Pergamon

Tetrahedron Letters 40 (1999) 931–934

TETRAHEDRON LETTERS

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

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Received 26 October 1998; revised 17 November 1998; accepted 20 November 1998

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.

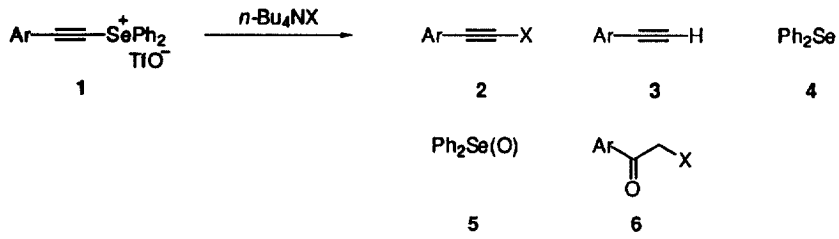
Keywords: selenonium ions; alkynyl halides; ammonium salts; hypervalent elements; coupling reactions

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

0040-4039/99/$ - see front matter
PII: S0040-4039(98)02492-7



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.

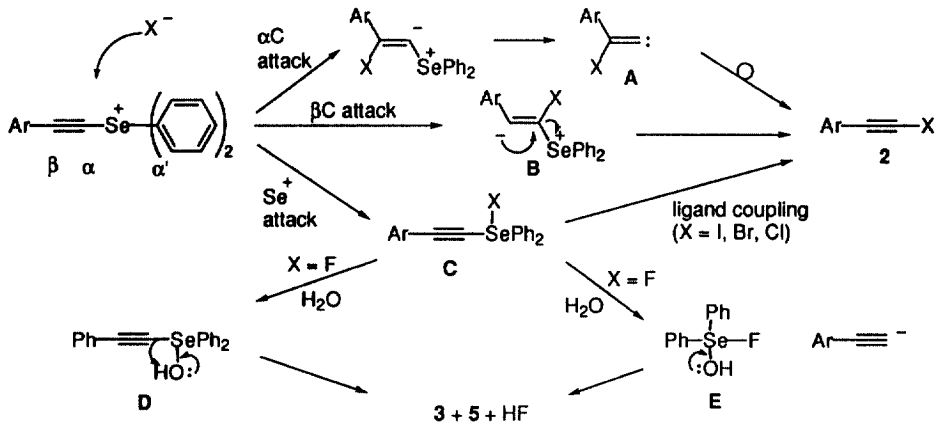
Entry	1	*n*-Bu_4NX	Solvent	Time	Products (%Yield) [a]		
1	**1a** : Ar=Ph	*n*-Bu_4NI	CH_2Cl_2	1 d	**2a** : Ar=Ph, X=I (74)	**4** (82)	
2 [b]	**1a**	*n*-Bu_4NI	CH_2Cl_2	1 d	**2a** (59)	**4** (77)	**6a** : Ar=Ph, X=I (2)
3	**1a**	*n*-Bu_4NBr	CH_2Cl_2	3 d	**2b** : Ar=Ph, X=Br (36)	**4** (73)	**6b** : Ar=Ph, 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.

Acknowledgment.

The authors thank Central Glass Co., Ltd, (Tokyo, Japan) for a generous gift of trifluoromethanesulfonic anhydride.

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