Tetrahedron Vol 36, pp 3317 to 3323
0040 4020/80 1115-3317 $02.00/0

SELENOLO[3,4-*b*]SELENOPHENE—THE THIRD "CLASSICAL" SELENOPHTENE

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(*Received in UK 22 April* 1980)

Abstract—Selenolo[3,4-*b*]selenophene (**3**) has been synthesized by two different routes using 2,3-bischloromethyl-5-carbomethoxyselenophene (**4**) or preferably 4-methylseleno-3-selenophene aldehyde (**10**) as the starting material. In marked contrast to its thiophene alogue thieno[3,4-*b*]thiophene, **3** was stable. Analysis of the ^{1}H, ^{13}C and, in particular, the ^{77}Se NMR gave strong evidence for the more positive nature of the Se-5 than the Se-1 atom of **3**.

INTRODUCTION

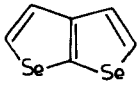
Previously[1] we have described the syntheses of selenolo[2,3-*b*]selenophene (**1**) and selenolo[3,2-*b*]selenophene (**2**) from the suitable selenienyl-1,3-dioxolanes *via* a ring-closure of the intermediate formyl selenienylselenoacetates with sodium ethoxide.

We now wish to report the synthesis of selenolo[3,4-*b*]selenophene (**3**), the third selenophtene with a "classical" structure. The isomeric selenophtenes **1**–**3** were claimed by Umezawa[2] to be present among the products of the reaction between acetylene and selenium. However, we were not able to provide evidence for the presence of any other selenophtene than selenolo[3,2-*b*]selenophene (**2**) among the more than 30 identified products of this reaction. Moreover, Umezawa's structural assignments were shown by us[1,3] to be erroneous and the synthesis of the third selenophtene **3** would be the final piece of evidence for the structures. There are few described synthetic routes leading to the sulfur analogues of selenophtenes **1-3**. The most common ones utilize a ring-closure of a suitably substituted thiophene leading directly to a derivative of the aromatic, fused system. Analogously, our syntheses of **1** and **2** were accomplished by Dieckmann cyclizations of the above-mentioned formyl selenienylselenoacetates. This synthetic approach was also successful for the preparation of 2-carboxythieno[3,4-*b*]thiophene,[4] (i.e. ring-closure on the 3- and 4-positions of the thiophene ring), but failed when applied to the synthesis of selenolo[2,3-*c*]-thiophene.[5] Also, our attempt to prepare selenolo-[3,4-*b*]selenophene (**3**) in a similar manner proved unsuccessful—only resinification products were obtained in the reaction of n-butyllithium with 2-(4-bromo-3-selenienyl)-1,3-dioxolane and subsequent treatment of the product with red selenium and methyl bromoacetate.

Other possible approaches might be a method of Wynberg and Zwanenburg,[6] who utilized a dehydration of a dihydrothienothiophene sulfoxide for a synthesis of thieno[3,4-*b*]thiophene, and the path of Litvinov *et al.*,[5] who synthesized selenolo[2,3-*c*]thiophene *via* quaternization of 4-methylseleno-3-thiophene aldehyde and ring-closure of the intermediate selenonium salt in pyridine and acetic anhydride.

Initially, we tried the approach of Wynberg and Zwanenburg,[6] partly because of our previous experience in preparing the "non-classical" [3,4-*c*]-annelated selenoloselenophenes (similarly via dehydration of dihydroselenoloselenophene selenoxides or the dehydrobromination of selenium dibromides[7]) and partly because, by starting from a thiophene derivative, this route could also lead to the fourth possible "classical" selenolothiophene, namely the currently unknown selenolo[3,4-*b*]thiophene. Work on its synthesis is now in progress in our laboratory. The synthesis of **3** along the route mentioned is outlined in Scheme 1.

This sequence is similar to that described by Wynberg *et al.*[8] for the synthesis of 2-carboxy-4,6-dihydrothieno[3,4-*b*]thiophene-5-oxide, with the exception that the hydrolysis of the ester function to an acid was done firstly on the aromatic system **8** and not on the dihydroselenophene derivative **5**. The reason for this was that the hydrolysis of **5**, even under very mild basic conditions, led to the corresponding acid in very low yields the dimer, trimer and even higher oligomers, as identified by mass spectroscopy, being the main products. This fact indicates the ease with which the dihydroselenophene ring in **5** undergoes (a base-induced) ring-opening, which might also account for the very low yield (<15%) of **5** in the cyclization reaction. This reaction gives primarily the dimeric product **6** in varying yields, depending on the conditions employed. We have carried out the cyclization of **4** at various temperatures, using a high dilution technique and varying the order of addition of the reagents, in such solvents as ethanol, water and dioxane but the yield of the desired monomeric product **5** never exceeded 15%. In contrast, a similar cyclization of a thio-



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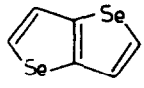

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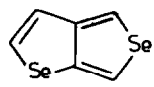

