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Original article

Potassium bromide or sodium chloride catalyzed acetoxyselenenylation of alkenes with diselenides and *m*CPBA

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ABSTRACT

KBr or NaCl is found to be a good catalyst in Se–Se bond cleavage of diselenides in the present of the oxidant *m*CPBA. The electrophilic addition of the *in situ* generated reactive electrophilic selenium species PhSeX (X = Br, Cl) to alkenes in AcOH provides a convenient access to 2-acetoxy-1-selenides. Compared with other catalysts, KBr or NaCl is less expensive and more environment-friendly.

1. Introduction

Organoselenium chemistry has developed as an important synthetic tool in the hands of synthetic chemists since the discovery of the selenoxide elimination in the early 1970s [1–5]. Because of their synthetic applications [6] and biological activities such as antitumor, antibacterial activities and other properties [7–14], selenium compounds have been increasing in importance in recent years. The introduction of organolseleno groups into organic molecules has been widely studied, in which the oxyselenenylation reaction is a very useful procedure for the anti-l,2-addition of an organylseleno group and an oxygen substituent (HO, RO, RCO_2) to an olefin [15–18]. In the electrophilic addition, the most common selenenylating reagents PhSeX (X = Br, Cl) are usually commercially available, or they are also prepared from oxidative cleavage of diphenyl diselenide by halogens [19]. However, due to the toxic and moisture-sensitive nature of PhSeX, nucleophilic halide anions are sometimes responsible for some undesirable processes such as addition of the halide ion and the decrease in stereoselectivity. To avoid the above drawbacks, some novel alternative reagents such as $PhSeO_2CCH_3$, $PhSeO_2CCF_3$, N-phenylselenophtalimide and N-phenylselenosuccinimide have been developed [20–23]. Since diphenyl diselenide is less expensive and less toxic, a much simpler way for formation of the electrophilic phenylselenium cation is oxidation of diphenyl diselenide with oxidants such as ammonium peroxydisulfate, *m*-nitrobenzenesulfonyl peroxide, $Pb(OAc)_4$, $Ce(NH_4)_2(NO_3)_6$ and $Cu^{2+}(Cu^{+})/O_2$ systems [24–30]. However, the metal oxidants also have toxicity and some oxidations require long reaction times or high reaction temperatures, which limit the applications. Therefore, the discovering of novel and convenient experimental conditions to carry out the cleavage of Se–Se bond is a really important target.

Recently, we have investigated the new acetoxyselenenylation of alkenes with a catalytic amount of hypervalent iodine reagent. We found that when the hypervalent iodine reagent was replaced by inorganic haloid salts combined with the oxidant *m*-chloroperbenzoic acid (*m*CPBA), the acetoxyselenenylation of alkenes was carried out smoothly and efficiently with high regioselectivity and good yields under mild conditions. In order to find cheaper and more environment-friendly catalysts, we have focused our attention on bromides and chlorides. Herein, we wish to report a novel and convenient acetoxyselenenylation of alkenes with diselenides and *m*CPBA using widely available KBr or NaCl as catalyst, and to the best of our knowledge, this electrophilic addition of the *in situ* generated reactive electrophilic selenium species PhSeX (X = Br, Cl) to alkenes has not been previously reported.

2. Experimental

A typical procedure for the catalytic acetoxyselenenylation of alkenes using KBr or NaCl as catalyst includes: In AcOH (AR, 99.5%,

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1.5 mL), alkene **1a** (0.6 mmol), diselenide **2a** (0.2 mmol), KBr (0.08 mmol) and *m*CPBA (0.4 mmol) were added successively. The suspension mixture was vigorously stirred at r.t. for 3 h. Upon completion, the reaction was quenched by addition of sat. aq $Na_2S_2O_3$ (2 mL), sat. aq Na_2CO_3 (8 mL) and H_2O (5 mL). The mixture was extracted with CH_2Cl_2 (3× 5 mL) and the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was then purified by TLC technique (4:1 (v/v) petroleum ether/ethyl acetate) to furnish 2-acetoxy-1-selenenylation compounds **3a** [31] in 90% yield.

