

Mass Spectrometry of Organo-Selenium Compounds

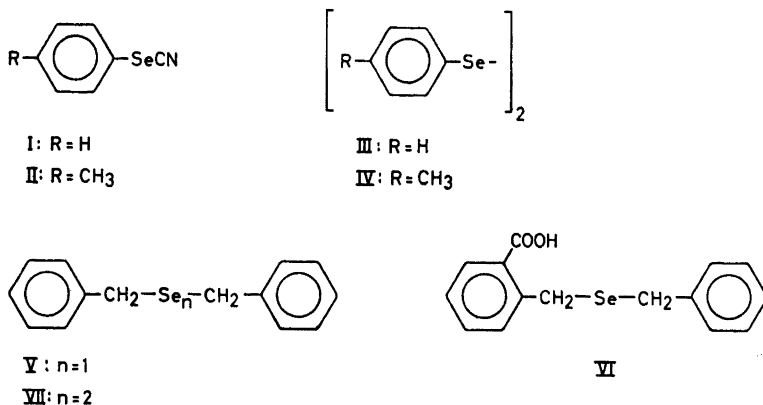
I. Investigation of Some Simple Aromatic Selenocyanates and the Corresponding Diselenides

LARS-BÖRGE AGENÄS

Chemical Institute, University of Uppsala, Uppsala, Sweden

The mass spectra of phenyl selenocyanate (I) and 4-methylphenyl selenocyanate (II) and the corresponding diselenides, diphenyl diselenide (III) and 4,4'-dimethyl-diphenyl diselenide (IV), have been recorded. The fragmentation of these compounds have been shown to be characteristic as regards the selenium containing substituent. The selenocyanates are splitting off the selenocyanato group in two steps and the remaining aromatic ion is fragmented in the usual way. Similarly, the diselenides are splitting off the two selenium atoms in two succeeding steps, forming an ion of biphenyl type, which is finally fragmented as earlier described. For comparison the spectra of dibenzyl selenide (V), 2-carboxy-dibenzyl selenide (VI), and dibenzyl diselenide (VII) have been recorded and are discussed in this paper. Their fragmentations are similar to what has been found for I-IV and the selenium atoms are split off after which the remaining ion is fragmented as described earlier for analogous compounds.

In the recent, very fast development of mass spectrometry as an analytical tool in organic chemistry, a large variety of compounds have been investigated. While many types of organic sulphur compounds have been investigated lately, only very few selenium compounds have so far been investigated by mass spectrometry. The spectrum of selenolane (tetrahydroselenophene), was reported in 1965 by Duffield, Budzikiewicz, and Djerassi.¹ Some selenadiazole derivatives have also been studied by mass spectrometry by Buu-Hoi *et al.*² and selenomethionine has been investigated by Svec and Junk.³ One reason for the paucity of studies within the field of mass spectrometry of organo-selenium compounds is no doubt the existence of six stable natural isotopes of selenium. This fact leads to fairly complicated spectra in many cases, especially when more than one selenium atom is present in the molecule. As a continuation of those investigations of different types of organo-selenium compounds, which have been performed during more than forty years in this Institute, the interest has now been directed towards mass spectrometry,



and a project leading to the investigation of the fragmentation of organo-selenium compounds by mass spectrometry was started lately. This paper is the first within a planned series and deals with the mass spectra of two simple aromatic selenocyanato substituted aromatic compounds, phenyl selenocyanate (I) and 4-methylphenyl selenocyanate (II), and their corresponding diselenides, diphenyl diselenide (III) and 4,4'-dimethyl-diphenyl diselenide (IV). The spectra have been compared with spectra recorded for some benzyl selenides, dibenzyl selenide (V), 2-carboxy-dibenzyl selenide (VI), and dibenzyl diselenide (VII). The discussion of the latter group of spectra is also given in this paper.

SELENOCYANATO COMPOUNDS

The mass spectra of the two selenocyanato compounds investigated are given in Figs. 1–2 and they show a series of very distinct peaks leading to the suggestion that the compounds are fragmented similarly. The peaks with greatest relative abundance are centered around m/e corresponding to molecular weight (M), $M-26$, $M-80$, and $M-106$. The selenium containing ions give groups of peaks with internal relative intensities well in agreement with the natural abundances for the selenium isotopes.*

Here and in the following discussion, the peaks corresponding to the main selenium isotope ^{80}Se will be considered as representing the selenium containing fragment in question. The series of peaks in Figs. 1–2 correspond to molecular weight (M), the loss of a cyano group, the selenium atom, and all the selenocyanato group, respectively. The base peak for phenyl selenocyanate (I) is the $M-106$ peak, while the base peak for 4-methylphenyl selenocyanate (II) is found at $M-80$. This fragmentation, drawn up for the phenyl selenocyanate (I), is given in Scheme 1.

