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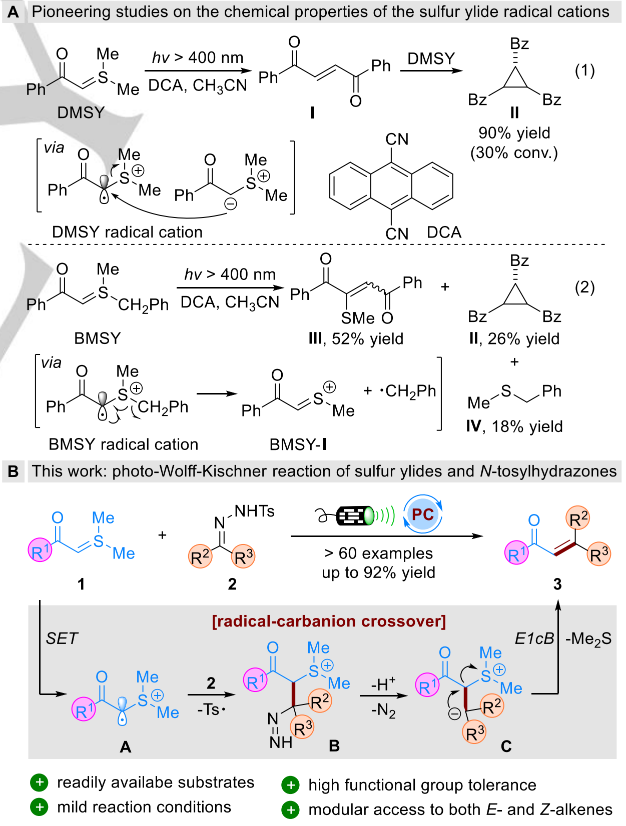
Alkene Synthesis by Photo-Wolff-Kischner Reaction of Sulfur Ylides and *N*-Tosylhydrazones

*Pan-Pan Gao, Dong-Mei Yan, Ming-Hang Bi, Min Jiang, Wen-Jing Xiao, and Jia-Rong Chen**

Abstract: *A visible-light-driven and room temperature photo-Wolff-Kischner reaction of sulfur ylides and N-tosylhydrazones has been developed for the first time to provide modular access to alkene synthesis. The high functional group tolerance and broad substrate scope were demonstrated by more than 60 examples. Both E- and Z-olefinic stereochemistry in the products could be controlled with excellent stereoselectivity. A series of mechanistic studies support that the reaction should proceed through a radical-carbanion crossover pathway, specifically involving addition of photo-generated sulfur ylide radical cations to N-tosylhydrazones to form carbanions and subsequent Wolff-Kischner process.*

Sulfur ylides, firstly reported in 1930 by Ingold and Jessop,[1] are a class of zwitterionic compounds characterized by a carbanion and a neighboring positively charged sulfur atom. Since the pioneering establishment of the synthetic prowess of these compounds in the Johnson−Corey−Chaykovsky epoxidation and cyclopropanation reactions,[2] the application of sulfur ylides as versatile one-carbon synthons in organic chemistry has undergone tremendous growth over the past decades, owing to their inherent unique chemical properties.[3] Many of these classical reactions have become textbook knowledge. Surprisingly, in sharp contrast to these ionic chemistry, the use of sulfur ylide radical cations, generated from the corresponding sulfur ylides by one-electron oxidation, in radical synthetic chemistry has been largely ignored.[4,5] The main reason may be attributed to the fact that the chemical properties of sulfur ylide radical cation depend primarily on the nature of the substituents on the sulfur, which often results in the formation of complex mixtures through various decomposition pathways. For example, Schuster was the first to investigate the reactivity modes of phenacyl sulfur ylides under photosensitization (λ> 400 nm) with 9,10-dicyanoanthracene (DCA) as the photocatalyst.[6] It was found that the outcome of the reactions depends remarkably on the structures of sulfur ylides because sulfur ylide radical cations were involved as the same intermediates (Scheme 1A). For instance, the DCA-sensitized photolysis of dimethylsulfur phenacylide (DMSY) led to formation of *trans*-1,2,3-benzoylcyclopropane **II** in 90% yield with 30% conversion via 1,2-dibenzoylethylene intermediate **I**, which is formed through nucleophilic attack of sulfur ylide radical cation by another molecule of DMSY [Eq. (1)]. By contrast, the reaction of benzylmethylsulfur phenacylide (BMSY) under the otherwise same conditions produced mixtures of 1,2-(dibenzoyl)vinyl methyl sulfide **III** (52%), *trans*-1,2,3-benzoylcyclopropane **II** (26%), and minor benzylmethyl sulfide (18% yield), indicative of different pathway of BMSY-derived sulfur ylide radical cation [Eq. (2)]. Specifically, BMSY sulfur ylide radical cation can undergo hemolytic C-S bond cleavage to form cation BMSY-**I** predominantly with release of benzylic radical; then the cation reacts with another molecule of sulfur ylide to lead to major 1,2-(dibenzoyl)vinyl methyl sulfide **III**. Despite these inspiring studies on the chemical properties of phenacyl sulfur ylide radical cations, surprisingly, the synthetic applications of such radical species have long been unexplored.



