THIOPYRANS AND THIOPYRYLIUM SALTS FROM 1,5-DIKETONES

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It has been established that with hydrogen sulfide and hydrogen chloride acyclic 1,5-diketones form thiopyrans, thiopyrylium chlorides, or mixtures of them, depending on their structure and the reaction conditions. Some reactions of thiopyrylium chlorides and thiopyrans obtained for the first time have been studied.

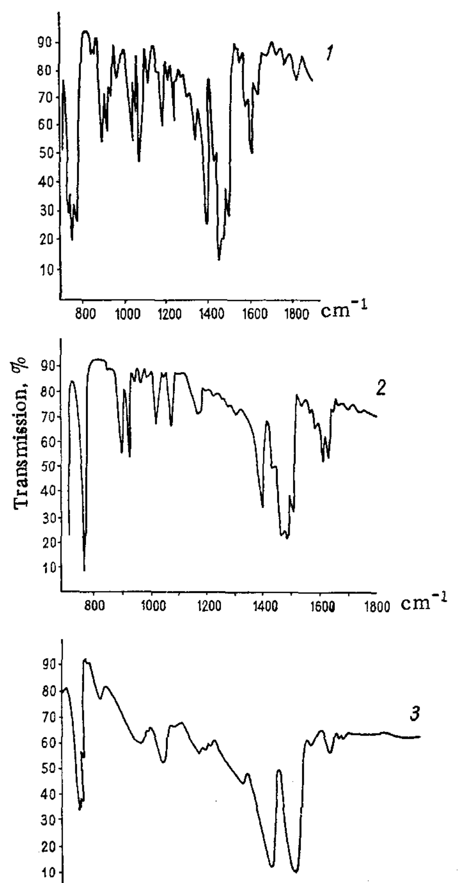
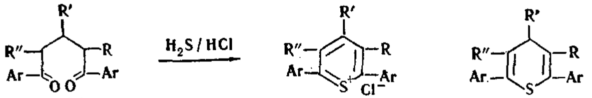


Fig. 1. IR spectra: 1) XVII; 2) XVI; 3) XVIII.

We were the first to establish that 1,3,5-substituted pentane-1,5-diones (I-IV) are capable of being converted by hydrogen sulfide and hydrogen chloride in acetic acid into thiopyrylium chlorides (VIII-XI) [1] or mixtures of the thiopyrylium chlorides and the corresponding γ-thiopyrans. Under the same conditions, tetra- and penta-substituted pentane-1,5-diones (V-VII) form thiopyrans (XIII-XV) with yields of up to 95%. With hydrogen sulfide and hydrogen chloride in methanol, the pentane-1,5-diones (I, II, V-VII) form γ-thiopyrans (XII-XVI), and only 3-methyl-1,5-diphenylpentane-1,5-dione (III) is converted into the thiopyrylium chloride (X).



I-VII VIII-XI XII-XVI

I, VIII, XII Ar = R' = C_6H_5, R = R' = H; II, IX, XV Ar = α-thienyl R' = C_6H_5, R = R'' = H; III, X Ar = C_6H_5, R' = CH_3, R = R'' = H; IV, XI Ar = C_6H_5, R' = $C_6H_4OCH_3$-p, R = R'' = H; V, XIII Ar = R' = C_6H_5, R = CH_3, R'' = H; VI, XIV Ar = R' = C_6H_5, R = R'' = CH_3; VII, XVI Ar = C_6H_5, R = R'' = CH_3, R' = H

We are the first to have shown that 1,5-diketones may be readily accessible starting materials for the preparation of thiopyrans and thiopyrylium salts. A study of the reactions mentioned above shows that the formation of thiopyrylium salts is favored by an acetic acid medium.

One of the causes for the favorable action of acetic acid on the formation of thiopyrylium chlorides is apparently the high solubility in acetic acid of the γ-thiopyrans arising as intermediates, while they are very sparingly soluble in methanol and are eliminated from the sphere of the reaction as they are formed.

