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Blue-light Induced Iron-Catalyzed Synthesis of γ,δ -Unsaturated Ketones.

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Abstract: A visible-light induced iron-catalyzed α -alkylation of ketones with allylic and propargylic alcohols as pro-electrophiles is reported. The diaminocyclopentadienone iron tricarbonyl complex plays a dual role by harvesting light and facilitating dehydrogenation and reduction steps, without the help of any exogenous photosensitizer. γ,δ -Unsaturated ketones can now be accessed through this borrowing hydrogen methodology at room temperature. Mechanistic investigations revealed that the steric hindrance on the δ -position of either the dienone or ene-ynone intermediate is the key feature to prevent or decrease the competitive 1,6-reduction (and consequently the formation of the saturated ketone) and to favour the synthesis of a set of non-conjugated enones and ynones.

Introduction

Hydrogen auto-transfer methodology or borrowing hydrogen is a thrilling area of research.^[1-2] This process is a greener and safer way to create new C-C or C-N bonds from environmentally benign alcohols. Plethora of complexes, including abundant metal-based ones, have been developed in the last decades.^[1-2] Among them, the diaminocyclopentadienone iron tricarbonyl complex has demonstrated its potency in the formation of both C-C and C-N bonds. This complex catalyzed not only the alkylation of ketones,^[3] indoles,^[4] oxindoles^[5] and alcohols,^[6] but also the *N*-alkylation of amines and amides.^[7] Whilst the hydrogen auto-transfer methodology is a successful technology in fine chemistry, some drawbacks, such as high reaction temperatures (90-150 °C), remain. Consequently, there is still room to improve such technology, to introduce new substrates and to develop unprecedented methodologies.

Photoinduced processes using visible light offer a great variety of catalytic transformations, open new retrosynthetic disconnection and, consequently, is an emerging toolbox in industry. Light, which can be seen as a clean and traceless reagent, can be exploited to access reactive intermediates in milder conditions

and at lower temperatures. Most of these reactions presuppose the excitation of a photosensitizer catalyst (PS) to initiate the transformation either by hydrogen-atom transfer (HAT), energy transfer or single-electron transfer.^[8] The merge of photoredox catalysis and transition metal catalysis (namely a dual catalysis) represents a second strategy and has extended the concept of the light activation.^[9] A third complementary approach is to take advantage of the inner coordination sphere of a transition metal complex able to harvest the visible light, without the help of any exogenous photosensitizer.^[10] Among the original light-induced methodologies using a chromophoric catalytic species, palladium-catalyzed cross-coupling reactions^[11] and the C-H functionalization are the most active areas.^[12]

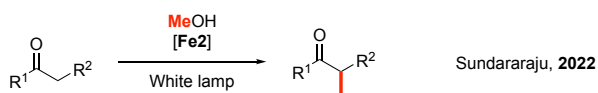
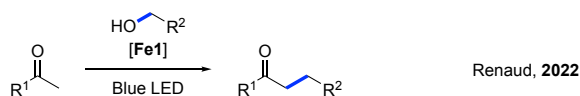
Recently, cyclopentadienone iron tricarbonyl complexes have showed their ability to perform alkylation reactions at room temperature under photoirradiation. Our group has recently disclosed a simple and robust visible light-induced iron-catalyzed α -alkylation of a variety of ketones with aliphatic and benzylic alcohols at room temperature (Scheme 1a).^[13] Almost simultaneously, Sundararaju used the Knölker's complex **Fe2** to perform the methylation of ketones with methanol, also at room temperature under white light irradiation (Scheme 1a).^[14] These results tend to demonstrate the versatility of the cyclopentadienone iron complexes, as the borrowing hydrogen strategy can now be applied either under thermal^[3-7] or visible light activation.

Homoallylic ketones or γ,δ -unsaturated ketones are relevant structures in organic synthesis as they can be intermediates in the synthesis of various (hetero)cycles, natural products or peptidomimetics.^[15] These derivatives might be synthesized from methyl ketones and allylic alcohols via the borrowing hydrogen strategy. However, allylic alcohol derivatives belong to a class of compounds which have been less evaluated in the hydrogen auto-transfer methodology.^[16] Indeed, the use of such alcohols remains a challenge because of a possible 1,4-reduction of the α,β -unsaturated aldehyde intermediates, leading to the saturated

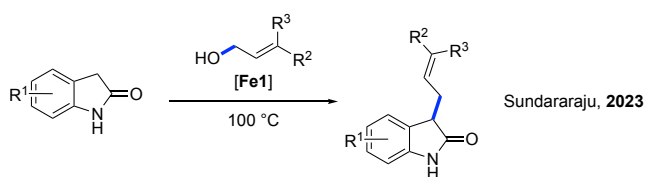
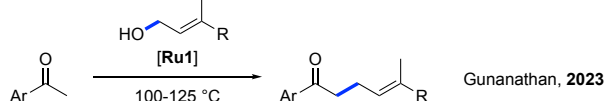
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products at the end of the reaction (Scheme 1b).^[16] Another problem to tackle with this class of compounds is that the dienone

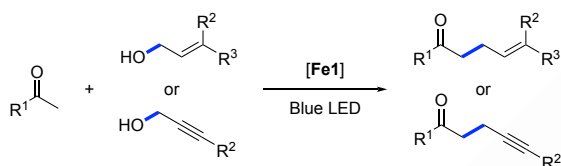
a) Light-induced alkylation of ketones:



