Tetrahedron Letters 55 (2014) 1788–1792

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Visible-light-induced cyanation of aza-Baylis–Hillman adducts: a Michael type addition

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ARTICLE INFO

Article history:
Received 31 December 2013
Revised 24 January 2014
Accepted 25 January 2014
Available online 5 February 2014

Keywords:
Air oxidation
Baylis–Hillman adducts
Cyanation
Michael adducts
Photoredox catalysis
Visible light

ABSTRACT

Visible-light-induced aerobic oxidative cyanation of aza-Baylis–Hillman (aza-BH) adducts providing valuable allylic cyanides in good to excellent yields has been developed. The protocol involves in situ formation of 4π conjugated iminium ion intermediates, which undergo cyanation at the γ-position to afford Michael type adducts. This is the first example of visible-light-induced catalytic functionalization of aza-BH adducts using air (O_2) as an economical and ecosustainable oxidant and TMSCN as a convenient and readily available cyanide source.

Recently, visible-light-induced catalytic oxidation of sp^3 C–H bonds adjacent to nitrogen providing reactive iminium ions has become a powerful toolkit for amine functionalization.[1] Amines often act as single electron donors in visible-light-induced photoredox processes and are oxidized to nitrogen radical cations to execute iminium ion formation under aerobic conditions. This has led to the development of several useful synthetic transformations of relevance to material and pharmaceutical sciences.[2]

However, the benzylic amine substrates acting as an electron donor are very limited and mostly realized on *N*-aryltetrahydroisoquinoline derivatives.[1] Thus, investigations on novel benzylic amine precursors for their exploitation in photosensitized SET (single electron transfer) processes are highly desirable. Baylis–Hillman adducts are useful substrates for diverse and highly functionalized molecules which are required for the synthesis of various interesting natural and unnatural products of medicinal importance.[3] Our continued efforts for implementation of new substrates in visible-light-photoredox reactions[4] and functionalization of BH adducts,[5] prompted us to choose aza-BH adducts for the present study as depicted in Scheme 1.

The development of new methods in synthetic organic chemistry using photoredox catalysis has attracted significant interest, as visible light is a ubiquitous, sustainable and clean source of energy.[1,2,6] The pioneering work from the groups of MacMillan,[7d] Yoon,[7e] and Stephenson[1h,7a–c] has demonstrated that ruthenium and iridium based polypyridyl complexes play a pivotal role in SET processes, as they possess well known photocatalytic properties and can readily be tuned by the choice of right ligands.[7] The photocatalytic aerobic oxidation of amino benzylic C–H bonds to generate reactive iminium ion intermediates has been frequently reported in the recent years.[1,6] Among different diverging approaches from this structural motif, the cyanation of sp^3 C–H bonds adjacent to a nitrogen atom represents one of the most straightforward and convenient methods for the synthesis of α-amino nitriles.[1d,g] Besides this, such highly reactive iminium ions have been subsequently trapped with diverse nucleophiles such as enol silane,[6a] TMSCF$_3$,[6b] phosphonates,[6c] indole,[6d] terminal alkynes,[6c,d] etc.[6]

The use of atmospheric oxygen as an oxidant in organic syntheses remains very limited although it is readily available, economical and ecosustainable oxidant.[8] The field of visible-light-photoredox catalysis has opened up a new route to utilize atmospheric oxygen, where it is mostly employed as an oxidant to regenerate Ru^{+2} from Ru^{+1} to complete the catalytic cycle and the superoxide radical ($O_2^{\cdot -}$) thus formed plays a key role in the synthetic process.[1,6]

In view of the above valid facts and widening the substrate scope for the visible-light-photoredox reactions, amino benzylic carbon in conjugation with a double bond was considered as a novel system for the present study. In the current photoredox catalytic process a 4π conjugated iminium ion is generated and

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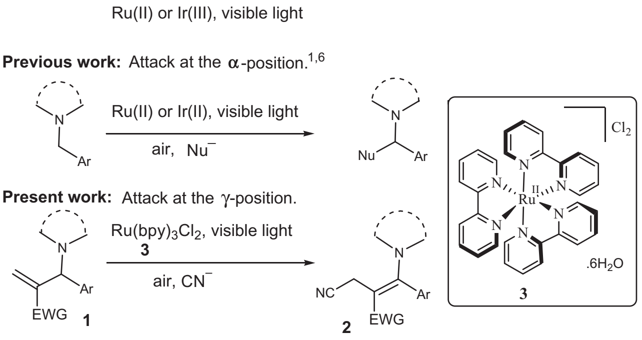
http://dx.doi.org/10.1016/j.tetlet.2014.01.121