Scheme 1. Chemical properties of sulfur ylide radical cation and new reaction design. DMSY = dimethylsulfur phenacylide, BMSY = benzylmethylsulfur phenacylide, DCA = 9,10-dicyanoanthracene, PC = photoredox catalysis.

Our research group is actively involved in developing valuable photoredox-catalyzed synthetic methods proceeding through radical pathways.[7,8] Furthermore, our continued interest in photocatalytic transformation of hydrazones[9] and inspiration

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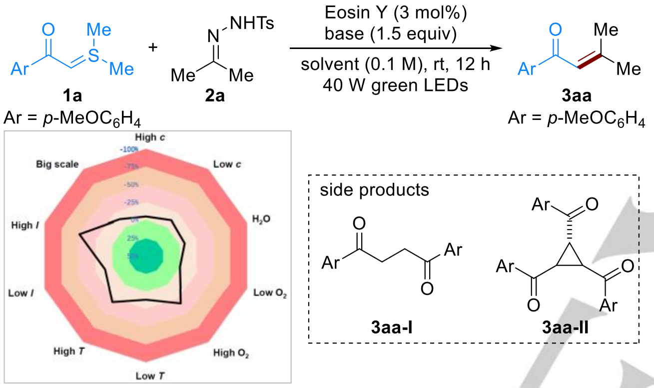
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) from the chemical and structural properties of sulfur ylide radical cations led to a novel route being envisioned for the modular access to alkenes by photo-Wolff-Kischner process (Scheme 1B). We assumed that adding a photo-generated sulfur ylide radical cation **A** to a hydrazone, and subsequent fragmentation of an arenesulfonyl radical could provide a diazene intermediate **B**. Then, intermediate **B** undergoes Wolff-Kischner-type N_2 extrusion to form carbanion **C**, which would undergo an *E1cB* elimination to afford alkene with loss of dimethyl sulfide. The feasibility of our design plan is corroborated by a recent study of König and co-workers, who demonstrated that trap of sulfur-centered radicals by *N*-sulfonyl hydrazones allowed formation of α–functionalized carbanion *via* a Wolff-Kischner process, thus leading to its subsequent intermolecular coupling with electrophilic CO_2 and aldehydes.[10] However, several competing reactions need to be overcome to achieve the desired reaction, such as 1) a range of sulfur ylide di- and trimerizations well established by Schuster;[6] 2) possible formation of hydrazonyl radicals observed in previous reports.[9]

Table 1: Optimization of the reaction conditions.[a]



