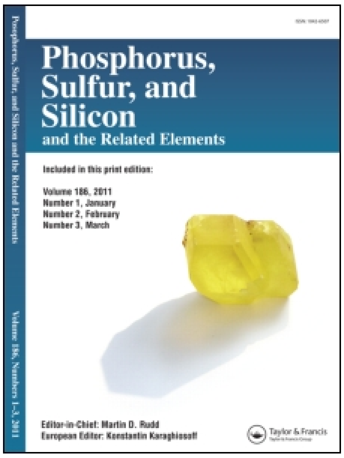

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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Yutaka Nishiyama[a]; Haruko Ohnishi[a]; Masako Iwamoto[a]; Noboru Sonoda[a]
[a] Department of Applied Chemistry, Faculty of Engineering, Kansai University, Osaka, Japan

To cite this Article Nishiyama, Yutaka , Ohnishi, Haruko , Iwamoto, Masako and Sonoda, Noboru(2010) 'A Convenient Synthetic Method of β-Bromo Alkenyl Phenyl Selenides by the Reaction of Alkynes with Diphenyl Diselenide and Copper(II) Bromide', Phosphorus, Sulfur, and Silicon and the Related Elements, 185: 5, 1021 — 1024

To link to this Article: DOI: 10.1080/10426501003772177

URL: http://dx.doi.org/10.1080/10426501003772177

Phosphorus, Sulfur, and Silicon, 185:1021–1024, 2010
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ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426501003772177

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A CONVENIENT SYNTHETIC METHOD OF β-BROMO ALKENYL PHENYL SELENIDES BY THE REACTION OF ALKYNES WITH DIPHENYL DISELENIDE AND COPPER(II) BROMIDE

Yutaka Nishiyama, Haruko Ohnishi, Masako Iwamoto, and Noboru Sonoda
Department of Applied Chemistry, Faculty of Engineering, Kansai University, Osaka, Japan

When alkynes were allowed to react with diphenyl diselenide in the presence of copper(II) bromide, bromophenylselenation of the carbon–carbon triple bond smoothly proceeded to give the corresponding β-bromo alkenyl phenyl selenides in moderate to good yields. Similarly, chlorophenylselenation of alkynes occurred by the use of copper(II) chloride as a copper salt giving β-chloro alkenyl phenyl selenides in good yields.

Keywords Alkyne; copper(II) bromide; diphenyl diselenide

INTRODUCTION

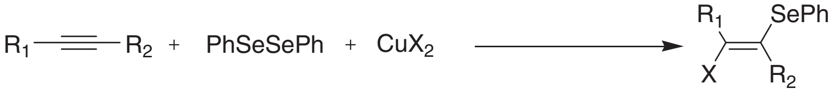
β-Halo alkenyl phenyl selenides such as β-chloro and β-bromo alkenyl phenyl selenides have been useful intermediates in organic synthesis.[1] Then, there have been some reports on the synthesis of β-halo alkenyl phenylselenides.[2] The addition of phenyselenenyl halides, such as phenylselenyl chloride (PhSeCl) and bromide (PhSeBr), to the carbon–carbon triple bond of alkynes is the one of the direct synthetic methods of β-halo alkenyl phenyl selenides (**2a–e**, **2g**, and **2h**). However, there are some disadvantages to the preparation and utilization of phenylselenyl halides: (i) low humidity conditions, (ii) the handling of chlorine and bromine, (iii) the use of phenylselnocyanate, and (iv) the formation of phenylselnenyl trihalides as byproducts.[3] As an approach to solve these problems, we investigated another generation method of phenyselenenyl halides and found that the treatment of dipehnyl diselenide copper(II) bromide and chloride is a useful in situ generation method of phenyselenenyl halides (Scheme 1).

Received 29 November 2008; accepted 1 January 2009.

Dedicated to Professor Naomichi Furukawa on the occasion of his 70th birthday.

This research was supported by a Grant-in-Aid for Science Research (No.18550100), Research and Development Organization of Industry-University Cooperation from the Ministry of Education, Culture, Sports, Science and Technology of Japan and Kansai University Grant-in-Aid for progress of research in graduate course, 2007.