A peculiarity of the behavior with respect to hydrogen chloride and hydrogen sulfide of the 1,5-diketone VII in acetic acid has been found. Under these conditions, VII, unlike I-VI, forms a

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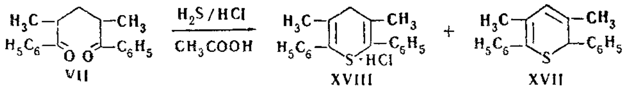
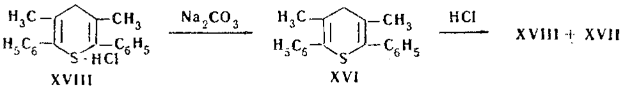
mixture of 3,5-dimethyl-2,6-diphenyl-α-thiopyran (XVII) and of the hydrochloride of 3,5-dimethyl-2,6-diphenyl-γ-thiopyran (XVIII):

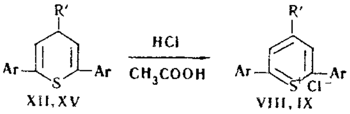


The structure of the hydrochloride XVIII was confirmed by the fact that the action of aqueous sodium carbonate solution on it formed the γ-thiopyran XVI. When an acetic acid solution of the γ-thiopyran XVI was saturated with hydrogen chloride, the hydrochloride XVIII and the α-thiopyran XVII were formed again.



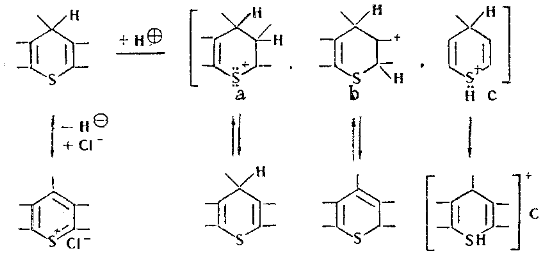
In the region of double-bond absorption in the IR spectrum of XVIII there is a weak split band with peaks at 1645 and 1652 cm^{-1}. The spectrum of the γ-thiopyran XVI contains medium-intensity absorption bands at 1603 and 1620 cm^{-1}. The shift in the absorption bands in the IR spectrum of XVIII in the high-frequency direction and the decrease in their intensity as compared with the spectrum of XVI can be explained by the participation of the free p electrons of the sulfur of XVIII in the formation of a bond with the hydrogen chloride, in contrast to the γ-thiopyran XVI, where there is conjugation of the p electrons of the π bond (see Fig. 1).

In contrast to the γ-thiopyran XVI, with hydrogen chloride in acetic acid solution 2,4,6-triphenyl-γ-thiopyran (XII) and 4-phenyl-2,6-dithienyl-γ-thiopyran (XV) form the corresponding thiopyrylium chlorides.



The results obtained show that with hydrogen sulfide noncyclic 1,5-diketones initially form γ-thiopyrans which, under the influence of hydrogen chloride and depending on the number, nature, and positions of the substituting groups, either do not change, are converted into thiopyrylium chlorides, or, as in the case of the γ-thiopyran XVI, give a mixture of the α-thiopyran XVII and the γ-thiopyran hydrochloride XVIII.

When the electron density in the C_4 position is sufficient, a splitting out of a hydride ion apparently takes place with the formation of a thiopyrylium cation which, becoming stabilized, forms a thiopyrylium chloride. Secondary reactions of the γ-thiopyran XVI under the influence of hydrogen chloride may be regarded as the result of the protonation of the sulfide with the formation of the carbocations *a* and b and the cation c which are stabilized by forming an α-thiopyran or the hydrochloride of a γ-thiopyran.



Apparently, the protonation of the γ-thiopyran ring not only at C_3 but also at C_2 is likely because of the +M effect of the phenyl group and of the free electron pairs of the sulfur:

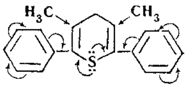
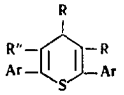
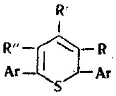