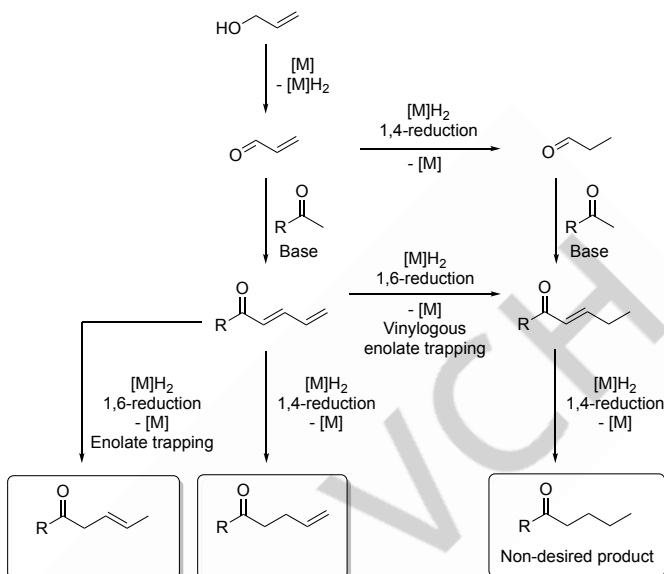
c) Previous alkylations using allylic alcohols as pro-electrophiles:



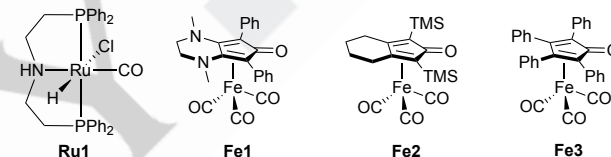
d) This work:



b) Challenges and pitfalls with the use of allylic alcohols as pro-electrophiles:



e) Organometallic complexes discussed:



Scheme 1. Previous work and outline of the blue-light induced Fe-catalyzed hydrogen autotransfer α -prenylation of ketones.

intermediates can also produce the saturated compounds via two consecutive reductions (an initial 1,6-reduction followed by a 1,4-reduction) as described in Scheme 1b.

The use of allylic alcohols as pro-electrophiles in the borrowing hydrogen approach was initially described by Gunanathan^[17] for the alkylation of ketones in the presence of a Ru-Macho complex at 100-125 °C. More recently, Sundararaju *et al.*^[18] reported a cyclopentadienone iron tricarbonyl complex **Fe1**-catalyzed the alkylation of oxindoles with some allylic alcohols at 100 °C (Scheme 1c). Following our previous works and our ongoing interest in hydrogen borrowing reactions, we report a visible-light-induced α -alkylation of ketones catalyzed by the iron complex **Fe1** at room temperature in the presence of allylic and propargylic alcohols as pro-electrophiles (Scheme 1d).

Results and Discussion

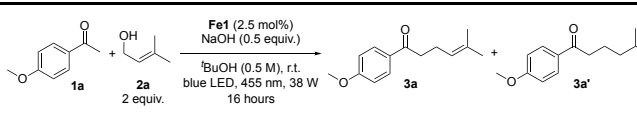
The reaction of 4-methoxyacetophenone with prenyl under blue light irradiation for 16 hours at room temperature in *tert*-butanol was chosen as a model reaction for the optimization (entry 1, Table 1). The alkylated ketones **3a** and **3a'** were obtained in 90% conversion and 70% isolated yield as an inseparable mixture. The over hydrogenated compound, namely the hydroxyl compound corresponding to the reduction of **3a**, was not obtained, distinct from the ruthenium-catalyzed prenylation reaction in thermal

conditions.^[17] The non-conjugated, β,γ -unsaturated ketone was never observed in these conditions, unlike in the thermal conditions.^[18] No alkylated product was formed without catalyst or in the dark (entry 2, Table 1). Optimization of the amount of alcohol showed an optimum with 2 equiv. of prenyl. This excess of pro-electrophile allows to reach reasonable conversions (entries 1, 3-4, Table 1). An investigation of the solvents showed up that *tert*-butanol and toluene led to the best conversions, albeit in lower selectivity in the latter (entries 1 and 5, Table 1). Prenylation in cyclopentyl methyl ether (CPME) and dichloromethane furnished ketones **3a** and **3a'** in lower conversions and lower selectivities (entries 6-7, Table 1). Finally, iron complexes **Fe2** and **Fe3** did not provide any alkylated product, demonstrating that the nature of the cyclopentadienone motive is decisive for the catalytic activity. In conclusion, the optimized conditions were as follow: one equivalent of 4-methoxyacetophenone reacts with two equivalents of prenyl in the presence of 0.5 equiv. of NaOH and 2.5 mol % of iron complex **Fe1** to give the alkylated product **3a** in mixture with **3a'** (74/26 molar ratio) in 70 % yield.

Having defined the optimal conditions, we commenced to outline the scope and limitation of this new visible light-mediated iron-catalyzed prenylation of ketones with allylic alcohols (Scheme 2). For the first series, a variety of substituted (hetero)aromatic ketones bearing electron-donating (methoxy, methyl, acetal) or

electron-withdrawing groups (halide, $-\text{CF}_3$) were employed as pronucleophiles in the hydrogen auto-transfer strategy under light