Address correspondence to Yutaka Nishiyama, Department of Applied Chemistry, Faculty of Engineering, Kansai University, Suita, Osaka 564-8680, Japan. E-mail: nishiya@kansai-u.ac.jp



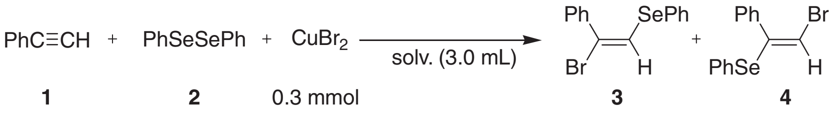
Scheme 1

RESULTS AND DISCUSSION

When phenylacetylene (**1**) was allowed to react with diphenyl diselenide (**2**) in the presence of copper(II) bromide in toluene solution at 25°C for 3 h under an atmosphere of air, bromophenylselenation of the carbon–carbon triple bond of **1** smoothly proceeded to give (*E*)-2-bromo-2-phenyl-1-phenylselenoethylene (**3**), which was an *anti*-addition product, in 88% yield along with the formation of small amount of regioisomers, 2-bromo-1-phenyl-1-phenyselenoethylene (**4**) (5%) (see entry 1 in Table I). To know the optimized reaction conditions, **1** was treated with **2** and copper(II) bromide under various reaction conditions, and these results were shown in Table I. Even when hexane, acetic acid, and acetonitrile were used as solvents, the addition products were formed in good yields; however, regioselectivity of the products was slightly decreased (Table I, entries 2–4). At lower reaction temperature (0°C), the yields of bromophenylselenation products were improved by the extending of the reaction time (15 h) (Table I, entries 5 and 6). The yield of **4** was also affected by the ratios of copper(II) bromide used (Table I, entries 8 and 9). The results have shown that both bromine atoms on copper(II) bromide were not introduced on the products. In contrast, it is interesting to note that both phenylseleno groups on diphenyl diselenide were efficiently utilized in the reaction (Table I, entry 9).[4,5]

A variety of alkynes were allowed to react with diphenyl diselenide and copper (II) bromide, and these results are shown in Table II.[6] The treatment of terminal alkyne, which was substituted with an alkyl group, gave the corresponding bromophenylselenated

Table I Reaction of phenylacetylene with diphenyl diselenide in the presence of $CuBr_2$

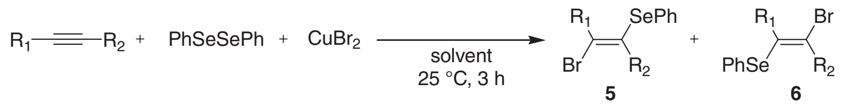


Entry	**1** (mmol)	**2** (mmol)	Solv.	Temp. (°C)	Time (h)	Yield (%)[a]	
						3	**4**
1	0.3	0.3	$C_6H_5CH_3$	25	3	88	5
2	0.3	0.3	C_6H_{14}	25	3	68	13
3	0.3	0.3	CH_3COOH	25	3	73	18
4	0.3	0.3	CH_3CN	25	3	60	27
5	0.3	0.3	$C_6H_5CH_3$	0	3	13	3
6	0.3	0.3	$C_6H_5CH_3$	0	15	62	7
7	0.3	0.3	$C_6H_5CH_3$	25	1	37	3
8	0.6	0.3	$C_6H_5CH_3$	25	3	35	11
9[b]	0.6	0.3	$C_6H_5CH_3$	25	3	75	24

[a] GC yield based on **1**.

[b] $CuBr_2$ (0.6 mmol) was used.

Table II Reaction of alkynes with diphenyl diselenide and $CuBr_2$[a]



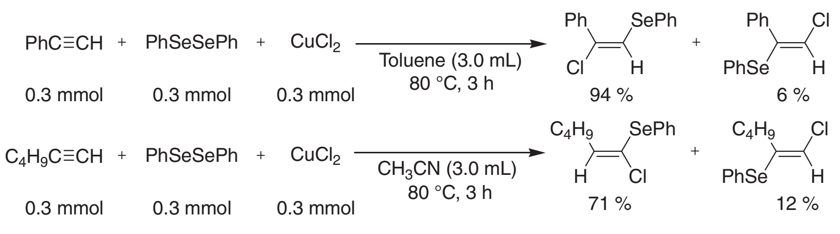
Entry	R_1	R_2	Solvent	Yield (%)[b] **5**	Yield (%)[b] **6**
1	Ph	H	$C_6H_5CH_3$	88	5
2	H	n-C_4H_9	CH_3CN	89	5
3	Ph	C_2H_5	$C_6H_5CH_3$	84	3
4	H	$COCH_3$	CH_3COOH	89	0
5	H	$COOC_2H_5$	CH_3COOH	72	0
6	c-C_6H_9	H	$C_6H_5CH_3$	72	22

[a] Reaction conditions: alkyne (0.6 mmol), PhSeSePh (0.3 mmol), $CuBr_2$ (0.6 mmol) and solvent (3.0 mL) at 25°C for 3 h.

