

# Visible-Light-Facilitated 5-*exo-trig* Cyclization of 1,6-Dienes with Alkyl Chlorides: Selective Scission of the C(sp<sup>3</sup>)–H Bond in Alkyl Chlorides

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A general and conceptually novel method for preparing polychloro-substituted pyrrolidin-2-ones and indeno[2,1-c]pyrrol-3(3a*H*)-ones is established by visible-light-facilitated 5-

Introduction

The cyclization of dienes is a continuing active field, because it is widely utilized for the construction of carbocyclic and heterocyclic compounds that are important components of multitudinous natural products, pharmaceutical molecules, and functional materials.<sup>[1–3]</sup> In this context, the cyclization of dienes through a radical strategy, particularly the generation of a carbon-centered radical from organohalides as the initial step, has attracted considerable attention.<sup>[2,3]</sup> Generally, organohalides (often alkyl halides) are transferred to the carbon-centered radicals by selectively splitting the carbon-halogen bonds by using a thermo- or photoinitiation strategy wherein radical initiators such as azobis(isobutyronitrile) (AIBN) and organotin reagents (often Bu<sub>3</sub>SnH) are usually used to accomplish these transformations (Scheme 1a).<sup>[2,3a–3e]</sup> To the best of our knowl-



Scheme 1. Cyclization of 1,6-dienes with alkyl chlorides. bpy = 2,2'-bipyridyl.

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exo-trig cyclization of 1,6-dienes with alkyl chlorides through selectively splitting the  $C(sp^3)$ –H bond adjacent to the chloride atom to form an alkyl radical.

edge, however, a method for the formation of carbon-centered radicals from organohalides by selectively abstracting the hydrogen atom, not the halide atom, has not been established. The reason may be that in organohalides the reactivity of the carbon-halogen bond is far higher than that of the carbon-hydrogen bond.

Herein we report an unprecedented visible-light-facilitated method for 5-*exo-trig* cyclization of 1,6-dienes with alkyl chlorides through selective scission of the C(sp<sup>3</sup>)–H bond adjacent to the chloride atom to form a chloro-substituted alkyl radical in the presence of aryldiazonium tetrafluoroborate radical initiators<sup>[4,5]</sup> (Scheme 1b). The results demonstrate that both visible-light and photoredox catalysts can facilitate this reaction.<sup>[4f-4i,5]</sup> Importantly, this new method provides an efficient way to synthesize various polychloro-substituted pyrrolidin-2-ones and indeno[2,1-*c*]pyrrol-3(3a*H*)-ones, which form the nuclei of many natural products and bioactive molecules.<sup>[6,7]</sup>

#### **Results and Discussion**

We began our investigation with the reaction of N-allyl-N-phenylmethacrylamide (1a) with dichloromethane (2a) to optimize the reaction conditions (Table 1).<sup>[8]</sup> Gratifyingly, treatment of diene 1a with chloride 2a, 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub>, and Na<sub>2</sub>CO<sub>3</sub> at 50 °C for 20 h afforded desired pyrrolidin-2-one 3 in 25% yield (Table 1, Entry 1), and its stereochemistry was determined by analysis by 2D NMR spectroscopy.<sup>[8]</sup> However, the reaction did not take place without a diazonium tetrafluoroborate (Table 1, Entry 2). The results suggest that the generation of the 4-methoxyphenyl radical from 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> is the key step in the 5exo-trig cyclization reaction. It is well known that visible light combined with a photoredox catalyst can trigger the transformation of aryldiazonium salts into aryl radicals.<sup>[4f-4i,5]</sup> Therefore, the effect of both visible light and the photoredox catalyst was tested: the yield of 3 was indeed enhanced to 35% under a 36W compact fluorescent light

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alone (Table 1, Entry 3) and was further increased to 58% in the presence of both  $Ru(bpy)_3Cl_2$  and a 36 W compact fluorescent light (Table 1, Entry 4). We found that the base affected the reaction, and Na<sub>2</sub>CO<sub>3</sub> was the most effective (Table 1, Entries 4-7). Notably, the absence of a base resulted in no detectable pyrrolidin-2-one 3 (Table 1, Entry 8). Among the reaction temperatures examined, it turned out that the reaction at 50 °C gave the best results (Table 1, Entries 4, 9 and 10). To our delight, a satisfactory yield was still achieved at an Ru(bpy)<sub>3</sub>Cl<sub>2</sub> loading of 2 mol-% (Table 1, Entry 11). Notably, the reaction proceeded in MeCO<sub>2</sub>nBu medium smoothly, although the product was obtained in a slightly lower yield (Table 1, Entry 12). Two other visible light photoredox catalysts, that is, Ir(ppy)<sub>3</sub> (ppy = 2-phenylpyridine) and Eosin Y, were tested (Table 1, Entries 13 and 14): Whereas Ir(ppy)<sub>3</sub> also displayed high catalytic activity, Eosin Y disfavored the reaction. Screening revealed that the amount of 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> had a fundamental influence on the reaction, and the yield decreased to 33% with 1 equiv. of the diazonium salt (Table 1, Entries 2, 4, and 15). Notably, the presence of an Ru catalyst alone affected the reaction slightly without light (Table 1, Entry 16).

