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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 1,4diphenylbutadiyne **5** and 1-(o-biphenylyl)-2-phenylethyne **7** in 25% and 15% yields, respectively. The latter product **7** was formed via the benzyne intermediate. © 1999 Elsevier Science Ltd. All rights reserved.

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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-Et₂O 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-



Scheme 1

 Table 1

 Reactions of Selenonium Salt 1a with Phenyllithium.

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

$$Ph = SePh_{2} + Ph = Li \qquad Ph_{2}Se + (Ph =)_{2}$$

$$THF \qquad THF \qquad r. t., 3h \qquad 4 \qquad 5$$

$$(94\%) \qquad (75\%)$$
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).



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 CH₂Cl₂ (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 Na₂S₂O₃ 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 cluting 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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