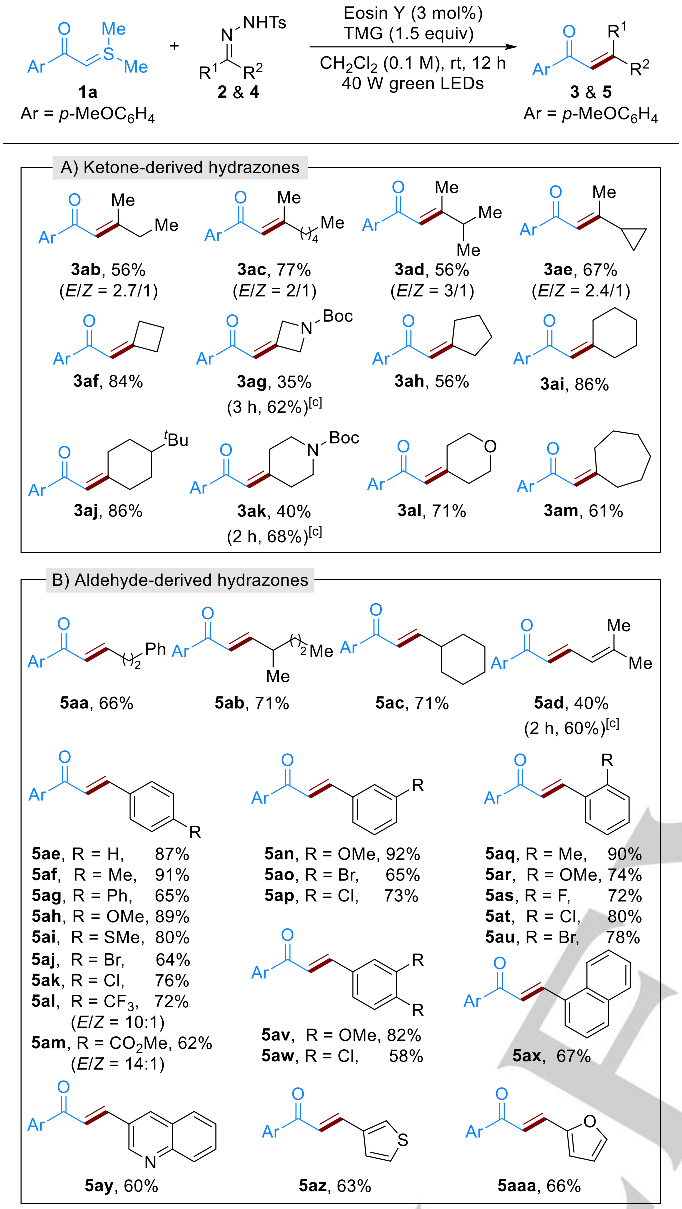
Entry	Base	Solvent	Conv [%][b] **2a**	Yield [%][b] **3aa-I/3aa-II**	Yield [%][b] **3aa**
1[c]	K_2CO_3	CH_2Cl_2	83	<5/25	46
2	DMAP	CH_2Cl_2	37	20/<5	36
3	DIPEA	CH_2Cl_2	<5	33/<5	<5
4	Et_3N	CH_2Cl_2	<5	13/<5	<5
5	TMG	CH_2Cl_2	>95	21/<5	95
6	DBU	CH_2Cl_2	64	37/<5	60
7	TMG	THF	>95	19/<5	95
8	TMG	MeCN	78	42/<5	78
9	TMG	Acetone	90	44/<5	80
10[d]	TMG	CH_2Cl_2	>95	18/<5	95 (81)
11[d]	-	CH_2Cl_2	68	<5/<5	29
12[d,e]	TMG	CH_2Cl_2	<5	<5/<5	<5
13[d,f]	TMG	CH_2Cl_2	<5	<5/<5	<5
14[d,g]	**TMG**	**CH_2Cl_2**	**>95**	**17/<5**	**95 (83)**
15[h]	TMG	CH_2Cl_2	>95	N.D.	(68)
16[d,g,i]	TMG	CH_2Cl_2	80	35/<5	(74)

[a] Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), Eosin Y (3 mol%), base (0.15 mmol, 1.5 equiv), solvent (1.0 mL), 40 W green LEDs (λ = 525 nm), Ar, rt, 12 h. [b] NMR yields with 1,3,5-trimethoxybenzene as an internal standard; values in parentheses are isolated yield. [c] Under irradiation of 7 W blue LEDs (λ = 455 nm). [d] Use of 1.2 equiv of **1a**. [e] Without Eosin Y. [f] Without visible-light irradiation. [g] 0.2 mmol scale. [h] Gram-scale: **1a** (15.0 mmol), **2a** (10.0 mmol, 1.5 equiv), 24 h. DMAP = 4-Dimethylaminopyridine. DIPEA = *N*,*N*-Diisopropylethylamine. TMG = 1,1,3,3-Tetramethylguanidine. DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene. N.D. = Not determined. [i] Use of 10 W green LEDs (λ = 525 nm).

We commenced the study by employing sulfur ylide **1a** and acetone-derived *N*-tosylhydrazone **2a** as model substrates for the condition optimization (Table 1).[11] Pleasingly, the target reaction indeed worked to afford the desired product **3aa** in 46% NMR yield, when using cost-effective Eosin Y as a photocatalyst under irradiation of 7 W blue LEDs at room temperature (entry 1).[12] In agreement with Schuster's study,[6] a significant amount of byproduct *trans*-1,2,3-benzoylcyclopropane **3aa-II** was also observed, which should be formed from three molecules of sulfur ylides. In contrast, irradiation of the reaction mixture with 40 W green LEDs in the presence of DMAP as a base resulted in a lower yield of **3aa**, while 1,4-diketone **3aa-I** was observed as the major byproduct instead (entry 2). With these challenges in mind, we then examined a range of organic bases (entries 3-6), and found that the base has played a crucial role in the reaction, with TMG being the best of choice (entry 5). Though the formation of byproduct **3aa-I** could not be fully suppressed, full conversion of **2a** and almost quantitative yield of **3aa** were achieved. A brief screening of solvents revealed that CH_2Cl_2 and THF were optimal, compared to MeCN and acetone (entries 8 and 9). When the equivalent ratio of **1a** to **2a** was decreased to 1.2:1, no loss of efficiency was observed and **3aa** was isolated in 81% yield (entry 10). Without addition of TMG, the conversion of **2a** dropped substantially, leading to **3aa** in only 29% yield (entry 11). As expected, in the absence of either the Eosin Y or visible-light irradiation, no desired product **3aa** was detected (entries 12 and 13). These results confirmed that each component is essential for the reaction. When performed on a 0.2 mmol scale reaction, comparable results were obtained (entry 14). Notably, when the reaction was performed at 10.0 mmol, product **4aa** can still be obtained in 68% isolated yield (1.3 g), highlighting the scalability of this protocol (entry 15). Decrease of the light intensity from 40 W to 10 W under otherwise same conditions led to lower conversion, giving **3aa** in 74% yield (entry 16). In order to explore the reproducibility and potential of this new photo-Wolff-Kischner reaction, we also performed condition-based sensitivity assessment developed by Glorius.[13] The intuitive, standardized presentation of the results in a radar diagram revealed that the reaction is only medium sensitive to light intensity, temperature and oxygen concentration (see Section 4 in the Supporting Information).

