Advanced
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To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701200

Link to VoR: http://dx.doi.org/10.1002/adsc.201701200

DOI: 10.1002/adsc.201((will be filled in by the editorial staff))

Sunlight-promoted direct irradiation of N-centred anion: the photocatalyst-free synthesis of pyrazoles in water

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Received: ((will be filled in by the editorial staff))

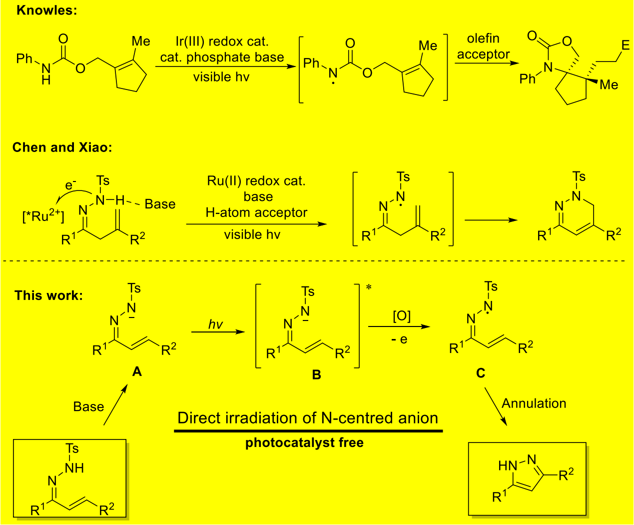
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.((Please delete if not appropriate))

Abstract. A practical method through sunlight mediated annulation of *α*, *β*-unsaturated hydrazones has been developed for the synthesis of pyrazole. Based on the analysis of UV-Vis absorption of the substrate, the reaction was designed to avoid the use of external photocatalysis and proceeds via direct irradiation of N-centred anion by sunlight. The key features of this reaction include operational simplicity, readily available reagents, and amenability to gram-scale synthesis.

Keywords: Sunlight-promoted; Photocatalyst-free; *N*-Radical; Pyrazole; Reaction in water

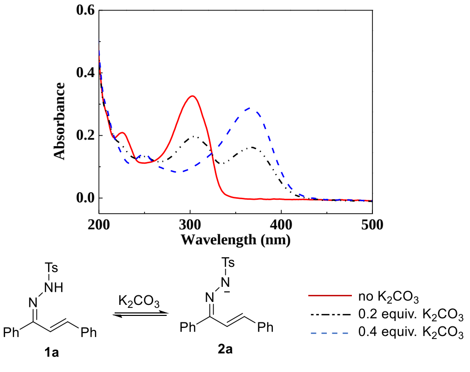
Pyrazole is a very important structural moiety frequently encountered in agrochemicals, pharmaceuticals, materials science, and synthetic chemistry. [1] In particular, a number of pyrazole-containing compounds exhibit a wide spectrum of therapeutic application and have progressed to the market, such as Celebrex[2a,b], Acomplia[2c], and Viagra[2d]. Owing to their prominent properties, pyrazoles have attracted much attention, and various procedures for their syntheses have been developed. [3] The most commonly used approaches for the acquisition of substituted pyrazoles is the condensation of hydrazine with 1, 3-dicarbonyl or α, β-unsaturated carbonyl compounds, and [3 + 2] cycloadditions of 1,3-dipoles to dipolarophiles like alkenes and alkynes. However, these methods have their own safety, eco-friendliness, scope, or efficiency limitations and usually involve reaction conditions like elevated temperature, microwave irradiation, transition-metal and hazard oxidants, which are contrary to the concept of green chemistry. Accordingly, synthetic methods for polysubstituted pyrazoles with high selectivity employing mild and green conditions are highly desirable.

