Review Article

Chemical Review and Letters
journal homepage: www.chemrevlett.com
ISSN (online): 2645-4947 (print) 2676-7279

Decarboxylative Cyanation and Azidation of Carboxylic Acids: An Overview

Evan Abdulkareem Mahmood [a], Bayan Azizi [a], Soma Majedi [a, *]

[a] *College of Health Sciences, University of Human Development, Sulaimaniyah, Kurdistan region of Iraq*
soma.majedi@uhd.edu.iq

ARTICLE INFO

Article history:
Received 30 December 2019
Received in revised form 23 January 2020
Accepted 13 February 2020
Available online 16 February 2020

Keywords:
Decarboxylative functionalization
Carboxylic acids
Organic nitriles
Organic azides
Single electron transfer

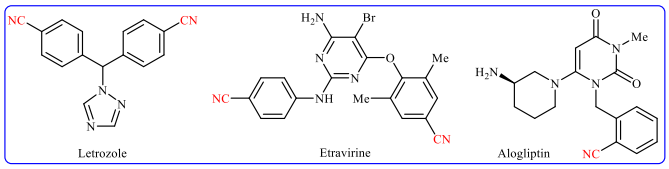
ABSTRACT

The present review gives an overview over the synthesis of organic nitriles and azides through the decarboxylative cyanation and azidation of carboxylic acids, respectively. Mechanistic features of the reactions are considered and discussed in detail.

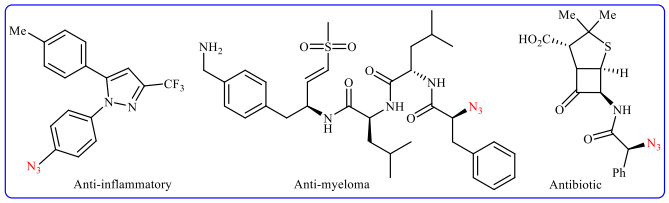
1. Introduction

Nitriles, or organic cyanides, are among the most important class of organic compounds that are widely found in natural products, pharmaceuticals, agrochemicals, herbicides, and dyes [1]. Moreover, they serve as versatile synthetic intermediates for the preparation of a number of value-added fine chemicals including amines, amides, aldehydes, ketones, carboxylic acids, and 1,2,3-triazole derivatives [2]. Interestingly, more than 30 currently marketed pharmaceuticals contain at least one cyano group in their structure (Scheme 1), while 20 more are in clinical trials [3]. In a similar way, organic azides are not only versatile intermediates in synthetic organic chemistry but are also of considerable industrial importance as plasticizers and high-energy materials [4]. Overall, compounds bearing this versatile functional group exhibit many kinds of biological activities (Scheme 2), such as antibiotic, anti-HIV, anti-inflammatory, and anti-myeloma activities [5]. Due to the wide importance of titled compounds in organic and medicinal chemistry, development of novel, practical, and truly efficient methods for their preparation is highly desirable.

Decarboxylative functionalization of carboxylic acids has recently received considerable attention as a novel and efficient method to construction of carbon-carbon and carbon-heteroatom bonds [6]. These reactions has several advantages [7]. Such as: (i) carboxylic acids are inexpensive and readily available reactants in great structural diversity. (ii) Decarboxylation can provides the reactive intermediates under neutral conditions, thus these reactions often show good tolerance to many sensitive functional groups. (iii) The only stoichiometric amount of by-product is carbon dioxide (CO_2), which is nonflammable, nontoxic, chemically inert and easily removed from the reaction medium.



Scheme 1. Selected examples of drugs bearing cyano group(s)



Scheme 2. Selected examples of biologically active organoazides

In contrast to well-documented formation of C-C and C-N bonds *via* decarboxylative coupling of carboxylic acids with various *C*-containing and *N*-containing reagents, respectively, decarboxylative functionalization of carboxylic acids into nitriles and azides has been almost untouched. In connection with our recent review articles on the fabrication of new C-C and C-X bonds through decarboxylative cross-coupling reactions [8], herein, we will highlight the most important advances

* Corresponding author. e-mail: soma.majedi@uhd.edu.iq

on the decarboxylative cyanation and azidation of carboxylic acids (Figure 1), by hoping that it will stimulate researchers to further thinking and research in these hot research topics.