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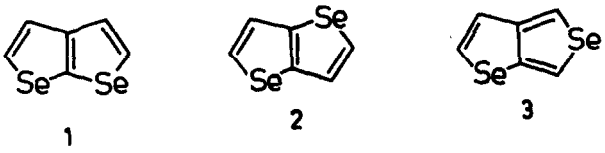
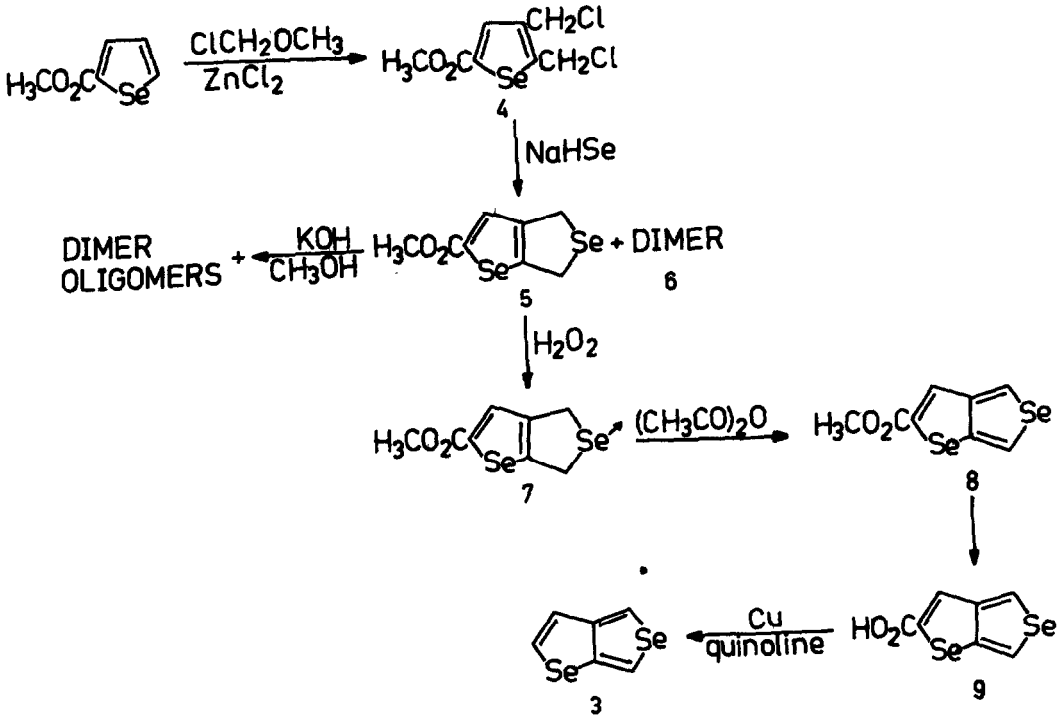
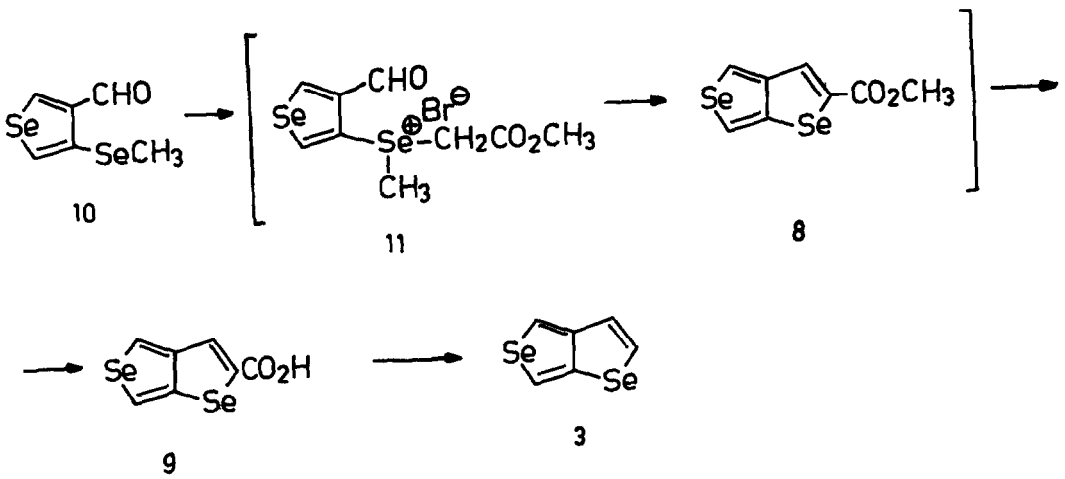


1 2 3



Scheme 1.



Scheme 2.

phene analogue of **4** with sodium sulfide in methanol gave the required dihydrothienothiophene in 66% yield.[8]

Nevertheless, the reaction sequence outlined in Scheme 1 was accomplished, the over-all yield of the selenophtene **3** being 2.6% from the bischloromethyl derivative **4** or 1.3% based on selenophene.

Because of the low, over-all yield in this multi-step synthesis, the approach of Litvinov *et al.*[5] was tried, giving selenolo [3,4-*b*]selenophene (**3**) in 44% yield when starting from the aldehyde **10** or in 18% from selenophene. The synthetic path is outlined in Scheme 2.

