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REACTION OF POLYSUBSTITUTED 4H-THIOPYRANS WITH TRIFLUOROACETIC ACID IN SALT-FORMATION AND IONIC-HYDROGENATION REACTIONS

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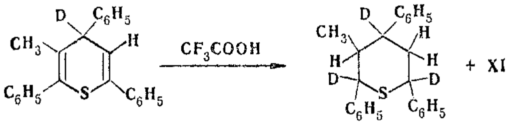
Depending on their structure, tetra- and pentasubstituted 4H-thiopyrans either undergo disproportionation or form salts with the participation of air oxygen upon reaction with trifluoroacetic acid. It is shown that these processes are competitive. The previously proposed scheme for the disproportionation of 4H-thiopyrans with protic acids was proved experimentally. The positions at which protonation of the double bonds of the heterorings occurs were established as a result of ionic hydrogenation of the 4H-thiopyrans.

The formation of thiapyrylium salts and thiacyclohexanes in a ratio of 2:1 in the reactions of di- and trisubstituted 4H-thiopyrans with protic acids made it possible to assume that disproportionation of the investigated sulfides, which includes initial protonation of the heteroring double bond and stabilization of the resulting carbonium ion due to hydride migration* from the 4H-thiopyran molecule, occurs in this case [1].

The proposed scheme has been confirmed experimentally by realization of the reaction of 4-deutero-3-methyl-2,4,6-triphenyl-4H-thiopyran (I-D) with trifluoroacetic acid. The reaction products were the corresponding trifluoroacetate XI and 2,4,6-trideutero-3-methyl-2,4,6-triphenylthiacyclohexane (VI-D).



I-D VI-D

As pointed out in [4], polysubstituted 4H-thiopyrans I-IV react with $HClO_4$ in acetic acid to give thiapyrylium salts with the participation of air oxygen via a mechanism that competes with disproportionation. At the same time, thiopyrans I, III, and IV undergo disproportionation in the usual manner upon reaction with trifluoroacetic acid, whereas thiopyran II does not undergo disproportionation even with trifluoroacetic acid. Whereas sulfide II is converted quantitatively to 3,5-dimethyl-2,4,6-triphenylthiapyrylium trifluoroacetate (XII) after 48 h upon reaction with CF_3COOH in air, virtually no reaction with trifluoroacetic acid occurs after the same period of time in a helium atmosphere. The results provide evidence that in this case, as in the reaction of thiopyrans I-IV with perchloric acid [4], air oxygen plays a substantial role in the formation of thiapyrylium salt XII. It should be noted that for the thiopyrans that undergo disproportionation with trifluoroacetic acid in air the absence of oxygen does not affect the direction of the process. Thus when this reaction is carried out in a helium atmosphere, sulfides I and V form disproportionation products (VI and XI and X and

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*Here and subsequently, the overall migration of a proton and two electrons is intended. The problem of the mechanism of hydride transfer, which has recently been the subject of active discussion [2, 3], is not discussed in the present communication.

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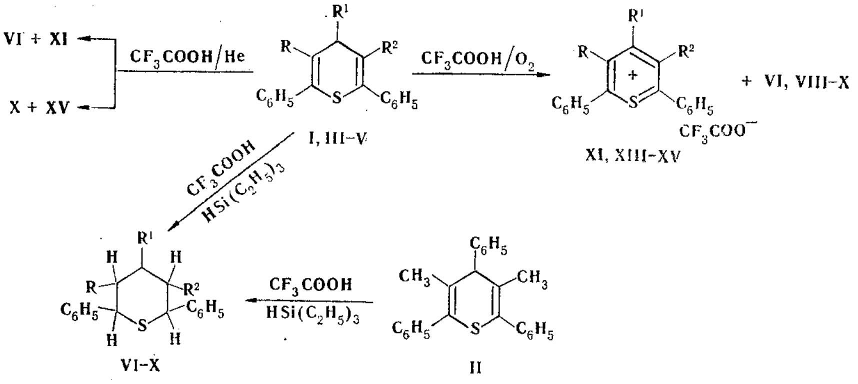
XV, respectively) after the same period of time as in air.



I, VI*, XI $R=CH_3$, $R^1=C_6H_5$, $R^2=H$; VII $R=R^2=CH_3$, $R^1=C_6H_5$; III, VIII, XIII $R=R^1=R^2=CH_3$; IV, IX, XIV $R=R^2=CH_3$, $R^1=C_2H_5$; V, X, XV $R=R^2=H$, $R^1=C_6H_5$

The ionic hydrogenation of 4H-thiopyrans by means of the trifluoroacetic acid—triethylsilane hydrogenating pair can be regarded as a model reaction for disproportionation. It was established that both thiopyrans I and III-V and thiopyran II are readily converted to the corresponding thiacyclohexanes VI-X upon reaction with $CH_3COOH/HSi(C_2H_5)_3$. The use of CF_3COOD in the ionic hydrogenation of thiopyrans I, II, and V made it possible to establish that, just as in the case of thiopyran V, the protonation of the double bonds of the heterorings of I and II, is realized in the $C_{(3)}$ and $C_{(5)}$ positions; trisubstituted thiopyran forms only 3,5-dideuterated thiacyclohexane Xa, while tetrasubstituted thiopyran I gives 3,5,5-trideuterated thiacyclohexane VIb in addition to the 3,5-dideuterated product (VIa). The PMR spectra of these compounds are presented in Fig. 1. These thiacyclohexanes (VIa, VIb) are also formed in the disproportionation of I with CF_3COOD. However, whereas the ratio of the trideutero-substituted (VIb) and dideutero-substituted (VIa) thiacyclohexanes is ∿1:2 in ionic hydrogenation, the fraction of the trideutero-substituted sulfide VIb increases significantly in the case of disproportionation.

