Advanced Synthesis & Catalysis

Accepted Article

Title: Visible Light Activated Radical Denitrative Benzoylation of β-Nitrostyrenes: A Photocatalytic Approach to Chalcones

Authors: Shubhangi Tripathi, Ritu Kapoor, and Lal Dhar Yadav

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: *Adv. Synth. Catal.* 10.1002/adsc.201701559

Link to VoR: http://dx.doi.org/10.1002/adsc.201701559

10.1002/adsc.201701559

COMMUNICATION

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

Visible Light Activated Radical Denitrative Benzoylation of β-Nitrostyrenes: A Photocatalytic Approach to Chalcones

Shubhangi Tripathi, Ritu Kapoor, Lal Dhar S. Yadav *

Green Synthesis Lab, Department of Chemistry, University of Allahabad, Allahabad 211002, India; e-mail: ldsyadav@hotmail.com; Fax: (+91)532-246-0533; Tel.: (+91)532-250-0652.

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

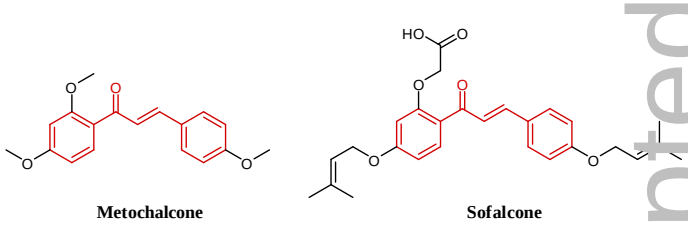
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201######.

Abstract: A metal-free, convenient photocatalytic approach to chalcones from β-nitrostyrenes and benzaldehydes via a radical denitrative benzoylation pathway is reported. The salient features of the protocol include the utilization of visible light as an inexpensive and ecosustainable energy source, *N*-hydroxyphthalimide (NHPI) as a reusable organophotocatalyst and acetonitrile as an acceptable green solvent to afford chalcones in excellent yields at room temperature in a one-pot procedure. Notably, this is the first application of β-nitrostyrenes as readily available substrates for chalcone synthesis and the first example of photocatalysis in this field.

Keywords: C-C bond formation; organic catalysis; photochemistry; radicals; synthetic methods; visible light.

Chalcones constitute a privileged family of compounds in the perspectives of medicinal and synthetic chemistry. They exhibit various useful biological activities such as analgesic, anti-viral, anti-inflammatory, anti-ulcerative, anti-fungal, anti-malarial, anti-bacterial and anticancer activities.[1] Some chalcone-based drugs are in clinical use, for example, metochalcone, a choleretic drug and sofalcone as anantiulcer and mucoprotective drug (Figure 1). Chalcones incorporate a very good synthon, which renders them valuable intermediates for the synthesis of flavonoids,[2] flavones[3] and a diverse range of heterocycles namely, thiazine, oxazine, isoxazole, pyrazole, diazepine, pyridine and pyrimidine.[4]

Owing to their tremendous chemical and biological importance, chalcones have been extensively studied, which is evident from the appearance of numerous reviews[5] thoroughly covering their synthesis, applications and biological significances from various angles. Traditionally, acids/bases catalysed homogeneous and heterogenous Claisen-Schmidt condensation was used for the practical synthesis of chalcones.[6] However, drawbacks of non-appositeness for the substrate bearing acid/base sensitive groups, slow reaction rate and very often generation of complex mixture during the condensation reaction, led to the development of many superior alternative methods for the synthesis of chalcones. In this context, different catalytic systems such as organolithium compounds,[7] modified phosphates,[8] zinc oxide,[9] KF-Al_2O_3,[10] phase transfer catalysts,[11] hydrotalcites and zeolites[12] have been employed for the synthesis of chalcones. Again, these processes suffer from the impediment of difficult catalyst recovery and purification of the desired products.



Metochalcone Sofalcone

Figure 1. Chalcone-based drugs in clinical use.

To overcome the difficulty associated with the foregoing routes, highly efficient, pioneering and celebrated cross coupling methodologies such as Suzuki,[13] Heck[14] and Julia-kocienski[15] cross couplings have been recently used for the synthesis of chalcones (Scheme 1a). Though these metal-catalysed couplings are very effective for chalcone synthesis, most of them are very expensive and hazardous to the environment. Thus, the development of a metal-free, environmentally benign, cost effective and sustainable method for the synthesis of chalcones is of course a welcome move.

Moreover, nitro-olefins are important building blocks for the synthesis of a wide variety of organic compounds,[16] possessing various biological and