TABLE 1


XIII–XVI


XVII

Compound	Ar	R	R′	R″	mp, °C	UV spectrum* λ_{max}, nm	UV spectrum* log ε	IR spec., $\nu_{C=C}$ alip, arom., cm^{-1} †	Empirical formula	Found, % C	Found, % H	Found, % S	Calc., % C	Calc., % H	Calc., % S	Yield, %
XIII	C_6H_5	CH_3	C_6H_5	H	102—104	210, 225	4,54 4,50	1577, 1602 1620	$C_{24}H_{20}S$	84,50	6,06	9,47	84,71	5,88	9,41	95
XIV	C_6H_5	CH_3	C_6H_5	CH_3	136—137	207, 222	4,16 4,06	1500, 1602 1630	$C_{25}H_{22}S$	84,69	6,51	8,72	84,75	6,21	9,04	46
XV	α-thienyl	H	C_6H_5	H	108—110			1520, 1600 1638	$C_{19}H_{14}S_3$	67,40	4,17	28,51	67,46	4,14	28,40	72
XVI	C_6H_5	CH_3	H	CH_3	121,5—123	220, 290	4,50 3,75	1587, 1603 1620	$C_{19}H_{18}S$	81,70	6,40	11,60	82,02	6,47	11,51	95
XVII	C_6H_5	CH_3	H	CH_3	65—67	217, 275 313	4,40 3,50 2,70	1575, 1602 1632	$C_{19}H_{18}S$	81,44	6,21	11,50	82,02	6,47	11,51	57

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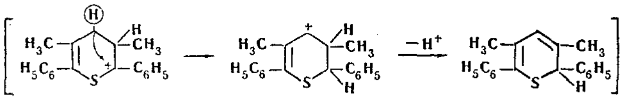
*The UV spectra were taken on a SP-700 spectrometer in hexane.

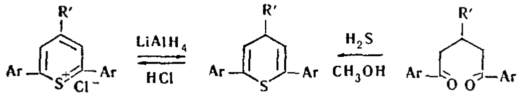
† The IR spectra were taken on a UR-10 spectrometer in paraffin oil.

However, it is possible that the isomerization of the γ-thiopyran into the α-thiopyran under the influence of hydrogen chloride is connected with an intramolecular β-hydride shift:

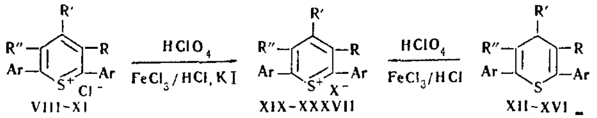


The formation of the hydrochloride XVIII – a compound of the sulfonium type – can be explained by the low degree of participation of the free electron pairs of the sulfur in conjugation with the π-electrons of the double bonds, as is shown by the high dipole moment of XVI, 1.83.*

The structure of the thiopyrylium chlorides VIII-IX that we obtained is confirmed by the results of analysis, by the smooth exchange reactions with KI, $HClO_4$, and $FeCl_3$ with the formation of known [3, 4] and new thiopyrylium salts which, in the case of the chlorides VIII and IX, are identical with salts obtained from the corresponding γ-thiopyrans XII and XV, and also by the fact that the thiopyrylium chlorides, like the thiopyrylium perchlorates [2], are reduced by $LiAlH_4$ to the corresponding γ-thiopyrans.



The structure of the γ-thiopyrans XII-XVI is confirmed by independent synthesis [2] of the known 2,4,6-triphenyl-γ-thiopyran and the conversion of XII-XVI with perchloric acid and ferric chloride into the known (XIX and XXII [3, 4]) and new thiopyrylium perchlorates and tetrachloroferrates.



XIX-XXV $X^- = ClO_4^-$; XXVI - XXX $X^- = FeCl_4^-$; XXXI-XXXVII $X^- = I^-$; XIX[5]; XXXI[3] Ar = R′ = C_6H_5, R = R″ = H; XX, XXVI, XXXII Ar = α-thienyl R′ = C_6H_5, R = R″ = H; XXI, XXVII, XXXIII Ar = C_6H_5, R′ = CH_3, R = R″ = H; XXII[5], XXXIV Ar = C_6H_5, R′ = $C_6H_4OCH_3$-p, R = R″ = H; XXIII, XXVIII, XXXV Ar = R′ = C_6H_5, R = CH_3, R″ = H; XXIV, XXIX, XXXVI Ar = R′ = C_6H_5, R = R″ = CH_3; XXV XXX, XXXVII Ar = C_6H_5, R = R″ = CH_3, R′ = H

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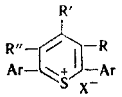
*Determined by E. N. Kharlamova of the Karpov Physicochemical Institute.