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



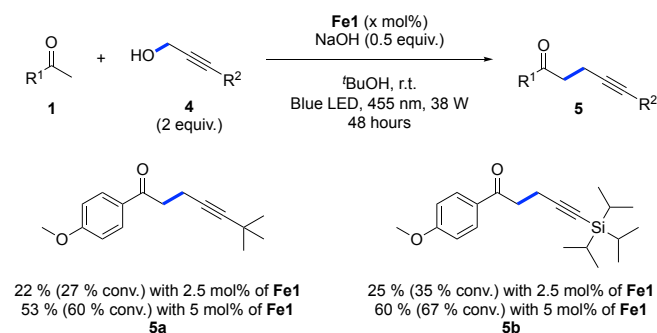
Entry ^[b]	Deviation from standard conditions	Conversion (isolated yield) ^[b,c]	3a+3a'	Selectivity 3a/3a'
1	None	90% (70%)		71/29
2	No light, or no complex ^d	N. R.		N. D.
3	1 equiv. of alcohol	N. R.		N. D.
4	3 equiv. of alcohol	77%		71/29
5	Toluene instead of tBuOH	76%		64/36
6	CH ₂ Cl ₂ instead of tBuOH	22%		73/27
7	CPME instead of tBuOH	44%		57/43
8	Complex Fe2 or Fe3 instead of Fe1	N. R.		N.D.

^[a] General conditions: 4-methoxyacetophenone (0.5 mmol), prenol (2 equiv.), NaOH (0.5 equiv.), Fe (2.5 mol%), and tBuOH (1 mL, 0.5 M), 38 watts Kessil blue LED lamp (455 nm), r.t., 16 h. ^[b] Conversions were determined by ¹H NMR analysis of the crude mixture. ^[c] Isolated yield. ^[d] N. R. no reaction. ^[e] N. D. not determined.

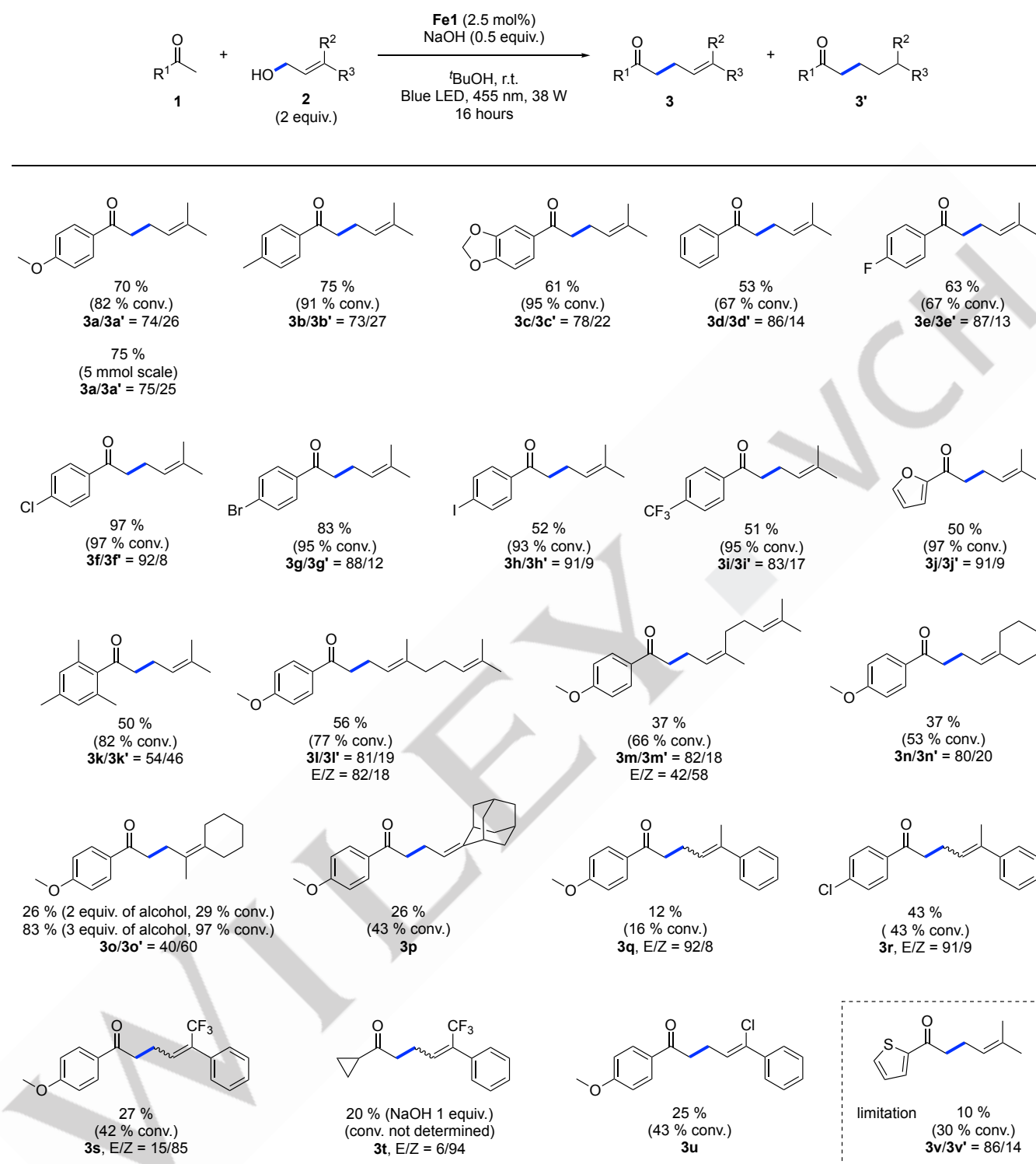
irradiation with prenol (Scheme 2). The saturated compound was always obtained as side product (Scheme 2). The alkylated products **3a-k** were synthesized in moderate to good yields (50-97 %, Scheme 2). The electronic properties of the substituent on the aromatic ring did not seem to bias the reactivity as the chemical yields were comparable (50-75% with electron-donating substituents vs. 50-97% with electron-withdrawing ones, Scheme 2). However, the steric hindrance on the pronucleophile seems to play a role in the selectivity as exemplified with alkylated ketone **3k/3k'** (54/46, Scheme 2). The steric factors might favor the 1,6-reduction of the unsaturated ketone intermediate or slow down the alkylation step, and consequently favor the reduction of the unsaturated aldehyde (see mechanistic investigations *vide infra*, Figure 1). Other 3,3'-disubstituted allylic alcohols can be introduced in this photo-induced iron-catalyzed alkylation. Compounds **3o-q** were prepared in 26-87% yield, albeit with a modest selectivity for the tetrasubstituted alkene (**3p/3p'**: 40/60, 83% yield, Scheme 2). Furthermore, worth to point out is that the lower yields with all these functionalized allylic alcohols are mainly due to lower reaction rates (leading consequently to lower conversions). Geraniol and nerol provided the corresponding alkylated ketones **3l/3l'** and **3m/3m'** in 56 and 37% yield, respectively (Scheme 2). Interestingly, isomerization of the unsymmetrically gem-disubstituted alkene was observed when

