

Convenient Synthesis of New Se,Se'-Disubstituted Derivatives of Benzene-1,2-diselenol

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The electrophilic cleavage of $(\eta^5\text{-Bu}^t\text{C}_5\text{H}_4)_2\text{ZrSe}_2\text{C}_6\text{H}_4\text{-}o$ leads easily to new Se,Se'-disubstituted derivatives of benzene-1,2-diselenol in good yield with quantitative recovery of the organometallic moiety of the reagent.

The last ten years have seen a worldwide explosion of interest in the development and uses of organoselenium methodology. Organoselenium compounds are very useful in various fields e.g. organic syntheses, molecular conductors, biology, and pharmacology.¹

Numerous routes of access to aryl selenides are available, most of them using the very bad smelling and toxic selenols. However, to the best of our knowledge, no general syntheses of functionalized *o*-diselenobenzenes are reported. Only some derivatives of this family have been synthesized, from the hard-to-prepare benzene *o*-diselenol dilithium salt or by an indirect method.²⁻⁵

In a recent paper,⁶ we described the easy access, in a good yield (75%), to the complex (1) by direct reaction between selenium and Bu^t-zirconocene diphenyl.

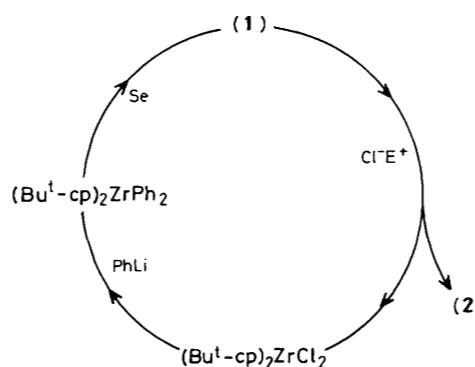
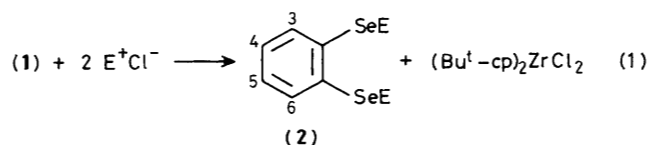
Taking into account the cleavage of Zr–chalcogen bonds by electrophilic reagents, the complex (1) containing the benzene-1,2-diseleno ligand represents a potential synthon in the synthesis of new diselenobenzene compounds. This paper deals with our first results in this field.

The complex (1) was treated with various electrophiles (chloro derivatives and acyl chlorides) according to equation (1) and Table 1. The transformations were complete in between a few minutes to some hours at room temperature. As the electrophiles were chloro reagents, the by-product formed was Bu^t-zirconocene dichloride, which was quantitatively recovered. This dichloride was used again many times and finally it took part in an overall cyclic transformation (Scheme 1).

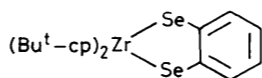
In a typical run under argon atmosphere, 1 mmol of the reagent E–Cl in tetrahydrofuran (THF; 10 ml) was added with stirring to a deep-red solution of (1) (0.5 mmol, 10 ml THF) at room temperature. Between a few minutes to some hours later, the red solution became lighter in colour indicating the end of the reaction. The solvent was evaporated

under reduced pressure and the crude compound (2) extracted from the residue with pentane or hexane leaving $(\text{Bu}^t\text{cp})_2\text{ZrCl}_2$. Then the crude product was purified by flash chromatography (silica gel, pentane–diethyl ether 8:2) and recrystallised (diethyl ether–pentane).

All the spectroscopic values for compounds (2) are perfectly in accordance with the structures expected.[†] The mass spectra



Scheme 1



(1) cp = $\eta^5\text{-C}_5\text{H}_4$

Table 1. Products from the reaction (1).

Product (2)	Electrophile E–Cl	% Yield (purified)
a	HCl (anaerobic)	100(crude)
b	PhCH ₂ Cl	67
c	NCCl ₂	60
d	MeCOCH ₂ Cl	65
e	PhCOCH ₂ Cl	75
f	MeCOCl	70
g	Furan-2-carbonyl chloride	68
h	Thiophene-2-carbonyl chloride	70
i	C ₅ H ₅ FeC ₅ H ₄ COCl	50

