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Synthesis of Areneselenenyl Benzenesulfinates and Benzenethiosulfonates, and Tetraphenylarsonium Areneselenenyl Sulfites and Thiosulfates

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A large number of stable aromatic selenenyl sulfur compounds, ArSeSR, have been isolated (for a review see Ref. 1). Many of these compounds have an NO_2-group in the *ortho* position of the areneselenenyl group.[2] The ability of Se(II) to achieve coordination numbers higher than two probably serves to make these compounds more stable due to an intramolecular bonding between the selenium atom and one of the oxygen atoms of the nitro group.[3]

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In this note we present the synthesis of some new aromatic selenenyl sulfur compounds which do not have any stabilizing groups in the *ortho* position. The various compounds are listed in Table 1.

Aromatic selenenyl benzenesulfinates were prepared from the corresponding aromatic selenenyl bromides and sodium benzenesulfinate in carbon tetrachloride, eqn. 1.

$$p\text{-}XPhSeBr + PhSO_2Na \rightarrow$$

$$p\text{-}XPhSeS(O)_2Ph + NaBr \qquad (1)$$

(X = H, Cl, and Me).
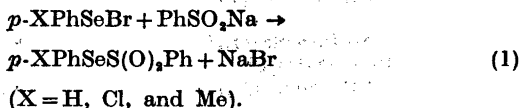
Aromatic selenenyl benzenethiosulfonates could be prepared from the corresponding aromatic selenenyl bromides and sodium benzenethiosulfonate in carbon tetrachloride, eqn. 2.
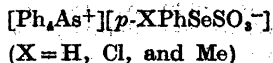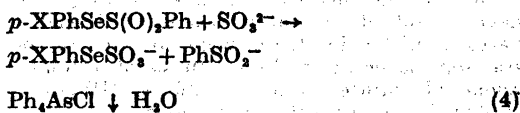
$$p\text{-}XPhSeBr + PhS(O)_2SNa \rightarrow$$

$$p\text{-}XPhSeSS(O)_2Ph + NaBr \qquad (2)$$

(X = H, Cl, and Me).
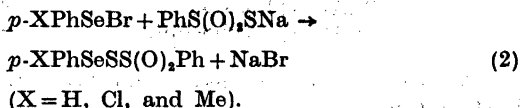
Analogous sulfur compounds, which have an NO_2-group in the *ortho* position of the arenesulfenyl group, have been isolated.[4]

Tetraphenylarsonium salts of aromatic selenenyl sulfites. A number of organic selenosulfates, seleno Bunte salts, have been prepared by the action of selenosulfate on alkyl chlorides or bromides in water or aqueous ethanol, eqn. (3) (see Ref. 1, p. 151).

$$R - X + SeSO_3{}^{2-} \rightarrow R - SeSO_3{}^- + X^- \qquad (3)$$
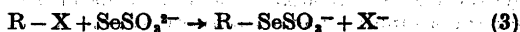
However, in most cases the resultant organic selenosulfate was converted *in situ* to the corresponding diselenide. Until now, no aromatic seleno Bunte salt has been reported. We found that tetraphenylarsonium salts of aromatic selenosulfates could be prepared according to eqn. 4, from the corresponding areneselenenyl benzenesulfinates dissolved in ether, by reaction with a mixture of sodium sulfite and tetraphenylarsonium chloride dissolved in water:

$$p\text{-}XPhSeS(O)_2Ph + SO_3{}^{2-} \rightarrow$$

$$p\text{-}XPhSeSO_3{}^- + PhSO_2{}^-$$

$$Ph_4AsCl \downarrow H_2O \qquad (4)$$

$$[Ph_4As^+][p\text{-}XPhSeSO_3{}^-]$$

(X = H, Cl, and Me)

The aromatic selenosulfate formed is immediately precipitated as a tetraphenylarsonium salt prior to the formation of any diaryldiselenide.

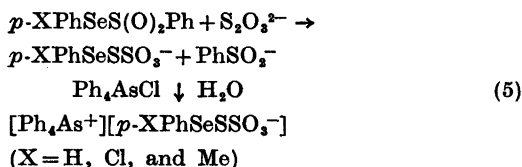Pyridinium *S*-aryl thiosulfates have been prepared by Baumgarten.[5]

Table 1. New selenenyl sulfur compounds prepared in this work.