4-Methylseleno-3-selenophene aldehyde (**10**) was obtained in 55% yield in two steps from 3,4-dibromoselenophene by halogen-metal exchange with n-butyllithium and reaction with dimethyl diselenide followed by another lithiation and formylation with N,N-dimethyl formamide. It was also obtained, though in lower yield, via 4-bromo-3-selenophene aldehyde by protecting the aldehyde function as an acetal, reacting with n-butyllithium and dimethyl diselenide and then hydrolyzing the acetal group. This route was more laborious not only because of the greater number of steps but also because the lithiation and subsequent formylation of 3,4-dibromoselenophene always gave a difficult-to-separate mixture of 4-bromo-3-selenophene aldehyde and the starting material, as previously pointed out by Paulmier *et al.*[9] The separation was best achieved after acetalization, from which the unreacted 3,4-dibromoselenophene could be recovered by distillation.[10] The methylseleno group of the aldehyde **10**, obtained in either way, was quaternized with methyl bromoacetate in toluene to give an intermediate selenonium salt **11**, which was then cyclized with acetic anhydride and pyridine to give the ester **8**. This was then, without isolation, hydrolyzed to the acid **9**, the whole sequence thus being a one-pot reaction from **10**, giving 2-carboxyselenolo [3,4-*b*]selenophene (**9**) in 61% yield. Decarboxylation with copper in quinoline gave selenolo [3,4-*b*]selenophene (**3**) as light yellow, glistening, volatile crystals, m.p. 46-47°, in 72% yield. The compound appeared to be indefinitely stable when kept in a refrigerator and at least for a week at room temperature in air, after which it began to darken. It was also stable in n-pentane solution.

This behaviour is in marked contrast to the behaviour of its sulfur analogue, thieno [3,4-*b*]thiophene, which rapidly turned yellow on standing in air and was only stable, for a few days, in petroleum ether solution or when kept at -40°.[6]

The greater stability of **3** compared with thieno [3,4-*b*]thiophene, together with our earlier observation that the non-classical selenoloselenophenes seemed to be more stable than their sulfur analogues,[7] indicate that selenophtenes are generally more stable than the corresponding thiophtenes. The structure of **3** was confirmed by its ^{1}H, ^{13}C and ^{77}Se NMR spectra, as well as by its mass spectrum. The ^{1}H NMR spectrum is of first order, quite similar to that observed for thieno [3,4-*b*]thiophene[6] with well separated signals for all four aromatic protons. Comparison of the chemical shifts of the protons of **3** and thieno [3,4-*b*]thiophene reveals that the resonances of all the protons occur at lower field for **3**.[12] The most striking difference between the spectra of these two compounds is that the relative positions of the signals attributed to H-4 and H-6 are reversed. As Wynberg *et al.*[6] did not observe the long-range coupling between H-3 and H-6, this difference could be due to their erroneous assignments of the chemical shifts of H-4 and H-6.

The decoupled ^{13}C NMR spectrum shows as expected six peaks: four of high intensity at δ 131.4 (C-2), 120.7 (C-3), 119.8 (C-4) and 117.9 (C-6) and two of low intensity, as expected for quaternary carbons, at δ 136.9 (C-7) and 152.2 (C-8). The assignments of signals were made from the undecoupled ^{13}C NMR spectrum in analogy with the assignments for selenolo [2,3-*c*]thiophene.[11] This spectrum is shown in Fig. 1. The decoupled ^{77}Se NMR spectrum of **3** shows two peaks, at δ 176.4 (Se-1) upfield from selenophene and δ 126.4 (Se-5) downfield from selenophene, as expected for the unsymmetrical structure of selenolo [3,4-*b*]selenophene. The assignments of signals were based on the comparison with the ^{77}Se NMR spectrum of selenolo [2,3-*c*]thiophene[11] (δ 173.8 upfield from selenophene), as well as on the analysis of the undecoupled ^{77}Se NMR spectrum, which is shown in Fig. 2. The signal at high field is split into two doublets, which is only compatible with the interactions between Se-1 and ring hydrogens H-2 and H-3, giving two different coupling constants $^2J_{Se\text{-}1\text{-}H2} = 47.1$ Hz and $^3J_{Se\text{-}1\text{-}H3} = 7.0$ Hz. The magnitude of these coupling constants is also in good agreement with the corresponding coupling constants in **1**[1] and **2**[3]. The signal at low field is split into a triplet, as expected for the coupling over two bonds between Se-5 and H-4 or H-6. Thus, $^2J_{Se\text{-}5\text{-}H4} = {}^2J_{Se\text{-}5\text{-}H6} = 48.1$ Hz. This coupling constant can also be obtained from the selenium satellites in the ^{1}H NMR spectrum. The ^{77}Se couplings to the hydrogens of the adjacent ring are not observed. It should be pointed out that none of the observed selenium signals falls into the ^{77}Se shift region of monosubstituted selenophenes,[13] although the resonances of both **1**[1] and **2**[3] are found there. The great shift difference of 302.8 ppm between Se-1 and Se-5 might be attributed to an appreciable charge separation in the molecule, with Se-5 being the more positively charged of the two Se atoms. Unfortunately, no calculations of the electron densities in **3** are available but the results of the SCF MO treatment by Dewar *et al.*[14] and of the PPP calculations by Skancke *et al.*[15], carried out on thieno [3,4-*b*]thiophene, indicate a similar charge distribution in this molecule. This is also confirmed by the fact that the resonance of Se-5 is only 6.6 ppm from that of the selenium atom in diphenyl selenoxide,[16] which has a partial positive charge. The resonance of the other selenium atom, Se-1, falls into the region of diarylselenides.[17]

