Synlett H. I. Jung, D. Y. Kim Letter

Synthesis of β-Selenylated Cyclopentanones via Photoredox-Catalyzed Selenylation/Ring-Expansion Cascades of Alkenyl Cyclobutanols

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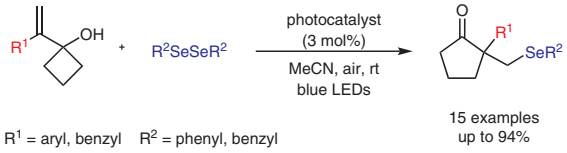


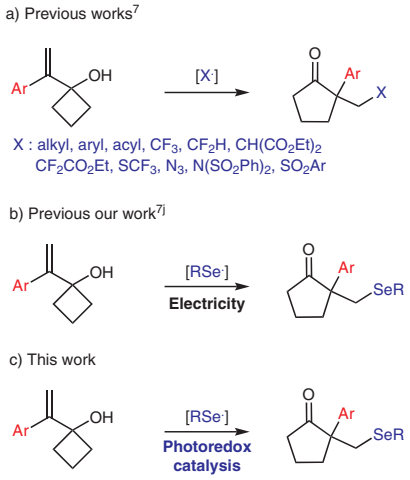
Received: 19.04.2019
Accepted after revision: 08.05.2019
Published online: 29.05.2019
DOI: 10.1055/s-0037-1611841; Art ID: st-2019-u0221-l

Abstract A photoredox strategy to access β-selenated cyclic ketone derivatives through the coupling reaction of 1-(1-arylvinyl)cyclobutanols with diselenides under blue LED irradiation and an air atmosphere was developed. This reaction employs the easily accessible and shelf-stable diselenides as a selenium radical source, and the reaction has advantages of mild reaction conditions and broad substrate scope.

Key words selenylation, semipinacol rearrangement, 1,2-alkyl migration, 1-(1-arylvinyl)cyclobutanols, photoredox reaction

Organoselenium compounds have attracted considerable attention in pharmaceutical and material sciences due to their biological and chemical properties.[1] It can also be used as a chemical intermediate for organic synthesis.[2] The widespread application of these compounds has led to intensive efforts to develop novel and convenient synthetic methods.[3] Deselenide, a reagent that is easily accessible and stable on the shelf, has emerged as a valuable selenium formulation for synthesizing organic selenium compounds. Various reactions of diselenides with alkene, boronic acid, aromatics, and diazonium salt have been used to supply a variety of organoselenium compounds.[4]

The radical-initiated addition reaction to alkenes provided a practical protocol for the difunctionalization of unactivated alkenes with high chemoselectivity.[5,6] Recently, several groups reported radical additions and ring-expansion cascades via semipinacol rearrangement of alkenyl alcohols with a variety of radicals, such as acyl, alkyl, amine, aryl, azido, difluoromethyl, phenylsulfonyl, and trifluoromethyl radicals, for the synthesis of β-functionalized carbonyl compounds (Scheme 1, a).[7]

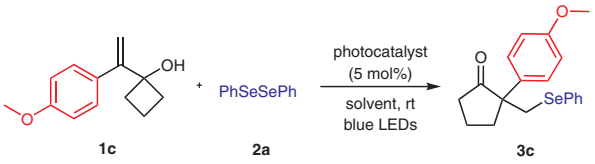


Scheme 1 Strategy for photoredox-catalyzed selenylation/ring-expansion sequences

Over the last decade, the visible-light-mediated photoredox catalysis has emerged as a powerful approach for organic chemists to introduce the functional group to organic compounds because of its environmentally friendly and practical properties.[8] Very recently, we have reported the electrochemical selenylation/ring-expansion sequences of alkenyl cyclobutanols (Scheme 1, b).[7j] Although this method has been achieved by this system, a more efficient, mild, and environmentally benign approaches for the selenylation/ring-expansion sequences of alkenyl alcohols are highly desired. We envisioned transformation of alkenyl cyclobutanols to β-selenated cyclopentanones by visible-light-mediated photoredox-catalyzed selenylation/ring-expansion sequence via semipinacol rearrangement with diselenides as selenium radical precursors (Scheme 1, c).

