Metal-Free Photochemical Olefin Isomerization of Unsaturated Ketones via 1,5-Hydrogen Atom Transfer

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Abstract: The photochemical isomerization of α,β- to β,γ-unsaturated ketones through a 1,5-hydrogen atom transfer mechanism under mild conditions with high efficiency and selectivity is reported. The reaction is carried out in the absence of metal catalysts or other additives, and its stereo-selectivity can be tuned by selecting appropriate solvent mixtures. The reaction's scope and tolerance towards func-tional groups, including light-sensitive halogens, free acids and alcohols, were studied, providing reliable access to a wide variety of β,γ-unsaturated ketones. This methodology details the deconjugation of a wide range of unsaturated ketones and, when combined with olefin metathesis, provides an efficient process for either dehomologation or one-carbon double-bond migration of terminal alkenes.

Introduction

Light is a valuable energy source for inducing a range of important and intricate chemical transformations. Notably, most photochemical transformations occur under relatively mild reaction conditions, demonstrate good functional group toler-ance, are usually highly atom economical and favorable to advance green chemistry principles. As a consequence, there has been a renaissance of photochemical organic reactions in academic and industrial research in recent years.[1] Alkenes are basic structural units present in various biologically active molecules and crucial intermediates in organic synthesis; thus, organic chemistry methodologies to produce and transform carbon-carbon double bonds abound.[2] Most procedures that make alkenes afford the thermodynamically more stable E isomers; however, various E to Z photoisomerizations have been reported (Scheme 1).[3,4] Other forms of alkene isomer-ization, including the controlled migration of the double bond along the carbon chain, are well established by using acids, bases, and transition metal complexes.[5] As noted, the trans-location of double bonds typically produces the thermodynami-cally stable E-isomers; nonetheless, a few reactions are also known to afford the Z-alkenes.[6] Within this framework, olefin isomerization has also been promoted photochemically, albeit with limited scope.[7,8] The first example of photoisomerization
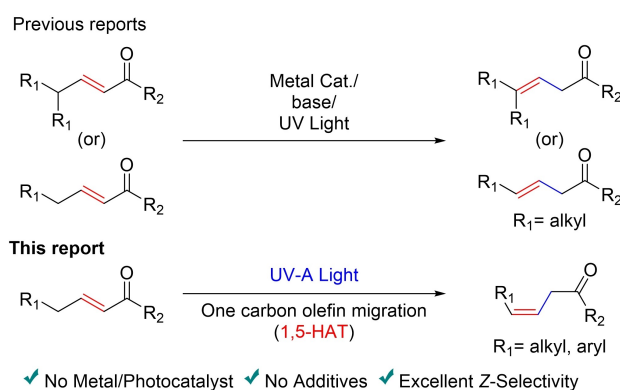
Scheme 1. General isomerization of alkenes.

of α,β-unsaturated to β,γ-carbonyl compounds was described by Jorgenson et al. in the early 1960's[7a] and the mechanism and kinetics of the reaction was then further investigated by several research groups.[7] Moreover, even an asymmetric version of the reaction was developed by Pete and co-workers.[8a–c] Finally, applications of this photochemical trans-formation in total synthesis have been reported in the literature.[8e–g] Notwithstanding these pioneering reports for the light-induced one carbon migration in unsaturated carbonyl compounds, they are typically restricted to substrates that produce either a symmetric regio-isomer, or the more thermo-dynamically stable E-stereoisomer.[7,8] Thus, taking into account its great potential and expediency, the controlled one carbon olefin migration via hydrogen atom transfer with good Z-selectivity has quite limited scope to date, especially in the absence of metal catalysts.

In recent years, 1,n photochemical hydrogen atom transfer (HAT) reactions are receiving considerable attention mainly because they provide excellent opportunities for the straightfor-ward activation of chemically inert aliphatic C–H bonds.[9] For example, a divergent light-mediated methodology for the synthesis of levulinates via photoinduced cross-metathesis

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followed by a photochemical 1,5-hydrogen atom transfer in the presence of phenanthrene as modulator.[9a]

Herein, we report a catalyst-free, UV–A light-induced isomerization of α,β-unsaturated ketones into largely Z-β,γ-unsaturated ketones via a solvent dependent 1,5-hydrogen atom transfer reaction. Moreover, we also take advantage of this effective methodology combined with olefin metathesis reactions to report a proof-of-concept dehomologation process and a one carbon double-bond migration for a broad scope of synthetically challenging substituted alkenes.