As we have already noted, thiopyran II, which does not undergo disproportionation with trifluoroacetic acid, readily undergoes ionic hydrogenation with $CH_3COOH/HSi(C_2H_5)_3$. It follows from this that protonation of the heteroring double bonds of II is realized in trifluoroacetic acid and that the corresponding carbonium ions, the stabilization of which due to hydride migration is possible only in the presence of an active hydride-ion donor such as triethylsilane, are formed as a result. Triethylsilane was also used as a hydride-ion supplier in the reaction of thiopyran I with perchloric acid. It is known that this thiopyran does not undergo disproportionation with $HClO_4$ in acetic acid [4]. Thiopyran I is converted to thiacyclohexane VI in 78% yield when triethylsilane is added to the reaction mixture.

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*In contract to thiacyclohexanes VI, VII, and X, the H atoms in the ring $C_{(3)}$ and $C_{(5)}$ positions are replaced by D atoms in thiacyclohexanes VIa, VIIa, and Xa.

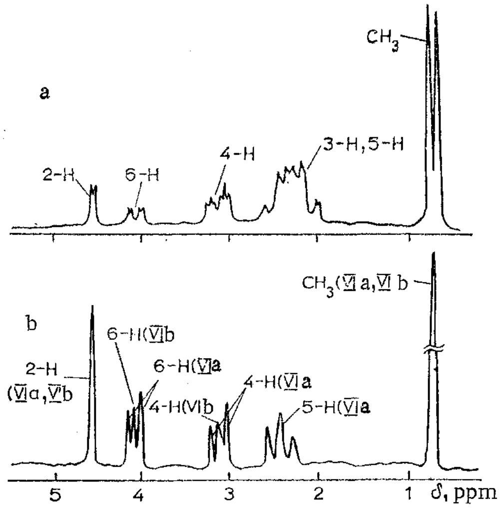

Fig. 1. PMR spectra of thiacyclohexanes VI: a) 3-methyl-2,4,6-triphenylthiacyclohexane (VI); b) mixture of 3,5-dideutero- and 3,5,5-trideutero-3-methyl-2,4,6-triphenylthiacyclohexanes (VIa, b) obtained in the reaction of thiopyran I with $CF_3COOD/HSi(C_2H_5)_3$.

On the basis of the data obtained it may be concluded that even when polysubstituted 4H-thiopyrans I and II do not form disproportionation products with strong acids, the double bonds of the heterorings are protonated. However, stabilization of the resulting carbonium ions as a result of hydride migration from the corresponding 4H-thiopyran molecule, which is characteristic for disproportionation, is hindered because of a change in the electron density in the ring and the steric hindrance that arises when methyl substituents are introduced in the $C_{(3)}$ or $C_{(3)}$ and $C_{(5)}$ positions of the heteroring. As a result, the formation of polysubstituted thiapyrylium salts occurs with the participation of air oxygen. Replacement of the phenyl substituent in the $C_{(4)}$ position of the pentasubstituted thiopyran ring of II by alkyl groups (thiopyrans III and IV) leads to an increase in the hydride lability in this position, which facilitates the disproportionation of sulfides III and IV with trifluoroacetic acid. Thus we have obtained confirmation that in the reaction of polysubstituted 4H-thiopyrans with protic acids the mechanisms of the formation of thiapyrylium salts as a result of the disproportionation of thiopyrans and with the participation of air oxygen are competitive. The direction of the process depends on both the nature of the starting thiopyran and the nature of the acid.

EXPERIMENTAL

The PMR spectra of solutions of the compounds in $CDCl_3$ were recorded with an RYa-2306 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

Thiopyran I-D. This compound, with mp 101-102°C [6] was obtained in 51% yield by the reaction of 3-methyl-2,4,6-triphenylthiapyrylium perchlorate with $LiAlD_4$. PMR spectrum (in $CDCl_3$): 1.60 (3H, s, CH_3), 6.0 (1H, s, 5-H), and 7.26 ppm (15H, m, C_6H_5).

Thiopyran III. This compound, with mp 141-143°C (from ethanol), was obtained in 54% yield by the reaction of 3,5-dimethyl-2,6-diphenylthiapyrylium perchlorate with methylmagnesium iodide by the method in [5]. PMR spectrum ($CDCl_3$): 1.32 (3H, d, J = 6.8 Hz, CH_3), 1.77 (6H, s, $=C{-}CH_3$), 2.88 (1H, q, J = 6.8 Hz, 4-H), and 7.27 ppm (12H, m, C_6H_5). Found: C 82.2; H 6.7; S 10.8%. $C_{20}H_{20}S$. Calculated: C 82.2; H 6.8; S 11.0%.