TABLE 2



Compound	Ar	R	R′	R″	X⁻	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
								Cl	I	S	Cl	I	S	
XIX	C_6H_5	H	C_6H_5	H	ClO_4	212—214*	$C_{23}H_{17}SClO_4$	—	—	—	—	—	—	61
XX	α-Thienyl	H	C_6H_5	H	ClO_4	303—305 (decomp.)	$C_{19}H_{13}S_3ClO_4$	22,02 22,08	—	8,42 8,64	21,99	—	8,11	88
XXI	C_6H_5	H	CH_3	H	ClO_4	218—220 †	$C_{18}H_{15}SClO_4$	9,82 9,56	—	8,74 8,95	9,79	—	8,82	91
XXII	C_6H_5	H	$C_6H_4OCH_3$	H	ClO_4	214—216 ‡								
XXIII	C_6H_5	CH_3	C_6H_5	H	ClO_4	182—184	$C_{24}H_{19}SClO_4$	8,91 9,23	—	7,80 7,93	8,73	—	7,87	60
XXIV	C_6H_5	CH_3	C_6H_5	CH_3	ClO_4	315—317	$C_{25}H_{21}SClO_4$	7,39 7,64	—	7,49 7,28	7,85	—	7,10	85
XXV	C_6H_5	CH_3	H	CH_3	ClO_4	165—166	$C_{19}H_{17}SClO_4$	9,66 9,74	—	8,63 8,77	9,43	—	8,50	66
XXVI	C_6H_5	H	C_6H_5	H	$FeCl_4$	271—274 (decomp.)	$C_{19}H_{13}S_3 \cdot FeCl_4$	26,51 26,43	—	17,92 17,64	26,54	—	17,94	94
XXVII	α-Thienyl	H	CH_3	H	$FeCl_4$	158,5—159	$C_{18}H_{15}S \cdot FeCl_4$	30,34 30,73	—	6,89 7,05	30,80	—	6,94	91
XXVIII	C_6H_5	CH_3	C_6H_5	H	$FeCl_4$	119—124,5	$C_{24}H_{19}S \cdot FeCl_4$	26,11 26,37	—	6,40 6,24	26,44	—	5,94	52

TABLE 2 (continued)

Compound	Ar	R	R′	R″	X⁻	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
								Cl	I	S	Cl	I	S	
XXIX	C_6H_5	CH_3	C_6H_5	CH_3	$FeCl_4$	171—172	$C_{25}H_{21}S \cdot FeCl_4$	25,97 25,46	—	5,74 6,11	26,77	—	5,75	74
XXX	C_6H_5	CH_3	H	CH_3	$FeCl_4$	197—198	$C_{19}H_{17}S \cdot FeCl_4$	29,87 30,31	—	6,75 7,01	29,89	—	6,74	88
XXXI	α-Thienyl	H	C_6H_5	H	I	206—213	$C_{19}H_{13}S_3 \cdot I$	—	27,26 27,84	20,55 20,91	—	27,37	20,47	92
XXXII	C_6H_5	H	CH_3	H	I	172 (decomp.)	$C_{18}H_{15}S \cdot I$	—	32,75 32,18	8,29 8,50	—	32,56	8,21	73
XXXIII	C_6H_5	H	$C_6H_4OCH_3$	H	I	205—207	$C_{24}H_{19}OS \cdot I$	—	26,60 26,54	7,05 6,69	—	26,35	6,63	70
XXXIV	C_6H_5	CH_3	C_6H_5	H	I	166—169 (decomp.)	$C_{24}H_{19}S \cdot I$	—	27,15 27,34	6,80 7,23	—	27,25	6,86	60
XXXV	C_6H_5	CH_3	C_6H_5	CH_3	I	286—288 (decomp.)	$C_{25}H_{21}S \cdot I$	—	26,39 26,40	6,84 6,62	—	26,46	6,66	78
XXXVI	C_6H_5	CH_3	H	CH_3	I	175—178 (decomp.)	$C_{19}H_{17}S \cdot I$	—	31,45 31,40	7,44 7,86	—	31,44	7,62	65

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*mp 211-212°C [2].

†mp 230-232°C [13].