Following optimization, the generaltiy of the reaction was firstly explored by reacting **1a** with various *N*-tosylhydrazones on a 0.2 mmol scale (Table 2). As summarized in Table 2A, a range of acyclic linear and α-branched aliphatic ketone-derived *N*-tosylhydrazones **2b-e** reacted smoothly with **1a**, giving the corresponding trisubstituted alkenes **3ab-ae** in reasonable yields with moderate *E*/*Z* ratios. Moreover, a series of *N*-tosylhydrazones **2f-m**, easily prepared from the related cyclic and heterocyclic ketones with various sizes, were all well accommodated. Products **3af-am** were afforded with moderate to good yields. As shown in the synthesis of **3ag** and **3ak**, the reaction efficiency could be significantly enhanced when performed in continuous-flow reactors,[14] increasing the yields to 62% and 68%, respectively.[11] Compared with the Vedejs' ionic strategy of alkene synthesis that relied on condensation of aldehyde-derived *N*-tosylhydrazones with stablilized carbanions in the presence of strong base,[15] good tolerance of these enolizable ketone-derived *N*-tosylhydrazones demonstrates obvious advantages of the current reaction system.

Table 2: Scope of the *N*-tosylhydrazones.[a,b]



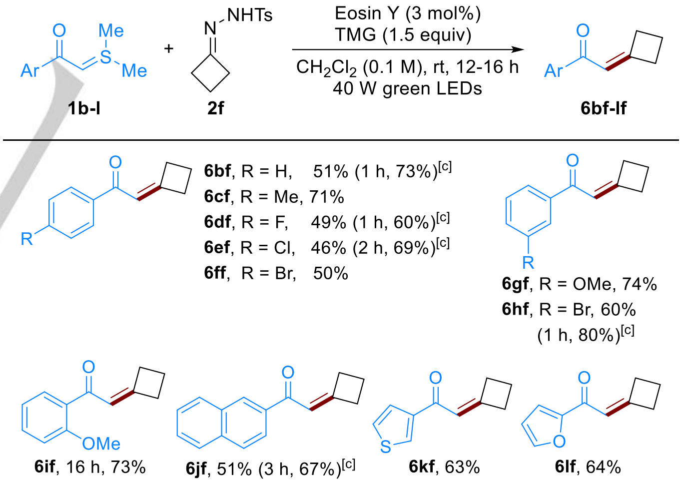
[a] Reaction conditions: **1a** (0.3 mmol), **2** or **4** (0.2 mmol), Eosin Y (3 mol%), base (0.15 mmol, 1.5 equiv), solvent (1.0 mL), 40 W green LEDs (λ = 525 nm), Ar, rt, 12 h. [b] Isolated yields. [c] Performed in continuous-flow reactors.

Gratifyingly, the catalytic system could be further extended to a wide variety of aldehyde-derived *N*-tosylhydrazones (Table 2B). For instance, the reactions of substrates **4a-c** prepared from linear, α-substituted and cyclic aliphatic aldehydes all worked well to produce 1,2-disubstituted alkenes **5aa-ac** with useful yields (66-71%). *N*-Tosylhydrazone **4d** derived from α,β-unsaturated aldehyde also proved to be suitable partner for the synthesis of valuable 1,3-dienes.[16] Then, we proceeded to examine an array of aromatic aldehyde-derived *N*-tosylhydrazones. It was found that a variety of electron-neutral, electron-donating (e.g., Me, Ph, OMe, SMe), and electron-withdrawing (e.g., Br, Cl, CF_3, CO_2Me) functional groups at the *para*-, *meta*-, or *ortho*-position of the phenyl ring were well tolerated. The desired 1,2-disubstituted alkene products **5ae-5au** were isolated with yields ranging from 62-92% and excellent *E*/*Z* selectivity. These examples also revealed that the substitution pattern of the phenyl ring has no obvious effect on the reaction.