[b] GC yield based on alkyne.

products, (E)-1-bromo-2-phenylseleno-1-hexene, in 89% yield with highly regioselectivity (Table II, entry 2). When alkynes bearing electron-withdrawing groups, such as but-3-yn-2-one and ethyl propiolate, were allowed to react with diphenyl diselenide in the presence of copper(II) bromide, β-bromo alkenyl phenyl selenides, in which the phenylseleno group was introduced on the α-carbon of the starting materials, were formed in 89% and 72% yields, respectively (Table II, entries 4 and 5).[7] The use of unsymmetrical 1,2-disubstituted alkyne also gave the addition products in 84% yield (Table II, entry 3). In the case of 1-ethynyl-cyclohex-1-ene, which has both carbon–carbon double and triple bonds, bromophenylselenation of the carbon–carbon triple bond occurred with selectivity to afford the mixture of 2-bromo-2-cyclohexenyl-1-phenylseleno ethylene (72%) and 2-bromo-1-cyclohexenyl-1-phenylseleno ethylene (22%) (Table II, entry 6).

Next, to investigate the application of the reaction, we examined the chlorophenylselenation of alkynes with diphenyl diselenide and copper chloride. When the reaction was carried out at 80°C, chlorophenylselenation of alkynes proceeded smoothly to give the corresponding β-chloro alkenyl phenyl selenides in good yields (Scheme 2).



Scheme 2

We cannot explain the reaction pathway in detail, but it was suggested that the formation of episelenium ion (**7**) was the first step in the reaction. The halogen ion (Br^- or Cl^-) attacked the **7** from the less hindered side to form *anti*-addition product. But in the case of 1-hexyne, the ring opening of **7** predominantly proceeded to form the vinyl cation intermediate (**8**). Then **8** reacted with the bromine anion to give the corresponding addition product. Therefore, the stability of **8** played an important role on the regioselectivity.

We find a new synthetic method of β-bromo and β-chloro alkenyl phenyl selenides by the reaction of alkynes with diphenyl diselenide and copper(II) bromide and chloride. The halogen atom on the copper (II) halide and both phenylseleno groups on the diphenyl diselenide are efficiently used in the reaction. The application of the reaction in organic synthesis is now progress.

EXPERIMENTAL

A toluene (3.0 mL) solution of diphenyl diselenide (0.3 mmol), alkyne (0.6 mmol), and $CuBr_2$ (0.6 mmol) was stirred at 25°C for 3 h under air. After the reaction, the resulting solution was extracted with ether (10 mL × 3). The organic layer was dried over $MgSO_4$ and filtered. The organic solvent was removed under reduced pressure. Purification of the residue by HPLC afforded the corresponding β-bromo alkenyl phenyl selenide.

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4. Recently, Taniguchi have reported the copper-catalyzed synthesis of β-halo alkenyl sulfides by the addition of disulfides to alkynes.[5] Then, we examined the reaction of phenylacetylene with diphenyl diselenide in the presence of CuBr; however, the reaction did not occur and starting materials were recovered.
5. N. Taniguchi, *Synlett*, 849 (2008).
6. Tomoda et al. have shown that the treatment of alkyne with phenylselenocyanate and copper (II) halides in the presence of triethylamine gave the corresponding (*E*)-β-halo alkenyl phenyl selenides. In this method, they have described that halogen atom came from the copper(II) halide [**2f**].
7. It was reported that the treatment of alkynes bearing electron-withdrawing groups with phenylselenyl halides (PhSeX: X = Cl and Br) gave β-halo alkenyl phenyl selenides, in which the phenylseleno group was introduced on the α-carbon of the starting materials [**2b**].