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Transformation of enals and enones into the glycoside-type derivatives by electrochemical generation of phenyl seleny cation

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The synthesis of tetrahydrofuran- and tetrahydropyran-type cyclic acetals has been achieved by electrochemical cyclization of Δ^4-unsaturated carbonyl compounds. The reaction is performed by electrolysis of these substrates and diphenyl diselenide in a saturated solution of KBr in methanol, by using an undivided cell, whereas graphite and Cu are used as an anode and a cathode, respectively.

The reaction of selenium containing electrophiles with the double bond of organic compounds followed by an attack of the suitable nucleophiles to α-arylselenocarbocations derived at the first stage of this reaction, is the well-known method for the synthesis of 1,2-bifunctional selenium containing organic compounds. This reaction became a powerful tool for organic synthesis because the selenium moiety can be easily removed from an organic molecule either by oxidative or by reductive processes, giving unsaturated or saturated products, respectively[1]. This technique is frequently used for the synthesis of naturally occurring compounds[2]. Further, many naturally occurring organic compounds contain cyclic acetal or ketal moieties, which facilitate the syntheses of glycoside-type compounds. Thus, several articles describing reactions of unsaturated carbonyl compounds with phenylselenenyl halides and corresponding alcohols giving cyclic acetals and ketals (some of which are naturally occurring products) have appeared in the literature[3].

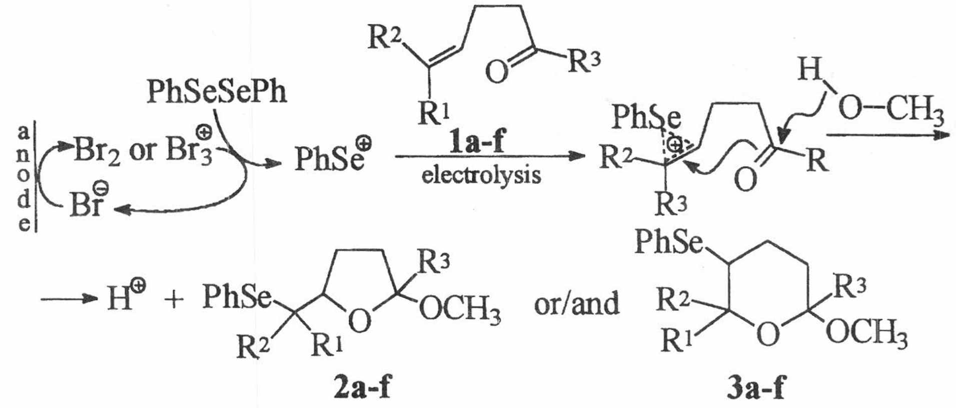
In continuation of our investigations of electrophilic reactions of functionalized[4] or simple alkenes[5] we report herein the transformation of unsaturated aldehydes and ketones into the corresponding cyclic acetals and ketals. According to above mentioned reports from the literature[3] and to our earlier experience gained from reactions of the electrochemically generated $PhSe^{\oplus}$ ion[4], we have chosen this ion as the key intermediate for such type of transformation.

We started our investigations by a constant current electrolysis of Δ^4-alkenals **1a-d** (Scheme I, Table I) in methanol solution of diphenyl diselenide and potassium bromide. The electrolysis was performed in an undivided cell by using a graphite stick as the anode, whereas the cathode was a copper spiral. As expected, the major reaction products were the corresponding selenated glycoside type-compounds, i.e. cyclic acetals containing tetrahydrofuran- or tetrahydropyran-type rings (**2a-d** or **3a-d**), yield 51-60%. These compounds were isolated by column chromatography and identified by IR and NMR spectral data. Besides these compounds, in some cases, small amounts of 2-methoxy-1-phenylseleno-5-alkanals or their actals were also isolated (up to 21 and 15%, respectively).

The data in Table I show that the nature of the double bond of the unsaturated aldehyde exhibit a strong influence on the size of the ring formed.

Table I—Electrochemical cyclization of enals and enones

Compd	R^1	R^2	R^3	Product	Yield (%)
1a	H	H	H	**2a**	56
1b	CH$_3$	H	H	**3b**	52
1c	H	CH$_3$	H	**2c**	54
1d	C$_5$H$_{11}$	H	H	**3d**	60
1e	H	H	CH$_3$	**2e**	59
1f	CH$_3$	CH$_3$	CH$_3$	**2f+3f**	51



R^1 and R^2 = H, CH_3 or C_5H_{11}; R^3 = H or CH_3

Scheme I

Thus, 4-pentenal **1a**, alkenal with the unsubstituted double bond, and *Z*-4-hexenal **1c**, give tetrahydrofuran-type products **2a** and **2c**, respectively whereas *E*-4-hexenal **1b** and *E*-4-decenal **1d** by this reaction give the tetrahydropyran-type products **3b** and **3d**, respectively. We believe that this reaction is stereospecific because each of the four products derived has only one singlet for the methoxyl group in the ^{1}H NMR spectra.

Two Δ^4-alkenones, namely 5-hexen-2-one **1e** and 6-methyl-5-hepten-2-one **1f**, also underwent this reaction. The compound **1e** gave the corresponding tetrahydrofuran-product **2e**, like alkenal **1a** (in 58% yield). On the other hand, the compound **1f** afforded a mixture of products which could not be separated. But on the basis of spectral data the major products obtained were five and six membered cyclic acetals (**2f** and **3f**) accompanied by some other products. Contrary to the cyclization of alkenals, in the case of akenone **1e** two diastereoisomers (*cis* and *trans*) were formed, because there were two singlets for the methoxy group and two for the methyl group in the ^{1}H NMR spectra. The ratio of two diasteroisomers was 39:61. Which one of the two is predominant is yet not known.

We suppose that the reaction starts by the oxidation of bromide ions at the anode for some species (bromine or bromonium ions) which are able to oxidize diphenyl diselenide to the phenylselenium cation. This cation, then, reacts with the double bond of the unsaturated carbonyl compound giving an α-phenylselenyl carbocation which undergo nucleophilic attack at the carbonyl oxygen. This process is probably supported by simultaneous nucleophilic attack of the methanolic oxygen to the carbonyl carbon (see Scheme I).

Experimental Section

In a typical procedure, 154 mg (1 mmole) of **1d** and 156 mg (0.5 mmole) of diphenyl diselenide was electrolyzed in 10 mL of saturated solution of KBr in methanol at a constant current (100 mA; 2 F/mol). At the end of the reaction the yellow colour of diphenyl diselenide disappeared and the solution became colourless. Methanol was evaporated and to the rest was added 20 mL of water. The mixture was extracted with ether and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the reaction mixture on column chromatography (SiO_2/pet. ether-ethyl acetate; 9:1) gave 205 mg of **3d** (60%) and 60 mg of dimethyl acetal of 4-methoxy-5-phenylselenyl-decanal (15%).

The above method used for preparing glycoside-type compounds, which does not require expensive and complex equipment, compares very favourably with existing methods and can be very useful for the synthesis of natural products.

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