



A new entry to α -alkylidene- β -lactams by 4-*exo-dig* cyclization of carbamoyl radicals

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ABSTRACT

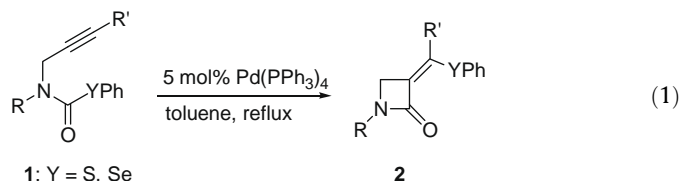
A new synthetic method of α -alkylidene- β -lactam frameworks has been developed. Irradiation of carbamotelluroates **5** having a propargylic group at the nitrogen atom with visible light afforded α -telluromethylene- β -lactams **6** by 4-*exo-dig* cyclization of carbamoyl radicals, generated by homolytic cleavage of carbamoyl carbon–tellurium bond of **5**, with internal C–C triple bond. Density functional theory (DFT) calculations on cyclization step indicate that 4-*exo-dig* cyclization of carbamoyl radicals is kinetically favored. The existence of a rapid equilibrium between carbamoyl and four-membered vinyl radicals was suggested by control experiments using the corresponding carbamoselenoate.

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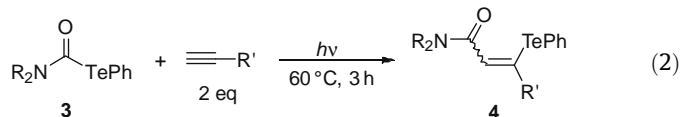
The α -alkylidene- β -lactam framework is a common structural feature found in various synthetic intermediates¹ and potent β -lactamase inhibitors² such as asparenomyins, Ro 15-1903, and 6-[(*Z*)-methoxymethylene]penicillanic acids. Classical methods for preparation of α -alkylidene- β -lactam include (i) addition of chlorosulfonyl isocyanate (CSI) to allenes,³ (ii) reaction of ketenes with imines,⁴ (iii) transition metal-catalyzed carbonylation of allyl- and propargylamines,⁵ (iv) cyclization by nucleophilic S_N2 attack of amino or amide nitrogen atom,⁶ (v) α -alkylideneation by elimination,⁷ and several other reactions.⁸ As for the radical cyclization approach to α -alkylidene- β -lactams, Pattenden and co-workers reported that 4-*exo-trig* cyclization of a carbamoyl radical, generated by irradiation of carbamoyl cobalt(salophen) complex with UV light, and subsequent β -elimination afforded α -methylidene- β -lactam in 25% yield.⁹ Ryu and co-workers revealed that intramolecular attack of acyl radicals, generated by carbonylation of azaenynes, at imino nitrogens led to α -alkylidene- β -lactams carrying a stannyl, silyl, or sulfenyl substituent.¹⁰

Recently we developed an efficient method for construction of this framework by palladium-catalyzed intramolecular addition of thio- and selenocarbamoyl groups to alkyne units (Eq. 1);¹¹ however, this system cannot be applied to carbamotelluroates under the same reaction conditions.

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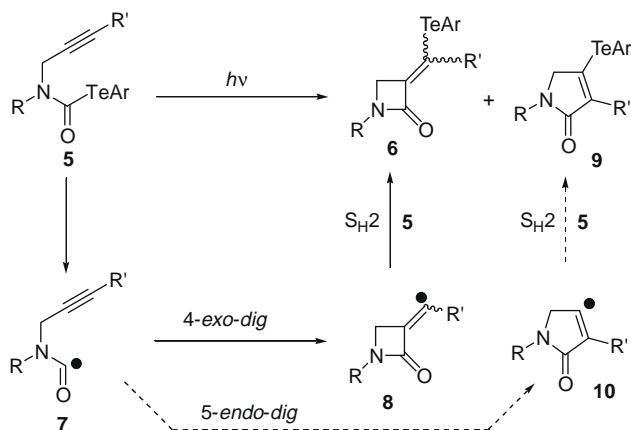


We also disclosed that carbamotelluroates **3** added to alkynes in an intermolecular fashion under irradiation of visible light yielding β -telluroacrylamides **4** regioselectively provably via photo-cleavage of the carbamoyl carbon–tellurium bond (Eq. 2).¹²