Remarkably, these products bearing halogen atoms (Cl, Br) on the phenyl ring also provide an easy handle for further synthetic elaboration at the respective positions. Again, substrates **4v** and **4w** with 3,4-disubstituted phenyl ring were also compatible with reaction, affording **5av** and **5aw** with good yields. *N*-Tosylhydrazones **4x** having sterically demanding 1-naphthyl group and **4y-aa** with heteroaromatic ring such as quinoline, thiophene, and furan all participated in the reaction well, with the expected products **5ax-aaa** being obtained in satisfactory yields.

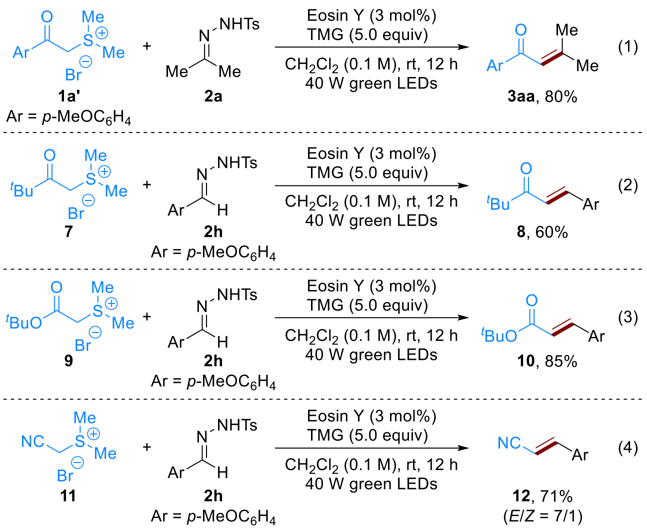
Encouraged by these results, we continued to simply evaluate the generality of this photo-Wolff-Kischner reaction by employing a representative range of sulfur ylides, which can be easily prepared from the α–bromo carbonyl compounds over two steps. As shown in Table 3, the reaction demonstrated a broad substrate scope and good functional group tolerance. Aside from **1a**, sulfur ylides **1b-h** with electron-neutral, electron-donating and electron-withdrawing substituent at the *para*-, *meta*- or *ortho*-position of the phenyl ring all reacted well with **2f**. The desired alkene products **6bf-if** were produced with moderate to good yields. Though the substrates with electron-donating groups resulted in higher yields, as shown in some cases (e.g., **6bf**, **6df-ef**, **6hf**), application of the technology of continuous-flow photochemistry to the substrates with electron-withdrawing groups at the aromatic ring also substantially improved the reaction efficiency compared to these performed in batch reactor. It is noteworthy that the reaction of 2-naphthyl-substituted sulfur ylide **1j** as well as 3-thiophenyl- and 2-furanyl-substituted sulfur ylides **1k** and **1l** also proved to be viable substrates for the reaction, giving **6jf-lf** with modest yields.

Table 3: Scope of the sulfur ylides.[a,b]



[a] Refer to footnote [a] of Table 2 with 1.5 equiv of **1b-l**. [b] Isolated yield. [c] Performed in continuous-flow reactors.

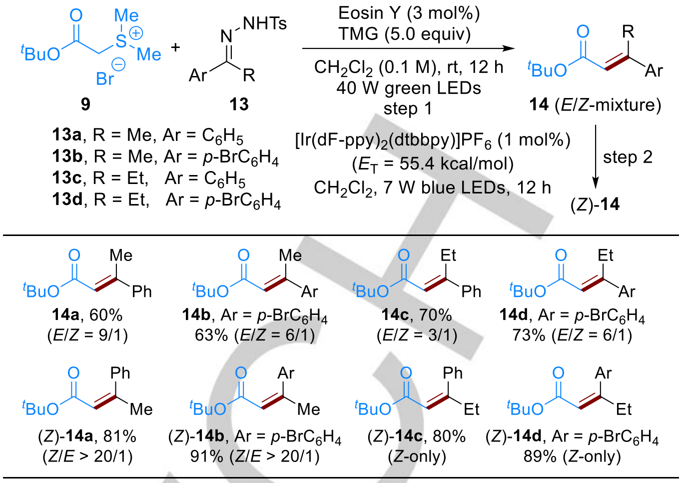
To further demonstrate the practicality of this protocol, we attempted to use sulfonium salts directly as precursors for *in situ* generation of the relevant sulfur ylides (Scheme 2). For example, upon slight increase of the base loading (5 equiv), the reaction between sulfonium salt **1a'** and **2a** also worked well to give product **3aa** with comparable yield [Scheme 2, Eq. (1)]. As a result, this one-pot process would allow the direct use of their precursors of certain otherwise-difficult-to-access sulfur ylides. As such, we further reacted sulfonium salts **7** and **9** that were prepared from 1-bromopinacolone and *tert*-butyl bromoacetate with *N*-tosylhydrazone **2h**; and the desired (*E*)-α,β–unsaturated ketone **8** and ester **10** were obtained exclusively with high yields [Scheme 2, Eq. (2) and (3)]. Notably, bromoacetonitrile-derived sulfonium salt **11** also proved to competent substrate, giving the corresponding valuable (*E*)-arylacrylonitrile **12** in 71% yield [Scheme 2, Eq. (4)].