There is therefore no doubt, that the selenophtene prepared by us has the structure of selenolo [3,4-*b*]selenophene (**3**). It is, however, still doubtful that any of the three isomeric selenophtenes described by Umezawa[2] really had the structure of **3**. Umezawa's structural assignments were mainly based on dipole moment measurements which were later shown to be erroneous.[3,18] He had also prepared picrates and tetrabromo derivatives of all three selenophtenes. In order to be able to compare all of the data given by Umezawa, we have repeated these experiments on **1-3**, and the results are collected in Table 1, together with data given in Ref. 2. The very good agreement of the m.p. for **1** and **2** and their derivatives and the striking

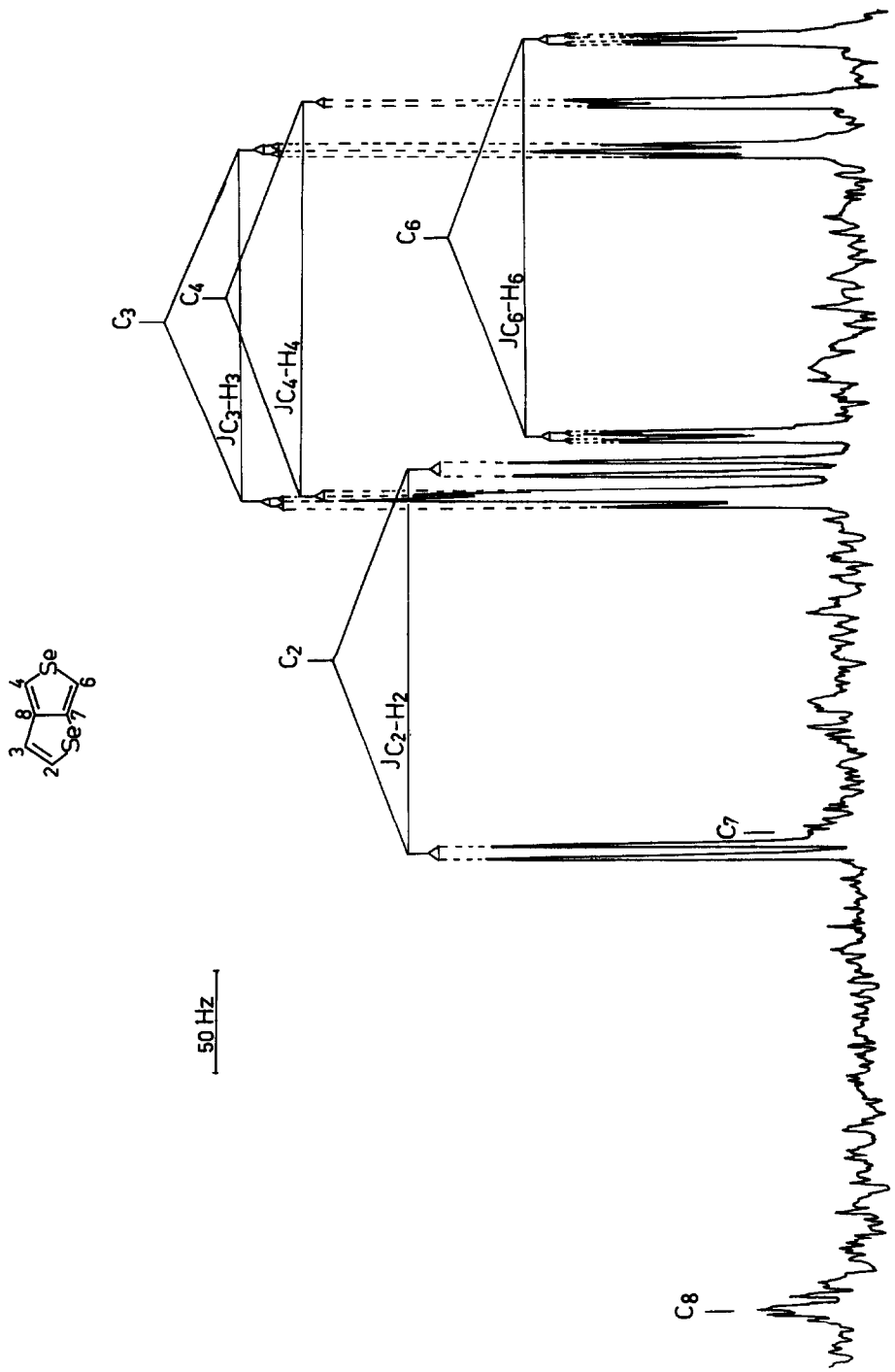


Fig. 1. ^{13}C NMR spectrum of selenolo[3,4-*b*]selenophene in acetone-d_6 at 15.04 MHz.

