

The diorgano dichalcogenides addition to benzyne under mild conditions

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Abstract—The reaction between diorgano dichalcogenides and *o*-(trimethylsilyl)phenyl triflate in the presence of CsF at room temperature produced *o*-bis(organochalcogenide)benzenes in moderate to good yields.

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Benzyne is an important reactive intermediate in organic chemistry, which has found application in mechanistic studies, total synthesis, and synthesis of functional materials.¹ Accordingly, benzyne has been generated by using several organic precursors.¹ However, we stand out *o*-(trimethylsilyl)phenyl triflate as a commercially available and bench stable reagent to generate benzyne under very mild reaction conditions.² In line with this, silylaryl triflates have emerged as outstanding reagents for generating arynes which have recently found use in a number of insertion reactions into σ bonds.³

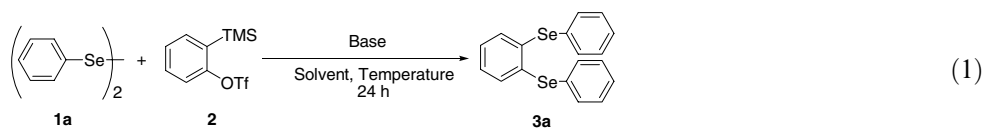
Although arynes generated under harsh conditions have reacted with diaryl dichalcogenides to give *o*-bis(aryl-

chalcogenide)benzenes,^{4,5} the published procedures are not general, and fail or give very low yields, when diphenyl dichalcogenides or electron-poor diaryl dichalcogenides are employed.^{4,5}

In the attempt to establish a more general procedure involving mild conditions for the insertion of benzyne into diorgano dichalcogenides, we decided to explore the reaction between dichalcogenides and *o*-(trimethylsilyl)phenyl triflate in the presence of a fluoride ion source.^{2,3}

Initially, allowing diphenyl diselenide (**1a**) to react with 1.5 equiv of *o*-(trimethylsilyl)phenyl triflate (**2**) and

Table 1. Optimization of the synthesis of *o*-bis(phenylselenide)benzene (**3a**) (Eq. 1)^a



Entry	2 (equiv)	Base (equiv)	Solvent	Temp (°C)	% isolated yield
1	1.5	CsF (3)	MeCN	rt	42
2	1.5	CsF (3)	MeCN	80	47 ^b
3	2	CsF (3)	MeCN	rt	53
4	2	CsF (4)	MeCN	rt	76
5	1.5	<i>n</i> -Bu ₄ NF (1.8)	THF	rt	16 ^c
6	1.5	KF/[18]crown-6 (1.5/1.5)	THF	0–rt	8
7	2		MeCN	rt	0

^a Reaction conditions: 0.3 mmol of diphenyl diselenide (**1a**), the indicated amount of benzyne precursor **2**, the indicated amount of base, and 3 mL of solvent were stirred at the temperature shown for 24 h.

^b This reaction was stirred for 12 h.

^c This reaction was stirred for 3 h.

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3 equiv of CsF in acetonitrile at room temperature, we obtained *o*-bis(phenylselenide)benzene (**3a**) in a 42% yield (Table 1, entry 1).

In an attempt to improve the yield, subsequent work focused on the optimization of these reaction conditions (Table 1). When the transformation was performed at 80 °C, compound **3a** was obtained in a slightly better yield of 47% (entry 2). By using 2 equiv of the benzyne precursor **2** at room temperature, we isolated **3a** in a 53% yield (entry 3). Treatment of diphenyl diselenide (**1a**) with 2 equiv of *o*-(trimethylsilyl)phenyl triflate (**2**) and 4 equiv of CsF in acetonitrile at room temperature

gave *o*-bis(phenylselenide)benzene (**3a**) in a 76% yield (Table 1, entry 4).⁶ In order to explore the effect of the fluoride source on the reaction, 1.8 equiv of tetrabutylammonium fluoride (TBAF) was added to a mixture of diphenyl diselenide (**1a**) and 1.5 equiv of *o*-(trimethylsilyl)phenyl triflate (**2**) in THF at room temperature. After 3 h, compound **3a** was obtained in a 16% isolated yield (entry 5). In line with this, diphenyl diselenide (**1a**) was treated with 1.5 equiv of *o*-(trimethylsilyl)phenyl triflate (**2**), 1.5 equiv of KF and 1.5 equiv of [18]crown-6 in THF initially at 0 °C with slow increase to room temperature, producing the *o*-bis(phenylselenide)benzene (**3a**) in an 8% isolated yield (entry 6). As can be seen in Table

Table 2. Synthesis of *o*-bis(organochalcogenide)benzenes (**3**) by the reaction of diorgano dichalcogenides (**1**) and *o*-(trimethylsilyl)phenyl triflate (**2**) in the presence of CsF^a

Entry	Diorgano dichalcogenide	Benzyne precursor	Product	% isolated yield
1				76
2		2		35
3		2		35
4		2		43
5		2		29 ^b
6		2		74 ^c
7		2		Traces
8		2		Traces

^a Reaction conditions: 0.3 mmol of diorgano dichalcogenide (**1**), 0.6 mmol of *o*-(trimethylsilyl)phenyl triflate **2**, 1.2 mmol of CsF, and 3 mL of MeCN were stirred at room temperature for 24 h.

