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Chemoselective light-induced reactivity of β-enaminones

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Abstract

The irradiation of β-enaminones, generated in situ from cyclic 1,3-diketones and activated alkenes leads to polyheterocyclic skeletons. The photoproduct chemoselectivity depends on the type of cyclic 1,3-diketones employed viz., 2-acetylcyclopentanone and 2-acetylcyclohexanone. The observed chemoselectivity was rationalized based on the Dieckmann-Kon rule.

KEYWORDS

enaminones photochemistry, excited state transformations, photochemistry, photophysics

INTRODUCTION

Stereoselective synthesis of complex carbon skeletons can be achieved through excited-state manipulation of chromophores that often facilitate reaction pathways that are typically not easily accessible by conventional methods.[1-3] Photocyclization reactions are one such class of reactions that yields heterocycles in a single step with multiple stereocenters.[4-9] Some of the classical examples include light-induced transformations featuring *conrotatory* 6π-ring closure and *disrotatory* 4π-ring closure.[10-14] Photoreactions are used to access natural products featuring structurally diverse skeletons.[1,6,7] Enaminones are one such scaffold used in the synthesis of heterocyclic natural products.[7,9] They are also known for their potential as prodrug analogs often used in physiologically active skeletons, featuring improved transport in various biological membranes.[15] Recently we reported a new photochemical reaction to access heterocyclic dihydropyran scaffolds (Scheme 1).[16] This reaction provided convenient access to the core structure of an anticancer drug candidate Marmycin (Scheme 1).[17-21] In the newly discovered reaction (Scheme 1), we postulated the involvement of an in situ-generated enaminone that underwent an excited-state intramolecular proton transfer (ESIPT) leading to the observed reactivity.

As enaminones often undergo facile *cis-trans* photoisomerization, we wanted to evaluate the influence of the isomerization process on this newly observed excited-state reactivity.[22] In this report we present our findings in which the chemoselectivity in the newly disclosed photoreaction

Abbreviations: DCM, dichloromethane; EA, ethyl acetate; ESI, electron spray ionization; ESIPT, excited-state intramolecular proton transfer; EtOH, ethanol; HRMS, high-resolution mass spectrometry; MeCN, acetonitrile; rt, room temperature; TLC, thin-layer chromatography; XRD, X-ray diffraction.

Lakshmy Kannadi Valloli and Kavyasree Manal contributed equally to this work.

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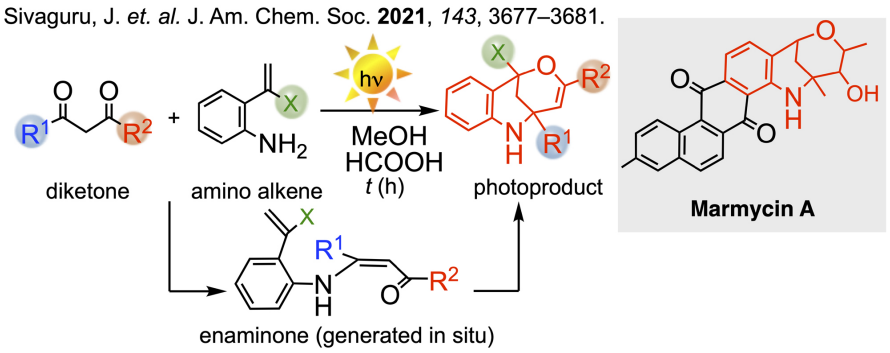
(Scheme 1) is dictated by the in situ generated β-enaminone derived from cyclic β-diketone (Scheme 2).