Results and Discussion

Because of its availability and ease of synthesis, (E)-5-phenyl-pent-3-en-2-one (**1a**-E) was selected as the model substrate to screen the optimal reaction parameters that could afford **2a**-Z (Table 1). After a few optimization experiments, we were pleased to discover that the reaction efficiently proceeded at room temperature under the proper conditions. As shown in Table 1, the solvent and substrate concentration were found to be crucial factors. In DCM, moderate selectivity and good yields were obtained at the higher dilutions (entry 1). As it is well known, dilute solutions lower the possibility of intermolecular interactions and may also avoid excited state quenching.[10] The addition of isopropanol or t-butanol was beneficial in increasing the selectivity ratio, with the optimal result found when a ratio of 9:1 DCM:IPA was used (entry 7). Similar reactivity was observed when isopropanol was replaced with t-butanol, ruling out the possibility of isopropanol acting as a donor for hydrogen transfer in this procedure (entry 8).[9i] Notably, irradi-

ation with 315 nm (UV–B) light afforded similar results (entry 9); however, other wavelengths, such as 254 nm (UV–C) and blue and green LED light, did not promote this reaction (Table 1, entries 10 and 11). It is important to mention that during the optimization studies, classical isomerization reagents such as K^tOBu, DBU, and $Ru(OAc)_3$[5d] afforded intractable mixtures of compounds.
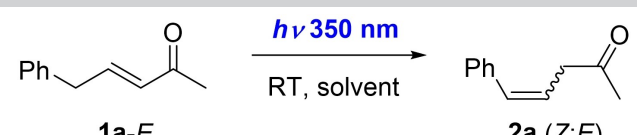
Thus, with the optimized reaction conditions in hand, a broader scope of substrates was examined first with various substituted methyl allylbenzene ketones (Scheme 2). Happily, the reaction was compatible with various photosensitive functional groups on the aromatic ring, such as F, Cl, and Br. It is significant to mention that the isomerization reaction yields relatively clean products without noticeable side reactions. Given the small R_f (retardation factor) difference in thin layer chromatography analysis between **2**-E and **2**-Z, the isomers could only be separated and purified by meticulous column chromatography procedures (see the Supporting Information).

One of the risks with photochemical reactions is the frequent occurrence of associated side-reactions, especially with photosensitive groups. Moreover, long-chain alkyl compounds may afford mixtures of several products due to multiple migration over the carbon chain.[5] Thus, substrates that could undergo recurrent double-bond migration were probed (Scheme 3). We were pleased to observe that a highly selective one carbon isomerization took place with excellent yields. However, compared to derivatives **1a–j**, substrates **1k–p** were found to be less Z-selective (close to a 1:1 ratio). This intriguing result strongly suggests that electronic factors play a crucial role in the more prominent Z-selectivity observed with the aromatic substrates.

Notably, bromide, hydroxy and carboxy substituents were also found to be compatible with the present reaction conditions for the long alkyl chain molecules. The scope of the reaction was augmented by replacing the methyl group in the series of methyl vinyl ketones by other substituents. Thus, substrates (**1q–1s**) containing a phenyl group, a 2-phenylethyl group and a bulky 1-phenylethyl group were tested. These experiments readily yielded the desired isomerized products in excellent yields with good Z-selectivity, highlighting the versatility of the reaction. Unfortunately, further expansion of the scope of starting materials to α,β-unsaturated esters or acids under our reaction conditions was unsuccessful (see the Supporting Information).
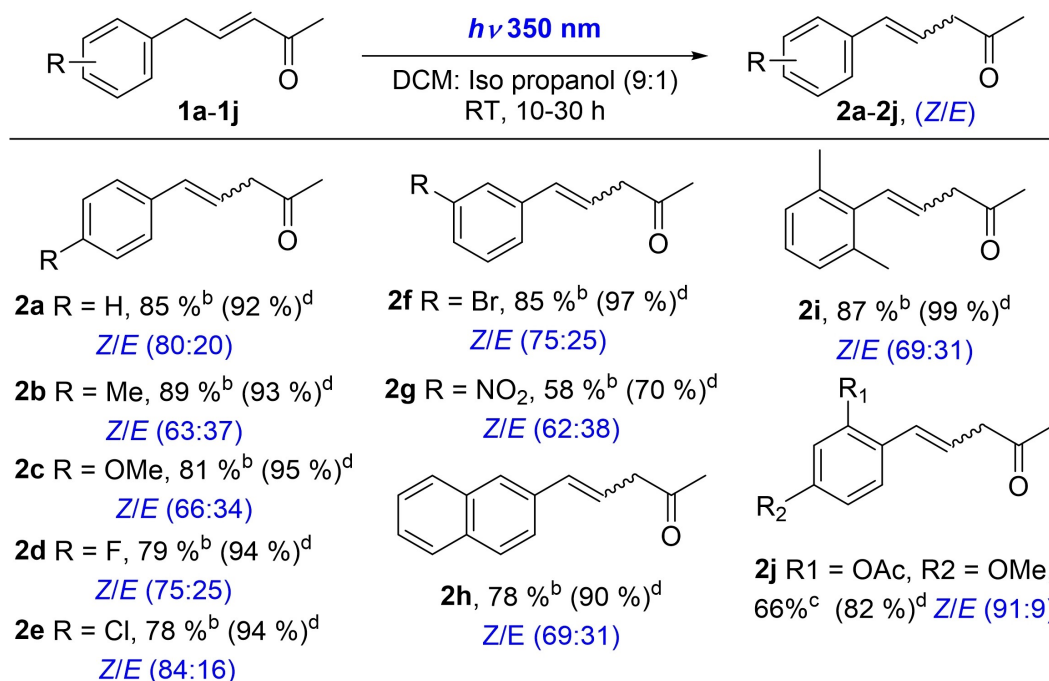
To gain further insight into the mechanism, control experiments were carried out (Scheme 4). At first, we analyzed whether **2a**-Z and **2a**-E interconvert during the reaction. Thus, in separate experiments, isolated **2a**-Z and **2a**-E were irradiated with UV–A light under the reaction conditions. Notably, no E/Z or Z/E isomerization could be observed, indicating that stereochemistry is unchanged after the reaction. In addition, the kinetics of the reaction of **1a**-E were carefully monitored using ^{1}H NMR spectroscopy (see Figure S2). At the early stages of the reaction, only **1a**-Z was formed. Then, the reaction proceeded further to afford the final product mixture of **2a**-Z and **2a**-E (that do not interconvert). These results clearly indicate that the fastest step is E/Z isomerization of **1a**-E, and that both migrated

