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Acyl Radicals from Benzothiazolines: Synthons for Alkylation, Alkenylation, and Alkynylation Reactions

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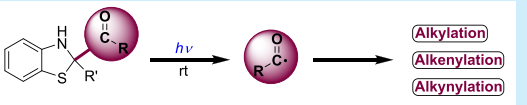
Supporting Information

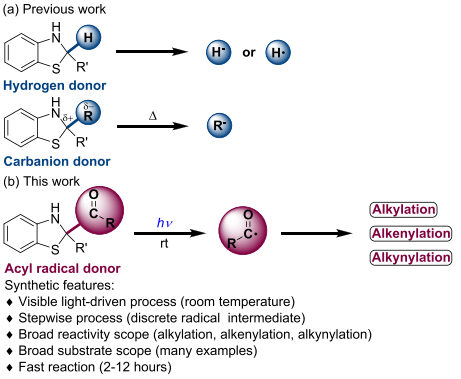
ABSTRACT: We describe herein a fundamentally new visible light-driven homolytic C−C bond breaking mode for the generation of acyl radicals from C2-acyl-substituted benzothiazolines. The reactive species can be used as versatile synthons for formal radical alkylation, alkenylation, and alkynylation reactions.



A central theme of organic synthesis is the invention of new bond breaking modes and use of reactive species generated thereof for forging new chemical bonds. Compared to C−H bonds, the scission of structurally closely related C−C bonds poses a significantly more demanding challenge due to their lower degree of polarization and lower affinity for transition metals.[1] However, the tempting prospect of discovering new reaction pathways, new retro-synthetic schemes, and powerful synthetic tools has prompted efforts for the identification of new C−C bond breaking modes.[2]

Benzothiazolines are extremely useful organic synthesis reagents and have been used, primarily, as a C2-hydrogen donor for various reductive processes under Brønsted acid or Lewis acid catalysis (Scheme 1a).[3] Only a single report briefly mentioned the possibility of thermally driven, concerted C2-alkyl transfer (heterolytic C−C bod cleavage), in the form of carbanion, to imines (with three examples) under high temperature and prolonged reaction time (∼2 days) (Scheme 1a).[4] With these precedents in mind, we have opted to pursue a different reaction course, exploiting aromatization as the enabling tool for homolytically cleaving C−C bonds and generating discrete carbon-centered radical intermediates for synthetic purpose. In particular, we demonstrate herein that C2-acyl groups, when assisted with hypervalent iodine reagents (HIRs),[5] can be converted into acyl radicals under visible light irradiation (Scheme 1b). The acyl radicals produced thereof can be utilized as versatile synthons for formal radical alkylation, alkenylation, and alkynylation reactions.

Scheme 1. Benzothiazolines as Donors of Reactive Species for Organic Synthesis



Acyl radicals are tremendously useful intermediates for organic synthesis.[6] Early thermal or photolytic acyl radical generation strategies generally witness harsh reaction conditions (e.g., strong oxidant, UV irradiation, high CO pressure, high temperature), thus inevitably restricting reactivity scope.[7] Visible light driven bond breakage has recently been adopted for the achievement of mild reaction conditions and expansion of reactivity profiles.[8] Albeit effective, a high-valued precious transition metal (Ir, Ru, etc.) or a toxic organic dye as photosensitizer is typically involved, which can be a drawback in certain synthetic contexts.[9] To address this issue, several efforts have been directed at transition metal- and organic dye-free conditions.[10] α-Ketoacids have been exploited in alkynylation reaction and oxindole synthesis through activation with HIRs.[11] However, the lability of α-ketoacids[12] raises serious concerns over their routine use as synthetic reagents. Aldehydes have been combined with *N*-hydroxyphthalimide[13] or 2-^{t}Bu-anthraquinone[14] for denitrative alkenylation reaction or coumarin synthesis, but only aromatic aldehydes can be tolerated. Hantzsch esters[15] have recently been added to the repertoire, but (1) their preparation involves complicated multiple reflux/high temperature steps, and (2) their utility is demonstrated only in organocatalysis-coupled, Giese-type addition reaction under prolonged irradiation. The acyl radical system reported herein provides an efficient, versatile visible light-driven platform for diverse C−C bond-forming reactions from benzothiazolines, the preparation of which involves minimum reagents and efforts.