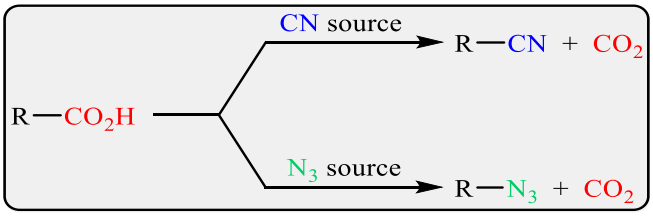


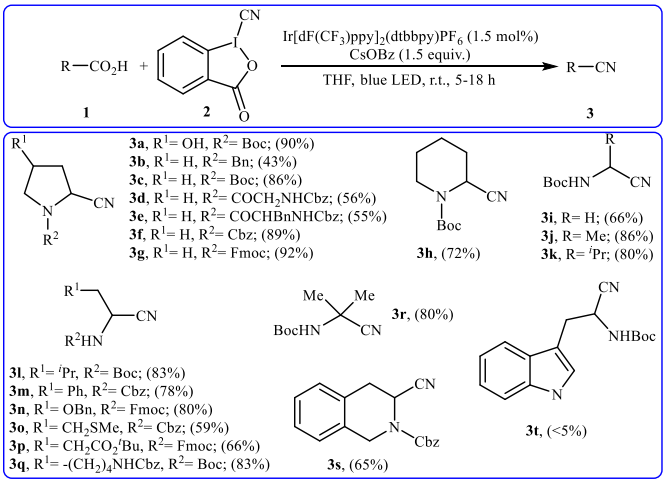
Figure 1. Decarboxylative cyanation and azidation of carboxylic acids

2. Decarboxylative cyanation of carboxylic acids

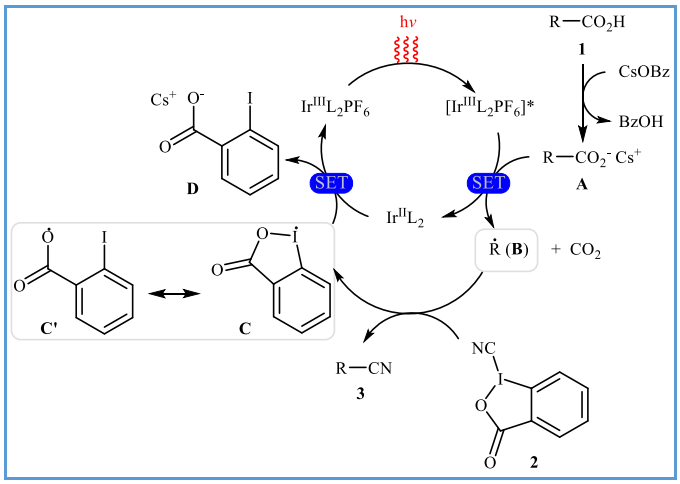
In the present section, we describe the available literature on the synthesis of organocyanide compounds through the decarboxylative cyanation of the corresponding carboxylic acids. The section is divided into two major sub-sections. The first will cover the decarboxylative cyanation of aliphatic carboxylic acids, while the second will discuss decarboxylative cyanation of aromatic carboxylic acids.

2.1. Aliphatic carboxylic acids

After pioneering work by Klein in 1971 on the synthesis of nitroalkanes from the corresponding carboxylic acids based on the acid−nitrile exchange reaction with 2-methylglutaronitrile (CNCH2CH2CHMeCN) [9]. Several research group utilized this procedure in the fabrication of various alkyl nitriles under both batch and continuous-flow conditions [10, 11]. However, all of the reported examples on this chemistry have been performed at evaluated temperatures. With the aim of designing a milder procedure to aliphatic nitriles from the respective carboxylic acids, Barton and colleagues have developed a two-step approach, which consists of conversion of carboxylic acids to the corresponding *N*-hydroxypyridine-2-thione esters synthesis and visible light promoted decarboxylative cyanation with *p*-toluenesulphonyl cyanide or methanesulfonyl cyanide [12]. The main drawback of this methodology is the requirement for an additional step for pre-functionalization of start materials, which may limit its range of application. In 2016, Waser and co-workers described the synthesis of a wide range of nitroalkanes **3** *via* photoredox-catalyzed direct decarboxylative cyanation of aliphatic carboxylic acids **1** using cyanobenziodoxolone **2** as a commercially available cyanating agent and Ir[dF(CF3)ppy]2(dtbbpy)PF6 as a photoredox catalyst [13]. The reactions were run at room temperature, tolerated various natural and non-natural α-amino and α-oxy acids, and provided the target nitroalkanes in moderate to excellent yields (Scheme 3). However, tryptophan derivatives and substrates bearing a sulfur atom in the β position failed to participate in this one-pot conversion. Interestingly, the methodology could also be scaled up to 1 mmol using only 0.1 mol% of catalyst, with a slight decrease of yield. According to a series of mechanistic studies, the authors proposed that this transformation proceeds by a single-electron transfer pathway (Scheme 4). Shortly afterwards, this catalytic system was successfully applied in the decarboxylative alkynylation of various aliphatic carboxylic acids by the same research group [14].

