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Direct vicinal oxy-azidation of unsaturated carbon-carbon bonds: a facile synthetic route to α-azido ketones

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ABSTRACT

α-Azido carbonyls include compounds that are known to possess wide range of biological activities or are important templates in medicinal chemistry. They are also extremely powerful building blocks for the efficient synthesis of diverse arrays of biologically important N-heterocyclic compounds. In the light of the importance of this family of organic azide compounds a great deal of attention has been given to their synthesis and, in the past years, several methods have been described in the literature allowing for the direct construction of these substances from easily accessible alkene and alkynes by vicinal oxy-azidation reactions. However, no comprehensive review on this chemistry has been published to date. In this light, here we intend to summarize the advances in this attractive field with special attention on mechanistic features of the reactions.

1. Introduction

Organic azides are privileged motifs that occur in various marketed drugs with diverse pharmacological activities [1]. They are also extremely powerful and versatile building blocks in a variety of synthetic transformations [2]. In particular, α-azido carbonyls are found in the structures of large numbers of approved drugs and clinical/preclinical candidates, with a wide range of activities including anti-bacterial, anti-viral, anti-myeloma, anti-AIDS and many more (Scheme 1) [3]. This class of azido compounds are also one of the most useful and versatile synthons in organic synthesis, as they can be easily transformed into numerous biologically important N-heterocycles including pyrroles, indoles, pyrazoles, imidazoles, triazoles, pyridines, pyrimidines, pyrazines, quinazolines, isoquinolines, etc [4]. As a result of this, numerous methods have been developed for the synthesis of α-azido carbonyls [5]. However, most of these methods rely upon the nucleophilic substitution of corresponding α-substituted ketone (e.g., α-halo ketones, α-tosyloxy ketones, α-nosyloxy ketones) with an azide anion. However, these methods suffer from some disadvantages such as requirement of pre-functionalized starting materials and liberation of hazardous by-products. Therefore, the development of efficient, convenient, and environmentally benign approaches that benefit from simple, low-cost and easily accessible starting materials for the construction of this specific class of organic azide compounds is still highly desirable in synthetic chemistry. Generally, the synthesis of nitrogen-included compounds is crucial in medicinal chemistry and material science. Nitrogen enhances diversity, reactivity, and solubility, aiding drug development and improving stability and specificity in biological interactions. Efficient nitrogen incorporation strategies remain a focus in synthetic chemistry [6-10].

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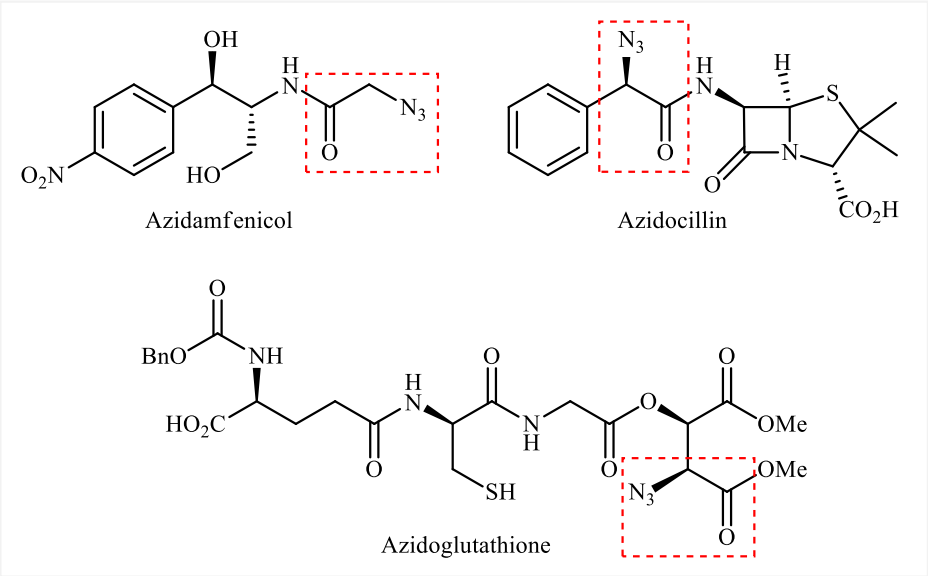


Scheme 1. Selected examples of bioactive compounds possessing an α-azido ketone unit.

The direct Oxy-functionalization of unsaturated hydrocarbons has emerged as a sustainable powerful, and step-economy synthetic strategy for the efficient construction of α-functionalized ketones in one step from simple and readily available feedstock chemicals [11-18]. In this context, the direct oxy-azidation reactions have recently become a highly valuable tool for preparing α-azido ketones from easily accessible alkenes and alkynes with high atom-, step-, and pot-economy (Figure 1). However, as far as we know, no comprehensive review on the direct synthesis of α-azido ketone derivatives from unsaturated hydrocarbons has been published to date. In this light, here we sum up the advances in this field with special attention on mechanistic implications of the reactions. It should be noted that this review does not cover literature data on the hydroxyazidation of alkenes since it recently highlighted by Shahimi and co-workers [19], in a paper entitled " Direct hydroxyazidation of alkenes: A viable strategy for the synthesis of β-azido alcohols ".

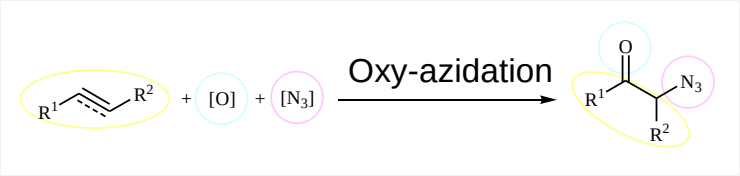
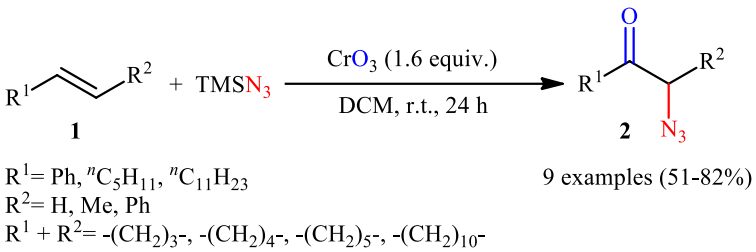


Fig. 1. Direct vicinal oxy-azidation of unsaturated carbon-carbon bonds.

