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OXIDATION REACTIONS OF 4H-CHALCOGENOPYRANS

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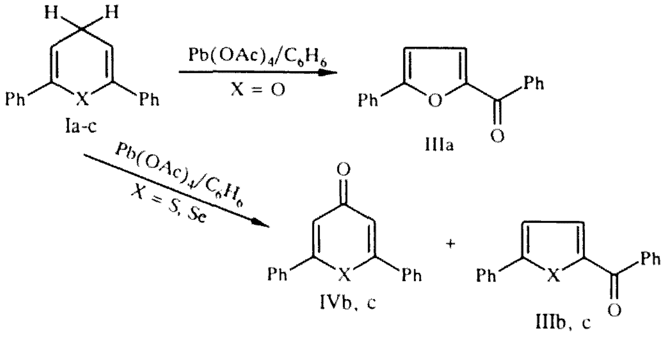
We have studied the oxidation of 4H-chalcogenopyrans and chalcogenopyrylium salts by lead tetraacetate. We have established that the major reaction products on oxidation of 2,6-diphenyl-4H-thiopyran and selenopyran are 2,6-diphenyl-4H-thio(seleno)pyran-4-ones, while 2-benzoyl-5-phenyl(seleno)thiophenes are formed as impurities. The major product on oxidation of 2,6-diphenyl-4H-pyran is 2-benzoyl-5-phenylfuran. We have shown that 2,4,6-triphenyl-4H-pyran does not undergo oxidation by hydrogen peroxide in neutral medium, in contrast to its S and Se analogs. This supports the hypothesis that the heteroatom participates in the oxidation process.

The 2,6-diaryl-4H-selenopyrans and -4H-thiopyrans unsubstituted in the 4 position of the heterocycle can undergo oxidation with formation of the corresponding 4H-seleno- and -thiopyran-4-ones [1-3] or aroylselenophenes and -thiophenes [3-5], depending on the oxidizing agent and the reaction conditions. For 4H-seleno- and thiopyrans aryl-substituted at the 4 position of the heterocycle, we have also established the possibility of conversion to benzoylselenophenes and -thiophenes [3-5], and oxidation of 2,4,6-triphenyl-4H-chalcogenopyrans by lead tetraacetate led to formation of 2-benzoyl-3,5-diphenylselenophene, thiophene, or furan [5]. We hypothesized that oxidation of 4H-selenopyrans and 4H-thiopyrans occurs through a stage of oxidation at the heteroatom [3, 5].

With the goal of determining the characteristics of the indicated reactions and the effect of the nature of the substituents and the heteroatom on the orientation of the oxidation processes, we studied the reaction with lead tetraacetate of 2,6-diphenyl-4H-pyran (Ia), 2,6-diphenyl-4H-thiopyran (Ib), and 2,6-diphenyl-4H-selenopyran (Ic), which due to the lack of substituents at the 4 position of the heterocycle may undergo conversion according to the two orientations indicated above [1-3]. Furthermore, in order to determine if formation of products of ring narrowing is possible during oxidation of chalcogenopyrylium salts by lead tetraacetate, we studied oxidation by this reagent of 2,4,6-triphenylpyrylium (IIa), 2,4,6-triphenylthiopyrylium (IIb), and 2,4,6-triphenylselenopyrylium (IIc) trifluoroacetates under conditions similar to the oxidation conditions for the corresponding 4H-chalcogenopyrans in [5].

We have established that on oxidation of the 4H-pyran Ia by lead tetraacetate, only the 2-benzoyl-5-phenylfuran (IIIa) is formed (besides unidentified products of exhaustive conversions), while the major products of oxidation of 4H-thiopyran Ib and 4H-selenopyran Ic under the same conditions are respectively 2,6-diphenyl-4H-thiopyran-4-one (IVb) and 2,6-diphenyl-4H-selenopyran-4-one (IVc); 2-benzoyl-5-phenylthiophene(IIIb) and 2-benzoyl-5-phenylselenophene (IIIc) are obtained in low yields as impurities (see Table 1).



