NEW REACTION OF COMPOUNDS OF THE FURAN SERIES WITH HYDROGEN SELENIDE

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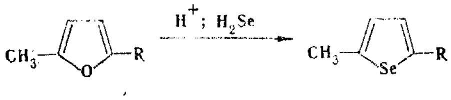
The reaction of 2,5-disubstituted furans with hydrogen selenide under acidic catalysis conditions, as a result of which the corresponding analogs of the selenophene series are formed, was studied.

We have previously shown that 2,5-disubstituted furans react readily with hydrogen sulfide under acidic catalysis conditions at room temperature to give the corresponding thiophene derivatives [1, 2].

In order to further study the new reaction involving the conversion of compounds of the furan series to other heteroanalogs and to solve the problem of its general character we investigated the possibility of their conversion to selenophenes.

The preparation of selenophene under severe conditions by passing furan and hydrogen selenide over aluminum oxide at 450°C is known [3]. However, it is not possible to arrive at functional derivatives of selenophene via this pathway.

We used 2,5-disubstituted furans I-X as the subjects of our investigation. We found that these furans are converted to the corresponding analogs (XI-XX) of selenophene in high yields when they are treated with hydrogen selenide in the presence of strong protic acids, viz, hydrochloric and perchloric acids and hydrogen chloride.



I-X XI-XX

The reaction was crrried out at 0 to 50°C.

The maximum yields of the products (51-67%) were obtained at 35-40°C. A further increase in the temperture leads to the appearance of an appreciable amount of elementary selenium in the composition of the reaction mixture. Methanol, ethanol, and acetic acid were used as the solvents. In addition to alcohols (XV-XX) of the selenophene series, the corresponding acetates are formed in the case of furan alcohols V-X when the reaction is carried out in acetic acid.

The process is realized in the presence of gaseous hydrogen chloride and perchloric and hydrochloric acids. The concentration of the acidic component in the reaction mixture was varied from 1.5 to 4.5 moles/liter — the best yields of the desired products were obtained at an acid concentration of 3 moles/liter.

In connection with the instability of hydrogen selenide in the presence of oxygen, a necessary condition for successful realization of the reaction is that it be carried out in an inert gas (argon) atmosphere.

The structure of the synthesized compounds of the selenophene series (XI-XX) was confirmed by the results of elementary analysis and data from the IR spectra, which contain absorption bands at 800, 1040, 1240, 1380, 1450, and 1520 cm^{1}, which are characteristic for vibrations of the selenophene ring [4]. The spectra of selenophene alcohols XV-XX also contain a broad band at 3200-3600 cm^{-1}, which is characteristic for an associated hydroxy group.

In our opinion, the reaction proceeds via two parallel pathways, the mechanisms of which are described by Schemes 1 and 2:

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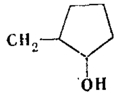
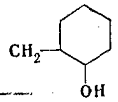
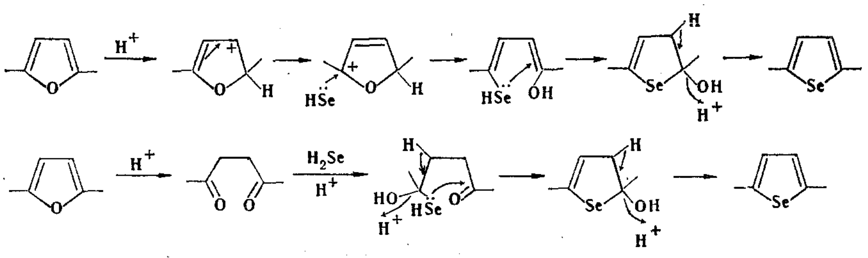
TABLE 1. 2,5-Disubstituted Selenophenes

Compound	R	bp, °C (mm)	n_D^{20}	Found, %		Empirical formula	Calc., %		Yield, %
				C	H		C	H	
XI[a]	CH_3	87—88 (70)	1,5442	45,4	5,3	C_6H_8Se	45,3	5,1	54
XII	C_2H_5	102—102,5 (70)	1,5318	48,8	6,1	$C_7H_{10}Se$	48,6	5,8	57
XIII	n-C_3H_7	85—86 (15)	1,5297	52,0	6,6	$C_8H_{12}Se$	51,3	6,6	51
XIV	n-C_4H_9	100,5—101,5 (15)	1,5230	54,1	6,9	$C_9H_{14}Se$	53,9	7,0	62
XV	$(CH_2)_2CH_2OH$	98—99 (1)	1,5550	47,1	6,3	$C_8H_{12}OSe$	47,3	6,0	56
XVI[b]	$(CH_2)_2CH(OH)CH_3$	105—106 (1)	1,5452	50,1	6,5	$C_9H_{14}OSe$	50,0	6,5	61
XVII[b]	$(CH_2)_2C(CH_3)_2OH$	134—137 (7)	—	52,2	6,9	$C_{10}H_{16}OSe$	52,0	7,0	61
XVIII	$(CH_2)_2CH(OH)C_6H_5$	178—180 (1)	—	60,5	6,1	$C_{14}H_{16}OSe$	60,2	5,8	67
XIX		144—145 (3)	1,5598	54,8	6,7	$C_{11}H_{16}OSe$	54,3	6,6	62
XX		147—148 (2)	1,5615	56,3	7,4	$C_{12}H_{18}OSe$	56,0	7,0	59

[a] The constants presented in the table are in agreement with the literature data [5]. [b] The substance crystallized upon standing.