Table 1. Optimization of reaction conditions.[a]

entry	Solvents	Conv. of **1a** [%]	Z:E ratio
1	DCM (0.1 M)	59	46:54
	(0.05 M)	67	49:51
	(0.02 M)	87	53:47
	(0.01 M)	99	68:32
2	Acetone	89	48:52
3	CH$_3$CN	84	48:52
4	IPA	75	80:20
5	Toluene	85	56:44
6	DCM:IPA (2:1)	98	78:32
7	DCM:IPA (9:1)	98(85)[b]	80:20
8	DCM:t-BuOH (9:1)	99	76:24
9[c]	DCM:IPA (9:1)	99	79:21
10[d]	DCM:IPA (9:1)	NR	–
11[e]	DCM:IPA (9:1)	NR	–
12[f]	DCM:IPA (9:1)	NR	–

[a] Reaction conditions: **1a**-E (0.15 mmol) in solvent (0.01 M) at rt under irradiation of UV–A (350 nm) for 10 h. [b] Isolated yield. [c] Irradiation at 315 nm. [d] Irradiation at 254 nm. [e] Irradiated with blue and green LED light. [f] Without irradiation (dark control). Z/E ratios calculated by ^{1}H NMR spectroscopy. DCM = dichloromethane. CH$_3$CN = acetonitrile. IPA = isopropanol. t-BuOH = $tert$-butyl alcohol.