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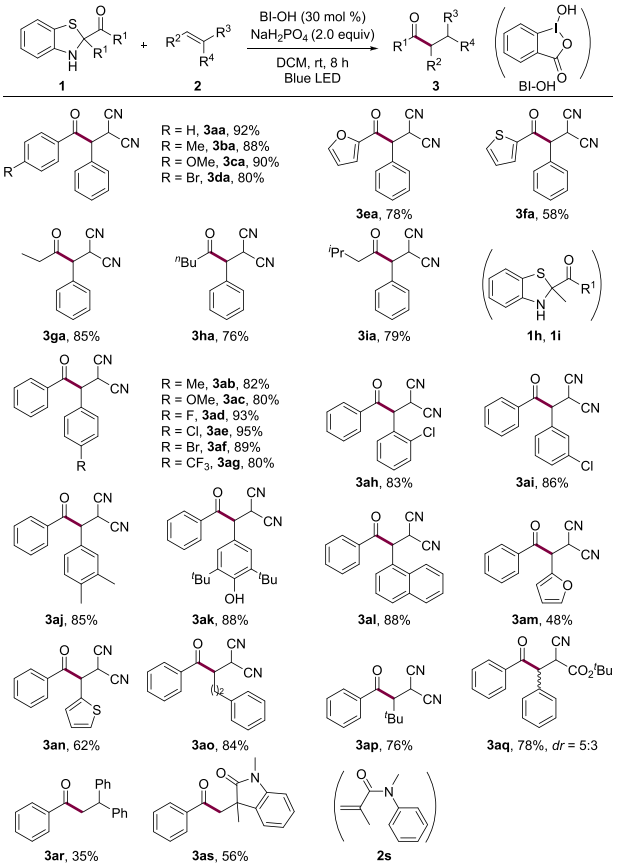
We set out to evaluate the feasibility of generating acyl radical from 2-benzoyl-2-phenylbenzothiazoline (**1a**) under visible light irradiation and, with electron-deficient 1,1-dicyano-2-phenylethylene (**2a**) as the acceptor, achieving formal radical alkylation (or alternatively, alkene hydroacylation) reaction. By using hydroxybenziodoxolone (BI−OH) (2.0 equiv) as the hypothetical **1a** N−H hydrogen (proton or hydrogen atom) abstraction reagent, initial screening experiments were performed against the photosensitizer (Table S1). The radical alkylation reaction can proceed quite easily under overnight blue light LED irradiation in DCM with the addition of a variety of transition metal complexes (2.5 mol %) as the photosensitizer and NaH_2PO_4 (2.0 equiv) as the base. However, the yield of target product **3aa** is generally not satisfactory ($Ru(ppy)_3(PF_6)_2$, 68%; $Ir(dtbbpy)(ppy)_2PF_6$, 76%; $Ir(ppy)_3$, 88%). The switching to the organic photosensitizer rhodamine B witnesses a reduction in the yield (44%). The adoption of 9-mesityl-10-methylacridinium perchlorate (Acr^+-Mes) provides a seemingly significant boost to the reactivity. Depending on the solvent (DCM, DCE, EtOAc, dioxane)/base (NaH_2PO_4, Na_2HPO_4, Na_3PO_4, NaH_2PO_4, NaOAc, $NaHCO_3$)/BI−OH derivative combination, the yield can be largely maintained, with a few exceptions, at the level of 80−92%. Further control experiments indicate, however, not surprisingly in hindsight from mechanistic standpoint, that photosensitizer can be completely eliminated from the system without negatively impacting the reaction. Compound **3aa** can be efficiently obtained in 92% yield even with the BI−OH quantity reduced to the 30 mol % catalytic level. No reaction occurs in the dark under otherwise identical conditions.