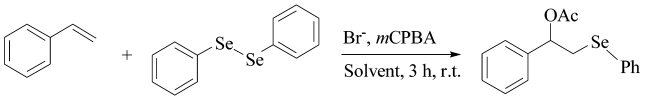
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (dd, 2H, J = 6.5, 2.9 Hz), 7.39–7.30 (m, 5H), 7.30–7.24 (m, 3H), 5.96 (dd, 1H, J = 8.0, 5.7 Hz), 3.40 (dd, 1H, J = 12.9, 8.0 Hz), 3.25 (dd, 1H, J = 12.9, 5.7 Hz), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ170.0, 139.4, 133.1, 129.8, 129.1, 128.5, 128.4, 127.2, 126.6, 75.2, 33.4, 21.0; IR (film, cm^{-1}): ν 3061, 3033, 1742, 1371, 1236, 1020, 738, 698; MS (EI, *m/z*, %): 320 (M^+, 1.8), 261 (100).

3. Results and discussion

To achieve the optimum reaction conditions, we first investigated the reaction of styrene (**1a**), diphenyl diselenide (**2a**) and oxidant *m*CPBA in the presence of a catalytic amount of KBr in acetic acid at r.t. When 0.2 equiv. of KBr was added to the mixture of 1.0 equiv. of **2a**, 1.2 equiv. of *m*CPBA and 1.5 equiv. of **1a** in acetic acid (1.5 mL) and the mixture was stirred for 3 h, the expected addition product 1-phenyl-2-(phenylselanyl)ethyl acetate **3a** was obtained in 83% yield (Table 1, entry 1). As a control experiment, the yield of **3a** was observed at only 5% in the absence of KBr (entry 2). Therefore, it was obvious that KBr played a key role in the reaction. Then, the acetoxyselenenylation of styrene with diphenyl diselenide and *m*CPBA using 0.2 equiv. of Br^- as catalyst at r.t. for 3 h was optimized (Table 1). As shown in Table 1, with 13 mmol AcOH (0.75 mL), the reaction was performed in CH_2Cl_2, CH_3CN, H_2O and EtOAc respectively; although the amount of AcOH was reduced to half, it was also greatly in excess, but the yields were not above 71%, which meant that the reaction was more proper in neat AcOH (entries 3–6). To reproduce this, the amount of AcOH was reduced to 3.0 equiv., and the reaction was carried out in CH_2Cl_2, CH_3CN and H_2O respectively, only rather poor yields were determined (entries 7–9). When NaOAc was substituted for AcOH in CH_3CN, no desired product was observed (entry 10). In neat AcOH, several kinds of bromide sources were studied. Among them, inorganic bromides usually gave appreciable results and KBr was the most effective while organic bromine compound led to low yield (entries 1, 11–15). Compared with *m*CPBA, other oxidants such as Oxone®, TBHP, $NaBO_3{\cdot}4H_2O$ and H_2O_2 usually resulted in moderate, or poor yields (entries 1, 16–19). The appropriate amount of *m*CPBA was 1.0 equiv., and when it was absent, no product was observed (entries 1, 20–23). Finally, the optimum amount of styrene was also determined, and at 1.5 equiv., it was the best choice (entries 21, 24–29).

In the similar model, we have also optimized the acetoxyselenenylation of styrene with diphenyl diselenide and *m*CPBA using 0.2 equiv. of Cl^- as catalyst in AcOH at r.t. The results showed that among several chlorides such as KCl, NaCl, NH_4Cl and CuCl, the most effective chloride was NaCl. The optimum amounts of styrene and *m*CPBA were 1.5 equiv. and 1.0 equiv., respectively, and the proper reaction time was 5 h.

Table 1
Optimization of the acetoxyselenenylation of styrene using KBr as catalyst.