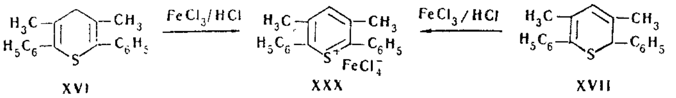
‡mp 214-216°C [2].

The IR spectra of XII-XVI contain absorption bands at 1600-1638 cm^{-1} which may be assigned to the stretching vibrations of the double bonds (absorption bands at 1600 and 1640 cm^{-1} are given for the known γ-thiopyran [5]).

The UV spectrum of VIII has λ_{max} in the same region as γ-thiopyran [5]: λ_{max}, nm (log ε) for γ-thiopyran 236-238, 278 (3.72, 3.38, 4.51) [5]; for 2,4,6-triphenyl-γ-thiopyran (XII) 236-237 (4.51).

The oxidation of XII-XVII by hydrogen peroxide in acetic acid gave sulfones only of XIV and XVII, and in the case of the other γ-thiopyrans products of far-reaching changes were produced. Some sulfones of tetrasubstituted γ-thiopyrans have been described in the literature, but the known sulfone of α-thiopyran was obtained only indirectly [6].

The structure of 3,5-dimethyl-2,6-diphenyl-α-thiopyran is confirmed by its IR spectrum which contains three absorption bands in the region of double bonds and the aromatic ring (1572, 1602, and 1632 cm^{-1}). The bands at 1602 and 1572 cm^{-1} are distinguished by a considerable intensity, which shows the presence of a conjugated system of double bonds. The spectrum of the isomeric γ-thiopyran (XVI) contains two medium-intensity bands in this region (at 1603 and 1620 cm^{-1}) and a weak band at 1581 cm^{-1}. The structure of the α-thiopyran XVII is also confirmed by the fact that it is formed with a yield of about 90% when an ethereal solution of XVI is saturated with hydrogen chloride, and with ferric chloride it gives a tetrachloroferrate identical with that obtained from the γ-thiopyran XVI, as was to be expected for such a type of isomer.



Unlike XVI, the isomer XVII forms a sulfone.

EXPERIMENTAL

The 1,5-diketones (I-VII) were obtained by known methods, and their melting points corresponded to those given in the literature [7-12].

2,4,6-Triphenylthiopyrylium Chloride (VIII). A solution of 5 g (0.015 mole) of I in 80 ml of glacial acetic acid was saturated with hydrogen sulfide at 14-15°C for 1 h and with a mixture of hydrogen sulfide and hydrogen chloride at 25-35°C for 3 h. The cooled reaction mixture was treated with 200 ml of ether, and the greenish-yellow crystalline precipitate of VIII that formed was separated off and carefully washed with ether. Yield 2.5 g (45%). After reprecipitation from acetic acid with ether, mp 133-136°C (decomp., in a sealed capillary). Found %: Cl 9.35, 9.63; S 8.65, 8.46. $C_{23}H_{17}ClS$. Calculated %: Cl 9.85; S 8.87. Evaporation of the ethereal extract gave almost colorless crystals of 2,4,6-triphenyl-γ-thiopyran (XII) in the form of needles. Yield 1.1 g (20%), mp 104-106°C (nitromethane); a mixture with authentic XII obtained by the method of Suld and Price [2] melted without depression.

4-Phenyl-2,6-dithienylthiopyrylium Chloride (XI). A solution of 5.5 g (0.016 mole) of II in 70 ml of CH_3COOH was saturated with H_2S and HCl as in the case of I, and the reaction mixture was kept for 24 h. This gave 2.05 g (37.2%) of dark red crystals which were reprecipitated by ether from dichloroethane, mp 139-141°C (decomp.). Found %: Cl 9.26, 9.33; S 25.23, 25.19. $C_{19}H_{13}ClS_3$. Calculated %: Cl 9.53; S 25.77. The filtrate yielded about 3 g (approximately 55%) of the initial II.

4-Methyl-2,6-diphenylthiopyrylium chloride (X) was obtained in a manner similar to IX. Yield about 40%. Yellowish green crystals, mp 162-165°C (decomp.). Found %: Cl 11.81, 11.48; S 10.90, 10.94. $C_{18}H_{15}ClS$. Calculated %: Cl 11.89; S 10.90.