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Scheme 2. Substrate scope for photoisomerizations of substituted (*E*)-5-arylpent-3-en-2-one.[a] [a] Reaction conditions: **1a–1j** (0.15 mmol, 0.01 M) at room temperature under UV–A (350 nm, distance from lamp ca. 5 cm). [b] Isolated combined yields of *Z* & *E* isomers (by column chromatography). [c] Isolated yield of pure *Z*-compound. [d] ¹H NMR yields of **2** (both isomers) in parentheses. *Z/E* ratios were calculated by ¹H NMR spectroscopy.
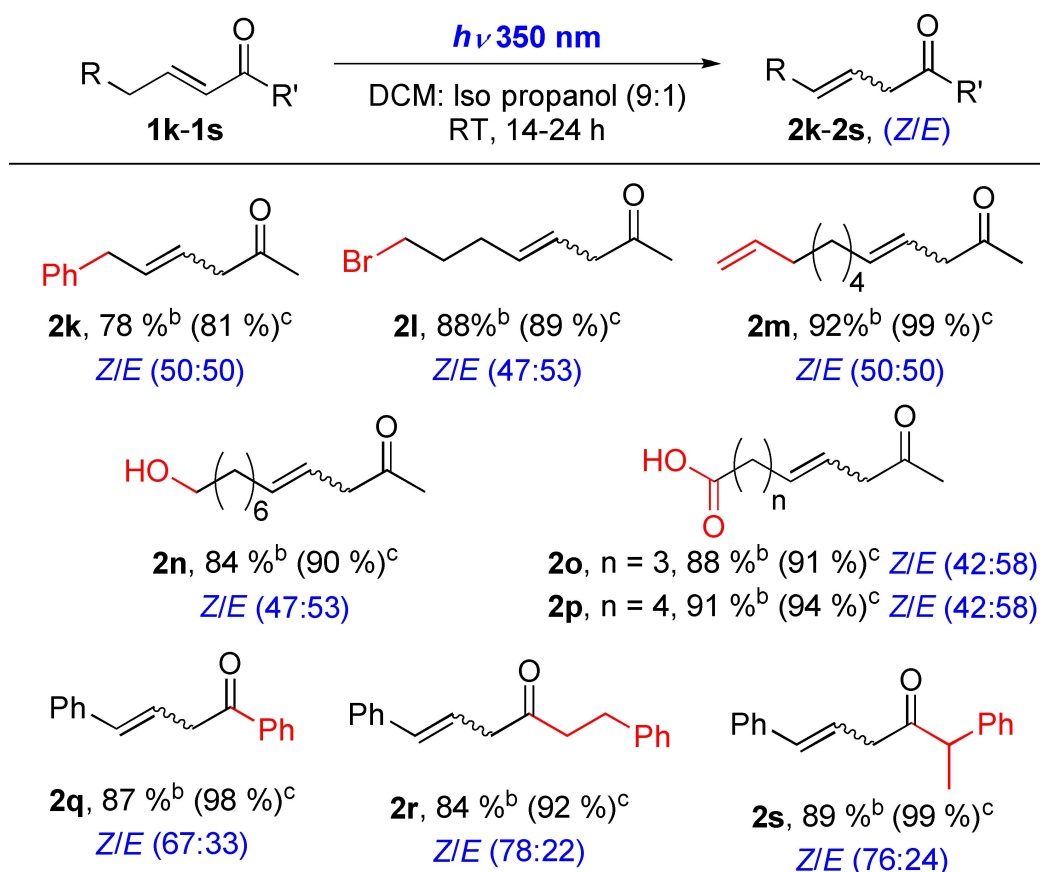
products **2a**-*Z* and **2a**-*E* can be obtained from **1a**-*Z*. For further confirmation, **1a**-*Z* was purified and subjected to the isomerization reaction conditions (Scheme 4b). As expected, the ratios of **2a**-*Z* and **2a**-*E* were the same as those obtained when the reaction was carried out beginning with **1a**-*E* (see Figure S3). Moreover, by monitoring the reaction, the NMR signals for the dienol species could be readily identified, naturally disappearing at the end of the reaction following the tautomerization (see Figure S4). These data strongly support the formation of dienol intermediates during the reaction procedure.

Based on our experimental results, and precedent literature reports,[7e] a plausible reaction mechanism for the isomerization reaction is proposed in Scheme 5. First, substrate **1**-*E* undergoes isomerization into **1**-*Z* in the presence of light. Subsequently, the carbonyl oxygen abstracts the allylic hydrogen atom via a 1,5-hydrogen atom transfer to afford the mixture of enols, which finally undergo keto-enol tautomerism to produce the mixture of **2**-*E* and **2**-*Z*.[7]

Higher *Z*-selectivity was obtained in the isomerization reaction of benzyl substituted alkenes (**1a–1j** and **1q–1s**) compared to other alkyl substituted alkenes (**1k–1p**). A possible explanation for the observed final stereoselectivity can be the existence of secondary orbital interactions during the stereo-determining 1,5-hydrogen atom rearrangement. While the more stable *E* isomer is obtained when the aromatic group is pointing away from the carbonyl group (preventing secondary orbital interactions), the more energetic *Z* isomer requires that the aromatic group be closer to the carbonyl; thus, this

interaction could explain the unusual stereoselectivity observed in the process.[9f]

Having shown the efficiency of the isomerization reaction, we envisioned a simple application for dehomologation of terminal olefin carbon chains by combining the light-induced migration process with olefin metathesis. We envisioned that cross-metathesis of a terminal alkene substrate with methyl vinyl ketone, followed by photochemical one carbon isomerization and ethenolysis could become a practical methodology to achieve dehomologations in a wide variety of terminal long chain alkenes (Scheme 6). Thus, alkenes containing bromo, alcohol and carboxylic acid functional groups were converted into the corresponding α,β-unsaturated conjugated ketones (**1l–1p**) via olefin cross-metathesis with methyl vinyl ketone. Next, the products were irradiated (UV–A) under the optimal conditions to afford the corresponding β,γ-unsaturated ketones (**2l–2p**). Finally, ethenolysis in the presence of Grubbs' second-generation catalyst, selectively afforded the dehomologated product with good overall yields (even before any careful optimization procedures were developed, detailed experimental procedures are given in the Supporting Information). Another important concern is the isomerization of terminal olefins to form internal olefins. Generally, this process requires costly precious metal catalysts, and enormous solvent volumes. Furthermore, by substituting 2-butene for ethylene in the final step of our reaction sequence, we were able to achieve a selective one-carbon migration of long-chain alkenes containing sensitive functional groups with good yields (even with internal olefins). When combined with stereoselective olefin