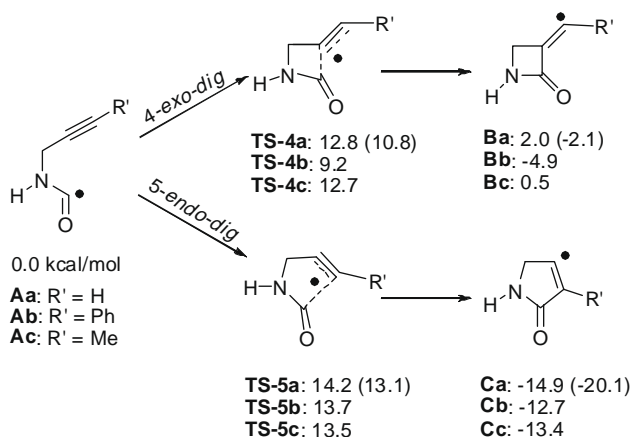


These results prompted us to examine 4-*exo-dig* cyclization of carbamoyl radicals aiming at the construction of α -alkylidene- β -lactam framework according to the reaction pathway as shown in Scheme 1. The first step is photo-induced generation of carbamoyl radicals **7** from carbamotelluroates **5** having a propargyl group at the nitrogen atom. Subsequent 4-*exo-dig* cyclization gives vinyl radicals **8**. S_H2 reaction at Te of **5** with **8** leads to α -alkylidene- β -lactams **6** and regenerates **7**. If 5-*endo-dig* cyclization proceeds, five-membered lactams **9** will be formed via vinyl radicals **10** Scheme 2.

Thus, we irradiated a toluene (2.5 mL) solution of **5a** (R = Bu, R' = H, Ar = Ph; 0.5 mmol) in a Pyrex flask with a tungsten lamp at 110 °C for 3 h. Usual workup of the resulting mixture using



Scheme 1. Intramolecular cyclization of carbamoyl radicals.



Scheme 2. Relative energies of radical intermediates calculated at UB3LYP/6-311G(d,p) and those at UB3PW91/cc-pVTZ in parentheses.

preparative TLC gave the corresponding α -methylidene- β -lactam **6a** in 40% yield ($E/Z = 61/39$) in pure form (Table 1, run 1). Unlike the case of intermolecular addition of carbamoyl radicals to alkynes, cyclization needs heating at 100 °C or above to proceed.^{13,14}

Table 1
4-*exo-dig* Cyclization of carbomoyl radicals^a

Run	5	R	R'	Ar	Isolated yield (E/Z ratio) ^b
1	5a	Bu	H	Ph	6a, 40% (61/39)
2	5b	Bu	H	<i>p</i> -MeC ₆ H ₄	6b, 39% (71/29)
3	5c	Bu	H	<i>p</i> -MeOC ₆ H ₄	6c, 58% (70/30)
4 ^c	5d	Me	H	<i>p</i> -BrC ₆ H ₄	6d, 42% (60/40)
5	5e	PhCH ₂	H	<i>p</i> -MeOC ₆ H ₄	6e, 50% (60/40)
6	5f	Bu	Ph	<i>p</i> -MeOC ₆ H ₄	6f, 83% (57/43) ^d
7 ^e	5g	Bu	Et	Ph	6g, 31% (83/17)

^a Conditions: **5** (0.5 mmol), toluene (2.5 mL), reflux, 3 h, irradiation with a tungsten lamp.

^b E/Z Ratio was determined by ¹H NMR.

^c 6 h.

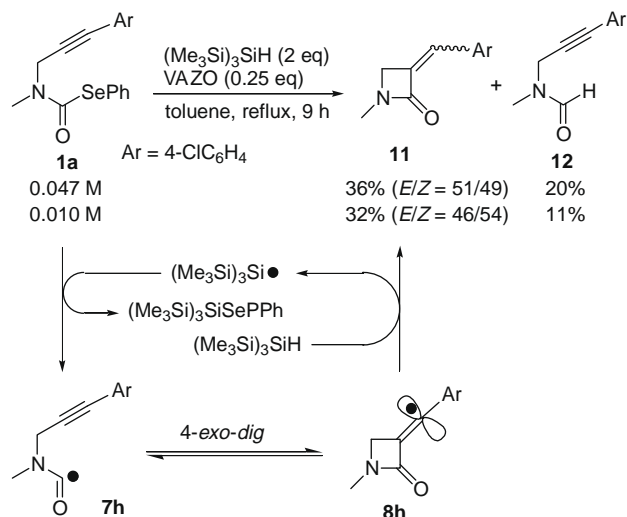
^d Major/minor ratio.