The same peaks in the spectrum of 4-methylphenyl selenocyanate (II) occur at 14 mass units higher. A metastable peak has been observed in the spectrum of II at m/e 69.5, which is in very good agreement with the calculated value

* ^{74}Se : 0.87, ^{76}Se : 9.02, ^{77}Se : 7.58, ^{78}Se : 23.52, ^{80}Se : 49.82, ^{82}Se : 9.19.⁴

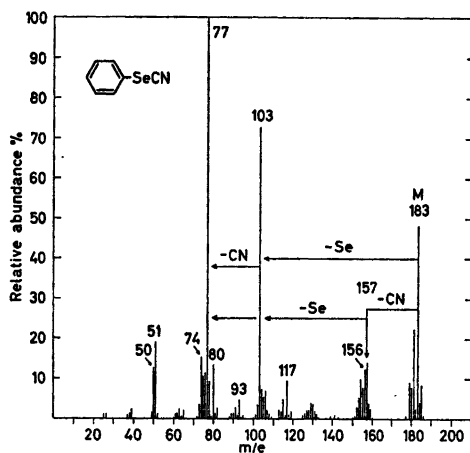


Fig. 1. Mass spectrum of phenyl selenocyanate (I), recorded with the ion source at 20°.

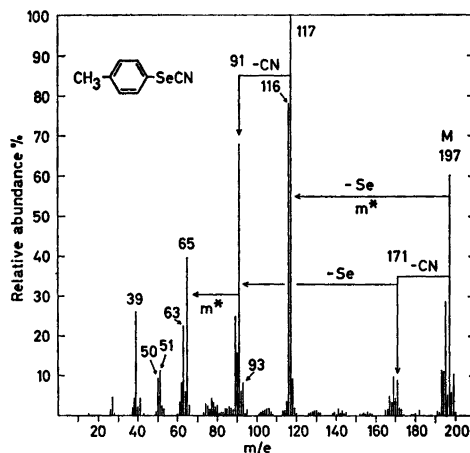
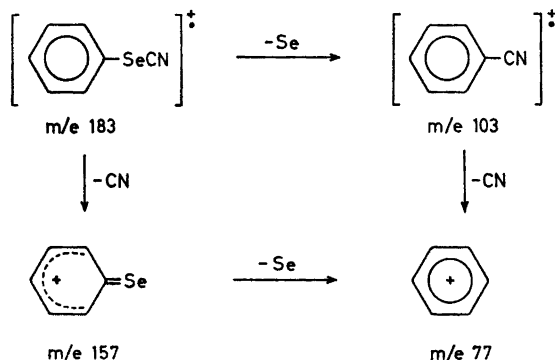


Fig. 2. Mass spectrum of 4-methylphenyl selenocyanate (II), recorded with the ion source at 25°.

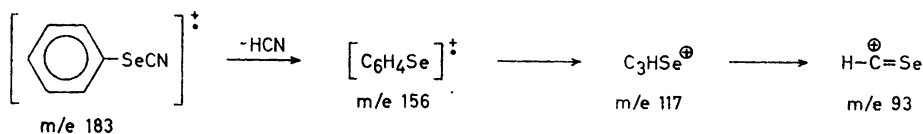
69.5 for the loss of a selenium atom from the molecular ion at m/e 197. The remaining aromatic hydrocarbon ion is finally fragmented in a way, which has been described earlier by many authors and their results have been reviewed in monographs.^{5,6} The parts of the spectra corresponding to this fragmentation will not be discussed in this paper. The fragmentation in Scheme 1 which is characteristic for aromatic selenocyanato substituted compounds, has been observed for other similar compounds, the spectra of which will be published elsewhere.^{7,8}

A detailed study of the spectra in Figs. 1—2 give information for paths of fragmentation other than the main paths discussed so far. In the spectrum of I, the group of peaks at m/e 157 has an appearance leading to the suggestion that it has its origin in two different fragments. Further, a selenium containing



Scheme 1.

fragment gives a group of peaks at m/e 117. The most probable explanation to these groups is the fragmentation in Scheme 2.