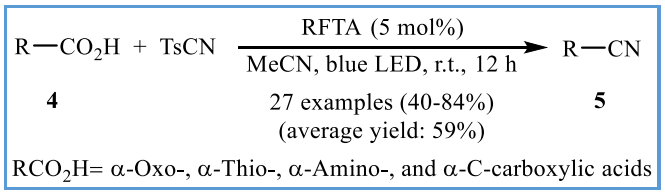


Scheme 3. Waser's synthesis of nitroalkanes **3**



Scheme 4. Proposed mechanism for the formation of nitroalkanes **3** *via* photoredox-catalyzed decarboxylative cyanation of aliphatic carboxylic acids **1**

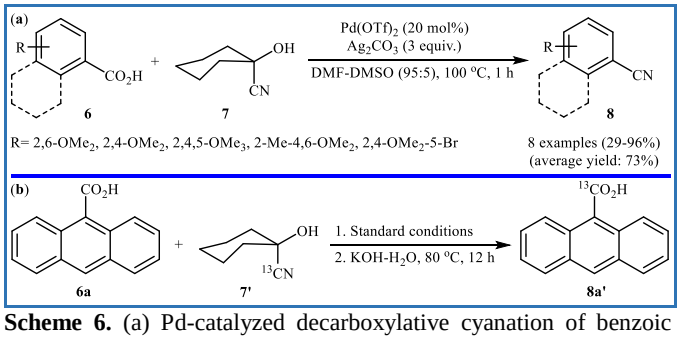
Very recently, the group of Gomez studied the similar decarboxylative cyanation of aliphatic carboxylic acids **4** using tosyl cyanide (TsCN) as cyanating reagent and riboflavin tetraacetate (RFTA) as an inexpensive organic photocatalyst in MeCN under visible-light irradiation ($\lambda_{max} \approx 455$ nm) [15]. Thereby, the expected nitroalkanes **5** were obtained in fair to high yields after 12 hours (Scheme 5). Noteworthy, the protocol can be adapted to flow conditions. The authors elegantly applied their methodology in the high yielding synthesis of idazoxan, a drug candidate that is under investigation as an adjunctive treatment in schizophrenia.



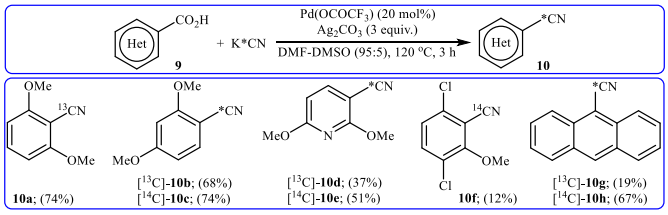
Scheme 5. RFTA-catalyzed decarboxylative cyanation of carboxylic acids **4** with TsCN

2.2. Aromatic carboxylic acids

In 2010, Taran and co-workers reported one of the first transition metal-catalyzed decarboxylative cyanation of aromatic carboxylic acids **6** into the corresponding aromatic nitriles **8** [16]. They carefully screened the reaction variables and found that 1-hydroxycyclohexane-1-carbonitrile **7** was more effective than other cyanating reagents [e.g., KCN, $Bu_4N^+CN^-$, CuCN, AgCN, $Zn(CN)_2$, $Hg(CN)_2$, $K_4Fe(CN)_6$] and compared to other palladium catalysts [e.g., $PdCl_2$, PdO, $PdSO_4$, $Pd(OAc)_2$, $Pd(acac)_2$], $Pd(OTf)_2$ was the best choice for this conversion. The reaction carried out in the presence of 3 equiv. of Ag_2CO_3 as a base in binary solvent DMF/DMSO with ratio 95:5 at 100 ºC, resulted in fast decarboxylative cyanation to give moderate to excellent isolated yields of aromatic nitriles **8** (Scheme 6a). The reaction, however, appears to be limited to the electron-rich carboxylic acids substrates. Of note, this procedure was successfully applied in the preparation of a ^{13}C-labeled compound using ^{13}C-labeled 1-hydroxycyclohexane-1-carbonitrile (Scheme 6b). Later, a similar decarboxylative cyanation of aromatic carboxylic acids using a cooperative catalytic system, consisting of $Pd(OCOCF_3)_2$ and Ag_2CO_3 was reported by Audisio and colleagues [17]. They showed that (hetero)aromatic carboxylic acids **9** underwent decarboxylative cyanation with [^{13}C] and [^{14}C]-KCN in the presence of $Pd(OCOCF_3)_2/Ag_2CO_3$ as a catalytic system in in a 95:5 mixture of DMF and DMSO to produce [^{13}C] and [^{14}C]-(hetero)aromatic nitriles **10** in satisfactory yields, respectively (Scheme 7).