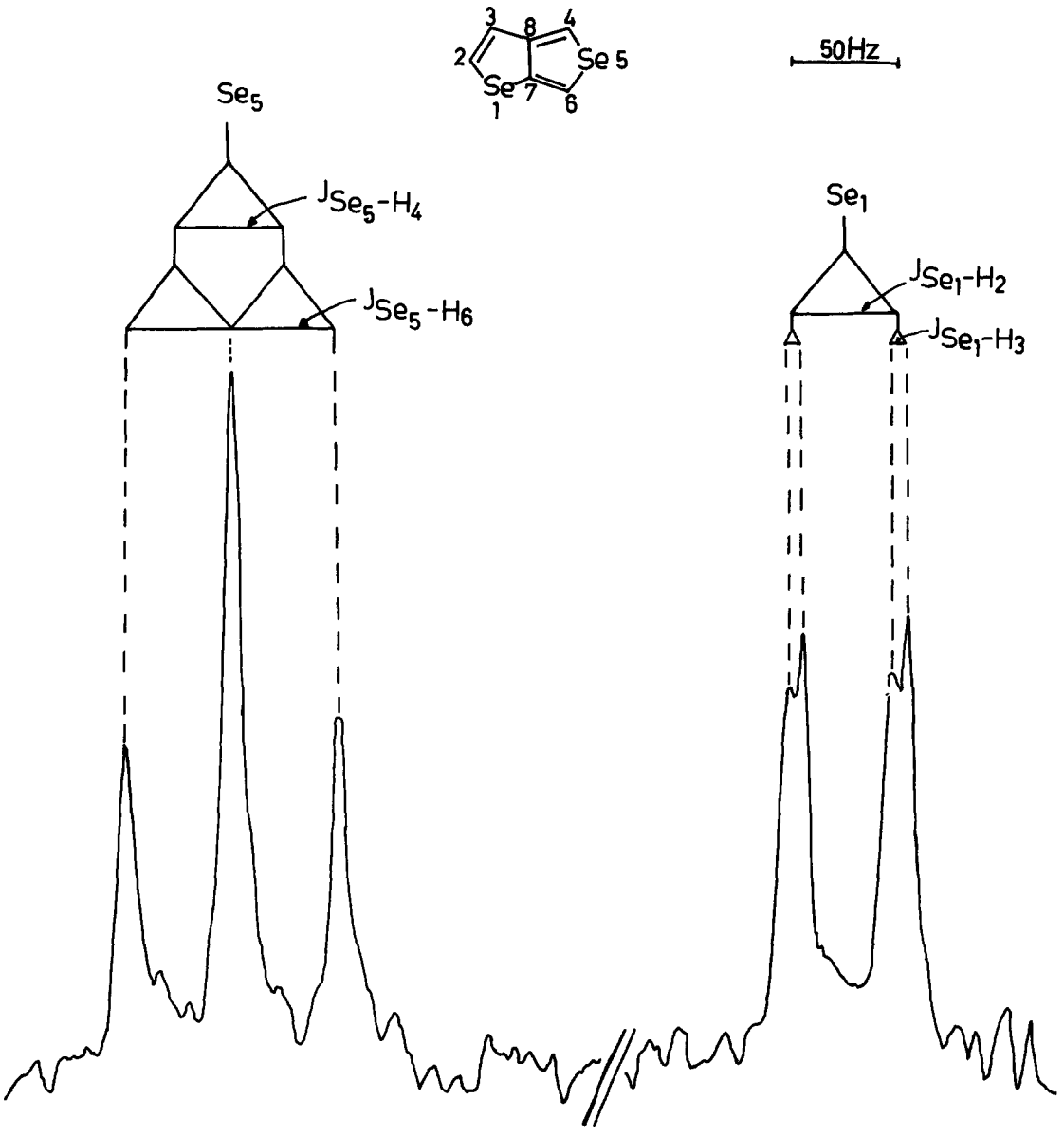


Fig. 2. ^{77}Se NMR spectrum of selenolo[3,4-*b*]selenophene in acetone-d_6 at 19.135 MHz.

Table 1. Comparison of melting points and assignments of the three isomeric selenoloselenophenes, as reported in Ref. 2 and by present authors

Item	M.p./b.p.		Picrate m.p.		Tetrabromo derivative m.p.		Assignment	
	Ref. 2	Refs. 1, 3 and this work	Ref. 2	This work	Ref. 2	This work	Ref. 2	This work
1	51-51.5°	56-57°	154-155.5°	152-154°	252.5-253°	252-254°	**2**	**1**
2	123-124.5°	127.5-128°	163-165°	162-164°	246-247.5°	246-248°	**3**	**2**
3	90-93°/14mmHg	46-47°	unstable oil	113°(dec.)	271-272°	*)	**1**	**3**

*) **3** decomposes rapidly when brominated with bromine in carbon disulfide under conditions of Ref. 2.

disagreement of the results obtained for **3** and its derivatives, make it most likely that the compound with b.p. 93-99°/14 mm Hg described by Umezawa, in spite of the results of the elemental analysis, was not selenolo[3,4-*b*]selenophene (**3**). Neither is it easy to believe that **3** would survive the conditions employed in the preparation of selenophene from acetylene and selenium, from which reaction Umezawa claimed isolation of all three selenophtenes **1-3**. On the other hand, it can now be concluded that both **1** and **2** were, in fact, isolated by Umezawa, though in our preparation of selenophene[19] only selenolo[3,2-*b*]selenophene (**2**) was formed.[1]

EXPERIMENTAL

The ^{1}H NMR spectra were obtained on a JEOL MH 100 high resolution spectrometer. The ^{13}CNMR spectra were obtained at 15.04 MHz with a JEOL JMN-60 spectrometer with a built-in JEOL 980A computer with 12K memory. The ^{77}Se NMR spectra were obtained at 19.135 MHz on a Varian XL-100-15 spectrometer equipped with frequency sweep, proton wide band decoupler and Fourier transform operation. Field-frequency control (lock) was effected by means of the deuterium resonance of hexadeuterioacetone or hexadeuteriodimethyl sulfoxide. Mass spectra were recorded on a Finnigan Model 4021 mass spectrometer and analytical glc was carried out with a Perkin–Elmer 900 gas chromatograph connected to a Varian 480 digital integrator. The integrator was not calibrated. A Dexil 300 3% on Chromosorb W AW column was used for all gas chromatographic analyses. The IR spectra were recorded on a Perkin–Elmer 257 instrument. Elemental analyses were carried out by Ilse Beetz, Mikroanalytisches Laboratorium, Kronach, Germany.