Scheme 2.

Further, a selenium containing fragment is causing a group of peaks at m/e 93. The most reasonable explanation to this group of peaks is a fragment analogous to the CHS^+ ion, frequently reported for organo-sulphur compounds, *e.g.* by Duffield, Budzikiewicz, and Djerassi.¹ The fragmentation of Scheme 2 has also been found to occur for other types of aromatic selenocyanato substituted compounds.⁷ The spectrum of II in Fig. 2 gives signs of the same peaks. The group of peaks at m/e 171 seems to be less complex than the corresponding group in Fig. 1, but nevertheless obviously has its origin in more than one fragment. The peak at m/e 117 is here predominantly caused by the loss of a selenium atom from the molecular ion, but a convincingly characteristic group of peaks with its origin in a selenium containing fragment is obtained at m/e 93.

Besides these main fragmentation paths, single peaks of interest are found. Thus in the spectrum of I, a peak at m/e 80 is seen, probably occurring from a selenium fragment. In the spectrum of II a very strong peak at m/e 116 is found which may be ascribed to the loss of an SeH fragment from the molecular ion. The strong peak at m/e 89 is certainly caused by the loss of a hydrogen molecule from the tropylium ion at m/e 91. The ion at m/e 89 is frequently found in the spectra of heterocyclic aromatic compounds.⁹

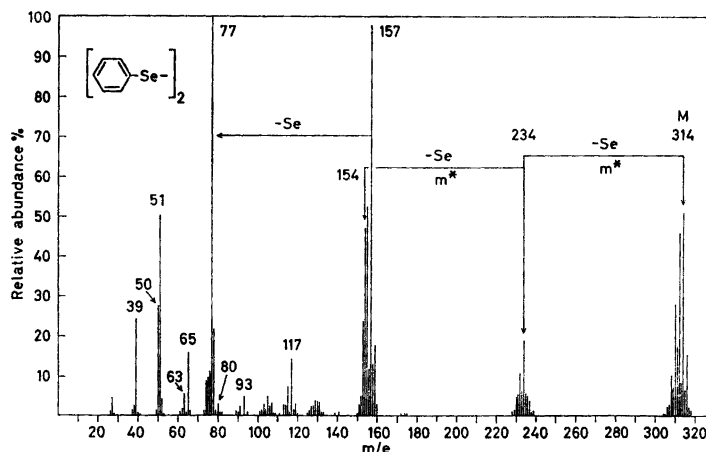


Fig. 3. Mass spectrum of diphenyl diselenide (III), recorded with the ion source at 40°.

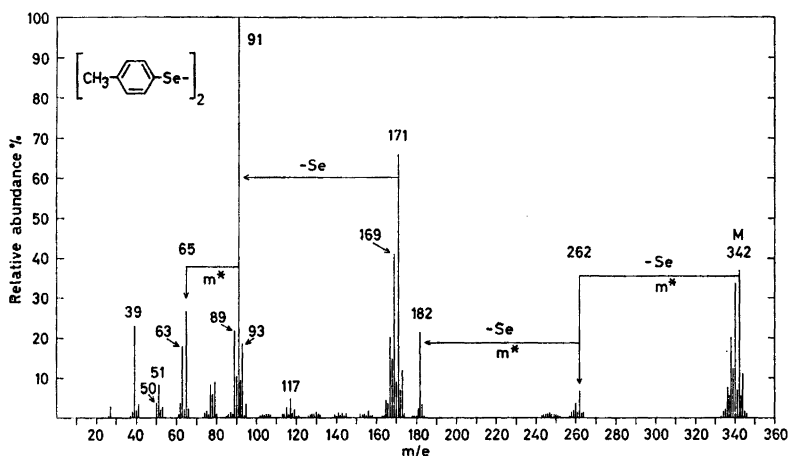
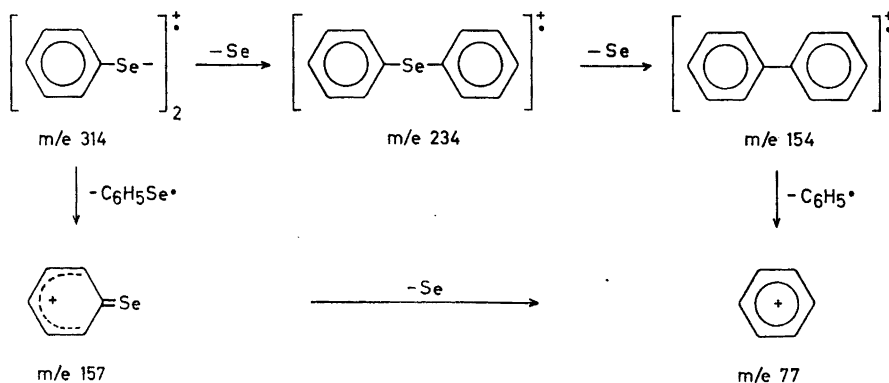