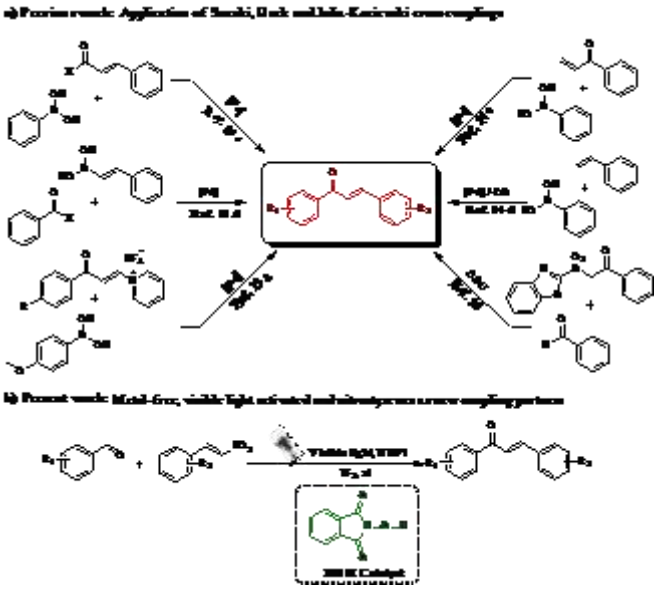
Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/adsc.201701559

pharmaceutical activities.[17] Among nitroalkenes, *β*-nitrostyrenes were extensively studied[18] because of their easy preparation (by Henry reaction) and inherent property to induce different functionalities via facile *ipso*-substitution of the nitro group through radical denitrative addition-elimination reaction.[18] The literature records very few reports for these reactions employing photochemical conditions.[18c,g] Therefore, further research for the fruition of this stable and easily available intermediate in conjuction with photocatalysis is highly desirable in organic synthesis.

In recent years, visible light photocatalysis has become a captivating way for designing and realising synthetically useful protocols,[19-23] because visible light is clean, inexpensive and unending natural energy source. The methodology development in this area is based on the seminal work of the research groups of MacMillan,[19] Yoon[20] and Stephenson,[21] who have demonstrated the powerful visible light photocatalytic property of $Ru(bpy)_3Cl_2$ (bpy = 2,2'-bipyridine) and $Ir(dtbbpy)_3Cl_2$ (dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine). Some organic dyes including eosin Y, rose Bengal, nile red, rhodamine B, perylene and fluorescein have also emerged as efficient visible light photocatalysts.[23] However, the high cost and potential toxicity of the transition metal-based photocatalysts makes them incompatible with the green chemistry demands. Similarly, organic dyes on prolonged irradiation undergo decomposition and suffer from the drawback of their tedious recovery for reuse.[23a] Very recently, our research group has disclosed the first utilization of *N*-hydroxyphthalimide (NHPI) as an efficient visible light organophotocatalyst,[24] which is free from the drawbacks of the aforementioned photocatalysts, hence we opted to use NHPI in the present study.



Scheme 1. Selected routes to access chalcones.

Considering the above points and our focus on the methodology development employing visible light organophotocatalysts,[23a,23b,24,25] we envisioned that benzoyl radicals could be easily generated photochemically from benzaldehydes using NHPI as catalyst and these could undergo cross coupling with *β*-nitrostyrene to afford chalcones (Scheme 1b). Notably, this is the first chalcone synthesis employing *β*-nitrostyrenes as coupling partners and the work also presents the first application of visible light photocatalysis to chalcone synthesis.

To realise the envisaged synthetic strategy and establish the optimal reaction conditions, our study began with the model reaction of (*E*)-*β*-nitrostyrene **1a** (1 mmol) with benzaldehyde **2a** (1 mmol) in acetonitrile (3 mL) in the presence of a catalytic amount of NHPI (10 mol%) under a nitrogen atmosphere and irradiation with 7 W white LEDs (White light emitting diodes) at room temperature. To our delight, the desired product chalcone **3a** was isolated in an excellent yield of 89% within 8 h of irradiation (Table 1, entry 1).

Encouraged by this initial success, we performed a series of control and screening experiments to confirm the requisite reaction parameters. It was found that there was no product formation when the reaction was conducted in the dark (Table 1, entry 1 versus 2). Similarly, in the absence of the catalyst NHPI, the product **3a** could not be obtained (Table 1, entry 1 versus 3). These results established that both visible light and NHPI are essential to realise the present protocol. Further, given the significance to the role of solvent for a chemical transformation, a series of experiments was performed to choose the best solvent for the present reaction and the results revealed that acetonitrile was the best among DCE, DMF and DMSO (Table 1, entry 1 versus 4, 5 and 6). Cumulatively, on decreasing the catalyst loading from 10 mol% to 5 mol%, a significant decrease in the yield of **3a** was observed (Table 1, entry 1 versus 7), while an increase in the catalyst loading from 10 mol% to 15 mol% does not affect the yield of the product (Table 1, entry 1 versus 8). Moreover, the catalyst NHPI also works under thermal conditions, but delivers a considerably lower yield of the desired product **3a** (Table 1, entry 1 versus 9). Advantageously, the catalyst could be recovered in high yield after the reaction (Table 1, entry 10) and reused with the same efficiency (Table 1, entry 11). Besides NHPI, the scope of other *N*-hydroxy catalysts was also examined but all of them were far less effective than NHPI (Table 1, entry 1 versus 12-14).

Having established the optimised reaction conditions for visible light mediated synthesis of chalcones, we continued to survey the generality and scope of the present protocol across a wide range of

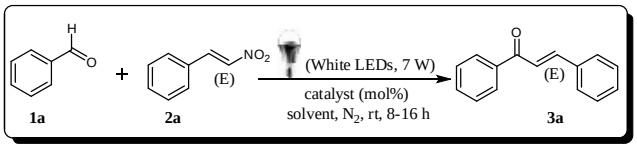
Accepted Manuscript

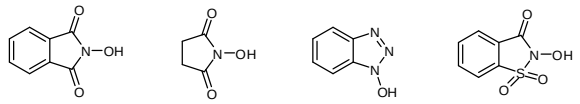
This article is protected by copyright. All rights reserved.

