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SYNTHESIS AND REACTIONS OF 1-ALKYL-SUBSTITUTED 1,5-DIKETONES WITH SULFUROUS REAGENTS

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1-Alkyl-substituted 1,5-diketones react with sulfurous reagents (H_2S and P_4S_{10}) to give thiopyrylium salts primarily via a mechanism that is competitive with disproportionation. The reaction depends on the nature of the acidic reagent. Some properties of the compounds obtained are described.

The character of the chemical transformations of 1,5-diarylpentanediones in reactions with nucleophilic reagents has recently been the subject of intensive study [1, 2]. In reactions with sulfurous reagents (P_xS_y, H_2S) thiopyrylium salts are formed via two competitive mechanisms that are determined by the structural peculiarities of the 1,5-dicarbonyl compounds and the reaction conditions [3]. The conversion of 1,5-dialdehydes (glutaraldehyde and its alkyl-substituted derivatives) with H_2S/HCl has been given an interpretation by Strating and Molenaar [4] that differs from what we have observed [1, 3]. One might have expected that 1,5-dialkyl- or 1,5-alkylarylpentanediones would display certain specific characteristics under acid-catalysis conditions.

Taking into account the information stated above, as well as the interest in thiopyrylium salts in connection with their extensive practical importance [5], we synthesized unsymmetrical α-alkyl-substituted 1,5-diketones I and II and studied their heterocyclization with sulfurous reagents, viz., hydrogen sulfide and phosphorus pentasulfide, under various conditions. The selection of 1,5-diketones I and II, which have a tert-butyl substituent in the α position relative to the carbonyl group, was due to the fact that the presence of other alkyl substituents such as a methyl or methylene group usually leads to carbocyclization [6]. The tert-butyl group in the α position of diketones I and II prevents carbocyclization of the latter; however, the Michael reaction is hindered as a consequence of steric factors, as a result of which the yields reach only 40-46%.

TABLE 1. Reaction of Alkyl-Substituted Diketones I and II with Sulfurous Reagents and of 4H-Thiopyrans IV and V with Acids

Starting compounds	Reagents	Solvent*	Reaction time, h	Reaction products (yield, %)
II	$H_2S/HClO_4$	CH_3COOH†	70	VIII (81)
I	P_4S_{10}	Dioxane	22	V (2,3) IX (80,5)
II	P_4S_{10}	Dioxane	17	IV (2) X (63)
I	P_4S_{10}	Pyridine	25	III (65)
II	P_4S_{10}	Pyridine	2,5	IV (72)
IV	CH_3COOH	CH_3COOH	20	XII (82)
V	CH_3COOH	CH_3COOH	25	XI (76)
IV	$HClO_4$	CH_3COOH†	70	VIII (83)
IV	CF_3COOH	Cl_3COOH†	30	VI (24) XV (61)

*The reaction was carried out at 100°C.
†At 20°C.

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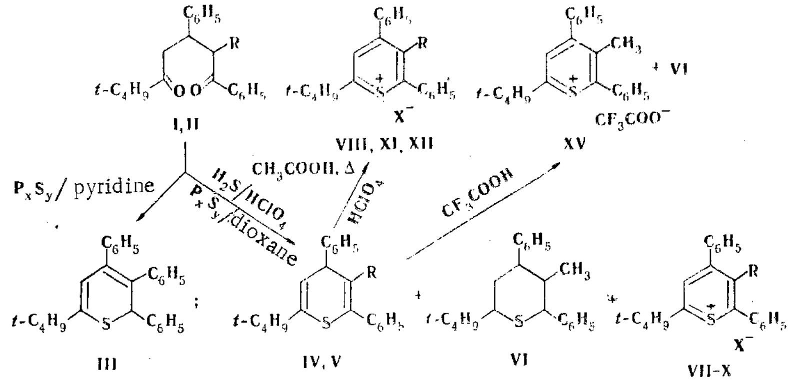
A study of the reactions of diketones I and II with sulfurous reagents, viz., P_xS_y and H_2S, demonstrated their low activity in nucleophilic reactions and the significant effect of the nature of the substituent in the 2 position on the latter (Table 1). We found that pentanedione I does not undergo nucleophilic reactions with hydrogen sulfide in the presence of acid catalysts such as perchloric acid or hydrogen chloride. Diketone II, which has a methyl group instead of a phenyl group in the 2 position, reacts with H_2S in the presence of perchloric acid to give thiopyrylium salt VIII in 81% yield.