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Scheme 3. Substrate scope for ketone isomerizations.[a] [a] Reaction conditions: **1k-1s** (0.15 mmol, 0.01 M) at room temperature under UV–A (350 nm, distance from lamp ca. 5 cm). [b] Isolated combined yields of pure Z & E (by column chromatography). [c] ^{1}H NMR yields of **2** (both isomers) in parentheses (dibromomethane as internal standard). Z/E ratios were calculated by ^{1}H NMR spectroscopy.
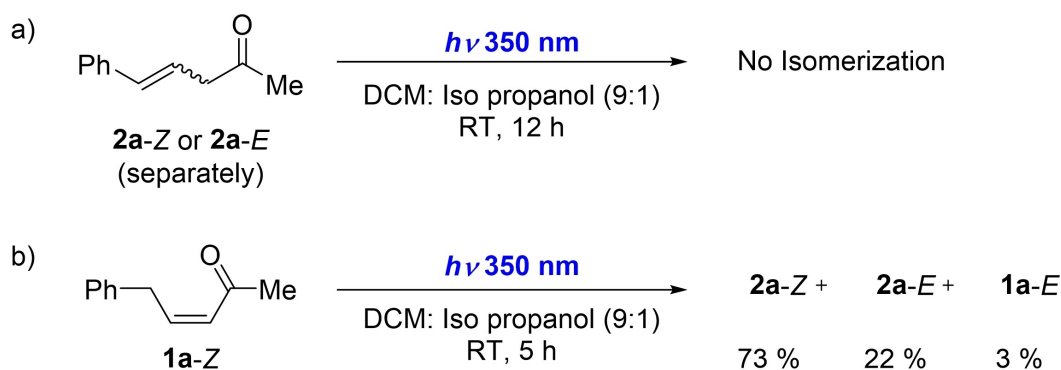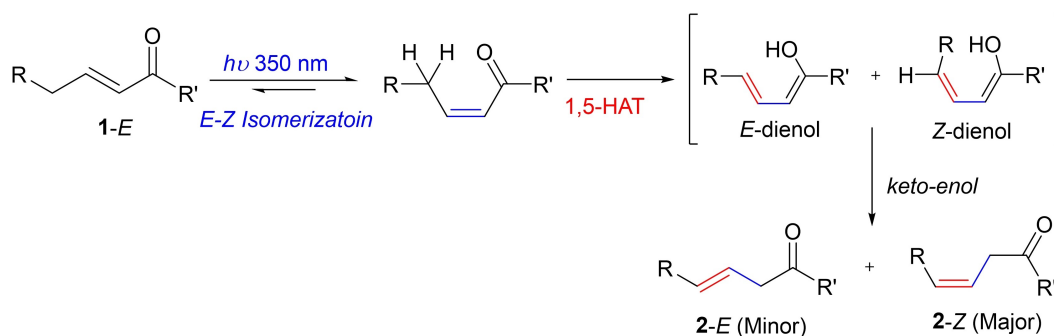

Scheme 4. Preliminary mechanistic investigations.