10.1002/adsc.201701559

(*E*)-*β*-nitrostyrenes and benzaldehydes, incorporating various functionalities like Me, OH, OMe, F, NO_2 or NH_2 (Table 2). The study reveals the splendid tolerance of both electron-donating and electron-withdrawing groups and regardless of differences in the electronic and steric properties of substrates, they produce the desired chalcones **3** in 76-96% yields. Electronically, (*E*)-*β*-nitrostyrenes **2** bearing an electron-withdrawing substituent on the aromatic nucleus appear to react faster and afford slightly higher yields in comparison to those possessing an electron-donating substituent (Table 2, product **3g** versus **3k**). However, benzaldehydes **1** with an electron-donating group on aromatic ring appear to react faster to afford marginally higher yields than those having an electron-withdrawing group (Table 2, products **3b**, **3c**, **3e**, **3n** versus **3d, 3f**, **3o**). The method also works well with heterocyclic aldehydes (Table 2, products **3l**, **3m**).

Table 1. Optimisation of reaction conditions [a]



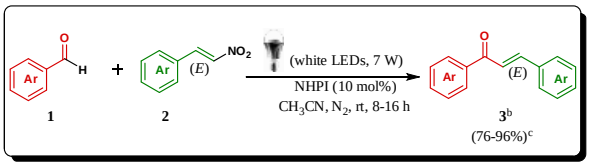


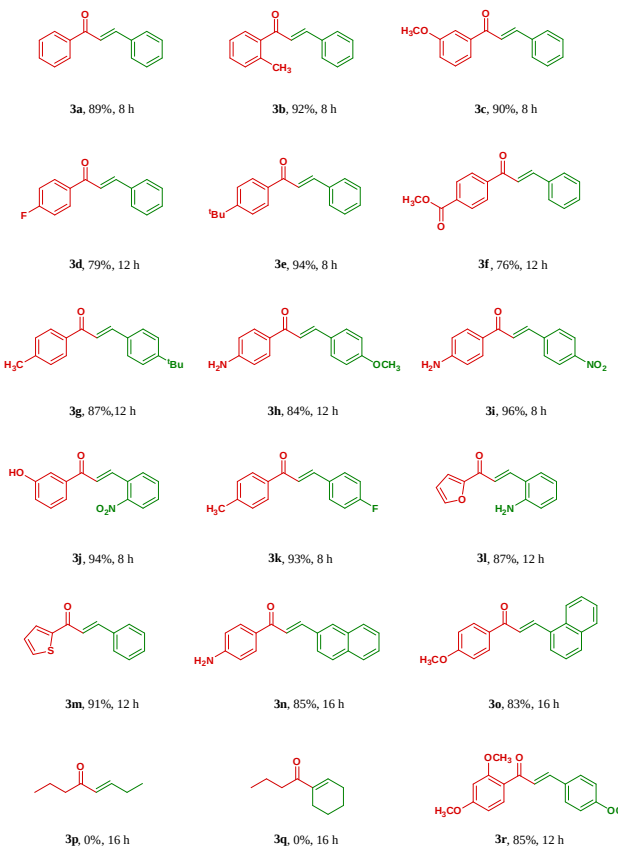
NHPI and related catalysts 4-7

Entry	Reaction conditions	Time (h)	Yield (%)[b]
1	**4** (10 mol%), CH_3CN, white LEDs	8	89
2	**4** (10 mol%), CH_3CN, in the dark	16	n.d.
3	**No catalyst**, CH_3CN, white LEDs	16	n.d.
4	**4** (10 mol%), DCE, white LEDs	8	58
5	**4** (10 mol%), DMF, white LEDs	8	67
6	**4** (10 mol%), DMSO, white LEDs	8	72
7	**4** (5 mol%), CH_3CN, white LEDs	8	53
8	**4** (15 mol%), CH_3CN, white LEDs	8	89
9	**4** (10 mol%), CH_3CN, in the dark	8	69[c]
10	**4** (10 mol%), CH_3CN, white LEDs	8	89[d]
11	**4** (10 mol%), CH_3CN, white LEDs	8	89[e]
12	**5** (10 mol%), CH_3CN, white LEDs	8	35
13	**6** (10 mol%), CH_3CN, white LEDs	8	21
14	**7** (10 mol%), CH_3CN, white LEDs	8	58

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), NHPI (5-15 mol%), in a 3 mL solvent irradiated under a nitrogen atmosphere at rt using high power white LEDs (7 W) for 8-16 h.
[b] Isolated yield of the pure product **3a** (For general procedure, see experimental section); n.d.= not detected.
[c] Reaction was conducted at 80 °C in the dark.
[d] Catalyst was recovered in 94% yield.
[e] Recovered catalyst was used.

Table 2. Substrate scope for the synthesis of chalcones [a]





[a] For general procedure, see Experimental section.
[b] All compounds are known and were characterised by comparison of their spectral data with those reported in the literature (see SI).
[c] Isolated yield of purified products **3**.