2. Oxy-azidation of alkenes

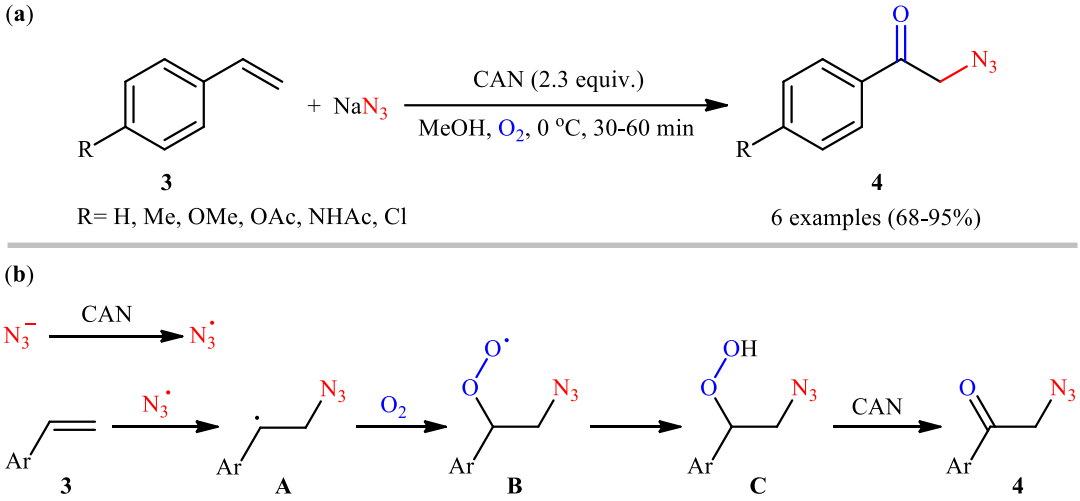
The possibility of direct oxy-adization of alkenes into corresponding α-azido ketones was first realized by Vankar and co-workers [20], who synthesized a range of cyclic and acyclic α-azido ketones 2 from the reaction of respective alkenes **1** with trimethylsilyl azide ($TMSN_3$) and chromium trioxide (CrO_3) under catalyst-/additive-free conditions. The reactions were carried out in DCM at room temperature, tolerated various terminal (aromatic or aliphatic) and internal (cyclic or acyclic) alkenes, and provided the desired products in moderate to high yields (Scheme 2). Notably, the reaction exhibited high degree of regioselectivity, in which azidation is exclusively took place on the carbon atom attached to the terminal carbon atom of the C–C double bond and those α-azido ketones that have carbonyls in the internal positions are formed selectively. Unfortunately, the authors did not unravel the plausible mechanistic scheme for this difunctionalization reaction.



R^1= Ph, $^nC_5H_{11}$, $^nC_{11}H_{23}$
R^2= H, Me, Ph
$R^1 + R^2$= -$(CH_2)_3$-, -$(CH_2)_4$-, -$(CH_2)_5$-, -$(CH_2)_{10}$-

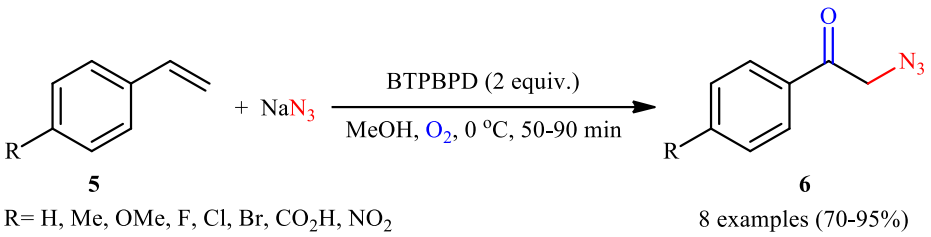
Scheme 2. Vankar's synthesis of α-azido ketones **2**.

Five year later, Nair and co-workers demonstrated that the same transformation could be achieved by using sodium azide (NaN_3) as the azide source and molecular oxygen (O_2) as the source of oxygen atom of carbonyl group [21]. Thus, in the presence of 2.3 equiv. of cerium ammonium nitrate (CAN) as a one-electron oxidant, the reaction of styrene derivatives 3 with NaN3 in MeOH under an oxygen atmosphere furnished corresponding phenacyl azides **4** in good to excellent yields. As shown in Scheme 3a, vinyl arenes possessing either electron-donating or electron-withdrawing functionalities were well tolerated by this protocol. However, only para-substituted styrenes have been examined in this study and no comment was made by the authors regarding the applicability of ortho- and meta-substituted substrates. The mechanistic course of this oxy-adization reaction is shown in Scheme 3b, and involves the initial formation of azido radical via one-electron oxidation of azide anion by CAN. Subsequently, addition of this radical to the styrene **3** leads to benzylic radical **A**, which after interaction with oxygen furnishes the peroxy radical **B**. Thereafter, the abstraction of a hydrogen atom from the solvent by newly generated radical B leads to an hydroperoxide intermediate **C**. Finally, oxidative cleavage of intermediate **C** by CAN affords the observed phenacyl azides **4**.