$I, V, VII, IX, XI\ R = C_6H_5;\ II, IV, VI, VIII, X, XII\ R = CH_3;\ VII, VIII\ X^- = ClO_4^-;\ XI, XII\ X^- = CH_3COO^-$

Both diketones I and II undergo heterocyclization under more severe conditions when they are heated with phosphorus polysulfide; as a result we obtained thiopyrylium phosphates IX and X in 80 and 63% yield, respectively, as well as very small amounts (∿2%) of 4H-thiopyrans IV and V. Unsaturated sulfide VI was detected in the reaction mixture by means of thin-layer chromatography (TLC) only in the case of diketone II. These results provide a basis for the assumption that the formation of unsymmetrical α-alkyl-substituted thiopyrylium salts occurs primarily via a mechanism that includes the participation of air oxygen and differs from the disproportionation of the resulting 4H-thiopyrans.

In order to confirm this assumption it was necessary to accomplish the synthesis of 4H-thiopyrans IV and V and to investigate their transformations under the influence of acids. However, we found that a 4H-thiopyran is formed only in the case of diketone II in the case of the reaction of diketcnes I and II with phosphorus pentasulfide in pyridine, whereas diketone I is converted to the corresponding 6H-thiopyran III. Isomerization of the resulting 4H-thiopyran evidently occurs in the latter case.

The isomerization of 4H-thiopyrans to the corresponding 2H-thiopyrans by heating in acetic acid has been descirbed [7]. We attempted to accomplish the isomerization of 4H-thiopyran IV to the corresponding 6H-thiopyran under similar conditions [7]. However, instead of the expected isomerization, thiopyran IV undergoes aromatization to give thiopyrylium acetate XII. Thiopyrylium acetate XI is similarly formed from 4H-thiopyran V.

The reaction of 4H-thiopyran IV in acetic acid in the presence of perchloric acid takes place without heating and terminates with the formation of the corresponding thiopyrylium perchlorate VIII, the yield of which is greater than 80%. The formation of other products is not observed in these cases. Consequently, the salt formation of unsymmetrical α-alkyl-substituted thiopyrans takes place via a mechanism that competes with disproportionation and includes air oxygen. The disproportionation of alkyl-substituted 4H-thiopyran IV occurs only in trifluoroacetic acid, in which case we isolated 3-methyl-2,4-diphenyl-6-tert-butylthiacyclohexane (VI) along with trifluoroacetate XV.

Thus the nature of the acidic reagent has a substantial effect on the salt formation of unsymmetrical α-alkyl-substituted thiopyrans.

The compositions and structures of the compounds obtained are confirmed by the results of elementary and spectral analyses (Table 2). Phosphates IX and X, which are mixtures of salts of phosphoric and thiophosphoric acids that are formed from P_4S_{10} during the reaction, and thiopyrylium trifluoroacetate XV were identified in the form of the corresponding perchlorates VII and VIII. The saltlike nature of thiopyrylium acetates XI and XII is confirmed by their conversion to the corresponding thiopyrylium iodides XIII and XIV under the influence of potassium iodide.

