REACTIONS OF 1,5-DIPHENYL-2,4-DIMETHYL-1,5-PENTANEDIONE WITH HYDROGEN SULFIDE

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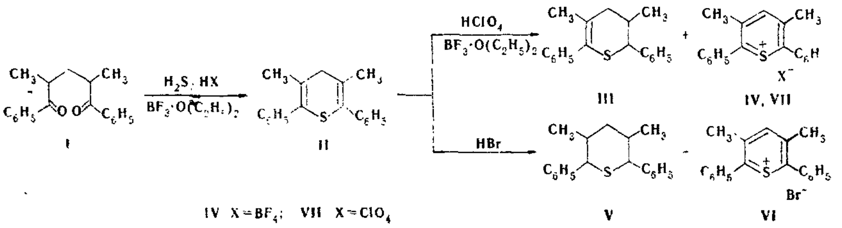
1,5-Diphenyl-2,4-dimethyl-1,5-pentanedione reacts with hydrogen sulfide in the presence of boron trifluoride etherate or 70% perchloric acid to give the corresponding thiapyrylium salts and 2,6-diphenyl-3,5-dimethyldihydrothiopyran; complete disproportionation to give 2,6-diphenyl-3,5-dimethylthiacyclohexane and 2,6-diphenyl-3,5-dimethylthiapyrylium bromide occurs in the presence of hydrogen bromide. The possibility of catalytic hydrogenation in the presence of 10% Pd/C of compounds with a thiopyran ring was established.

In the reaction of 1,5-diketones with hydrogen sulfide and hydrogen chloride in acetic acid media 4H-thiopyrans are usually formed in the first 2-3 h, after which they undergo disproportionation as a result of intermolecular hydride ion transfer to give thiacyclohexanes and thiapyrylium salts [1]. However, in the case of 1,5-diphenyl-2,4-dimethyl-1,5-pentanedione (I) this sort of disproportionation is observed only when the reaction is carried out in the presence of a stronger protonating reagent – trifluoroacetic acid [2].

We have studied the reaction of 1,5-diketone I with hydrogen sulfide in the presence of an aprotic catalyst – boron trifluoride etherate – and also in the presence of strong protic acids such as perchloric acid or hydrogen bromide, the acidities of which in nonaqueous solvents are two orders of magnitude higher than the acidity of hydrogen chloride.

Considering the aprotic character of boron trifluoride etherate, one might have expected the formation of the corresponding thiopyrans or complexes of the latter with boron trifluoride as a result of its reaction with 1,5-diketones. It was found that the reaction of diketone I with hydrogen sulfide and boron trifluoride etherate in absolute ether gives 2,6-diphenyl-3,5-dimethyldihydrothiopyran (III) and 2,6-diphenyl-3,5-dimethylthiapyrylium tetrafluoroborates (IV).



The reaction proceeds more actively in acetic acid and is complete in a shorter time.

It was observed by thin-layer chromatography (TLC) of the reaction mixture that diketone I reacts initially with hydrogen sulfide and boron trifluoride etherate to give 4H-thiopyran II, which is converted to dihydrothiopyran III and thiapyrylium tetrafluoroborate IV under the reaction conditions. This is also confirmed by the conversion of 4H-thiopyran with boron trifluoride etherate to dihydrothiopyran III and thiapyrylium tetrafluoroborate IV.

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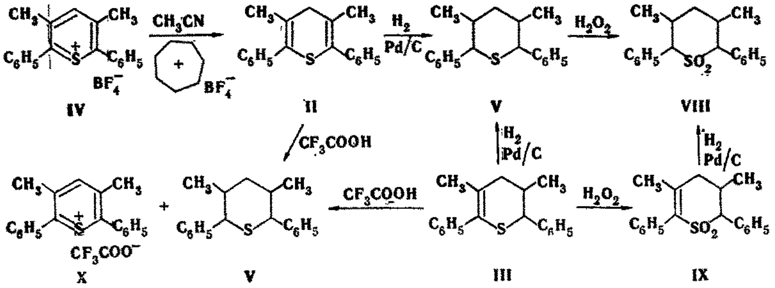
The reaction of diketone I with hydrogen sulfide in the presence of hydrogen bromide proceeds with the formation of products of complete disproportionation – thiacyclohexane V and thiapyrylium bromide VI.

Bromide VI and 2,6-diphenyl-3,5-dimethylthiapyrylium tetrafluoroborate (IV) react with perchloric acid to give thiapyrylium perchlorate VII. The structure of tetrafluoroborate IV was confirmed by comparison with a sample of the thiapyrylium salt obtained as a result of the reaction of thiopyran II with tropylium tetrafluoroborate. This reaction constitutes evidence for the greater hydride lability of the hydrogen in 4H-thiopyran II.