Table 1. Screening for the optimal conditions.<sup>[a]</sup>

| ~                  |                           |                                 |                       |                   |              |  |
|--------------------|---------------------------|---------------------------------|-----------------------|-------------------|--------------|--|
|                    | NO + H-CHC<br>Ph 2a<br>1a | I <sub>2</sub> [M], ba          | ase                   | NO<br>Ph<br>cis-3 |              |  |
| Entry              | [M] (mol-%)               | Base                            | Solvent               | <i>Т</i><br>[°С]  | Yield<br>[%] |  |
| 1 <sup>[b]</sup>   | _                         | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 25           |  |
| 2 <sup>[b,c]</sup> | _                         | $Na_2CO_3$                      | neat                  | 50                | 0            |  |
| 3                  | _                         | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 35           |  |
| 4                  | $Ru(bpy)_3Cl_2(5)$        | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 58           |  |
| 5                  | $Ru(bpy)_3Cl_2(5)$        | NaHCO <sub>3</sub>              | neat                  | 50                | 50           |  |
| 6                  | $Ru(bpy)_3Cl_2(5)$        | $Cs_2CO_3$                      | neat                  | 50                | 21           |  |
| 7                  | $Ru(bpy)_3Cl_2(5)$        | Et <sub>3</sub> N               | neat                  | 50                | 17           |  |
| 8                  | $Ru(bpy)_3Cl_2(5)$        | _                               | neat                  | 50                | 0            |  |
| 9                  | $Ru(bpy)_3Cl_2(5)$        | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 30                | 50           |  |
| 10                 | $Ru(bpy)_3Cl_2(5)$        | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 70                | 32           |  |
| 11                 | $Ru(bpy)_3Cl_2(2)$        | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 40           |  |
| 12 <sup>[d]</sup>  | $Ru(bpy)_3Cl_2(5)$        | Na <sub>2</sub> CO <sub>3</sub> | MeCO <sub>2</sub> nBu | 50                | 48           |  |
| 13                 | $Ir(ppy)_3(5)$            | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 50           |  |
| 14                 | Eosin Y (5)               | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 10           |  |
| 15 <sup>[e]</sup>  | $Ru(bpy)_3Cl_2(5)$        | $Na_2CO_3$                      | neat                  | 50                | 33           |  |
| 16 <sup>[b]</sup>  | $Ru(bpy)_3Cl_2(5)$        | Na <sub>2</sub> CO <sub>3</sub> | neat                  | 50                | 28           |  |

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (15 mmol), [M], 4-Me-OC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (2 equiv.), and base (2 equiv.) with 36 W compact fluorescent light under argon for 20 h. Two diastereoisomers were observed by GC–MS analysis of the crude products, and the *dr* value was 9.8:1; however, only the *cis* isomer was isolated upon purification. Yields of the isolated products are given. [b] Without additional light. [c] Without 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub>. [d] Compound **2a** (6 mmol) and MeCO<sub>2</sub>*n*Bu (anhydrous, 0.5 mL). [e] 4-Me-OC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (1 equiv.).

We next set out to examine the effect of the diazonium salt (Scheme 2). Three other aryldiazonium salts displayed high reactivity, but they were less efficient than 4-Me $OC_6H_4N_2BF_4$  (Scheme 2 versus Table 1, Entry 4). However, the common radical initiator, AIBN, had no effect on the reaction.



Scheme 2. Screening of the diazonium salts.