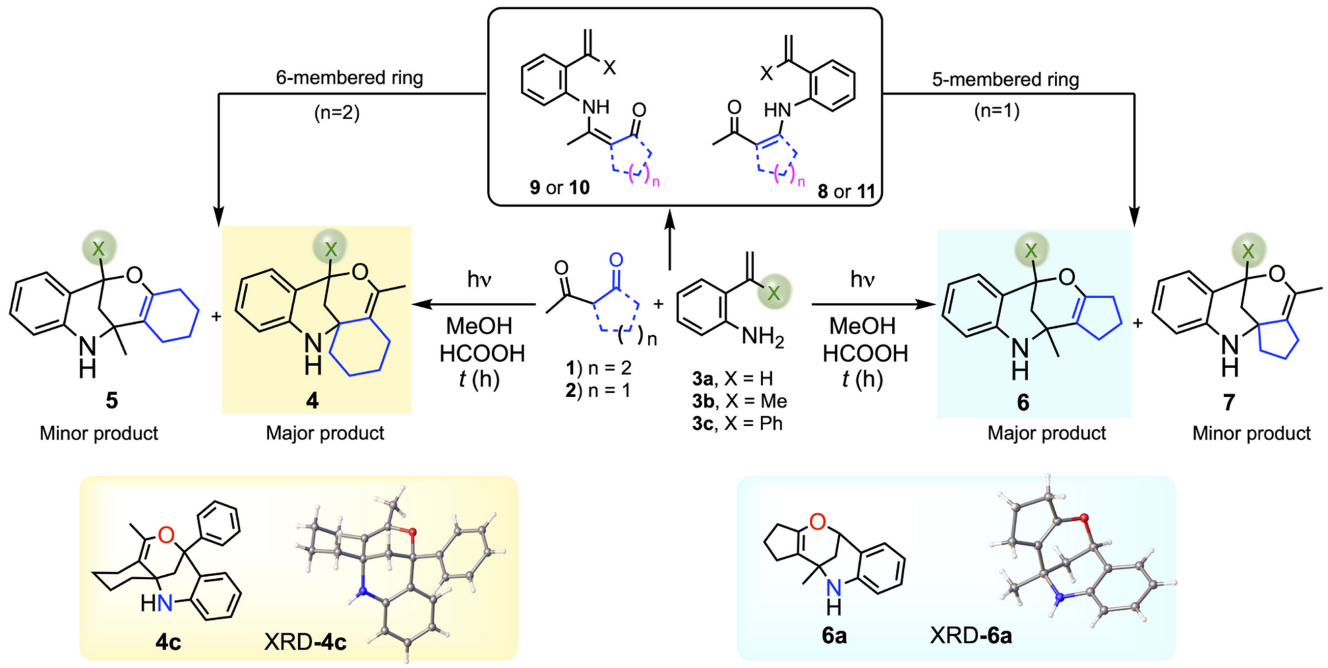
MATERIALS AND METHODS

General methods

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros organics®, and TCI America® and were used as received without further purification. Spectrophotometric grade solvents (e.g., acetonitrile and ethanol) were purchased from Sigma-Aldrich® and used without further purification for emission measurements. Unless stated otherwise, reactions were conducted in oven-dried glassware under nitrogen atmosphere. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on Bruker 500 MHz (126 MHz for ^{13}C-NMR) spectrometers. Data from the NMR spectroscopic measurements are reported as chemical shifts (δ ppm) with the corresponding integration values. Coupling constants (*J*) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s (singlet), b (broad), bs (broad singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Data for ^{13}C-NMR spectra are reported in terms of chemical shift (δ ppm). High-resolution mass spectrometry (HRMS) was performed using a Waters ToF instrument, model SYNAPT G2-Si using electron spray ionization (ESI) on positive mode. When necessary, the compounds were purified by chromatography using a Combiflash SI-3 system equipped with a dual wavelength UV–Vis absorbance detector (Teledyne ISCO) using hexanes:ethyl acetate solvent mixture as the mobile phase and Redisep® cartridge



SCHEME 1 Newly discovered photochemical reaction to access the core of an anticancer drug candidate, Marmycin.



SCHEME 2 Achieving regioselectivity in the photoproduct by tuning the ring size of 1,3-diketones.

filled with silica (Teledyne ISCO) as stationary phase. Unless indicated, the Retention Factor (Rf) values were recorded using 5%–50% hexanes:ethyl acetate as mobile phase and on Sorbent Technologies®, silica Gel TLC plates (200 mm thickness w/UV254). To record the IR spectrum Thermoscientific iD7 Nicolet iS5 was used and the analysis was performed using the EZ OMNIC software.

Photophysical methods

Spectrophotometric solvents (Sigma-Aldrich®) were used whenever necessary unless otherwise mentioned. UV-quality fluorimeter cells (with a range until 190 nm) were purchased from Starna®. Absorbance measurements were performed using a Cary 300 UV–Vis spectrophotometer. Time-resolved phosphorescence spectra recorded on an FLS1000 Spectrometer (Edinburgh Instruments). Ethanol sample solutions in 3-mm quartz tubes (inner diameter) were frozen in a quartz liquid nitrogen Dewar (77 K) and excited with a pulsed xenon lamp.

X-ray crystal structure determination

Single crystal X-ray diffraction data of the compounds **4c**, **8c**, and **6a** were collected on a Bruker Apex Duo diffractometer with an Apex 2 CCD area detector at $T = 105$ K. Cu radiation was used. All structures were processed with Apex 3 v2019.1–0 software package (SAINT v. 8.38A) and Olex 2 v 1.3.0.[1] XT[2] structure solution program based on Intrinsic Phasing was used to solve the structures after multi-scan absorption corrections and refined with the XL[3] refinement package using least squares minimization.

Irradiation procedures for photoreactions

General procedure for the one-pot reaction of hexacyclic diketone **1** with amino alkenes **3a-c**

Amino alkenes **3a-c** (0.34 mmol, 1 equiv.), hexacyclic diketone **1** (1.1 equiv.) and formic acid (0.01 equiv.) were dissolved in methanol (15 mL) in a round bottom flask. The solution was stirred at room temperature for 4 h for the formation of enaminone. The completion of the reaction for the enaminone formation was confirmed by ^{1}H NMR spectroscopy. The reaction mixture was dissolved in 120 mL of methanol and was transferred to 8 Pyrex test tubes and degassed with nitrogen for 15 min. It was followed by irradiation in a Rayonet reactor with a light source of ~350 nm and a merry-go-round. Progress of the reaction was monitored by crude ^{1}H NMR spectroscopy of the reaction mixture. After the completion of reaction, solvent was removed under reduced pressure. The crude product was purified by chromatography (Combiflash) using ethyl acetate/hexanes mixture as a mobile phase. All the reported values carry an error of ~5%.

General procedure for the one-pot reaction of pentacyclic diketone **2** with amino alkenes **3a-c**

Amino alkenes **3a-c** (0.34 mmol, 1 equiv.), pentacyclic diketone **2** (1.1 equiv.) and formic acid (0.01 equiv.) were dissolved in methanol (15 mL) in a round bottom flask. The solution was stirred at room temperature for 4 h for the formation of enaminone. The completion of the reaction for the enaminone formation was confirmed by ^{1}H NMR spectroscopy. The reaction mixture was dissolved in 120 mL of methanol and was transferred to 8 Pyrex test tubes and degassed with nitrogen for 15 min. It was followed by irradiation in a Rayonet reactor with a light source of ~350 nm and merry-go-round. Progress of the reaction was monitored by crude ^{1}H NMR spectroscopy of the reaction mixture. After the completion of the reaction solvent was removed under reduced pressure. The crude product was purified by chromatography (Combiflash) using ethyl acetate/hexanes mixture as a mobile phase.