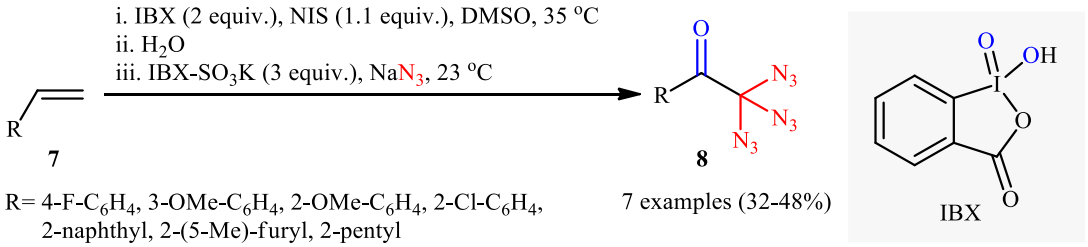
Scheme 3. (a) Nair's synthesis of phenacyl azides **4**; (b) Possible mechanism for the formation of phenacyl azides **4**.

The synthesis of a library of phenacyl azides **6** in good to excellent yields (up to 95 %) was also reported by Badri and Gorjizadeh through the direct oxy-adization of corresponding styrene derivatives **5** with NaN_3 under an atmosphere of oxygen using cis-1,4-bis(triphenylphosphonium)-2-butene peroxodisulfate (BTPBPD), as an inexpensive and environmentally safe oxidation reagent (Scheme 4) [22]. The reaction showed good functional group tolerance, including fluoro, chloro, bromo, nitro, acid and ether functionalities that would allow further elaboration of the products. When compared to the CAN-mediated protocol, the current methodology presents higher average yields using similar substrates.



Scheme 4. Badri-Gorjizadeh's synthesis of phenacyl azides **6**.

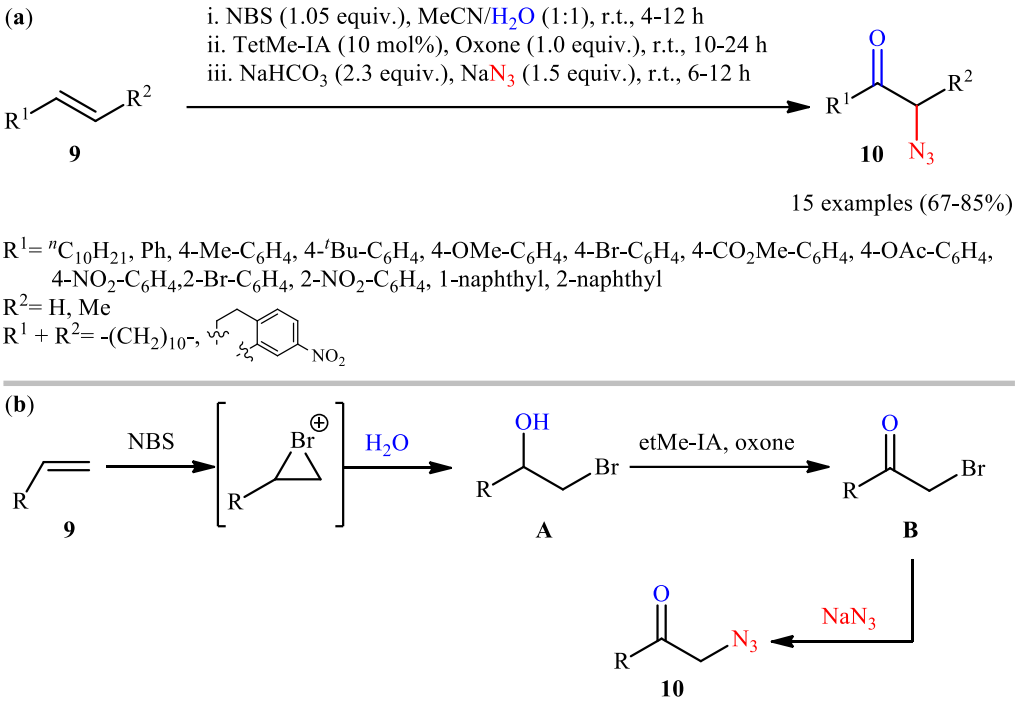
In a significant contribution in this field, Kirsch's research group developed an efficient protocol for the synthesis of geminal triazides **8** from terminal alkenes **7** as shown in Scheme 5 [23]. Optimal reaction conditions for this transformation were found to be in situ preparation of the corresponding iodomethyl ketones by reaction of alkenes with 2-iodoxybenzoic acid (IBX) and N-iodosuccinimide (NIS). Then the reaction was followed by addition of water, filtration and addition of NaN_3 and IBX-SO_3K. The reactions showed good tolerance to both aliphatic and aromatic terminal alkenes. Notably, when internal alkenes were used as substrates under the identical conditions, the corresponding oxy-diazidated products were obtained in high yields. It should be mentioned that, due to its lower oxidative power, IBX-SO3K cannot be used in place of IBX as the oxidizing agent in oxy-iodination step. On the other hand, the use of IBX instead of IBX-SO3K in the azidation step results in a strongly exothermic reaction that is uncontrollable, and ends in the complete decomposition of the starting material and the evolution of gas.



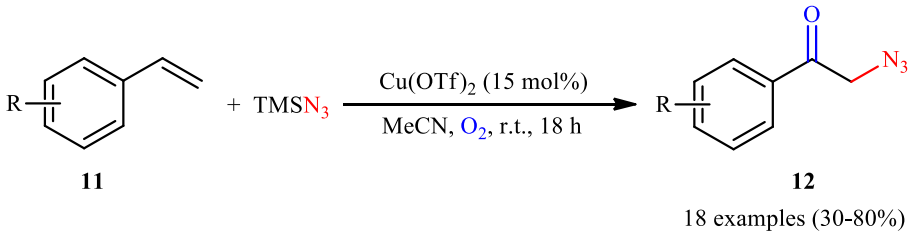
Scheme 5. Kirsch's synthesis of geminal triazides **8**.

