REACTIONS OF 4H-SELENOPYRANS WITH HALOGENS

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The reactions of 2,4,4,6-tetraphenyl-4H-selenopyran with chlorine or bromine give the corresponding 1,1dichloro- or 1,1-dibromo-4H-selenopyrans, whereas the reaction of 2,4,6-triphenyl-4H-selenopyran with bromine gives 2,4,6-triphenylselenopyrylium tribromide.

It is known that selenopyrylium salts or the products from addition of the halogens at the double bonds of the selenopyran ring are formed during the halogenation of 4H-selenopyrans [1]. During the halogenation of chalcogenopyrans having an sp^2 carbon atom at the γ position of the heterocycle or of 4H-chalcogeno-4-pyranones the 1,1-dihalogeno derivatives were only isolated for the tellurium-containing heterocycles [2, 3]. In reactions with halogens, 4,4-diaryl-substituted 4H-pyrans and thiopyrans form the products from substitution of the hydrogen atom at the β position of the heterocycle [4, 5].

In order to obtain evidence for the possibility of the formation of 1,1-dihalogeno-4H-selenopyrans as intermediates in the heteroaromatization of 4H-selenopyrans, we studied the reaction of 2,4,4,6-tetraphenyl-4H-selenopyran (I) and 2,4,6-triphenyl-4H-selenopyran (II) with halogens.

It was found that the selenopyran (I) reacts with chlorine and bromine in dichloromethane with the formation of 1,1dichloro- and 1,1-dibromo-2,4,4,6-tetraphenyl-4H-selenopyrans (III) and (IV) respectively. The formation of the dihalogeno derivatives (III) and (IV) is reversible, as shown by the formation of the selenopyran (I) during recrystallization of the dibromide (IV) from acetonitrile. In reaction with bromine, the selenopyran (II) formed 2,4,6-triphenylselenopyrylium tribromide (V).



I, III, IV R = Ph; II R = H; III Hal = Cl; IV Hal = Br

The facts set out above give reason to conclude that the 1,1-dihalogeno derivatives of selenopyrans have greater stability than the thiopyrans. This is confirmed by the production of compounds (III) and (IV), the analogs of which for 4H-thiopyrans are unknown [3, 4]. It can be supposed that the salt (V) is formed in two directions.

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Com-	Molecular	Found % Calculated %			mp, °C	IR spectrum,	PMR spectrum,	Yield,
pound	formula	с	н	Hal	-	$\nu, {\rm cm}^{-1}$	δ, ppm	%
I	C29H22Se	<u>77.92</u> 77,50	<u>5.17</u> 4,93		138139	3020, 1488, 1444, 1156, 1076, 1032, 768, 750, 722, 700	6,43 s, 2H, β -H, 7,317,52 m,20H, Ph	40
ш	C29H22Cl2Se	<u>67.22</u> 66,94	<u>4.50</u> 4,26	<u>13.32</u> 13,63	147149 (decomp.)	3060, 3028, 1492, 1444, 1344, 1328, 1070, 1025, 936, 760, 750, 692, 572	6,58 s, 2H, β-H, 7,337,77 m, 20H, Ph	83
IV	C29H22Br2Se	<u>57.05</u> 57,17	<u>3.88</u> 3,64	<u>26.51</u> 26,23	135136 (decomp.)	2924, 1492, 1444, 1070, 1025, 758, 748, 696, 572	6,68 s, 2H, β -H, 7,427,81 m, 20H, Ph	94
v	C ₂₃ H ₁₅ Br ₃ Se	<u>44.96</u> 45,13	<u>2.51</u> 2,80	<u>38.91</u> 39,16	178180 (decomp.)	1568, 1556, 1470, 1448, 1434, 1340, 756, 722, 682	7,338,24 m, 15H, Ph, 8,60 s, 2H, β-H	69
Direction A								
$\Pi \xrightarrow{Br_2} Ph \xrightarrow{Ph} H \xrightarrow{Ph} H$								
$\begin{bmatrix} Br & Br & Br & Br^{-} \end{bmatrix}$								
Direction B								

TABLE 1. Elemental Analysis and PMR and IR Spectra of Compounds (I, III-V)

It should be mentioned that oxidation in direction A with the formation of an intermediate of type (VI) probably takes place more slowly than oxidation of the selenopyran by the mechanism with electron transfer (direction B) [6].

Thus, data were obtained which confirm the previous suggestions about the intermediate formation of the products from oxidation at the heteroatom in the oxidation of 4H-(seleno)thiopyrans by hydrogen peroxide, potassium permanganate, or lead tetraacetate [7, 8]. The high stability of the 1,1-dihalides of the 4H-selenopyrans compared with the 1-oxides and 1,1-diacetates made it possible to isolate and characterize compounds (III) and (IV) but only in the case of initial compound (I) as a result of the presence of the two substituents at the γ position not having the ability to enter into heteroaromatization.

EXPERIMENTAL

The PMR spectra were recorded on a Varian FT-80A spectrometer with deuterochloroform as solvent and TMS as internal standard. The IR spectra were recorded on a Specord M-80 spectrophotometer in Vaseline oil and hexachlorobutadiene. The reactions and the individuality of the products were monitored by TLC on Silufol UV-254 plates with a 3:1:1 (by volume) mixture of hexane, ether, and chloroform as eluant and iodine vapor as developer.

The yields of the products, their melting points, elemental analyses, and PMR and IR spectroscopic data are given in Table 1. 2,4,6-Triphenylselenopyrylium tetrafluoroborate was obtained by the method in [9].

Synthesis of 2,4,4,6-Tetraphenyl-4H-selenopyran (I). To a solution of 50 mmole of phenylmagnesium bromide in 100 ml of absolute diethyl ether, prepared from 1.22 g (50 mmole) of magnesium filings and 8.64 g (55 mmole) of distilled bromobenzene by the standard procedure for the synthesis of Grignard reagents, we added in small portions with stirring 11.48 g (25 mmole) of 2,4,6-triphenylselenopyrylium tetrafluoroborate. When all the salt had been added, the reaction mixture was stirred for 30 min and diluted with 150 ml of ether. The excess of the Grignard reagent was neutralized with cold water, and

the ether solution was extracted with water $(3 \times 150 \text{ ml})$. The ether layer was separated and dried with anhydrous sodium sulfate, and the solvent was removed. The crystallized selenopyran (I) was separated and recrystallized from acetic acid.

Reaction of 2,4,4,6-Tetraphenyl-4H-selenopyran (I) with Chlorine (bromine). We dissolved 0.45 g (1 mmole) of the selenopyran (I) in 5 ml of dichloromethane. A stream of dry chlorine was passed through the solution (or bromine was added drop by drop) with stirring until the initial selenopyran (I) had disappeared according to TLC. After removal of the solvent the obtained crystals of the dichloride (III) [or the dibromide (IV)] were washed with 10 ml of hexane and dried under vacuum.

Reaction of 2,4,6-Triphenyl-4H-selenopyran (II) with Bromine. We dissolved 0.37 g (1 mmole) of the selenopyran (II) in 5 ml of dichloromethane and added bromine with stirring until the initial selenopyran (I) had disappeared according to TLC. The reaction mixture was kept for 2 h. After removal of the solvent the obtained crystals of the salt (V) were washed with hexane $(3 \times 10 \text{ ml})$ and dried under vacuum.

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