General procedure for the photoreaction of enaminones **8a-c** (with minor isomer **9a-c**) at ~350 nm to form the corresponding photoproducts **4a-c** (with minor isomer **5a-c**)

Enaminone solution (~0.02–0.015 mmol, depending on the enaminone) was taken in a Pyrex test tube and was purged with nitrogen for ~15–30 min. It was then irradiated in a Rayonet reactor at ~350 nm. Progress of the reaction was monitored at a regular interval of time by recording the crude ^{1}H NMR spectra of the reaction mixture. After the completion of the reaction, the solvent was evaporated and concentrated under reduced pressure. The crude product was purified by chromatography (Combiflash) using ethyl acetate/hexanes mixture as a mobile phase.

General procedure for the photoreaction of enaminones **10a-c** (with minor isomer **11a-c**) at ~350 nm to form the corresponding photoproducts **6a-c** (with minor isomer **7a-c**)

Enaminone solution (0.02–0.016 mmol depending on the enaminone) was taken in a Pyrex test tube and was purged

with nitrogen for ~15–30 min. It was then irradiated in a Rayonet reactor at ~350 nm. Progress of the reaction was monitored at a regular interval of time by recording the crude ^{1}H NMR spectra of the reaction mixture. After the completion of the reaction, the solvent was evaporated and concentrated under reduced pressure. The crude product was purified by chromatography (Combiflash) using an ethyl acetate/hexanes mixture as a mobile phase.