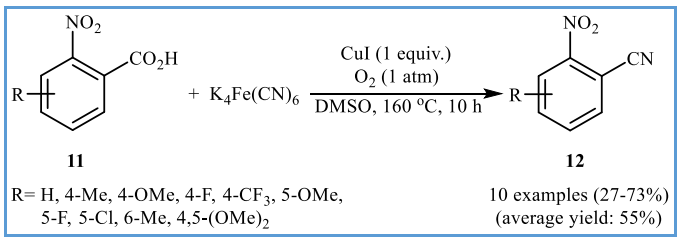


Scheme 6. (a) Pd-catalyzed decarboxylative cyanation of benzoic acids **6** with 1-hydroxycyclohexane-1-carbonitrile **7**; (b) synthesis of ^{13}C-labeled anthracene-10-carboxylic acid **8a'** from the corresponding carboxylic acid **6a** and ^{13}C-labeled cyanating agent **7'**



Scheme 7. Synthesis of labeled (hetero)aryl nitriles **10** through decarboxylative cyanation of (hetero)aromatic carboxylic acids **9** using [^{13}C] and [^{14}C]-KCN

Along this line, the group of Cai's described the synthesis of benzonitriles *via* a Cu-mediated decarboxylative cyanation of electron-deficient aryl carboxylic acids with $K_4Fe(CN)_6$ as a low-cost, nontoxic, and green cyanide source under an oxygen atmosphere [18]. Several catalysts, additives, and solvents were tested, and the system CuI/DMSO was found to be superior. Under optimized condition, a number of *ortho*-nitrobenzoic acids **11** were examined and the corresponding benzonitriles **12** were obtained in moderate to good yields (Scheme 8). However, the substrates having Me group at the C3- and C5-positions gave poor results under this reaction conditions. It should be mentioned that heteroaromatic carboxylic acids were also compatible with this green procedure. Of note, electron-rich aryl carboxylic acids completely failed to provide the corresponding benzonitrile products under this condition. The authors properly and elegantly solved this limitation using $Pd(OAc)_2$ instead of CuI catalyst, which afforded decent yields of the target nitro products. It is noted that both of these catalytic systems were also successfully applied in the synthesis of aryl halides from the respective (hetero) aryl carboxylic acids employing readily available halogen sources CuX (X = I, Br, Cl). Unfortunately, the mechanism of this transformation has not been elucidated yet. Later, the same authors improved the efficiency of their protocol in the term of product yields by performing the process in the presence of $Ag_2SO_4/Cu(OAc)_2$ combination as a catalytic system [19].

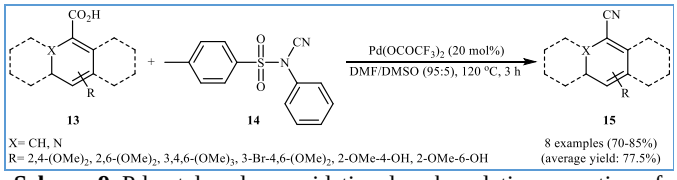


Scheme 8. Cu-mediated decarboxylative cyanation of electron-deficient aryl carboxylic acids **11** with $K_4Fe(CN)_6$

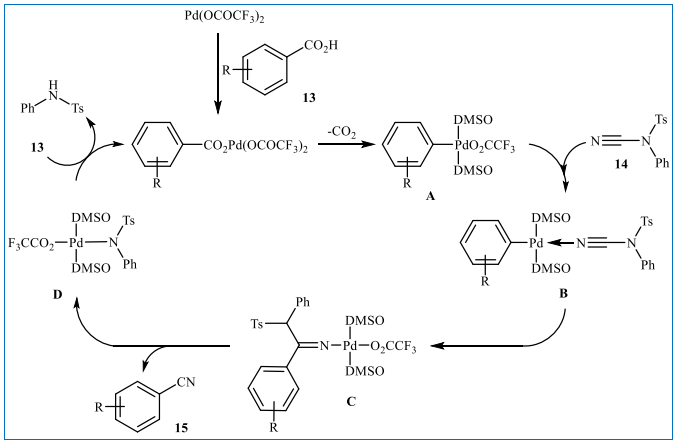
In 2017, Song, Salter, and Chen reported an interesting Pd-catalyzed nonoxidative decarboxylative cyanation of aromatic carboxylic acids **13** with the electrophilic cyanating reagent *N*-cyano-*N*-phenyl-ptoluenesulfonamide **14** (NCTS) as the cyano source

∗ Corresponding author. e-mail: soma.majedi@uhd.edu.iq

employing $Pd(OCOCF_3)$ as a catalyst in the absence of any oxidant [20]. Just like previous $Pd(OCOCF_3)$-catalyzed decarboxylative cyanation reaction, this reaction was also performed in DMF/DMSO (95:5) at 120 °C and afforded the expected benzonitriles **15** in good to high yields (Scheme 9); however, the substrate scope was generally limited to the electron-rich aryl carboxylic acids bearing at least one *ortho* substituent. It should be noted that no product was formed by using nucleophilic cyanating agents such as KCN and BtCN. The authors also demonstrated that their catalytic system can effectively promote the carboxylative cyanation of a small series of aliphatic and aromatic carboxylic acids with the isotopically labeled electrophilic cyanating reagent [$^{13/14}$CN]-NCTS to furnish the corresponding labeled nitrile products in good yield. The mechanistic course of this reaction is shown in Scheme 9, and involves the initial formation of arylpalladium trifluoroacetate **A** *via* decarboxylative palladation of starting aryl carboxylic acid **13**. The coordination of NCTS (**14**) to Pd affords the complex **B**, which afte insertion of C-N triple bond into aryl-Pd bond converts to the intermediate **C**. Next, rearrangement of **C** produces the benzonitrile product **15** along with the species **D**. Finally, aryl carboxylate displacement followed by decarboxylation affords the arylpalladium trifluoroacetate **A** to complete the catalytic cycle.



