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SYNTHESIS OF SELENIUM-CONTAINING CROWN ETHERS AND RELATED COMPOUNDS

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The synthesis of the first examples of selenium-containing crown ethers from the benzene diselenolate anion and dichalcogenated ethers is reported. The reaction is highly dependent on the experimental conditions, particularly the concentration. ¹H NMR and mass spectrometry were used to confirm the structures of the new compounds.

Key words: Benzene diseleno crown ethers; benzene diselenopolyethers; ¹H NMR

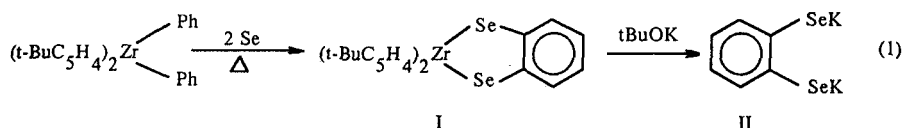
INTRODUCTION

A large variety of crown ethers have been synthesized in the past and this area of chemistry has developed rapidly, mainly because of the interesting properties of these compounds as complexing agents.¹ These macrocycles differ largely in ring size and in the number and type of heteroatoms (O, N, S). Most of the thia-macrocyclic compounds that have been prepared exhibit a great affinity for transition metal cations and as such can be used as a class of host molecules.^{2,3}

With regard to the interesting properties of sulphur-containing macrocycles, we were incited in conducting some experiments on the selenium series for which the stabilization properties of metals in low oxidation states could be very efficient. Recent articles in this field^{4,5} have prompted us to report our first results.⁶ This paper deals with the synthesis of the first crown ethers from the benzenediselenolate anion.

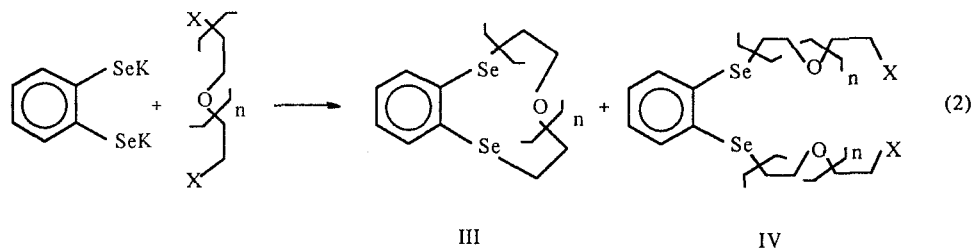
RESULTS

We have shown previously⁷ that the benzene diselenolate anion II is obtained by the nucleophilic cleavage of metallacycle I, which is formed on heating diphenyl-zirconocene in the presence of grey selenium powder (Equation 1).



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On reacting a diluted tetrahydrofuran solution of compound **II** ($5 \cdot 10^{-2} \text{ mol l}^{-1}$) with bis(chloroethyl)ether $\text{ClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{Cl}$, the crown ether **III** is isolated in a low yield (less than 10%). Simultaneously another product is formed (30% yield) for which spectroscopic data (from ^1H NMR and mass fragmentation) confirm the open structure **IV** (Equation 2).



a, $n = 1$, $\text{X} = \text{Cl}$

b, $n = 2$, $\text{X} = \text{Cl}$

c, $n = 3$, $\text{X} = \text{Br}$

The ratio **IV/III** obtained is dependent of the concentration for $n = 1, 2$ ($\text{X} = \text{Cl}$). The dichloride **IV_a** was formed almost exclusively (>95%) in concentrated solution (40% yield of isolated product), whereas the macrocycle **I_a** (20%) was obtained by the high dilution technique (pushed syringe).

In using these latter experimental conditions with the ether dichloride $\text{Cl}(\text{CH}_2\text{CH}_2\text{O})_2\text{CH}_2\text{CH}_2\text{Cl}$ ($n = 2$), there were no significant changes in the results (overall yield 35%, **III_b/IV_b** = 30/70).

On the contrary, if the dichloride is replaced by the dibromide $\text{Br}(\text{CH}_2\text{CH}_2\text{O})_3\text{CH}_2\text{CH}_2\text{Br}$ ($n = 3$),⁸ the reaction proceeds very differently. Even in concentrated solution and with two moles of dibromide per mole of benzenediselenolate, **III_a** was formed in an appreciable yield (46% isolated). Only small amounts of the open selenoether **IV_c** were obtained.

The spectroscopic data establish the structures of the different products.

As it would be predicted, the ^1H NMR of compounds **III** exhibits two double doublets related to the A_2B_2 aromatic protons. The methylene protons appear in the 3.00–3.70 ppm range as two triplets but the resolution in this spectral region becomes poorer as the size of the macrocycle increases.

The mass spectra also confirm the proposed structures and the molecular peak is always observed. The orthocondensed ring in compounds **III** is cleaved immediately, with further fragmentation typical of $\text{C}_6\text{H}_4\text{Se}_2$. In contrast compounds **IV** show the successive cleavage of the two chains followed by the fragmentation of the benzodiselenide part.