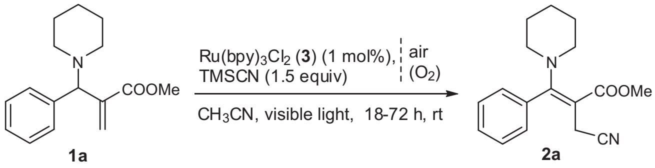


Scheme 1. Visible-light-induced functionalization of benzylic amines.

subsequently attacked by the cyanide ion at the γ-position to afford an allylic cyanide, whereas in the previous cases the attack takes place at the α-position (Scheme 1).[1,6] The known methods available for the cyanation of amines involve the use of hypervalent-iodine[9]/I_2,[10] tropolium ion[11] and copper[12] catalysis and electrolysis,[13] which are of limited scope and selectivity.

In order to verify the practicability of the envisaged protocol for the target molecule, a model reaction was carried out with aza-Baylis–Hillman adduct **1a**, in CH_3CN containing 1 mol % of $Ru(bpy)_3Cl_2$ (**3**) as a photocatalyst and TMSCN (1.5 equiv) as a cyanide source. The reaction mixture was open to an air atmosphere (but no air bubbling) and irradiated with visible light (blue light emitting diodes (blue LEDs),[14] λ_{max} = 447.5 nm) at rt. It was highly satisfying that the reaction delivered the desired allylic cyanide **2a** in 85% isolated yield after 18 h (Table 1, entry 1). Following this experiment, a series of control experiments were performed, which demonstrated that either there was no product formation or it was formed in traces in the absence of any one of the reagents/catalyst (Table 1, entries 2–4). Only a trace of product was detected under an N_2 atmosphere (Table 1, entry 5). Moreover, the use of another catalyst $Ir(bpy)_3PF_6$ (1 mol %) or eosin Y (2 mol %) was not as effective as $Ru(bpy)_3Cl_2$ (1 mol %) (Table 1, entry 1 vs 6 and 7). Irradiation with a household light (18 W CFL) produced considerably lower yield in a longer time as compared to blue LEDs irradiation (Table 1, entry 1 vs 8). The presence of O_2 (air) was found to be essential, because only a trace of product formation was detected under the degassed condition or in an N_2 atmosphere (Table 1, entry 1 vs 4 and 5). Moreover, the reaction was quenched with TEMPO (1 mol %) (Table 1, entry 9) showing that it follows a radical reaction pathway.

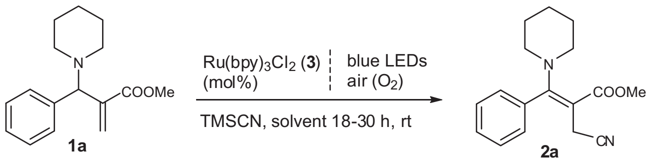
Table 1
Screening and control experiments[a]



Entry	Visible light	Photocatalyst	Air	Time (h)	Yield[b] (%)
1	+	+	+	18	85
2	–	+	+	24	n.r.[c]
3	+	–	+	24	n.r.
4	+	+	–	24	Trace[d]
5	+	+	N_2	24	Trace
6	+	+	+	18	72[e]
7	+	+	+	18	57[f]
8	+	+	+	24	55[g]
9	+	+	+	72	Trace[h]

[a] Reaction conditions: **1** (1 mmol), **3** (1 mol %), CH_3CN (3 mL), TMSCN (1.5 equiv), open to air (without bubbling air), irradiation through the flask's bottom side using Luxeon Rebel high power blue LEDs.
[b] Isolated yield of pure product **2a**.
[c] Reaction was carried out in dark; n.r. = no reaction.
[d] Reaction was performed under degassed condition.
[e] $Ir(bpy)_3PF_6 \cdot 6H_2O$ (1 mol %) was used as the catalyst.
[f] Eosin Y (2 mol %) was used as the catalyst.
[g] Reaction was performed using 18 W CFL (compact fluorescent lamp, Philips).
[h] Reaction was quenched with TEMPO (1 mol %).

Table 2
Optimization of reaction conditions[a]



Entry	**3** (mol %)	Solvent	Time (h)	Yield[b] (%)
1	1	CH_3CN	18	85
2	1	DMF	18	80
3	1	DMSO	18	65
4	1	THF	18	43
5	1	EtOH	18	47
6	1	DCE	18	55
7	2	CH_3CN	18	85
8	0.5	CH_3CN	30	67

[a] Reaction conditions: **1** (1 mmol), **3** (0.5-2 mol %), solvent (3 mL), TMSCN (1.5 equiv), open to air (without bubbling air, irradiation through the flask's bottom side using Luxeon Rebel high power blue LEDs.
[b] Isolated yield of pure product **2a**.