Visible light photoredox catalysis (VLPC) has been demonstrated to be a powerful tool in synthetic organic chemistry over the last decade.[4,5] As an inexpensive, abundant, renewable, and non-polluting light source, sunlight can be applied in light activated reactions, which represents an ideal way for the development of green synthetic methods.[6,7] In 2008, Yoon group developed an efficient sunlight-promoted Ru-catalyzed formal [2+2] enone cycloaddition reaction for the synthesis of cyclobutane-containing bicyclic dione.[8] Jiao group reported an aerobic oxidation of benzyl halides in the presence of $Ru(bpy)_3Cl_2$ irradiated by sunlight.[9] Additionally, elegant works by Wang[10] and Hashmi[11] demonstrated the possibility of radical alkynylation coupling reaction driven by sunlight in the presence of hypervalent iodine reagent and gold catalyst. Most recently, Pan group reported a sunlight-driven catalyst-free cascade radical iodination and cyclization reaction of aryl alkynoates with *N*-iodosuccinimide, providing a green pathway to 3-halocoumarins derivatives. [12] On the other side, the use of visible-light photocatalysis in generating N-centred radicals by N–H bond activation began to receive increasing academic attention. The Knowles' group recently reported an elegant combination of iridium photocatalyst and phosphate base for a direct homolytic cleavage of strong N–H bonds of N-arylamides to access amidyl radicals by a concerted proton coupled electron transfer, which allowed an efficient radical cascade reaction towards N-heterocycle synthesis[13] The Chen and Xiao's group reported a visible-light photocatalytic oxidative deprotonation electron transfer/TEMPO-mediation strategy for catalytic N-radical cascade reaction of unsaturated hydrazones to synthesize 1,6-dihydropyradazines.[14] As a continuation of our interest in developing green synthetic method for heterocycles,[15] we hypothesized that the *N*-centred anion A generated from corresponding hydrazone could be directly irradiated by visible-light to its excited state **B** due to the red shift of the UV-Vis absorption. In the presence of electron acceptor, **B** would lose one electron to form radical **C**, which could undergo radical annulation to form pyrazole (Scheme 1).



Scheme 1. Application of visible-light photocatalysis in generating N-centred radicals.

At the outset of our investigation to assess the validity of this hypothesis, the UV-Vis absorption of hydrazone **1a** was studied. As shown in scheme 2, hydrazone **1a** has a maxim absorption at 302 nm which probably accounts for the $n\rightarrow\pi^*$ excitation (red, solid line). This absorption peak was partly red shifted when 0.2 equivalents of K_2CO_3 was added, as a new peak at 373 nm appeared on the spectrum (black, long dashed dotted line). Furthermore, the absorption was totally red shifted to 373 nm in the presence of 0.4 equivalents of K_2CO_3 (blue, dashed line). This phenomena of red shift can be attributed to the lone pair of electrons on the *N*-centred anion of **2a** which consists of an extended πsystem. Since 373 nm is almost within the spectrum of visible-light, it could be confirmed that hydrazone **1a** can be irradiated in the presence of catalytic amount of base by low-energy light like household LEDs and regular sunlight, instead of UV.



Scheme 2. UV-Vis absorption: Red shift of hydrazone **1a** in the presence of base.

So we went on to test the reactivity of **1a** by irradiating it with visible light in the presence of base and air as the oxidant. Initially the desired product **3a** was isolated in 60% yield from the reaction employing Na_2CO_3 (1.2 equiv.) as the base in MeCN at room temperature under the irradiation of 7 W blue LEDs (Table 1, entry 1). As the next step, we investigated the influence of base, solvent and light source on the efficiency of the reaction (Table 1). Different inorganic and organic bases were scanned for this reaction (entries 1−9), and almost all of them gave desired product with decent yields. Only pyridine led to trace amount of product (entry 9), and the highest yield (94%) was obtained from the reaction using K_2CO_3 as the base (entry 2). Then the ratio of K_2CO_3 *vs* substrate **1a** was studied, and it is found that reducing K_2CO_3 loading led to inferior outcomes (entries 10−12), but at least a yield of 60% was secured even when K_2CO_3 loading was reduced to 20 mol% (entry 10). Then the reaction was examined in various solvents (entries 13−17), among which DMSO and DMF gave comparable yields (entries 14−15), while H_2O can also be the solvent for this reaction and led to the desired product with 56% yield (entry 16). The co-solvent of MeCN-H_2O (*v*/*v*, 1:1) can give a yield of 68% (entry 18). Finally, the light sources, such as white LEDs and red LEDs, were tested, but they gave no better results (entries 19 and 20). From an environmental and practical point of view, we were intrigued to use abundant sunlight for activating this chemical transformation. To our delight, the reaction under sunlight could complete within 8 h with excellent chemical yield (98%, entry 21).

