zoxazin-4-ones. Treatment of the reaction mixture with $NaHCO_3$ solution, washing of the precipitate with water, and recrystallization from ethanol gave 0.53 g (33%) of a substance with mp 65.2-66.0°C. Found: C 79.1; H 7.8; N 3.6%. $C_{24}H_{29}NO_2$. Calculated: C 79.3; H 8.0; N 3.8%.

2-(4-Octyloxyphenyl)-6-n-butyl-4H-3,1-benzoxazin-4-one. This compound was obtained from 0.9 g (5 mmole) of 5-n-butylanthranilic acid and 2.68 g (0.01 mole) of 4-octyloxybenzoyl chloride by a method similar to that used in the preparation of the preceding compound. Crystallization from ethanol gave 0.5 g (25%) of a substance with mp 86-87°C. Found: C 76.5; H 8.1; N 3.3%. $C_{26}H_{33}NO_2$. Calculated: C 76.6; H 8.2; N 3.4%.

2-(trans-4-Pentyl-2-cyclohexyl)-6-(trans-4-pentylcyclohexanoyloxy)-4H-3,1-benzoxazin-4-one. This compound was obtained from 1.68 g (11 mmole) of 5-hydroxyanthranilic acid and 7.4 g (0.034 mole) of trans-4-pentylcyclohexane-1-carboxylic acid chloride in 50 ml of pyridine by a method similar to that used to prepare 2-aryl-6-aroyloxy-4H-3,1-benzoxazin-4-ones. Two crystallizations from ethanol gave 1.4 g (25%) of a substance with mp 214-215°C. Found: C 75.3; H 9.1; N 2.7;. $C_{31}H_{45}NO_4$. Calculated: C 75.1; H 9.1; N 2.8%.

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# DISPROPORTIONATION OF CONDENSED THIOPYRANS WITH TRIFLUOROACETIC AND DEUTEROTRIFLUOROACETIC ACIDS

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The disproportionation of isomeric 2,4-diphenyl-5,6-tetramethylene-4H-thiopyran, -6H-thiopyran, and 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene with trifluoroacetic and deuterotrifluoroacetic acids was investigated for the first time. The direction of protonation of the sulfides was established, and this made it possible to form a judgment regarding the structure of the intermediate carbonium ions, which are hydride-ion acceptors. The correctness of the mechanism of disproportionation of condensed two-ring sulfides with a 4H-thiopyran ring was proved. A mechanism for the disproportionation of isomeric 2,4-diphenyl-5,6-tetramethyl-6H-thiopyran and 2,4-diphenyl-5,6,7,9-tetrahydrothiochromene was proposed.

The reactions of 2,4-diphenyl-5,6-tetramethylene-6H-thiopyran (I), -4H-thiopyran (II), and 2,4-diphenyl-5,6,7,9-tetrahydro-4H-thiochromene (III)* with trifluoroacetic and deuterotrifluoroacetic acids have been investigated for the first time. It was established that 2,4-diphenyl-5,6-tetramethylenethiopyrylium trifluoroacetic (IV) and 3,5-diphenyl-2-thiabicyclo[4.4.0]decane (V)† are formed in the disproportionation of isomeric sulfides I-III with trifluoroacetic acid.

TABLE 1. PMR Spectra of Sulfides V, IX, and XI

| Compound | δ, ppm | | | | | J, Hz | | |
|---|---|---|---|---|---|---|---|---|
| | 1-H | 3-H | 5-H | Ar | $(CH_2)_n$ | $J_{3,4}$ | $J_{4,5}$ | $J_{5,6}$ |
| V | 3,50 m | 3,97 dd | 2,90 dt | 7,22 | 1,84 m | 3,0; 12,0 | 12,0 | 3,0 |
| IX | 3,63 m | 4,04 dt | 2,91 m | 7,22 | 1,83 m | 3,0; 4,2 | | |
| XI | 3,60 m | 4,04 dt | 2,90 m | 7,22 | 2,0—1,0 | 3,0; 4,2 | | |

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*See [1] for the structures of II and III.

†In the text and in Table 1, V, VII-IX, and XI are numbered in conformity with the system adopted for thiabicyclanes.