Two absorption maxima characteristic for the absorption of the thiapyrylium cation – λ_{max}, nm (log ε): 247 (4.23) and 370 (4.12) – are present in the UV spectra of thiapyrylium salts IV and VI. Intense absorption bands at 1380, 1455, 1470, and 1560 cm^{-1}, which are characteristic for the thiapyrylium cation, are observed in the IR spectra, and the intense absorption of the BF_4^- anion at 1060 cm^{-1} is noted for salts IV.

One might have expected that products of disproportionation of V, VII would be formed in the reaction of diketone I with hydrogen sulfide in the presence of perchloric acid. However, it was found that protonation of the initially formed thiopyran II in the presence of 70% perchloric acid is realized only at one double bond to give a dihydrothiopyran and thiapyrylium perchlorate VII. These same products are also obtained in the direct reaction of thiopyrans II with 70% perchloric acid. This unexpected course of the reaction can be explained by the fact that the disproportionation of thiopyran II occurs in a stepwise manner, and, as a result of the low solubility in acetic acid of dihydrothiopyran III, which is formed during protonation of one double bond, its further conversion becomes impossible. However, upon reaction with trifluoroacetic acid, dihydrothiopyran III is relatively readily converted to thiacyclohexane V and thiapyrylium trifluoroacetate X. The latter was identified in the form of the corresponding perchlorate (VII).

In order to confirm the structure of thiacyclohexane V and dihydrothiopyran III we accomplished the catalytic hydrogenation of thiopyran II, dihydrothiopyran III, and sulfone IX over 10% Pd/C.



The substances obtained in the catalytic hydrogenation of thiopyran II and dihydrothiopyran III were identical to one another and identical to sulfide V obtained by disproportionation of II and III with trifluoroacetic acid.

The IR spectrum of sulfide V does not contain bands in the region of C=C bond absorption (1600-1700 cm^{-1}), and this constitutes evidence for the saturated character of the heteroring.

Absorption of a C=C bond at 1628 cm^{-1}, the position of which was established by means of PMR spectroscopy, is observed in the IR spectrum of III. The singlet at δ 7.22 ppm in the PMR spectrum of dihydrothiopyran III is affiliated with the equivalent protons of phenyl groups. The signals of 2-H and (3-4)-H protons are found at δ 4.09 and 2.17 ppm, respectively. The protons of the methyl group attached to C-3 give a doublet at δ 0.86 ppm. The presence in the spectrum of a singlet at 1.60 ppm, which is related to the $=C-CH_3$ group, and the absence of the signal of a vinyl proton make it possible to assign the 5,6 position to the double bond in dihydrothiopyran III.

The ratio of the integral intensities is in agreement with the proposed structure.

Sulfone IX – the product of oxidation of dihydrothiopyran II – is converted to sulfone VIII as a result of hydrogenation. Sulfone VIII is identical to the sulfone obtained by oxidation of sulfide V.

In addition to absorption at 1150 and 1230 cm^{-1}, which corresponds to the symmetrical and asymmetrical vibrations of the SO_2 group, absorption for a C=C bond at 1620 cm^{-1} is noted in the IR spectrum of sulfone IX. The PMR spectrum of sulfone IX is similar to the spectrum of starting sulfide III. However,

TABLE 1. Reaction of 1,5-Diketone I and 4H-Thiopyran III with Acidic Reagents

Starting compound	Medium	Acidic reagent	Reaction product	Yield, %
I	Absolute ether	$BF_3 \cdot OEt_2$	III and IV	47 and 47
I	CH_3COOH	$BF_3 \cdot OEt_2$	III and IV	49 and 51
I	CH_3COOH	HBr	V and VI	27 and 60
II	$BF_3 \cdot OEt_2$	$BF_3 \cdot OEt_2$	III and IV	46,6 and 47
II	CH_3COOH	$HClO_4$	III and VII	20 and 55
II	CH_3COOH	HBr	V and IV	28 and 60
II	CF_3COOH	CF_3COOH	V and X*	26 and 56
III	CF_3COOH	CF_3COOH	V and X*	35 and 40

*Identified in the form of the corresponding perchlorate (VII).

the presence of a SO_2 group in IX leads to a certain shift in all of the signals to strong field, particularly for the signal for $=C-CH_3$ (by 0.19 ppm) and $-C-CH_3$ (by 0.26 ppm) fragments.

EXPERIMENTAL METHOD

The IR spectra of mineral oil and hexachlorobutadiene suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of acetonitrile solutions (10^{-3} M) were recorded with an SF-4A spectrophotometer. The PMR spectra of CCl_4 solutions were recorded with an RYa-2306 spectrometer with hexamethyldisiloxane as the internal standard.