2,3-*Bischloromethyl-5-carbomethoxyselenophene* (**4**). A soln of 66.2 g (0.35 mol) of 2-carbomethoxyselenophene (b.p.$_{15}$ 98-99°, n_D^{20} 1.5731; lit.[20]: b.p.$_{18}$ 95.5-96°C, n_D^{20} 1.5732) in 50 ml chlorodimethyl ether was added dropwise to a stirred suspension of 47.7 g (0.35 mol) of water-free $ZnCl_2$ in 400 ml chlorodimethyl ether. The temp rose to about 50° during the addition. After the addition was complete, the mixture was refluxed for 6 hr. During the first hr of reflux, the colour changed from nearly colourless to deep red. The red soln was then cooled to room temp and poured onto 800 g crushed ice, with stirring. After stirring for 2 hr, the initially formed light-brown oil solidified. The solid was removed by filtration, washed with cold water and dried in a rotatory evaporator at 40°, cooling the receiver in ice. The dried solid was crystallized from petroleum ether (b.p. 40-60°), which furnished 87.1 g (87%) of light-yellow needles, m.p. 55-56°. NMR ($CDCl_3$): δ 3.87 (s, 3 H, CH_3), 4.55 (s, 2 H, CH_2), 4.84 (s, 2 H, CH_2), 7.98 (s, 1 H, H_4) (Found: C, 33.71; H, 2.87; Cl, 24.71; Se 27.75. Calc. for $C_8H_8Cl_2O_2Se$: C, 33.60; H, 2.82; Cl, 24.79; Se, 27.61%).

2-*Carbomethoxy*-4 H,6 H-*dihydroselenolo*[3,4-b]*selenophene* (**5**). To a colourless soln of 0.55 mol sodium hydrogen selenide in 750 ml abs EtOH prepared according to Ref. 21, 19.3 g (0.050 mol) of solid **4** was added in small portions during 5 hr with stirring at room temp under N_2. After complete addition, the mixture was stirred overnight at room temp and the NaCl was filtered off. The filtrate was concentrated to about 200 ml and poured into 1 l. water. The resulting white suspension was extracted with $CHCl_3$ and then the combined extracts were dried over $MgSO_4$ and concentrated, affording 10.3 g (70%) of a yellow, crystalline residue, the mass spectrum of which indicated the presence of **6**. Separation of the desired **5** from its dimer **6** could be achieved by fractional crystallization from aqueous EtOH, which gave 1.8 g (12%) of the dihydroselenophtene as light yellow needles, m.p. 85-86°. NMR ($CDCl_3$): δ 3.84 (s, 3 H, CH_3), 7.71 (s, 1 H, H_3) and a strongly coupled AA'BB' spectrum of the methylene protons centred at 4.03 and 4.26. (Found: C, 32.65; H, 2.72; Se, 53.66. Calc. for $C_8H_8O_2Se_2$: C, 32.67; H, 2.74; Se, 53.70%). Dimer **6**, 7.8 g; 53%) m.p. 227-229°, was obtained after recrystallization from pyridine/water (9:1). Owing to its low solubility in organic solvents, no NMR spectrum could be recorded. Both the mass spectrum and the elemental analysis were in agreement with the dimeric structure of **6**. In the mass spectrum, the peaks centred at *m/e* 592 (M^+) and at *m/e* 296 (base peak), showed the same pattern as a spectrum simulated for four and for two selenium atoms, respectively. (Found: C 32.67; H 2.89; Se 53.54. Calc. for $C_{16}H_{16}O_4Se_4$: C 32.67; H 2.74; Se 53.70%).

2-*Carbomethoxy*-4 H,6 H-*dihydroselenolo*[3,4-b]*selenophene 5-oxide* (**7**). To a soln of 1.5 g (5.1 mmol) of **5** in 10 ml dry THF, placed at -22° in the freezing room, a soln of 1.0 g (8.8 mmol) 30% H_2O_2 in 5 ml dry THF was added dropwise with stirring. After stirring overnight at -22°, the colourless ppt was filtered off giving 1.1 g of the selenoxide. The filtrate was concentrated *in vacuo* and filtered to give an additional 0.2 g of the selenoxide, i.e. 82% yield, m.p. 80-83° (dec). All attempts at purification resulted in decomposition. (Found: C, 31.35; H, 2.72; Se, 50.03. Calc. for $C_8H_8O_3Se_2$: C, 30.99; H, 2.60; Se, 50.93). Due to the low solubility of the selenoxide in $CDCl_3$, $CDBr_3$ and C_6D_6, the NMR spectrum could only be recorded in DMSO-d_6 solution. If the spectrum was recorded immediately after dissolving the compound, the expected signals of the methylene protons appeared as two singlets at δ 3.80 and 3.82, together with a singlet for the aromatic proton H_3 at δ 7.92 and a singlet at δ 3.86 (s, 3 H, CH_3). If, however, the spectrum was recorded after a short period of time the intensity of the methylene signals decreased and the aromatic part of the spectrum indicated formation of the selenolo[3,4-*b*]selenophene system. Thus, the two α-protons of the selenophene ring appeared at δ 8.81 (d, 1H, H_4) and 8.42 (2d, 1H, H_6) with the coupling constant $J_{H4\text{-}H6}$ = 2.4 Hz and a long-range coupling to the β-proton of the other ring, $J_{H3\text{-}H6}$ = 0.8 Hz. This proton gave a signal at δ 8.12 (d, 1H, H_3), and the carbomethoxy group at δ 3.88 (s, 3H, CH_3).