We are currently optimising the synthesis of the compounds described here and are preparing larger macrocycles starting from open chain products **IV**. The behavior of the macrocycles **III** towards complexation to transition metals is also being investigated.

EXPERIMENTAL

Typical experimental procedure: All reactions were carried out under an argon atmosphere using standard techniques and infusions pump (Precidor type 5003) for slow introduction of reagents. Solvents were distilled from sodium-benzophenone complex before use.

Two solutions (compound II: 2 mmol in THF 25 mL) and (dichloroether: 2 mmol in THF 25 mL) were simultaneously and very slowly added (8 h) to 200 mL of preheated THF at reflux under vigorous stirring. Stirring and reflux were maintained overnight. Evaporation of the solvent led to a residue which was flash-chromatographed (eluents: pentane and then pentane/diethyl ether mixtures).

All products gave satisfactory microanalyses. ^1H NMR were measured at 100 MHz from CDCl_3 solutions.

Compound III_a: ^1H NMR δ 7.41 (dd, 2H), 7.13 (dd, 2H), 3.76 (t, 4H), 3.05 (t, 4H); MS 308 (M^+ , 59%).

Compound IV_a: ^1H NMR δ 7.41 (dd, 2H), 7.15 (dd, 2H), 3.68 (m, 12H), 3.68 (m, 12H), 3.05 (t, 4H); MS 450 (M^+ , 14%).

Compound III_b: ^1H NMR δ 7.58 (dd, 2H), 7.15 (dd, 2H), 3.64 (t, 4H), 3.48 (s, 4H), 3.20 (t, 4H); MS 352 (M^+ , 15%).

Compound IV_b: ^1H NMR δ 7.38 (dd, 2H), 7.12 (dd, 2H), 3.66 (m, 20H), 3.05 (t, 4H); MS 538 (M^+ , 15%).

Compound III_c: ^1H NMR δ 7.47 (dd, 2H), 7.14 (dd, 2H), 3.80 (t, 4H), 3.58 (m, 8H), 3.09 (t, 4H); MS 396 (M^+ , 24%).

Compound IV_c: ^1H NMR δ 7.39 (dd, 2H), 7.14 (dd, 2H), 3.73 (m, 24H), 3.46 (t, 4H), 3.06 (t, 4H); MS 714 (M^+ , 4%).

REFERENCES

1. R. M. Izatt and J. J. Christensen, "Synthetic Multidentate Macrocyclic Compound," Academic Press, New York (1974).
2. For example: a) J. R. Meadow and E. E. Reid, *J. Amer. Chem. Soc.*, **56**, 2177 (1934); b) W. Rosen and D. H. Busch, *Inorg. Chem.*, **9**, 262 (1970); c) W. Rosen and D. H. Busch, *J. Amer. Chem. Soc.*, **91**, 4694 (1969); d) D. St. C. Black and I. A. Malean, *Tetrahedron Lett.*, 3961 (1969); e) L. A. Ochrymowycz, C. P. Mark and J. D. Michna, *J. Org. Chem.*, **39**, 2079 (1974); f) J. S. Bradshaw and J. Y. K. Hui, *J. Heterocyclic Chem.*, **11**, 649 (1974).
3. For example: a) K. Travis and D. H. Busch, *Inorg. Chem.*, **13**, 2591 (1974); b) T. E. Jones, L. L. Zimmer, L. L. Diddario, D. B. Rorabacker and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, **97**, 7163 (1975); c) T. E. Jones, D. B. Rorabacker and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, **97**, 7485 (1975); d) E. R. Dockal, T. E. Jones, W. F. Sokol, R. J. Engerer, D. B. Rorabacker and L. A. Ochrymowycz, *J. Amer. Chem. Soc.*, **98**, 4324 (1976); e) T. F. Lai and C. K. Poon, *J. Chem. Soc. Dalton Trans.*, 1465 (1982); f) S. C. Rawle, R. Yagbasan, K. Prout and S. R. Cooper, *J. Amer. Chem. Soc.*, **109**, 6181 (1987); g) G. J. Grant, J. P. Carpenter, W. N. Setzer and D. G. Van Derveer, *Inorg. Chem.*, **28**, 4128 (1989).
4. S. Tomoda and M. Iwaoka, *J. Chem. Soc. Chem. Commun.*, 231 (1990).
5. R. J. Batchelor, F. W. B. Einstein, I. D. Gay, J. H. Gu, B. M. Pinto and X. Zhou, *J. Amer. Chem. Soc.*, **112**, 3706 (1990).
6. This work has been partly presented (poster n° 264) to the XIII International Conference on Organometallic Chemistry, Turin, September (1988).
7. a) B. Gautheron, G. Tainturier, S. Pouly, F. Théobald, H. Vivier and A. Laarif, *Organometallics*, **3**, 1495 (1984); b) P. Meunier, B. Gautheron and A. Mazouz, *Phosphorus and Sulfur*, **33**, 33 (1987).
8. J. R. Dann, P. P. Chiesa and J. W. Gates, *J. Org. Chem.*, **26**, 1991 (1961).