these natural allylic alcohols were used as pro-electrophiles. Starting from pure E-isomer (geraniol), **3l** was isolated as an 82/18 mixture of E/Z isomers, when the same reaction from the pure Z-isomer (nerol) led to a mixture of E/Z isomers in a ratio of 42/58. This isomerization might be due to a photoinduced process on the dienone intermediate, as already reported in literature.^[19] A second set of allylic alcohols was then evaluated. Starting from cinnamyl type allylic alcohols as pro-electrophiles and aromatic ketones as pro-nucleophiles, the corresponding non-conjugated enones were synthesized in lower conversions (16-43%) and, therefore, in lower yields (12-43%). However, some key points have to be stressed. First, **3q-3u** were obtained selectively, no saturated ketone was formed from such allylic alcohols. Second, functionalities (such as CF₃ group, or halide substituent) on the alkene moiety can be tolerated (Scheme 2). Finally, the cyclopropyl methyl ketone was engaged in the borrowing hydrogen transfer with a cinnamyl type alcohol and the corresponding alkylated ketone **3t** was isolated in 20% yield (the conversion was not determined by ¹H NMR analysis of the crude mixture in this case due to the volatility of the starting ketone). To show up the practicability of this methodology, the visible-light mediated prenylation was carried out on a 5 mmol scale between 4-methoxyacetophenone and prenol at room temperature for 16h. Ketones **3a/3a'** were prepared in full conversion, good yield (74%) and selectivity (75/25).

Having delineated the scope of this reaction with allylic alcohols, we thought to extend this methodology to propargylic alcohols. To the best of our knowledge, such pro-electrophiles have not yet been reported in hydrogen auto-transfer methodology. Again, the steric parameter was the key feature to allow the formation of the alkylated product. While no reaction was observed with 2-butylnol and low yield (6 %) was obtained from 3-phenyl propargyl alcohol, sterically hindered alkynes open the way to the hydrogen auto-transfer reaction (Scheme 3). As examples, *tert*-butyl or tris-isopropylsilyl group substituted-propargylic alcohols led chemoselectively to the corresponding non-conjugated ynones **5a** and **5b** in moderate conversions (27 and 35%, respectively) and yields (22 and 25%, respectively, Scheme 3). A rapid optimization of the reaction conditions showed that both conversions and yields could be improved by using 5 mol% of iron complex (Scheme 3). The γ,δ -ynone **5a** and **5b** were then isolated in 53 and 60% yields. Increasing the amount of base (1 equiv.) or catalyst (> 5 mol%) led to a turbid solution and consequently to a drop of the conversions.



Scheme 3. Blue-light-induced alkylation of ketones with substituted propargylic alcohols.



Scheme 2. Scope of the blue-light-induced alkylation of ketones with allylic alcohols.

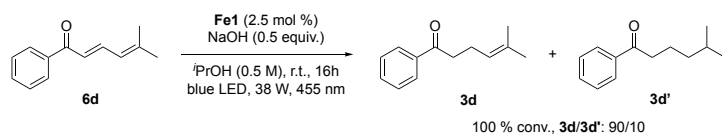
To acquire more insight into the mechanism of this light-mediated iron-catalyzed prenylation, several experiments were conducted (Scheme 4).

First, the dienone **6d**, prepared from acetophenone and 3-methylbutenal (prenal), was reduced in *iso*-propanol at room

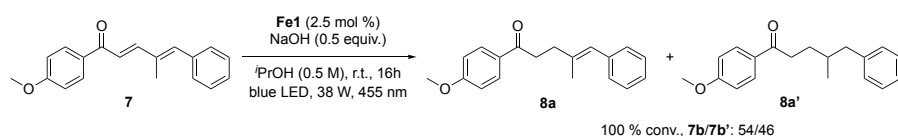
temperature under blue light irradiation.^[20] A 9/1 mixture of **3d/3d'** was obtained in full conversion. The selectivity was comparable to the one in the catalytic alkylation (86/14) and confirmed that the 1,6-reduction of the dienone intermediate is a competitive side pathway. Second, the reduction of the dienone **7**, prepared from

4-methoxyacetophnone and α -methyl trans cinnamaldehyde, led to **8a/8a'** in a 54/46 ratio in the same reaction conditions.

