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The First Example of Formation of the Benzyne Intermediate from the Reactions of Selenonium Salts with Phenyllithium

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Abstract

The reaction of diphenyl(phenylethynyl)selenonium salt **1a** with 1.0 equiv. of phenyllithium afforded 1,4-diphenylbutadiyne **5** and 1-(*o*-biphenylyl)-2-phenylethyne **7** in 25% and 15% yields, respectively. The latter product **7** was formed via the benzyne intermediate.

Keywords: selenonium ions; hypervalent elements; arynes; coupling reactions

Reactions of triarylsulfonium salts with aryllithiums have been widely studied [1]. Recently, many hypervalent chalcogen compounds, of which the chalcogen atom formally possesses more than eight valence electrons, have been synthesized [2]. Among them, sulfuranes and selenuranes with only carbon ligands can be prepared from the reactions of triarylsulfonium and selenonium salts with aryllithiums [3]. Khim and Oae reported that the reactions of tritolylsulfonium bromide with phenyllithium proceeded via the aryne formation as well as the nucleophilic attack of the phenyl anion on the sulfur [4]. However, there has been no report that aryne intermediates are generated from the reactions of selenonium salts with nucleophiles. In the course of our research on diphenylalkynylselenonium salts [5], we found, and report here, the first example of the benzyne formation from the reaction of diphenylalkynylselenonium salt with phenyllithium.

We examined the reaction of diphenyl(phenylethynyl)selenonium triflate **1a** with phenyllithium in THF (Scheme 1, Table 1). In a typical procedure, a solution of phenyllithium in cyclohexane-Et_2O was added to a stirred solution of **1a** (290 mg, 0.6 mmol) in THF (10 ml) at room temperature. The mixture was stirred for 3 h at ambient temperature, quenched by addition of water (5 ml), and extracted with hexane. Yields of the products were analyzed by HPLC (DEVELOSIL 60-5, hexane, 1.0 ml/min). These reactions revealed four interesting results: (1) 1,4-diphenylbutadiyne **5** was obtained in all cases; (2) 1-

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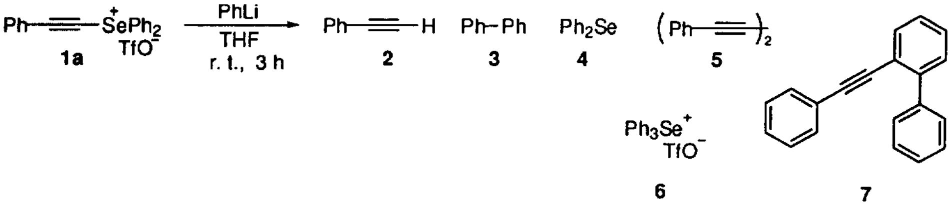