2-*Carbomethoxyselenolo*[3,4-b]*selenophene* (**8**). The selenoxide **7** (1.1 g, 3.5 mmol) was dissolved in 15 ml Ac_2O, whereupon a spontaneous exothermic reaction took place and the soln became very dark. After stirring at room temp for 0.5 hr, the Ac_2O was hydrolyzed with water, the mixture was extracted with ether and the ether extracts were washed with sat $NaHCO_3$aq and water, dried over $MgSO_4$ and concentrated. Recrystallization of the half-crystalline residue from petroleum ether (b.p. 40-60°) gave 0.56 g (55%) of the title compound, m.p. 74-76°. All spectroscopic data were in accordance with those for 2-carbomethoxyselenolo[3,4-*b*]selenophene prepared by esterification of the acid **9** with diazomethane, where the acid was obtained by the independent route (see below) of Scheme 2.

2-*Carboxyselenolo*[3,4-b]*selenophene* (**9**). The ester **8** (0.29 g, 1.0 mmol) was dissolved in 20 ml 10% KOHaq in MeOH and warmed to 50° for 2 hr, with stirring under N_2. After cooling to 0°, the soln was acidified with ice-cold 1 N HCl and the yellow ppt was filtered off and then recrystallized from acetone. 0.19 g (68%) of the acid **9** was obtained. All physical and spectroscopic properties were in accordance with those for 2-carboxyselenolo[3,4-*b*]selenophene prepared by the independent route of Scheme 2 (see below).

Decarboxylation of **9** with copper in quinoline is described below.

4-*Bromo-3-methylselenoselenophene*. A soln of 70.0 g (0.242 mol) of 3,4-dibromoselenophene[22] in 250 ml of dry ether was cooled to −70° and 159 ml of 1.53 N n-butyllithium (0.243 mol) in hexane diluted with 100 ml of dry ether was added dropwise with stirring under N_2 at such a rate that the temp did not exceed −69°. The addition took 1 hr and, after stirring for an additional 30 min at −70°, a soln of 45.1 g (0.240 mol) of dimethyl diselenide in 100 ml dry ether was added dropwise at −70°. The mixture was allowed to reach +5° and was hydrolyzed with 350 ml of ice-cold 2 N HCl. After stirring for 1 hr, the aqueous phase was separated, extracted twice with ether and the combined ethereal solns washed with $NaHCO_3$aq and water, then dried over $MgSO_4$

and concentrated. The dark residue was distilled under N_2 at 12 mm Hg, giving, after a small fore-run of the starting 3,4-dibromoselenophene, 55.8 g (76.1%) of the title compound as a light yellow, viscous oil, b.p.$_{12}$ 159-160°. NMR ($CDCl_3$): δ 2.32 (s, 3H, -$SeCH_3$), $J_{^{77}Se-CH_3}$ = 11.6 Hz; 7.62 (d, 1H, H_2), 7.93 (d, 1H, H_5); J_{H2-H5} = 3.0 Hz. Assignments of the chemical shifts of the two aromatic protons were based on known substituent-caused shifts. (Found: C, 19.91; H, 1.80; Se, 52.07. Calc. for $C_5H_5BrSe_2$: C, 19.82; H, 1.66; Se, 52.13%).

4-*Methylseleno-3-selenophene aldehyde* (**10**). To a soln of 108 ml of 1.53 N n-butyllithium (0.165 mol) in hexane diluted with 100 ml dry ether was added, dropwise with stirring, 45.4 g 0.150 mol) 4-bromo-3-methylselenoselenophene in 100 ml dry ether, under N_2 at −70°, at such a rate that the temp did not exceed −68°. After an additional 30 min at −70°, 12.4 g (0.170 mol) of freshly distilled dimethylformamide in 100 ml dry ether was added dropwise and the mixture was allowed to reach room temp, then cooled to +5° and hydrolyzed with 300 ml ice-cold 2 N HCl. After stirring for 1 hr, the mixture was worked up as in the synthesis of 4-bromo-3-methyl-selenoselenophene and the very dark residue obtained was fractionated under N_2 at 1.5 mm Hg, giving 27.2 g (71.9%) of 4-methylseleno-3-selenophene aldehyde as an orange oil, b.p.$_{1.5}$ 141–144.5°. Another distillation gave a fraction with b.p.$_{1.5}$ 144–144.5°, which solidified on standing. The orange solid yielded, after recrystallization from ligroin, fine yellow needles with m.p. 39–40°. NMR ($CDCl_3$): δ 2.30 (s, 3H, -$SeCH_3$), $J_{^{77}Se-CH_3}$ = 12.7 Hz; 7.50 (2d, 1 H, H_5), 9.00 (d, 1H, H_2), 9.91 (d, 1H, CHO), J_{H2-H5} = 2.9 Hz, J_{H5-CHO} = 0.8 Hz. These assignments are in good agreement with the published NMR spectrum of 4-methylseleno-3-thiophene aldehyde.[23] (Found: C, 28.71; H, 2.34; Se, 62.71. Calc. for $C_6H_6OSe_2$: C, 28.59; H, 2.40; Se, 62.66).