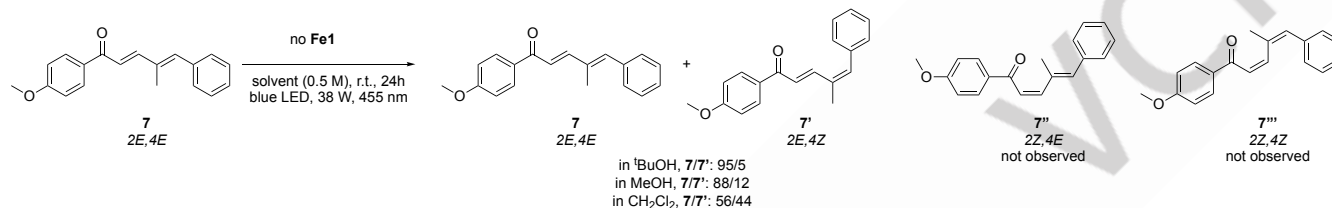
a) Investigation on the 1,6-reduction of the dienone intermediate



b) Investigation on the importance of the substitution at the δ -position of the dienone intermediate



c) Investigation on the light-induced cis-trans isomerisation



Scheme 4. Mechanistic investigations.

This result demonstrates that the steric hindrance on the δ -position of the intermediate is a key feature to prevent or slow down the 1,6-reduction. The last experiment was set up to unveil the role of light for the alkene isomerization. After photoirradiation for 24 hours, the dienone **7** was obtained in a mixture of isomers **7** and **7'** in a ratio depending on the solvent and on the solubility of the dienone. No other isomer was observed in these conditions. When the dienone **7** is poorly soluble in alcoholic solvents (^tBuOH, MeOH), little isomerization was noticed under blue light irradiation for 24 h. The ratio between **7/7'** decreases in dichloromethane in the same reaction conditions.

Based on the above-mentioned experiments and previous works on the borrowing hydrogen methodology,^[3-7,13] a plausible mechanism for the prenylation of ketone **1d** with **2a** is reported in Figure 1. Following the decarbonylation procedure used by Knölker in basic conditions,^[21] Fe1 could generate the 16-electron deficient intermediate species **I**. Coordination of the alcohol **2a** could afford the intermediate **II**. Light-mediated dehydrogenation would liberate the intermediate **III** and prenal **9a**.^[13] A condensation step between prenal **9a** and the ketone **1d** could furnish the dienone **10a**. Reaction of the later with **III** could provide two intermediates **IV** and **VI**. A 1,6-photoinduced reduction could liberate the unsaturated ketone **11a** via intermediate **V**. The 1,4-photoinduced reduction would lead to ketone **3a** via intermediate **VI**. The conjugated ketone **11a** could then re-enter in a second catalytic cycle to finally generate the saturated compound **3d'** via a 1,4-photoinduced reduction.^[13] A second pathway to produce the side product **3d'** could be the following one. Prenal **9a** could be reduced into 3-methylbutanal **12a** thanks to a visible light-mediated activation of **III**. Further condensation of **10a** with **1d** (leading to **11a**) and a second reduction step could furnish **3d'** (Figure 1).

Conclusion

In conclusion, we have reported a novel visible-light-induced α -alkylation of ketones using allylic alcohols as pro-electrophiles. Extension of the reaction to propargylic alcohols, as pro-electrophiles, allowed for the first time the obtention of the corresponding alkylated ketones through a hydrogen borrowing process. Mechanistic investigations confirmed the presence of a 1,6-reduction of the dienone intermediate leading to the saturated product, and a light-induced isomerization of the alkene. Further work on the mechanistic understanding is in progress in our group.

Supporting Information ((optional))

The authors have cited additional references within the Supporting Information.^[22-43]

Experimental Section

General. Commercial reagents were used without further purification. All air- and moisture-sensitive manipulations were carried out using standard vacuum line Schlenk tubes techniques. The photocatalyzed reactions were carried out in an Hepatochem HCK1006-01-025 PhotoredoxBox or PhotoredoxBox Duo irradiated with a 38 W A 160WE Tuna Blue Kessil lamp (455 nm). Solvents were degassed prior to use by bubbling argon gas directly in the solvent. NMR spectra were recorded on a Brücker

spectrometer (500 MHz or 600 MHz). ^1H NMR chemical shifts are referenced to the residual hydrogen signals of the deuterated