With the visible light-driven, photosensitizer-free reaction conditions established, we next proceeded to the assessment of substrate scope (Scheme 2). The substrate scope for benzothiazolines with respect to C2-acyl substituent was examined by coupling with **2a**. Both electron-donating (*p*-Me, **1b**; *p*-OMe, **1c**) and electron-withdrawing (*p*-Br, **1d**) groups can be tolerated on the phenyl ring, affording corresponding products in 80−90% yields. The use of a heterocyclic substituent such as 2-furyl (**1e**) or 2-thienyl (**1f**) only leads to a slight reduction of the yield. Notably, an alkyl substituent (**1g**, **1h**, **1i**) provides an effective reaction system (85% yield). The substrate scope for trisubstituted alkenes with respect to C2-substituent was explored by coupling with **1a**. The yields stay at a high level (80−95%) irrespective of the electronic character of the substituent on the phenyl ring. The electron-donating groups (*p*-Me, **2b**; *p*-OMe, **2c**) exert a slightly negative effect on the product yields as compared to the electron-withdrawing groups (*p*-F, **2d**; *p*-Cl, **2e**; *p*-Br, **2f**; *p*-CF_3, **2g**; *o*-Cl, **2h**; *m*-Cl, **2i**). This is understandable since electron deficiency is the prime parameter governing alkene reactivity as acceptors for nucleophilic acyl radicals. The product yields for alkenes bearing di- (**2j**) and trisubstituted (**2k**) phenyl rings are comparable to those bearing monosubstituted ones. The replacement of phenyl group with the bulky naphthyl group (**2l**) poses no hurdle for the reaction. However, a heterocyclic group (2-furyl, **2m**; 2-thienyl, **2n**) significantly retards the reaction. Switching to the alkyl group (**2o**, **2p**) also shows compatibility with the reaction. The replacement of one cyano group to an ester group (**2q**) decreases the reactivity. Significantly, two fundamentally different types of alkene substrates also exhibit the coupling reactivity (**2r**, **2s**).

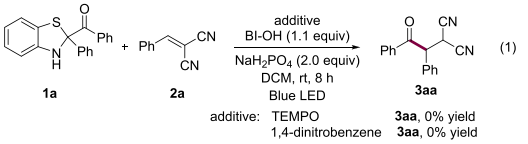
With the substrate scope surveyed, preliminary mechanistic experiments were conducted and are consistent with a radical

Scheme 2. Substrate Scope of Formal Radical Alkylation Reaction[a,b]



[a]Reaction conditions: **1** (0.12 mmol), **2** (0.1 mmol), DCM (2 mL). [b]Isolated yield.

reaction pathway. The reaction between **1a** and **2a** can be completely inhibited by the addition of a radical scavenger of either (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) or 1,2-dinitrobenzene (eq 1). Together with the isolation of 2-



phenylbenzothiazole and 2-iodobenzoic acid, the following reaction mechanism is proposed (Scheme 3): the reaction between **1a** and BI−OH generates intermediate **I**; the I−N bond of **I** is cleaved under visible light irradiation, leading to the formation of radical intermediate **II** and BI• radical **III**; aromatization of **II** provides the driving force for C−C bond cleavage and formation of acyl radical **IV**; nucleophilic attack of **IV** on **2a** generates intermediate **V**; abstraction of hydrogen atom by **V** from **1a** generates **3aa** as the formal alkylation product and reinitiates the formation of **I** for the next chain reaction cycle; BI• radical **III** can also abstract the hydrogen atom from **1a** to initiate the radical reaction. Dicyano groups are versatile reactive functionalities toward further elaboration (with or without the incorporation of two cyano groups into target products).[16] As an illustration, **3aa** can be conveniently transformed into **3aa-t1** (eq 2) and **3aa-t2** (eq 3).