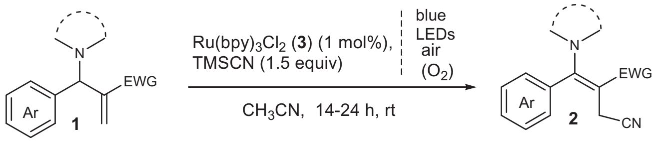
Then, the reaction was optimized for an effective solvent system and catalyst loading (Table 2). CH_3CN was found to be the best among the tested solvents DMF, DMSO, DCE, EtOH, and THF, hence it was used throughout the present study (Table 2, entry 1 vs 2–6). The optimum catalyst loading delivering the highest yield in minimum reaction time was 1 mol %, because lowering the amount of the catalyst to 0.5 mol % decreases the yield significantly and takes a longer reaction time (Table 2, entry 1 vs 8), while there was no effect on the yield and reaction time on increasing the catalytic loading from 1 to 2 mol % (Table 2, entry 7).

To investigate the scope of the substrate, we tried various types of aza-BH adducts **1**, which successfully underwent the reaction to produce the corresponding allylic nitriles in good to excellent yields (Table 3). Many functionalities like MeO, NO_2, Cl, Br, CN, and COOMe are well tolerated in the present reaction conditions. The aza-BH adducts **1** bearing an electron-withdrawing group on the aromatic ring undergo slower reaction and give slightly lower yields as compared to those containing an electron-donating group (Table 3, entries 2 and 3 vs 4–6). The requisite aza-BH adducts **1** were prepared by the method reported in the literature.[12b,16]

Based on the above observations and the literature precedents,[1,7,10,12] a plausible mechanistic pathway is depicted in Scheme 2. The benzylic tertiary amine **1** undergoes SET to generate the radical cation **A** and Ru(I) with activated Ru(II)* in the presence of blue LEDs. Ru(I) is oxidized to Ru(II) with atmospheric oxygen, which is reduced to superoxide radical anion ($O_2^{\cdot-}$) to complete the photoredox cycle. The radical cation **A** is converted into iminium ion **B** by H-abstraction from the benzylic position by the superoxide radical anion ($O_2^{\cdot-}$). The conjugated iminium ion thus generated in situ undergoes nucleophilic addition with the cyanide ion to afford the desired allylic cyanides **2**.

In conclusion, we have disclosed aza-BH adducts as a novel substrate for visible-light-mediated functionalization at the γ-position with respect to the amino group. The protocol involves an aerobic oxidative photocatalytic γ-cyanation of aza-BH adducts to provide