metathesis, this procedure could potentially provide the desired stereochemistry in the final product (Scheme 6).
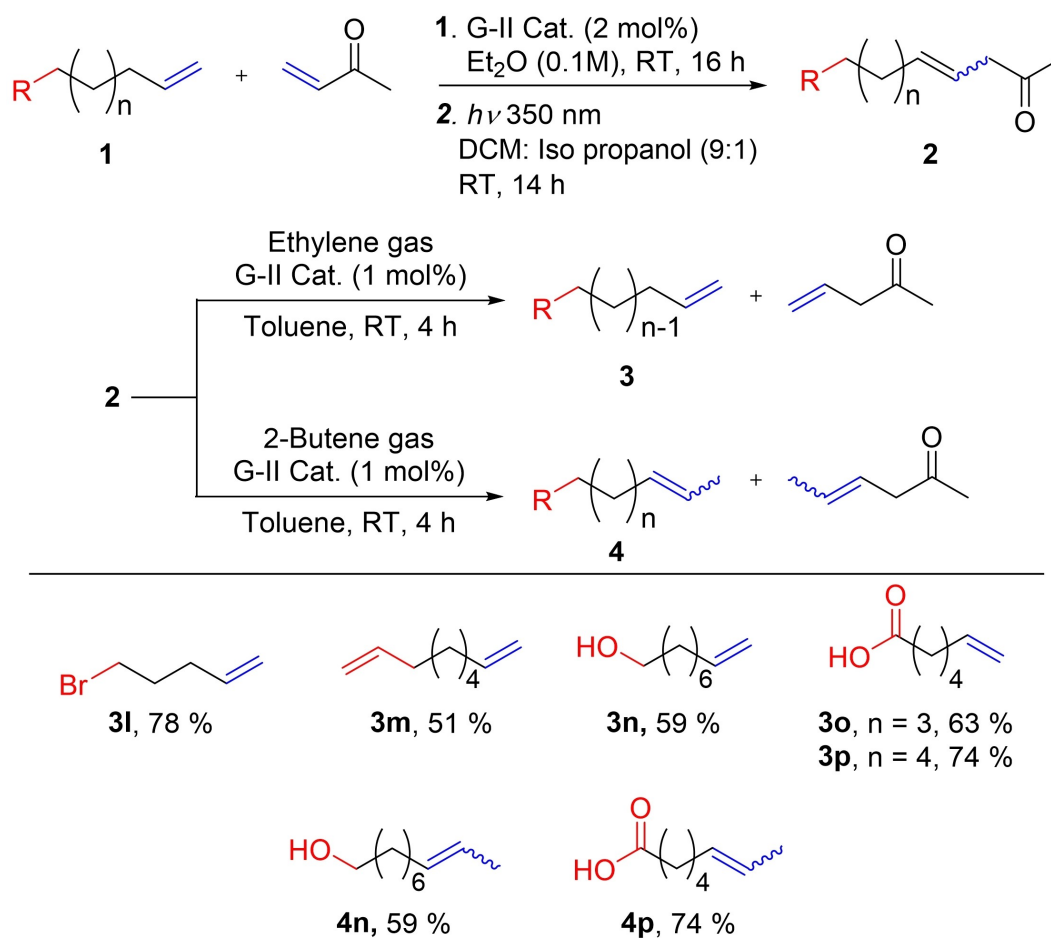
Conclusion

In conclusion, we show a mild and efficient UV-light induced method for the regioselective one-carbon double-bond migration of α,β-unsaturated ketones without the need for external additives or metal catalysts. Various unsaturated ketones with broad functional group compatibility are tolerated in this protocol to provide the desired isomerized products in moderate to high yields with good selectivity. Mechanistic investigations determined that the E to Z isomerization is the first step in the reaction, followed by a 1,5-hydride shift and consequent tautomerization to produce the corresponding isomerized products. A dehomologation and olefin migration reactions of synthetically challenging linear alkenes shows an

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Scheme 5. Proposed mechanism.

Scheme 6. Dehomologation and olefin migration procedure.

important practical application for this method. Moreover, a high Z-selectivity was observed for the allyl benzene compounds (e.g., **1a–1j**) which may be further utilized in future Z-selective cross-metathesis reactions to afford more complex final products. Further explorations of light-induced isomerizations involving 1,n-migration of different olefin substrates is currently underway in our laboratory.

Experimental Section

General procedure for olefin migration of vinyl ketones with light: In a 25-mL vial with a septum containing the solution of vinyl ketone **1** (0.2 mmol) in 0.01 M of DCM and Isopropanol (9:1 ratio) was evacuated and purged with nitrogen gas three times. Then the septum was covered with Teflon, and the vial was irradiated with 350 nm light in a Luzchem photo reactor for 10–36 h. The reaction was monitored by GC, after completion of the reaction solvent was removed under reduced pressure. The NMR yields and E/Z ratios were calculated by analyzing the crude products by ^{1}H NMR using

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dibromomethane as an internal standard. The residue could be purified through column chromatography on silica gel to provide the desired products with good, isolated yields.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

[1] a) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527–532; b) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev.* **2013**, *113*, 5322–5363; c) D. M. Schultz, T. P. Yoon, *Science.* **2014**, *343*, 985–994; d) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* **2016**, *81*, 6898–6926; e) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034–10072; f) C.-S. Wang, P. H. Dixneuf, J.-F. Soulé, *Chem. Rev.* **2018**, *118*, 7532–7585; g) F. Glaser, O. S. Wenger, *Coord. Chem. Rev.* **2020**, *405*, 213129; h) S. K. Pagire, T. Föll, O. Reiser *Acc. Chem. Res.* **2020**, *53*, 782–791; i) R. Cannalire, S. Pelliccia, L. Sancineto, E. Novellino, G. C. Tron, M. Giustiniano, *Chem. Soc. Rev.* **2021**, *50*, 766–897; j) Y. Abderrazak, A. Bhattacharyya, O. Reiser, *Angew. Chem. Int. Ed.* **2021**, *60*, 2–18; k) M. Vellakkaran, S. Hong, *Asian J. Org. Chem.* **2021**, *10*, 1012–102.

