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Anti-Markovnikov Hydroazidation of Alkenes by Visible Light Photoredox Catalysis

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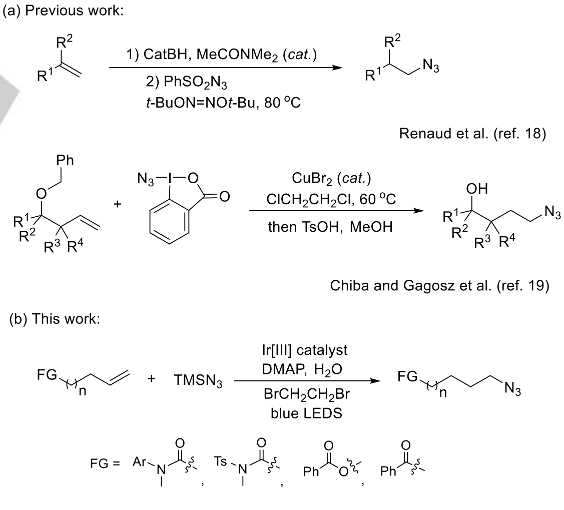
Dedication ((optional))

Abstract: The anti-Markovnikov hydroazidation of alkenes has been accomplished under visible light irradiation by using [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as photocatalyst and trimethylsilyl azide as azidating agent. The reactions were greatly facilitated by water, whose beneficial effect can be attributed to its participation in the reaction as the hydrogen donor, as indicated by deuterium isotope experiments. The reactions can be effected under solvent free conditions in the presence of water. 4-Dimethylaminopyridine also exhibited a beneficial effect on the reactions. The present method enabled hydroazidation of several types of unactivated alkenes with good yield and high regionselectivity.

Hydroamination of readily available alkenes constitutes a direct and atom-economical means to gain access to amine derivatives.[1] Despite its apparent simplicity, implement of this type of reactions has proven to be a nontrivial task as demonstrated by the enormous efforts made towards this goal.[1,2] Particularly challenging in this line is to realize these transformations in an anti-Markovnikov manner. While transition metal catalysis provides viable solutions to this problem,[3-7] radical-mediated addition reactions have also been applied to effect anti-Markovnikov hydroamination.[8] Recent investigations by Nicewicz et al.[9,10] and Knowles et al.[11] show that visible light photoredox catalysis constitutes a powerful means for the anti-Markovnikov hydroamination of both activated and unactivated alkenes under mild catalytic conditions, and these excellent studies well illustrate the usefulness of the photochemical protocols in the synthesis of chain amines and sulfonamides.

Olefin azidation reactions are highly effective for the synthesis of organic azides.[12] However, compared with olefin difunctionalization azidation reactions, hydroazidation of alkenes,[13,14] a variant type of hydroamination, has much less been explored. There have only been several studies addressing this issue during the last two decades.[15-19] In 2005, Waser and Carreira developed a Markovnikov olefin hydroazidation strategy featuring a cobalt-catalyzed radical hydrogen addition and azidyl transfer process.[16] Later on, Boger et al. realized similar transformations by using iron as catalyst.[17] Besides their applications in Markovnikov hydroazidation, radical reactions have also been employed for the anti-Markovnikov hydroazidation (Scheme 1, (a)). In 2011, Renaud et al. reported a one-pot procedure towards this goal: the alkene is first hydroborated to give an organoborane which is then azidated with benzenesulfonyl azide via radical-mediated azidyl transfer.[18] Recently, Chiba and Gagosz developed another radical procedure for the anti-Markovnikov hydroazidation of functionalized alkenes.[19] This method involves the addition of azidyl radical onto the alkene moiety followed by intramolecular hydrogen atom transfer from an internal benzyl protecting group. Although these studies provide effective means for the hydroazidation of alkenes, simple straightforward anti-Markovnikov hydroazidation protocols are still lacking, and more approaches are needed to meet various synthetic demands. In this concern, herein we report a visible light-induced anti-Markovnikov hydroazidation of unactivated alkenes (Scheme 1, (b)). Our method features the use of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as photocatalyst and TMSN$_3$ as azidating agent. Moreover, water and 4-dimethylaminopyridine were employed to facilitate the reaction. This system allowed us to prepare some functionalized primary azides with good yield and high selectivity.