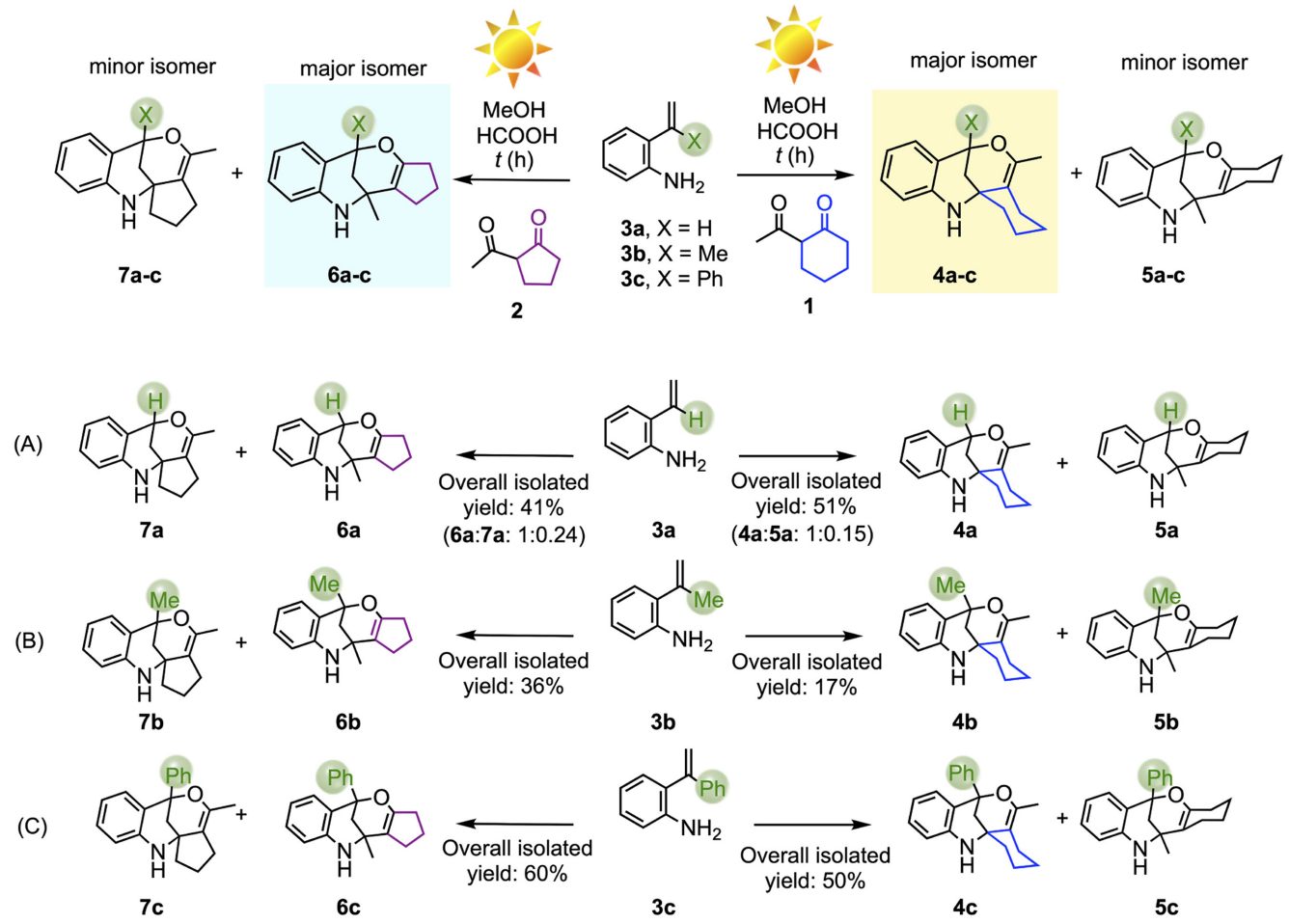
RESULTS AND DISCUSSION

Excitation of cyclic β-diketones in the presence of alkenes often leads to the well-established de Mayo reaction from which a diverse set of natural products have been synthesized.[4] Building on this precedence we envisioned introducing cyclic β-diketones with varying ring sizes to specifically tune the regioselectivity of the photoproduct in our newly discovered photochemical transformation.[16] We targeted to utilize the Dieckmann-Kon rule[23,24] in which six-membered enaminone ring systems generally prefer endocyclic double bonds as compared to five-membered enaminone ring systems, which favor exocyclic double bonds.[23,24] The application of the Dieckmann-Kon rule has been exploited for various thermal reactions as demonstrated by Yu and coworkers who investigated the effect of ring size on the product formation of the Schiff base reaction with diamino alkanes.[25] The 2-acetylcyclohexanone yielded the major product with an endocyclic double bond as compared to 2-acetylcyclopentanone which yielded the exocyclic double bond as the major product.[25] Braibante and coworkers reported the selective synthesis of unsymmetrical β-enamino ketones with cyclic β-diketones, where they reported the formation of the endocyclic enaminone on reaction with six-membered diketone and an exocyclic enaminone on reaction with the five-membered diketone.[26] We envisioned exploiting the Dieckmann-Kon rule[23,24] to direct reactivity of enaminones in the newly observed photochemical reaction (Schemes 1 and 2).[23,24]

We began our evaluation by investigating the photoreaction of 2-acetylcyclohexanone **1** and 2-acetylcyclopentanone **2** with *o*-vinlyanilines **3a-c** (Schemes 2 and 3). A methanolic solution of commercially available 2-acetylcyclohexanone **1** and **3a** was allowed to equilibrate at room temperature in the presence of catalytic amounts of formic acid and was irradiated at ~350 nm under nitrogen atmosphere.[27] This irradiated mixture was concentrated under reduced pressure and purified by column chromatography.[27] There were uncharacterized minor products that were observed that were reflected in the moderate to lower isolated yields. The purified photoproduct was analyzed by various analytical techniques and was characterized to be a mixture of **4a** (featuring a vinylic methyl substituent) as the major isomer and **5a** as the minor isomer (featuring a bridge head methyl substituent) with an overall isolated yield of 51% (Scheme 3A-right). The ratio determined by ^{1}H-NMR spectroscopy of the photoproduct, that is, **4a**:**5a** was 1:0.15 (Scheme 3A-right). To gauge the effect of different substituents on the activated alkene, we investigated with methyl substituted *o*-vinlyaniline **3b** and phenyl substituted *o*-vinlyaniline **3c** (Schemes 3B-right and 3C-right). Irradiation of 2-acetylcyclohexanone **1** with methyl substituted *o*-vinlyaniline **3b** gave both photoproducts, **4b** as major isomer and **5b** as minor isomer with an overall isolated yield of 17% (Scheme 3B-right). Similarly, irradiation of 2-acetylcyclohexanone **1** with phenyl substituted *o*-vinlyaniline **3c** yielded the corresponding photoproduct **4c** as major isomer and **5c** as minor isomer with an overall isolated yield of 50% (Scheme 3C-right). The structure of the photoproduct **4c** was decisively confirmed using single crystal XRD (Scheme 2).[27]

To gauge the effect of ring size, six-membered 1,3-diketone was employed instead of a five-membered 1,3-diketone viz, acetylcyclohexanone **1** instead of acetylcyclopentanone **2** and its photoreactivity was evaluated with *o*-vinlyanilines **3a-c** (Scheme 3-left). Irradiation of 2-acetylcyclopentanone **2** with amine **3a** gave the corresponding photoproduct **6a** featuring a bridge head methyl substituent as major isomer and **7a** featuring a vinylic methyl substituent as minor isomer with an overall isolated yield of 41% (Scheme 3A-left). The ratio determined by ^{1}H-NMR spectroscopy of the photoproduct, that is, **6a**:**7a** was 1:0.24 (Scheme 3A-left). The structure of the photoproduct **6a** was unequivocally confirmed using single crystal XRD (Scheme 2).[27] To gauge the effect of different substituents on the activated alkene during reactivity with 2-acetylcyclopentanone **2**, we investigated with methyl substituted *o*-vinlyaniline derivative **3b** and phenyl substituted *o*-vinlyaniline derivative **3c** (Schemes 3B-left and 3C-left). Irradiation of 2-acetylcyclopentanone **2** with methyl substituted *o*-vinlyaniline **3b** yielded both photoproducts **6b** as major isomer and **7b** as minor isomer with an overall isolated yield of 36% (Scheme 3B-left). Similarly, irradiation of 2-acetylcyclopentanone **2** with phenyl substituted *o*-vinlyaniline **3c** gave the corresponding photoproduct **6c** as major isomer and **7c** as minor isomer with an overall isolated yield of 60% (Scheme 3C-left).