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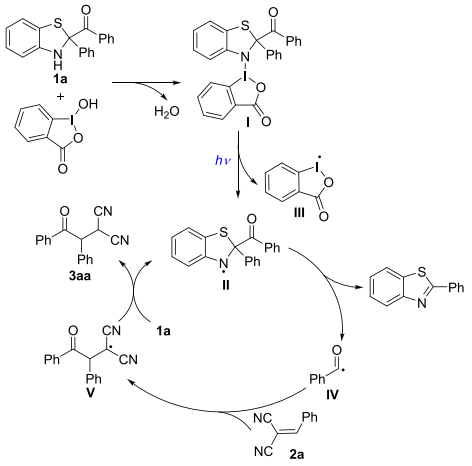
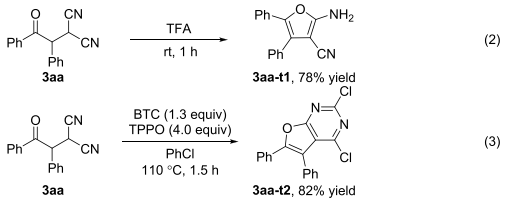
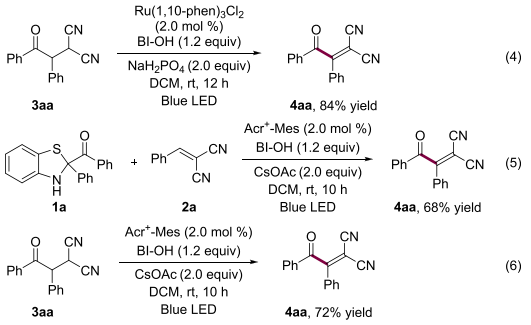
Scheme 3. Mechanistic Proposal for the Formal Radical Alkylation Reaction





Even though photosensitizer has proven to be an unnecessary component for the radical alkylation reaction, during the course of reaction condition screening, we have identified an interesting formal radical alkenylation reaction (Table S2). The reaction between **1a** and **2a** can proceed to the stage of **4aa** in 80% yield, with the restoration of BI−OH quantity to 1.2 equiv. and the additional participation of $Ru(1,10\text{-phen})_3Cl_2$ (2.0 mol %),[17] under blue light LED irradiation. Preliminary substrate scope inspection (Scheme 4) suggests the reaction compatibility of phenyl substitution on both the C2-acyl side (**1b**) and alkene C2 side (**2b**, **2c**, **2d**, **2e**, **2f**, **2j**). The product yields for radical alkenylation are generally inferior to those for radical alkylation, and again, electronic deficiency on the alkene C2 phenyl ring dictates the reaction outcome. Careful control experiments illustrate a stepwise mechanism for the radical alkenylation reaction. The radical alkylation product **3aa** can be converted to **4aa** under the radical alkenylation condition employed herein (eq 4). Monitoring with thin layer chromatography (TLC)

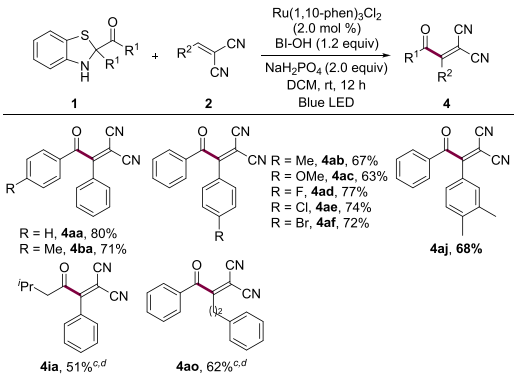


shows that the reaction between **1a** and **2a** features an initial rapid accumulation of **3aa** (within 2 h) and subsequent formation of **4aa** at the expense of **3aa**. The transition metal photosensitizer $Ru(1,10\text{-phen})_3Cl_2$ can be changed to the organic photosensitizer Acr^+-Mes without affecting the transformation (eqs 5 and 6). Alternatively, the formal alkenylation product (**4ia**, **4ao**) can be directly obtained from the corresponding alkylation product (**3ia**, **3ao**) under DDQ oxidative conditions (Scheme 4).

With both radical alkylation and alkenylation reactions demonstrated, we further pursued the possibility of achieving radical alkynylation. To this end, alkynylbenziodoxolone (BI-alkyne) is selected as the potential source of alkynyl group. Initial screening was carried out using **1a** and BI-phenylacetylene (**5a**) as the coupling partners, Acr^+-Mes (2.0 mol %) as the photosensitizer, and NaH_2PO_4 (2.0 equiv) as the base (Table S3). With the quantity of **5a** first set at 2.0 equiv, a variety of solvents (DCM, DCE, EtOH, EtOAc, THF, CH_3CN) was scrutinized. DCM proves to be the best reaction medium, with the yield of product **6aa** reaching 84% after 2 h of blue light LED irradiation. The reaction can still proceed smoothly when the quantity of **5a** is decreased to either 1.5 or 1.2 equiv, albeit with a slightly lower yield. The increase of **5a** quantity to 3.0 equiv is not beneficial. As in the case of benzothiazoline/BI−OH system, the acyl radical generation from benzothiazoline/BI-alkyne system does not require the participation of Acr^+-Mes. Without Acr^+-Mes, **6aa** can be obtained from **1a** and **5a** in 89% yield.