Scheme 1. Anti-Markovnikov hydorazidation.

At the initial stage of this research, we envisioned that alkenes might be hydroazidated with an azide anion in an anti-Markovnikov manner under the conditions of visible light photoredox catalysis. In this view, we began our investigation by searching for a suitable catalytic system to realize this goal. After extensive exploration of reaction conditions with several olefins as substrates and TMSN$_3$ as the azidating agent, we found that when [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ was used as the catalyst, compound *N*-phenylpent-4-enamide (**1a**) could be converted to the desired hydroazidation product **2a** in low yield in acetonitrile in the presence of 4-dimethylaminopyridine

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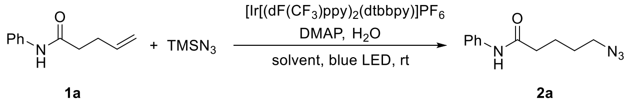
(DMAP). On the basis of this result, the reaction conditions were further explored with **1a** as the model compound and [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ as photocatalyst. The representative results are summarized in Table 1.

Table 1. Screening of the conditions for the reaction of **1a**[a]

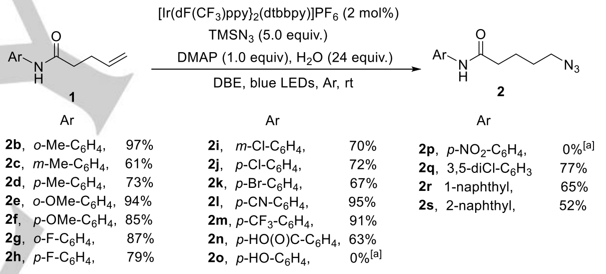


Entry	TMSN$_3$ (mmol)	DMAP (mmol)	H$_2$O (mmol)	Solv.	Yield of **2a** (%)
1	0.4	0.04	--	CH$_3$CN	10
2	0.4	--	--	PhCF$_3$	0
3	0.4	0.04	--	PhCF$_3$	23
4	0.4	0.2	--	PhCF$_3$	26
5	1.0	0.2	4.8	PhCF$_3$	53
6	1.0	0.2	4.8	toluene	23
7	1.0	0.2	4.8	CH$_2$Cl$_2$	56
8	1.0	0.2	0.6	CH$_2$Cl$_2$	46
9	1.0	0.2	56	CH$_2$Cl$_2$	36
10	1.0	0.2	4.8	DCE[b]	44
11	1.0	0.2	4.8	CHCl$_3$[b]	78
12	1.0	0.2	4.8	DBE[b]	87
13	1.0	0.1	4.8	DBE[b]	76
14	1.0	0.2	4.8	DBE	62
15	1.0	--	4.8	DBE[b]	48
16	1.0	--	--	DBE[b]	0[c]
17	1.0	0.2	4.8	DBE[b]	78
18	0.6	0.2	4.8	DBE[b]	48
19	0.8	0.2	4.8	DBE[b]	70
20[d]	1.0	0.2	4.8	DBE[b]	69
21[e]	1.0	0.2	4.8	DBE[b]	N. R.
22[f]	1.0	0.2	4.8	DBE[b]	N. R.
23	1.0	0.2	4.8	CH$_3$OH	N. R.
24	1.0	0.2	4.8	MeCN	Trace[g]

[a] The reactions were performed on a 0.2 mmol scale in 2 mL solvent under an argon atmosphere with 2 mol% of photocatalyst unless otherwise specified. The yields given are isolated yields. [b] The reaction was performed in 0.5 mL solvent. [c] **1a** decomposed. [d] 1 mol% of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ was used. [e] Control experiment in the dark. [f] Control experiment in the absence of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$. [g] Most of **1a** recovered. DCE = 1,2-dichloroethane; DBE = 1,2-dibromoethane.