^e Five-membered lactam **9g** (12%) was formed.

Representative results are summarized in Table 1.¹⁵ Electron-donating substituent, methoxy group, at the para position of the phenyl ring increased the yield of the product (run 3 vs runs 1, 2, and 4); probably because of lower homolytic bond dissociation energy between carbamoyl carbon and tellurium. As for the substituents on nitrogen atom, **5d,e** having methyl and benzyl groups also afforded the expected products (runs 4 and 5). It is noteworthy that when phenyl group was introduced at the end of C–C triple bond, desired β -lactam **6f** was obtained in 83% yield due to stabilization of a vinyl radical intermediate **8f** (run 6), whereas, **5g** having ethyl group underwent 5-*endo-dig* cyclization, although as a minor process, to afford five-membered lactam **9g** in 12% yield along with 31% of **6g** (run 7).^{16–18}

In order to gain insight into the effect of substituents at the acetylenic terminus in cyclization step, we performed computational studies. **Aa–c**, **Ba–c**, and **Ca–c** are model compounds for the reactions of **5a**, **5f**, and **5g**, respectively, and **TS-4a–c** and **TS-5a–c** are transition-state structures of 4-*exo-dig* and 5-*endo-dig* cyclizations. All geometries were optimized at the UB3LYP/6-311G(d,p) level using GAUSSIAN 03 program.¹⁹ Structures of **Aa**, **Ba**, **Ca**, **TS-4a**, and **TS-5a** were also optimized at the UB3PW91/cc-pVTZ level. These computations show that 4-*exo-dig* processes are favored kinetically than 5-*endo-dig* processes. For example, activation barrier of **TS-4a** is ca. 1.4 kcal/mol lower than that of **TS-5a**. When Ph group was introduced at the acetylenic terminus, $\Delta\Delta E_a$ increased to 4.5 kcal/mol, and on the contrary **Ac** (R' = Me) reduced $\Delta\Delta E_a$ to 0.8 kcal/mol. These results do not conflict with the experimental results.

Under similar conditions, carbamoselenoate **1a** did not undergo photo-induced cyclization. So we attempted to generate carbamoyl radical **7h** by abstraction of PhSe moiety from **1a** using silyl radical that should lead to cyclization in the presence of hydrogen donor and would provide information on the existence of equilibrium between carbamoyl radical **7** and vinyl radical **8**. Thus, when a solution of **1a** in toluene (0.047 M) was heated at reflux using 0.25 equiv of VAZO[®] (1,1'-azobis(cyclohexanecarbonitrile)) as a radical initiator and 2 equiv of (Me₃Si)₃SiH as a hydrogen donor, β -lactam **11** was formed in 36% yield together with 20% of formamide **12** (Scheme 3). These products **11** and **12** are considered to be formed by hydrogenation of vinyl radical **8h** and carbamoyl radical **7h**, respectively. To suppress the formation of **12**, the reaction was carried out under more diluted conditions (0.010 M); however, product ratio was not largely improved. These results suggest that

Scheme 3. Reaction of carbamoselenoate **1a**.

there might be a rapid equilibrium between vinyl radical **8h** and carbamoyl radical **7h** in this reaction system.²⁰

In contrast to 5- and 6-*exo* cyclization processes that have been employed widely in organic synthesis,²¹ 4-*exo* cyclization process has been rarely involved in synthetic reactions due to unfavorable torsional strain and rapid reverse processes; opening of four-membered rings.²² Since Araki reported the first example of 4-*exo*-*trig* radical cyclization,²³ this cyclization has been studied by several groups.²⁴ However only two systems are known for 4-*exo*-*dig* cyclization so far.²⁵ Here we revealed 4-*exo*-*dig* cyclization of carbamoyl radicals onto alkynes proceeds efficiently to afford α -alkylidene- β -lactams. Reduced ring strain by the incorporation of two sp² carbon atoms in the ring may facilitate this unique 4-*exo*-*dig* cyclization. Equilibrium between carbamoyl radicals and vinyl radicals is also suggested.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.03.071.

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