Tetrahedron 65 (2009) 798–801

Contents lists available at ScienceDirect

Tetrahedron

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

The reaction of mono-aryl substituted methylenecyclobutanes with diphenyl diselenide in the presence of iodosobenzene diacetate and H_2O

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ARTICLE INFO

Article history:
Received 8 October 2008
Received in revised form 18 November 2008
Accepted 19 November 2008
Available online 24 November 2008

Keywords:
Mono-aryl substituted methylenecyclobutanes
Diphenyl diselenide
Iodobenzene diacetate
Aryl-(1-phenylselanylcyclobutyl)-methanones

ABSTRACT

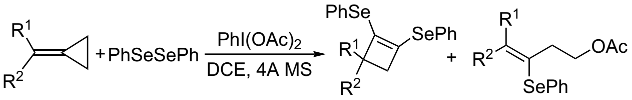
The mono-aryl substituted methylenecyclobutanes undergo an interesting reaction with diphenyl diselenide in the presence of iodosobenzene diacetate and H_2O at 40 °C in 1,2-dichloroethane to give the corresponding aryl-(1-phenylselanylcyclobutyl)methanones in moderate to good yields within 30 h. A plausible reaction mechanism has been discussed on the basis of the control and ^{18}O-labeling experiments.

1. Introduction

Organoselenium compounds have become attractive synthetic targets because of their unique chemo-, regio-, and stereo-selectivities in organic synthesis and their useful biological activities.[1] Furthermore, organoselenium compounds can also be used as precursor for the introduction of a wide variety of functional groups by selenoxide *syn*-elimination[2] and [2,3]-sigmatropic rearrangement,[3] thus avoiding protection group chemistry.[4] Previously, our group reported the reaction of *gem*-aryl disubstituted methylenecyclopropanes (MCPs) with diphenyl diselenide to give the corresponding 1,2-bis(arylselanyl)-3,3-diarylcyclobut-1-ene, a four-membered ring, along with a ring-opened product in the presence of iodosobenzene diacetate [$PhI(OAc)_2$] in moderate to good yields under mild conditions (Scheme 1)[5] as well as the reaction of vinylidenecyclopropanes with diphenyl diselenide catalyzed by iodosobenzene diacetate to produce the corresponding addition products in good yields.[6] In this paper, we wish to report that the mono-aryl substituted methylenecyclobutanes (MCBs)[7] can react with diphenyl diselenide in the presence of iodosobenzene diacetate and H_2O at 40 °C in 1,2-dichloroethane (DCE) to give the corresponding aryl-(1-phenylselanylcyclobutyl)methanones in moderate to good yields rather than the ring-expanded or ring-opened products.

2. Results and discussion

At first, we investigated the reaction of mono-aryl substituted methylenecyclobutane **1a** with diphenyl diselenide in the presence of iodosobenzene diacetate and H_2O to develop the optimal conditions.[8] The results of these experiments are summarized in Table 1. Using mono-aryl substituted MCB(**1a**, 1.0 equiv) with PhSeSePh (**2**, 1.0 equiv), $PhI(OAc)_2$ (**3**, 2.0 equiv), and H_2O (1.0 equiv) in DCE at 40 °C, **4a** was produced in 71% yield after 30 h under ambient atmosphere (Table 1, entry 1). When the temperature was changed to room temperature (20 °C), the corresponding product **4a** was produced in trace (Table 1, entry 2). Raising the reaction temperature to 60 °C afforded **4a** in 20% yield (Table 1, entry 3). Changing the ratio of **1a**/**2**/**3**/H_2O to 1:1:1:1 or 1:1.5:3:1 provided **4a** in 35% and 26% yield, respectively (Table 1, entries 4 and 5). Thus, the ratio of 1:1:2:1 for **1a**/**2**/**3**/H_2O is the best one for this reaction to give **4a** in 71% yield in DCE at 40 °C (Table 1, entries 1–5). Further examination of solvent effects revealed that DCE was the best one for this transformation (Table 1, entries 9–14). In tetrahydrofuran (THF), acetonitrile (CH_3CN), and toluene, **4a** was obtained in 47%, 35%, and 52% yield at 40 °C after 30 h, respectively



Scheme 1. Reactions of *gem*-aryl disubstituted methylenecyclopropanes with diaryl diselenide in the presence of iodosobenzene diacetate.