The conversion of the diketones was monitored by TLC on Silufol UV 254 in hexane–ether (6 : 1) with development in iodine vapors. The 10% Pd/C catalyst was prepared by the method in [4].

Reaction of 1,5-Diphenyl-2,4-dimethyl-1,5-pentanedione with Hydrogen Sulfide and Boron Trifluoride Etherate (or 70% Perchloric Acid). A solution of 4.76 g (0.017 mole) of 1,5-diketone I in 60 ml of absolute ether (or glacial acetic acid) was saturated with hydrogen sulfide at 20° for 2 h, after which 10 ml (0.07 mole) of boron trifluoride etherate or 10 ml (0.16 mole) of 70% $HClO_4$ was added. The mixture was then allowed to stand for 40 h for complete conversion of the starting diketone (chromatographic monitoring). The resulting precipitate was removed by filtration, washed with alcohol, air-dried, and reprecipitated from acetic acid solution by the addition of ether to give 2.92 g (47%) of thiapyrylium tetrafluoroborate IV with mp 157-158°. Found: C 62.5; H 4.8; S 8.6%. $C_{19}H_{17}SBF_4$. Calculated: C 62.7; H 4.7; S 8.8%. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 247 (4.35) and 370 (4.12). PMR spectrum, δ, ppm: 2.64 s (6H, CH_3), 7.52 m (10H, C_6H_5), and 8.40 s (1H, C-4). Thiapyrylium perchlorate VII [2.8 g (46%)], with mp 152-155°, was similarly isolated. Found: C 60.8; H 4.5; S 8.8%. $C_{19}H_{17}SClO_4$. Calculated: C 60.5; H 4.5; S 8.5%. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 246 (4.06) and 370 (3.92). PMR spectrum, δ, ppm: 2.33 s (6H, CH_3), 7.24 m (10 H, C_6H_5), and 8.40 s (1H, C-4).

The ether filtrate obtained after separation of salt IV (or VII) was washed with water and dried with Na_2SO_4, after which the ether was removed by distillation. The resulting precipitate was removed by filtration, washed with alcohol, dried, and recrystallized from alcohol to give 2.2 g (47%) of dihydrothiopyran III with mp 64-64.5°. Found: C 81.4; H 7.0; S 11.2%. $C_{19}H_{20}S$. Calculated: C 81.4; H 7.1; S 11.4%.

Reaction of 1,5-Diphenyl-2,4-dimethyl-1,5-pentanedione with Hydrogen Sulfide and Hydrogen Bromide. A solution of 4.1 g (0.15 mole) of diketone I in 50 ml of glacial acetic acid was saturated successively with hydrogen sulfide at 20° for 2 h and with a mixture of hydrogen sulfide and hydrogen bromide for another 2 h. The mixture was then allowed to stand for 30 h for complete conversion of the starting diketone (chromatographic monitoring), after which it was poured into 150 ml of ether. The resulting precipitate was removed by filtration, washed with ether, dried, and reprecipitated from acetic acid solution by the addition of ether to give 2.54 g (60%) of thiapyrylium bromide VI. Found: C 63.7; H 4.6; Br 22.2; S 8.9 %. $C_{19}H_{17}SBr$. Calculated: C 63.9; H 4.8; Br 22.3; S 8.9%. UV spectrum (CH_3CN), λ_{max}, nm (log ε): 246 (4.06) and 370 (3.92). PMR spectrum δ, ppm: 2.4 s (6H, CH_3), 7.45 m (10H, C_6H_5), and 8.4 s (1H, C-4).

The ether filtrate remaining after isolation of salt VI was washed with water and dried with Na_2SO_4, after which the ether was removed by distillation. The resulting precipitate was removed by filtration, washed with alcohol, dried, and recrystallized from alcohol to give 1.12 g (27%) of thiacyclohexane V with mp 167-168°. Found: C 80.8; H 7.7; S 11.3%. $C_{19}H_{22}S$. Calculated: C 80.9; H 7.8; S 11.3%. PMR spectrum, δ, ppm: 7.23 s (10H, C_6H_5), 4.36 d (2H, C-2, C-6), 1.66 m (4H, C-3, C-4, and C-5), and 0.97 d (6H, CH_3).

2,6-Diphenyl-3,5-dimethylthiapyrylium Tetrafluoroborate (IV). A 0.32-g (2 mmole) sample of tropylium fluoroborate was added to a solution of 0.544 g (2 mmole) of 4H-thiopyran II in 10 ml of acetonitrile, and the resulting mixture was refluxed for 5-10 min. It was then cooled and poured into 50 ml of ether. The resulting precipitate was removed by filtration, washed with ether, dried and purified by the reprecipitation method described above to give 0.632 g (93%) of thiapyrylium tetrafluoroborate IV, which with respect to its melting point and IR, UV, and PMR spectra was identical to IV obtained by reaction of diketone I with hydrogen sulfide and boron trifluoride etherate.