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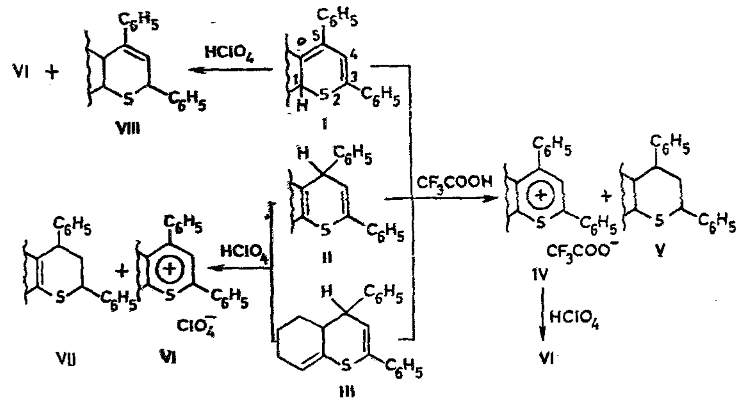
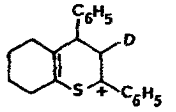


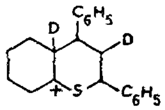
At the same time, it is known that 4H-thiopyran II reacts with perchloric acid to give perchlorate VI and 3,5-diphenyl-3-thiabicyclo[4.4.0]dec-$\Delta^{1,6}$-ene (VII), whereas isomeric 6H-thiopyran I under similar conditions gives perchlorate VI and 3,5-diphenyl-2-thiabicyclo-[4.4.0]dec-4-ene (VIII) [2, 3]. The action of perchloric acid on sulfide III, just as in the case of 4H-thiopyran II, leads to perchlorate VI and dihydrothiopyran VII.

Thus the double bonds of the heteroring during disproportionation are reduced in sulfide II in the 1 and 2 positions and in sulfide I in the 1 and 4 positions. Hydrothiochromene III is converted to salt VI and dihydrothiopyran VII through intermediate 4H-thiopyran II.

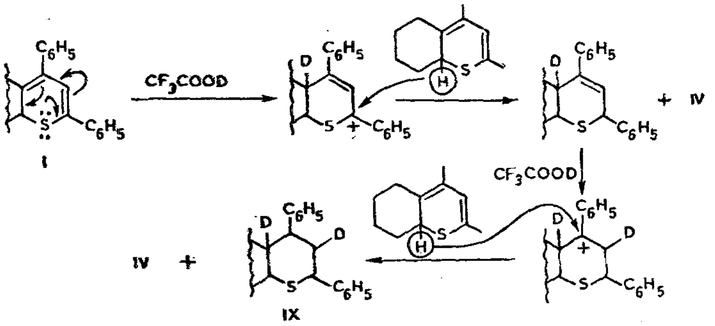
A study of the reactions of the indicated isomers with deuterotrifluoroacetic acid made it possible to establish the direction of protonation during disproportionation. It was found that both 4H-thiopyran II and 6H-thiopyran I react with $CF_3COOD$ to form trifluoroacetate IV and 4D,6D-3,5-diphenyl-2-thiabicyclo[4.4.0]decane (IX).

The formation of deuterated product IX gives an idea of the structure of the intermediate carbonium ions, which are hydride-ion acceptors. Carbonium ions A and B are evidently formed in the disproportionation of 4H-thiopyran II, and this confirms the overall scheme of the disproportionation of 4H-thiopyrans, including condensed 4H-thiopyrans [4-6].

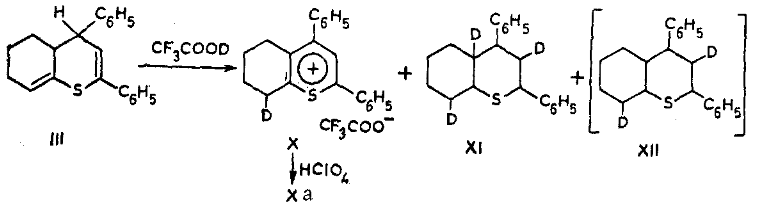

A


B

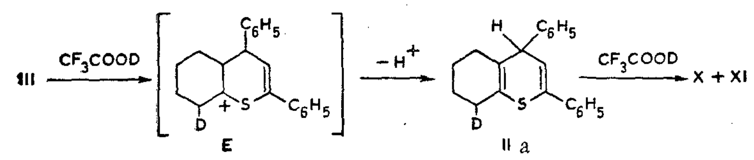
The formation of sulfide IX from 6H-thiopyran I serves as evidence for a mechanism for its disproportionation through an intermediate 6D-3,5-diphenyl-2-thiabicyclo[4.4.0]dec-4-ene, which is formed as a result of the reduction of the diene system of bonds in the 1 and 4 positions.