In 2017, Moorthy and co-workers developed an interesting one-pot–three-step approach comprising bromohydroxylation-oxidation-azidation for the conversion of alkenes **9** into α-azido ketones **10** under ambient conditions (Scheme 6) [24]. Step one of this process involves initial formation of bromohydrins **A** by the reaction of alkenes **9** with N-bromosuccinimide (NBS) in aqueous acetonitrile which then undergoes oxidation with Oxone in the presence of a catalytic amount of 3,4,5,6-tetramethyl-2-iodoxybenzoic acid (TetMe-IBX) leading to α-bromoketones **B** followed by a nucleophilic substitution with NaN_3 to form the target α-azido ketones **10**. The one-pot conversions are versatile for a variety of olefins that include cyclic as well as acyclic aliphatic olefins and electron-rich and electron-deficient styrenes. This protocol was compatible with a variety of alkenes that include cyclic as well as acyclic aliphatic olefins and electron-rich and electron-deficient styrenes.

In 2018, Xiong and co-workers realized the first metal-catalyzed direct oxy-adization of alkenes by using low-cost $Cu(OTf)_2$ as the catalyst, $TMSN_3$ as the azide source, and molecular oxygen both as an oxidant and a source of an oxygen atom [25]. Under the optimized conditions, various styrene derivatives **11** bearing sensitive functional groups such as fluoro, chloro, bromo, cyano, nitro, ether, and ester showed fair to high yields of the corresponding phenacyl azide products **12** (Scheme 7). However, hydroxyl-substituted styrenes were incompatible in the reaction and applicability of aliphatic alkenes was not investigated in this study. In order to extend the generality of their methodology, the authors also investigated several vinylic substituted styrene derivatives. β-Alkyl and nitrile substituted substrates were inert under the standard conditions, but stilbene gave the corresponding product in only 45%, which indicates that this protocol is specific for terminal alkenes.



Scheme 6. Moorthy's synthesis of α-azido ketones **10**.

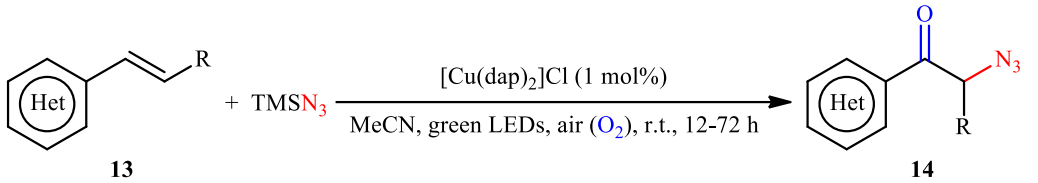


Scheme 7. Xiong's synthesis of geminal triazides **12**.

Concurrently, an elegant visible-light-accelerated Cu-catalyzed direct oxy-azidation of vinyl (hetero)arenes **13** with $TMSN_3$ was reported by Hossain et al. [26]. No organic oxidant was used and only 1 mol% of organic dye [Cu-(dap)2]Cl (dap=2,9-bis(p-anisyl)-1,10-phenanthroline) was enough for preparation of a panel of 28 functionalized 2-azido-1-arylethanones **14** in 10–85% yields (Scheme 8). These reactions were run under green LED irradiation at ambient temperature and tolerated both terminal and internal alkenes with either electron-donating or electron-withdrawing substituents. However, the steric hindrance produced by the substituents has a significant influence on the reaction yield. For instance, while *para*-substituted nitrostyrene produced 51% yield, the *meta*-substituted one produced 29% yield. Moreover, a substrate with two Cl substituents at C2 and C6-positions gave the product in only 10% yield. Allylbenzene did not take part in the reaction and therefore no other aliphatic alkenes were examined in the protocol. By observing the lack of conversion for the unactivated olefin, the authors provided an interesting example to highlight chemoselectivity of their methodology. When 1-allyl-4-vinylbenzene was subjected to these reaction conditions, oxy-azidation occurred exclusively over the vinylic C-C double bond when allylic C-C double bond was also present. Gratifyingly, 1-(chloromethyl)-4-vinylbenzene was also successfully oxy-azidated and the reactive chloride remained untouched, highlighting the excellent chemoselectivity of the reaction. The authors assume that the mechanistic pathway of this light-accelerated oxy-azidation reaction involves the initial formation of [Cu(I)]* complex **A'** via the excitation of [Cu(dap)2]Cl

complex **A** under light irradiation, which after oxidation by O_2 leads to catalytically active species