Table 1. Optimization of Reaction Conditions[a]

entry	solvent	base (equiv.)	light source	yield [b] (%)
1	MeCN	Na_2CO_3 (1.2)	7 W blue LEDs	60
2	MeCN	K_2CO_3 (1.2)	7 W blue LEDs	94
3	MeCN	Cs_2CO_3 (1.2)	7 W blue LEDs	88
4	MeCN	DBU (1.2)	7 W blue LEDs	90
5	MeCN	DABCO (1.2)	7 W blue LEDs	78
6	MeCN	$^iPr_2NEt$ (1.2)	7 W blue LEDs	82
7	MeCN	Et_3N (1.2)	7 W blue LEDs	60
8	MeCN	Imidazole (1.2)	7 W blue LEDs	40
9	MeCN	Pyridine (1.2)	7 W blue LEDs	trace
10	MeCN	K_2CO_3 (0.2)	7 W blue LEDs	61
11	MeCN	K_2CO_3 (0.4)	7 W blue LEDs	67
12	MeCN	K_2CO_3 (1)	7 W blue LEDs	89
13	DCM	K_2CO_3 (1.2)	7 W blue LEDs	85
14	DMSO	K_2CO_3 (1.2)	7 W blue LEDs	90
15	DMF	K_2CO_3 (1.2)	7 W blue LEDs	93
16	H_2O	K_2CO_3 (1.2)	7 W blue LEDs	56
17	MeOH	K_2CO_3 (1.2)	7 W blue LEDs	80
18	MeCN-H_2O[c]	K_2CO_3 (1.2)	sunlight	68
19	MeCN	K_2CO_3 (1.2)	7 W white LEDs	75
20	MeCN	K_2CO_3 (1.2)	7 W red LEDs	72
21	MeCN	K_2CO_3 (1.2)	sunlight	98

[a] 0.5 mmol of **1a**, 2 mL of solvent, room temperature, open flask. [b] isolated yield. [c] MeCN-H_2O (*v*/*v*, 1:1)

After establishing suitable conditions, the scope of the reaction with respect to the variation of *α*, *β*-unsaturated hydrazones was explored (Table 2). Under optimized condition (condition A), a wide range of *α*,