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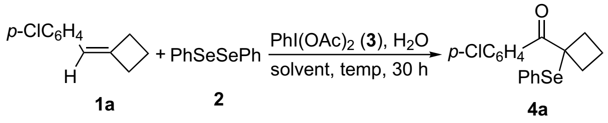
doi:10.1016/j.tet.2008.11.052

Table 1
Optimized reaction conditions of MCB **1a** with PhSeSePh in the presence of PhI(OAc)$_2$



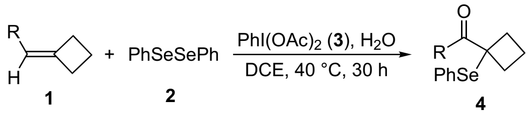
Entry[a]	**1a**/**2**/**3**/H$_2$O	Solvent	Temp (°C)	Yield[b] of **4a** (%)
1	*1:1:2:1*	*DCE*	*40*	*71*
2	1:1:2:1	DCE	rt	Trace
3	1:1:2:1	DCE	60	20
4	1:1:1:1	DCE	40	35
5	1:1.5:3:1	DCE	40	26
6	1:1:2:1	THF	40	47
7	1:1:2:1	Toluene	40	52
8	1:1:2:1	CH$_3$CN	40	35
9	1:1:2:1	CH$_2$Cl$_2$	30	25
10	1:1:2:1	Et$_2$O	30	20

[a] Reaction conditions: **1a** (0.3 mmol), **2** (0.3 mmol), **3** (0.6 mmol), solvent (2.0 mL), and H$_2$O (0.3 mmol); and the reactions were carried out at various temperatures.
[b] Isolated yields.

(Table 1, entries 6–8). In dichloromethane or ether at 30 °C, **4a** was formed in only 25% and 20% yield, respectively (Table 1, entries 9 and 10).

Under these optimal reaction conditions, we next carried out the reactions of a variety of MCBs **1** with diphenyl diselenide in the presence of H$_2$O and iodosobenzene diacetate to examine the scope and limitations. We found that the corresponding products **4** were obtained in moderate to good yields within 30 h in spite of MCBs **1** bearing electron-rich, electron-neutral, and electron-poor substituents on the benzene rings (Table 2). For mono-aryl substituted MCBs **1b**–**1f** having an electron-poor substituent at the *para* or *meta* position of benzene ring, the corresponding products **4b**–**4f** were obtained in 75%–82% yields (Table 2, entries 1–5). But for mono-aryl substituted MCB **1g** having an electron-poor substituent at the *ortho* position of benzene ring, the corresponding product **4g** was obtained in slightly lower yield (61%), presumably due to the steric reason (Table 2, entry 6). Using MCBs **1h**–**1j** bearing an electron-rich substituent on the benzene ring as the substrates afforded the corresponding products **4h**–**4j** in 62%–68% yields under the standard conditions (Table 2, entries 7–9). However, when using mono-aliphatic substituted MCB **1k** as the substrate, the reaction produced complex product mixtures without the formation of **4k**, suggesting that an aromatic group is required in this transformation (Table 2, entry 10).

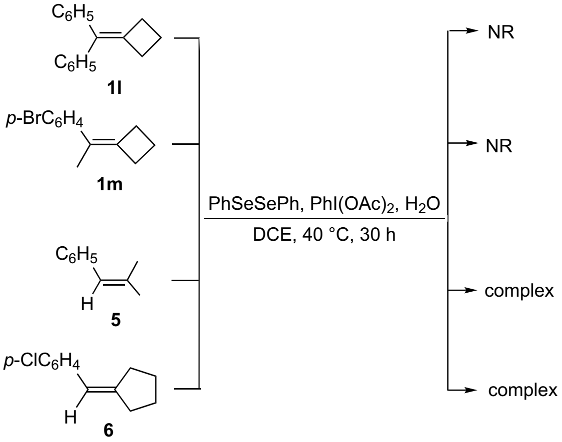
Table 2
Reaction of MCBs **1** with PhSeSePh in the presence of PhI(OAc)$_2$ and H$_2$O