[2] a) S. Patai, J. Zabicky, *The chemistry of the alkenes*, Interscience Publishers, New York, **1964**; b) R. C. Larock, *Comprehensive organic transformations: a guide to functional group preparations, 2nd ed.*; Wiley-VCH: New York, **1999**; c) A. B. Flynn, W. W. Ogilvie, *Chem. Rev.* **2007**, *107*, 4698–4745.

[3] a) G. S. Hammond, Jack. Saltiel, *J. Am. Chem. Soc.* **1962**, *84*, 4983–4984; b) Jack. Saltiel, G. S. Hammond, *J. Am. Chem. Soc.* **1963**, *85*, 2515–2516; c) R. S. H. Liu, A. E. Asato, M. Denny, *J. Am. Chem. Soc.* **1983**, *105*, 4829–4830; d) R. S. H. Liu, D. Mead, A. E. Asato, *J. Am. Chem. Soc.* **1985**, *107*, 6609–6614; e) F. D. Lewis, C. L. Stern, B. A. Yoon, *J. Am. Chem. Soc.* **1992**, *114*, 3131–3133; f) Tatsuo. Arai, Katsumi. Tokumaru, *Chem. Rev.* **1993**, *93*, 23–39; g) T. Arai, M. Moriyama, K. Tokumaru, *J. Am. Chem. Soc.* **1994**, *116*, 3171–3172; h) A. M. Müller, S. Lochbrunner, W. E. Schmid, W. Fuß, *Angew. Chem. Int. Ed.* **1998**, *37*, 505–507.

[4] a) K. Singh, S. J. Staig, J. D. Weaver, *J. Am. Chem. Soc.* **2014**, *136*, 5275–5278; b) J. B. Metternich, R. Gilmour, *J. Am. Chem. Soc.* **2015**, *137*, 11254–11257; c) D. C. Fabry, M. A. Ronge, M. Rueping, *Chem. Eur. J.* **2015**, *21*, 5350–5354; d) J. B. Metternich, R. Gilmour, *Synlett* **2016**, *27*, 2541–2552; e) A. Singh, C. J. Fennell, J. D. Weaver, *Chem. Sci.* **2016**, *7*, 6796–6802; f) W. Cai, H. Fan, D. Ding, Y. Zhang, W. Wang, *Chem. Commun.* **2017**, *53*, 12918–12921; g) C. M. Pearson, T. N. Snaddon, *ACS Cent. Sci.* **2017**, *3*, 922–924; h) J. J. Molloy, J. B. Metternich, C. G. Daniliuc, A. J. B. Watson, R. Gilmour, *Angew. Chem. Int. Ed.* **2018**, *57*, 3168–3172; i) M. Marazzi, A. F. Monerris, M. Mourer, A. Pasc, A. Monari, *Phys. Chem. Chem. Phys.* **2020**, *22*, 4749–4757.

[5] a) Y. Yamamoto, T. Miyairi, T. Ohmura, N. Miyaura, *J. Org. Chem.* **1999**, *64*, 296–298; b) S. Hanessian, S. Giroux, A. Larsson, *Org. Lett.* **2006**, *8*, 5481–5484; c) H. J. Lim, C. R. Smith, T. V. Rajan Babu, *J. Org. Chem.* **2009**, *74*, 4565–4572; d) C. R. Larsen, D. B. Grotjahn, *J. Am. Chem. Soc.* **2012**, *134*, 10357–10360; e) M. Hassam, A. Taher, G. E. Arnott, I. R. Green, W. A. L. van Otterlo, *Chem. Rev.* **2015**, *115*, 5462–5569; f) X. Yu, H. Zhao, P. Li, M. J. Koh, *J. Am. Chem. Soc.* **2020**, *142*, 18223–18230.

[6] a) T. Ohmura, Y. Yamamoto, N. Miyaura, *Chem. Commun.* **1998**, 1337–1338; b) F.-A. Alphonse, A. K. Yudin, *J. Am. Chem. Soc.* **2006**, *128*, 11754–11755; c) L.-G. Zhuo, Z.-K. Yao, Z.-X. Yu, *Org. Lett.* **2013**, *15*, 4634–4637; d) C. Chen, T. R. Dugan, W. W. Brennessel, D. J. Weix, P. L. Holland, *J. Am. Chem. Soc.* **2014**, *136*, 945–955; e) A. Schmidt, A. R. Nödling, G. Hilt, *Angew. Chem. Int. Ed.* **2015**, *54*, 801–804.