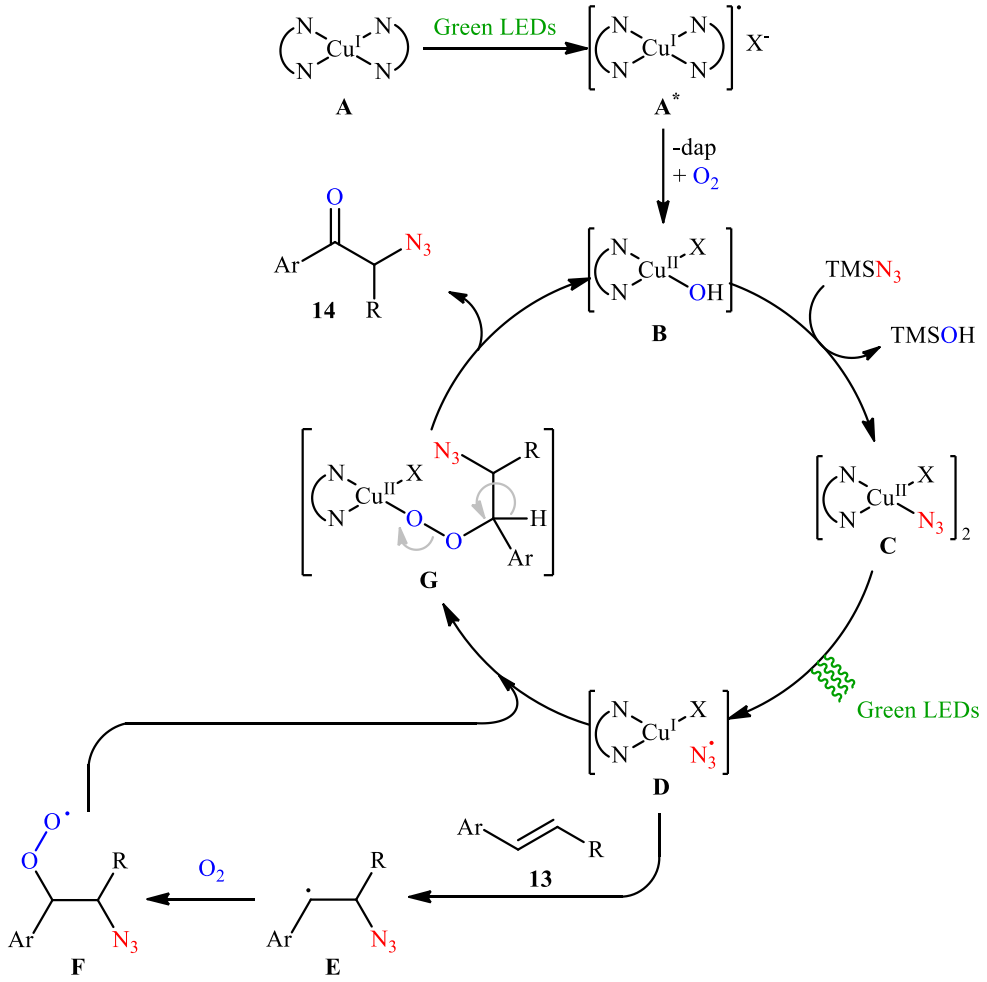
B. Next, reaction of newly generated complex **B** with the azide anion give azide-bridged dimer **C**, which after the homolytic dissociation affords Cu(I) species **D** and an azide radical. Subsequently, addition of the azide radical to the substrate **13** provides C-centered radical **E** (confirmed by TEMPO trapping), which further reacts with oxygen to form O-centered radical **F**. Afterwards, peroxy radical intermediate F binds to **D** to give Cu(II) species **G**. Finally, elimination of active species **B** from this intermediate furnishes the target oxy-azidated product **14** (Scheme 9).



(Het)Ar= Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-OAc-C_6H_4, 4-NH_2-C_6H_4, 4-NHAc-C_6H_4, 4-NO_2-C_6H_4, 4-CN-C_6H_4, 3-OMe-C_6H_4, 3-Cl-C_6H_4, 2-Me-C_6H_4, 2-OMe-C_6H_4, 2-NO_2-C_6H_4, 2-CF_3-C_6H_4, 3,5-$(OMe)_2$-C_6H_3, 3,4-(OBn)-C_6H_3, 2,6-$(Cl)_2$-C_6H_3, 3,4,5-$(OMe)_2$-C_6H_2, 2-Cl-3,4-$(OMe)_2$-C_6H_2, 2-naphthyl, 2-thienyl, 2-benzofuryl

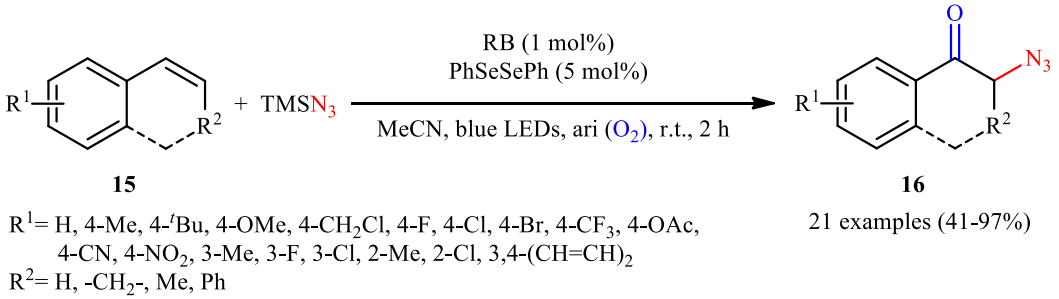
R= H, Me

Scheme 8. Visible-light-accelerated Cu-catalyzed synthesis of 2-azido-1-arylethanones **14**.



Scheme 9. Plausible reaction mechanism for the formation of 2-azido-1-arylethanones **14**.

In the same year, Wei and co-workers reported a conceptually analogous oxy-azidation using low-toxic and inexpensive organic dye, Rose Bengal (RB) as a photocatalyst and diphenyl diselenide (PhSeSePh) as co-catalyst [27]. Thus, a panel of twenty-one vinyl arenes **15** reacted well with $TMSN_3$ under the standard conditions [RB (1 mol%), PhSeSePh (5 mol%), MeCN, blue LEDs, air, r.t., 2 h] to produce the corresponding 2-azido-1-arylethanones **16** in moderate to almost quantitative yields (Scheme 10). The method showed a broad substrate scope including α,β-unsubstituted and β-substituted styrenes (cyclic and acyclic) bearing either electron-withdrawing or electron-donating groups on the phenyl ring periphery. Interestingly, the presence of different substituting patterns in *o*-, *m*-, or *p*-positions on the phenyl ring did not have almost any impact on the reaction outcome. However, when aliphatic alkenes such as hex-1-ene and cyclopentene were used as the substrates under the identical conditions, none of the desired products were detected.



Scheme 10. Wei's synthesis of 2-azido-1-arylethanones **16**.