Reactions of Thiopyrans I-D and I-V with Trifluoroacetic Acid in Air. These reactions were realized by the method in [1].

Reaction of Thiopyran II with Trifluoroacetic Acid in a Helium Atmosphere. A 7.5-ml sample of absolute trifluoroacetic acid, which had been degassed by freezing and thawing three times in vacuo [10^{-5} mm (mercury column)], was added to 0.5 g (1.4 mmole) of thiopyran II in a special apparatus in vacuo, and the reaction mixture was maintained in a helium atmosphere for 48 h. It was then worked up by the method in [1] to give 0.44 g (89%) of starting thiopyran II.

Reactions of Thiopyrans I and V with Trifluoroacetic Acid in a Helium Atmosphere. These reactions were realized by the method presented above.

General Method for the Ionic Hydrogenation of Thiopyrans I-V. A 5-mmole sample of absolute trifluoroacetic acid (or CF_3COOD) was added dropwise to a mixture of 1 mmole of thiopyran

TABLE 1. Characteristics of the New Sulfur-Containing Compounds*

Compound	mp,† °C	Found, %			Empirical formula	Calc., %		
		C	H	S		C	H	S
VII	111,5—113	83,8	7,1	8,8	$C_{25}H_{26}S$	83,8	7,3	8,9
VIII	174—175,5	80,9	8,1	10,7	$C_{20}H_{24}S$	81,1	8,1	10,8
IX	143,5—145	81,2	8,4	10,4	$C_{21}H_{26}S$	81,3	8,4	10,3
XIV	42—46	65,0	4,7	6,8	$C_{23}H_{21}F_3O_2S$	66,0	5,0	7,6

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*Trifluoroacetate XIII was an oil. It was identified from the IR spectral data and through the known 3,4,5-trimethyl-2,6-diphenylthiapyrylium perchlorate.

†Compounds VII-IX were crystallized from ethanol, while salt XIV was reprecipitated from solution in chloroform by the addition of petroleum ether.

I-V and 3 mmole of triethylsilane. At the end of the reaction the precipitated crystals of thiacyclohexanes VI-X were separated (see Table 1).

Reaction of Thiopyran I with Perchloric Acid and Triethylsilane. A 0.65-g (5.6 mmole) sample of triethylsilane and 0.5 ml (8.4 mmole) of $HClO_4$ were added successively to a suspension of 0.5 g (1.4 mmole) of thiopyran I in 15 ml of glacial acetic acid. At the end of the reaction (as monitored by thin-layer chromatography on Silufol) the precipitated crystals of the known thiacyclohexane VI were separated. The product, with mp 116-117°C (from ethanol) [1], was obtained in 78% yield.

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CONDENSED HETEROCYCLES WITH A THIAZOLE RING.

4.* THIAZOLO[3',4':1,2]PYRIMIDO[6,5-b]QUINOLINES

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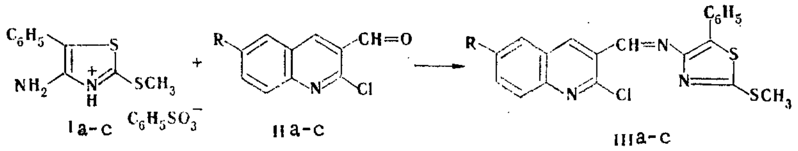
Derivatives of a new heterocyclic system that are suitable for the synthesis of dyes were obtained by condensation of 4-amino-2-methylthiazolium salts with 2-chloro-3-formylquinolines.

In an investigation of the possibility of the use of condensed heterocycles with a thiazole ring in the synthesis of dyes we studied the reaction of 4-amino-2-methylthio-5-phenylthiazoliumbenzenesulfonate (I) with 2-chloro-3-formylquinolines IIa-c.

We found that condensation products IIIa-c are readily formed when this reaction is carried out in acetic acid or dimethylformamide (DMF) at room temperature:



Absorption bands of N-H and C=O bonds at 3200-3400 and 1610-1750 cm^{-1} are absent in the IR spectra of the condensation products; thus the reaction leads to condensation rather than hetarylation of I, in which 2-methylthio-5-phenyl-4-(6-R-3-formyl-2-quinolyl)aminothiazole hydrochlorides (IV) or 4-amino-2-methylthio-5-phenyl-3-(6-R-3-formyl-2-quinolyl)thiazolium chlorides (V), which have similar elementary analysis data, might have been formed. The synthesized III do not form the corresponding monomethylidynecyanine and nullomethylidynemerocyanine dyes upon condensation with 2-methyl-3-ethylbenzothiazolium tosylate, and this constitutes evidence in favor of a structure of the III type for the condensation products, since it is known that quaternary salts of 4-amino-2-methylthio-5-phenylthiazole [2] and 2-methylthio-3-hetarylthiazolium salts [3] react under the same conditions. It should be noted that

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*See [1] for Communication 3.

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