It can be seen from Table 1 that the desired reaction took place in solvents such as PhCF$_3$, toluene, CH$_2$Cl$_2$, CHCl$_3$, 1,2-dichloroethane (DCE) and 1,2-dibromoethane (DBE), but not in CH$_3$OH. It is noteworthy that water exhibited conspicuous beneficial effect on the reaction. The reaction was also facilitated by DMAP, but it was not indispensable (entry 15). The reaction did not take place when both water and DMAP were absent (entry 16). Although DMAP helped to improve the yield, it also prolonged the reaction time to some extent (see Table 1 in Supporting Information (SI)). The best result was obtained in DBE (0.4 M for **1a**) under the conditions of 5.0 equiv. of TMSN$_3$, 1.0 equiv. of DMAP and 24 equiv. of water: not only the yield of **2a** was raised to 87%, the reaction also proceeded quite fast (3 h, entry 12). Besides TMSN$_3$, tetrabutyl ammonium azide and sodium azide were also tested, but they were literally ineffective under in the present circumstances (For detailed information about optimization of reaction conditions, see Tables 1 and 2 in Supporting Information (SI)).

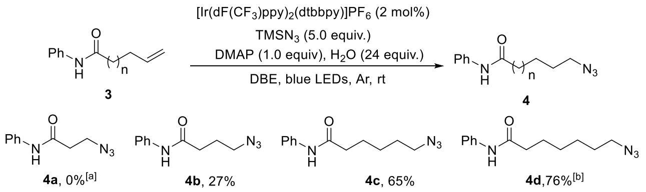
The optimized conditions (Table 1, entry 12) were then applied to variously unsaturated *N*-aryl amides to test the scope of this hydroazidation protocol, and the result is presented in Schemes 2-3 and Table 2. For γ,δ-unsaturated anilides bearing a substituent at the phenyl ring, the reaction took place smoothly in most cases, giving rise to the anti-Markovnikov products in good to excellent yields (Scheme 2). The only exceptions were substrates bearing a *p*-OH or *p*-NO$_2$ group, in which case the no desired products **2o** and **2p** were obtained.



The Reactions were conducted on a 0.2 mmol scale. The yields given are isolated yields.
[a] No reaction took place.

Scheme 2. Effect of substituent at the *N*-phenyl group.

Subsequent experiments revealed that the distance between the double bond and the amidyl group has a crucial effect on the reaction. As such, while compound **4c** and **4d** were obtained in good yield, the yield of **4b** dropped to 27%. Compound **4a**, on the other hand, cannot be formed from the corresponding precursor under the current conditions (Scheme 3).

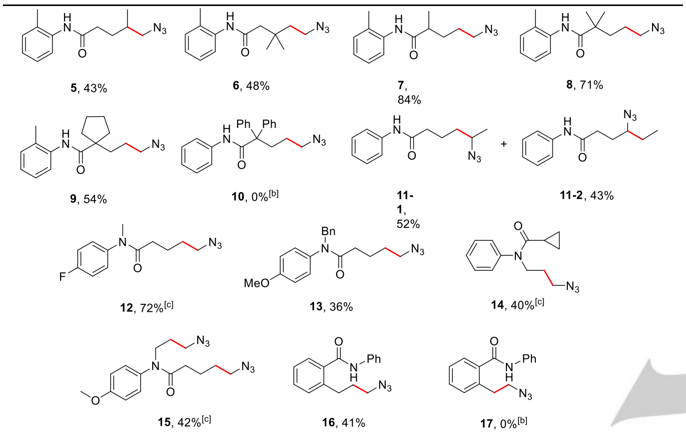


The Reactions were conducted on a 0.2 mmol scale unless otherwise specified. The yields given are isolated yields. [a] Substrate decomposed. [b] The reaction was performed on a 0.5 mmol scale.