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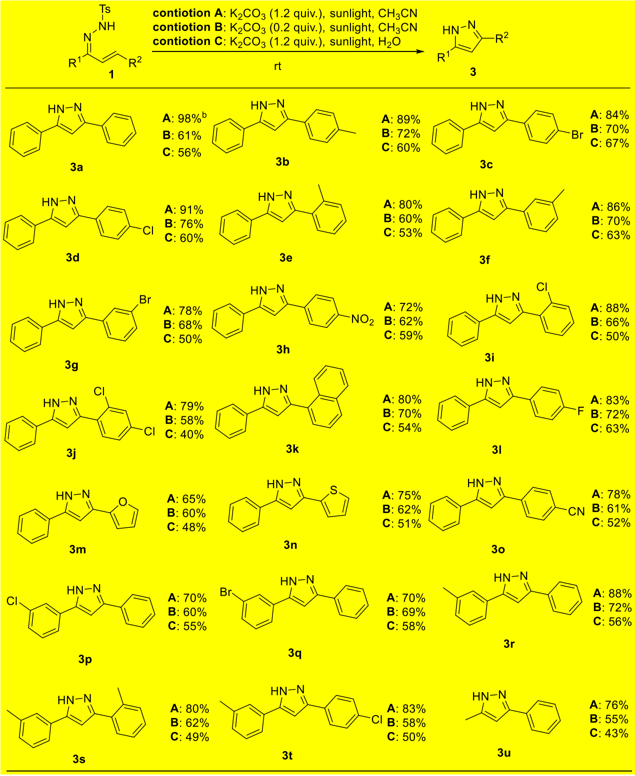
β-unsaturated hydrazones were applicable and good to exellent isolated yields of the products were achieved (**3a**–**3t**). Aromatic substrates with R^1 bearing different electron-withdrawing or electron-donating groups at different positions were all compatible with this reaction (**3a-3o**). A series of functional groups, such as nitro, cyano, and halogen, were all well tolerated under the reaction conditions. Impressively, α, β-unsaturated hydrazons containing other aromatic rings including naphthalene, furan and thiophen were found to be suitable substrates, leading to corresponding pyrazoles (**3k**, **3m-3n**) in moderate to good yields. On the other side, the variation of R^2 was also possible (**3a-3o**), leading to desired products **3p**–**3t** in good yields. Notably, substrate **1u** bearing methyl group also underwent the reaction smoothly to give **4u** with 76% yield.

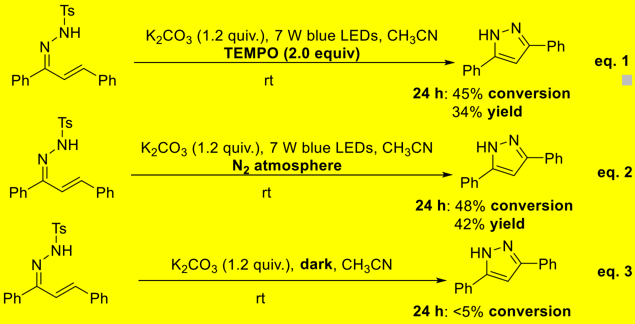
To demonstrate the practicality of our method, all the substrates were studied under condition B (catalytic K_2CO_3) and condition C (H_2O as the solvent). Both conditions can generate desired products with synthetically useful yields, and a yield of 76% (**3d**) was obtained when substrate **1d** was subjected to condition B, while the yield can be up to 67% (**3c**) under condition C. Notably the reaction of α, β-unsaturated hydrazone **1a** was scaled up to 20 mmol under condition A and the desired product **3a** was obtained without loss in the yield.

Table 2. Substrate scope of the reaction[a]



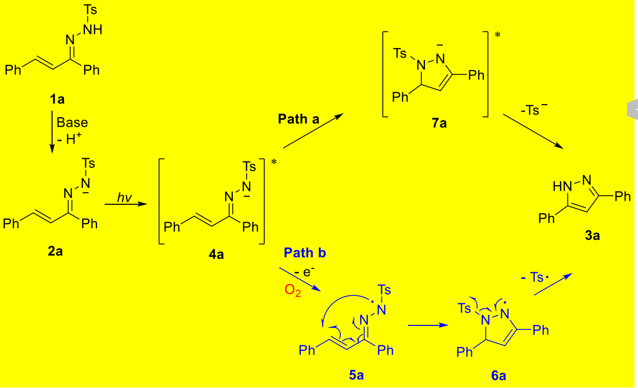
[a] Condition A: 0.5 mmol of **1a**, 0.6 mmol of K_2CO_3, air (open flask), and MeCN (2 mL) at room temperature under the irradiation of sunlight; Condition B: 0.5 mmol of **1a**, 0.1 mmol of K_2CO_3, air (open flask), and MeCN (2 mL) at room temperature under the irradiation of sunlight; Condition C: 0.5 mmol of **1a**, 0.6 mmol of K_2CO_3, air (open flask), and H_2O (2 mL) at room temperature under the irradiation of sunlight. [b] Reaction scaled up to 20 mmol.