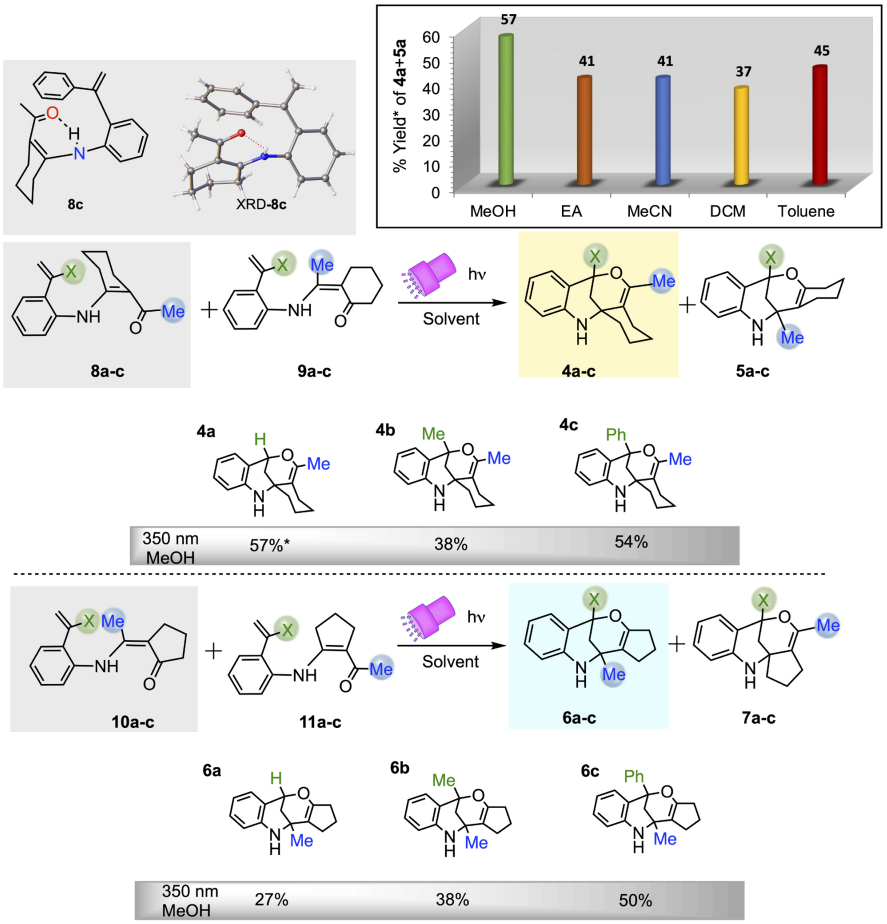
It was clear that there was a reversal in chemoselectivity when the diketone was changed from 2-acetylcyclohexanone **1** to 2-acetylcyclopentanone **2**, that is, the photoproduct featuring the vinylic methyl substituent was preferred in hexacyclic system (product **4** over **5**), while the photoproduct featuring the bridge head methyl substituent was preferred in pentacyclic system (product **6** over **7**). As we had postulated the formation



SCHEME 3 Evaluating the photoreaction of acetylcylcohexanones and acetylcyclopentanones with different *o*-vinlyanilines.

of enaminone (assisted by catalytic amounts of formic acid) that was generated in situ during the course of the photoreaction (Scheme 1), we independently synthesized the enaminone by thermal method.[27,28] Analysis of the enaminones derived from the thermal reaction of cyclic β-diketones **1**/**2** with *o*-vinlyanilines **3a-c** showed that the endocyclic enaminone-**8** was favored over exocyclic enaminone-**9** for 2-acetylcyclohexanone **1**, while the exocyclic enaminone-**10** was favored over endocyclic enaminone-**11** for 2-acetylcyclopentanone **2**.[27] This was in line with the Dieckmann-Kon rule[23,24] where the endocyclic systems are favored over the exocyclic systems for reaction involving six-membered skeletons while the reversal is true for five-membered systems.

The formation of endocyclic and exocyclic enaminones was unambiguously determined by single crystal XRD analysis as we were successful in crystalizing endocyclic enaminone **8c** (Scheme 4).[27] We then subjected the enaminones (synthesized by thermal methods)[27,28] to our standard irradiation conditions. Irradiation of methanolic solution of as synthesized endocyclic enaminone **8a** (with traces of isomer exocyclic enaminone **9a**) at ~350 nm under nitrogen atmosphere yielded the photoproduct **4a** (featuring a vinylic methyl substituent) as the major isomer and **5a** as the minor isomer (featuring a bridge head methyl substituent) with an overall yield of 57% (Scheme 4-top). The photochemical reactivity of enaminones was monitored by ^{1}H-NMR spectroscopy. The vinylic hydrogens were used as an NMR handle to gauge the *endo*/*exo* cyclic enaminones ratios (Figure 1-left) and the bridge head hydrogen was used as an NMR handle to determine the ratio of the isomeric photoproducts (Figure 1-right). This overall yield determined by ^{1}H-NMR spectroscopy for irradiation of enaminones derived from **1** and **3a** in methanol was 57%, which was similar to the overall isolated yield of 51% for the reaction of **1** with **3a** (compare yields in Scheme 3A-right and Scheme 4-top). To gauge the influence of solvents, we evaluated the photoreactivity of enaminones thermally derived from **1** and **3a** in various solvents. Irradiation of enaminone **8a** (with traces of isomer **9a**) in various solvents resulted in photoproducts with the corresponding yields (overall yield of **4a**/**5a**) varying from 37% to 57% (Scheme 4). Irradiation of a methanolic solution of



SCHEME 4 Top and bottom: Evaluation of photoreactivity of enaminones under various conditions, yields of major isomer provide. *=yield from ^{1}H-NMR spectroscopy with triphenylmethane as internal. EA, Ethyl acetate.

as synthesized enaminone **8b/9b** (**8b**:**9b** = 1:0.5 by ^{1}H-NMR spectroscopy) under nitrogen atmosphere resulted in the corresponding photoproduct **4b** and **5b** with an overall yield of 38%. Similarly, irradiation of deoxygenated methanolic solution of the synthesized enaminone **8c/9c** (with traces of isomer exocyclic enaminone-**9c**) resulted in the corresponding photoproduct **4c** and **5c** with a yield of 54% (Scheme 4).