Scheme 3. Effect of chain length in the unsaturated anilides.

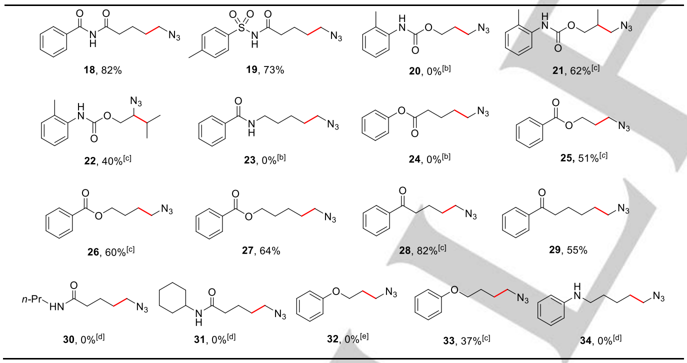
Variation of the substituent at other positions also influences the reaction consequence. As shown in Table 2, while this protocol is applicable to the preparation of compounds **5**-**9** and **11**-**16**, it is ineffective when used to prepare compounds **10**. For substrates bearing a terminal double bond, the reaction proceeded exactly in the anti-Markovnikov pattern. For substrates bearing an internal 1,2-disubsituted double bond, the azidyl was introduced to both positions in roughly the same efficacy (**11-1** and **11-2**). It is noteworthy that when an allyl group was tethered to the nitrogen group or to the *ortho*-position of the phenyl group, the carbon-carbon double bond was hydroazidated as well (**14**-**16**). *N*-phenyl-2-vinylbenzamide, on the other hand, cannot be converted under the same conditions.

Table 2. Scope of alkenes-1[a]



[a] The reactions were conducted on a 0.2 mmol scale unless otherwise specified. The yields given are isolated yields. [b] A complex mixture was generated. [c] The Reaction was performed on 0.5 mmol scale.

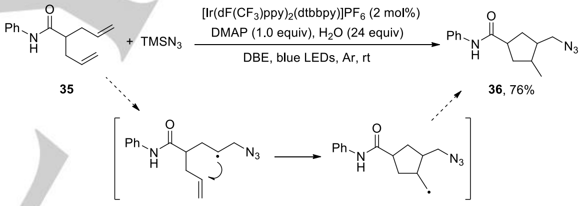
Table 3. Scope of alkenes-2[a]



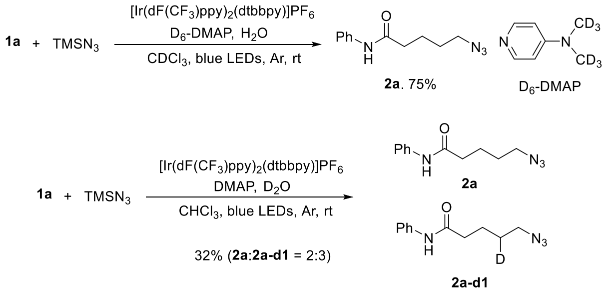
[a] The reactions were conducted on 0.2 mmol scale unless otherwise specified. The yields given are isolated yields. [b] Substrate decomposed. [c] The reaction was performed on 0.5 mmol scale. [d] A complex mixture was generated. [e] No reaction took place.

To further evaluate the scope of this method, more functionalized alkenes were subjected to this protocol, and the result is presented in Table 3. The method is applicable to the preparation of **18**, **19**, **21**, **22**, **25**-**29** and **33**, but failed in the cases of **23**, **24**, **30**-**32** and **34**. Styrene, allylbenzene, *N*-vinylbenzenesulfonamide, ethoxyethene, and limonene also cannot be hydroazidated in this way, for which either a complex mixture was obtained or substrates decomposed (See SI).

