THIAPYRYLIUM AND PYRYLIUM SALTS WITH FURYL SUBSTITUENTS

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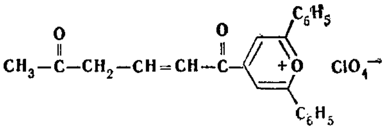
The possibility of obtaining pyrylium and thipyrylium salts that contain acidophobic furyl substituents by the action of protic acids on the corresponding 1,5-diketones in acetic acid or methanol, depending on the position of the furan rings relative to the carbonyl groups, was established.

Recent research on the synthesis and properties of thiapyrylium salts shows that these relatively accessible compounds have a number of very interesting properties, in particular, high photosensitizing activity and antimicrobial activity [1, 2]. At the same time, very little study has been devoted to thiapyrylium salts with furyl substituents in the 2, 4, and 6 positions.

One's attention is directed to unsuccessful attempts [3] to synthesize pyrylium salts with acidophobic furyl substituents in the 4 position. Thus in the case of the reaction of perchloric acid with 1,5-diphenyl-3-(2-furyl)pentane-1,5-dione in acetic anhydride a product of opening of the furan ring, viz., 2,6-diphenyl-4-(4-acetylbut-2-en-1-onyl)pyrylium perchlorate with the formula:



is obtained, according to the authors, instead of the expected 2,6-diphenyl-4-(2-furyl)-pyrylium perchlorate. In another case, in order to avoid the destructive effect of an acidic reagent on the acidophobic furyl substituents the authors use triphenylmethyl perchlorate as the cyclizing agent [4]. If the furyl substituents are in the 1 and 5 positions of the starting 1,5-diketone, the formation of the pyrylium salt proceeds smoothly. A difficult-to-separate mixture of saltlike tritylation products is formed when a furyl substituent is present in the 3 position, and a pyrylium salt with a furyl substituent cannot be isolated.

In order to study the behavior of 1,5-diketones with furyl substituents under the influence of protic acids we synthesized the diketones presented in Table 1; diketones Ia, b, d, e were obtained for the first time.

TABLE 1. 1,5-Diketones $RCOCH_2CHR'CH_2COR$

Compound	R	R′	mp, °C	IR spectrum, ν, cm⁻¹ (C=O)	Found, %		Empirical formula	Calc., %		Yield, %
					C	H		C	H	
Ia	5-Methyl-α-furyl	p-Methoxyphenyl	93—94	1670	72,0	6,0	$C_{22}H_{22}O_5$	72,1	6,3	60
Ib	5-Methyl-α-furyl	α-Thienyl	96—97	1675	67,5	5,1	$C_{19}H_{18}O_4S$	67,1	5,3	65
Ic [4]	α-Furyl	Phenyl	90—91	1685	72,9	5,4	$C_{18}H_{16}O_4$	73,1	5,5	63
Id	Phenyl	5-Methyl-α-furyl	77—78	1695	79,8	6,0	$C_{22}H_{20}O_3$	79,6	6,2	65
Ie	α-Thienyl	5-Methyl-α-furyl	69—70	1670	62,8	4,6	$C_{18}H_{16}O_3S_2$	62,8	4,5	90
If [5]	α-Thienyl	α-Furyl	94,5—96,5	1670	63,2	4,8	$C_{17}H_{14}O_3S_2$	63,7	4,4	92
Ig [6]	Phenyl	α-Furyl	97—98	1695	79,1	5,8	$C_{21}H_{18}O_3$	79,2	5,6	61

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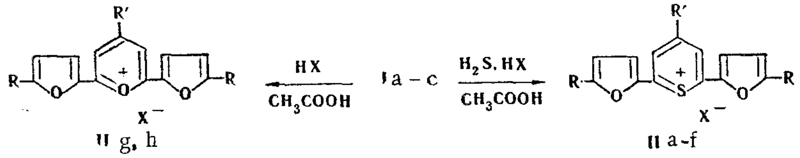
TABLE 2. Thiapyrylium and Pyrylium Salts (IIa-o)