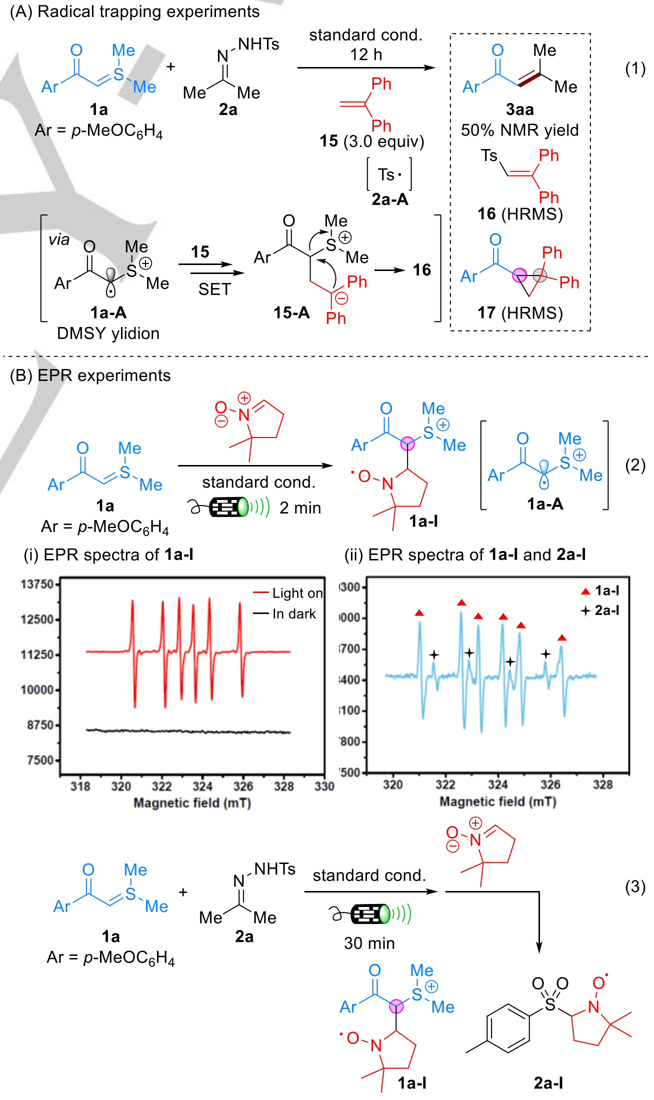
Scheme 2. Photo-Wolff-Kischner reaction of sulfonium salts and *N*-tosylhydrazones. Use of 5 equiv of sulfonium salts.

In recent years, visible-light-driven photosensitization has been established as a robust tool for switching of the *cis*/*trans* selectivity of alkenes.[17] In particular, isomerization-based strategies to enable stereodivergent construction of (*E*)- and (*Z*)-isomers of target alkenes from the identical set of starting materials remain conspicuously underdeveloped. Thus, we turned our attention to the development of a sequential photo-Wolff-Kischner reaction and geometrical isomerization for synthesis of (*Z*)-alkenes by merger visible-light-driven single-electron-transfer (SET) and energy transfer catalysis.[18] To our delight, as shown in Table 4, sulfonium salt **9** reacted well with a series of sterically congested arylalkyl ketone-derived *N*-tosylhydrazones **13a-d** under photo-Wolff-Kischner reaction conditions. The corresponding trisubstituted α,β-unsaturated esters **14a-d** were produced in good yields (60-73%) with *E*-selectivity. Notably, when these alkenes were further subjected to a catalytic amount of photocatalyst [Ir(dF-ppy)$_2$(dtbbpy)]PF_6 (1 mol%) under irradiation of 7 W blue LEDs for 12 h, the corresponding thermodynamically unfavored α,β-unsaturated esters (*Z*)-**14a-d** were obtained with 80-91% yields and excellent *Z*-selectivity (*Z*/*E*>20:1). These results showed that both *E*- and *Z*-olefinic stereochemistry in the products could be accessible by simple combination of photocatalytic systems. When we tried to use photocatalyst [Ir(dF-ppy)$_2$(dtbbpy)]PF_6 alone to promote both steps, surprisingly, it was found that such a catalyst showed lower overall reaction efficiency (47% yield, *Z*/*E* = 5/1) (results not shown).