Along this line, very recently, the Cui-Liu laboratory designed and synthesized two supramolecular metal−organic cages **I** and **II** with the general formula $\{[Ni_4(\mu_4\text{-}H_2O)(\mu_2\text{-}OH)(TBSC)]_8[Ni_4(\mu_4\text{-}H_2O)(TBSC)]_2(CuL_2)_8\}\cdot(PF_6)_8$ and $\{[Ni_4(\mu_4\text{-}H_2O)(\mu_2\text{-}OH)(TBSC)]_4[Ni_4(\mu_4\text{-}H_2O)\text{-}(TBSC)]_7(CuL_2)_8(NiLCl_2)_3L\}\cdot(PF_6)_8$ from proper mixtures of H_2L, H_4TBSC, $[Cu(CH_3CN)_4]\text{-}PF_6$ and $NiCl_2\cdot 6H_2O$ [28]. They showed that treatment of a Cu(I) bis-dmp linker or a mixture of dmp and Cu(I) bis-dmp linkers with a Ni_4-*p*-*tert*-butylsulfonylcalix[4]arene cluster affords the quadruply interlocked double cage **I** consisting of two identical tetragonal pyramids and the quadruply heterointerlocked cage **II** consisting of a tetragonal pyramid and an octahedron, respectively (Figure 2). With photoredox-active $[Cu(dmp)_2]^+$ in the structures, both cages exhibited remarkable performance as supramolecular photocatalysts for oxy-azidation of vinyl arenes with $TMSN_3$ under irradiation of green LEDs at room temperature.

In 2021, the group of Handa described a beautiful micelle-mediated synthesis of α-azido ketones **18** through a one-pot two-step sequence from styrene derivatives **17**, NBS, and NaN_3 in water (Scheme 11) [29]. In the first step, the reaction of alkenes with NBS in the presence of an amphiphile PS-750-M that structurally mimics the dipolar-aprotic solvents resulted in the formation of corresponding α-bromo ketones, and in the second step, the treatment of resulted α-bromo ketones with NaN_3 furnished the expected α-azido ketones. In this report, 10 α-azido ketones were synthesized in fair to good yields (52-85%) using either electron-rich or electron-poor styrene derivatives. In addition, a gram-scale synthesis of 2-azido-1-phenylethanone was successfully performed under the standard reaction conditions (1.3 g, 85% yield). Noteworthy, this synthetic strategy was also successfully extended to the preparation of different α-substituted ketones using different nucleophiles other than azide. Mechanistic investigations indicated that this oxy-azidation reaction proceeds through the following key steps (Scheme 12): (i) addition of NBS to alkene **17** to generate radical intermediate **A** and a succinimide radical; (ii) the hydrogen atom transfer radical abstraction from water by succinimide radical to produce to produce α-hydroxy bromide **B**; (iii) hydrogen atom exchange between NBS and α-hydroxy bromide **B** to form α-bromo ketone **D** through intermediate **C**; and (iv) nucleophilic addition of N_3^- to intermediate **D** to provide the final product **18**.

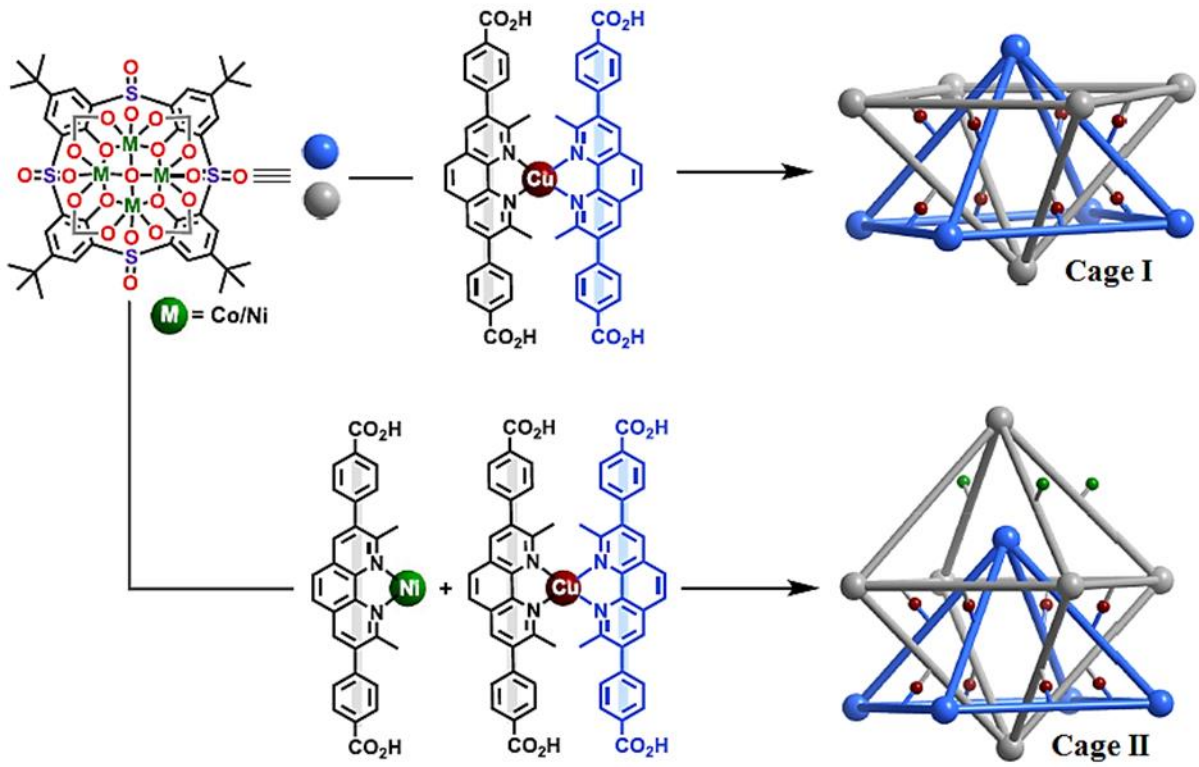
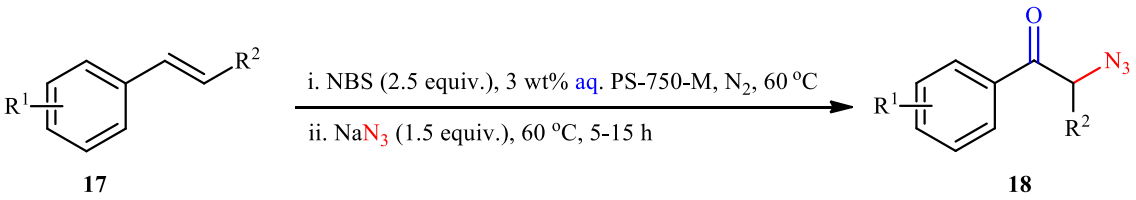