Deuterated salt X and a mixture of two saturated deuterated sulfides, viz., XI and, evidently, XII, from which 4D,6D,10D-3,5-diphenyl-2-thiabicyclo[4.4.0]decane (XI) was isolated and characterized, are formed in the reaction of hydrothiochromene III and $CF_3COOD$.



These results constitute evidence for isomerization of hydrothiochromene III to 4H-thiopyran IIa, which subsequently undergoes disproportionation via the general scheme



Carbonium ion E can evidently act as a hydride-ion acceptor. Hence, one might expect the formation of 4D,10D-3,5-diphenyl-2-thiabicyclo[4.4.0]decane (XII), which, however, we were unable to isolate in individual form.

Absorption bands at 2110 and 2200 $cm^{-1}$, which correspond to stretching vibrations of the C—D bond, are observed in the IR spectra of IX and XI and perchlorate Xa. The structure of sulfides IX and XI is confirmed by their PMR spectra and the spectrum of thiabicyclodecane V (Table 1), which attest to a change in the form of the signals of the 3-H and 5-H protons in deuterated analogs IX and XI. The signal of the 3-H proton from the double doublet at 3.97 ppm with spin—spin coupling constants (SSCC) 3.0 and 12.0 Hz in the spectrum of sulfide IX without changing its position. The signal of the 5-H proton from the double triplet at 2.90 ppm in the spectra of sulfide V is converted to a multiplet in deuterated analog IX. Since splitting of the signals with SSCC 12 Hz is absent in the spectrum of sulfide IX, it should be assumed that the deuterium attached to $C_4$ is axially oriented.*.

The position and form of the signals in the spectrum of sulfide XI are similar. The principal difference in the spectra of IX and XI is displayed in the 1.0-2.0 ppm region. The form of the signals of the methylene protons in the spectrum of sulfide XI is complicated, and this evidently indicates replacement of one of the alicyclic protons by deuterium.

## EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in $CCl_4$ were recorded with a Tesla BS-477 spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The course of the reaction was monitored by means of thin-layer chromatography (TLC) on Silufol UV-254 in a hexane—ether system (25:1).

The starting isomeric sulfides I-III were obtained as described in [8-10].

Disproportionation of Sulfides I-III with Trifluoroacetic Acid. A 1-g sample of sulfide I-III was refluxed in 3 ml of trifluoroacetic acid for 3-18 h (until complete disappearance of the intermediate dihydrothiopyrans). The reaction mixture was then diluted with 10 ml of ether, cooled, and treated with 2 ml of 70% $HClO_4$. Workup gave perchlorate VI in 62% yield [11]. The ether extract was washed with water, dried, and evaporated to give 628 mg (28%) of thiabicyclodecane V [11].

The disproportionation of sulfides I-III with D-trifluoroacetic acid was carried out similarly.

4D,6D-3,5-Diphenyl-2-thiabicyclo[4.4.0]decane (IX). This compound had mp 130-131°C (from ethanol). Found: C 81.0; H 8.3; S 10.2%. $C_{21}H_{21}D_3S$. Calculated: C 81.3; H 8.4; S 10.3%.

4D,6D,10D-3,5-Diphenyl-2-thiabicyclo[4.4.0]decane (XI). This compound was obtained in 13% yield and had mp 121-123°C (from acetone). Found: C 80,5; H 8.6; S 10.1%. $C_{21}H_{21}D_3S$. Calculated: C 80.1; H 8.7; S 10.3%.

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*See [7] for information regarding the structures of sulfides V and IX.

8D-2,4-Diphenyl-5,6,7,8-tetrahydrothiochromylium Perchlorate (Xa). This compound was obtained in 55% yield and had mp 179-181°C (from acetic acid). Found: C 62.4; H 4.3; S 7.6%. $C_{21}H_{18}ClDO_4S$. Calculated: C 62.5; H 4.5; S 7.9%.

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