Compound	Mp. °C	Sulfur, % Calc.	Found [a]
p-MePhSeS(O)$_2$Ph	54	10.3	10.5
PhSeS(O)$_2$Ph	51	10.7	11.2
p-ClPhSeS(O)$_2$Ph	75 – 77	9.7	10.2
p-MePhSeSS(O)$_2$Ph	89 – 90	18.7	19.0
PhSeSS(O)$_2$Ph	43 – 45	19.5	19.9
p-ClPhSeSS(O)$_2$Ph	84	17.6	18.0
[Ph$_4$As$^+$][p-MePhSeSO$_3^-$]	206	5.1	5.4
[Ph$_4$As$^+$][PhSeSO$_3^-$]	160	5.2	5.7
[Ph$_4$As$^+$][p-ClPhSeSO$_3^-$]	179	4.9	5.0
[Ph$_4$As$^+$][p-MePhSeSSO$_3^-$]	171	9.6	10.0
[Ph$_4$As$^+$][PhSeSSO$_3^-$]	164	9.8	10.2
[Ph$_4$As$^+$][p-ClPhSeSSO$_3^-$]	130	9.3	10.5

[a] The analyses were performed at Ilse Beetz, Mikroanalytisches Laboratorium, 8640 Kronach/OFR., West Germany.

Tetraphenylarsonium salts of aromatic selenenyl thiosulfates. Foss [2] has prepared the potassium salt of o-nitrobenzeneselenenyl thiosulfate, and we earlier have prepared the tetraphenylarsonium salt of the analogous sulfenyl thiosulfate.[6] Tetraphenylarsonium salts of *para* substituted benzeneselenenyl thiosulfates were synthesised in an analogous way as described for the aromatic seleno Bunte salts, eqn. 5.

$$p\text{-}XPhSeS(O)_2Ph + S_2O_3^{2-} \rightarrow$$

$$p\text{-}XPhSeSSO_3^- + PhSO_2^-$$

$$\begin{array}{r} Ph_4AsCl \downarrow H_2O \end{array} \qquad (5)$$

$$[Ph_4As^+][p\text{-}XPhSeSSO_3^-]$$

$$(X = H, Cl, \text{ and } Me)$$

The product immediately separates as a tetraphenylarsonium salt prior to the formation of any diselenide.

Due to the fact that [Ph$_4$As$^+$][PhSO$_2$S$^-$] is nearly insoluble in water,[7] selenenyl thiosulfonates, p-XPhSeSS(O)$_2$Ph, were not used as the starting materials in the synthesis of aromatic selenenyl sulfites and thiosulfates. [Ph$_4$As$^+$]-[PhSO$_2^-$] is easily soluble in water.

Experimental. Water-free PhSO$_2$Na was obtained from Fluka. Water-free PhS(O)$_2$SNa was prepared by dissolving the salt in absolute ethanol containing some benzene. The solvent was removed in vacuum, and the residue was dried carefully.

p-XPhSeCN. The aromatic selenocyanates were prepared from diazotized anilines and potassium selenocyanates: PhSeCN,[8] p-MePhSeCN,[9] and p-ClPhSeCN.[9]

(p-XPhSe)$_2$. The aromatic diselenides were prepared from the respective selenocyanates and potassium hydroxide in ethanol.[10]

p-XPhSeBr. The aromatic selenenyl bromides were synthesised from the diselenides and bromide in dry chloroform.[11] The compounds were recrystallized from light petroleum (40 – 60 °C) and stored in a freezer.

p-XPhSeS(O)$_2$Ph. The general procedure is analogous to the one used by Foss [12] to prepare aromatic sulfinates of divalent selenium. It consists in dissolving 2.0 × 10^{-3} mol of the aromatic selenenyl bromide in 45 ml of dry CCl$_4$. 2.2 × 10^{-3} mol, i.e., 10 % excess of finely powered, dry sodium benzenesulfinate was added to the deep red selenenyl bromide solution. The mixture was stirred at room temperature until the solution became yellow. Sodium bromide and excess of sodium benzenesulfinate were filtered off, and the solvent was removed in vacuum. The product, which appeared as a semi-solid oil, was dissolved in about 25 ml of ether. About 5 ml of light petroleum (40 – 60 °C) was added, and the solution was left in a freezer and then in a dry-ice acetone mixture. The product crystallized as a stable yellowish-green compound. Yield 80 – 85 % based on the amount of aromatic selenenyl bromide.