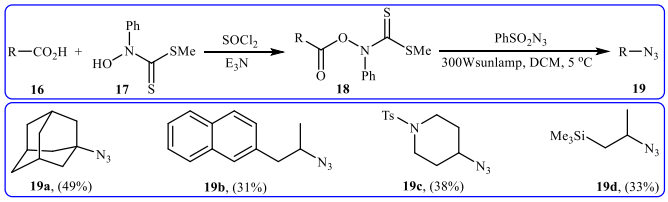
Scheme 9. Pd-catalyzed nonoxidative decarboxylative cyanation of aromatic carboxylic acids **13** with NCTS (**14**)



Scheme 10. Proposed mechanism for the formation of benzonitriles **15** from the reaction of aromatic carboxylic acids **13** with NCTS (**14**)

3. Decarboxylative azidation of carboxylic acids

In 2008, Nyfeler and Renaud developed the synthesis of aliphatic azids from the respective aliphatic carboxylic acids *via* a two steps process [21]. Thus, at the first step, esterification of aliphatic carboxylic acids **16** with *N*-hydroxy-*S*-methyl-*N*-phenyldithiocarbamate **17** in the presence of $SOCl_2$ gives thiohydroxamate esters **18** (MPDOC esters), which undergoes decarboxylative azidation with benzenesulfonyl azide ($PhSO_2N_3$) under irradiation with a 300W sunlamp to produce the target aliphatic azids **19** in moderate yields (Scheme 11). Decarboxylative azidation of a small library of α-amino and α-alkoxy acids using their corresponding MPDOC esters was also investigated under the standard conditions. However, due to low stability of this kind of MPDOC esters, all attempts were failed. The authors nicely solved this problem by using Kim's MMDOC esters instead of MPDOC esters. According to the authors proposed mechanism, the key steps of the reaction involves the generation of alkyl radicals from MPDOC esters and trapping of these radicals by $PhSO_2N_3$.



Scheme 11. Decarboxylative azidation of aliphatic carboxylic acids **16** using MPDOC esters **18**

Seven years later, Li and co-workers disclosed the first example of one-step and direct decarboxylative azidation of carboxylic acids [22]. They showed that the reaction of various aliphatic carboxylic acids **20** with tosyl azide or pyridine-3-sulfonyl azide in the presence of $AgNO_3$ as the catalyst and $K_2S_2O_8$ as the oxidant in aqueous MeCN solution afforded the corresponding alkyl azides **21** in moderate to almost quantitative yields (Scheme 12a). The reaction took place under relatively mild reaction conditions (50 °C) in air and tolerated a number of sensitive functional group including chloro, bromo, anitro, amino, ester, ketone, and ether functionalities, which provided the opportunity to further functionalization of end products. The synthetic utility of this new procedure was illustrated by the practical synthesis of (-)-indolizidine 209D and 167B. The mechanism shown in Scheme 11b was proposed by the authors for this C-N bond forming reaction. It consists of the following key steps:

(i) Generation of Ag(II) intermediate *via* the oxidation of Ag(I) by persulfate.

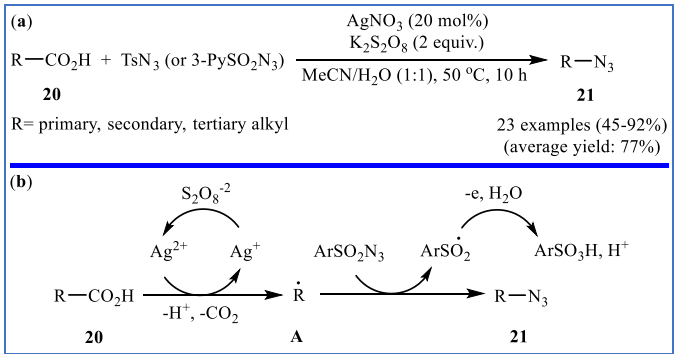
(ii) Reduction of Ag(II) through a single electron transfer with a carboxylate to form the carboxyl radical intermediate and regenerate Ag(I).

(iii) Decarboxylation of the carboxyl radical gives the corresponding alkyl radical **A**.

(iv) Trapping of the alkyl radical by the sulfonyl azide affords the expected alkyl azide **21** along with the generation of a sulfonyl radical.

