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# The Anodic Acetoxylation of Alkylarylselenides

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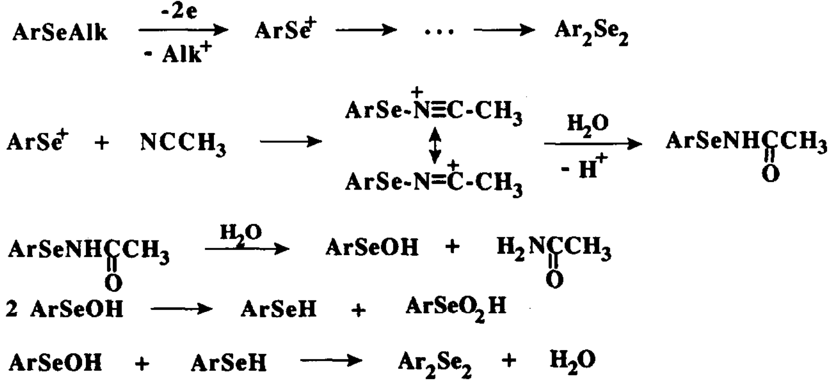
***Abstract:*** *Electrooxidation of alkylarylselenides in methanol in the presence of sodium acetate leads to the acetoxylation of the methylene group of selenides*

The organic compounds of selenium, particularly phenylseleno compounds,[2] can be of wide use in the processes of electrochemical functionalization of organic molecules.[3] As a rule, the transformations do not affect the phenylseleno group, and it is the organic saturated radical on the selenium that undergoes functionalization. Generally, these reactions result in the formation of a double bond between α and β carbon atoms after elimination of the phenylseleno fragment. We have shown, however, that this is just one of the two possible reaction pathways of the cation radicals of alkylphenylselenides, the two pathways being rupture of a Se-$C_{sp^3}$ bond (dealkylation) and deprotonation[4].

For a large number of alkylarylselenides, carrying ArSe moiety, the primary products of electrooxidation in "dry" acetonitrile were shown by commutative voltammetry at the rotating disk electrode to be cation radicals. While radical cations of thioanisoles and arylsulfides, being relatively stable, react in second order reactions[5], a consecutive reaction of the cation radicals of isologous selenides occurs very rapidly as a first order one ($\Delta E_{1/2}/\ \Delta \lg \omega = 30$mV).

Exhaustive electrooxidation of arylselenides with different alkyl substituents on the selenium produces corresponding diaryldiselenides as the final selenium-containing products. A sequence of transformations leading to diaryldiselenide begins with the fission of the Se-$C_{sp^3}$ bond of the cation radical. The resulting $ArSe^+$ cation exists for some time in solution, probably as a complex with acetonitrile; hydrolysis of this complex by residual water leads to a diselenide:[6]



$$ArSeAlk \xrightarrow[-\ Alk^+]{-2e} ArSe^+ \longrightarrow \cdots \longrightarrow Ar_2Se_2$$

$$ArSe^+ + NCCH_3 \longrightarrow \begin{matrix} ArSe\text{-}\overset{+}{N}\equiv C\text{-}CH_3 \\ \updownarrow \\ ArSe\text{-}N{=}\overset{+}{C}\text{-}CH_3 \end{matrix} \xrightarrow[-\ H^+]{H_2O} ArSeNH\underset{\overset{\|}{O}}{C}CH_3$$

$$ArSeNH\underset{\overset{\|}{O}}{C}CH_3 \xrightarrow{H_2O} ArSeOH + H_2N\underset{\overset{\|}{O}}{C}CH_3$$

$$2\ ArSeOH \longrightarrow ArSeH + ArSeO_2H$$

$$ArSeOH + ArSeH \longrightarrow Ar_2Se_2 + H_2O$$

Seleninic acid, being a strong oxidant, reacts with components of the solution to give $Ar_2Se_2$ as well.

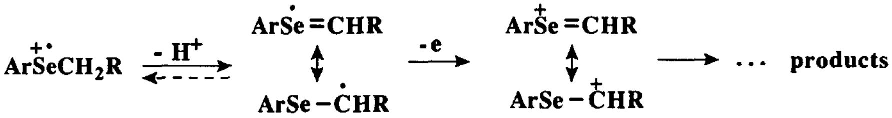
When increasing the water content of the solution, syn-elimination of selenoxide becomes more important in the formation of diselenide. This reaction affects all alkylarylselenides, exept selenoanisole and selenides lacking β-methylene protons. In the case of arylselenide with *tert*-butyl radical, which is known to be a more stable leaving group, it is rupture of the bond which takes place, but not syn-elimination. The results of electrolyses are summarized in Table 1.