Fig. 4. Mass spectrum of 4,4'-dimethyl-diphenyl diselenide (IV), recorded with the ion source at 20°.

AROMATIC DISELENIDES

The spectra of the diselenides corresponding to I and II, diphenyl diselenide (III) and 4,4'-dimethyl-diphenyl diselenide (IV), have been recorded and are given in Figs. 3—4. These two spectra show, like the spectra of the selenocyanato compounds investigated, a series of very characteristic groups of peaks, establishing the similarity on fragmentation of III and IV. The most abundant peaks are centered around molecular weight (M), $M-80$, $M-160$, $M/2$, $(M/2)-80$. This series corresponds to the successive loss of the two selenium atoms leading to the formation of the corresponding monoselenide ion and finally the biphenyl at $M-160$. The symmetrical molecule is then split into halves, and the resulting ion is then decomposed by the loss of its selenium



Scheme 3.

atom, giving as result a simple aromatic fragment ion. The fragment ion at $(M/2)-80$ can be formed by two alternative fragmentation paths, which are given for III in Scheme 3. The loss of the two selenium atoms in two succeeding steps are supported by the metastable peaks observed at m/e 174.5 and 101.5, in good agreement with the calculated values 174.4 and 101.8.

The corresponding peaks at 14 or 28 mass units higher are found in the spectrum on IV in Fig. 4. Metastable peaks, analogous to those observed for III have been found at m/e 201 and 126.5, similarly in agreement with the calculated values 200.7 and 126.4 for the loss of the two selenium atoms. The finally obtained aromatic fragment ion is further fragmented along well known paths.^{6,7} The base peak of both spectra is an $M/2-80$ fragment. The mass spectrum of the corresponding diphenyl disulphide has been studied by Bowie *et al.*¹⁰ and shows a similar fragmentation. A recent study by Bergman¹¹ of diphenyl selenide gives further support to the fragmentation given here.

Considering the spectrum of III in detail, there is reason to mention that the group of peaks at m/e 157 is caused by two different fragments, which is illustrated by the fragmentation given in Scheme 3. The groups of peaks originating from the fragments m/e 157 and 154 are of course overlapping. Further, selenium containing fragments give rise to peaks at m/e 117 and 93, the origin of which must be the same as was stated for the selenocyanato analogue in Scheme 2. Finally, a fragment at m/e 80 is found analogous to the spectrum of I, which may be ascribed to a selenium fragment.

In the spectrum of IV the group of peaks at m/e 171 has to be studied in detail. This group, more prominent than in the spectrum of II, has an appearance more complex than what is expected from a fragment containing one selenium atom. The formation of a selenium substituted tropylium ion at m/e 169 can be the reason, which also shall be considered in the case of II.

As in the spectrum of III, the peaks characteristic for the fragmentation in Scheme 2 are found at m/e 117 and 93.

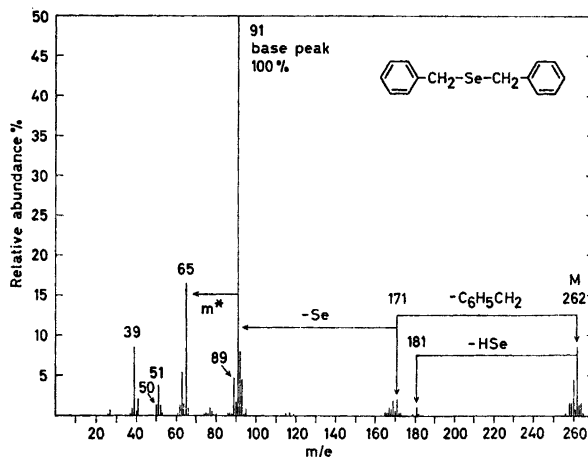


Fig. 5. Mass spectrum of dibenzyl selenide (V), recorded with the ion source at 20°.