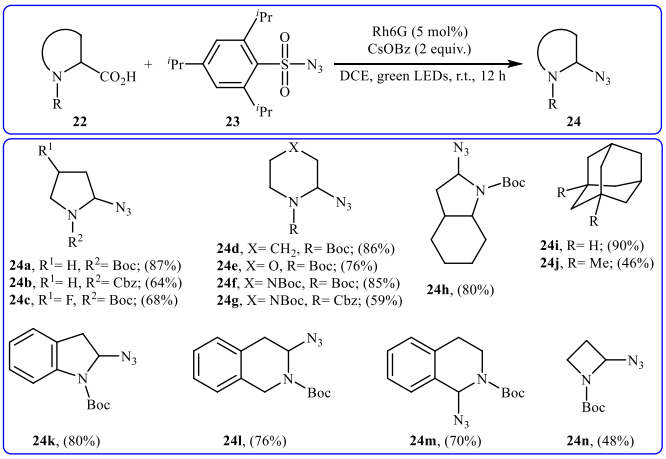
(v) Oxidation of the resulting sulfonyl radical leads to the formation of arenesulfonic acid.

In a closely related study, Song, and Jiao along with their co-workers synthesized a library of alkyl azides through the decarboxylative azidation of the corresponding aliphatic carboxylic acids using $PhSO_2N_3$ as the nitrogen source and $AgF/K_2S_2O_8$ combination as the catalytic system [23]. Later, this catalytic system was successfully utilized by Warner and colleagues in the decarboxylative azidation of carboxylic acid-functionalized detonation nanodiamond (dND) with TsN_3 [24].

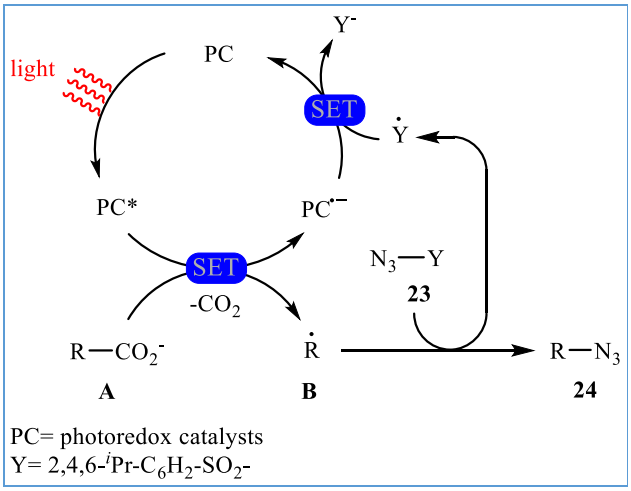


Scheme 12. (a) Ag-catalyzed decarboxylative azidation of aliphatic carboxylic acids **20** in aqueous solution; (b) mechanistic proposal for the formation of alkyl azides **21**

Very recently, Leonori's research team extended the scope of carboxylic acids to α-amino acids [25]. Thus, a variety of C-2-azidated cyclic aliphatic amines **24** were synthesized in moderate to excellent yields *via* the visible-light mediated organo-photoredox catalyzed decarboxylative azidation of cyclic α-amino acids **22** employing 2,4,6-triisopropylbenzenesulfonyl azide **23** as an azidating reagent and rhodamine 6G (Rh6G) as the catalyst at room temperature (Scheme 13). However, acyclic α-amino acids were not compatible with the reaction conditions. Other organo-photoredox catalysts such as MesAcr•$HClO_4$, 4CzIPN, riboflavin, methylene blue, and Eosin Y could also promote this azidation reaction; however, in lower yields. Of note, metallo-photoredox catalysts (e.g., $Ir(ppy)_3$, $Ru(bpy)_3Cl_2$) failed to promote this transformation. The authors proposed reaction mechanism for this conversion is illustrated in Scheme 14 that involves the initial formation of excited state species PC* *via* the excitation of PC under visible light irradiation, which leads to the single electron transfer oxidation of a carboxylate starting material **A**. Subsequently, a fast decarboxylation of this intermediate produces the alkyl radical **B**. Finally, the interception of radical **B** by 2,4,6-triisopropylbenzenesulfonyl azide **23** gives the desired product **24**.



Scheme 13. Photoinduced decarboxylative azidation of cyclic amino acids **22** with 2,4,6-triisopropylbenzenesulfonyl azide **23**



Scheme 14. Mechanism that accounts for the formation of C-2-azidated cyclic aliphatic amines **24**

4. Conclusion

Nitriles and azides are of great interest to medicinal chemistry due to their broad spectrum of biological activity. Therefore, many scientists have been working on developing novel and improved methods for their construction. In recent years, decarboxylative functionalization of carboxylic acids has emerged as a novel, selective, and powerful strategy to create various C-C and C-X bonds. Along this line, synthesis of nitriles and azides through the decarboxylative cyanation and azidation of carboxylic acids has got much attention over the past few years. As illustrated, using this step- and atom-economical synthetic process, various alkyl and aryl nitriles and alkyl azides have been successfully synthesized from the corresponding carboxylic acids. This synthetic methodology is still under development and we believe that the highly efficient and improved procedures for the synthesis of structurally diverse nitriles and azides will be attainable in the near future.