Table 4: Visible-light-driven sequential Photo-Wolff-Kischner reaction and isomerization for synthesis of *Z*-alkenes.[a,b,c]



[a] Conditions of Step 1: **8** (0.3 mmol), **2a** (0.2 mmol), Eosin Y (3 mol%), TMG (1.0 mmol, 5.0 equiv), CH_2Cl_2 (2.0 mL), 40 W green LEDs (λ = 525 nm), Ar, rt, 12 h. Conditions of Step 2: **13** (0.2 mmol), Ir(dFppy)$_2$(dtbbpy)PF_6 (1 mol%), CH_2Cl_2 (2.0 mL), 7 W blue LEDs, 12 h. [b] Isolated yield. [c] *E*/*Z* ratio was determined by ^{1}H NMR analysis of the crude mixture.

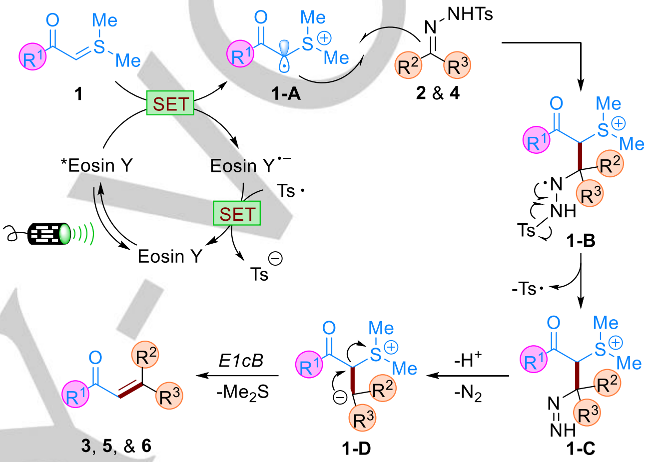


Scheme 3. Mechanistic studies. (A) Radical trapping experiments. (B) EPR experiments. (i) EPR spectra of 1**a-I**. (ii) EPR spectra of **1a-I** and **2a-I**.

To gain some insight into the mechanism, we conducted a series of experimental mechanistic investigations (Scheme 3). When stoichiometric radical acceptor, 1,1-diphenylethylene **15**, was added to the model reaction of **1a** and **2a** under the standard conditions, the yield of product **3aa** dropped drastically [Scheme 3A, Eq. (1)]. However, tosyl-substituted 1,1-diphenylethylene **16** and cyclopropane **17** were detected by HMRS, which implied that sulfonyl radical **2a-A** and sulfur ylide radical cation **1a-A** might be involved in the process. We postulated that cyclopropane **17** should be formed by radical addition of **1a-A** to **15**, followed by SET reduction and intramolecular cyclization. Addition of stoichiometric TEMPO as radical scavenger inhibited the formation of **3aa** completely, further suggesting that the reaction may involve a radical process (see Section 6.2 in the Supporting Information).[11]

To further confirm a radical pathway that might be engaged in this photo-Wolff-Kischner reaction, we then exploited electron paramagnetic resonance (EPR) in the presence of a radical spin-trap agent, 5,5-dimethyl-pyrroline *N*-oxide (DMPO), to trap radical species possibly involved in the process (Scheme 3B). In a mixture of **1a** and DMPO performed under standard conditions for 2 min, the formation of persistent radical adduct **1a-I** was identified according to EPR signals with six lines ($g = 2.0041$; $A_N = 1.45$ mT, $A_H = 2.21$ mT), implying the involvement of radical intermediate, sulfur ylide radical cation **1a-A** [Scheme 3B, Eq. (2)]. Moreover, with addition of DMPO to the model reaction of **1a** and **2a** that was firstly irradiated for 30 min, two sets of EPR signals were observed [Scheme 3B, Eq. (3)]. Specifically, signals with six lines ($g = 2.0041$; $A_N = 1.45$ mT, $A_H = 2.21$ mT) were identified as EPR signals of adduct **1a-I**, while signals with four lines ($g = 2.0044$; $A_N = 1.45$ mT, $A_H = 1.42$ mT) were observed and identified as adduct **2a-I**, respectively. All of these results confirmed the formation of sulfur ylide radical cation **1a-A** and sulfonyl radical **2a-A**. Moreover, Schuster previously reported that aryl sulfur ylides demonstrated an irreversible one-electron wave with a peak at around +0.5 V,[6] which means that the excited-state *Eosin Y ($E_{1/2}^{red}$ = +0.83 V *vs* SCE) is sufficiently oxidizing to undergo SET reduction by the sulfur ylides to give the corresponding radical species. We also carried out Stern−Volmer luminescence quenching experiments of the photocatalyst Eosin Y using each reaction component (see Figure S3 in the Supporting Information).[11] It was found that that it is only the sulfur ylide that can efficiently quench the excited photocatalyst. Collectively, these observations suggested that the photocatalytic cycle should commence with SET oxidation of sulfur ylide in a reductive quenching photocatalytic cycle. The quantum yield of the model reaction was determined to be $\phi = 0.341$, which suggested a truly photocatalytic pathway though a short radical chain cannot be excluded.[11]