Unfortunately, aliphatic nitroalkenes such as (*E*)-1-nitro-1-butene and 1-nitrocyclohex-1-ene do not react

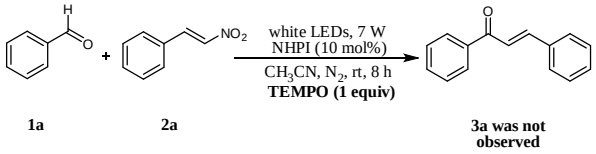
Accepted Manuscript

This article is protected by copyright. All rights reserved.

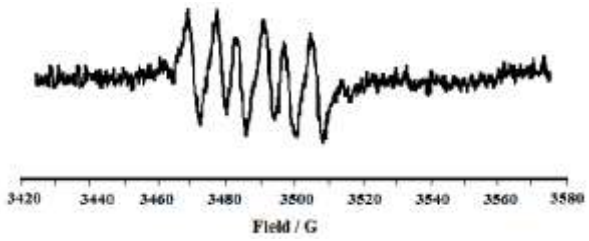
with an aliphatic aldehyde, butyraldehyde to give the desired products (**3p** and **3q**) under the present reaction conditions. This is probably due to the significantly lower stability of alkyl and aliphatic acyl radicals than benzyl and benzoyl radicals. We also prepared a choleretic drug, metochalcone (**3r**) which further improves the appeal of our designed protocol.

On addition of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl), a traditional radical scavenger, the reaction was quenched (Scheme 2a); indicating that it might follow a radical pathway. The formation of benzoyl-TEMPO adduct during quenching was confirmed by its isolation and MS (HRMS (EI) calcd for $C_{16}H_{23}NO_2$: 261.1729, found 261.1726). To gain

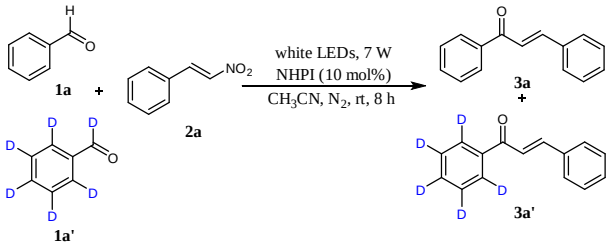
a) Trapping Experiment



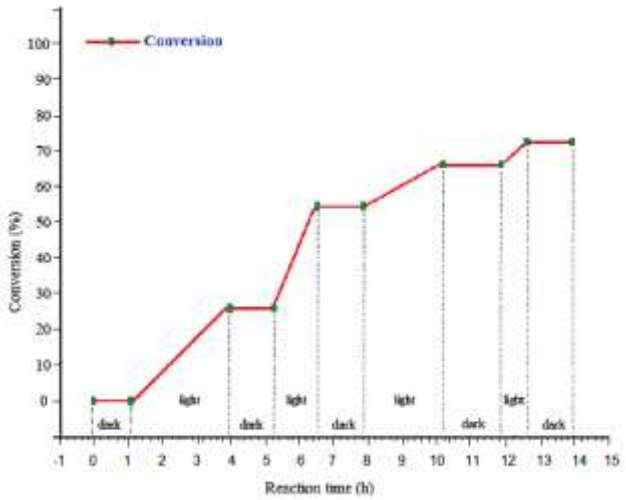
b) Electron Paramagnetic Resonance (EPR) Experiment



c) Kinetic Isotope Effect (KIE) Experiment



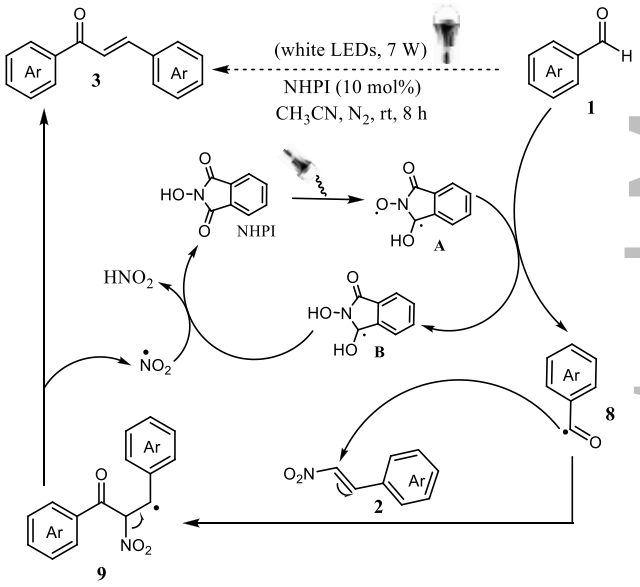
d) Evidence in support of continuous irradiation



Scheme 2. Preliminary mechanistic investigations.

further insight into the mechanism of the reaction, electron paramagnetic resonance (EPR) experiments were also conducted. A complicated spectrum, displaying a resonance characteristic of organic radical, was recorded on the addition of 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) to the reaction mixture of benzaldehyde (1.0 mmol), (*E*)-*β*-nitrostyrene (1.0 mmol) and NHPI (10 mol%) under the standard reaction conditions (Scheme 2b). Both the results established the involvement of radical species in the reaction.