∗ Corresponding author. e-mail: soma.majedi@uhd.edu.iq

References

[1] (a) F. Fleming, Nitrile-containing natural products, *Nat. Prod. Rep*, 16 (1999) 597-606; (b) F.F. Fleming, L. Yao, P. Ravikumar, L. Funk, B.C. Shook, Nitrile-containing pharmaceuticals: efficacious roles of the nitrile pharmacophore, *J. Med. Chem*., 53 (2010) 7902-7917; (c) A. Kleemann, Pharmaceutical substances: Syntheses, Patents, Applications, 4th ed.; Thieme: Stuttgart, 2001.

[2] (a) J. Wang, F. Xu, T. Cai, Q. Shen, Addition of amines to nitriles catalyzed by ytterbium amides: An efficient one-step synthesis of monosubstituted *N*-arylamidines, *Org. Lett.*, 10 (2008) 445-448; (b) T. Horneff, S. Chuprakov, N. Chernyak, V. Gevorgyan, V.V. Fokin, Rhodium-catalyzed transannulation of 1, 2, 3-triazoles with nitriles, *J. Am. Chem. Soc.*, 130 (2008) 14972-14974; (c) S. Lu, J. Wang, X. Cao, X. Li, H. Gu, Selective synthesis of secondary amines from nitriles using Pt nanowires as a catalyst, *Commun. Chem*., 50 (2014) 3512-3515; (d) X. Wang, Y. Huang, Y. Xu, X. Tang, W. Wu, H. Jiang, Palladium-catalyzed denitrogenative synthesis of aryl ketones from arylhydrazines and nitriles using O2 as sole oxidant, *J. Org. Chem.*, 82 (2017) 2211-2218.

[3] U. Dutta, D.W. Lupton, D. Maiti, Aryl nitriles from alkynes using *tert*-butyl nitrite: Metal-free approach to C-C bond cleavage, *Org. Lett*., 18 (2016) 860-863.

[4] (a) T. Cheng, Review of novel energetic polymers and binders–high energy propellant ingredients for the new space race, Des. *Monomers Polym.*, 22 (2019) 54-65; (b) W.R. Martin, D.W. Ball, Small organic azides as high energy materials: Perazidoacetylene,-ethylene, and-allene, *ChemistrySelect*, 3 (2018) 7222-7225.

[5] (a) T.-S. Lin, W.H. Prusoff, Synthesis and biological activity of several amino analogs of thymidine, *J. Med. Chem*., 21 (1978) 109-112; (b) D.B. Smith, G. Kalayanov, C. Sund, A. Winqvist, T. Maltseva, V.J.-P. Leveque, S. Rajyaguru, S.L. Pogam, I. Najera, K. Benkestock, The design, synthesis, and antiviral activity of monofluoro and difluoro analogues of 4′-azidocytidine against hepatitis C virus replication: the discovery of 4′-azido-2′-deoxy-2′-fluorocytidine and 4′-azido-2′-dideoxy-2′, 2′-difluorocytidine, *J. Med. Chem*., 52 (2009) 2971-2978; (c) J.A. Raeburn, J.D. Devine, Pharmacological findings during azidocillin treatment of chest infections, *Scand. J. Infect. Dis*., 5 (1973) 135-139; (d) P.P. Geurink, W.A. van der Linden, A.C. Mirabella, N. Gallastegui, G. de Bruin, A.E. Blom, M.J. Voges, E.D. Mock, B.I. Florea, G.A. van der Marel, Incorporation of non-natural amino acids improves cell permeability and potency of specific inhibitors of proteasome trypsin-like sites, *J. Med. Chem.*, 56 (2013) 1262-1275.

[6] (a) N. Rodriguez, L.J. Goossen, Decarboxylative coupling reactions: a modern strategy for C–C-bond formation, *Chem. Soc. Rev.*, 40 (2011) 5030-5048; (b) J. Schwarz, B. König, Decarboxylative reactions with and without light–a comparison, *Green Chem*., 20 (2018) 323-361.

[7] R. Shang, Transition metal-catalyzed decarboxylation and decarboxylative cross-couplings, in: New Carbon–Carbon Coupling Reactions Based on Decarboxylation and Iron-Catalyzed C–H Activation, *Springer*, 2017, pp. 3-47.

[8] (a) S. Arshadi, S. Ebrahimiasl, A. Hosseinian, A. Monfared, E. Vessally, Recent developments in decarboxylative cross-coupling reactions between carboxylic acids and N–H compounds, *RSC Adv*., 9 (2019) 8964-8976; (b) A. Monfared, S. Ebrahimiasl, M. Babazadeh, S. Arshadi, E. Vessally, Recent advances in decarboxylative trifluoromethyl (thiol) ation of carboxylic acids, *J. Fluor. Chem*., 220 (2019) 24-34; (c) A. Hosseinian, F.A.H. Nasab, S. Ahmadi, Z. Rahmani, E. Vessally, Decarboxylative cross-coupling reactions for P(O)–C bond formation, *RSC Adv*., 8 (2018) 26383-26398; (d) A. Hosseinian, P.D.K. Nezhad, S. Ahmadi, Z. Rahmani, A. Monfared, A walk around the decarboxylative C–S cross-coupling reactions, *J. Sulfur Chem.*, 40 (2019) 88-112.