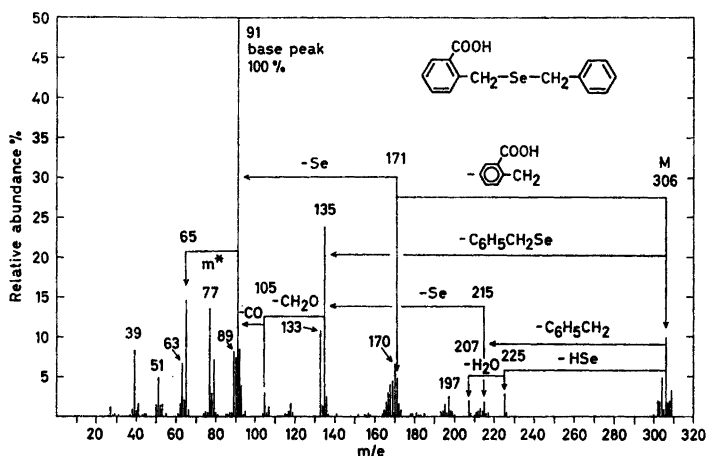


Fig. 6. Mass spectrum of 2-carboxy-dibenzyl selenide (VI), recorded with the ion source at 80° .

The further fragmentation of the finally obtained aromatic hydrocarbon ions proceed along expected paths, which is obvious from those parts of the spectra below m/e 80.

BENZYL COMPOUNDS

The third group of compounds investigated by mass spectroscopy within this part of the project are dibenzyl selenide (V), 2-carboxy-dibenzyl selenide (VI), and dibenzyl diselenide (VII), the spectra of which are given in Figs. 5–7. The general appearance of these spectra is different from what is found

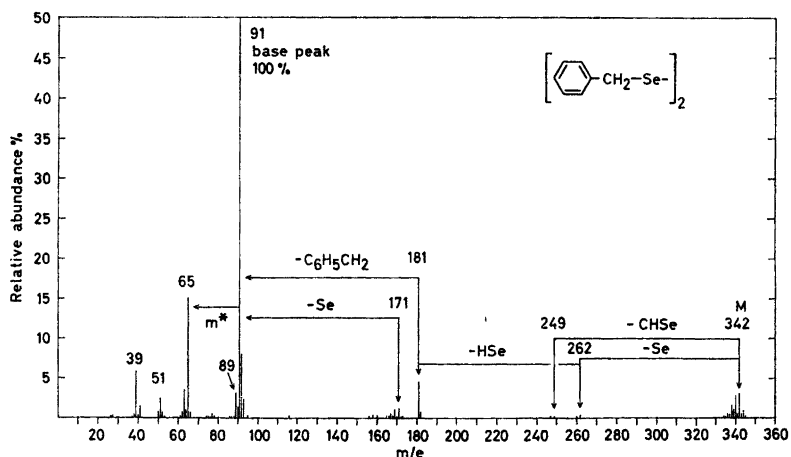
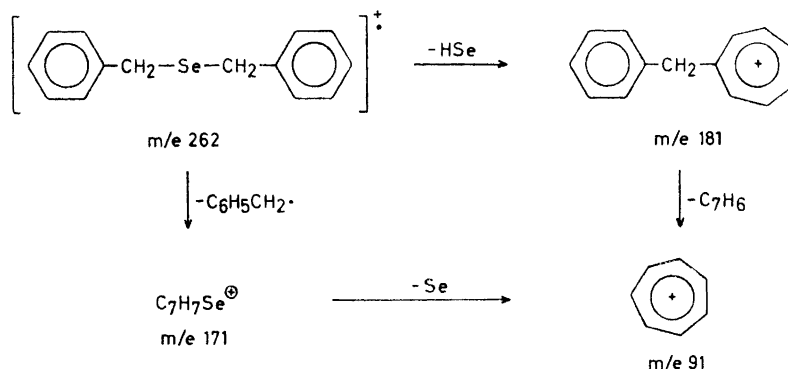


Fig. 7. Mass spectrum of dibenzyl diselenide (VII), recorded with the ion source at 35° .



