

1,1,3,3-Tetramethylindan-2-selone–Benzyne Adduct: An Isolable 2*H*-Benzoselenete

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The synthesis and mechanistic studies of ortho-quinoid compounds have received much attention over the past decades.¹ 2*H*-Benzothietes (**1**) are one of the important valence isomers of these orthoquinoid compounds (**2**), which have been especially interested in the reaction with dienophiles.² Benzooxetes (**3**) were prepared from benzofuran oxide derivatives,³ which are labile and reverted to the quinone methides (**4**) and benzofuran epoxides upon prolonged storage (Scheme 1).⁴ However, to our knowledge, there is no report on the synthesis of 2*H*-benzoselenete (**5**), which was postulated as an intermediate on the photolysis of 3-diazobenzo[*b*]-selenophen-2(3*H*)-one.⁵ 2*H*-Benzoselenete (**5a**) was found to be labile and revert to dibenzodiselenocin derivative, dimer of selenoquinone methide (**6a**).

Recently, we have reported the reaction of thiones with benzyne, which provided a convenient method for the synthesis of 2*H*-benzothietes (**1**).⁶ These results prompted us to investigate the possibility to synthesize 2*H*-benzoselenete (**5**) from selones (**7**) and benzyne. We herein report the first isolation of substituted benzoselenete derivatives, **5**, in the reaction of selones, **7**, with benzyne.

A solution of 1,1,3,3-tetramethylindane-2-selone (**7a**)⁷ and *o*-trimethylsilylphenyl trifluoromethanesulfonate (**8**)⁸ in dichloromethane was treated with tetrabutylammonium fluoride in THF at room temperature, and then the solvent was removed in vacuo. Separation on silica gel chromatography and recrystallization from methanol led to the colorless crystals (mp 83–84 °C), which was found to be benzoselenete (**5b**) in 70% yield. The structure of **5b** was determined by its ¹H NMR, ¹³C NMR (Table 1).

When **7a** was treated with benzenediazonium 2-carboxylate (**9**) in refluxing benzene, compound **5b** was obtained in 27% along with the rearranged product (**10**) in 7% yield (Scheme 2).

Scheme 1

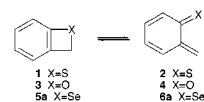


Table 1. Spectral Data of **5b**

¹ H NMR	¹³ C NMR
1.23 (s, 6H, Me), 1.62 (s, 6H, Me)	25.33 (2 × Me), 34.62 (Me),
6.03 (d, 1H, Ar), 6.87 (t, 1H, Ar), 7.05 (t, 1H, Ar), 7.14 (d, 1H, Ar), 7.18–7.29 (m, 4H, Ar)	34.65 (Me), 47.69 (Me-C), 82.98 (Se-C), 122.52 (Ar CH), 123.25 (Ar CH), 123.65 (Ar CH), 124.37 (Ar CH), 127.24 (Ar CH), 127.76 (Ar CH), 128.26 (Ar C), 148.06 (Ar C), 149.77 (Ar C)

Scheme 2

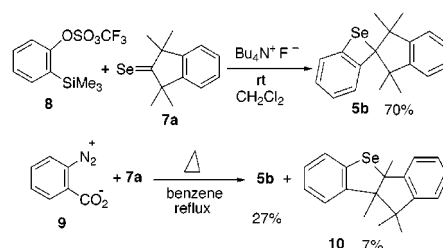


Table 2. Selected Distances and Angles of **5b**

bond length (Å)		
	C(1)–Se	1.92 (1)
	C(7)–Se	2.00 (1)
	C(1)–C(6)	1.39 (2)
	C(6)–C(7)	1.49 (2)
	C(7)–C(15)	1.62 (2)
	C(7)–C(8)	1.59 (2)
bond angles (deg)	C(1)–Se–C(7)	70.4 (6)
	Se–C(1)–C(6)	96.4 (9)
	C(1)–C(6)–C(7)	103.1 (1)
	Se–C(7)–C(6)	89.9 (8)

Since **5b** is the first isolated benzoselenete, X-ray crystallographic analysis of **5b** was carried out (Figure 1).⁹ The molecule lies in a crystallographic mirror plane, with Se, C, C(1), C(2), and the aromatic ring from benzyne in this plane. On the contrary, the indane plane is perpendicular to this plane. C–Se bonds were 2.02 and 1.89 Å, respectively (Table 2).

The first isolation of benzoselenete **5b** and its crystallographic structure prompted us to investigate the molecular orbital studies.¹⁰ The stabilities of the strained benzenoid form (**5a**) and the *o*-quinoid form (**6a**) are compared (see Figure 2). With the geometry optimization of the 6-31G basis set, **5a** is calculated to be 58.41 kJ/mol (13.96 kcal/mol) more stable than **6a** in the ground-state S₀. Bond lengths (C=Se) of the calculated value are quite similar to the observed single X-ray crystallographic data (2.032 and 1.935 Å, respectively).

By analyzing the calculated data, the conversion between benzoselenete **5a** and *o*-quinoid structure **6** at elevated temperature proceeds very likely. Actually, Yamazaki et al. reported the photolysis of 3-diazobenzo[*b*]selenophene-2(3*H*)-one (**11**) in methanol gave dimethyl 1,5-dibenzo[*b,f*]diselenocine-2,6-dicarboxylate (**12**)

(9) The X-ray crystallographic analyses of **5b**, **10**, and **15** were carried out by using Enraf-Nonius CAD4 diffractometer.