Having ascertained the reactivity of the enaminone 8/9 derived from 2-acetylcyclohexanone **1**, we then evaluated the reactivity of the enaminone 10/11 derived from 2-acetylcyclopentanone **2** (Scheme 4-bottom). Irradiation of a deoxygenated methanolic solution of as synthesized exocyclic enaminone **10a** (with traces of minor isomer endocyclic enaminone **11a**) at ~350 nm yielded the photoproduct **6a** as the major isomer (featuring a bridge head methyl substituent) and **7a** (featuring a vinylic methyl substituent) as the minor isomer and with an overall yield of 27% (Scheme 4-bottom). This overall yield was similar to the overall isolated yield for the reaction of **2** with **3a** (compare yields in Scheme 4-bottom and Scheme 3A-left). Similarly, irradiation of a deoxygenated methanolic solution of the synthesized enaminone **10b/11b** (**10b**:**11b** = 1: 0.56 by ^{1}H-NMR spectroscopy) resulted in the corresponding photoproduct **6b** and **7b** with an overall yield of 38%. Irradiation of deoxygenated methanolic solution of the synthesized enaminone **10c/11c** (with traces of minor isomer endocyclic enaminone **11c**) resulted in the corresponding photoproduct **6c** and **7c** with a yield of 50% (Scheme 4-bottom).

Further to understand the chemoselectivity, we evaluated the photoreaction of cyclic β-diketone **1/2** with **3** by changing the reaction temperature (room temperature, 60 and −20°C) in different solvents (Tables 1 and 2). By using the vinylic hydrogen in the enaminone(s) and the corresponding bridgehead hydrogen in the photoproduct(s) as the NMR handle, the ratio of the isomeric reactants and photoproducts were evaluated respectively (Figure 1). In the case of photoreaction of 2-acetylcyclohexanone **1** with **3a**, the ratio of the minor photoproduct **5a** increased upon lowering the temperature in all the investigated solvents (MeOH, MeCN, and toluene; Table 1). For example, in toluene, the ratio of **4a**:**5a** was 1:0.33 when the reaction was performed at 60°C (Table 1; entry 6). The ratio of **4a**:**5a**

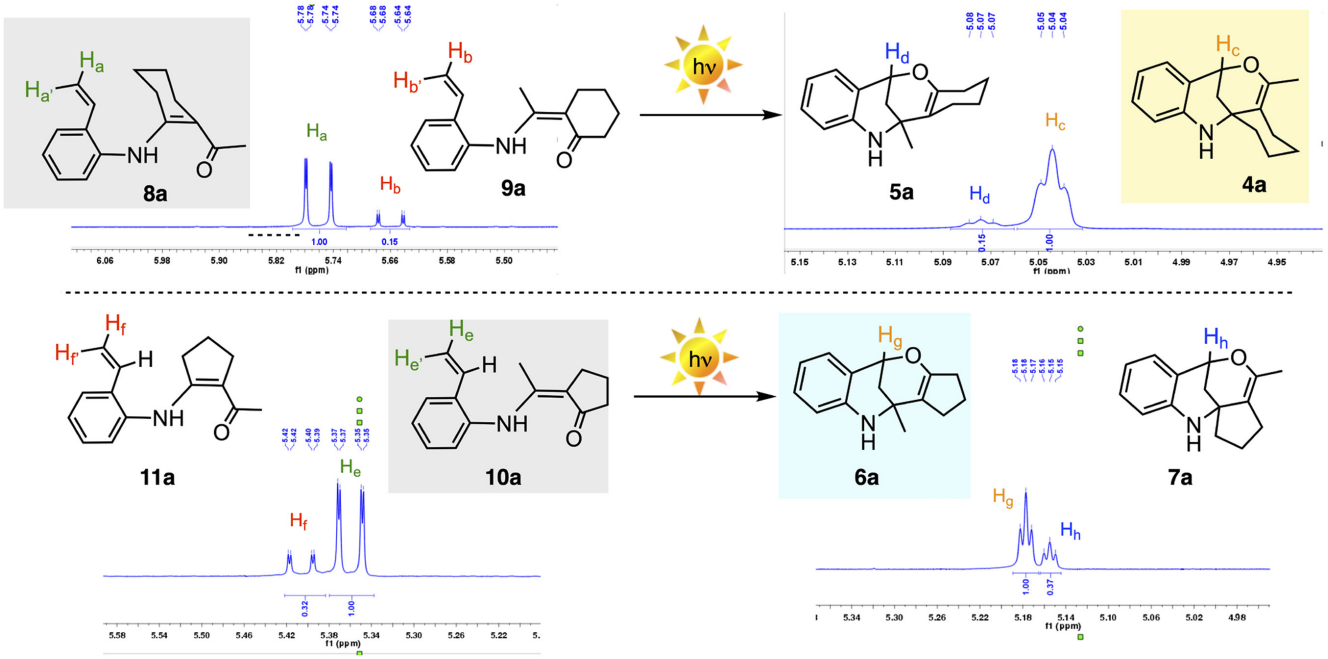
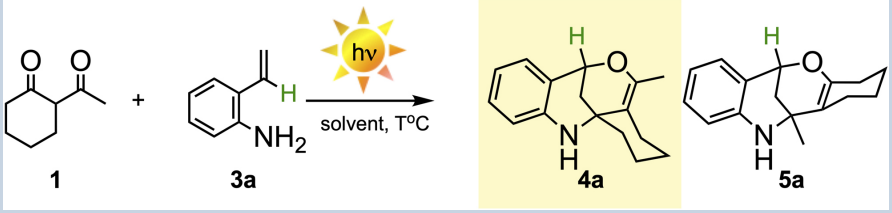


