THIAPYRYLIUM TRIFLUOROACETATES AND THIACYCLOHEXANES FROM 1,5-DIKETONES

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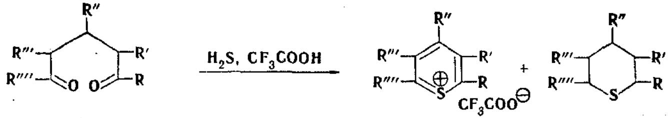
1,5-Diketones react with hydrogen sulfide and trifluoroacetic acid to give a mixture of thiapyrylium trifluoroacetates or sym-octahydrothiaxanthylium trifluoroacetates with thiacyclohexanes or perhydrothiaxanthenes, respectively.

To elucidate the mechanism of the reaction of 1,5-diketones with hydrogen sulfide and protic acids [1,2], we have studied the reaction of pentane-1,5-diones (I-VI) and alkylidenecyclohexanones (VII-VIII) with hydrogen sulfide and trifluoroacetic acid. It can be assumed that 1,5-diketones V-VI, which form only α- or γ-thiapyrans with H_2S/HCl in acetic acid, will be converted with H_2S and the stronger trifluoroacetic acid to a mixture of the corresponding thiacyclohexanes and thiapyrylium trifluoroacetates.

Trifluoroacetic acid served as the medium and reagent in this reaction. It was found that 1,3,5-triaryl- and 1,5-diaryl-3-alkylpentane-1,5-diones I-IV react smoothly with H_2S and CF_3COOH to give a mixture of crystalline thiapyrylium trifluoroacetates (IX-XII) and thiacyclohexanes (XVII-XX). 1,2,4,5- and 1,2,3,5-Arylalkyl-substituted pentane-1,5-diones (V-VI) and alkylidenedicyclohexanones (VII-VIII) readily react with H_2S and CF_3COOH to form readily crystallized thiacyclohexanes (XXI and XXII) and perhydrothiaxanthenes (XXIII and XXIV) but with difficulty form either uncrystallizable thiapyrylium trifluoroacetates (XI and XII) or octahydrothiaxanthylium trifluoroacetates (XV, XVI).



I-VIII IX-XVI XVII-XXIV

I, IX, XVII $R=R''''=C_6H_5$, $R'=R'''=H$, $R''=CH_3$; II, X, XVIII $R=R''=R''''=C_6H_5$, $R'=R'''=H$; III, XI, XIX $R=R''''=\alpha$ thienyl $R'=R'''=H$, $R''=C_6H_5$; IV, XII, XX $R=R''''=C_6H_5$, $R'=R'''=H$, $R''=C_6H_4OCH_3$-p; V, XIII, XXI $R=R''''=C_6H_5$, $R'=R'''=CH_3$, $R''=H$; VI, XIV, XXII $R=R''=R''''=C_6H_5$, $R'=CH_3$, $R'''=H$; VII, XV, XXIII $R+R'=R'''+R''''=(-CH_2-)_4$, $R''=H$; VIII, XVI, XXIV $R+R'=R'''+R''''=(-CH_2-)_4$, $R''=CH_3$

The results obtained for diketones I-VIII, particularly for V and VI, confirm the role of trifluoroacetic acid as a strong protonating reagent and make it possible to conclude that the reaction [1] of 1,5-diketones with H_2S and protic acids is general in character. The results are also indirect proof of the mechanism that we proposed in [1,2] for the reaction, which includes a step involving the protonation of γ- or α-thiapyrans to form carbonium ions that act as hydride-ion acceptors (see scheme on following page).

Compounds IX-XVI are dark-red or green substances. The salt-like nature of IX-XVI is confirmed by their capacity to enter into anion-exchange reactions with KI and $HClO_4$ to give known salts – thiapyrylium iodides [2,3] and perchlorates [3] or sym-octahydrothiaxanthylium iodides and perchlorates [2].

