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Reactions of Alkynylselenonium Salts with Tetrabutylammonium Halides: Apparent Umpolung of Alkynyl Moiety

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Abstract

The reactions of alkynylselenonium salts with *n*-Bu_4NX (X = I, Br, Cl) in CH_2Cl_2 gave 1-halo-1-alkynes or phenacyl halide derivatives and selenide, while the reaction with F^- afforded a terminal alkyne and a selenoxide. Seemingly, the selenonium salts acted as alkynyl cations in the former case and as alkynyl anions in the latter case.

Keywords: selenonium ions; alkynyl halides; ammonium salts; hypervalent elements; coupling reactions

1-Halo-1-alkynes are useful intermediates in organic synthesis [1] and are usually prepared by the substitution reaction of alkynylmetallics with the halogenation reagents [2]. Recently, it has been shown that alkynyliodinanes (or iodonium salts) reacted with various nucleophiles to give the corresponding alkynes [3]. However, there has been known only one report on the formation of an alkynyl chloride by decomposition of phenyl(β-phenylethynyl)iodonium chloride [4].

We previously reported that diphenyl(phenylethynyl)selenonium triflate **1a** reacted with sodium benzenesulfinate in alcohols to give exclusively (*Z*)-β-alkoxy-α-phenylsulfonylstyrenes via an addition-elimination process [5] different from the reactions of the iodinanes via alkylidene carbenes [6, 7]. This paper describes the reactions of alkynylselenonium salts with tetrabutylammonium halides, affording alkynyl halides or terminal alkynes via the σ-selenuranes.

Nucleophilic alkynylic substitution of the alkynylselenonium salt **1** with tetrabutylammonium halides was carried out (Scheme 1). To a solution of the selenonium salt **1a** [5] in CH_2Cl_2, 3 equivalents of *n*-Bu_4NI were added. The mixture was stirred at room temperature for 1 d under Ar and extracted with ether. The solvent was evaporated under

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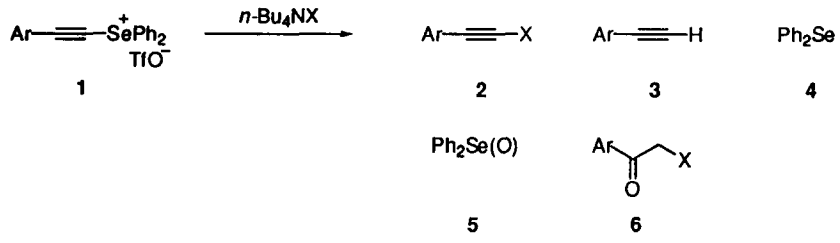


1 2 3 4 5 6

Scheme 1

reduced pressure and purification by preparative TLC afforded the alkynyl iodide **2a** in 74% yield (Table 1). *n*-Bu_4NBr and *n*-Bu_4NCl were less reactive than *n*-Bu_4NI. The alkynyl bromide **2b** was obtained in only 36% yield because of its volatility, but the alkynyl halides **2c, 2d** with higher boiling points were isolated in better yields than **2a**, **2b**, respectively (entries 6 and 7). Alkynyl chloride was not obtained from the reaction of **1a** or **1b** [1] with *n*-Bu_4NCl but 2-chloroacetophenone derivatives **6c** and **6d** were given in low yields. In contrast, the reaction with *n*-Bu_4NF in CH_2Cl_2 gave diphenyl selenoxide **5** in good yield. The counterpart, phenylacetylene **3a**, was analyzed directly by HPLC (DEVELOSIL 60-5, hexane, 1 ml/min) of the reaction mixture in 88% yield (entry 5). In entry 9, the reaction of **1b** with *n*-Bu_4NF afforded *p*-chlorophenylacetylene **3b** in 56% yield. Diphenyl selenide **4** was not converted into **5** by treatment with *n*-Bu_4NF.

Table 1

Reactions of Selenonium Salts **1** with Tetrabutylammonium Halides in Aprotic Solvents.