Scheme 4.

for the aromatic compounds III and IV. Very few peaks are found and thus the fragmentation of V—VII proceeds along paths different from what has been found for the aromatic diselenides in this investigation.

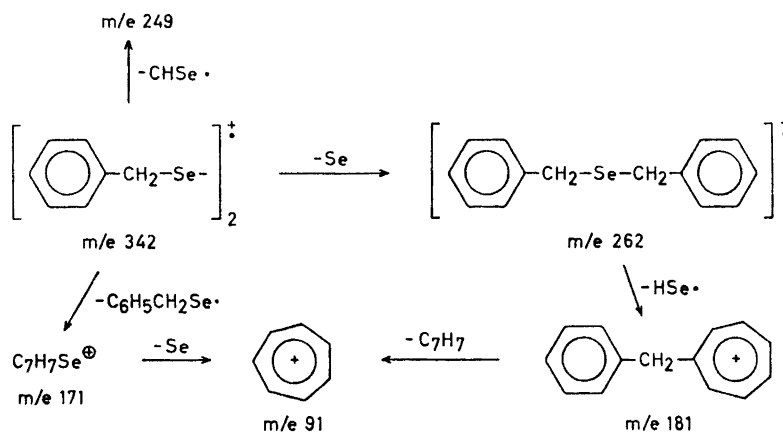
Studying the spectrum of V in Fig. 5 leads to the conclusion that the compound is fragmented in a simple way. Besides the comparatively strong peaks from the fragmentation of the benzyl fragment at m/e 91, only three groups of peaks are found. The molecular ion at m/e 262 gives two fragments at m/e 181 and 172 leading to the suggestion of the fragmentation in Scheme 4.

In the spectrum of VI in Fig. 6, a more complex fragmentation is present due to the carboxyl group in the molecule and to the fact that the molecule is unsymmetric. The fragmentation as far as the selenium substituent is concerned is largely the same as was stated for V. The molecular ion at m/e 306 is split on both sides of the selenium atom. The different possible fragments, together with known fragmentation paths for carboxylic acids,¹² leads to the fragmentation paths as indicated in Fig. 6.

Considering the spectrum further, it is found that the peaks at m/e 171 seems to be caused by two different fragments. The second fragment may be formed by the loss of a hydrogen atom from the first fragment leading to the complex group of peaks. A similar complication is found at m/e 133, where a comparatively strong peak is found. This may be explained by the loss of a hydrogen molecule from the fragment at m/e 135.

Finally, the spectrum of VII in Fig. 7 is very similar to that of the corresponding monoselenide V. The few groups of peaks obtained lead to the fragmentation given in Scheme 5.

As in the fragmentation of the aromatic diselenides III and IV, the two selenium atoms are lost by succeeding fragmentation steps, but the distinction is that the second selenium atom is lost together with a hydrogen atom as an HSe-fragment. In addition to what was found for III and IV, the molecular structure of VIII makes it possible to split off a CHSe-fragment from the molecular ion, causing the peak at m/e 249. The corresponding dibenzyl disulphide has been investigated by mass spectroscopy by Bowie *et al.*¹⁰ and the fragmentation of the diselenide follows mainly the same path as the disulphide.



Scheme 5.

EXPERIMENTAL

The mass spectra were recorded with an LKB 9000 A gas chromatograph-mass spectrometer using the direct inlet technique. This was also used when the spectrum of I was recorded which was made possible by using a special technique (*vide infra*). The electron energy was 70 eV.

The purity of the materials was determined by microanalysis for selenium, using a method developed by Bengtsson,¹³ which is very similar to the method of Gould.¹⁴

Phenyl selenocyanate (I) was prepared as described by Behaghel and Seibert.¹⁵ The product was purified by repeated redistillation with the addition of copper powder to the crude liquid in order to remove impurities. B.p. 128–130°/15 mm.

In order to record the mass spectrum of I a small amount was dissolved in methylene chloride and added to aluminium oxide. (Woelm neutral, grade I, for chromatography). The solvent was carefully removed and the resulting mixture was used for mass spectrometry using the direct inlet technique.

4-Methylphenyl selenocyanate (II) was prepared as described by Behaghel and Rollmann.¹⁶ After repeated recrystallization from petroleum ether, the pure product was obtained; m.p. 51–52°.