As part of a study for redox reaction and ring closure, we have reported internal redox reactions[9] and radical additions/ring-expansion sequences under mild conditions.[7d–m]

Table 1 Optimization of Reaction Conditions[a]



1c 2a 3c

Entry	Photocatalyst	Solvent	Time (h)	Yield (%)[b]
1	eosin Y	MeCN	12	37
2	Na_2eosin Y	MeCN	16	46
3	eosin B	MeCN	16	24
4	rhodamine B	MeCN	12	29
5	rhodamine 6G	MeCN	16	30
6	*fac*-Ir(ppy)$_3$	MeCN	12	41
7	F(Ir)pic[c]	MeCN	12	45
8	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	11	94
9	Ru(bpy)$_3$(PF$_6$)$_2$	MeCN	11	37
10	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMSO	22	trace
11	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DMF	22	trace
12	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeOH	21	trace
13	Ru(bpy)$_3$Cl$_2$·6H$_2$O	H_2O	21	20
14	Ru(bpy)$_3$Cl$_2$·6H$_2$O	Acetone	21	32
15	Ru(bpy)$_3$Cl$_2$·6H$_2$O	PhMe	24	24
16	Ru(bpy)$_3$Cl$_2$·6H$_2$O	EA	21	22
17	Ru(bpy)$_3$Cl$_2$·6H$_2$O	THF	11	37
18	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DCM	22	65
19	Ru(bpy)$_3$Cl$_2$·6H$_2$O	DCE	21	55
20[d]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	14	94
21[e]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	14	78
22[f]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	21	66
23[g]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	21	64
24[h]	–	MeCN	24	0
25[i]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	24	0
26[j]	Ru(bpy)$_3$Cl$_2$·6H$_2$O	MeCN	24	25

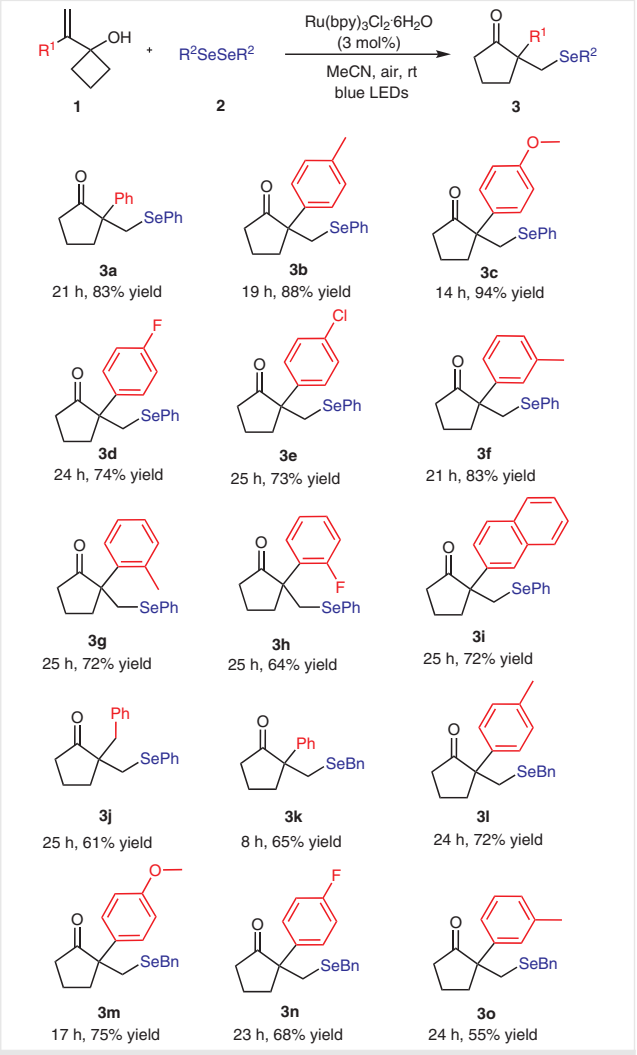
[a] Reaction conditions: 1-[1-(4-methoxyphenyl)vinyl]cyclobutanol (**1c**, 0.1 mmol), diphenyl diselenide (**2a**, 0.06 mmol), photocatalyst, solvent (1 mL), blue LEDs, room temperature under air.
[b] Isolated yields.
[c] F(Ir)pic = bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl) iridium (III).
[d] 3 mol% photocatalyst loading.
[e] 1 mol% photocatalyst loading.
[f] White LEDs instead of blue LEDs.
[g] Green LEDs instead of blue LEDs.
[h] Without photocatalyst.
[i] The reaction was performed in the dark.
[j] The reaction was performed under N_2.