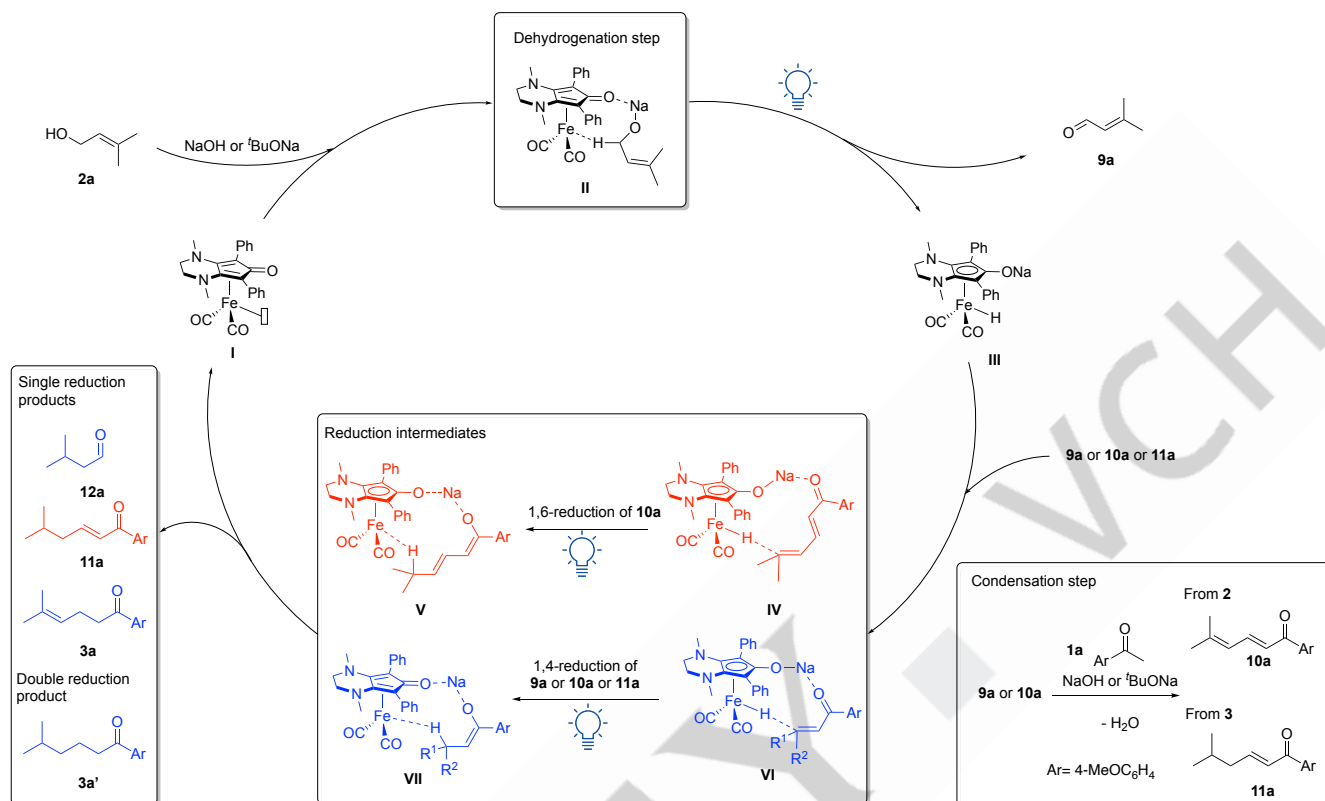


Figure 1. Proposed mechanism.

solvent (7.26 ppm for CDCl_3). The ^{13}C NMR chemical shifts are referenced to the ^{13}C signals of the deuterated solvent (77 ppm for CDCl_3). (^1H) NMR information is given in the following format: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant(s) (J) in Hertz (Hz), number of protons, type. Carbon (^{13}C) NMR spectra are reported in ppm (δ) relative to CDCl_3 unless noted otherwise. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer. HRMS (ESI-TOF) analyses were performed by Laboratoire de Chimie Moléculaire et Thioorganique analytical facilities. Emission spectra were measured at room temperature in liquid state on a Perkin Elmer LS 55 spectrofluorometer. UV-visible absorption spectrum in solution was measured at room temperature on a Perkin Elmer Lambda 40 UV-visible spectrometer

General procedure: In a 10 mL vial, were added under argon atmosphere ketone **1** (0.5 mmol, 1.0 equiv.), alcohol (1.0 mmol, 2 equiv.), NaOH (10 mg, 0.25 mmol, 0.5 equiv.), **Fe1** (2.5 mol%, 5.8 mg, 0.0125 mmol), $t\text{BuOH}$ (1.0 mL). The reaction tube was sealed. The mixture was stirred at room temperature and irradiated by a 38W blue LED lamp for 16 hours. The mixture was filtrated on celite, eluted with diethyl ether and concentrated under reduced pressure. The conversion was determined by ^1H NMR spectroscopy. The residue was purified by flash chromatography using pentane/ethyl acetate as eluent to afford the desired product.

Acknowledgements

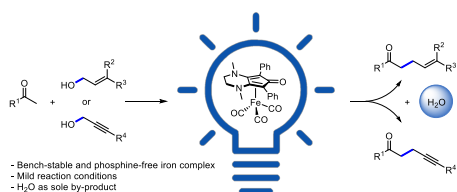
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Keywords: light activation • iron complex • hydrogen auto-transfer • γ,δ -unsaturated ketones

- [1] For recent reviews see: a) F. Huang, Z. Liu, Z. Yu, *Angew. Chem. Int. Ed.* **2016**, *55*, 862. b) G. Chelucci, *Coord. Chem. Rev.* **2017**, *331*, 1. c) A. Corma, J. Navas, M. J. Sabater, *Chem. Rev.* **2018**, *118*, 1410. For recent works, see: d) W. M. Akhtar, C. B. Cheong, J. R. Frost, K. E. Christensen, N. G. Stevenson, T. J. Donohoe, *J. Am. Chem. Soc.* **2017**, *139*, 2577. e) S. Thiyagarajan, C. Gunanathan, *J. Am. Chem. Soc.* **2019**, *141*, 3822.
- [2] For recent reviews on the use of Earth-abundant metal-based complexes in auto-transfer strategy, see: a) T. Irrgang, R. Kempe, *Chem. Rev.* **2019**, *119*, 2524-2549. b) B. G. Reed-Berendt, K. Polidano, L. C. Morrill, *Org. Biomol. Chem.* **2019**, *17*, 1595. For recent examples, see: c) P.