To provide some insights into the mechanism of this reaction, control experiment [16] in the presence of radical trapper TEMPO (2.0 equiv.) was carried out. The reaction was found to become much slower, and only 45% starting α, β-unsaturated hydrazon **1a** was consumed after 24 h, resulting in the desired pyrazole **3a** with a yield of 34% (eq.1, scheme 3). Similarly, the reaction under N_2 atmosphere was also found to be deactivated, leading to lower conversion and yield (eq.2, scheme 3). Notably, visible light is essential for this reaction, as the reaction in dark only generated trace amount of desired product (eq.3, scheme 3).



Scheme 3. Mechanistic study

These experiments indicated that both radical and excited-state addition maybe involved in this reaction (Scheme 4). Specifically, the reaction is initiated by deprotonation of **1a**, leading to the formation of N-centred anion **2a**. Then **2a** is irradiated by visible-light to its excited state **4a**. The intermediate **4a** can either directly undergo intramolecular addition to form another excited-state intermediate **7a** via path a, or lose one electron to form radical **5a**, followed by intramolecular radical addition to generate **6a** via path b. Finally, the elimination of Ts motif can generate pyrazole **3a** from both **7a** and **6a**. Oxygen may serve as a SET oxidant to oxidize the in situ-formed nitrogen anion **4a** into **5a**[17], which is confirmed by the similar loss of activity in the control reaction (eq.1 and 2, scheme 3)



Scheme 4. Plausible mechanistic pathway for the formation of pyrazoles

In conclusion, we have described a practical method for the synthesis of pyrazoles through sunlight promoted annulation of *α*, *β*-unsaturated hydrazones. This protocol features mild sustainable reaction conditions, and broad substrate scope for aromatic compounds. Based on the analysis of UV-Vis absorption of the substrate, this reaction was designed to avoid the use of external photocatalysis and proceeds via direct irradiation of N-centred anion by sunlight. Taken together with its operational simplicity, readily available reagents, and amenability to gram-scale synthesis, this green reaction will find practical applications for the synthesis of pyrazole derivatives.

Experimental Section

General Procedure for Synthesis of 3a under condition A: To a solution of *α*, *β*-unsaturated hydrazine **1a** (0.5 mmol) in MeCN (2 mL) was added K_2CO_3 (0.6 mmol). The reaction mixture was stirred at 25℃ under air atmosphere (open vial) and irradiated by sunlight. The reaction was monitored by thin layer chromatography (TLC). When the reaction was completed, it was diluted with water and extracted with ethyl acetate 3 times. Removal of solvent followed by column chromatography afforded desired product **3a**[18]. A light yellow solid (108 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.70 (m, 4H), 7.37-7.29 (m, 6H), 6.82 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 131.3, 128.9, 128.1, 125.7, 100.1.

Acknowledgements

We acknowledge the Qing Lan Project of Jiangsu Province and Jiangsu University Foundation (No. 13JDG059), the National Natural Science Foundation of China (61604069), the National Key R&D Program of 'Strategic Advanced Electronic Materials' (No. 2017YFA0204704) for finance support.

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[16] All the control experiments were carried out using blue LEDs instead of sunlight as the light source due to the 24 h reaction time.

[17] We acknowledge all the inspiring comments by the reviewers during the submission of this paper, including the one about the role of oxygen.

[18] L.-L. Wu, Y.-C. Ge, T. He, L. Zhang, X.-L. Fu, H.-Y Fu, H. Chen and R.-X. Li, *Synthesis*. **2012**, *44*, 1577.

COMMUNICATION

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Adv. Synth. Catal. **Year**, *Volume*, Page – Page

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