4-(p-Methoxyphenyl)-2,6-diphenylthiopyrylium chloride (XI) was obtained in a manner similar to IX with a yield of 38%. Dark red crystals, mp 136-138°C (decomp., precipitated by ether from chloroform). Found %: Cl 9.15, 9.30; S 8.60, 8.45. $C_{24}H_{19}ClOS$. Calculated %: Cl 9.09; S 8.20.

Reaction of 2-Methyl-1,3,5-triphenylpentane-1,5-dione (V) with H_2S and HCl. A suspension of 10.26 g (0.03 mole) of the diketone V in 70 ml of CH_3COOH was saturated with hydrogen sulfide and hydrogen chloride as in the experiments described above. The V gradually went into solution, and after some time a crystalline precipitate began to deposit which was separated off after the reaction mixture had been kept at 20°C for 14 h. Yield of colorless plates corresponding to 3-methyl-2,4,6-triphenyl-γ-thiopyran (XIII) 9.77 g.

Reaction of 2,4-Dimethyl-1,3,5-triphenylpentane-1,5-dione (VI) with H_2S under the Influence of Hydrogen Chloride. A suspension of 7.12 g (0.02 mole) of the diketone VI in 50 ml of glacial CH_3COOH was saturated with hydrogen sulfide and hydrogen chloride and then, as described above, 3.3 g (46%) of 3,5-dimethyl-2,4,6-triphenyl-γ-thiopyran (XIV) and 3.7 g of the initial VI were isolated. The mixture was separated satisfactorily by recrystallization from gasoline. The diketone precipitated from the hot gasoline solution of the mixture, and the γ-thiopyran (XIV) remained after the filtrate had been evaporated.

The Reaction of 2,4-Dimethyl-1,5-diphenylpentane-1,5-dione (VII) with H_2S and HCl. A solution of 15 g (53 mmoles) of VII in 50 ml of glacial CH_3COOH was treated as in the above-described experiments, giving yellow crystals corresponding to the hydrochloride of 3,5-dimethyl-2,6-diphenyl-γ-thiopyran (XVI), yield 30%, mp 121-123°C (reprecipitated from dichloroethane with ether). Found %: Cl 11.39, 11.43; S 10.57, 10.56. $C_{19}H_{17}ClS$. Calculated %: Cl 11.28; S 10.17. The filtrate was poured into water and the ethereal layer was separated off, washed with sodium carbonate solution and with water, dried with Na_2SO_4, and filtered, and the ether was distilled off, whereupon the residue crystallized, giving 3,5-dimethyl-2,6-diphenyl-α-thiopyran (XV).

3,5-Dimethyl-2,6-diphenyl-α-thiopyran S,S-dioxide was obtained by oxidizing a solution of 0.62 g (2.3 mmoles) of XV in 7 ml of glacial acetic acid with 3 ml of 30% hydrogen peroxide at 20°C (the reaction mixture was allowed to stand for 24 h). Yield 0.62 g (92.5%), mp 137-139°C (ethanol). Found %: C 73.54; H 6.08; S 10.45. $C_{19}H_{18}O_2S$. Calculated %: C 73.55; H 5.81; S 10.32.

The reactions of the diketones I-VII with hydrogen sulfide and hydrogen chloride in methanolic solution were carried out as in acetic acid solution at the same concentration of the diketones in methanol. The yields of the γ-thiopyrans XII-XIV obtained in methanol were, respectively, 87, 88, and 46%. Mixtures with the respective authentic samples of II-XIV melted without depression. Under these conditions, 2,4-dimethyl-1,5-diphenylpentane-1,5-dione (VII) and 4-phenyl-1,5-dithienylpentane-1,5-dione (II) were converted into the corresponding γ-thiopyrans, which were not obtained when the reaction was performed in acetic acid. The properties and analytical results for the thiopyrans obtained are given in Table 1.

Isomerization of 3,5-Dimethyl-2,6-diphenyl-γ-thiopyran (XVI) into 3,5-Dimethyl-2,6-diphenyl-α-thiopyran (XVII). A solution of 1 g (3.5 mmoles) of XVI in 25 ml of acetic acid was saturated with hydrogen chloride for an h, and then 100 ml of ether was added to precipitate 0.15 g (15%) of XVIII, mp 120-121°C, a mixture with the authentic hydrochloride XVIII melting without depression. The ethereal solution was washed with water and dried, and the ether was distilled off, and the residue consisted of crystals of XVII (yield 15%), mp 65-67°C, a mixture with authentic XVII melting without depression.