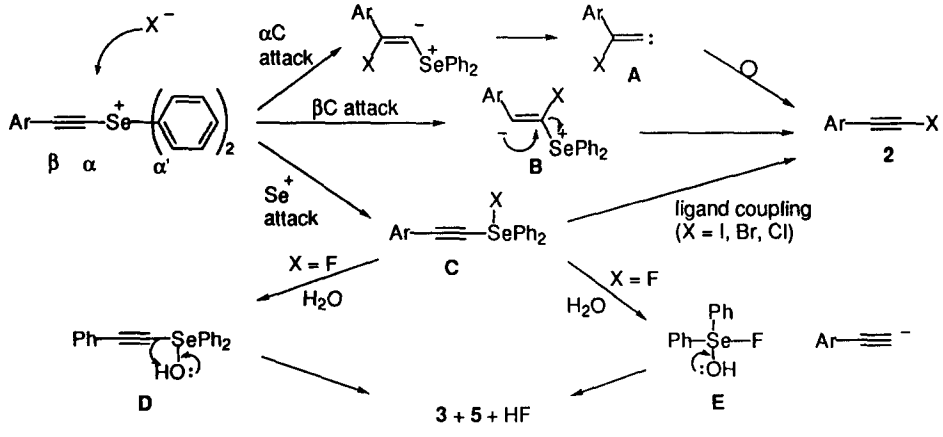
Entry	1	*n*-Bu_4NX	Solvent	Time	Products (%Yield) [a]		
1	**1a** : Ar=Ph	*n*-Bu_4NI	CH_2Cl_2	1 d	**2a** : Ar=Ph, X=I (74)	**4** (82)	
2 [b]	**1a**	*n*-Bu_4NI	CH_2Cl_2	1 d	**2a** (59)	**4** (77)	**6a** : Ar=Ph, X=I (2)
3	**1a**	*n*-Bu_4NBr	CH_2Cl_2	3 d	**2b** : Ar=Ph, X=Br (36)	**4** (73)	**6b** : Ar=Ph, X=Br (8)
4	**1a**	*n*-Bu_4NCl	CH_2Cl_2	3 d	**4** (34)	**6c** : Ar=Ph, X=Cl (23)	
5	**1a**	*n*-Bu_4NF	CH_2Cl_2	1 d	**3a** : Ar=Ph (88) [c]	**4** (10) [c]	**5** (62)
6	**1b** : Ar=*p*-ClC_6H_4	*n*-Bu_4NI	CH_2Cl_2	1 d	**2c** : Ar=*p*-Cl C_6H_4, X=I (84)	**4** (82)	
7	**1b**	*n*-Bu_4NBr	CH_2Cl_2	3 d	**2d** : Ar=*p*-Cl C_6H_4, X=Br (49)	**4** (73)	
8	**1b**	*n*-Bu_4NCl	CH_2Cl_2	3 d	**4** (36)	**6d** : Ar=*p*-Cl C_6H_4, X=Cl (21)	
9	**1b**	*n*-Bu_4NF	CH_2Cl_2	1 d	**3b** : Ar=*p*-Cl C_6H_4 (56)	**4** (9)	**5** (60)
10	**1a**	*n*-Bu_4NI	CH_3CN	1 d	**2a** (66)	**4** (69)	
11	**1a**	*n*-Bu_4NBr	CH_3CN	3 d	**2b** (20)	**4** (43)	
12	**1a**	*n*-Bu_4NCl	CH_3CN	3 d	**4** (32)	**6c** (22)	
13	**1a**	*n*-Bu_4NF	CH_3CN	1 d	**3a** (93) [c]	**4** (2) [c]	**5** (72)

[a] Isolated yield. [b] A drop of H_2O was Added. [c] Determined by HPLC.

[1] Selenonium salt **1b** was prepared from trimethyl(*p*-chlorophenylethynyl)silane and diphenyl selenoxide **5** with trifluoromethanesulfonic anhydride in a similar manner to that for **1a**.

On the other hand, the results of the reactions in CH_3CN, which is a kind of dipolar aprotic solvent, were similar to those in nonpolar aprotic CH_2Cl_2. Irrespective of the polarity of the solvents, the rate of substitutions of **1** with *n*-Bu_4NX decreased in order of $I^- > Br^- > Cl^-$, while *n*-Bu_4NF did not bring about the substitution and afforded terminal alkynes **3** together with selenoxide **5** (entry 10-13). In order to clarify the origin of the oxygen atom in the selenoxide **5**, a mixture of **1a** and *n*-Bu_4NF was stirred in CH_3CN containing $H_2{}^{18}O$, and $Ph_2Se(^{18}O)$ was obtained in good yield. This result showed that a trace amount of water in *n*-Bu_4NF was responsible for the oxygen atom in the selenoxide **5**.

Three possible reaction pathways for formation of alkynyl halides **2** can be considered: 1,2-migration via an alkylidene carbene intermediate **A** [6], an addition-elimination route via a betaine **B** [8], and a ligand coupling on a selenurane intermediate **C** [9]. If these reactions are carried out in a nucleophilic solvent such as an alcohol, the solvent would react with the intermediate **A** or **B** [5, 7, 10]. Thus, we examined the reaction of **1a** with *n*-Bu_4NX in methanol (Table 2).



Scheme 2

Table 2

Reactions of Selenonium Salt **1a** with Tetrabutylammonium Halides in MeOH.

Entry	*n*-Bu_4NX	Time	Products (%Yield)		
1	*n*-Bu_4NI	1 d	**2a** (53)	**4** (62)	
2	*n*-Bu_4NBr	3 d	**2b** (5)	**4** (39)	**6b** (18)
3	*n*-Bu_4NCl	3 d		**4** (2)	
4	*n*-Bu_4NF	1 d		**4** (17)	**5** (0)

The reactions in MeOH were slower than those in CH_2Cl_2. Especially, *n*-Bu_4NCl hardly reacted and the reaction with *n*-Bu_4NF did not afford selenoxide because the halide ion was solvated by MeOH. In any case, the solvent-incorporated products were not obtained. The result indicates that the reaction pathway via the selenurane intermediate **C** is the most feasible. A halide ion initially attacks the selenium atom to form selenurane intermediate **C**, and the subsequent ligand coupling reaction between the alkynyl group and the halogen atom gives the alkynyl halide **2** and selenide **4**. The fluorine intermediate **C** (X=F) would be more susceptible to hydrolysis than the other haloselenuranes or undergo hydrolysis because of the slower ligand coupling than the others. Water attacks the selenurane **C** (X=F) and the resulting hydroxyselenurane **D** decomposes to the terminal alkyne **3** and selenoxide **5**. Another possible pathway contains the nucleophilic attack of water at the selenium atom of **C** (X=F). The reaction causes the ligand exchange to form phenylacetylide and selenurane **E**, which finally changes into diphenyl selenoxide **5** and hydrogen fluoride. Thus, the alkynyl moiety of **1** acted as the alkynyl cation or the acetylide ion depending upon the kind of halide ion and we could find apparent umpolung of the alkynyl moiety.

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