The substrate scope for benzothiazolines and BI-alkynes was then investigated (Scheme 5). For benzothiazolines, the electronic character of C2-acyl phenyl ring, whether electron-rich (**1b**, **1c**) or electron-poor (**1d**), does not significantly influence the reactivity. The change of phenyl ring to a heterocycle (**1e**) or an alkyl group (**1g**) provides a less effective reaction system. The reactions using benzothiazolines constructed from unsymmetrical 1,2-diketones (**1j**, **1k**, **1l**) demonstrate that an aromatic ring on the C2 position is not required for achieving the high reactivity. For BI-alkynes, the effect of phenylacetylene substitution was comprehensively studied. For the *para* substitution, an electron-donating group (*p*-Me, **5b**) is generally not as ideal as an electron-withdrawing group (*p*-F, **5c**; *p*-Cl, **5d**; *p*-$C(O)CH_3$, **5e**; *p*-CH(O), **5f**; *p*-CO_2Me, **5g**), but with a notable exception (*p*-CN, **5h**). The *ortho* substitution (*o*-Cl, **5i**) provides a more reactive substrate as compared to the *para* counterpart. The *meta* substitution (*m*-Cl, **5j**; *m*-OMe, **5k**; *m*-OCF_3, **5l**) also enables the generation of respective product in high yield. Extension of the single phenyl ring to the 1,1′-biphenyl ring (**5m**) largely preserves the

Scheme 4. Substrate Scope of Formal Radical Alkenylation Reaction[a,b]



[a]Reaction conditions: **1** (0.12 mmol), **2** (0.1 mmol), DCM (2 mL). [b]Isolated yield. [c]Compounds **3ia** and **3ao** as starting material. [d]DDQ (2.0 equiv), O_2 balloon, $CHCl_3$ (1 mL).

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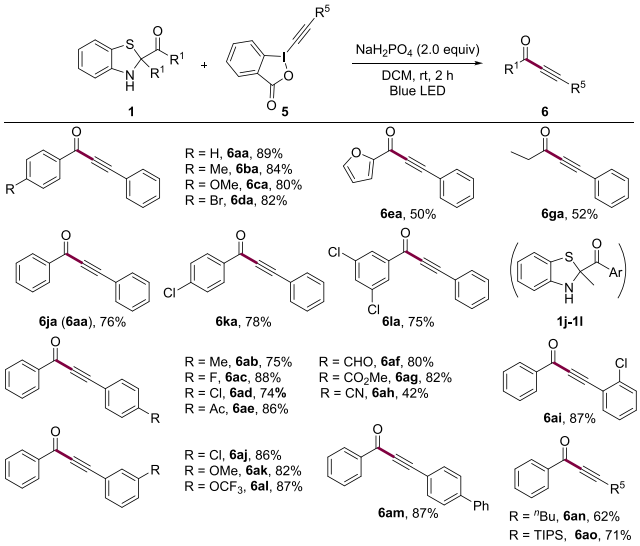
Scheme 5. Substrate Scope of Formal Radical Alkynylation Reaction[a,b]



[a]Reaction conditions: **1** (0.1 mmol), **5** (0.2 mmol), DCM (2 mL). [b]Isolated yield.

reactivity. Delightfully, an alkyl substitution (**5n**) or a silyl substitution (**5o**) on the acetylene unit can also be tolerated.

In conclusion, we have developed herein an acyl radical generation strategy from benzothiazolines under visible light irradiation. This not only provides a mechanistically distinct C−C bond breaking mode but also enables the efficient achievement of radical alkylation, alkenylation, and alkynylation reactions. These findings promise the discovery of more aromatization-derived synthetic systems.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01717.

Experimental procedures and product characterization; copies of the ^{1}H and ^{13}C NMR spectra of selected products (PDF)

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Notes

The authors declare no competing financial interest.

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