Entry[a]	MCBs (R)	Yield[b] of **4** (%)
1	**1b**, (*p*-BrC$_6$H$_4$)	**4b**, 78
2	**1c**, (*p*-FC$_6$H$_4$)	**4c**, 75
3	**1d**, (*m*-ClC$_6$H$_4$)	**4d**, 78
4	**1e**, (*m*-BrC$_6$H$_4$)	**4e**, 77
5	**1f**, (*m*-NO$_2$C$_6$H$_4$)	**4f**, 82
6	**1g**, (*o*-ClC$_6$H$_4$)	**4g**, 61
7	**1h**, (*p*-MeC$_6$H$_4$)	**4h**, 68
8	**1i**, (*p*-EtC$_6$H$_4$)	**4i**, 65
9	**1j**, (*m*-CH$_3$C$_6$H$_4$)	**4j**, 62
10	**1k**, (C$_4$H$_9$)	**4k**, -

[a] Reaction conditions: **1** (0.3 mmol), **2** (0.3 mmol), **3** (0.6 mmol), DCE (2.0 mL), and H$_2$O (0.3 mmol); and the reactions were carried out at 40 °C.
[b] Isolated yields.

To further clarify the scope and limitations of this transformation, the reactions of MCBs **1l**, **1m**, alkene **5**, and methylenecyclopentane **6** with diphenyl diselenide in the presence of iodosobenzene diacetate and H$_2$O have been also examined under identical conditions. However, we found that either none of the corresponding product was formed or complex product mixtures were obtained after 30 h under the standard conditions, indicating that the four-membered cyclobutane ring, an aromatic ring, and a hydrogen atom in MCBs are essential for this reaction (Scheme 2).

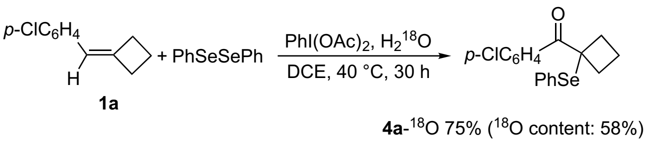


Scheme 2. Reaction of **1l**, **1m**, **5**, **6** with diphenyl diselenide in the presence of iodosobenzene diacetate and H$_2$O.

The structures of all these products reported in this paper were determined by ^{1}H, ^{13}C NMR spectroscopic data, HRMS, or microanalysis. In addition, these products can be easily transformed to the corresponding cyclobutenyl methanones by oxidation.[9]

In order to clarify the reaction mechanism, H$_2^{18}$O (^{18}O content 97.7%) was used in the reaction of **1a** with diphenyl diselenide and iodosobenzene diacetate under the standard conditions. It was found that the corresponding product **4a**-^{18}O was obtained in 75% yield along with 58% of ^{18}O content, indicating that the oxygen atom is indeed derived from water (Scheme 3). The lower ^{18}O content of **4a** (58%) is due to that the ambient moisture (H$_2$O) takes part into the reaction as well.

The reaction mechanism is outlined in Scheme 4 on the basis of the ^{18}O-labeling and control experiments. Initially, the diphenyl diselenide was oxidized by iodosobenzene diacetate to generate intermediate PhSe$^+$,[10] which was added into substrate **1** to form intermediate **A**.[5,6,10] Then, alcohol **B** is formed by the nucleophilic attack of water[11] at the position a of intermediate **A**. Further oxidization of alcohol **B** by iodosobenzene diacetate[12] affords the corresponding product **4**. A hydrogen atom at position *a* can facilitate the nucleophilic attack by water as well as the subsequent oxidation by PhI(OAc)$_2$ to give a ketone. Moreover, the four-membered cyclobutane moiety and an aromatic ring in MCBs can stabilize intermediate **A**, driving the reaction forward. Therefore, the four-membered cyclobutane, an aromatic ring, and a hydrogen atom in MCBs are essential for this reaction.



Scheme 3. Isotopic labeling experiment using H$_2^{18}$O under the reaction conditions.