Figure 2. Schematic diagram showing the formation of cage **I** and cage **II**.



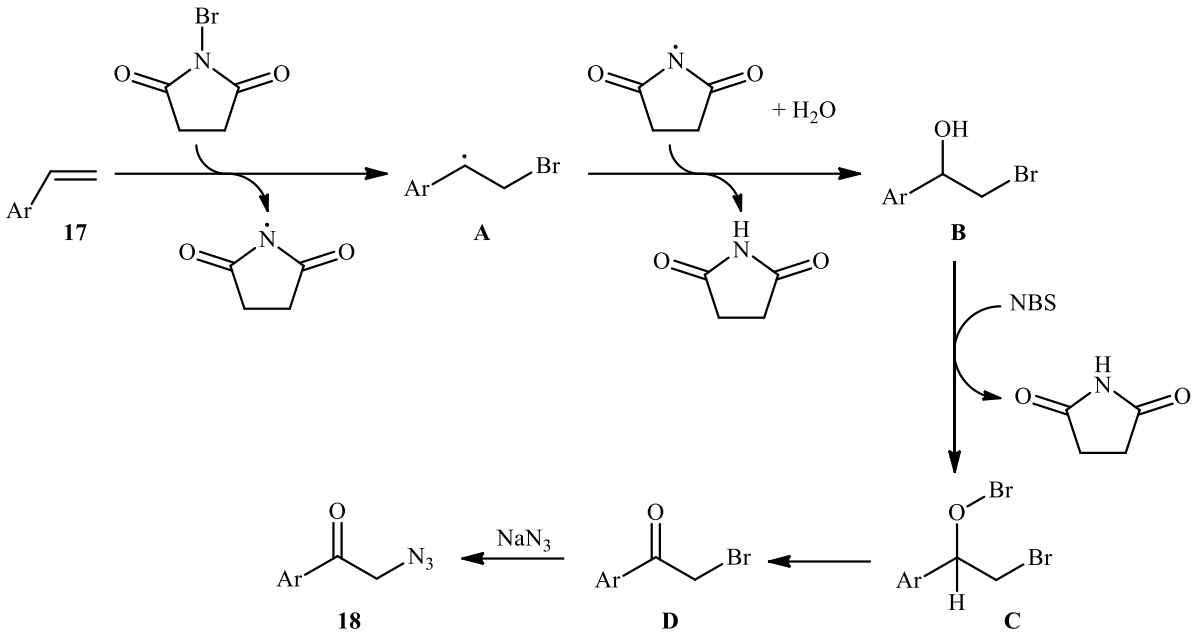
17 **18**

R^1= H, 4-Me, 4-^{t}Bu, 4-Ph, 4-(2-naphthyl), 4-F, 4-Cl, 4-Br, 3-Br-4-F
R^2= H, Me

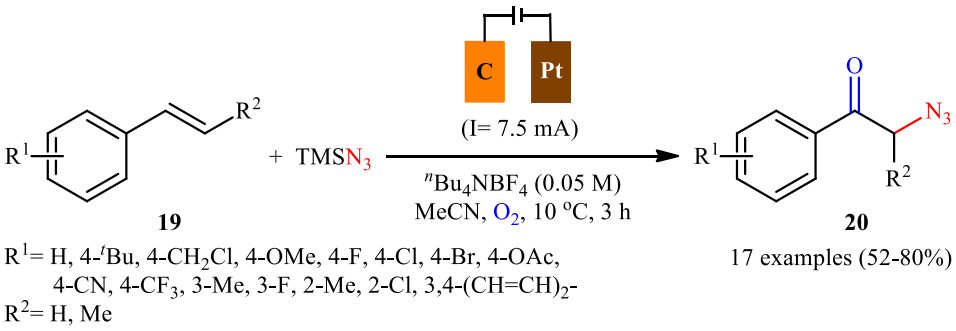
10 examples (52-85%)

Scheme 11. Handa's synthesis of α-azido ketones **18**.

In an important contribution in this field, Zhang and colleagous developed a catalyst-free electrochemical approach for oxy-azidation of styrene derivatives **19** with $TMSN_3$ and molecular under mild conditions [30]. The authors identified a reticulated vitreous carbon (RVC) and a platinum plate as the optimal anode and cathode, respectively, and tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte. The established electro-difunctionalization was conducted in MeCN under the oxygen atmosphere, tolerated both terminal and internal vinyl arenes, and provided the target α-azido ketones **20** in moderate to high yields (Scheme 13). The 1,1-disubstituted styrenes were also subjected to the reaction but, surprisingly, corresponding ketones were obtained instead in excellent yields *via* olefin cleavage.