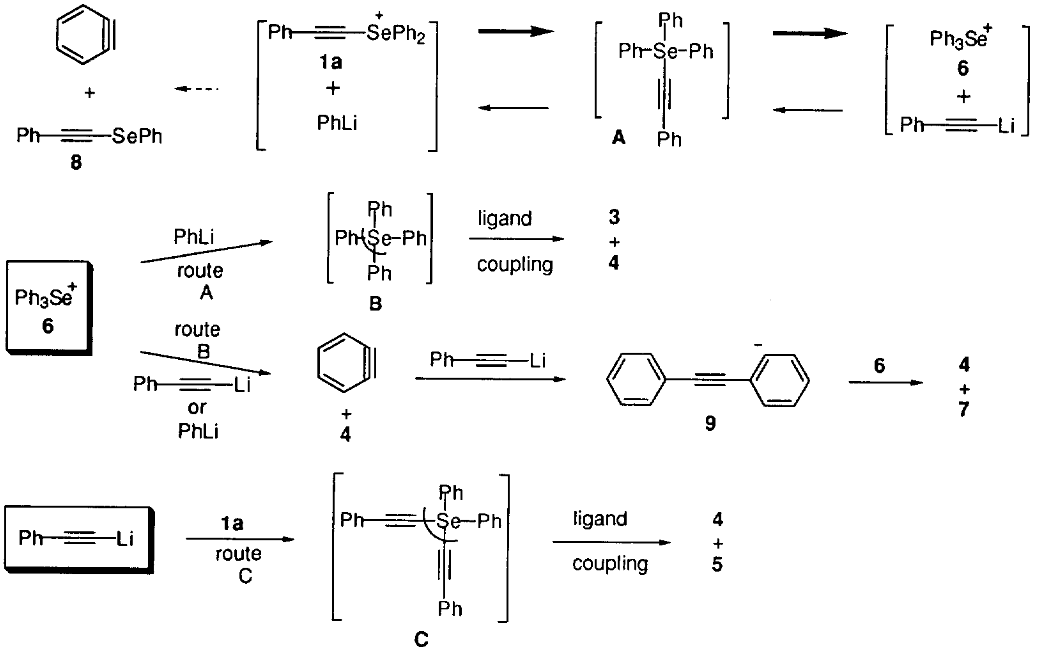
Scheme 1

Table 1
Reactions of Selenonium Salt **1a** with Phenyllithium.

Entry	Phenyllithium	Products (% yield)[a]					
1	0.5 equiv.	**2** (10)		**4** (56)	**5** (34)	**6**[b] (18)	
2	1.0 equiv.	**2** (14)	**3** (20)	**4** (92)	**5** (25)		**7** (15)
3	2.0 equiv.	**2** (38)	**3**[c]	**4** (99)	**5** (13)		**7** (7)
4	3.0 equiv.	**2** (51)	**3**[c]	**4** (104)	**5** (2)		**7** (5)
5	5.0 equiv.	**2** (60)	**3**[c]	**4** (100)	**5** (2)		**7** (4)

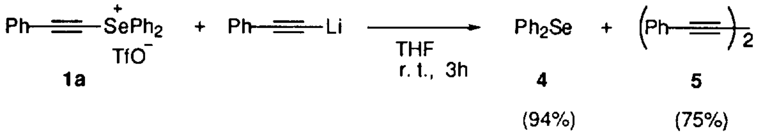
[a] Determined by HPLC. [b] Isolated yield. [c] Biphenyl **3** was also obtained from the coupling of phenyllithiums and, therefore, the yield of **3** is meaningless.

(*o*-biphenylyl)-2-phenylethyne **7** [1] was given in low yields (entries 2-5); (3) when 0.5 equivalent of phenyllithium was used, the starting material **1a** was not recovered but triphenylselenonium triflate **6** was obtained (entry 1); (4) when the quantity of phenyllithium was increased, the yields of diyne **5** and alkyne **7** were decreased and phenylethyne **2** was increased.



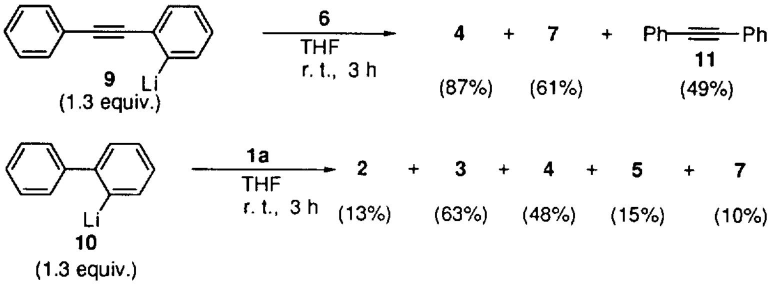
Scheme 2

On the basis of these results, we propose a plausible mechanism as shown in Scheme 2. Phenyllithium as a nucleophile initially attacks the selenium atom to form selenurane intermediate **A**, but this intermediate would not cause ligand coupling reaction because the ligand coupling products such as 1-phenyl-2-(phenylseleno)ethyne **8** [6] and 1,2-diphenylethyne were not obtained. The nucleophilic attack of phenyllithium at the selenium of **1a** gives rise to ligand exchange to form triphenylselenonium salt **6** and phenylethynyllithium concertedly (or via the selenurane **A**). The resulting selenonium salt **6** reacts with phenyllithium to generate the selenurane intermediate **B**, which subsequently brings about the ligand coupling reaction [7] to produce **3** and **4** (route A). On the other hand, the eliminated phenylethynyllithium reacts with **1a** to form selenurane intermediate **C**, whose two ethynyl ligands couple to afford **4** and **5** (route C). The route C was experimentally supported by the result that the reaction of **1a** with phenylethynyllithium gave **4** (94%) and **5** (75%) (Scheme 3).