**Table 1.** Formation of Diaryldiselenides during the course of Electrooxidation of Alkylarylselenides

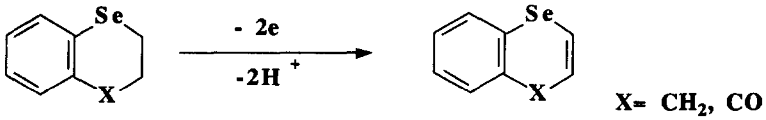
| Entry | Selenide | E, V[a] | F/mol | Yield, (%)[b] |
|---|---|---|---|---|
| 1 | $C_6H_5SeCH_3$ | 1.00 | 2.0 | 5-10 |
| 2 | $C_6H_5SeCH_3$[c] | 1.00 | 2.0 | trace |
| 3 | $p\text{-}CH_3C_6H_4SeCH_3$ | 0.90 | 2.0 | 17 |
| 4 | $p\text{-}BrC_6H_4SeCH_3$ | 1.10 | 2.0 | 11 |
| 5 | $p\text{-}NO_2\text{-}C_6H_4SeCH_3$ | 1.20 | 2.1 | 5 |
| 6 | $C_6H_5SeC_2H_5$ | 1.00 | 2.0 | 47 |
| 7 | $C_6H_5SeC_3H_7$ | 1.05 | 2.0 | 68 |
| 8 | $C_6H_5SeC_3H_7\text{-}i$ | 1.05 | 2.1 | 83 |
| 9 | $C_6H_5SeC_4H_9\text{-}i$ | 1.10 | 2.0 | 88 |
| 10 | $C_6H_5SeC_5H_{11}$ | 1.10 | 2.1 | 70 |
| 11 | $C_6H_5SeC_5H_{11}\text{-}i$ | 1.10 | 2.1 | 78 |
| 12 | $C_6H_5SeC_6H_{13}$ | 1.10 | 2.0 | 71 |
| 13 | $C_6H_5SeC_4H_9\text{-}t$ | 1.12 | 2.2 | 97 |

a ) controlled potential of electrolysis *vs*. Ag/ 0.1 M $AgNO_3$ in acetonitrile. b) yields are based on isolated products. c) pyridine in excess was added.

During the oxidation of methyl and ethyl phenylselenides a considerable amount of unidentified resin was formed; this resin was shown by the colour reaction[7] and by IR-spectroscopy to contain a selenonium group. These products were formed as a result of polymerisation of cationic intermediates after deprotonation of the original radical cation. Individual products of deprotonation have not been described so far.



The only example of deprotonation yielding a stable product, is formation of selenochromene and selenochromenone by anodic oxidation of selenochromane and selenochromanone, respectively[8]:



In the absence of external nucleophiles the deprotonation leads to unsaturated derivatives. The yield of selenochromenone is greater than that of selenochromene while the carbonyl group at the γ-position to selenium favours the deprotonation of the β–carbon and protects the final product from further oxidation.

The yields of diselenides, reflecting the relative rates of dealkylation and deprotonation of radical cationes, are self-explanatory; the reactivity of radical intermediates is determined by localization of the positive charge on the selenium atom, which is affected by such factors as electron-donor properties of the substituents on the aromatic ring, both inductive and steric effects of the alkyl group attached to the selenium (i.e. the stability of the alkyl leaving group), as well as the nucleophilicity and basicity of the medium.[9]

As can be seen, the reactivity of the radical cations of alkylarylselenides is quite different from that of alkylarylsulfides,[10] for which an oxidative rupture of $S\text{-}C_{cp}3$ bond is less typical[11] and α-functionalization of sulfides occurs smoothly in good yields[12]. In contrast, α-functionalization of selenides by anodic substitution was reported only for arylselenides bearing electron-withdrawing groups.[13] Methyl and ethyl phenylselenides devoid of such groups afford only a trace amount of the acetoxylated product; fluorinated product was not obtained at all.[13b] Nevertheless, keeping in mind the reversibility of deprotonation, one can achieve the α-functionalization of the selenides in question too. Thus, the acetoxylation of the methyl group of some selenides, related to selenoanisole, was carried out. The electrophilic center in the selenide has been electroinduced as a result of the deprotonation of the cation radical of selenoanisole, formed by a two electron anodic oxidation of the latter. The conditions of electrolyses and the yields of products are collected in the Table 2.

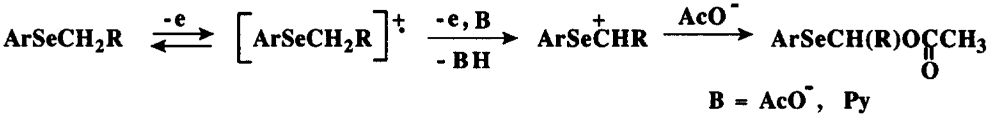
**Table 2.** Anodic Acetoxylation of Alkylarylselenides[14]