Compound	mp, °C	IR spectrum, ν, cm⁻¹		Found, %				Empirical formula	Calculated, %				Yield, %
		cation	anion	C	H	Cl	S		C	H	Cl	S	
IIa	242—244	1575	1100	57,1	4,1	7,9	6,7	$C_{22}H_{19}Cl_7S$	57,1	4,1	7,7	6,9	60
IIb	219—220	1575	1080	66,6	5,1	9,4	7,8	$C_{22}H_{19}ClO_3S$	66,2	4,7	9,0	8,0	64
IIc	226—228	1580	1100	56,4	4,0	8,1	7,5	$C_{19}H_{15}ClO_6S_2$	56,1	3,7	8,3	7,9	65
IId	211—213	1580	1075	66,3	4,6	10,1	7,1	$C_{19}H_{15}ClO_2S_2$	66,6	4,4	10,4	7,6	57
IIe	266—268	1570	1080	67,0	4,1	10,4	9,8	$C_{19}H_{13}ClO_2S$	66,9	3,8	10,6	9,7	61
IIf	290—292	1570	1100	60,3	3,3	9,6	8,4	$C_{19}H_{13}ClO_6S$	60,0	3,4	9,3	8,4	62
IIg	187—189	1640	1100	58,8	4,0	8,1		$C_{22}H_{19}ClO_8$	59,1	4,2	7,9		57
IIh	172—175	1630	1090	69,4	4,7	9,3		$C_{22}H_{19}ClO_4$	69,1	4,9	9,2		63
IIi	228—230	1590	1100	48,8	3,1	8,3	22,0	$C_{18}H_{13}ClO_5S_3$	49,0	2,9	8,1	21,7	95
IIj	136—137	1585	1080	57,8	3,7	9,3	25,3	$C_{18}H_{13}ClOS_3$	57,5	3,4	9,4	25,5	72
IIk	165—167	1590	1070	56,6	3,2	9,4	26,2	$C_{17}H_{11}ClOS_3$	56,3	3,0	9,8	26,5	75
II*l*	230—232	1590	1100	47,6	2,9	8,2	21,9	$C_{17}H_{11}ClO_5S_3$	47,8	2,6	8,4	22,5	92
IIm	227—229	1580	1080	71,2	4,5	9,8	9,4	$C_{21}H_{15}ClOS$	71,0	4,3	10,1	9,1	67
IIn	209—210	1640	1070	76,1	4,7			$C_{22}H_{17}ClO_2$	75,9	4,9			65
IIo	192—195	1640	1100	59,9	4,1			$C_{22}H_{17}IO_2$	60,0	3,9			97

All of the diketones were synthesized by alkaline condensation of the corresponding aldehydes and ketones in alcohol in the presence of a 40% solution of alkali [6]. The structures of the 1,5-diketones were confirmed by the IR spectra. (The presence of bands with absorption maxima at 1670-1690 cm^{-1} is characteristic for the stretching vibrations of a group conjugated with an aryl or hetaryl substituent [7].)

Thiapyrylium salts IIa-f (Table 2), which were formed from diketones Ia-c, were obtained in good yields in the case of a sevenfold excess of perchloric acid or dry hydrogen chloride in glacial acetic acid in a hydrogen sulfide atmosphere.

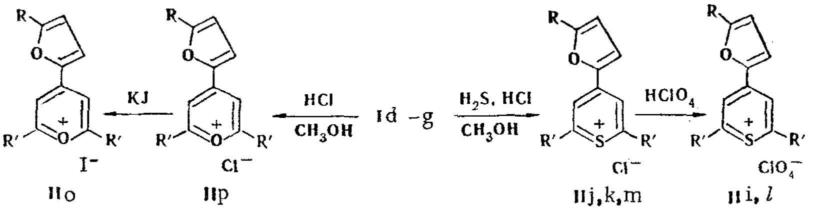


IIa,b,g,h R=CH_3, R'=p-$CH_3OC_6H_4$; c,d R=CH_3, R'=α-тиенил; e,f R=H, R'=C_6H_5;
a,c,f,g X^-=ClO_4^-; b,d,e,h X^-=Cl^-

The corresponding pyrylium salts IIg, h were obtained from diketone Ia by the action of a sevenfold excess of perchloric acid or dry hydrogen chloride in glacial acetic acid.