Moreover, an intermolecular competing kinetic isotope effect (KIE) experiment was also carried out which gives a prominent KIE with k_H/k_D = 5.2, suggesting thereby the activation of aldehydic C-H bond in the rate determining step (Scheme 2c). In addition, an on/off experiment was conducted to check the role of visible light in promoting the process and the graph thus obtained establishes the necessity of continuous irradiation with visible light to realise the present protocol (Scheme 2d). The UV-vis specrtum



Scheme 3. Plausible reaction mechanism for NHPI catalysed synthesis of chalcones.

of the catalyst NHPI is also given in see SI for ready reference.

In accordance with our observations and the literature precedents,[18,24,25b] a plausible mechanistic pathway for visible light-mediated synthesis of chalcones is depicted in Scheme 3. On irradiation with visible light using 7 W white LEDs under a nitrogen atmosphere, H atoms of NHPI migrate from O to the carbonyl groups of the imide chromophore and by that process liberate the reactive O radical **A**

Accepted Manuscript

This article is protected by copyright. All rights reserved.

for hydrogen transfer from aldehyde **1.** This forms acyl radical **8** along with radical **B.** The radical **8** reacts with (*E*)-*β*-nitrostyrene **2** to generate the benzylic radical **9**. Subsequently, the radical **9** easily eliminates the stable NO_2· radical to afford the desired product **3**. The NO_2· radical abstracts a hydrogen atom from **B** to give NHPI to complete the catalytic cycle.

In summary, we have disclosed a convenient, metal-free one-pot photocatalytic approach to chalcones through visible light activated radical cross coupling of *β*-nitrostyrenes and aromatic aldehydes. The protocol presents the first application of nitrostyrenes as readily available substrates and the first example of photocatalysis in chalcone synthesis. Its desirable features include the utilization of visible light as a clean, inexpensive and ecosustainable energy source and NHPI as a reusable organophotocatalyst to afford the desired product in excellent yields at room temperature.

Experimental Section

General Remarks

All commercially available reagents were obtained from commercial suppliers and used without further purification. Solvents were purified by the usual methods and stored over molecular sieves. All reactions were performed using oven-dried glass ware. Organic solutions were concentrated using a Buchi rotary evaporator. Flash chromatography was carried out over silica gel (Merck 200–300 mesh) and TLC was performed using silica gel GF254 (Merck) plates. Melting points were determined by open glass capillary method and are uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AVII spectrometer in $CDCl_3$ using TMS as internal reference with chemical shift values being reported in ppm. All coupling constants (*J*) are reported in Hertz (Hz). MS (EI) spectra were recorded on double focusing mass spectrometer. Luxeon Rebel high power white LEDs (7 W) were used as visible light source.

General procedure for the synthesis of chalcones 3a-o

A mixture of an aromatic aldehyde **1** (1 mmol), *β*-nitrostyrene **2** (1 mmol) and CH_3CN (3 mL) was taken in a round bottom flask and stirred under a nitrogen atmosphere and irradiation with white LEDs, at rt for 8-16 h (Table 2). After the completion of reaction (as indicated by TLC), it was quenched with saturated aqueous sodium hydrogen carbonate (5 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic phases were dried over anhyd. $MgSO_4$, filtered and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate-hexane to afford an analytically pure sample of **3**. All the products are known compounds and were characterised by comparison of their spectral data with those reported in the literature. [14c,d,26,27,28]

Acknowledgements

Acknowledgements We sincerely thank SAIF, Punjab University, Chandigarh, for providing microanalyses and spectra. S.T. is grateful to the UGC, New Delhi, for the award of a Junior Research Fellowship (File No. 21/06/2015(i)EU-V). R.K is grateful to the DST-SERB, New Delhi, for the award of a Start-Up-Grant project (Ref no. CS-271/2014) and financial assistance.

References

[1] a) C. J. Zheng, S. M. Jiang, Z. H. Chen, *Archiv der Pharmazie*. **2011**, *344*, 689; b) B. A. Bhat, K. L. Dhar, S.C Puri, *Bioorg. Med. Chem. Lett*. **2005**, *15*, 3177; c) Y. M. Lin, Y. Zhou, M. T. Flavin, *Bioorg. Med. Chem.* **2002**, *10*, 2795; d) Y. Xia, Z. Y. Yang, P. Xia, *Bioorg. Med. Chem. Lett*. **2000**, *10*, 699; e) J. J. Ares, P. E. Outt, J. L. Randall, *Bioorg. Med. Chem. Lett.* **1996**, *6*, 995; f) R. J. Anto, K. Sukumaran, G. Kuttan, *Cancer Lett*. **1995**, *97*, 33; g) R. Li, X. Chen, B. Gong, *J. Med. Chem.* **1995**, *38*, 5031; h) J. F. Ballesteros, M. J Sanz, A. Ubeda, *J. Med. Chem*. **1995**, *38*, 2794.

[2] R. A. Dixon, N. L. Paiva, *Plant Cell*, **1995**, *7*, 1085.

[3] J. Li, *Name Reactions in Heterocyclic Chemistry*, Wiley-Interscience Publication, **2005**, pp. 262.

[4] a) N. A. Al-Jaber, A. S. Bougasim, M. S. Karah, *J. Saudi Chem. Soc*. **2012**, *16* , 45; b) R. Kalirajan, S U. Sivakumar, S. Jubie, *Int. J. Chem. Res.* **2009**, *1*, 27.