With the optimal conditions in hand, the scope of dienes 1 and alkyl halides 2 for the 5-exo-trig cyclization reaction was investigated (Table 2 and Scheme 3). In the presence of Ru(bpy)<sub>3</sub>Cl<sub>2</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, and a 36 W compact fluorescent light, diene 1a successfully reacted with various alkyl chlorides, that is, 1,1-dichloroethane (2b), chloroform (2d), 1,1,2-trichloroethane (2e), and 1,1,2,2-tetrachloroethane (2f), to provide pyrrolidin-2-ones 4, 6, 8, and 9, respectively, in good yields (Table 2, Entries 1, 3, 5, and 6). However, 1-chlorobutane (2c) was unreactive in this reaction (Table 2, Entry 2). By using diene 1b, a moderate yield of the product was still achieved (Table 2, Entry 4). Interestingly, the selectivity of the products from dienes 1c and 1d bearing a phenyl group at the 2-position depended on chlorides 2 (Table 2, Entries 7-11). For example, diene 1c reacted with chlorides 2a and 2f to afford indeno[2,1-c]pyrrol-3(3aH)-ones 10 and 11 through a cascade of three C-C bond-formation reactions (Table 2, Entries 7 and 9), but chloride 2d gave only pyrrolidin-2-one 12 in moderate yield (Table 2, Entry 8). Notably, treatment of diene 1d with chloride 2a provided a mixture of tricyclic product 13 and spirocyclic product 14 in 41 and 36% yield, respectively (Table 2, Entry 10). By using chloroform (2d), only pyrrolidin-2-one 15 was isolated from diene 1d in moderate yield (Table 2, Entry 11).

To understand the mechanism, some control experiments were performed (Scheme 3). By using CDCl<sub>3</sub> (2d-D1) instead of CHCl<sub>3</sub> (2d), both monodeuterated pyrrolidin-2-one 6-D1 and anisole 16-D1 were observed by GC-MS analysis [Equation (1)].<sup>[8]</sup> This suggests that the reaction is triggered by the 4-methoxyphenyl radical from  $4\text{-MeOC}_6\text{H}_4\text{N}_2\text{BF}_4$ and is finished by abstraction of a hydrogen atom from the alkyl halide. To verify this, the reaction between 4-Me-OC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> and CDCl<sub>3</sub> (2d-D1) was tested. Without Ru, base, or light, 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> was stable. However, 90% of this diazonium salt was decomposed by Na<sub>2</sub>CO<sub>3</sub> into monodeuterated anisole 16-D1, which was obtained in 75% yield with 83% deuterium, because the diazonium salt (neat at 50 °C) decomposed smoothly with the aid of Na<sub>2</sub>CO<sub>3</sub> to generate the aryl radical. This may also justify the 25% yield of pyrrolidin-2-one that was found in the absence of both [Ru] and visible light (Table 1, Entry 1). As expected, the decomposition was selectively promoted by using Ru and light: 95% of the diazonium salt was converted into



Table 2. 5-*exo-trig* cyclization of 1,6-dienes 1 with alkyl chlorides  $2^{[a]}$ 

[a] Reaction conditions: 1 (0.3 mmol), 2 (15 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (5 mol-%), 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (2 equiv.), and Na<sub>2</sub>CO<sub>3</sub> (2 equiv.) with a 36 W compact fluorescent light under argon at 50 °C for 20 h. The *dr* (*cis/trans*) values are given in parentheses, and they were determined by GC–MS analysis of the crude products. The yields are those of the *cis* isomers only, because only the *cis* isomers were isolated after purification. Moreover, some side products, including C–N bond-decomposition products and noncyclizing products, were observed by GC–MS analysis.



Scheme 3. Control experiments.

**16**-D1 (91% yield). These deuteration experiments imply that the yield of the present reaction is based on the selectivity of the generation of the aryl radical, and the photocatalysts/visible-light system mainly effects the reaction by facilitating the generation of the aryl radical. Notably, a stoichiometric amount of two radical inhibitors (2 equiv.), that is, TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide) and 2,6-di-*tert*-butylphenol, was added to the reaction mixture, and this resulted in no conversion of diene **1a**. All of the results described above support that the reaction includes a radical process.

Consequently, possible mechanisms outlined in Scheme 4 are proposed.<sup>[2-4]</sup> Initially, 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> is readily converted into the 4-methoxyphenyl radical by base/ Ru(bpy)<sub>3</sub>Cl<sub>2</sub>/visible light under heating conditions.<sup>[4,5]</sup> Subsequently, selective hydrogen-atom abstraction of CH<sub>2</sub>Cl<sub>2</sub> cation radical A, in situ generated from CH<sub>2</sub>Cl<sub>2</sub> (2a) by visible-light catalysis, by the 4-methoxyphenyl radical offers the 'CHCl<sub>2</sub> radical. Addition of the 'CHCl<sub>2</sub> radical to the activated alkene yields radical intermediate B; cyclization of **B** with another alkene through a single-electron-transfer process gives rise to radical intermediate C. Finally, hydrogen-atom abstraction of A by C takes place to yield the 'CHCl<sub>2</sub> radical and product 3. The photoinduced mechanism is also supported by the quantum yield ( $\Phi_x = 0.073$ ).<sup>[9]</sup> Notably, the CHCl<sub>2</sub> radical can be directly generated from the reaction of  $CH_2Cl_2$  (2a) with the 4-methoxyphenyl radical if the reaction is conducted without an Rh catalyst or light.