I, III, IV a X = O, b X = S, c X = Se

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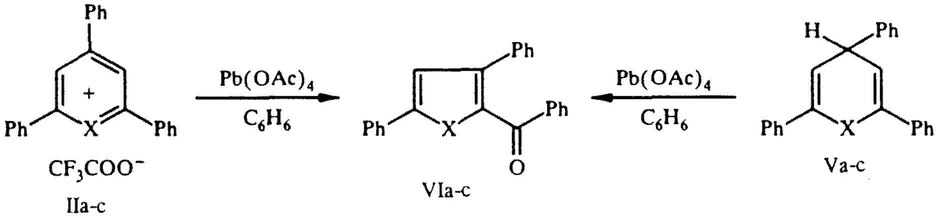
Bearing in mind that narrowing of the ring is possible if a compound with a 2H-pyran structure is an intermediate in the oxidation reaction, we can conclude that such a structure is formed during oxidation of 4H-chalcogenopyrans Ia-c. The results obtained are quite consistent with data from an investigation of the reactions of addition of nucleophiles to chalcogenopyrylium salts [6], leading to formation of a mixture of isomers with the 2H- and 4H-pyran structure. The amount of 2H-isomer in the mixture of reaction products depended on the heteroatom of the starting salt and increased on going from Se to O. Thus both types of products (IIIa-c and IVb,c) are probably formed on addition of a nucleophile to the intermediates: chalcogenopyrylium salts followed by oxidation of the adducts formed, as we suggested in [5]. Intermediate formation of chalcogenopyrylium salts in oxidation of 4H-chalcogenopyrans by lead tetraacetate (which we also suggested in [5] based on the fact that 4H-chalcogenopyrans can be oxidized by oxygen from the air in acid media or one-electron oxidizing agents with formation of chalcogenopyrylium salts [7]) was supported experimentally by TLC.

We demonstrated the ability of chalcogenopyrylium salts to undergo oxidation by lead tetraacetate, by carrying out the experiment on oxidation of 2,4,6-triphenylchalcogenopyrylium trifluoroacetates IIa-c under conditions similar to the oxidation conditions for the corresponding 4H-chalcogenopyrans (Va-c) [5]. We have established that the reactions lead to formation of the same products: 2-benzoyl-3,5-diphenylfuran VIa, 2-benzoyl-3,5-diphenylthiophene VIb, and 2-benzoyl-3,5-diphenylselenophene VIc, and on oxidation of chalcogenopyrylium salts the product yields were higher than on oxidation of 4H-chalcogenopyrans (see Table 1).



II, V, VI a X = O, b X = S, c X = Se

We know that oxidation of 4H-pyrans in acid media leads to formation of pyrylium salts. Such a process also occurs on oxidation of 4H-pyrans by lead tetraacetate [5]. Earlier, by studying the oxidation reactions of 4H-selenopyrans in neutral media, we showed that on oxidation of 2,4,6-triphenyl-4H-selenopyran Vc by hydrogen peroxide in benzene, the corresponding 2-benzoyl-3,5-diphenylselenophene VIc is formed [3]. We discussed the hypothesis that the intermediate in this reaction is the 1-oxide of 4H-selenopyran. Based on this hypothesis, the pyran Va should not undergo oxidation under such conditions, while thiopyran Vb should be oxidized by hydrogen peroxide in benzene to 2-benzoyl-3,5-diphenylthiophene VIb, which also was confirmed experimentally: thiophene VIb is formed during oxidation under the given conditions (along with products of exhaustive conversions) and was isolated from the reaction mixture in 26% yield (see Table 1), while the pyran Va did not undergo oxidation under these conditions over a 30 day period.

$$\mathrm{VIa}\ \cancel{\xleftarrow[X\,=\,O]{H_2O_2/C_6H_6}}\ \mathrm{V}\ \xrightarrow[X\,=\,S,\,Se]{H_2O_2/C_6H_6}\ \mathrm{VIb,\,c}$$

EXPERIMENTAL

The starting 4H-chalcogenopyrans were synthesized by the familiar techniques in [8] (Ia), [9] (Ib, Ic, Vb), and [10] (Va). The chalcogenopyrylium salts IIa-c were synthesized according to the technique in [11]. The ^1H NMR spectra were recorded on a Varian FT-80A spectrometer. The solvent was $CDCl_3$, internal standard TMS. The IR spectra were recorded on a Specord M-80 spectrophotometer in vaseline oil and hexachlorobutadiene. The course of the reactions and the purity of the compounds obtained were monitored by TLC on Silufol UV-254 plates. The eluents were mixtures of hexane, ether, and chloroform 3:1:1 and acetonitrile and chloroform 3:1 (by volume). Iodine vapor was the visualizing agent.