Herein, we report photoredox catalytic selenylation/ring-expansion cascades via semipinacol rearrangement of alkenyl cyclobutanols. To determine optimized reaction conditions for visible-light-mediated photoredox catalytic selenylation/1,2-alkyl-migration sequences of alkenyl cyclobutanol derivatives, we choose 1-[1-(4-methoxyphenyl)vinyl] cyclobutanol (**1c**) and diphenyl diselenide (**2a**) as the model substrates. The reaction proceeded in visible-light irradiation using blue LED (5 W, λ_{max} = 455 nm) in acetonitrile with 5 mol% of photocatalyst. The reaction was conducted with various organic and metal photocatalysts (Table 1, entries 1–9), among which a ruthenium complex, Ru(bpy)$_3$Cl$_2$·6H$_2$O, afforded the optimal result (94% yield, Table 1, entry 8). An intensive screening revealed that the reaction is best conducted in acetonitrile (Table 1, entries 8 and 10–19). The reaction tolerates photocatalyst loading down to 3 mol% without a decrease in yield (Table 1, entries 20 and 21). Using white or green LEDs to replace blue LEDs led to a slight decrease in reaction yields (Table 1, entries 22 and 23). The controlled experiments showed that the reaction completely suppressed in the absence of photocatalyst or light source (Table 1, entries 24 and 25).

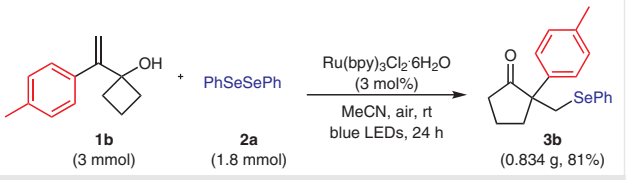
We turned our attention to study the substrate scope of 1-(1-arylvinyl)cyclobutanols **1** with diphenyl diselenide (**2a**, Scheme 2). The reactions of cyclobutanol substrates **1a–h** showed that a variety of functional groups were well tolerated, including methyl, methoxy, fluoro, and chloro; and the corresponding cyclopentanone products **3a–h** were obtained with 64–94% yields (Scheme 2). The electronic effect on the aryl of cyclobutanols **1** is important to the reactivity of this selenylation and ring-expansion sequences: cyclopentanones containing electron-donating-substituted aryl groups had higher yields than those with electron-withdrawing ones. The 2-naphthyl-substituted cyclobutanol **1i** provided the corresponding product **3i** in 72% yield. Notably, this radical selenylation/1,2-alkyl-migration reaction with alkyl-substituted alkenyl cyclobutanol gave 61% yield of corresponding product **3j** under the optimized reaction conditions. Next, dibenzyl diselenide (**2b**) was also effective in the reaction, resulting in the corresponding products **3k–o** were obtained in moderate to high yields (55–75%, Scheme 2).

The practical synthesis of β-selenated cyclic ketones has been achieved by the photoredox-catalyzed selenylation and ring-expansion cascades of 1-(1-arylvinyl)cyclobutanol derivatives with diselenides. Under the optimized reaction conditions, 1-[1-(*p*-tolyl)vinyl]cyclobutanol (**1b**) with diphenyl diselenide (**2a**) afford the desired β-selenated cyclopentanone **3b** with 81% yield (Scheme 3). It is noteworthy that this cascade can also be conducted on gram scale.

To demonstrate the feasibility of this protocol, we decided to further investigate synthetic utility of β-selenated cyclopentanones **3** through Dowd–Beckwith-type ring expansion to afford ring-enlarged cyclohexanone derivatives



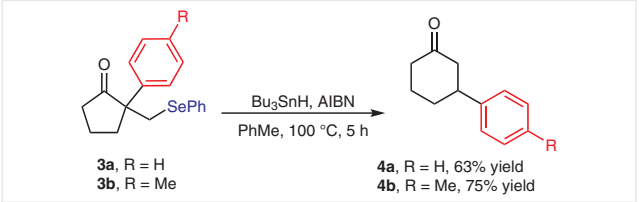
Scheme 2 Substrate scope. Reaction conditions: allylic alcohol **1** (0.1 mmol), R^2SeSeR^2 **2** (0.06 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (3 µmol), MeCN (1 mL), blue LEDs, room temperature under air. Isolated yields are given.



Scheme 3 Gram-scale synthesis of **3b**

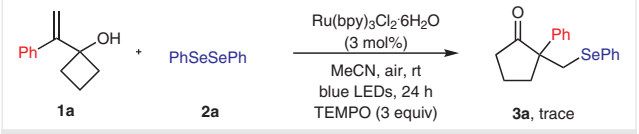
4.[10] The reaction of cyclopentanones **3** with Bu_3SnH and azobis(isobutyronitrile) (AIBN) affords high yields of ring-enlarged cyclohexanones **4** in toluene at 100 °C for 5 hours (Scheme 4).