[5] For reviews on chalcones, see: a) C. Zhuang, W. Zhang, C. Sheng, W. Zhang, C. Xing, *Chem. Rev*. **2017**, *117*, 7762; b) M. Das, K. Manna, *J. Toxicol*. **2016**, *2016*, 7651047; c) D. K. Mahapatra, S. K. Bharti, *Life Sci.* **2016**, *148*, 154; d) M. J. Matos, S. Vazquez-Rodriguez, E. Uriarte, L. Santana, *Expert Opin. Ther. Pat*. **2015**, *25*, 351; e) A. J. Leon-Gonzalez, N. Acero, D. Munoz-Mingarro, I. Navarro, C. Martin-Cordero, *Curr. Med. Chem*. **2015**, *22*, 3407; f) D. K. Mahapatra, V. Asati, S. K. Bharti, *Eur. J. Med. Chem*. **2015**, *92*, 839; g) D. K. Mahapatra, S. K. Bharti, V. Asati, *Eur.J. Med. Chem*. **2015**, *101*, 496; h) D. K. Mahapatra, S. K. Bharti, V. Asati, *Eur. J. Med. Chem*. **2015**, *98*, 69; i) B. Zhou, C. Xing, *Med. Chem*. **2015**, *5*, 388; j) P Singh, A. Anand, V. Kumar, *Eur. J. Med. Chem*. **2014**, *85*, 758; k) D. Kumar, M. Kumar, A. Kumar, S. K. Singh, *Med. Chem*. **2013**, *13*, 2116; l) S. N. Bukhari, S. G. Franzblau, I. Jantan, M. Jasamai, *Med. Chem*. **2013**, *9*, 897; m) A. Kamal, M. K. Reddy, A. Viswanath, *Expert Opin. Drug Discovery*. **2013**, *8*, 289; n) V. Sharma, V. Kumar, P. Kumar, *Med. Chem*. **2013**, *13*, 422; o) N. K. Sahu, S. S. Balbhadra, J. Choudhary, D. V. Kohli, *Curr. Med. Chem*. **2012**, *19*, 209; p) N. Abbas, S. N. Bukhari, M. Jasamai, I. Jantan, *Med. Chem*. **2012**, *12*, 1394; q) A. Boumendjel, X. Ronot, J.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

Boutonnat, *Curr. Drug. Targets.* **2009**, *10*, 363; r) C. Kontogiorgis, M. Mantzanidou, D. Hadjipavlou-Litina, *Med. Chem*. **2008**, *8*, 1224; s) M. L. Go, X. Wu, X. L. Liu, *Curr. Med. Chem*. **2005**, *12*, 483; t) J. R. Dimmock, D. W. Elias, M. A. Beazely, N. M. Kandepu, *Curr. Med. Chem*. **1999**, *6*, 1125.

[6] a) V. Calvino, M. Picallo, A. J. Lopez-Peinado, R. M. Martın-Aranda, C. J. Duran-Valle, *Appl. Surf. Sci.* **2006**, *252*, 6071; b) L. Claisen, A. Claparède, *Ber. Dtsch. Chem. Ges*. **1881**, *14*, 2460.

[7] J. B. Daskiewicz, G. Comte, D. Barron, A. D. Pietro, F. Thomasson, *Tetrahedron Lett*. **1999**, *40*, 7095.

[8] S. Sebti, A. Solhy, R. Tahir, S. Boulaajaj, J. A. Mayoral, J. M. Fraile, A. Kossir, H. Oumimoun, *Tetrahedron Lett*. **2001**, *42*, 7953.

[9] S. Saravanamurugan, M. Palanichamy, B. Arabindoo, V. Murugesan, *Catal. Commun*. **2005**, *6*, 399.

[10] J. T. Li, W. Z. Yang, Z. X. Wang, S. H. Li, T.S. Li, *Ultrason. Sonochem*. **2002**, *9*, 237.

[11] J. Yang, G. Ji, H. Liu, Y. Lian, *Chem. Abstr*. **2013**, *160*, 33884.

[12] M. J. Climent, A. Corma, S. Iborra, J. Primo, *J. Catal*. **1995**, *151*, 60.

[13] a) K. R. Buszek, N. Brown, *Org. Lett*. **2007**, *9*, 707; b) S. Eddarir, N. Cotelle, Y. Bakkour, C. Rolando, *Tetrahedron Lett*. **2003**, *44*, 5359; c) N. A. Bumagin, D. N. Korolev, *Tetrahedron Lett*. **1999**, *40*, 3057; d) M. Haddach, J. R. McCarthy, *Tetrahedron Lett*. **1999**, *40*, 3109.

[14] a) X. F. Wu, H. Neumann, M. Beller, *Chem. Asian J*. **2012**, *7*, 282; b) P. Hermange, T. M. Gogsig, A. T. Lindhardt, R. H. Taaning, T. Skrydstrup, *Org. Lett*. **2011**, *13*, 2444; c) X. F. Wu, H. Neumann, A. Spannenberg, T. Schulz, H. Jiao, M. Beller, *J. Am. Chem. Soc*. **2010**, *132*, 14596; d) X. F. Wu, H. Neumann, M. Beller, *Angew. Chem. Int. Ed*. **2010**, *49*, 5284; e) G. Zou, J. P. Guo, Z. Y. Wang, W. Huang, J. Tang, *Dalton T.* **2007**, *28*, 3055; f) A. Bianco, C. Cavarischia, M. Guiso, *Eur. J. Org. Chem*. **2004**, *13*, 2894; g) R. F. Heck, J. P. Nolley, *J. Org. Chem*. **1972**, *37*, 2320; h) T. Mizoroki, K. Mori, A. Ozaki, *Bull. Chem. Soc*. **1971**, *44*, 581.