(10) Ab initio MO calculations were made by using the GAUSSIAN 94 program at B3LYP/6-31++G (2d,p) basis set. Trisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Montgomery, B. G. A.; Raghabachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*, revision B.1; Gaussian, Inc.: Pittsburgh, PA, 1995.

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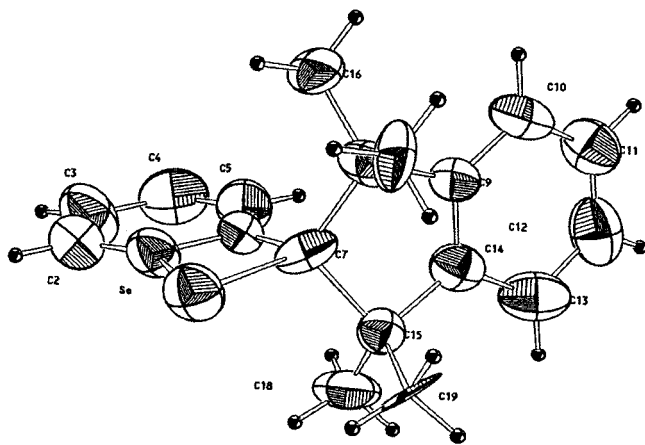
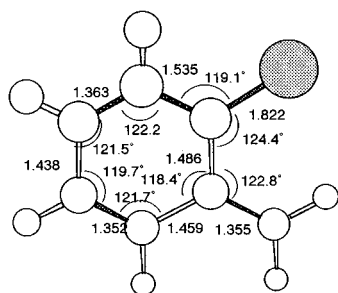
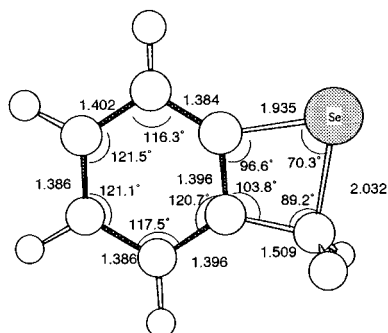
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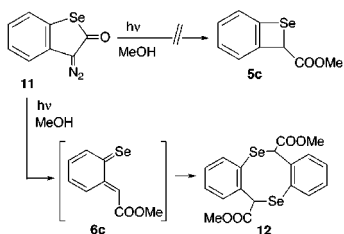
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Figure 1. X-ray crystallographic structure of **5b**.Figure 2. Calculated formula and selected data of **5a** and **6a**.

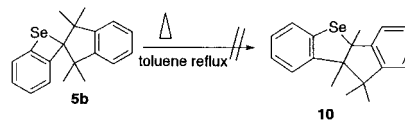
Scheme 3



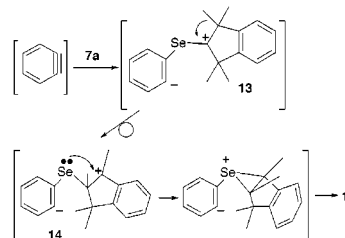
instead of methyl 2*H*-1-benzoselenite-2-carboxylate (**5c**).⁵ They have shown that the formation of selenocine **12** might be formed from the corresponding *o*-quinoid structure **6c** (Scheme 3).

To confirm the possibility of the formation of *o*-quinoid form **6b**, thermolysis of **5b** was carried out in refluxing toluene, which resulted in almost recovery of starting **5b**, suggesting that bulky 1,1,3,3-indanyl moiety prevents the formation of the *o*-quinoid structure (Scheme 4). When the reaction was carried out in the presence of dimethyl acetylenedicarboxylate in refluxing toluene,

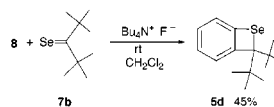
Scheme 4



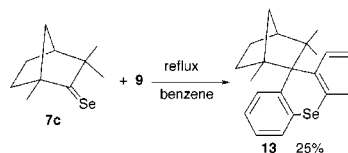
Scheme 5



Scheme 6



Scheme 7



starting **5b** was recovered almost quantitatively. Therefore, it is noteworthy that there is no tautomeric interconversion between **5** and **6** under our experimental conditions.

Tetramethylindane-2-selone, **7a**, reacted with benzyne to give **5b** via a [2 + 2] manner at room temperature. By using **9** as a benzyne precursor, **10** might be formed as follows: Selenide of selone **7a** attacked the electron-deficient carbon of benzyne to afford the corresponding betaine (**13**). Methyl migration of **13** followed by the addition of selenide resulted in the formation of episelenonium ion (**14**), which finally afforded **10** (Scheme 5).

Another sterically crowded selone, di-*tert*-butyl selenoketone (**7b**)¹¹ afforded a similar result. When **8** was treated with di-*tert*-butyl selenoketone, **7b**, followed by the addition of tetrabutylammonium fluoride, the corresponding benzoselenete (**5d**) was isolated in 45% yield (Scheme 6).

Interestingly, treatment of selenofenone (**7c**)¹¹ with benzenediazonium 2-carboxylate, **9**, resulted in the formation of 2:1 adduct (spiro[fenchone-9,9'-selenoxanthene]) (**15**) (Scheme 7). The structure of **15** was confirmed by its ¹H and ¹³C NMR, elemental analysis, and X-ray crystallographic analysis.

Thus, benzyne-mediated synthesis appears to be the only viable route for **5b**, the structure of which was confirmed by X-ray crystallographic analysis. The molecular orbital study of **5a** suggests that the benzoselenete structure is more stable than that of *o*-selone methide **6a**.

Supporting Information Available: Experimental procedures, spectroscopic characterization for the products **5b**, **5d**, **10**, and **15**, and X-ray crystallographic data for **5b**, **10**, and **15** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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