FIGURE 1 Monitoring the photochemical reactivity of enaminones by ^{1}H-NMR spectroscopy. The vinylic hydrogens were used as an NMR handle to gauge the *endo*/*exo* cyclic enaminones ratios (left) and the bridge head hydrogen was used as an NMR handle to determine the ratio of the isomeric photoproducts (right).

TABLE 1 Photochemical reactivity of 2-acetyl cyclohexanone **1** with *o*-vinlyanilines **3a-c**.



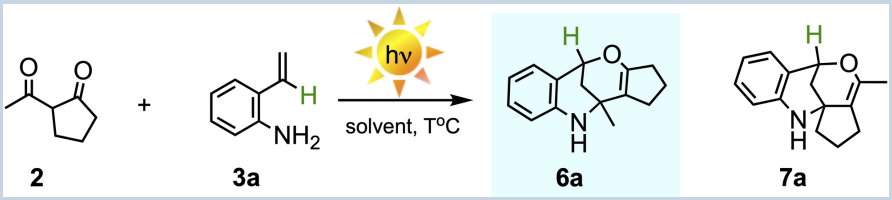
Entry	Reactants	Solvents	*T* °C	Ratio of isomers (4a:5a)[a]
1	**1**+**3a**	MeOH	rt	1:0.15
2			−20	1:0.55
3		MeCN	60	1:0.33
4			rt	1:0.31
5			−20	1:0.50
6		Toluene	60	1:0.33
7			rt	1:0.43
8			−20	1:0.63

[a]The ratio was established by ^{1}H-NMR spectroscopy in $CDCl_3$ as the solvent.

changed to 1:0.43 when the reaction was performed at room temperature (Table 1; entry 7) and the ratio of **4a**:**5a** was 1:0.63 when the reaction was performed at −20°C (Table 1; entry 8). It is very likely that the rates of reactivity of the enaminone leading to isomeric products are impacted by the change in reaction temperature (Scheme 5; vide infra). Contrary to the observed temperature dependent product ratios during reactivity of 2-acetylcyclohexanone **1** and *o*-vinlyaniline **3a**, the photoreactivity of 2-acetylcyclopentanone **2** with *o*-vinlyaniline **3a** did not show significant temperature dependence in all the investigated solvents (Table 2).

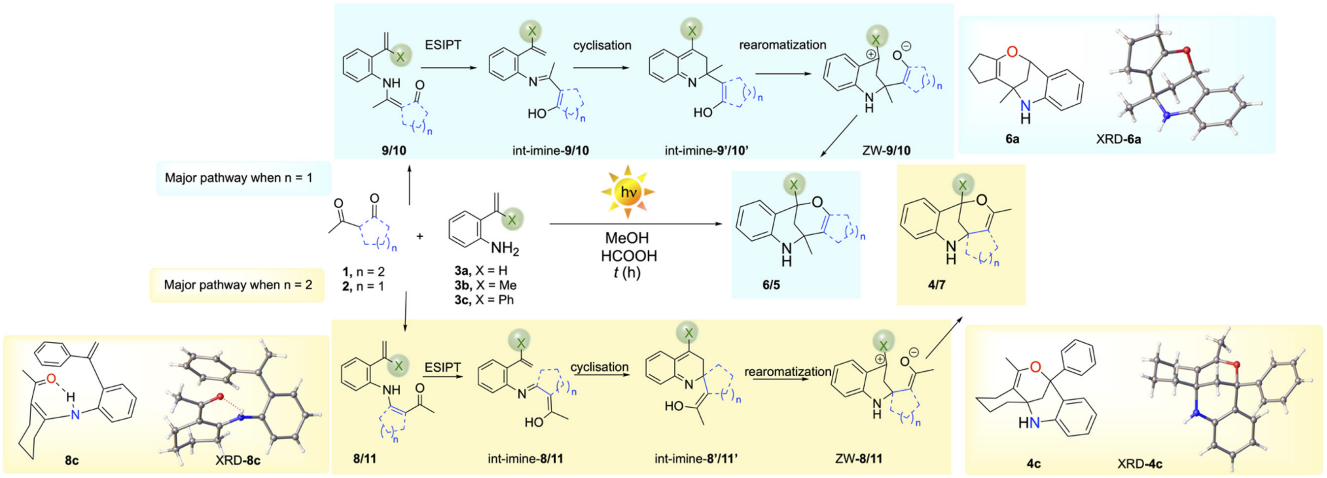
We then investigated the luminescence properties of cyclic β-enaminones to gauge the nature of the excited state. Only negligible fluorescence was observed at room temperature for enaminones **8a**/**9a** and **10a**/**11a** with

TABLE 2 Photochemical reactivity of 2-acetyl cyclopentanone **2** with *o*-vinlyanilines **3a-c**.