Diphenyl diselenide (III) was prepared following the method of Behaghel and Seibert.¹⁵ Phenyl selenocyanate (I) was dissolved in methanol and a small amount of dilute sodium hydroxide solution was added until the colour of the solution had turned dark yellow. After addition of water, the product was precipitated as an oil which solidified upon standing. Repeated recrystallization from ethanol gave the pure product; m.p. 61–61.5°.

4,4'-Dimethyl-diphenyl diselenide (IV) was prepared as described by Behaghel and Seibert¹⁵ for III. 4-Methylphenyl selenocyanate(II) was dissolved in ethanol and dilute sodium hydroxide solution was added until the solution turned intensely yellow. Addition of a large amount of water precipitated the product as a red-yellow oil which solidified upon standing. The crude material was repeatedly recrystallized from ethanol, giving the pure product as dark yellow prisms; m.p. 45.5–46°.

Dibenzyl selenide (V) was prepared as described by Painter *et al.*¹⁷ The slightly yellowish product was repeatedly recrystallized from absolute ethanol, giving the pure product as almost white needles; m.p. 46–46.5°.

2-Carboxy-dibenzyl selenide (VI) was prepared as described by Agenäs and Persson.¹⁸ The crude material was repeatedly recrystallized from benzene, giving the pure product as white crystals; m.p. 144–144.5°.

Dibenzyl diselenide (VII) was prepared as described by Painter *et al.*¹⁷ The crude material was repeatedly recrystallized from absolute ethanol, giving the pure product as bright yellow leaves; m.p. 93–94°.

Acknowledgements. I wish to express my sincere thanks to Professor Arne Fredga for his interest in this investigation and for many valuable discussions. I am also very grateful for the facilities he has placed at my disposal. I am indebted to Dr. K. Olsson for very valuable discussions and to Dr. S.-O. Lawesson for his kind interest and advice. My thanks are also due to Professor Folke Nydahl for the facilities he has placed at my disposal, making the microanalysis for selenium possible. A grant from *AB Astra, Södertälje, Sweden*, is gratefully acknowledged. The selenium analyses were performed by Mrs. Marie Ljungquist.

REFERENCES

1. Duffield, A. M., Budzikiewics, H. and Djerassi, C. *J. Am. Chem. Soc.* **87** (1965) 2920.
2. Buu-Hoi, N. P., Jacquignon, P. and Mangane, M. *Chem. Commun.* **1965** 624.
3. Svec, H. J. and Junk, G. A. *J. Am. Chem. Soc.* **89** (1967) 790.
4. Beynon, J. H. *Mass Spectrometry and its Application to Organic Chemistry*, Elsevier, Amsterdam 1960, p. 558.
5. Budzikiewicz, H., Djerassi, C. and Williams, D. H. *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, Inc., San Francisco 1964, p. 162.
6. Beynon, J. H. *Mass Spectrometry and its Application to Organic Chemistry*, Elsevier, Amsterdam 1960, p. 340.
7. Agenäs, L.-B. *Acta Chem. Scand.* **22** (1968) 1773.
8. Agenäs, L.-B. *To be published.*
9. Pandit, U. K., Hofman, H. J. and Huisman, H. O. *Tetrahedron* **20** (1964) 1679.
10. Bowie, J. H., Lawesson, S.-O., Madsen, J. Ø., Nolde, C., Schroll, G. and Williams, D. H. *J. Chem. Soc. Sect. B* **1966** 946.
11. Bergman, J. *Acta Chem. Scand.* **22** (1968) 1883.
12. Beynon, J. H. *Mass Spectrometry and its Application to Organic Chemistry*, Elsevier, Amsterdam 1960, p. 371.
13. Bengtsson, A. *To be published.*
14. Gould, E. S. *Anal. Chem.* **23** (1951) 1502.
15. Behaghel, O. and Seibert, H. *Ber.* **65** (1932) 812.
16. Behaghel, O. and Rollmann, M. *J. prakt. Chem.* [2] **123** (1929) 336.
17. Painter, E. G., Franke, K. W. and Gortner, R. A. *J. Org. Chem.* **5** (1940) 579.
18. Agenäs, L.-B. and Persson, B. *Acta Chem. Scand.* **21** (1967) 835.

Received January 24, 1968.