[15] A. Kumar, S. Sharma, V. D. Tripathi, S. Srivastava, *Tetrahedron* **2010**, *66*, 9445.

[16] a) L. Q. Lu, J. R. Chen, W. J. Xiao, *Acc. Chem. Res*. **2012**, *45*, 1278; b) M. A. Reddy, N. Jain, D. Yada, C. Kishore, J. R. Vangala, R. P. Surendra, A. Addlagatta, S. V. Kalivendi, B. Sreedhar, *J. Med. Chem*. **2011**, *54*, 6751; c) H. Uehara, R. Imashiro, G. Hernandez Torres, C. F. Barbas, *Proc. Natl. Acad. Sci*. **2010**, *107*, 20672; d) H. Feuer, A. Nielsen, *Nitro Compounds: Recent Advances in Synthesis and Chemistry*, VCH, New York, **1990**; e) A. G. M. Barrett, G. G. Graboski, *Chem. Rev*. **1986**, *86*, 751.

[17] a) J. Zheng, D. Wang, S. Cui, *Org. Lett*. **2015**, *17*, 4572; b) P. Cheng, Z. Y. Jiang, R. R. Wang, X. M. Zhang, Q. Wang, Y. T. Zheng, J. Zhou, J. J. Chen, *Bioorg. Med. Chem. Lett*. **2007**, *17*, 4476; c) S. Kaap, I. Quentin, D. Tamiru, M. Shaheen, K. Eger, H. J. Steinfelder, *Biochem. Pharmacol*. **2003**, *65*, 603; d) J. H. Kim, J. H. Kim, G. E. Lee, J. E. Lee, I. K. Chung, *Mol. Pharmacol*. **2003**, *63*, 1117; e) Y. Meah, V. Massey, *Proc. Natl. Acad. Sci*. **2000**, *97*, 10733; f) T. A. Alston, D. J. T. Porter, H. J. Bright, *Bioorg. Chem*. **1985**, *13*, 375; g) P. Talalay, M. J. De Long, H. J. Prochaska, *Proc. Natl. Acad. Sci*. **1988**, *85*, 8261.

[18] a) A. K. Yadav, K. N. Singh, *New J. Chem*. **2017**, DOI: 10.1039/C7NJ02997G; b) T. Keshari, R. Kapoor, L. D. S. Yadav, *Eur. J. Org. Chem*. **2016**, 2695; c) N. Zhang, Z. -J. Quan, Z. Zhang, Y. -X. Da, X. -C. Wang, *Chem. Commun*. **2016**, *52*, 14234; d) S.-R. Guo, Y. -Q. Yuan, *Synlett* **2015**, *26*, 1961; e) J. -F. Xue, S. -F. Zhou, Y. -Y. Liu, X. Pan, J. -P. Zou, O. T. Asekun, *Org. Biomol. Chem*. **2015**, *13*, 4896; f) S. Guo, Y. Yuan, J. Xiang, *New J. Chem*. **2015**, *39*, 3093; g) P. Schroll, D. P. Hari, B. König, *ChemistryOpen* **2012**, *1*, 130; h) Y. -J. Jang, Y. -K. Shih, J. -Y. Liu, W. -Y. Kuo, C. -F. Yao, *Chem. Eur. J*. **2003**, *9*, 2123.

[19] a) A, Noble, D. W. C. MacMillan, *J. Am. Chem. Soc*. **2014**, *136*, 11602; b) J. A. Terrett, M. D. Clift, D. W. C. MacMillan, *J. Am. Chem. Soc*. **2014**, *136*, 6858; c) M. T. Pirnot, D. A. Rankic, D. B. C. Martin, D. W. C. MacMillan, *Science* **2013**, *339*, 1593; d) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc*. **2009**, *131*, 10875; e) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77.

[20] a) J. Du, T. P. Yoon, *J. Am. Chem. Soc*. **2009**, *131*, 14604; b) M. A. Ischay, M. E. Anzovino, J. Du, T. P. Yoon, *J. Am. Chem. Soc*. **2008**, *130*, 12886.

[21] a) M. D. Konieczynska, C. Dai, C. R. J. Stephenson, *Org. Biomol. Chem.* **2012**, *10*, 4509; b) C. Dai, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem*. **2011**, *3*, 140; c) A. G. Condie, J. C. Gonzâlez-Gólez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464; d) J. W. Tucker, J. M. R. Narayanam, S. W. Krabbe, C. R. J. Stephenson, *Org. Lett.* **2010**, *12*, 368; e) J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *J. Am. Chem. Soc*. **2009**, *131*, 8756.