The IR spectra of trifluoroacetates IX-XVI contain absorption bands at 1400-1410, 1470-1490, and 1560-1580 cm^{-1}, which are characteristic for the thiapyrylium cation. The first two bands are overlapped with the absorption bands of the aryl groups. The band at 1560-1580 cm^{-1} is distinguished by a very high

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TABLE 1. Characteristics of the Synthesized Compounds

Starting diketone	Reaction time, h	Compounds obtained[a]	mp, °C	Emprical formula	Found, %			Calc., %			Yield, %
					C	H	S	C	H	S	
I	50	Trifluoroacetate (IX)	76—77	$C_{20}H_{15}F_3O_2S$			8,8			8,5	66
		Thiacyclohexane (XVII)	63—64[b]								27,3
II	48	Trifluoroacetate (X)	176—177	$C_{25}H_{17}F_3O_2S$			7,2			7,3	51
		Thiacyclohexane (XVIII)	106—108[b]								30
III	50[c]	Trifluoroacetate (XI)	69—70	$C_{21}H_{13}F_3O_2S_3$			21,7			21,3	60,6
IV	50	Trifluoroacetate (XII)	133—134	$C_{26}H_{19}F_3O_3S$			6,2			6,8	65,4
		Thiacyclohexane 1,1-dioxide (XXa)	274—276	$C_{24}H_{24}O_2S$	73,2	6,2	7,9	73,5	6,1	8,1	24
V	72	Trifluoroacetate (XIII)[d]	—	—	—	—	—	—	—	—	56
		Thiacyclohexane (XXI)	166—167	$C_{19}H_{22}S$	80,8	7,7	11,2	80,9	7,8	11,4	25
		Thiacyclohexane 1,1-dioxide (XXIa)	254—255	$C_{19}H_{22}O_2S$	72,4	7,1	10,0	72,6	7,0	10,2	85
VI	72[c]	Trifluoroacetate (XIV)[d]	—	—	—	—	—	—	—	—	63,7
		Thiacyclohexane (XXII)	122—123	$C_{24}H_{24}S$	84,6	7,3	9,3	83,7	7,0	9,3	25
		Thiacyclohexane 1,1-dioxide (XXIIa)	265—266	$C_{24}H_{24}O_2S$	76,1	7,0	8,4	76,6	6,4	8,5	90
VII	12—14	Trifluoroacetate (XV)	98—102[e]								45
		Perhydrothiaxanthene (XXIII)	70—71[b]								15
VIII	48—50	Trifluoroacetate (XVI)[d]									60
		9-Methylperhydrothiaxanthene (XXIV)	126—128[b]								11

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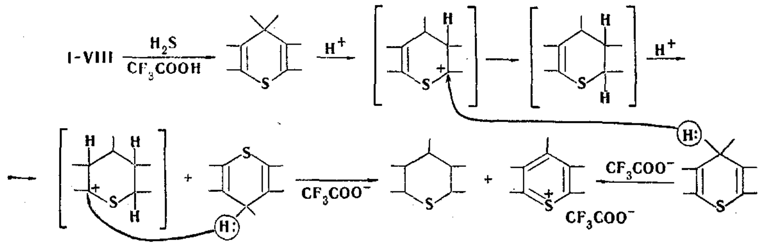
[a] Compounds XVII-XXIII and XXa, XXIIa, and XXIIIa were crystallized from alcohol, IX-XII were purified by precipitation from chloroform or acetic acid by the addition of hexane or ether. [b] Identified by mixed-melting-point determination with an authentic sample [1,2]. [c] The reaction mixture was worked up in the presence of traces of unchanged 1,5-diketone in the mixture. [d] The trifluoroacetate did not crystallize and was identified through the corresponding iodide and perchlorate [2,3]. [e] The trifluoroacetate was hard to crystallize and readily deliquesced in air. The melting point presented here is that of the unreprecipitated crystals.



intensity (up to 90%) and makes it possible to readily detect the thiapyrylium cation. In the case of the sym-octahydrothiaxanthylium cation, this band is of medium intensity but is clearly isolated, since there are no other absorption bands in this region. We will assign the strong bonds at 1140-1200 cm^{-1} to the deformation vibrations of the C—F bond in the CF_3 group [4]. The 1680-1780 cm^{-1} region contains a broad intense band with two or three peaks, which is characteristic for ν_{as} C—O in the CF_3COO^- ion [4].