In an anhydrous medium the conversion of furans to selenophenes can be represented by Scheme 1. The formation of an intermediate 1,4-dicarbonyl compound is possible in the presence of water — a second nucleophile [Scheme 2]. The formation of this intermediate in the case of furan I was confirmed by the results of elementary analysis and data from the IR spectra (two bands at 1690-1720 cm^{-1}).

The rigorous substantiation of the proposed mechanism requires special studies, particularly kinetic studies; this will be the subject of our future research.

EXPERIMENTAL

The IR spectra of thin layers of XI-XVI, XIX, and XX and suspensions of XVIII and XVII in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer. Analysis of the synthesis compounds by gas—liquid chromatography (GLC) was accomplished with a Tsvet-101 chromatograph with a flame-ionization detector; the 1000 × 3 mm steel column was packed with 15% Apiezon L on Chromaton N-AW, the carrier gas was helium, the flow rate was 2 liters/h, and the temperature was 180°C.

Synthesis of 2,5-Disubstituted Selenophenes XI-XX. A solution of 0.05 mole of furan I-X in 30 ml of ethanol was placed in a thermostatted reactor equipped with a gas inlet tube, a dropping funnel, a reflux condenser, and a magnetic stirrer, and argon was passed through the system for 1 h. The reaction mixture was then saturated with hydrogen selenide for 1-1.5 h, after which 0.15 mole of hydrochloric or perchloric acid was added dropwise in the course of 10-15 min without interrupting the passage of hydrogen sulfide. The reaction was carried out until the starting furan was no longer present in the mixture (according to GLC data). When gaseous hydrogen chloride was used, the reaction was carried out similarly with simultaneous passage of the latter and hydrogen selenide into the mixture. At the end of the reaction the solution was neutralized with saturated sodium carbonate solution, and the liberated oil was separated. The aqueous solution was extracted with ether, the ether extracts were combined with the oil, and the ether solution was washed with water and dried with calcined magnesium sulfate. The ether was removed, and the residue was distilled *in vacuo*. The characteristics of the synthesized substances are presented in Table 1.

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SATURATED NITROGEN-CONTAINING HETEROCYCLES.

9.* SYNTHESIS AND STUDY OF OPTICALLY ACTIVE PYRROLIDINYLALKANOLS AND THEIR TARTRATES

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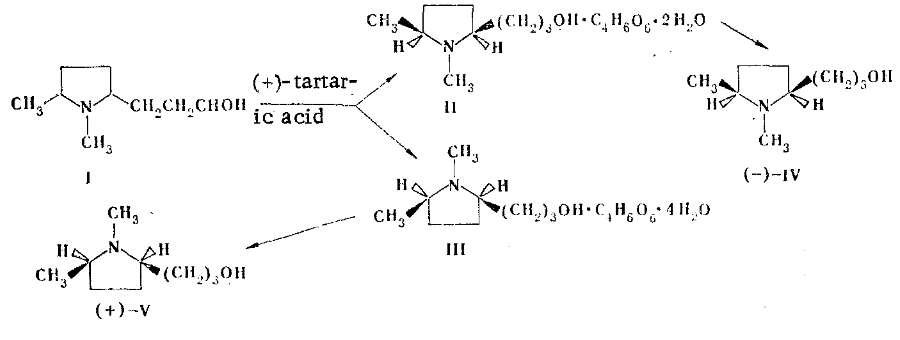
Optically active 3-(5-methyl-2-pyrrolidinyl)-1-propanols and their tartrates were synthesized. The stereochemical structures of the latter were established by x-ray diffraction analysis and PMR and IR spectroscopy. The absolute configuration was determined for (−)-cis-3-(1,5-dimethyl-2-pyrrolidinyl)-1-propanol (+)-bitartrate dihydrate, and the conformational and structural peculiarities of the pyrrolidinium cation and the tartrate anion were studied.

We have previously reported a new reaction involving the formation of alkyl- and aryl-substituted 3-(2-pyrrolidinyl)-1-alkanols by catalytic hydrogenation of the corresponding amines of the furan series in acidic solutions [1]. It was established that the reaction is stereospecific and that the degree of realization of the principal geometrical form is 80-90% when two or more substituents are present in the pyrrolidine ring.

Pyrrolidinylalkanols are biologically active compounds [2, 3], and the study of their three-dimensional structure is therefore of practical value. Since this problem cannot be solved by PMR spectroscopy, we used x-ray diffraction analysis.

On the basis of the racemate of the geometrical isomer of 3-(1,5-dimethyl-2-pyrrolidinyl)-1-propanol (I) and (+)-tartaric acid we synthesized two hydrates (II and III) of diastereomeric bitartrates, from which optically active alcohols (−)-IV and (+)-V were isolated by treatment with alkali.



Bitartrate dihydrate II, which was obtained in the form of well-formed crystals, was subjected to x-ray diffraction analysis. The geometries of the pyrrolidinium cation and the bitartrate anion (in the absolute configuration) with the bond lengths and torsion angles in

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*See [1] for communication 8.

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