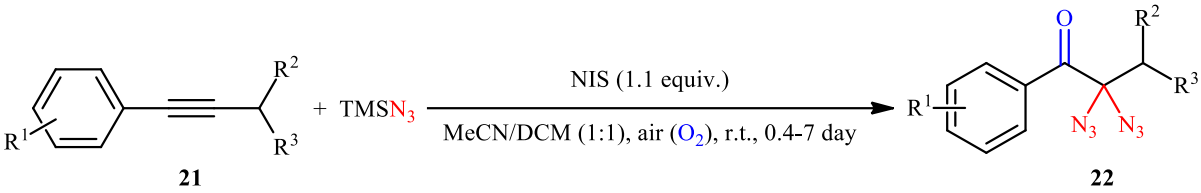
Scheme 12. A plausible mechanism for the formation of α-azido ketones **18**.



Scheme 13. Zhang's synthesis of α-azido ketones **20**.

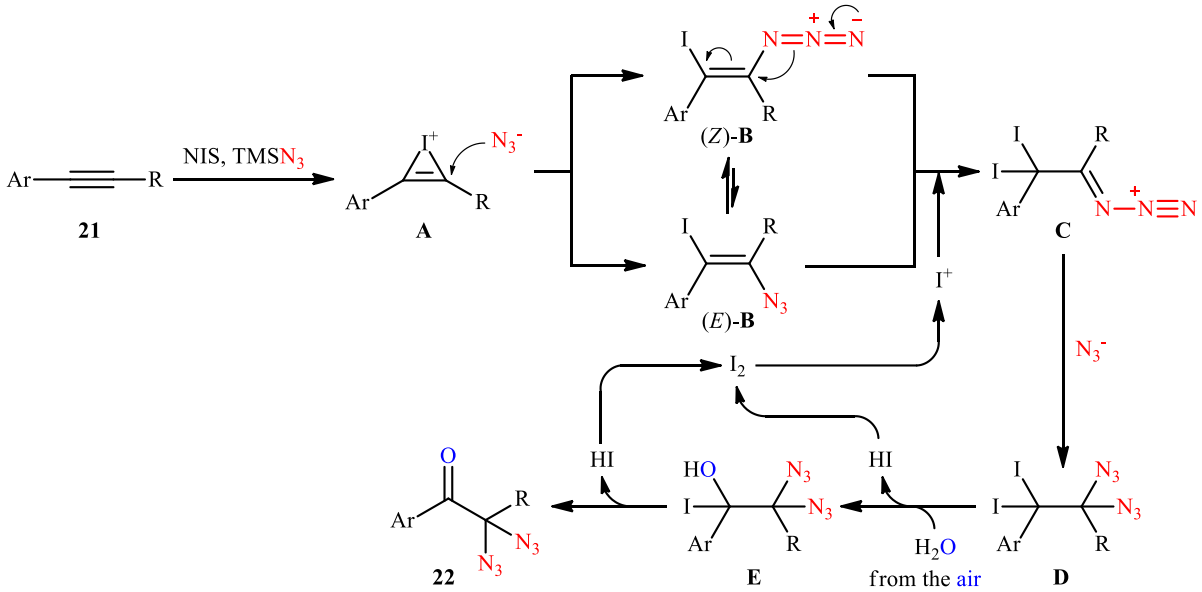
3. Oxy-azidation of alkynes

Although, synthesis of α-azido ketones through the direct oxy-azidation of alkenes has been well known, direct oxy-azidation of alkynes was less developed. In fact, only one example of such a reaction was reported in the literature up to now. In this study, the Yanada laboratory disclosed that the treatment of aryl alkyl alkynes **21** with $TMSN_3$ in the presence of 1.1 equiv. of *N*-iodosuccinimide (NIS) in the binary solvent MeCN/DCM under an open air atmosphere afforded α,α-diazidoketones **22** with yield ranging from 17% to 73% (Scheme 14) [31]. In the investigation of the scope of this transformation, it was found that the reaction is very dependent on the steric- and electronic-factors of the substituents on the aromatic ring of substrates. Generally, alkynes with electron-donating groups showed better activity in comparison with those containing strong electron-withdrawing groups. However, regardless of the electronic-characters of the substituents, *ortho*-substituted aryl alkynes totally failed to participate in this conversion. On the other hand, although aryl alkyl alkynes possessing either primary or secondary alkyl groups were compatible in the reaction, substrates with a tertiary alkyl groups did not take part in the reaction. The authors suggested that the plausible mechanism for the formation of α,α-diazidoketones **22** includes the initial formation of iodonium ion intermediate **A** through the reaction of alkyne **21** with NIS. Thereafter, *syn* or *anti* addition of the azide ion to this intermediate **A** affords regiochemically unusual alkene (*Z*)-**B** or (*E*)-**B**. Subsequently, reaction of **B** with I^+ results in the formation of intermediate **C**, which after a quick reaction with the azide ion delivers diazide intermediate **D**. In the next step, this intermediate **D** undergoes hydrolysis by moisture from the air to generate β-diazido alcohol intermediate **E**, which after elimination of HI affords the observed products (Scheme 15).



R^1= H, 4-Me, 4-F, 4-CF_3, 3-OMe
R^2= ^{n}Pr, ^{c}Hex, -$(CH_2)_2$OBz, -$(CH_2)_3$OBz, OBz, OBn, OAc, OCO_2Et, OCO-(4-Br-C_6H_4), OTBS
R^3= H, Me, Ph

Scheme 14. Yanada's synthesis of α,α-diazidoketones **22**.



Scheme 15. Mechanism proposed to explain the formation of α,α-diazidoketones **22**.

4. Conclusion

In this overview we have presented the recent advances in direct oxy-azidation of unsaturated hydrocarbons, showing this methodology to be an established process to access biologically and synthetically important α-azido ketones within a single click. Some salient features of this page of α-azido ketones are: i) simple and readily available starting materials; ii) high atom- and step-economy; iii) minimal waste generation; and iv) high yield and reioselectiviy.

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