In order to gain insight into the reaction mechanism, some control experiments were performed. When the reaction was carried out under anhydrous nitrogen, significantly

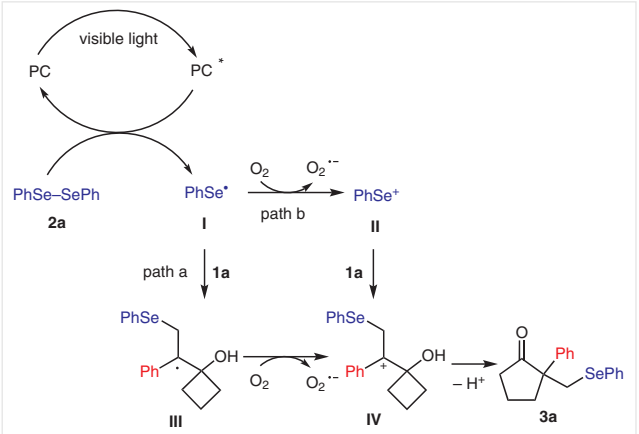


Scheme 4 Dowd–Beckwith rearrangement of **3**

reducing yield of product was obtained (Table 1, entry 26). This result indicates that the oxygen plays an important role in the reaction. In addition, when 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), as a radical inhibitor, was added into the reaction, no desired product was detected (Scheme 5). This outcome was consistent with our hypothesis that a radical pathway can be involved in this cascade reaction. We propose the reaction mechanism as shown in Scheme 6 based on the results of the experiment and related literature.[11] A photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ is converted into the excited state $[Ru(bpy)_3Cl_2·6H_2O]^*$ under visible-light irradiation. Energy-transfer process then occurs to diphenyl diselenide (**2a**) and would generate ground-state $Ru(bpy)_3Cl_2·6H_2O$ and selenium radicals **I**. After that, selenium radical **I** react with 1-(1-phenylvinyl) cyclobutanol (**1a**) to give carbon radical **III**, which is oxidized to cation intermediate **IV** by oxygen (path a). The semipinacol rearrangement through 1,2-alkyl migration of intermediate **IV** affords the cyclopentanone **3a**. Alternatively, radical **I** can also be oxidized by oxygen to selenium cation **II** which react with 1-(1-phenylvinyl) cyclobutanol (**1a**) to give corresponding cation **IV** (path b).



Scheme 5 Radical-trapping experiment



Scheme 6 Proposed reaction mechanism

In conclusion, we have developed a practical synthesis of β-selenated cyclopentanone derivatives **3** via photoredox-catalyzed selenylation and ring-expansion cascade of alkenyl cyclobutanol derivatives **1** with diselenides.[12,13] This approach is environmentally friendly by using shelf-stable diselenides as selenium radical source and visible light as source of energy. This synthetic method affords a facile way to prepare β-selenated cyclopentanone derivatives.

Funding Information

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (Grant-No. NRF-2016-R1D1A1B03933723) and Soonchunhyang University Research Fund.

Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611841.

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(12) **General Procedure for Photoredox Selenylation/Ring-Expansion Sequences of Alkenyl Cyclobutanols**

An oven-dried flask equipped with a magnetic stir bar was charged with 1-(1-arylvinyl)cyclobutanols **1** (0.1 mmol), diselenide **2** (0.06 mmol), $Ru(bpy)_3Cl_2·6H_2O$ (2.2 mg, 3 μmol), and acetonitrile (1 mL) under air. The reaction mixture was stirred for 8–25 h under irradiation of blue LEDs (5 W, 455 nm). The reaction mixture was concentrated under vacuum and purified by chromatography on silica gel (ethyl acetate/*n*-hexane = 1:20) to afford β-selenated cyclic ketone derivatives **3**.

(13) **2-Phenyl-2-[(phenylselanyl)methyl]cyclopentanone (3a)**

Yield 83%; yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.37 (m, 4 H), 7.34–7.30 (m, 2 H), 7.27–7.23 (m, 1 H), 7.21–7.18 (m, 3 H), 3.39 (d, *J* = 12 Hz, 1 H), 3.30 (d, *J* = 12.4 Hz, 1 H), 2.70–2.65 (m, 1 H), 2.40–2.20 (m, 3 H), 2.00–1.90 (m, 1 H), 1.84–1.73 (m, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 217.9, 138.4, 132.6, 131.0, 128.9, 128.7, 127.4, 126.8, 126.7, 57.8, 37.8, 37.4, 33.6, 18.4. HRMS (ESI): *m/z* calcd for $C_{18}H_{18}OSe$ $[M]^+$: 330.0523; found: 330.0527.