According to TLC, ^1H NMR, and IR spectra, the compounds obtained (IIIc, IVb,c, VIa-c) were identical to the compounds obtained and described in [1-5]. The product yields and their melting points are given in Table 1.

Oxidation of 2,6-diphenyl-4H-chalcogenopyrans (Ia-c) by lead tetraacetate. Lead tetraacetate (3.318 g, 7.5 mmoles) was added with stirring to a solution of 4H-chalcogenopyran (3 mmoles) in 20 ml benzene. The reaction mixture was stirred at a temperature of 20°C for 24 h, after which 0.332 g (0.75 mmoles) more lead tetraacetate was added. The reaction

TABLE 1. Characteristics of Oxidation Products of Chalogenopyrans Ia-c, Va-c, and Chalocogenopyrylium Salts IIa-c

Starting compound	Oxidizing agent	Product	mp. °C	Yield, %
Ia	$Pb(OCOCH_3)_4$	IIIa	95-96	28
Ib	$Pb(OCOCH_3)_4$	IIIb[†] IVb	124-126, 128-130	6, 43
Ic	$Pb(OCOCH_3)_4$	IIIb, IVc	136-138, 145-147	8, 46
IIa (Va)	$Pb(OCOCH_3)_4$	VIa	108-110	86 (58)
IIb (Vb)	$Pb(OCOCH_3)_4$	VIb	96-98	55 (37)
IIc (Vc)	$Pb(OCOCH_3)_4$	VIc	111-113	74 (69)
Vb	H_2O_2	VIb	95-97	26
Vc	H_2O_2	VIc	109-112	27 [3]

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[*] Found, %: C 82.46, H 4.80. $C_{17}H_{12}O_2$. Calculated, %: C 82.25, H 4.87. IR spectrum: 1640 cm^{-1} (C═O). PMR spectrum ($CDCl_3$): 6.83 (1H, d, J = 3.8 Hz, 4-H), 7.30-8.08 (11H, m, 3-H+two Ph).

[†] Found, %: C 77.65, H 4.54. $C_{17}H_{12}OS$. Calculated, %: C 77.24, H 4.57. IR spectrum: 1624 cm^{-1} (C═O). PMR spectrum ($CDCl_3$): 7.32-7.95 (12H, m, 3-H+4-H+two Ph).

mixture was stirred for 6 h, poured into 100 ml dichloromethane, and washed with distilled water (3 × 100 ml). The suspension of lead dioxide was filtered off and the result was dried with anhydrous sodium sulfate. The residue was separated by column chromatography on a column with Silicagel L 100/150 (1 × 20 cm). The eluents were hexane—ether, 10:1, 5:1, 2:1, ether, chloroform.

Oxidation of 2,4,6-triphenylchalcogenopyrylium trifluoroacetates (IIa-c) by lead tetraacetate. A mixture of lead tetraacetate (0.831 g, 1.875 mmoles) and the chalcogenopyrylium salt (1.5 mmoles) in 20 ml benzene was stirred at 20°C for 24 h, then poured into 100 ml dichloromethane and washed with distilled water (3 × 100 ml). The dichloromethane layer was removed and it was dried with anhydrous sodium sulfate. The residue after removal of the solvent for oxidation of the salts IIa,c was colorless crystals of compounds VIa,c, which were washed with a small amount of hexane. For oxidation of the salt IIb, the residue is an oil; the thiophene VIb was crystallized on trituration of this oil in a 5:1 hexane—ether mixture.

Oxidation of 2,4,6-triphenyl-4H-chalcogenopyrans (Vb,c) by hydrogen peroxide. 10 ml 30% hydrogen peroxide was added to a solution of 1 mmole of the 4H-chalcogenopyran in 10 ml benzene and this was vigorously stirred until disappearance of the thiopyran according to TLC. The benzene layer was removed and it was dried with anhydrous sodium sulfate, and the solvent was evaporated. The residue was separated by column chromatography on a column with Silicagel L 100/150 (1 × 20 cm), eluent hexane—ether 10:1. For oxidation of 4H-pyran Va, after 30 days we did not observe formation of appreciable amounts of any reaction products. The reaction mixture was a solution of the starting 4H-pyran.

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