There are two possible mechanisms that might work for the present hydroazidation reactions. One involves the initial oxidation of $TMSN_3$ by the photoexcited iridium catalyst to generate the azidyl radical, which then adds onto the carbon-carbon double bond from the less substituted side.[11,19] The other is via the intermediacy of alkene radical cations generated by single-electron oxidation of the alkenes.[9,10] Both mechanism can explain the observed anti-Markovnikov selectivity. To see which mechanism operates under the current conditions, luminescence quenching experiments[20,21] were conducted with both $TMSN_3$ and **1a** as the quenchers (Figure 1 in SI). It was found that luminescence of the excited Ir[III] catalyst can be quenched by $TMSN_3$, While **1a** has no such effect. Subsequent cyclic voltammetry experiment shows that **1a** has a high oxidation potential (E_p = 1.65 V, vs SCE, see SI), and thus its oxidation by the photoexcited $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ ($E_{1/2}^{red}$[*Ir(III)/Ir(II) = +1.21 V vs SCE in MeCN][20,21] should be endergonic. $TMSN_3$, on the other hand, has an oxidation potential of 0.66 V (vs. SCE),[22] and can be oxidized by photoexcited $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$. Thus, we conclude that the present reactions probably proceeded following a mechanism where the azidation step involves addition of azidyl radical onto the alkene double bond to give a carbon radical. Evidence supporting the formation of this carbon radical can be found in the reaction of compound **35**, where cyclized product **36** was produced in good yield as a mixture of diastereoisomers (Scheme 4). Luminescence quenching experiments indicate that DMAP can also quench the excited state of the photocatalyst, and that explains why the reaction became slower in the presence of DMAP.

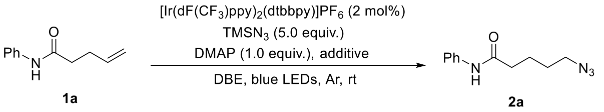


Scheme 4. Evidence supporting the involvement of a carbon radical.



Scheme 5. Experiment with deuterated reagents.

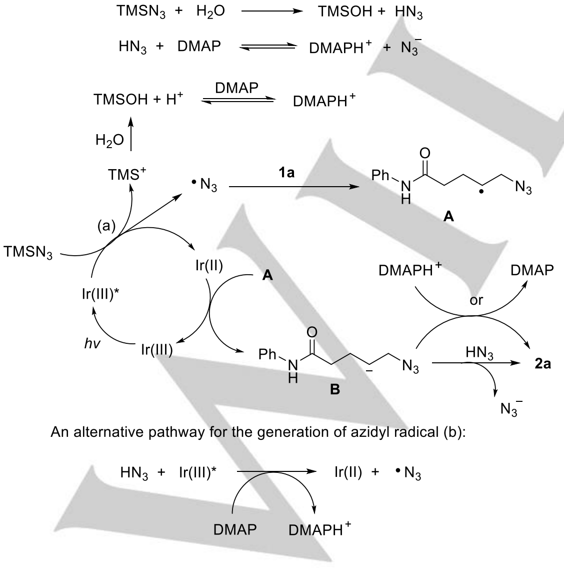
To determine where the added hydrogen atom in the products came from, experiments were conducted by using deuterated reagents. As shown in Scheme 5, the reaction was unaffected by the use of $CDCl_3$ and D_6-DMAP, whereas using D_2O in place of H_2O brought forth a big change: not only a deuterium atom was introduced into the product, the yield also decreased significantly. This result confirms that water is a source of the hydrogen atom that appears in the product, probably brought in via protonation. Organic acids such as acetic acid and benzoic acid are also effective proton donors for the reaction (Scheme 6), but they were detrimental to the reaction when used in large amount.



