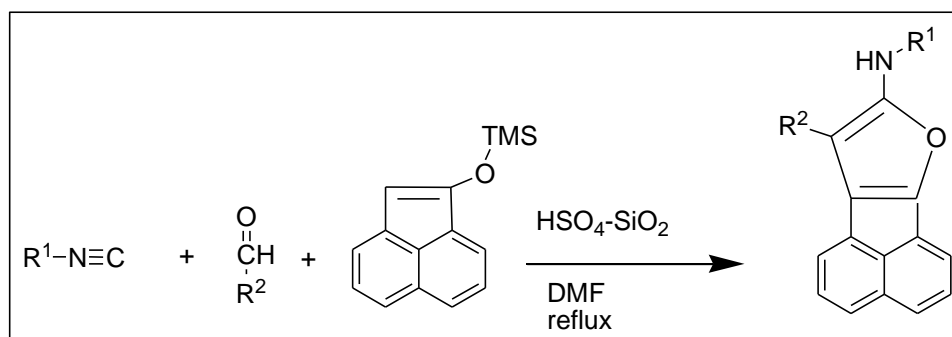
Scheme. II .A.25. Synthesis of quinoxalines from benzil with 1, 2-diamine

Kantevary et.al.³⁹ explored one-pot , highly efficient, four-component synthesis of 1, 2, 4, 5-tetrasubstituted imidazoles from the condensation of diverse aldehydes, benzil, aromatic or aliphatic primary amines and ammonium acetate, catalyzed by perchloric acid adsorbed on silica-gel ($\text{HClO}_4\text{-SiO}_2$) as catalyst under solvent-free condition. The yield was reported to be excellent and $\text{HClO}_4\text{-SiO}_2$ exhibited remarkable catalytic activity regarding reaction time (2-20min) and amount of catalyst (**Scheme. II .A.26**)



Scheme. II .A.26. Synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by $\text{HClO}_4\text{-SiO}_2$

Cycloaddition reaction of various aldehydes, isocyanides with (acenaphthylen-1-yloxy) trimethylsilane into acenaphtho [1, 2-b]furan derivatives was catalyzed by silica-supported ionic liquid. Sandaroos et.al⁴⁰ reported this one-pot transformation (**Scheme. II .A.27.**)



Scheme. II .A.27. Synthesis of acenaphtho [1,2-b] furan derivatives by silica-supported ionic liquid

II .A.10. Conclusion

Nitriles are important bio-active compounds. Besides this, nitriles are useful organic intermediate for the functional group transformations give rise to several nitrogen containing heterocyclic compounds. A lot of catalytic system are reported in literature for the synthesis of nitrile intermediate from different functional group. But most of the methodologies in literature suffer from a few drawbacks e.g. long reaction time, lack of straight-forward process, use and generation of hazardous side-product, tedious work-up process , use of strong oxidizing agents and use of expensive catalyst. Therefore, author explored an easy, low-cost and straight forward protocol by the use of less expensive and environmental friendly reagents for the one-pot synthesis of nitriles.

II .A.11. Reference

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