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STUDY OF OXIDATION REACTIONS OF 4H-SELENOPYRANS

B. I. Drevko, M. I. Smushkin, L. A. Fomenko,
and V. G. Kharchenko

The oxidation of 4H-4R-2,6-diphenylselenopyrans was studied. This reaction was found to depend on the presence of substituents at $C_{(4)}$ of the heterocycle and the reaction conditions.

We have reported that 4H-thio- and 4H-selenopyrans unsubstituted at $C_{(4)}$ of the heterocyclic ring undergo oxidation by potassium permanganate in acetone or acetonitrile to give 4H-thio- or 4H-selenopyranones [1, 2]. Ring contraction with formation of 2-aroyl-3,5-diarylthio- or 2-aroyl-3,5-diarylselenophenes occurs in the oxidation of 2,4,6-triaryl-4H-thio- or 2,4,6-triaryl-4H-selenopyrans by selenium dioxide [3].

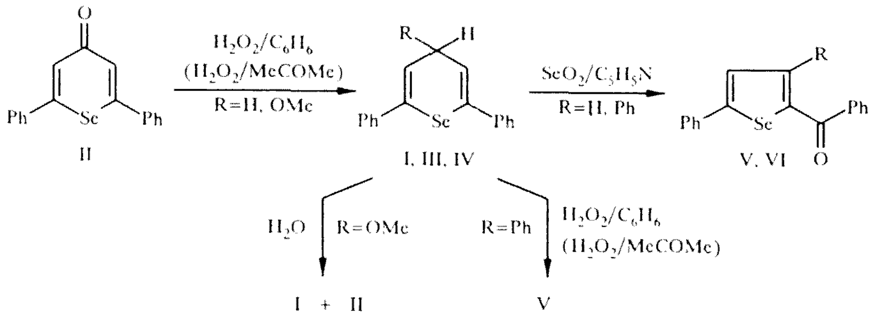
In the present work, we attempted to elucidate the effect of the oxidizing agent, structure of the starting 4H-selenopyran, and reaction conditions on the direction of the oxidation reaction.

Hydrogen peroxide in acetic acid oxidizes polysubstituted thiopyrans to give the corresponding 1,1-dioxides, i.e., the oxidation proceeds at the heteroatom [4]. We carried out the hydrogen peroxide oxidation of 2,6-diphenyl-4H-selenopyran (I) in acetone and benzene (heterogeneous medium). In both cases, we obtained the same product, namely, selenopyran-4-one (II). We should note that II is also formed in the oxidation of 2,6-diphenyl-4-methoxy-4H-selenopyran (III) under analogous conditions.

This transformation of selenopyran III may be attributed to its hydrolysis under the reaction conditions to give 2,6-diphenyl-4-hydroxy-4H-selenopyran and disproportionation of the latter to give selenopyran I and selenopyran-4-one II. Examples of such transformations have been reported for 4-hydroxythio- and 4-hydroxyselenoxanthenes [5]. The capacity of III to undergo hydrolysis may be evaluated relative to its conversion upon storage in solution into a mixture of selenopyran I and selenopyran-4-one II, which is presumably the result of disproportionation of 4-hydroxy-2,6-diphenyl-4H-selenopyran formed in the hydrolysis.

Upon replacement of the methoxy group by a phenyl group, i.e., in the case of 2,4,6-triphenyl-4H-selenopyran (IV), the action of hydrogen peroxide in benzene is accompanied by ring contraction to give 2-benzoyl-3,5-diphenylselenophene (V). Such an oxidation process also occurs using selenium dioxide in pyridine as the oxidizing agent [3]. Hence, we might have expected that pyranone II would be formed upon the action of 4H-selenopyran I, which is unsubstituted at $C_{(4)}$, by selenium dioxide but ring contraction is observed with the formation of 2-benzoyl-5-phenylselenophene (VI) in 34% yield.

Thus, ring contraction is observed for 4H-selenopyrans upon oxidation by selenium dioxide in pyridine whether or not there is a substituent at $C_{(4)}$ of the heterocycle, while 4H-selenopyran I, which lacks a substituent at $C_{(4)}$ of the heterocycle, is oxidized to selenopyranone II when hydrogen peroxide is used.



I, VI R = H; III R = OMe; IV, V R = Ph

N. G. Chernyshevskii Saratov State University, 410600 Saratov. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 1, pp. 24-26, January, 1995. Original article submitted October 10, 1994.