Thus the furan and 5-methylfuran rings are retained in acidic media in the synthesis of thiapyrylium and pyrylium salts, evidently due to the stabilizing effect of the carbonyl groups in the 1 and 5 positions. However, furan rings in the 3 position of 1,5-diketones, which are remote from the carbonyl groups, decompose under similar conditions, and one cannot obtain thiapyrylium and pyrylium salts from diketones Id-g, which contain furyl substituents in the 3 position, in acetic acid under the influence of mineral acids.

Systematic studies enabled us to find conditions for the preparation of salts IIj, k, m from 1,5-diketones Id-g by the action of dry hydrogen chloride and hydrogen sulfide in methanol on the latter.



IIi,j R=CH_3, R'=α-thienyl k, *l* R=H, R'=α-thienyl m R=H, R'=C_6H_5; n,o R=CH_3,
R'=C_6H_5

Under similar conditions in the absence of hydrogen sulfide we found that it was possible to obtain pyrylium salt IIa from 1,5-diketone Id. Opening of the furan ring in methanol does not occur. Salt formation probably prevails significantly over opening of the furan ring under these conditions, and, as a result, the furan ring is stabilized due to conjugation with the pyrylium or thipyrylium cation.

Thiapyrylium and pyrylium salts readily undergo anion-exchange reactions, and we used this method to obtain the corresponding perchlorates IIi, *l* and iodide IIo from chlorides IIj, k, n.

The presence of intense absorption bands of thiapyrylium cations at 1560-1590 cm^{-1}, of pyrylium cations at 1620-1640 cm^{-1}, and of the anions at 1080-1100 cm^{-1} is characteristic for the IR spectra of the thiapyrylium and pyrylium salts.

Thus for the first time we have established the possibility of the preparation of pyrylium and thiapyrylium salts that contain acidophobic furyl and α-methylfuryl substituents by the action of the protic acids cited above on the corresponding 1,5-diketones in acetic or methanol. The peculiarities of the cyclization of furyl-substituted 1,5-diketones as a function of the position of the furan rings relative to the carbonyl groups were established, and new possibilities for the synthesis and transformations of pyrylium and thiapyrylium salts are thus opened up.

EXPERIMENTAL

The IR spectra of suspensions of the compounds in mineral oil and hexachlorobutadiene were recorded with a UR-20 spectrometer.

Thiapyrylium Perchlorates and Chlorides (IIa-f, j, k, m). A suspension of 0.01 mole of 1,5-diketone Ia-c in 50 ml of glacial acetic acid (in 50 ml of methanol in the case of Ie-g) was saturated with hydrogen sulfide for 2 h, after which dry hydrogen chloride was bubbled through the mixture for 8 h, or a sevenfold excess of 70% perchloric acid was added dropwise (Ie-g reacted very slowly with perchloric acid). Ether (100 ml) was added to the reaction mixture, and the precipitated crystals of the thiapyrylium salt were removed by filtration and purified by reprecipitation from methylene chloride by the addition of ether.

Pyrylium Perchlorates and Chlorides (IIg, h, n). The pyrylium salts were obtained by the method presented above from the corresponding 1,5-diketones Ia, d in the absence of hydrogen sulfide.

Thiapyrylium Perchlorates (IIi, l). A 0.01-mole sample of thiapyrylium chloride IIj, k was dissolved in the minimum amount of methanol, a 10% excess of 70% perchloric acid was added, and the precipitated crystals of the perchlorate were removed by filtration and dried.

Pyrylium Iodide (IIo). A 0.01-mole sample of chloride IIn was dissolved in the minimum amount of a 50% solution of acetone in water, and a solution of 0.03 mole of KI in 10 ml of water was added. The precipitated crystals of the iodide were removed by filtration and purified by reprecipitation from methylene chloride by the addition of ether.

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