Table 3
Substrates scope



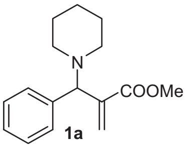
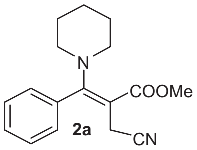
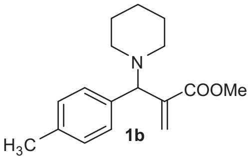
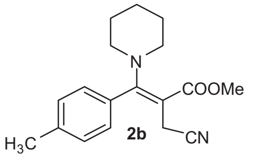
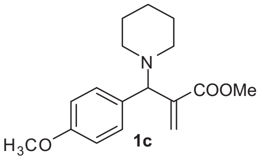
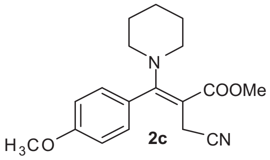
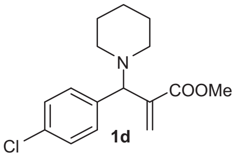
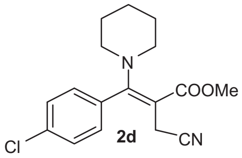
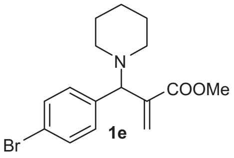
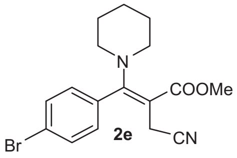
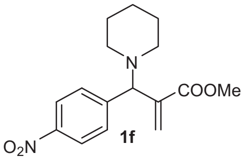
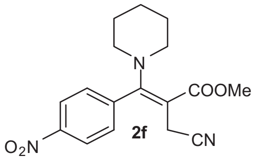
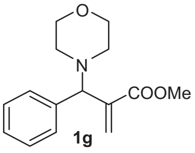
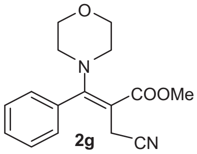
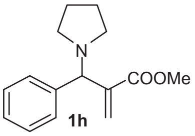
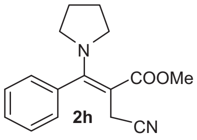
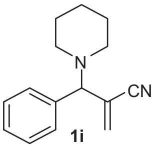
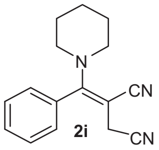
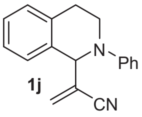
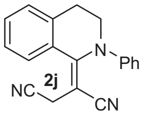
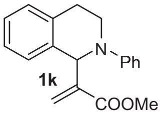
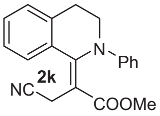
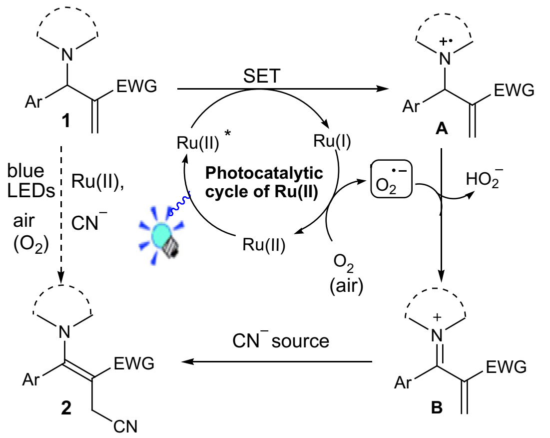
Entry[a]	Substrate **1**	Product **2**	Time (h)	Yield[b] (%)
1	 **1a**	 **2a**	18	85
2	 **1b**	 **2b**	14	89
3	 **1c**	 **2c**	14	92
4	 **1d**	 **2d**	20	80
5	 **1e**	 **2e**	20	82
6	 **1f**	 **2f**	24	73
7	 **1g**	 **2g**	18	80
8	 **1h**	 **2h**	18	84
9	 **1i**	 **2i**	18	79
10	 **1j**	 **2j**	14	80

Table 3 (*continued*)

Entry[a]	Substrate **1**	Product **2**	Time (h)	Yield[b] (%)
11			14	85

[a] Reaction conditions: **1** (1.0 mmol), **3** (1.0 mol %), TMSCN (1.5 equiv) in CH_3CN (3 mL) open to air, irradiation with blue LEDs irradiation (for the detailed procedure, see: Ref. 15).

[b] Isolated yields of pure products **2** after column chromatography.



Scheme 2. Plausible mechanistic pathway for cyanation of aza-BH adducts.

allylic cyanides in good to excellent yields. Mild reaction conditions, low catalyst loading, and use of atmospheric oxygen and visible light as cost effective, readily available and ecosustainable reagents to afford Michael type addition products are the attractive features of the methodology.

Acknowledgments

We sincerely thank the SAIF, Punjab University, Chandigarh, for providing spectra. V.P.S. is grateful to the Department of Science and Technology (DST) Govt. of India, for the award of a DST-Inspire Faculty position (Ref. IFA-11CH-08) and financial support and A.K.Y. is grateful to the CSIR, New Delhi, for the award of a Senior Research Fellowship.

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14. Blue LEDs (4.45 W, 447.5 nm) Rebel LED, mounted on a 25 mm cool base was purchased from commercial supplier Luxeon Star LEDs Quadica Developments Inc. 47 6th Concession Rd. Brantford, Ontario N 32 5L7 Canada.
15. *General procedure for the visible-light-induced cyanation of aza-Baylis–Hillman adducts to afford allylic cyanides* **2** (Table 3): To a solution of aza-Baylis–Hillman adduct **1** in CH_3CN (3 mL) was added $Ru(bpy)_3Cl_2$ (1 mol %) and TMSCN (1.5 equiv). The reaction mixture was irradiated with blue LEDs with stirring at rt for 14–24 h (Table 3). After completion of the reaction (as monitored by TLC), water (5 mL) was added and the mixture was extracted with EtOAc (3 × 5 mL). The combined organic phase was dried over $MgSO_4$, filtered, and evaporated

under reduced pressure. The resulting product was purified by silica gel column chromatography using a gradient mixture of hexane/ethyl acetate as eluent to afford an analytically pure sample of **2**. The characterization data of representative compounds **1** and **2** are given below:

Compound ***1a:*** (Yellow oily liquid); IR (neat liquid): ν_{max} = 3440, 3062, 3023, 2950, 2924, 2856, 2719, 1960, 1728, 1619, 1572, 1490, 1438, 1379, 1263, 1009, 765, 712 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.01 (m, 5H), 6.27 (s, 1H), 5.60 (s, 1H), 4.12 (s, 1H), 3.76 (s, 3H), 1.54–1.43 (t, 4H), 1.02–0.92 (br′ s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0 139.4, 128.3, 126.7, 124.9, 122.1, 93.7, 83.1, 51.5, 51.1, 25.6, 24.3; HRMS (EI): calcd for $C_{16}H_{21}NO_2$ 259.1572, found 259.1570.

Compound ***1g***. (Yellow oily liquid); IR (neat liquid): ν_{max} = 3449, 3065, 3028, 2946, 2918, 2850, 2713, 2219, 1956, 1727, 1621, 1570, 1490, 1437, 1375, 1262, 1198, 1141, 1018, 767, 709 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.28-7.04 (m, 5H), 6.17 (s, 1H), 5.59 (s, 1H), 4.32 (s, 1H), 3.67 (s, 3H), 2.54–2.43 (br′ s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 139.8, 136.0, 128.8, 127.3, 126.1, 82.7, 74.8, 67.5, 52.4, 52.1; HRMS (EI): calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1361.

Compound ***1j***:[12b] (Yellow oily liquid); IR (neat liquid): ν_{max} = 3063, 3026, 2913, 2851, 2221, 1623, 1595, 1508, 1473, 1387, 1324, 1300, 1224, 1157, 1115, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.21 (m, 5H), 7.18–7.16 (m, 1H), 6.85 (d, J = 8.4 Hz, 2H), 6.82 (dd, J = 7.6, 7.6 Hz, 1H), 5.95 (s, 1H), 5.85 (d, J = 1.2 Hz, 1H), 5.27 (s, 1H), 3.74 (ddd, J = 11.2, 5.2, 5.2 Hz, 1H), 3.50 (ddd, J = 13.2, 8.4, 4.8 Hz, 1H), 3.02–2.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.0, 135.7, 132.3, 130.4, 129.0, 128.3, 127.9, 127.6, 126.4, 125.3, 118.4, 117.8, 114.2, 62.3, 43.5, 28.2; HRMS (EI): calcd for $C_{18}H_{16}N_2$ 260.1314, found 260.1315.

Compound ***2a:*** (Yellow oily liquid); IR (neat liquid): ν_{max} = 3440, 3060, 3024, 2217, 2952, 2923, 2850, 2717, 1962, 1729, 1614, 1576, 1492, 1436, 1377, 1261, 1003, 767, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.31(m, 5H), 3.59 (s, 3H), 3.09 (s, 2H), 1.32–1.25 (t, 4H), 1.07–0.97 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 156.4, 133.9, 128.7, 127.3, 126.8, 116.0, 95.9, 54.2, 52.3, 26.8, 24.0, 11.9; HRMS (EI): calcd for $C_{17}H_{20}N_2O_2$ 284.1525, found 284.1520.

Compound ***2g:*** (Yellow oily liquid); IR (neat liquid): ν_{max} = 3446, 3058, 3022, 2952, 2917, 2853, 2712, 2223, 1960, 1726, 1619, 1578, 1490, 1432, 1375, 1260, 1190, 1143, 1021, 760, 711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.23 (m, 5H), 3.69 (s, 3H), 2.81–2.14 (br′ s, 8H), 1.97 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.7, 154.6, 132.9, 127.8, 126.7, 116.0, 95.7, 66.1, 51.3, 48.6, 24.3, 12.7; HRMS (EI): calcd for $C_{16}H_{18}N_2O_3$ 286.1317, found 286.1315.

Compound ***2j:*** (Yellow oily liquid); IR (neat liquid): ν_{max} = 3107, 3068, 3023, 2959, 2921, 2856, 2713, 2219, 2232, 1968, 1723, 1615, 1572, 1497, 1438, 1379, 1264, 1197, 1148, 1013, 760, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.15 (m, 4H), 7.24 (t, 2H), 7.21 (m, 2H), 7.20 (q, 1H), 6.77 (t, 1H), 3.39 (d, 2H), 3.08 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.7, 135.4, 134.1, 132.9, 127.3, 126.1, 124.6, 120.0, 118.3, 117.7, 115.8, 72.9, 50.3, 43.3, 27.6, 24.2, 12.3; HRMS (EI): calcd for $C_{19}H_{15}N_3$ 285.1266, found 285.1263.

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