Entry	Styrene (equiv.)	Oxidant (equiv.)	Br^- (equiv.)	AcOH	Solvent	Yield (%)[a]
1	1.5	*m*CPBA (1.2)	KBr (0.2)	1.5 mL	–	83
2	1.5	*m*CPBA (1.2)	–	1.5 mL	–	5
3	1.5	*m*CPBA (1.2)	KBr (0.2)	0.75 mL	CH_2Cl_2	63
4	1.5	*m*CPBA (1.2)	KBr (0.2)	0.75 mL	CH_3CN	66
5	1.5	*m*CPBA (1.2)	KBr (0.2)	0.75 mL	H_2O	35
6	1.5	*m*CPBA (1.2)	KBr (0.2)	0.75 mL	EtOAc	71
7	1.5	*m*CPBA (1.2)	KBr (0.2)	3.0 equiv.	CH_2Cl_2	10
8	1.5	*m*CPBA (1.2)	KBr (0.2)	3.0 equiv.	CH_3CN	11
9	1.5	*m*CPBA (1.2)	KBr (0.2)	3.0 equiv.	H_2O	0
10	1.5	*m*CPBA (1.2)	KBr (0.2)	3.0 equiv.	CH_3CN	0[b]
11	1.5	*m*CPBA (1.2)	NaBr (0.2)	1.5 mL	–	81
12	1.5	*m*CPBA (1.2)	$(C_4H_9)_4NBr$ (0.2)	1.5 mL	–	75
13	1.5	*m*CPBA (1.2)	CuBr (0.2)	1.5 mL	–	69
14	1.5	*m*CPBA (1.2)	NH_4Br (0.2)	1.5 mL	–	73
15	1.5	*m*CPBA (1.2)	$CH_3(CH_2)_3Br$ (0.2)	1.5 mL	–	31
16	1.5	Oxone (1.2)	KBr (0.2)	1.5 mL	–	67
17	1.5	TBHP (1.2)	KBr (0.2)	1.5 mL	–	68
18	1.5	$KBO_3{\cdot}4H_2O$ (1.2)	KBr (0.2)	1.5 mL	–	35
19	1.5	H_2O_2 (1.2)	KBr (0.2)	1.5 mL	–	61
20	1.5	*m*CPBA (1.4)	KBr (0.2)	1.5 mL	–	66
21	1.5	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	90
22	1.5	*m*CPBA (0.8)	KBr (0.2)	1.5 mL	–	85
23	1.5	–	KBr (0.2)	1.5 mL	–	0
24	1.0	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	80
25	1.1	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	80
26	1.2	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	83
27	1.3	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	84
28	1.4	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	86
29	1.8	*m*CPBA (1.0)	KBr (0.2)	1.5 mL	–	89

[a] Isolated yield.
[b] 3.0 equiv. of NaOAc was added.

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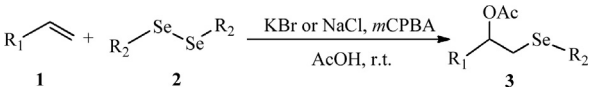
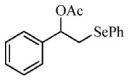
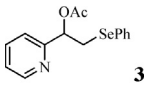
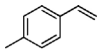
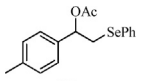
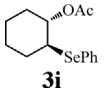
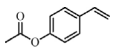
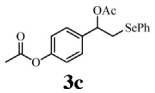
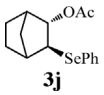
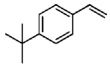
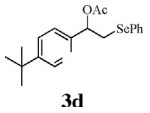
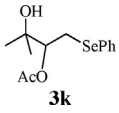
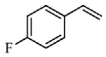
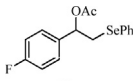
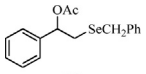
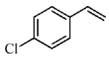
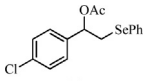
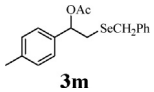
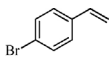
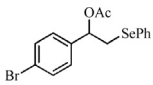
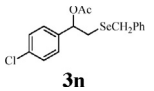
Table 2
Preparation of 2-acetoxy-1-selenenylation compounds **3**.



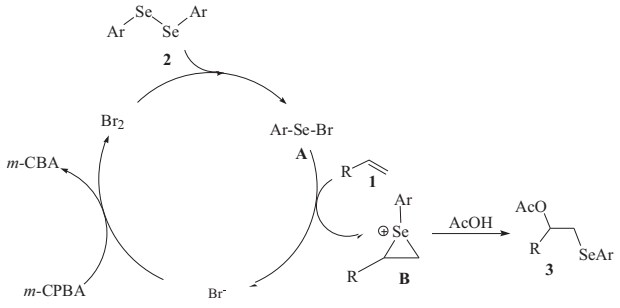
Entry	1	2	3	Yield (%)[a]	Entry	1	2	3	Yield (%)[a]
1	 **1a**	PhSeSePh **2a**	 **3a**	90 (88)[b]	8	 **1h**	**2a**	 **3h**	65 (54)[b]
2	 **1b**	**2a**	 **3b**	85 (79)[b]	9	 **1i**	**2a**	 **3i**	94 (92)[b]
3	 **1c**	**2a**	 **3c**	72 (70)[b]	10	 **1j**	**2a**	 **3j**	44
4	 **1d**	**2a**	 **3d**	81 (94)[b]	11	 **1k**	**2a**	 **3k**	62
5	 **1e**	**2a**	 **3e**	86	12	**1a**	$(PhCH_2Se)_2$ **2b**	 **3l**	71 (78)[b]
6	 **1f**	**2a**	 **3f**	84 (83)[b]	13	**1b**	**2b**	 **3m**	80 (79)[b]
7	 **1g**	**2a**	 **3g**	88 (86)[b]	14	**1f**	**2b**	 **3n**	78 (78)[b]