^b This reaction was stirred for 48 h.

^c This reaction was carried out at 50 °C.

1, entry 7, product **3a** was not obtained and the starting materials **1a** and **2** were recovered when the reaction was carried out in the absence of CsF. This experiment clearly shows that the success of the reaction depends on the presence of a fluoride ion source.

Employing the optimal conditions shown in Table 1, entry 4, we examined the scope of this process using some diorgano dichalcogenides (Table 2). The reaction using the electron-poor diaryl dichalcogenide **1b** with the benzyne precursor **2**, gave *o*-bis(*p*-chlorophenylselenide)benzene (**3b**) in a 35% isolated yield (entry 2). The same yield was obtained for **3c**, when the reaction was carried out using the diaryl diselenide **1c**, bearing fluoro groups (entry 3). When dithienyl diselenide (**1d**) was allowed to react with **2**, the product was isolated in a 43% yield (entry 4). Allowing diphenyl disulfide (**1e**) to react with 2 equiv of the benzyne precursor **2** and 4 equiv of CsF in acetonitrile at room temperature for 24 h, we obtained *o*-bis(phenylsulfide)benzene (**3e**) in a 27% isolated yield. Increasing the reaction time to 48 h, product **3e** was formed in a similar yield of 29% (entry 5). For our surprise, when the electron-rich diaryl dichalcogenide **1f** was subjected to the reaction with *o*-(trimethylsilyl)phenyl triflate (**2**), *o*-bis(*p*-tolylselenide)benzene (**3f**) was obtained in a very low yield of 15%. In the attempt to increase this yield, the same reaction was performed at 50 °C, and compound **3f** was isolated in a good yield of 74% (Table 2, entry 6). When dibenzyl diselenide (**1g**) was allowed to react with the benzyne precursor **2** in the presence of CsF in acetonitrile at room temperature for 24 h, traces of the product **3g** were obtained along with some by-products. The starting materials were completely consumed, and no attempts were made to identify the by-products. On the other hand, when dibutyl diselenide (**1h**) was submitted to the same reaction conditions, it was almost completely recovered after 24 h.

The structures of compounds **3a–f** were assigned according to its LRMS, IR, ¹H, and ¹³C NMR spectra. All new compounds (**3b–d**) provided elemental analyses that agree with the proposed structures.

In summary, a simple and more general procedure involving mild conditions for the insertion of benzyne into diorgano dichalcogenides has been developed, and *o*-bis(organochalcogenide)benzenes were prepared in moderate to good yields.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.09.111.

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- Experimental procedure for the synthesis of *o*-bis(organochalcogenide)benzenes (**3**): To a vial (20 mL) were added the appropriate diorgano dichalcogenide **1a–h** (0.3 mmol), *o*-(trimethylsilyl)phenyl triflate (**2**) (178.8 mg, 0.6 mmol), acetonitrile (3 mL) and CsF (182.4 mg, 1.2 mmol). The vial was sealed using a cap and the mixture was stirred for 24 h at room temperature unless otherwise indicated. Afterwards, brine (30 mL) was added to the mixture, which was extracted with ethyl acetate (3 × 30 mL). The organic phase was dried over MgSO₄. After filtration, the solvent was evaporated under reduced pressure. The residue was purified by preparative thin layer chromatography using silica gel and hexane as eluent, affording the desired products **3a–f**. *o*-Bis(*p*-chlorophenylselenide)benzene (**3b**): yield 48.0 mg (35%); light yellow solid; mp 97–100 °C; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.44–7.40 (m, 4H), 7.30–7.24 (m, 4H), 7.21–7.17 (m, 2H), 7.13–7.09 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ (ppm) 135.6, 135.1, 134.2, 133.2, 129.7, 128.7, 128.3; IR (KBr, cm⁻¹) 3070, 3046, 1559, 1469, 1438, 1088, 1009, 817, 745; LRMS (*m/z*, %) 422 (29), 232 (78), 152 (72), 40 (100); Anal. Calcd for C₁₈H₁₂Cl₂Se₂: C, 47.30; H, 2.65. Found: C, 47.32; H, 2.81.