| Entry | Selenide | Solvent // supporting electrolyte | E, V[a] | F/mol | Yield, (%)[b] |
|---|---|---|---|---|---|
| 1 | $C_6H_5SeCH_3$ | $CH_3CN + CH_3COOH$ // $CH_3COONa$ | 0.99 | 2.4 | 5-10 |
| 2 | $C_6H_5SeCH_3$ | $CH_3CN$ // $NaClO_4 + CH_3COONa$ | 0.99 | 2.2 | 17 |
| 3 | $C_6H_5SeCH_3$ | $CH_3CN$[c] // $NaClO_4 + CH_3COONa$ | 0.99 | 2.0 | 32 |
| 4 | $C_6H_5SeCH_3$ | $CH_3CN$ // $NaClO_4 + CF_3COOH$ | 0.99 | 1.4 | -[d] |
| 5 | $C_6H_5SeCH_3$ | $CH_3OH$ // $CH_3COONa$ | 0.99 | 2.1 | 87 |
| 6 | $p\text{-}CH_3C_6H_4SeCH_3$ | $CH_3OH$ // $CH_3COONa$ | 0.90 | 2.3 | 63 |
| 7 | $p\text{-}CH_3C_6H_4SeCH_3$ | $CH_3CN$ // $NaClO_4 + CF_3COOH$ | 0.90 | 1.5 | -[e] |
| 8 | $p\text{-}O_2NC_6H_4SeCH_3$ | $CH_3OH$ // $CH_3COONa$ | 1.20 | 2.1 | 92 |
| 9 | $C_6H_5SeC_2H_5$ | $CH_3OH$ // $CH_3COONa$ | 1.00 | 2.4 | 34 |
| 10 | $C_6H_5SeC_2H_5$ | $CH_3OH$ // $CH_3COONa + Na_3PO_4$ | 1.00 | 2.2 | 56 |

a ) *vs* . Ag/ 0.1 M $AgNO_3$ in acetonitrile. b) isolated yields. c) 0.8g of pyridine as a base have been added.d) $Ph_2Se_2$ was obtained in 30% yield. e) ditolyl diselenide was obtained in 47% yield.

A typical procedure was as follows. 1.7 g of selenoanisole (10 mmol) were dissolved in 30 ml of absolute methanol, containing 2.5 g (30 mmol) of molten anhydrous sodium acetate as a source of a nucleophile as well as a supporting salt. In acetonitrile, sodium perchlorate was used as supporting electrolyte while the anhydrous sodium acetate is very poorly soluble in this solvent. The oxidation was carried out in a divided cell at a platinum cylinder (area 45 cm$^2$) as anode and a nickel rod cathode. After passing ca. 2.0 F/mol of electricity, the anolyte was diluted with 50 ml of an aqueous saturated solution of sodium chloride and extracted three times by 30 ml of ether. Evaporation of the solvent and distillation under reduced pressure gave the final product. IR: 1740 $cm^{-1}$ (COO), 1190 $cm^{-1}$ ($CH_3COO$); $^1$H-NMR 60 MHz (ppm, TMS): 1.9 (s,3H), 5.0 (s,2H), 6.6-7.0 (m,5H).

We have tried to employ this process with selenides other than selenoanisoles, for which the deprotonation of the β–position also takes place. Indeed, when selenochromanone was taken as selenide, a mixture of α and β acetoxylated products was obtained in 37% yield. The regioselectivity of the process has not, as yet, been determined. As a whole, anodic acetoxylation of selenides occurs according to the scheme:



$$\mathrm{ArSeCH_2R} \xrightleftharpoons{-e} \left[\mathrm{ArSeCH_2R}\right]^{+\cdot} \xrightarrow[-BH]{-e,\,B} \mathrm{ArSe\overset{+}{C}HR} \xrightarrow{AcO^-} \mathrm{ArSeCH(R)O\underset{\underset{O}{\|}}{C}CH_3}$$

$$B = AcO^-,\ Py$$

For anodic α–functionalization of alkylarylselenides a sufficiently polar non-acid solvent must be chosen in order to favor the solvatation of ionic intermediates but not to suppress their deprotonation equilibrium. For this reason it is more convenient to use the acetoxylating agent in the form of a salt, because the acetoxy anion can also act as a base in this process, trapping the protons to be eliminated, as the weakly dissociated acetic acid.

## References and notes:

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6. Bulk reactions yielding diselenide are relatively slow, because the oxidation wave of the diselenide does not appear on voltammograms of alkylarylselenide recortded at sweep rates higher than 10 mV/s.
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8. Jouikov, V.; Latypova, V.; Postnikova, M.; Kargin, Y. *Zhurn. Obsch. Khim.*, **1987**, *57*, 609.
9. The reactivity of radical cations of alkylarylselenides can be dramatically altered by the presence of electron donor groups, which reduce the positive charge on selenium by trans-annular effect; this study will be reported elsewhere.
10. In the case of selenides, the positive charge of the radical cation is more localized on the heteroatom than in corresponding sulfides; it favours the nucleophilic reactions on this reaction center. For the same reason, while $Ph_2S$ affords sulfonium salts upon oxidation, $Ph_2Se$ provides $Ph_2SeO$. Anodic formation of trisarylselenonium salts also occurs very readily (see Jouikov, V.V. *Electrochemical oxidation of organic sulfides and selenides*, University of Kazan, **1985**).
11. The oxidative rupture of the $S\text{-}C_{cp}3$ bond affording $Ph_2S_2$ in 48% yield was reported only for $Ph_3CSPh$ (see Torii, S.; Uneyama, K. *Tetrahedron Lett.*, **1971**, *4*, 329).
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14. Alkylarylselenides were prepared by described methods, and were distilled prior to use. The identities of the products were established by $^1$H NMR and IR spectroscopy and by element analysis.

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