Scheme 3

1-(*o*-Biphenylyl)-2-phenylethyne **7** would be produced via benzyne. If phenyllithium abstracts the *o*-proton of the phenyl group of selenonium salt **1a**, benzyne and selenide **8** should be obtained. However, the selenide **8** was not obtained (Table 1). Therefore, benzyne would be generated from the reaction of **6** with phenyllithium or phenylethynyllithium. Benzyne reacts with phenylethynyllithium to form an ethynylphenyllithium **9**. The reaction of **9** with selenonium salt **6** gives selenide **4** and alkyne **7**. In order to confirm these pathways, we conducted the reactions of selenonium salt **6** with carbanion **9** and selenonium salt **1a** with carbanion **10** in THF at room temperature for 3 h (Scheme 4).



Scheme 4

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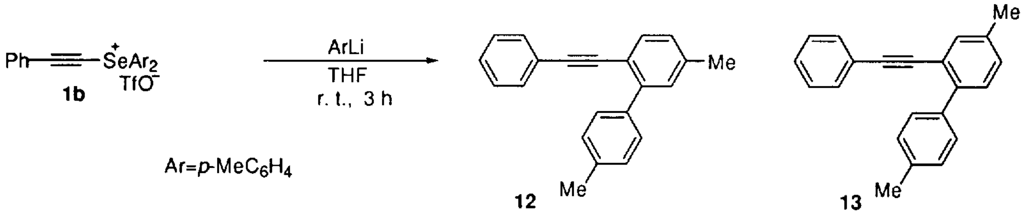
[1] 1-(*o*-Biphenylyl)-2-phenylethyne **7** was prepared by an alternative method: A solution of 2-(2-phenylethenyl)-*o*-biphenyl (400 mg, 1.56 mmol) [8] in CH_2Cl_2 (20 ml) at room temperature under Ar was treated with bromine (0.1 ml, 1.94 mmol) for 2 h. The reaction mixture was quenched with a saturated $Na_2S_2O_3$ solution. After the usual workup, 221 mg (46%) of 2-(1,2-dibromo-2-phenylethyl)-*o*-biphenyl was obtained. To a stirred solution of this compound (75 mg, 0.18 mmol) in *t*-BuOH (5 ml), 90% *t*-BuOK (60 mg, 0.48 mmol) was added at room temperature and then the mixture was refluxed for 6 h. After the usual workup, the residue was purified by preparative TLC on silica gel eluting with hexane to give 45 mg (98%) of 1-(*o*-biphenylyl)-2-phenylethyne **7**.

The former reaction afforded ligand coupling products **4** (87%) and **7** (61%), while the latter gave some products together with **7** (10%). This result showed that alkyne **7** would be mainly produced by the reaction of **6** with **9**. When more than 2 equivalents of phenyllithium were used, excess phenyllithium, which is more nucleophilic than acetylide, reacted with benzyne and selenonium salt **6** faster than phenylethynyllithium, and consequently the yield of **7** was decreased.

In order to confirm the formation of an aryne we planned to conduct the reaction of di-*p*-tolyl(phenylethynyl)selenonium triflate **1b** [9] with *p*-tolyllithium in THF (Scheme 5). If an unsymmetrical aryne, 3-methylbenzyne is formed, two types of alkynylbiphenyls would be produced from the aryne. The products were separated by preparative TLC to give a mixture of alkynylbiphenyls **12** and **13** in 13% yield (**12**:**13**=3:2) as we had expected. This result strongly supported the formation of an aryne.



Scheme 5

In summary, we have shown that the first step of the reaction of **1a** with phenyllithium quickly caused the ligand exchange reaction to form selenonium salt **6** and phenylethynyllithium, followed by the evolution of benzyne. This is the first example of the formation of benzyne in the reaction of selenonium salts with nucleophiles.

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