[7] a) N. C. Yang, M. J. Jorgenson, *Tetrahedron Lett.* **1964**, *5*, 1203–1207; b) K. J. Crowley, R. A. Schneider, J. Meinwald, *J. Chem. Soc. C Org.* **1966**, 571–572; c) J. A. Barltrop, J. Wills, *Tetrahedron Lett.* **1968**, *9*, 4987–4990; d) R. M. Duhaime, A. C. Weedon, *J. Am. Chem. Soc.* **1985**, *107*, 6723–6724; e) M. Marjerrison, A. C. Weedon, *J. Photochem.* **1986**, *33*, 113–122; f) R. M. Duhaime, A. C. Weedon, *Can. J. Chem.* **2011**, *65*, 1867–1872; g) R. M. Duhaime, A. C. Weedon, *J. Am. Chem. Soc.* **1987**, *109*, 2479–2483; h) P. K. Freeman, L. Siggel, *Tetrahedron* **1988**, *44*, 5065–5074; i) A. Rudolph, A. C. Weedon, *J. Am. Chem. Soc.* **1989**, *111*, 8756–8757; j) R. R. Rando, W. v. E. Doering, *J. Org. Chem.* **1968**, *33*, 1671–1673; k) R. Ricard, P. Sauvage, C. S. K. Wan, A. C. Weedon, D. F. Wong, *J. Org. Chem.* **1986**, *51*, 62–67; l) S. L. Eng, R. Ricard, C. S. K. Wan, A. C. Weedon, *J. Chem. Soc. Chem. Commun.* **1983**, 236–238; m) Q.-Y. Meng, T. E. Schirmer, K. Katou, B. König, *Angew. Chem. Int. Ed.* **2019**, *58*, 5723–5728.

[8] a) J.-P. Pete, F. Henin, R. Mortezaei, J. Muzart, O. Piva, *Pure Appl. Chem.* **1986**, *58*, 1257–1262; b) O. Piva, R. Mortezaei, F. Henin, J. Muzart, J. P. Pete, *J. Am. Chem. Soc.* **1990**, *112*, 9263–9272; c) O. Piva, J.-P. Pete, *Tetrahedron Lett.* **1990**, *31*, 5157–5160; d) F. Hénin, S. Létinois, J. Muzart, J. Wirz, *Photochem. Photobiol. Sci.* **2006**, *5*, 426–431; e) M. M. Hinman, C. H. Heathcock, *J. Org. Chem.* **2001**, *66*, 7751–7756; f) L. Raffier, O. Piva, *Beilstein J. Org. Chem.* **2011**, *7*, 151–155; g) W. M. Horspool, F. Lenci, Eds., in *CRC Handb. Org. Photochem. Photobiol. Vol. 1 2*, CRC Press, **2003**; h) H. Yonezawa, S. Tashiro, T. Shiraogawa, M. Ehara, R. Shimada, T. Ozawa, M. Shionoya, *J. Am. Chem. Soc.* **2018**, *140*, 16610–16614.

[9] a) R. L. Sutar, S. Sen, O. Eivgi, G. Segalovich, I. Schapiro, O. Reany, N. G. Lemcoff, *Chem. Sci.* **2018**, *9*, 1368–1374; b) G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu, R. R. Knowles, *Nature* **2016**, *539*, 268–271; c) J. C. K. Chu, T. Rovis, *Nature* **2016**, *539*, 272–275; d) K. L. Skubi, T. R. Blum, T. P. Yoon, *Chem. Rev.* **2016**, *116*, 10035–10074; e) W. Shu, C. Nevado, *Angew. Chem. Int. Ed.* **2017**, *56*, 1881–1884; f) D. V. Vidhani, J. R. Gillett, Y. Cusido, I. V. Alabugin, *J. Phys. Chem. A* **2020**, *124*, 6016–6028; g) M. Nechab, S. Mondal, M. P. Bertrand, *Chem. Eur. J.* **2014**, *20*, 16034–16059; h) S. Sarkar, K. P. S. Cheung, V. Gevorgyan, *Chem. Sci.* **2020**, *11*, 12974–12993; i) E. Baráth, *Catalysts* **2018**, *8*, 671–697.

[10] B. F. Lui, N. T. Tierce, F. Tong, M. M. Sroda, H. Lu, J. Read de Alaniz, C. J. Bardeen, *Photochem. Photobiol. Sci.* **2019**, *18*, 1587–1595.