[†] The new species (2a–i) were characterized by elemental analysis, i.r. and n.m.r. spectroscopy, and mass spectrometry. Selected spectroscopic data [i.r. in KBr, n.m.r. in CDCl₃, coupling constants in Hz, mass (abundance)]: (2a), ¹H n.m.r. δ 2.01 (s, 2H, SeH), 7.04 (dd, 2H, H-4, H-5), 7.50 (dd, 2H, H-3, H-6); mass 236 ($M^{+} - 2$) (48). (2b), ¹H n.m.r. δ 4.09 (s, 4H, CH₂), 7.09 (dd, 2H, H-4, H-5), 7.23 (m, 10H, Ph), 7.31 (dd, 2H, H-3, H-6); mass 418 (M^{+}) (2). (2c), ¹H n.m.r. δ 3.46 (s, 4H, CH₂), 7.37 (dd, 2H, H-4, H-5), 7.60 (dd, 2H, H-3, H-6); mass 316 (M^{+}) (23); $\nu(\text{CN})$ 2240s cm⁻¹. (2d), ¹H n.m.r. δ 2.30 (s, 6H, Me), 3.62 (s, 4H, CH₂), 7.19 (dd, 2H, H-4, H-5), 7.45 (dd, 2H, H-3, H-6); mass 350 (M^{+}) (55); $\nu(\text{CO})$ 1700s cm⁻¹. (2e), ¹H n.m.r. δ 4.17 (s, 4H, CH₂), 7.16 (dd, 2H, H-4, H-5), 7.45 (m, 10H, Ph), 7.85 (dd, 2H, H-3, H-6); mass 474 (M^{+}) (18); $\nu(\text{CO})$ 1672s cm⁻¹. (2f), ¹H n.m.r. δ 2.45 (s, 6H, Me), 7.35 (dd, 2H, H-4, H-5), 7.71 (dd, 2H, H-3, H-6); mass 322 (M^{+}) (3); $\nu(\text{CO})$ 1714s cm⁻¹. (2g), ¹H n.m.r. δ 6.56 (dd, 2H, *J* 3.6 and 1.7, H-4'), 7.20 (dd, 2H, *J* 3.6 and 0.7, H-5'), 7.47 (dd, 2H, H-4, H-5), 7.60 (dd, 2H, *J* 0.7 and 1.7, H-3'), 7.82 (dd, 2H, H-3, H-6); mass 426 (M^{+}) (27); $\nu(\text{CO})$ 1685s cm⁻¹. (2h), ¹H n.m.r. δ 7.14 (dd, 2H, *J* 5 and 3.8, H-4'), 7.45 (dd, 2H, H-4, H-5), 7.89 (dd, 2H, *J* 5 and 1.1, H-5'), 7.83 (m, 4H, H-3, H-6, and H-3'); mass 458 (M^{+}) (0.2); $\nu(\text{CO})$ 1660s and 1680s cm⁻¹. (2i), ¹H n.m.r. δ 4.33 (s, 5H, FeC₅H₅), 4.50 (t, 2H, FeC₅H₄), 4.85 (t, 2H, FeC₅H₄), 7.41 (dd, 2H, H-4, H-5), 7.79 (dd, 2H, H-3, H-6); mass 660 (M^{+}) (24); $\nu(\text{CO})$ 1678s cm⁻¹.

exhibit isotopic distribution patterns typical of ions containing two selenium atoms and the fragmentation gives prominence to the $C_6H_4Se_2^+$ ion. The 1H n.m.r. spectra reveal two double doublets (A_2X_2 system) consistent with a 1,2-disubstituted phenyl group. Other signals are related to the new part of the molecule coming from the electrophile reagent. I.r. spectra show the usual $C=O$ and $C\equiv N$ frequencies. The carbonyl absorption of (**2h**) is split into two bands probably accounting for two different conformations of the carbonyl groups with reference to the heterocyclic rings. Such behaviour has already been mentioned.⁷⁻⁹

The methodology described in this report offers synthetically valuable entries to linearly substituted *o*-diselenobenzenic derivatives from (**1**) and monohalogeno derivatives.

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References

- 1 D. L. Klayman and H. H. Günther, 'Organic Selenium Compounds,' John Wiley, New York, 1973, and references therein.
- 2 K. Lerstrup, M. Lee, F. M. Wiygul, J. Kistenmacher, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 1983, **6**, 294.
- 3 I. Johannsen, K. Bechgaard, K. Mortensen, and C. Jacobsen, *J. Chem. Soc., Chem. Commun.*, 1983, **6**, 295.
- 4 O. Schmitz-Dumont and B. Ross, *Angew. Chem., Int. Ed. Engl.*, 1967, **6**, 1071.
- 5 E. J. Miller, A. L. Rheingold, and T. B. Brill, *J. Organomet. Chem.*, 1985, **282**, 399.
- 6 B. Gautheron, G. Tainturier, S. Pouly, F. Theobald, H. Vivier, and A. Laarif, *Organometallics*, 1984, **3**, 1495.
- 7 R. Grigg and M. V. Sargent, *Tetrahedron Lett.*, 1965, **19**, 1381.
- 8 Y. Mollier, F. Terrier, and N. Lozac'h, *Bull. Soc. Chim. Fr.*, 1964, **8**, 1778.
- 9 R. Grigg, *J. Chem. Soc.*, 1965, 5149.