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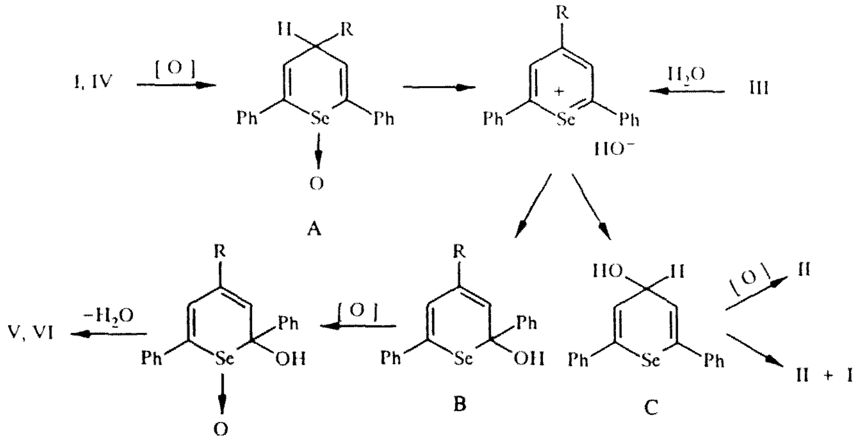
TABLE 1. Results of the Oxidation of Selenopyrans I, III, and IV under Different Conditions

Starting selenopyran	Oxidizing agent	Solvent	Reaction product	Yield, %
I	SeO_2	Pyridine	VI	34
I	H_2O_2	Benzene	II	40
I	H_2O_2	Acetone	II	48
III	H_2O_2	Benzene	II	38
IV	SeO_2	Pyridine	V	68 [3]
IV	H_2O_2	Benzene	V	27
IV	H_2O_2	Acetone	V	25

We may propose that the oxidation reactions of 4H-selenopyrans I and IV proceed through formation of the corresponding 4H-selenopyran 1-oxides A, which, analogously to selenoxanthene 1-oxides, rearrange to give hydroxyselenopyrans B and C [5]. Upon further oxidation, intermediates B may undergo transformations leading to ring contraction products V and VI, while intermediate C may undergo oxidation or disproportionation to give selenopyran-4-one II.



Such a scheme has been proposed for the oxidation of 4H-thiopyrans in our previous work [2-4].

EXPERIMENTAL

The PMR spectra were taken on a Varian FT-80A spectrometer at 30°C with TMS as the internal standard and $CDCl_3$ as the solvent. The IR spectra were taken on a Specord spectrophotometer in vaseline mull or hexachlorobutadiene.

The reaction course and purity of the products obtained were monitored by thin-layer chromatography on Silufol UV-254 plates in 3:1:1 or 5:1:1 hexane–ether–chloroform. Silica gel L5/40 was used for the chromatographic separation of the products.

Products I, III, and IV were prepared according to our previous procedures [6, 7].

Products II and V, were found to be identical in their PMR and IR spectra, thin-layer chromatography, melting point, and elemental analysis to the compounds described in our previous work [1, 3].

The reaction conditions are given in Table 1.

Oxidation of 2,6-Diphenyl-4-selenopyran I by Selenium Dioxide. A mixture of 1.48 g (5 mmoles) selenopyran I and 0.55 g (5 mmoles) selenium dioxide in 5 ml abs. pyridine was maintained on a steam bath for 2 h and then an additional 0.55 g (5 mmoles) selenium dioxide was added. The mixture was heated at reflux for 3 h and then poured into a mixture of

70 ml water, 30 ml concentrated hydrochloric acid, 100 ml ether, and 30 g ice. After 30 min, the ethereal layer was separated, thoroughly washed with water, and dried over sodium sulfate. Ether was evaporated and the residue was subjected to chromatography on a 2.5 × 40-cm column using 10:1 hexane–ether as the eluent.

2-Benzoyl-5-phenylselenophene (VI, $C_{17}H_{12}OSe$). mp 137-138°C. IR spectrum, $\nu_{C=O}$: 1616 cm^{-1}. PMR spectrum in $CDCl_3$, δ, ppm: 7.28-7.82 (12H, m, H_{arom}).

Oxidation of Selenopyrans I, III, and IV by Hydrogen Peroxide in Benzene. A sample of 10 ml 30% hydrogen peroxide was added to a solution of 1 mmole selenopyran in 10 ml benzene and vigorously stirred for 24 h. The benzene layer was separated, dried over sodium sulfate and evaporated. The residue was subjected to chromatography on a 1.5 × 40-cm column using 10:1 and 3:1 hexane–ether as the eluents.

Oxidation of Selenopyrans I and II by Hydrogen Peroxide in Acetone. A sample of 2 ml 30% hydrogen peroxide was added to a solution of 1 mmole selenopyran in 20 ml acetone and stirred for 24 h. Acetone was evaporated. The residue was dissolved in ether, washed with water, dried over sodium sulfate, and separated on a 1.5 × 40-cm column using 10:1 and 3:1 hexane–ether as the eluents.

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