[22] For leading reviews on visible light photocatalysis, see: a) C. K. Prier, D. A. Rankic, D. W. C. MacMillan, *Chem. Rev*. **2013**, *113*, 5322; b) Y. Xi, H. Yia, A. Lei, *Org. Biomol. Chem.* **2013**, *11*, 2387; c) J. Xuan, W. -J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 6828; d) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Soc. Rev*. **2011**, *40*, 102; e) F. Collect. Teply, *Czech. Chem. Commun.* **2011**, *76*, 859; f) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; g) K. Zeitler, *Angew. Chem. Int. Ed*. **2009**, *48*, 9785; h) J. K. Kochi, *Angew. Chem. Int. Ed*. **1988**, *27*, 1227; i) R. G. Salomon, J. K. Kochi, *J. Am. Chem. Soc*. **1974**, *96*, 1137; j) R. Srinivasan, *J. Am. Chem. Soc*. **1963**, *85*, 3048.

[23] For recent examples using organic dyes as the photocatalyst, see: a) V. P. Srivastava, A. K. Yadav, L. D. S. Yadav, *Synlett* **2014**, *25*, 665; b) A. K. Yadav, V. P. Srivastava, L. D. S. Yadav, *RSC Adv*. **2014**, *4*, 4181; c) X. -J. Yang, B. Chen, L. -Q.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

10.1002/adsc.201701559

Zheng, L. -Z. Wu, C. -H Tung, *Green Chem*. **2014**, *16*, 1082; d) Y. C. Teo, Y. Pan, C. H. Tan, *ChemCatChem*. **2013**, *5*, 235; e) D. -T. Yang, Q. -Y. Meng, J. -J. Zhong, M. Xiang, Q. Liu, L. -Z. Wu, *Eur. J. Org. Chem.* **2013**, 7528; f) M. Rueping, C. Vila, T. Bootwicha, *ACS Catal*. **2013**, *3*, 1676; g) Y. -Q. Zou, J. -R. Chen, X. -P. Liu, L. -Q. Lu, R. L. Davis, K. A. Jørgensen, W. -J. Xiao, *Angew. Chem. Int. Ed*. **2012**, *51*, 784; h) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc*. **2012**, *134*, 2958; i) D. P. Hari, T. Hering, B. König, *Org. Lett*. **2012**, *14*, 5334; j) T. Hering, D. P. Hari, B. König, *J. Org. Chem*. **2012**, *77*, 10347; k) Q. Li, Y. -N. Li, H. -H. Zhang, B. Chen, C. -H. Tung, L. -Z. Wu, *Chem. - Eur. J*. **2012**, *18*, 620; l) K. Fidaly, C. Ceballos, A. Falguieres, M. S. -I. Veitia, A. Guy, C. Ferroud, *Green Chem*. **2012**, *14*, 1293; m) J. Yu, L. Zhang, G. Yan, *Adv. Synth. Catal*. **2012**, *354*, 2625; n) M. Neumann, S. Fuldner, B. König, K. Zeitler, *Angew. Chem. Ins. Ed*. **2011**, *50*, 951; o) D. P. Hari, B. König, *Org. Lett*. **2011**, *13*, 3852; p) Y. Pan, C. W. Kee, L. Chen, C. -H. Tan, *Green Chem*. **2011**, *13*, 2658; q) Y. Pan, S. Wang, C. W. Kee, E. Dubbuisson, Y. K. Yang, P. Loha, C.-H. Tan, *Green Chem*. **2011**, *13*, 3341.

[24] A. K. Yadav, L. D. S. Yadav, *Chem. Commun*. **2016**, *52*, 10621.

[25] a) R. Kapoor, S. Tripathi, S. N. Singh, T. Keshari, L. D. S. Yadav, *Tetrahedron Lett*. **2017**, *58*, 3814; b) A. K. Yadav, L. D. S. Yadav, *Tetrahedron Lett*. **2017**, *58*, 552; c) S. Tripathi, S. N. Singh, L. D. S. Yadav, *RSC Adv*. **2016**, *6*, 14547; d) A. K. Yadav, L. D. S. Yadav, *Green Chem*. **2016**, *18*, 4240; e) V. K. Yadav, V. P. Srivastava, L. D. S. Yadav, *Tetrahedron Lett*. **2016**, *57*, 155.

[26] K. C. Bharadwaj, *Tetrahedron* **2017**, *73*, 5690.

[27] T. Narender, K. P. Reddy, *Tetrahedron Lett*. **2007**, *48*, 3177.

[28] M. B. Santos, V. C. Pinhanelli, M. A. R. Garcia, G. Silva, S. J. Baek, S. C. França, A. L. Fachin, M. Marins, L. O. Regasini, *Eur. J. Med. Chem*. **2017**, *138*, 884.

Accepted Manuscript

This article is protected by copyright. All rights reserved.

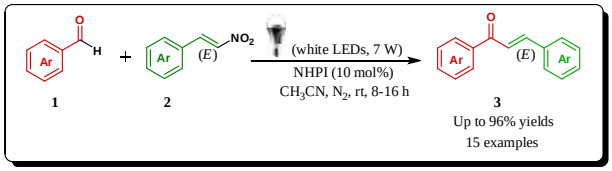
10.1002/adsc.201701559

COMMUNICATION

Visible Light Activated Radical Denitrative Benzoylation of β-nitrostyrenes: A Photocatalytic Approach to Chalcones

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

Shubhangi Tripathi, Ritu Kapoor, L. D. S. Yadav*



Accepted Manuscript

This article is protected by copyright. All rights reserved.