Scheme 4. Possible mechanisms.

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### Conclusions

We illustrated a novel, general method for the synthesis of polychloro-substituted pyrrolidin-2-ones and indeno[2,1-c]pyrrol-3(3aH)-ones by a visible light photoredox catalyst facilitated 5-*exo-trig* cyclization of dienes with alkyl chlorides involving a C(sp<sup>3</sup>)–H functionalization process. Importantly, this method represents a significant conceptual advance that is achieved by selective scission of the C–H bond adjacent to the chloride atom of the carbon-centered radical by using a single-electron-transfer strategy. Investigation of the applications of diazonium salts as potential triggers in organic synthesis are currently underway in our laboratory.

## **Experimental Section**

**General Methods:** All the materials and solvents were purchased from commercial suppliers and used without additional purification. IR measurements were performed with an FTIR Shimadzu DR-8000 spectrometer fitted with a Pike Technologies MIRacle single reflection ATR adapter. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX-500 spectrometer (<sup>1</sup>H at 500 MHz and <sup>13</sup>C at 125 MHz) or a Bruker DRX-400 spectrometer (<sup>1</sup>H at 400 MHz and <sup>13</sup>C at 100 MHz). NMR spectroscopic data were obtained in CDCl<sub>3</sub> unless otherwise noted. High-resolution mass spectra were recorded with a Bruker microTOF-QII (ESI) spectrometer. Preparative thin-layer chromatography was performed on silica gel plates with PF254 indicator. Flash column chromatography was performed with silica gel 60N unless otherwise noted.

Typical Experimental Procedure for the Visible-Light-Facilitated 5exo-trig Cyclization of 1,6-Dienes with Alkyl Chlorides: A Schlenk tube was charged with *N*-allyl-*N*-phenylmethacrylamide (1a, 0.3 mmol), dichloromethane (2a, 15 mmol), Ru(bpy)<sub>3</sub>Cl<sub>2</sub> (5 mol-%), Na<sub>2</sub>CO<sub>3</sub> (2 equiv.), and 4-MeOC<sub>6</sub>H<sub>4</sub>N<sub>2</sub>BF<sub>4</sub> (4-methoxybenzenediazonium tetrafluoroborate, 2 equiv.). Then, the tube was charged with argon, and the mixture was stirred at 50 °C under visible light for the indicated time until complete consumption of starting material, as monitored by TLC and/or GC–MS analysis. Upon completion of the reaction, the mixture was diluted with diethyl ether and concentrated in vacuo, and the resulting residue was purified by silica gel column chromatography (hexane/ethyl acetate, 20:1) to afford desired product *cis*-**3**.

*cis*-3-(2,2-Dichloroethyl)-3,4-dimethyl-1-phenyl-pyrrolidin-2-one (3): Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.61 (d, J = 4.8 Hz, 2 H), 7.38 (t, J = 3.6 Hz, 2 H), 7.16 (d, J = 7.2 Hz, 1 H), 6.14 (t, J = 6.0 Hz, 1 H), 3.81 (dd, J = 8.0, 9.6 Hz, 1 H), 3.42 (t, J = 9.6 Hz, 1 H), 2.76 (dd, J = 6.4, 15.2 Hz, 1 H), 2.70–2.64 (m, 1 H), 2.50 (dd, J = 6.0, 15.6 Hz, 1 H), 1.13–1.12 (m, 6 H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.8, 139.2, 128.9 (2 C), 124.6, 119.8, 70.1, 52.0, 49.2, 47.6, 33.6, 17.7, 12.0 ppm. IR (KBr):  $\tilde{v}$  = 1693, 1597, 1461 cm<sup>-1</sup>. LRMS (EI, 70 eV): *mlz* (%) = 287 (5) [M + 2]<sup>+</sup>, 285 (7) [M]<sup>+</sup>, 190 (6), 189 (47), 175 (13), 174 (100). HRMS (ESI): calcd. for C<sub>14</sub>H<sub>18</sub><sup>35</sup>Cl<sub>2</sub>NO [M + H]<sup>+</sup> 286.0760; found 286.0751.

**Supporting Information** (see footnote on the first page of this article): <sup>1</sup>H and <sup>13</sup>C NMR spectra for all products **3**, **4**, and **6–16**.

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