- Chakraborty, M. K. Gangwar, B. Emayavaramban, E. Manoury, R. Poli B. Sundararaju, *ChemSusChem* **2019**, *12*, 3463. d) S. Waiba, S. K. Jana, A. Jati, A. Jana, B. Maji, *Chem. Commun.* **2020**, *56*, 8376.
- [3] a) L. Bettoni, C. Seck, M. D. Mbaye, S. Gaillard, J.-L. Renaud, *Org. Lett.* **2019**, *21*, 3057. b) L. Bettoni, S. Gaillard, J.-L. Renaud, *Chem. Commun.* **2020**, *56*, 12909. c) L. Bettoni, S. Gaillard, J.-L. Renaud, *Org. Lett.* **2020**, *22*, 2064.
- [4] C. Seck, M. D. Mbaye, S. Gaillard, J.-L. Renaud, *Adv. Synth. Catal.* **2018**, *360*, 4640.
- [5] M. B. Dambatta, K. Polidano, A. D. Northey, J. M. Williams, L. C. Morrill, *ChemSusChem* **2019**, *12*, 2345.
- [6] a) L. Bettoni, S. Gaillard, J.-L. Renaud, *Org. Lett.* **2019**, *21*, 8404. b) K. Polidano, J. M. J. Williams, L. C. Morrill, *ACS Catal.* **2019**, *9*, 8575.
- [7] a) K. Polidano, B. D. W. Allen, J. M. J. Williams, L. C. Morrill, *ACS Catal.* **2018**, *8*, 6440. b) A. Lator, S. Gaillard, A. Poater, J.-L. Renaud, *Org. Lett.* **2018**, *20*, 5985.
- [8] a) J. Großkopf, T. Kratz, T. Rigotti, T. Bach, *Chem. Rev.* **2022**, *122*, 1626. b) L. Capaldo, D. Ravelli, M. Fagnoni, *Chem. Rev.* **2022**, *122*, 1875. c) N. Holmberg-Douglas, D. A. Nicewicz, *Chem. Rev.* **2022**, *122*, 1925. d) F. Juliá, T. Constantini, D. Leonori, *Chem. Rev.* **2022**, *122*, 2292. e) S. P. Pitre, L. E. Overman, *Chem. Rev.* **2022**, *122*, 1717. f) K. Kwon, R. T. Simons, M. Nandakumar, J. L. Roizen, *Chem. Rev.* **2022**, *122*, 2353.
- [9] A. Y. Chan, I. B. Perry, N. B. Bissonnette, B. F. Buksh, G. A. Edwards, L. I. Frye, O. L. Garry, M. N. Lavagnino, B. X. Li, Y. Liang, E. Mao, A. Millet, J. V. Oakley, N. L. Reed, H. A. Sakai, C. P. Seath, D. W. C. MacMillan, *Chem. Rev.* **2022**, *122*, 1485.
- [10] For a recent review, see: a) K. P. S. Cheung, S. Sarkar, V. Gevorgyan, *Chem. Rev.* **2022**, *122*, 1543. b) Y. Xiong, S. Li, H. Xiao, G. Zhang, *Synthesis* **2021**, *53*, 4327.
- [11] For recent reviews, see: a) G. A. M. Jardim, J. A. Dantas, A. A. Barboza, M. W. Paixão, M. A. B. Ferreira, *Synthesis* **2022**, *54*, 4629. b) P. Chuentragool, D. Kurandina, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2019**, *58*, 11586. For some examples, see: c) Z. Zhang, N. Kvasovs, A. Dubrovina, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2022**, *61*, e202110924. d) H.-M. Huang, P. Bellotti, P. M. J. Pflüger, L. Schwarz, B. Heidrich, F. Glorius, *J. Am. Chem. Soc.* **2020**, *142*, 10173. e) A. D. Marchese, A. G. Durant, C. M. Reid, C. Jans, R. Arora, M. Lautens, *J. Am. Chem. Soc.* **2022**, *144*, 20554.
- [12] a) P. Gandeepan, J. Koeller, K. Korvorapun, J. Mohr, L. Ackermann, *Angew. Chem., Int. Ed.* **2019**, *58*, 9820. b) A. Sagadevan, M. F. Greaney, *Angew. Chem., Int. Ed.* **2019**, *58*, 9826. c) K. Korvorapun, J. Struwe, R. Kuniyil, A. Zangarelli, A. Casnati, M. Waeterschoot, L. Ackermann, *Angew. Chem., Int. Ed.* **2020**, *59*, 18103. d) A. Sagadevan, A. Charitou, F. Wang, M. Ivanova, M. Vuagnat, M. F. Greaney, *Chem. Sci.* **2020**, *11*, 4439. e) J. Kim, D. Kim, S. Chang, *J. Am. Chem. Soc.* **2020**, *142*, 19052. f) J. Thongpaen, R. Manguin, V. Dorcet, T. Vives, C. Duhayon, M. Mauduit, O. Baslé, *Angew. Chem. Int. Ed.* **2019**, *58*, 15244. g) L. Britton, J. H. Dochert, A. P. Dominey, S. P.; Thomas, *Molecules* **2020**, *25*, 905. h) L. Britton, M. Skrodzki, G. S. Nichol, A. P. Dominey, P. Pawluć, J. H. Docherty, S. P. Thomas, *ACS Catal.* **2021**, *11*, 6857. i) S. Sar, R. Das, S. Sen, *Adv. Synth. Catal.* **2021**, *363*, 3521. j) Y. Wang, S. Chen, X. Chen, A. Zangarelli, L. Ackermann, *Angew. Chem. Int. Ed.* **2022**, e202205562. k) K. P. S. Cheun, J. Fang, K. Mukherjee, A. Mihranyan, V. Gevorgyan, *Science* **2022**, *378*, 1207.