p-XPhSeSS(O)$_2$Ph. The procedure for the preparation of aromatic selenenyl benzenethiosulfonates is analogous to the one described for the selenenyl sulfinates. 7.3 × 10^{-3} mol of the aromatic selenenyl bromide was dissolved in about 20 ml of CCl$_4$, and 8.0 × 10^{-3} mol of finely powered, dry sodium benzenethiosulfonate was added. The solution was

stirred at room temperature until it became yellowish-green. The product was recrystallized from 10 ml of ether. Yield 70 – 75 % based on the amount of the selenenyl bromide.

[Ph_4As^+][p-$XPhSeSO_3^-$]. The aromatic seleno Bunte salts were prepared from the corresponding selenenyl benzenesulfinates, $Na_2SO_3.7H_2O$, and $Ph_4AsCl.2H_2O$ according to the following procedure. A solution, made by dissolving 3.4×10^{-3} mol of the aromatic selenenyl sulfinate in 15 ml of ether, was added under vigorous stirring at room temperature to a solution containing 3.8×10^{-3} mol of each of the reagents $Na_2SO_3.7H_2O$ and $Ph_4AsCl.2H_2O$ in 25 ml of water. The reaction mixture was stirred for 5 min, and the product separated as a white crystalline compound. The salt was filtered off, washed carefully with cold water and drained well. The product was recrystallized from about 10 ml of warm acetonitrile by the addition of some ether. Yield ca. 85 % based on the amount of selenenyl sulfinate.

[Ph_4As^+][p-$XPhSeSSO_3^-$]. The tetraphenylarsonium salts of aromatic selenenyl thiosulfates were prepared from the corresponding selenenyl benzenesulfinates, $Na_2S_2O_3.5H_2O$, and $Ph_4AsCl.2H_2O$. The procedure is analogous to that described above for the preparation of the corresponding selenenyl sulfite salts. The products, which appeared as yellowish-green compounds, were recrystallized from acetonitrile by the addition of some ether. Yield 85 – 90 % based on the amount of the selenenyl benzenesulfinate.

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On Comparisons of Structural Information Obtained from Microwave Spectroscopy and from Electron-diffraction Studies of Gaseous Chlorobutatriene and Chlorobutenynes

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In recent electron-diffraction studies on the molecular structures of gaseous C_4H_3Cl isomers [1-4] the moments of inertia calculated from the structural results were compared to values obtained from microwave spectroscopy.[5-9] The comparisons were based upon the assumption that the average distances r_α and r_z [10] are comparable quantities, and the corresponding moments of inertia are given in Table 1. They were derived from the operational parameters, respectively, for electron diffraction (r_a) and microwave spectroscopy (r_0) [10] using similar force fields for computation of the necessary correction terms as described previously.[1-9]

However, r_α should be corrected to r_α^0 in order to represent the distance between the mean positions of a pair of atoms in the zero-point level as does the r_z parameter.[10]

$$r_\alpha^0 = r_\alpha + (K - K_0) - \tfrac{3}{2}a(l^2 - l_0^2) \qquad (1)$$

where K_0 and l_0 are the perpendicular amplitude correction coefficient and the root-mean-square amplitude of vibration at absolute zero, and a is an anharmonicity constant which for bond distances is usually about 2 Å^{-1}.[10] The correction is dominated by the $K - K_0$ term and r_α is therefore smaller than r_α^0 by an amount which was assumed to be negligible. A closer examination of the moments of inertia for all five isomers (Table 1) reveals, however, that those obtained from the electron-diffraction data (r_α) are all smaller than the corresponding microwave ones (r_z). Although the discrepancies are smaller than the estimated error limits,[1-4] the similar trend indicates the presence of some systematic error. The approximation applied by using r_α rather than r_α^0 was therefore reconsidered. The K_0- and l_0-values were computed from the force fields described previously for the five compounds [1-4] and the corresponding moments of inertia based upon r_α^0-parameters ($a = 2$ Å^{-1}) are given in Table 1. The correction introduced removed