On the basis of the above experimental evidence and mechanistic pathways reported about the reactivity mode of carbanion in Wolff−Kishner reaction,[10,19] we postulated a plausible mechanism as depicted in Scheme 4 for the current photo-Wolff-Kischer reaction. Initially, the reaction begins with a SET-mediated oxidation of sulfur ylide **1** by the photoexcited *Eosin Y, affording the radical species sulfur ylide radical cation **1-A** and the reduced form of the photocatalyst (Eosin Y$^{\cdot-}$), respectively. Subsequent radical addition of electrophilic sulfur ylide radical cation **1-A** to the C=N bond of *N*-tosylhydrazones forms the aminyl radical intermediate **1-B**.[20] Then, the intermediate **1-B** undergoes a homolytic N-S bond fragmentation to generate leaving group-containing diazene intermediate **1-C** with release of arylsulfonyl radical.[21] Upon base-mediated deprotonation, **1-C** further undergoes a Wolff−Kishner type N_2 extrusion process to give zwitterionic species **1-D**. Another SET transfer from the reduced form of the photocatalyst to arylsulfonyl radical to furnish a sulfinate anion with regeneration of the ground state photocatalyst Eosin Y, closing the photocatalytic cycle. Finally, an intramolecular *E1cB* elimination of **1-D** occurred to give the alkene products with release of dimethyl sulfide. Taken together, key to the success of the reaction was the modulating the reactivity mode of photo-generated sulfur ylide radical cations and the radical-carbanion crossover mechanism.[22] Notably, the overall reaction is redox-neutral process and does not need any external oxidant.



Scheme 4. Proposed mechanism for the photo-Wolff-Kischer alkene synthesis.

In summary, we have developed for the first time a visible-light-driven photo-Wolff-Kischner reaction for the practical and modular access to diverse alkenes, starting from readily available and bench-stable sulfur ylides and *N*-tosylhydrazones. The high functional group tolerance and broad substrate scope were demonstrated by more than 60 examples. Both *E*- and *Z*-olefinic stereochemistry in the products could be controlled with excellent stereoselectivity. A series of mechanistic studies support that the reaction was enabled by control the chemical property of sulfur ylide radical cations and a radical-carbanion crossover mechanism. Thus, this strategy opened a new way for the exploration of sulfur ylides in synthetic radical chemistry. Studies in this area are currently underway in our laboratory.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

Keywords: photoredox catalysis • hydrazones • radical reactions • sulfur ylides • photo-Wolff-Kischner reaction

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Layout 2:

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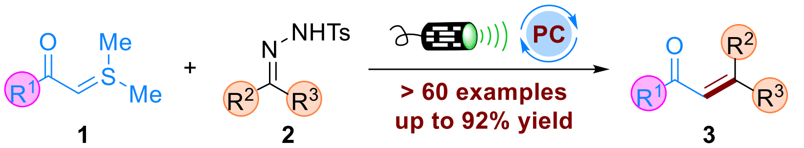

- readily availabe substrates
- mild reaction conditions
- high functional group tolerance
- modular access to both *E*- and *Z*-alkenes

P.-P. Gao, D.-M. Yan, M.-H. Bi, M. Jiang, W.-J. Xiao, J.-R. Chen*

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Alkene Synthesis by Photo-Wolff-Kischner Reaction of Sulfur Ylides and N-Tosylhydrazones

A visible-light-driven and room temperature photo-Wolff-Kischner reaction of sulfur ylides and *N*-tosylhydrazones has been developed for the first time to provide modular access to alkene synthesis. The high functional group tolerance and broad substrate scope were demonstrated by more than 60 examples. Both *E*- and *Z*-olefinic stereochemistry in the products could be controlled with excellent stereoselectivity. A series of mechanistic studies support that the reaction should proceed through a radical-carbanion crossover pathway, specifically involving addition of photo-generated sulfur ylide radical cations to *N*-tosylhydrazones to form carbanions and subsequent Wolff-Kischner process. PC = photoredox catalysis. SET = single-electron transfer.