2-*Carboxyselenolo*[3,4-b]*selenophene* (**9**). A mixture of 12.6 g (0.050 mol) of 4-methylseleno-3-selenophene aldehyde, 7.6 g (0.050 mol) of methyl bromoacetate and 7 ml toluene was heated at 120° under N_2 for 2 days. The toluene was then distilled off under reduced pressure and 40 ml freshly distilled Ac_2O and 25 ml dry pyridine were added to the dark residue, whereupon the mixture was refluxed under N_2 for 4 hr. The solvents were then evaporated *in vacuo* and a soln of 10 g KOH in 70 ml dry MeOH was added to the residue. After 2 hr refluxing, the mixture was concentrated to dryness, dissolved in water, filtered, cooled and acidified with dil HCl leaving 8.5 g (61%) of brown, amorphous solid. Recrystallization from aqueous acetone gave 6.7 g (48%) of light yellow, glistening crystals, decomposing above 204° into elemental Se without melting. NMR (DMSO-d_6): δ 7.81 (d, 1H, H_3), 8.23 (2d, 1H, H_6), 8.69 (d, 1H, H_4), J_{H4-H6} = 2.3 Hz, J_{H3-H6} = 0.75 Hz. IR (C=O): 1650 cm^{-1}. (Found: C, 30.36; H, 1.54; Se, 56.91. Calc. for $C_7H_4O_2Se_2$: C, 30.24; H, 1.45; Se, 56.80). ^{13}C NMR (DMSO-d_6): δ (ppm) relative to TMS as an internal standard: 139.8 (C-2), 127.1 (C-3), 128.1 (C-4), 120.8 (C-6), 136.0 (C-7), 150.2 (C-8), 165.2 (CO_2H). $^1J_{C3-H3}$ = 170.9 Hz, $^1J_{C4-H4}$ = 192.9 Hz, $^1J_{C6-H6}$ = 195.3 Hz.

2-*Carbomethoxyselenolo*[3,4-b]*selenophene* (**8**). Esterification of 280 mg (0.001 mol) of the acid with diazomethane gave 260 mg (89%) of the methyl ester, m.p. 74–76°. NMR ($CDCl_3$): δ 3.88 (s, 3H, -CO_2CH_3), 7.82 (d, 1H, H_3), 7.92 (2 × d, 1H, H_6), 8.15 (d, 1H, H_4); J_{H4-H6} = 2.4 Hz, J_{H3-H6} = 0.8 Hz. IR (C=O): 1655 cm^{-1}. (Found: C, 33.01; H, 1.98; Se, 54.24. Calc. for $C_8H_6O_2Se_2$: C, 32.90; H, 2.07; Se, 54.07).

Selenolo[3,4-b]*selenophene* (**3**). To a soln of 1.40 g (5.0 mmol) of **9** in 50 ml freshly distilled quinoline, 0.50 g (7.8 mmol) copper bronze was added and the mixture heated to 180 under N_2 until the calculated volume of CO_2 (112 ml) was collected over sat NaCl aq. This took about 0.5 hr, whereupon the quinoline and liquid selenophtene were distilled off at reduced pressure, diluted with ether and cooled to 0°. The colourless soln was then carefully washed with ice-cold 1 N HCl holding the temp at 0°, as **3** is sensitive to acid. The ether soln was washed with water to neutral pH, dried over $MgSO_4$ and concentrated to give 0.85 g (72%) of a light brown oil, which solidified on cooling. Recrystallization of **3** could be achieved, though with some decomposition, by dissolving it in warm pentane and cooling to −70°, which gave analytically pure, slightly yellow, glistening crystals, m.p. 46–47°. NMR ($CDCl_3$): δ (ppm) 8.03 (d, 1H, H_4), 7.84 (2d, 1H, H_6), 7.78 (d, 1H, H_2), 7.00 (2d, 1H, H_3), J_{H2-H3} = 6.2 Hz, J_{H4-H6} = 2.4 Hz, J_{H3-H6} = 0.8 Hz.

In the mass spectrum, the peaks centred at *m/e* 236 (M^+ and base peak) showed the same pattern as a spectrum simulated for two Se atoms. Single-atom Se patterns were observed at *m/e* 156 (M^+-Se), *m/e* 117 (C_3HSe), *m/e* 105 (C_6HSe) and *m/e* 93 (CHSe).

^{13}C and ^{77}Se NMR spectra of **3** were described in the text. (Found: C, 30.94; H, 1.81; Se, 67.63. Calc. for $C_6H_4Se_2$: C, 30.80; H, 1.72; Se, 67.48).

Acknowledgements—Grants from the Swedish Natural Science Research Council to S.G. are gratefully acknowledged.

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