TABLE 2. Characteristics of the Synthesized Compounds

Compound	mp, °C	IR spectrum, cm^{-1}				PMR spectrum, δ, ppm	Found, %				Empirical formula	Calculated, %				Yield, %
		νC=O	νC=C	ν of cation	ν of anion		C	H	Cl	S		C	H	Cl	S	
I	154—155	1680—1710					84,2	7,8			$C_{27}H_{28}O_2$	84,4	7,6			41
II	126—127	1685—1700					82,1	8,0			$C_{22}H_{26}O_2$	82,0	8,0			46
III	113—114		1560			6,25 s (C_3—H), 4,62 s (C_6—H)	84,9	6,9		8,6	$C_{27}H_{26}S$	84,8	6,8		8,4	65
IV	86,5—87		1620			5,78 d (C_3—H), 4,41 d (C_4—H)	82,2	7,3		9,8	$C_{22}H_{24}S$	82,4	7,5		10,0	72
V	121—121,5		1615			5,69 d (C_3—H), 4,06 d (C_4—H)	84,6	7,0		8,6	$C_{27}H_{26}S$	84,8	6,8		8,4	2
VI	110—111						81,3	8,6		9,6	$C_{22}H_{28}S$	81,4	8,7		9,9	24
VII	265—266			1540	1100				7,0	6,6	$C_{27}H_{25}ClO_4S$			7,3	6,7	79
VIII	238—239			1555	1080—1110				8,5	7,8	$C_{22}H_{23}ClO_4S$			8,4	7,6	83
XI	243—245			1560	1700—1710		79,3	6,3		7,6	$C_{29}H_{28}O_2S$	79,1	6,4		7,3	76
XII	236—238			1560	1700—1720		70,1	6,4		7,4	$C_{24}H_{26}O_2S$	70,2	6,3		7,8	82
XIII	300			1560			64,3	5,1		6,4	$C_{27}H_{25}IS$	63,8	4,9		6,3	79
XIV	270—271			1560			59,1	5,0		6,4	$C_{22}H_{23}IS$	58,8	4,8		6,7	81

The IR spectra of thiopyrylium salts VII-XIV at 1540-1560 cm^{-1} contain bands that are characteristic for the vibrations of the thiopyrylium cation, and absorption of ClO_4^- and CH_3COO^- anions for perchlorates VII and VIII and acetates XI and XII is observed at 1080-1100 and 1700-1720 cm^{-1}, respectively.

The position of the double bonds in thiopyrans III-V was established on the basis of data from IR and PMR spectroscopy. The IR spectrum of III contains absorption bands of conjugated double bonds of the heteroring at 1560 cm^{-1}. Two signals of heteroring protons, viz., a singlet of a vinyl 3-H proton at 6.25 ppm and a singlet at 4.25 ppm, which corresponds to the 6-H proton, are observed in the PMR spectrum of III; this confirms the 6H-thiopyran structure of this compound. The IR spectra of IV and V contain bands at 1620 and 1615 cm^{-1}, respectively, which are due to the vibrations of unconjugated double bonds of the heteroring in 4H-thiopyrans. The chemical shifts and the character of the signals of the PMR spectrum — doublets of 3-H and 4-H protons at 5.78 and 5.69 ppm and at 4.41 and 4.06 ppm — constitute evidence in favor of the 4H-thiopyran structure of IV and V.

EXPERIMENTAL

Diketones I and II were obtained by condensation of benzalpinacoline with deoxybenzoin or propiophenone under the conditions of the Michael reaction [8]. The course of the conversion of the diketones was monitored on Silufol UV-254 plates in a hexane—ether—chloroform system (3:1:1). The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer with a KBr prism. The PMR spectra of 30% solutions of the substances in CCl_4 were obtained with a Tesla BS-477 spectrometer (60 MHz) with hexamethyldisiloxane as the internal standard.

Reaction of Diketone II with Hydrogen Sulfide and Perchloric Acid. A suspension of 5 g (0.015 mole) of diketone II in 30 ml of acetic acid was saturated with hydrogen sulfide for 1 h, after which 2.8 g (0.03 mole) of 70% $HClO_4$ was added. After 70 h, the reaction mixture was diluted with 100 ml of ether, and the crystalline precipitate of thiopyrylium perchlorate VIII was removed by filtration. The yield of product with mp 238-239°C (from alcohol) was 2.7 g (81%). Found: Cl 8.5; S 7.9%. $C_{22}H_{23}ClO_4S$. Calculated: Cl 8.4; S 7.6%.