- [13] M.-S. Abdallah, N. Joly, S. Gaillard, A. Poater, J.-L. Renaud, *Org. Lett.* **2022**, *24*, 5584.
- [14] B. Emayavaramban, P. Chakraborty, P. Dahiya, B. Sundararaju, *Org. Lett.* **2022**, *24*, 6219.
- [15] a) A. Douchez, A. Geranurimi, W. D. Lubell, *Acc. Chem. Res.* **2018**, *51*, 2574. b) G. Casiraghi, L. Battistini, C. Curti, G. Rassu F. Zanardi, *Chem. Rev.* **2011**, *111*, 3076.
- [16] D. E. Latham, K. Polidano, J. M. J. Williams, L. C. Morrill, *Org. Lett.* **2019**, *21*, 7914.
- [17] R. V. Sankar, D. Manikpuri, C. Gunanathan, *Org. Biomol. Chem.* **2023**, *21*, 273.
- [18] P. Chakraborty, S. Pradhan, J. R. Premkumar, B. Sundararaju, *J. Catal.* **2023**, *421*, 309.
- [19] N. Kozukue, M.-S. Park, S.-H. Choi, S.-U. Lee, M. Ohnishi-Kameyama, C. E. Levin, M. Friedman, *J. Agric. Food Chem.* **2007**, *55*, 7131.
- [20] For a thermal reduction in *iso*-propanol with Fe¹, see: A. Lator, S. Gaillard, A. Poater, J.-L. Renaud, *Chem. Eur. J.* **2018**, *24*, 5770.
- [21] H.-J. Knölker, E. Baum, H. Goesmann, R. Klauss, *Angew. Chem. Int. Ed.* **1999**, *38*, 2064.
- [22] S. W. Kim, T. Wurm, G. A. Brito, W.-O. Jung, J. R. Zbieg, C. E. Stivala, M. J. Krische, *J. Am. Chem. Soc.* **2018**, *140*, 9087.
- [23] S. P. Chavan, K. P. Pawara, S. Garaia, *RSC Adv.* **2014**, *4*, 14468.
- [24] M. Koy, P. Bellotti, F. Katzenburg, C. G. Daniliuc, F. Glorius, *Angew. Chem. Int. Ed.* **2020**, *59*, 2375.
- [25] A. Mukherjee, O. Wu, W. J. le Noble, *J. Org. Chem.* **1994**, *59*, 3270.
- [26] a) J. Jacob, J. H. Espenson, J. H. Jensen, M. S. Gordon, *Organometallics* **1998**, *17*, 1835. b) H. Li, H. Chen, Y. Zhou, J. Huang, J. Yi, H. Zhao, W. Wang, L. Jing, *Chem. Asian J.* **2020**, *15*, 555.
- [27] M. Kimura, T. Yamazaki, T. Kitazume, T. Kubota, *Org. Lett.* **2004**, *6*, 4651.
- [28] C. Herbivo, A. Comel, G. Kirsch, M. M. M. Raposo, *Tetrahedron*, **2009**, *65*, 2079.
- [29] X. Zhou, G. Zhang, R. Huang, H. Huan, *Org. Lett.* **2021**, *23*, 3659.
- [30] V. Sinka, D. A. Cruz, V. S. Martín, J. I. Padrón, *Org. Lett.* **2022**, *24*, 5271.
- [31] H. C. Brown, G. A. Molander, S. M. Singh, U. S. Racherla, *J. Org. Chem.* **1985**, *50*, 1577.
- [32] H.-S. Sim, X. Feng, J. Yun, *Chem. Eur. J.* **2009**, *15*, 1939.
- [33] T. Narender, S. Sarkar, K. Rajendar, S. Tiwari, *Org. Lett.* **2011**, *13*, 6140.
- [34] D. Shen, D. L. Pool, C. C. Shotton, A. F. Kornahrens, M. P. Healy, T. J. Donohoe, *Angew. Chem. Int. Ed.* **2014**, *54*, 1642.
- [35] C.-L. Wu, W.-Y. Chen, C.-S. Chu, *Nat. Prod. Commun.* **2007**, *2*, 361.
- [36] J.-J. Cao, F. Zhou, J. Zhou, *Angew. Chem. Int. Ed.* **2010**, *49*, 4976.
- [37] N. Kalutharage, C. S. Yi, *Angew. Chem. Int. Ed.* **2013**, *52*, 13651.
- [38] J. Wang, Y.-B. Pang, N. Tao, R.-S. Zeng, *J. Org. Chem.* **2019**, *84*, 15315.
- [39] L. Feng, T. Jialin; A. Guizhen, WO2022160637A1, **2022**.
- [40] J.Hood, Kumar KC Sunil, O. Kibar, C. Barroga (Samumed LLC), WO2016029021A1, **2016**.
- [41] J. R. Frost, C. B. Cheong, W. M. Akhtar, D. F. J. Caputo, N. G. Stevenson, T. J. Donohoe, *J. Am. Chem. Soc.* **2015**, *137*, 15664.
- [42] B. Yuan, D. Ding, C. Wang, *ACS Catal.* **2022**, *12*, 4261.
- [43] C.-Y. Wang, R.-J. Song, Y.-X. Xie, J.-H. Li, *Synthesis* **2016**, *48*, 223.

Entry for the Table of Contents



A cyclopentadienone iron tricarbonyl complex, able to harvest light and catalyze both dehydrogenation and reduction, allows the synthesis of γ,δ -unsaturated ketones using the borrowing hydrogen strategy in the presence of various substituted primary allylic or propargylic alcohols as alkylating reagents.

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