Hydrolysis of the Hydrochloride of 3,5-Dimethyl-2,6-diphenyl-γ-thiopyran (XVIII). A solution of 0.1 g of Na_2CO_3 in 10 ml of H_2O was poured onto 0.1 g (0.3 mmole) of XVIII, and after 30 min the reaction product was extracted with ether; evaporation of the extract gave 0.07 g (70%) of crystals with mp 121-123°C, a mixture of which with authentic 3,5-dimethyl-2,6-diphenyl-γ-thiopyran (XVI) melted without depression.

Reaction of 2,4,6-triphenyl-γ-thiopyran (XII) with Hydrogen Chloride. A solution of 0.5 g (1.5 mmole) of XII in 30 ml of glacial CH_3COOH was saturated with dry HCl for 3 h, and then the reaction mixture was kept for 12 h (about 20°C) and 150 ml of ether was added. Yellow crystals with mp 130-134°C (decomp.) (0.3 g; about 57%) deposited; in admixture with the authentic chloride VIII they melted without depression.

Reaction of 4-Phenyl-2,6-dithienyl-γ-thiopyran (XV) with Hydrogen Chloride. As in the case of the γ-thiopyran XII, a solution of 1.5 g (5.3 mmoles) of XV in 10 ml of CH_3COOH yielded 1.3 g (80%) of the chloride IX, mp 141-143°C (decomp.), a mixture with an authentic sample melting without depression.

The thiopyrylium perchlorates (XIX-XXV) were obtained from the γ-thiopyrans (XII-XVI) or the thiopyrylium chlorides (VIII-XI) by the action of a six- to eightfold excess of 70% $HClO_4$ in glacial CH_3COOH. After 24 h, crystals separated out which were washed with acetic acid and ether. The perchlorates obtained are given in Table 2.

The Thiopyrylium Tetrachloroferrates (XXVI-XXX). To a solution of 2-4 mmoles of one of the γ-thiopyrans XII-XVI or one of the chlorides VIII-XI in 5-10 ml of acetic anhydride was added a 4- to 5-molar excess of ferric chloride and a mixture of 5 ml of hydrochloric and 5 ml of acetic acids. The resulting mixture was kept at 20°C for 12 h, and the crystals were separated off and were washed with glacial acetic acid and with ether. The tetrachloroferrates obtained are given in Table 2.

The thiopyrylium iodides (XXXI-XXXVI) were obtained by double decomposition with potassium iodide in aqueous acetone from the chlorides IX-XI and the perchlorates XXIII-XXV.

LITERATURE CITED

1. V. G. Kharchenko, V. I. Kleimenova, N. M. Kupranets, N. V. Polikarpova, and A. Ya. Yakoreva, ZhOrKh, 4, 2054 (1968).
2. B. G. Suld and C. C. Price, J. Am. Chem. Soc., 11, 2090 (1962).
3. R. Wizinger and R. Ulrich, Helv. Chim. Acta, 39, 207 (1956).
4. K. Kanai et al., J. Chem. Soc. Japan, Pure Chem. Sect., 84, 432, A-30 (1963); RZhKh (1964), 21Zh96.
5. I. Strating, I. H. Keijer, E. Molenar, and L. Brandsma, Angew. Chem., 74, 465 (1962).
6. E. Molenar and J. Strating, Rec. Trav. Chim., 86, 1047 (1967).
7. S. Kostanecki and G. Rossbach, Ber., 29, 1488 (1896).
8. W. Steinkopf and W. Popp, Lieb. Ann., 24, 540 (1939).
9. M. N. Tilichenko, ZhOKh, 25, 2503 (1955).
10. W. Dilthey and R. Taucher, Ber., 53, 252 (1920).
11. R. D. Abell, J. Chem. Soc., 83, 360 (1903).
12. M. N. Tilichenko and N. K. Astakhova, Dokl. Akad. Nauk SSSR, 74, 951 (1950).
13. R. Wizinger and H. I. Angliker, Helv. Chim. Acta, 49, 2046 (1966).