[9] D.A. Klein, Nitrile synthesis *via* the acid-nitrile exchange reaction, *J. Org. Chem*., 36 (1971) 3050-3051.

[10] D. Cantillo, C.O. Kappe, Direct preparation of nitriles from carboxylic acids in continuous flow, *J. Org. Chem*., 78 (2013) 10567-10571.

[11] D. Cartigny, A. Dos Santos, L. El Kaim, L. Grimaud, R. Jacquot, P. Marion, Nitrile synthesis through catalyzed cascades involving acid–nitrile exchange, *Synthesis*, 46 (2014) 1802-1806.

[12] D.H. Barton, J.C. Jaszberenyi, E.A. Theodorakis, The invention of radical reactions. Part XXIII new reactions: Nitrile and thiocyanate transfer to carbon radicals from sulfonyl cyanides and sulfonyl isothiocyanates, *Tetrahedron*, 48 (1992) 2613-2626.

[13] F. Le Vaillant, M.D. Wodrich, J. Waser, Room temperature decarboxylative cyanation of carboxylic acids using photoredox catalysis and cyanobenziodoxolones: a divergent mechanism compared to alkynylation, *Chem. Sci*., 8 (2017) 1790-1800.

[14] F.L. Vaillant, J. Waser, Decarboxylative alkynylation and cyanation of carboxylic acids using photoredox catalysis and hypervalent iodine reagents, *Chimia*, 71 (2017) 226-230.

[15] N.P. Ramirez, B. König, J.C. Gonzalez-Gomez, Decarboxylative cyanation of aliphatic carboxylic acids *via* visible-light flavin photocatalysis, *Org. Lett*., 21 (2019) 1368-1373.

[16] K. Ouchaou, D. Georgin, F. Taran, Straightforward conversion of arene carboxylic acids into aryl nitriles by palladium-catalyzed decarboxylative cyanation reaction, *Synlett*, (2010) 2083-2086.

[17] O. Loreau, D. Georgin, F. Taran, D. Audisio, Palladium-catalyzed decarboxylative cyanation of aromatic carboxylic acids using [^{13}C] and [^{14}C]-KCN, *J. Label. Compd. Radiopharm.*, 58 (2015) 425-428.

[18] Z. Fu, Z. Li, Y. Song, R. Yang, Y. Liu, H. Cai, Decarboxylative halogenation and cyanation of electron-deficient aryl carboxylic acids via cu mediator as well as electron-rich ones through pd catalyst under aerobic conditions, *J. Org. Chem*., 81 (2016) 2794-2803.

[19] Z. Fu, L. Jiang, Z. Li, Y. Jiang, H. Cai, Ag/Cu-mediated decarboxylative cyanation of aryl carboxylic acids with K4Fe (CN) 6 under aerobic conditions, *Synth. Commun*., 49 (2019) 917-924.

[20] F. Song, R. Salter, L. Chen, Development of decarboxylative cyanation Reactions for C-13/C-14 carboxylic acid labeling using an electrophilic cyanating reagent, *J. Org. Chem.*, 82 (2017) 3530-3537.

[21] E. Nyfeler, P. Renaud, Decarboxylative radical azidation using MPDOC and MMDOC esters, *Org. Lett*., 10 (2008) 985-988.

[22] C. Liu, X. Wang, Z. Li, L. Cui, C. Li, Silver-catalyzed decarboxylative radical azidation of aliphatic carboxylic acids in aqueous solution, *J. Am. Chem. Soc*., 137 (2015) 9820-9823.
[23] Y. Zhu, X. Li, X. Wang, X. Huang, T. Shen, Y. Zhang, X. Sun, M. Zou, S. Song, N. Jiao, Silver-catalyzed decarboxylative azidation of aliphatic carboxylic acids, *Org. Lett*., 17 (2015) 4702-4705.
[24] Z.C. Kennedy, C.A. Barrett, M.G. Warner, Direct functionalization of an acid-terminated nanodiamond with azide: enabling access to 4-substituted-1, 2, 3-triazole-functionalized particles, *Langmuir*, 33 (2017) 2790-2798.
[25] D.C. Marcote, R. Street-Jeakings, E. Dauncey, J.J. Douglas, A. Ruffoni, D. Leonori, Photoinduced decarboxylative azidation of cyclic amino acids, *Org. Biomol. Chem*., 17 (2019) 1839-1842.

∗ Corresponding author. e-mail: soma.majedi@uhd.edu.iq