Reaction of Diketone I with Phosphorus Pentasulfide. A mixture of 5.5 g (0.015 mole) of diketone I with 3.5 g (0.01 mole) of P_4S_{10} in 50 ml of dioxane was refluxed for 22 h, after which it was cooled and diluted with 100 ml of ether. The crystalline precipitate was separated and was identified as a mixture of thiopyrylium phosphates. The yield was 5.1 g (80.5%). The mother liquor was washed with water and dried over Na_2SO_4, and the solvent was removed by distillation to give 0.15 g (2.3%) of 4H-thiopyran V (Table 2).

Salt X and 4H-thiopyran IV (Table 2) were obtained by the reaction of diketone II with P_4S_{10} under similar conditions. Thiopyrylium phosphates IX and X were identified in the form of the corresponding perchlorates VII and VIII.

1-tert-Butyl-4,5,6-triphenyl-6H-thiopyran (III). A mixture of 5 g (0.015 mole) of diketone I and 3.5 g (0.01 mole) of P_4S_{10} in 50 ml of pyridine was refluxed for 25 h, after which it was cooled and diluted with ether. The ether mixture was washed with water and dried with Na_2SO_4, and the solvent was removed by distillation. The precipitated thiopyran III was removed by filtration and recrystallized from alcohol (Table 2).

4-H-Thiopyran IV was obtained by the reaction of 5.5 g (0.015 mole) of diketone II with 3.5 g (0.01 mole) of P_4S_{10} under similar conditions (Table 2).

1-tert-Butyl-4,5,6-triphenylthiopyrylium Acetate (XI). A solution of 3.8 g (0.01 mole) of thiopyran V in 30 ml of acetic acid was refluxed for 20-25 h, after which the mixture was cooled and diluted with 50 ml of ether, and the resulting precipitate of thiopyrylium acetate XI was removed by filtration and recrystallized from alcohol (Table 2).

Thiopyrylium acetate XII was obtained under similar conditions from 3.2 g (0.01 mole) of thiopyran IV in 30 ml of acetic acid (Table 2).

Thiopyrylium Perchlorates VII and VIII. A) A 1.4-g (15 mmole) sample of 70% $HClO_4$ was added to a solution of 2 g (7 mmole) of thiopyran IV in 30 ml of acetic acid. After 70 h, the mixture was diluted with ether, and the crystalline precipitate of thiopyrylium perchlorate VIII was separated. The yield was 2.25 g (83%), and the product was identical to the perchlorate obtained by the reaction of diketone II with H_2S and $HClO_4$.

B) A 0.7-g sample of 70% $HClO_4$ was added to 1 g of thiopyrylium salt IX, X, or XV in 20 ml of acetic acid. After 2-3 h, the mixture was diluted with ether, and the crystalline precipitate of perchlorate VII or VIII was removed by filtration (Table 2).

Thiopyrylium Iodides XIII and XIV. A 0.83-g (3 mmole) sample of KI was added to 1.3-1.5 g (3 mmole) of thiopyrylium acetate XI or XII in 20 ml of acetone. After 2-3 h, the reaction mixture was poured into 50 ml of ether, and the precipitated thiopyrylium iodide XIII or XIV was removed by filtration (Table 2).

Reaction of Thiopyran IV with Trifluoroacetic Acid. A solution of 2 g (7 mmole) of thiopyran IV in 30 ml of CF_3COOH was allowed to stand for 30 h, after which it was diluted with 50 ml of ether. The resulting oily thiopyrylium trifluoroacetate XV was identified in the form of perchlorate VIII. The mother liquor was washed with water and dried over Na_2SO_4, and the solvent was removed by distillation. The precipitated sulfide VI was removed by filtration and recrystallized from alcohol (Table 2).

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