OXIDATION OF 2,4,6-TRIARYL-4H-THIO(SELENO)PYRANS WITH SELENIUM DIOXIDE

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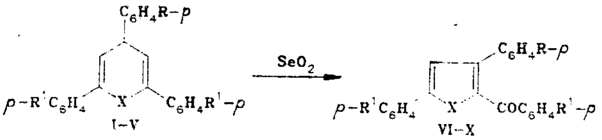
The oxidation of 2,4,6-triaryl4-H-thio(seleno)pyrans with selenium oxide in pyridine was studied. It is shown that the corresponding 2,4-diaryl-5-aroylthiophenes and -selenophenes are formed as a result of the oxidation.

According to the literature data, thiopyrylium salts are converted to carbonyl-containing thiophenes on oxidation with manganese dioxide [1]. Similar transformations are also known for thio- and selenochromylium salts, which, as a result of the reaction, form the corresponding carbonyl derivatives of benzothiophenes and benzoselenophenes [2, 3]. The oxidation of thiochromenes, selenochromenes, and tellurochromenes is also accompanied by contraction of the heterocyclic ring; the corresponding carbonyl derivatives of benzothiophenes, benzoselenophenes, and benzotellurophenes are obtained [4-6]. It is also known that 4H-thiopyrans that do not contain substituents in the 4 position of the heteroring give thiopyrones on oxidation with potassium permanganate [7].

In the present research we studied the reaction of 4-substituted 4H-thiopyrans and aryl-substituted 4H-selenopyrans. which have become accessible only in recent years [8], with selenium dioxide.

It was established that the corresponding 2,4-diaryl-5-benzoylthiophenes VI and VII and 2,4-diaryl-5-aroylselenophenes VIII-X are formed in the reaction of 2,4-6-triarylthiopyrans I and II and 2,4,6-triarylselenopyrans III-V with selenium dioxide in pyridine.



I, VI $R=R^1=H$, X=S; II, VII $R=OCH_3$, $R^1=H$, X=S; III, VIII $R=R^1=H$, X=Se; IV, IX $R=OCH_3$, $R^1=H$, X=Se; V, X $R=H$, $R^1=OCH_3$, X=Se

One might assume that the mechanism of the oxidation of thio- and selenopyrans with selenium dioxide is similar to the known mechanism of the oxidation of alkenes to allyl alcohols: this reaction is regarded as a process that takes place through the hydrated form of SeO_2 [9]. According to the indicated scheme, the reaction proceeds up to intermediate A, after which, by virtue of the specific characteristics of the indicated systems [5], the heteroring opens with the formation of the corresponding hydroseleno- or mercapto derivatives B, which undergo cyclization to intermediate C. The corresponding thiophene or selenophene ketone, elementary selenium, and water are obtained as a result of decomposition of intermediate C.

Characteristic absorption bands of a conjugated carbonyl group at 1640-1650 cm^{-1} are observed in the IR spectra of the VI-X obtained. A signal of a carbonyl carbon atom is also recorded in the ^{13}C NMR spectra at 190 ppm; this is also characteristic for a conjugated carbonyl group [10]. In an analysis of the ^1H NMR spectra of VI-X it was established that they correspond to the proposed structures. Thus signals of two phenyl groups that are characteristic for p-substituted phenyl rings (four doublets) are observed in the spectrum of X. The proton of the thiophene ring is recorded as a singlet at 7.52 ppm. Confirmation of the indicated structure is provided by the appearance of the protons of an unsubstituted phenyl ring in the form of a narrow multiplet (7.11-7.24 ppm); this indicates

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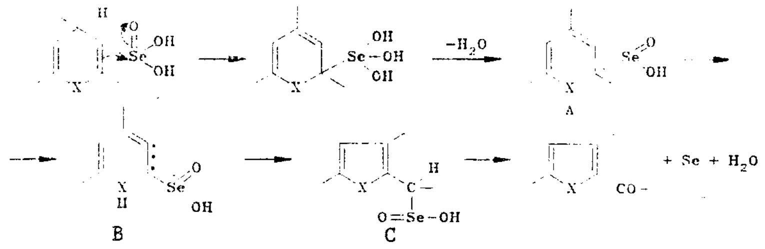
TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C	^{1}H NMR spectrum: chemical shift, ppm	^{1}H NMR spectrum: J, Hz	Yield, %
V	$C_{25}H_{22}SeO_2$	84...85	7,51...7,20 (9H, m, arom)	—	76
			6,83 (4H, d, C_6H_4R-p)	8,77	
			6,12 (2H, d, β-H)	4,13	
			4,24 (1H, t, γ-H)	4,21	
			3,78 (3H, s, OCH_3)	—	
VI	$C_{23}H_{16}OS$	84...85,5	7,70...7,08 (m, arom.)	—	65
VII	$C_{24}H_{18}O_2S$	92,5...94	7,69...7,13 (13H, m, arom.)	—	68
			6,68 (2H, d, C_6H_4R-p)	8,76	
			3,71 (3H, s, OCH_3)	—	
VIII	$C_{23}H_{16}OSe$	85...86,5	7,62 (1H, s, selenophene	—	68
			7,58...7,07 (15H, m, arom.)	—	
IX	$C_{24}H_{18}O_2Se$	90...92	7,76...7,20 (13H, m, arom.)	—	59
			6,88 (2H, d, C_6H_4R-p)	9,05	
			3,82 (3H, s, OCH_3)	—	
X	$C_{25}H_{20}O_3Se$	135...137	7,60 (2H, d, C_6H_4R-p)	8,85	55
			7,55 (2H, d, C_6H_4R-p)	8,77	
			6,91 (2H, d, C_6H_4R-p)	8,78	
			6,60 (2H, d, C_6H_4R-p)	8,83	
			7,24...7,11 (5H, m, C_6H_5)	—	
			7,52 (1H, s, selenophene	—	
			3,82 (3H, s, OCH_3)	—	
			3,72 (3H, s, OCH_3)	—	

steric interaction with the adjacent substituents (in the 2 and 3 positions). In the case of VIII the signal of the proton of the selenophene ring deviates from the region of absorption of phenyl protons and shows up at 7.62 ppm; this is in agreement with the literature data [11].



EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer. The ^{1}H and ^{13}C NMR spectra of solutions in $CDCl_3$ were obtained with a Varian 80MT spectrometer. The purity of the products obtained was monitored by TLC on Silufol UV-254 plates in a hexane—ether—chloroform system (3:1:1).

Compounds I and II [12] and III and IV [8] were synthesized by known methods. The characteristics of the compounds obtained are presented in Table 1. The results of elementary analysis of V-X for C, H, and S were in agreement with the calculated values.

4-Phenyl-2,6-di(p-methoxyphenyl)-4H-selenopyran (V) was obtained in 76% yield by the method proposed in [8].

Oxidation of 4H-Seleno(thio)pyrans I-V with Selenium Dioxide in Pyridine. A mixture of 5 mmole of 4H-seleno(thio)pyran and 5 mmole of selenium dioxide in 5 ml of absolute pyridine was heated on a boiling-water bath for 2 h, after which another 5 mmole of selenium dioxide was added, and the mixture was heated for ~ 3 h [until the seleno(thio)pyran had vanished, according to TLC]. The reaction mixture was poured into previously mixed 70 ml of water, 30 ml of concentrated HCl, 100 ml of ether, and several chunks of ice. After 30 min, the ether layer was separated, washed throughly with water, and dried with calcined magnesium sulfate. The ether was evaporated, and the residue was separated with a column packed with Silica gel L5/40 (2.5 by 40 cm) and a mixture of hexane and ether (10:1) as the eluent.

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