Reaction of 2,6-Diphenyl-3,5-dimethyl-4H-thiopyran (II) with Trifluoroacetic Acid. A solution of 1.5 g (5 mmole) of thiopyran II in 10 ml of trifluoroacetic acid was stirred for 2-3 h, and the resulting precipitate was removed by filtration, washed with alcohol, dried, and recrystallized from alcohol to give 0.4 g (26%) of thiacyclohexane V; according ot its melting point and IR spectrum, this product was identical to sulfide V obtained by reaction of diketone I with H_2S and HBr. The filtrate was poured into 50 ml of hexane, and the resulting oily product was separated, washed with hexane, dried, and identified in the form of perchlorate VII. The yield was 56%. The reaction of 2,6-diphenyl-3,5-dimethyldihydrothiopyran III with trifluoroacetic acid was carried out similarly. The yield of thiacyclohexane V, with mp 166-166.5° (from alcohol), was 35%. The yield of thiapyrylium trifluoroacetate X was 40% (identified in the form of perchlorate VII) was also obtained in 85-90% yields by anion exchange reaction of thiapyrylium salts IV, VI, and X with 70% $HClO_4$.

Reaction of 2,6-Diphenyl-3,5-dimethyl-4H-thiopyran (II) with Boron Trifluoroide Etherate. A solution of 1.5 g (5 mmole) of thiopyran II in 15 ml of boron trifluoride etherate was held at 20° for 12 h, after which the resulting precipitate was removed by filtration, washed with alcohol, dried, and recrystallized from alcohol to give 0.5 g (46.6%) of dihydrothiopyran III. The filtrate was poured into ether, and the resulting precipitate was removed by filtration, washed with ether, dried, and reprecipitated from acetic acid solution by the addition of ether to give 0.6 g (47%) of thiapyrylium tetrafluoroborate IV.

The reaction of 4H-thiopyran II with 70% $HClO_4$ was carried out similarly. The yield of dihydrothiopyran III, with mp 64-64.5° (alcohol), was 20%. The yield of thiapyrylium perchlorate VII, with mp 152-153° (reprecipitated from acetic acid solution by the addition of ether), was 55%.

2,6-Diphenyl-3,5-dimethylthiacyclohexane S,S-Dioxide (VIII). Oxidation of 1 g (5 mmole) of thiacyclohexane V with hydrogen peroxide [2] gave 0.98 g (90%) of sulfone VIII with mp 244-246° (alcohol). Found: C 72.6; H 7.1; S 10.1%. $C_{19}H_{22}SO_2$. Calculated: C 72.6; H 7.0; S 10.2%. PMR spectrum, δ, ppm: 7.23 s (10H, C_6H_5), 4.36 d (2H, C-2, C-4), 1.66 m (4H, C-3, C-4, and C-5), and 0.97 d (6H, CH_3).

2,6-Diphenyl-3,5-dimethyldihydrothiopyran S,S-dioxide (IX), with mp 137.5-138° (alcohol) was similarly obtained in 87% yield. Found: C 73.0; H 6.5; S 10.2%. $C_{19}H_{20}SO_2$. Calculated: C 73.1; H 6.4; S 10.3%. PMR spectrum, δ, ppm: 7.02 (10H, C_6H_5), 4.20 d (1H, C-2), 3.69 m (1H, C-3), 20.7 m (2H, C-4), 1.41 s (3H, $=C-CH_3$), and 0.58 d (3H, $-C-CH_3$).

2,3-Diphenyl-3,5-dimethylthiacyclohexane (V). A solution of 1 g (4 mmole) of 4H-thiopyran II in 50 ml of alcohol was placed in an autoclave, and 1 g of a 10% Pd/C catalyst was added to the solution. The compound was hydrogenated at an initial hydrogen pressure of 50 atm at 100° for 5.5 h. The catalyst was then removed by filtration, and the precipitate that formed during evaporation of the filtrate was separated, washed with alcohol, dried, and recrystallized from alcohol to give 0.6 g (59%) of thiacyclohexane V with mp 166.5-167°.

A total of 0.7 g (60%) of a compound identical to sulfide V with respect to its melting point and IR and PMR spectra was similarly obtained from 1 g (4 mmole) of dihydrothiopyran III.

2,6-Diphenyl-3,5-dimethylthiacyclohexane S,S-dioxide (VIII) was obtained by catalytic hydrogenation of 1.6 g (5 mmole) of 2,6-diphenyl-3,5-dimethyldihydrothiopyran IX as in the preceding experiment. The yield of VIII was 1.2 g (70%).

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