Additive (equiv.)	Yield
acetic acid (5.0)	71%
acetic acid (24)	57%
benzoic acid (5.0)	60%
benzoic acid (24)	30%

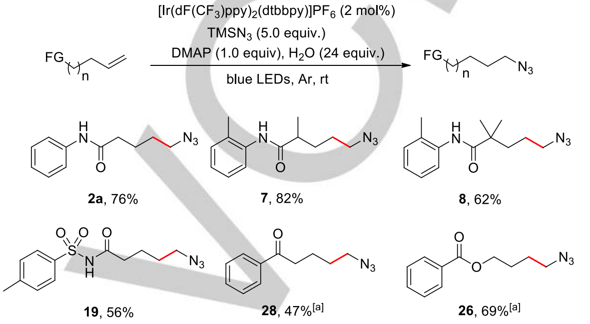
Scheme 6. Reaction of **1a** in the presence of an acid.

On the basis of these primary mechanistic investigations, a plausible mechanism is proposed to rationalize the observed results. As illustrated in Scheme 7 with **1a** taken as an example, the initiation step is believed to be the oxidative generation of azidyl radical from $TMSN_3$ by the action of photoexcited $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$. As $TMSN_3$ can react readily with H_2O to form HN_3 and TMSOH, it is also possible that the azidyl radical derives from HN_3 via single electron oxidation (path (b)). The azidyl radical then adds onto **1a** to give carbon radical **A**. Subsequent single electron transfer (SET) between **A** and the reduced iridium (II) catalyst affords carbon anion intermediate **B,** from which product **2a** is formed by capturing a proton from HN_3. Meanwhile the photocatalyst is recovered and enters into the next catalytic cycle.[23] As the yield of **2a** decreased considerably when D_2O was used in place of H_2O (Scheme 5), there must exist some other pathways to compete with the last protonation step. The protonation needs to be fast to guarantee a clean transformation and high yield; using D_2O would slow down protonation of **B**, thus resulting in decrease of the yield. This protonation step, on the other hand, might be facilitated by DMAP, which can act as proton carrier ($DMAPH^+$) to transfer it to intermediate **B** in the organic phase.



Scheme 7. Proposed mechanism.

As shown in Table 1, the reactions are quite sensitive to the reaction media, with DBE and $CHCl_3$ being superior to other solvents. Initially we speculated that the beneficial effect of these two solvents might be caused by their participation in the reactions as electron acceptor. However, subsequent experiments show that the reactions can take place as well under solvent free conditions as long as water is used (Scheme 8). Thus, we conclude that this beneficial effect is mainly related to their solvating capacity.



The reactions were conducted on a 0.2 mmol scale unless otherwise specified. [a] The Reaction was performed on 0.5 mmol scale.

Scheme 8. Reactions under solvent-free conditions.

In summary, we have developed a photochemical protocol for the anti-Markovnikov hydroazidation of unactivated alkenes. The reactions were implemented by means of visible light photoredox catalysis with $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as photocatalyst and trimethylsilyl azide as azidating agent. Water was found to exhibit a crucial beneficial effect on the reaction, which can be attributed to its role as hydrogen donor. This method provides a simple and straightforward means to convert terminal alkenes to structurally important primary azides. Notably, the present reactions can take place as well under solvent-free conditions, which is highly preferable from the point of view of green chemistry.[24] Further work is being done in our laboratory to improve on the reactions and expand the scope of this method.

Acknowledgements

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Keywords: hydroazidation • photoredox catalysis • radical reactions • trimethylsilyl azide • water

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Entry for the Table of Contents

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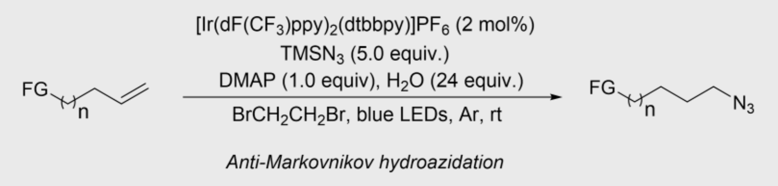

Text for Table of Contents

*Juan-juan Wang, Wei Yu**

Page No. – Page No.

Anti-Markovnikov Hydroazidation of Alkenes by Visible Light Photoredox Catalysis