Entry	Reactants	Solvents	*T* °C	Ratio of isomers (6a:7a)[a]
1	**2** + **3a**	MeOH	60	1:0.13
2			rt	1:0.20
3			−20	1:0.08
4		MeCN	60	1:0.16
5			rt	1:0.17
6			−20	1:0.20
7		Toluene	60	1:0.16
8			rt	1:0.40
9			−20	1:0.15

[a]The ratio was established by ^{1}H-NMR spectroscopy in $CDCl_3$ as the solvent.



SCHEME 5 Proposed mechanism of photo reactivity of pentacyclic and hexacyclic enaminones.

quantum yields of approximately 0.0003 (Figure S45). Even at 77 K in frozen ethanol matrix only weak phosphorescence was observed for enaminone **8a**/**9a** (Figure 2) indicating a fast deactivation of its excited state. This is consistent with previous studies of the acyclic enaminone **14** where after N-Boc protection, **15**, the phosphorescence increased substantially (Figure 2). We rationalized that this fast deactivation has its origin in ESIPT.[16]

The preliminary photophysical investigations of the observed photo reactivity were discussed in the previous work by Sivaguru and coworkers.[16] Based on this precedence, the enaminones derived from the corresponding six and five-membered β-diketones dictate the mode of reactivity. The enaminone formation from the cyclic β-diketone **1**/**2** and *o*-vinlyaniline adheres to the Dieckmann-Kon rule.[23,24] In the case of the reactivity involving 2-acetylcyclohexanone **1** and *o*-vinlyaniline **3**, the formation of endocyclic six membered enaminone **8** (Scheme 5) is preferred over exocyclic six membered enaminone **9**. The ratio of these two enaminones **8**/**9** are dictated by the type of substituents on the reactive substrates. For example, in the case of *o*-vinlyaniline featuring phenyl (**3c**) substitution at the vinyl group, exclusive formation of the corresponding endocyclic enaminone **8c** is preferred. On the other hand, *o*-vinlyaniline featuring H (**3a**) or methyl (**3b**) substitution at the vinyl group, both the *endo*-enaminone **8a**/**8b** and

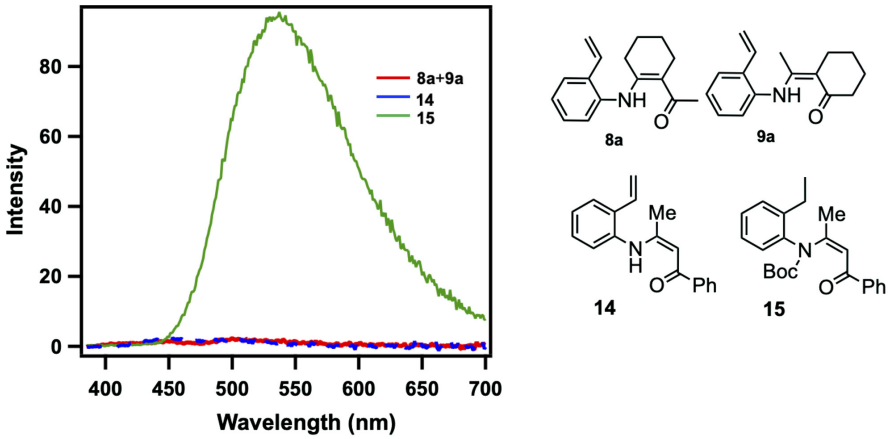


FIGURE 2 Phosphorescence of cyclic β-enaminones **8a/9a** in EtOH at 77 K. For comparion of the luminescence, the emission of acyclic β-enaminones **14** and **15** is provided.[16]

exo-enaminone **9a**/**9b** are generated in situ during the reaction. Photoexcitation of endocyclic enaminone **8** results in ESIPT enroute to the formation of int-imine-**8** that undergoes cyclization to the corresponding int-imine-**8′**. This intermediate int-imine-**8′** rearomatizes enroute to the formation of the corresponding photoproduct **4**. A similar mechanism can be envisioned for exocyclic five-membered enaminone **10** which is preferred over endocyclic five-membered enaminone **11** (Scheme 5-top). The key question that needs to be answered related to the above mechanism is the observed temperature dependence of reactivity in the six-membered system derived from 2-acetylcyclohexanone **1** compared to the five-membered system derived from 2-acetylcyclopentanone **2**. We conjecture that the enaminone generated from acetylcyclohexanone is dependent on the temperature with higher temperatures preferring the formation of the enaminone featuring endocyclic double bond, while at lower temperature a gradual shift towards the formation of the exocyclic enaminone is observed. On the other hand, the pentacyclic β-diketone prefers the formation of exocyclic enaminone in the temperature range investigated which is reflected in the minimal change in our product ratios upon changing the temperature.

CONCLUSION

Our investigation has revealed that β-enaminones can be utilized for accessing photoproducts in which the ring system in the enaminone size (hexa- vs. penta-cyclic system) dictates the mode of photochemical reactivity. Further efforts are underway in our lab to exploit this phenomenon to tailor excited-state reactivity.

AUTHOR CONTRIBUTIONS

The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

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SUPPORTING INFORMATION

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