The structure of thiacyclohexanes XVII-XVIII and XXIII-XXIV was confirmed by a comparison with authentic samples of thiacyclohexanes [1] and perhydrothiaxanthenes [2]. Thiacyclohexanes XXI-XXII were obtained for the first time. The structure of the latter was confirmed by the results of elementary analysis and by their conversion to the corresponding sulfones (XXIa and XXIIa) on oxidation with hydrogen peroxide. Thiacyclohexanes XXI and XXII and their sulfones (XXIa and XXIIa) are colorless, readily crystallizable, stable substances. Their IR spectra do not contain bands in the region of C=C bond absorption (1600-1700 cm^{-1}), which attests to the saturated character of the heteroring.

2,6-Diphenyl-4-(p-methoxyphenyl)thiacyclohexane (XX) was identified through the sulfone – 2,6-diphenyl-4-(p-methoxyphenyl)thiacyclohexane 1,1-dioxide (XXa). 1,5-Diketone III readily forms a crystalline thiapyrylium trifluoroacetate (XI), but the expected thiacyclohexane cannot be preparatively isolated, although the chromatogram attests to its presence in the reaction mixture.

EXPERIMENTAL

Reaction of Pentane-1,5-dione (I) with Hydrogen Sulfide and Trifluoroacetic Acid. A 16-g (0.06 mole) sample of pentane-1,5-dione I was dissolved in 50 ml of CF_3COOH, and the solution was saturated with hydrogen sulfide at 20° for 4 h. The mixture was held at room temperature until the spot of diketone I vanished on the thin-layer chromatogram. Petroleum ether or n-hexane was then added to precipitate green crystals of thiapyrylium trifluoroacetate IX. The crystals were washed with the same solvent and dried to constant weight in vacuo to give 14.9 g (66%) of a product with mp 76-77° [reprecipitated from chloroform—ether (2:1) by the addition of hexane] (see Table 1).

The ether or hexane extracts were washed with sodium carbonate solution and water and dried over Na_2SO_4. The solvent was removed by distillation, and the residue was crystallized to give 4.4 g (27%) of colorless crystals of 2,6-diphenyl-4-methyl-1-thiacyclohexane (XVII) with mp 63-64° (from alcohol) (Table 1). The reaction of 1,5-diketones II-VIII with H_2S in CF_3COOH was carried out similarly (Table 1).

Anion-Exchange Reaction of Thiapyrylium Trifluoroacetate IX with Potassium Iodide. A 0.2-g sample of salt IX was dissolved in 3 ml of acetone, and a solution of 0.3 g of KI in 5 ml of water was added to precipitate 2,6-diphenyl-4-methylthiapyrylium iodide. It was removed by filtration, washed with water, and dried to give 0.18 g (90%) of a product with mp 172° (from acetic acid). This product did not depress the melting point of an authentic sample [3].

The anion-exchange reactions of thiapyrylium trifluoroacetates X-XIV and sym-octahydrothiaxanthylium trifluoroacetates XV-XVI with potassium iodide were carried out similarly. The corresponding thiapyrylium and sym-octahydrothiaxanthylium iodides were identified by mixed-melting-point determinations with the iodides obtained by the methods in [2,3].

Anion-Exchange Reaction of 2,6-Diphenyl-3,5-dimethylthiapyrylium Trifluoroacetate (XIII) with Perchloric Acid. A 6.55-g sample of oily trifluoroacetate XIII was dissolved in 6 ml of acetic acid, and 8.5 ml of 70% perchloric acid was added to give a yellow crystalline precipitate of 2,6-diphenyl-3,5-dimethylthiapyrylium perchlorate. To ensure complete precipitation, 50 ml of ether was added, and the crystals were removed by filtration to give 5.5 g (88%) of a product with mp 165-166° (from acetic acid). This product did not depress the melting point of an authentic sample [3].

The perchlorates obtained by the action of perchloric acid on thiapyrylium trifluoroacetates IX-XII and XIV and sym-octahydrothiaxanthylium trifluoroacetate XV were identified by fusion of mixtures of them with authentic samples obtained by the methods described in [2, 3].

Sulfones (XXIa-XXIIa) of Thiacyclohexanes XXI-XXII. These compounds were obtained by oxidation of XXI and XXII with 30% hydrogen peroxide in acetic acid, as described in [3] (Table 1).

The IR spectra of mineral-oil suspensions were recorded with a UR-10 spectrometer.

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