[a] Isolated yields from Method 1.
[b] Yields from Method 2.

Having established the optimum conditions, the acetoxyselenenylation of 1.0 equiv. of diselenides (**1**), 1.5 equiv. of alkenes (**2**) and 1.0 equiv. of *m*CPBA with 0.2 equiv. of KBr in AcOH at r.t. for 3 h (Method 1), or with 0.2 equiv. of NaCl in AcOH at r.t. for 5 h (Method 2) was carried out, a series of corresponding 2-acetoxy-1-selenenylation compounds (**3**) were obtained; the results are summarized in Table 2.

As shown in Table 2, the reaction was compatible with most of the studied alkenes except bicyclo[2.2.1]hept-2-ene (**1j**), which provided the corresponding 2-acetoxy-1-selenenylation compounds in good to excellent yields (entries 1–14). It was also determined that the groups on the benzene ring, no matter whether they were electron-donating or electron-withdrawing groups, did not influence the yield (entries 2–7, 13, 14). When treated under the same conditions, the addition to cyclohexene (**1i**) and **1j** proceeded in a *trans* fashion and the single stereoisomers were isolated with an excellent yield for **3i** (entry 9) and a poor yield for **3j** due to the steric hinderance effect of the methylene group (entry 10). Compared with **2a**, the dibenzyl diselenide (**2b**), an aliphatic diselenide, also reacted easily with alkenes, but the yields were slightly lower (entries 12–14). From Table 2, it is obvious that the yields for most products **3** were higher when KBr was used as catalyst as opposed to NaCl, so the catalytic effect of KBr is better than NaCl in the acetoxyselenenylation of alkenes.

A proposed catalytic cycle for the KBr or NaCl mediated acetoxyselenenylation of alkenes is shown in Scheme 1. Thus, KBr is first oxidized by *m*CPBA to molecular bromine, which reacts with diselenide **2** to furnish the electrophilic reagent **A**. Then, the following an electrophilic addition of the *in situ* generated active ArSeBr to alkenes results in a cyclic intermediate **B**. After a solvolysis of **B** in AcOH, the desired product 2-acetoxy-1-selenenylation compound **3** as a single isomer is obtained *via* an S_N1 mechanism for the aromatic alkenes. When aliphatic alkenes such as **1i** and **1j** are used as alkene substrates, the reaction provides the *trans* single stereoisomers *via* an S_N2 mechanism,



Scheme 1. Proposed mechanism for the catalyzed acetoxyselenenylation.

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which supports the initial formation of the cyclic selenium intermediate **B**, then the acetate anion attacks the cyclic intermediate affording the corresponding anti-l,2-addition product **3**. In order to validate our protocol, we checked our reaction in the absence of KBr, and only 5% yield of **3a** was observed (Table 1, entry 2). We also examined the reaction of styrene with *m*CPBA and KBr or NaCl in acetic acid without diphenyl diselenide, and determined the addition product of Br_2 or Cl_2 to styrene was obtained in good yield, which supports the proposed mechanism.

4. Conclusion

In summary, we have developed a novel and efficient catalytic procedure for the synthesis of 2-acetoxy-1-selenenylation compounds by the electrophilic addition of alkenes with diselenides and *m*CPBA in the presence of a catalytic amount of KBr or NaCl in AcOH at r.t. This method using widely available and less expensive KBr or NaCl as catalyst, has some advantages such as mild reaction conditions and simple procedure. Furthermore, the scope of catalytic use of inorganic haloids in acetoxyselenenylation of alkenes could be extended.

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