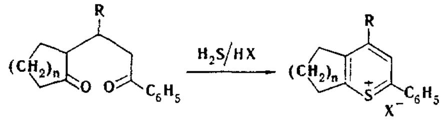
5,6-TRIMETHYLENETHIAPYRYLIUM AND 5,6,7,8-TETRAHYDROTHIOCHROMYLIUM SALTS

V. G. Kharchenko, S. K. Klimenko,
and M. N. Berezhnaya

UDC 547.818.222:543.422.4

5,6-Trimethylenethiapyrylium salts have been obtained for the first time. 5,6-Trimethylene-γ-thiopyrans (or 5,6,7,8-tetrahydro-γ-thiochromenes), which belong to a previously unknown series of two-ring sulfides, are formed by reaction of the 5,6-trimethylenethiapyrylium salts (or 5,6,7,8-tetrahydrothiochromylium salts) with Grignard reagents and lithium aluminum hydride.

1,5-Diketones react with hydrogen sulfide and hydrogen chloride to give thiapyrylium, tetrahydrothiochromylium, or sym-octahydrothioxanthylium chlorides [1]. We have established that "semicyclic" 1,5-diketones I-III are cyclized to 5,6-trimethylenethiapyrylium (IV, V, VII, and VIII) or 5,6,7,8-tetrahydrothiochromylium (VI and IX) salts in 40-65% yields on reaction with hydrogen sulfide and acids (hydrogen chloride and perchloric acid) in glacial acetic acid or ether at 20-40°C.

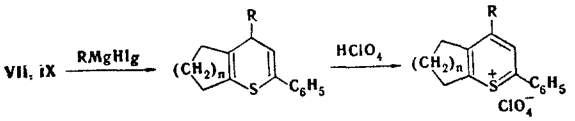


I-III IV-IX

IV X=Cl, n=1, R=H; V X=Cl, n=1, R=C_6H_5; VI X=Cl, n=2, R=H; VII X=ClO_4, n=1, R=H; VIII X=ClO_4, n=1, R=C_6H_5; IX X=ClO_4, n=2, R=H

The formation of salts from 1,5-diketones I-III and perchloric acid is complete after 6-7 h, while up to 3 days are required for the formation of salts with hydrogen chloride at 20-25°. The completion of the reaction can be judged from the disappearance of the starting 1,5-diketone and the corresponding sulfide with a thiopyran ring in the reaction mixture.

Chlorides IV-VI exchange an anion with perchloric acid, potassium iodide, or ferric chloride at 20° and undergo conversion to, respectively, perchlorates VII-IX, iodides X-XII, or tetrachloroferrates XIII and XIV. Iodides X-XII and tetrachloroferrates XIII and XIV, respectively, are similarly obtained from the reaction of perchlorates VII-IX with potassium iodide and a hydrochloric acid solution of ferric chloride (Table 1). Perchlorates VII and IX add methyl-, benzyl-, and phenylmagnesium halides to give 2,4-disubstituted 5,6-trimethylene-γ-thiopyrans (XV and XVI) or 5,6,7,8-tetrahydro-γ-thiochromenes (XVII-XIX). They are oxidized to the corresponding 2,4-disubstituted salts XX-XXIII (Table 1) by the action of 70% perchloric acid.



XV-XIX VIII, XX-XXIII

XV, XX R=CH_3, n=1; XVI, XXI R=$CH_2C_6H_5$, n=1; XVII, XXII R=CH_3, n=2; XVIII, XXIII R=$CH_2C_6H_5$, n=2; XIX R=C_6H_5, n=2

N. G. Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 489-492, April, 1974. Original article submitted November 15, 1972.

TABLE 1. 5,6-Trimethylenethiapyrylium and 5,6,7,8-Tetrahydrothiochromylium Salts

Compound	R	X	mp, °C[a]	Empirical formula	Found, %		Calc., %		Yield, %
					Cl	S	Cl	S	
IV	H	Cl	49—50	$C_{14}H_{13}ClS$	14,5	12,9	14,3	12,9	51
VII	H	ClO_4	154—156	$C_{14}H_{13}ClO_4S$	11,3	10,4	11,3	10,2	65
X	H	I	164—165	$C_{14}H_{13}IS$[b]	—	9,4	—	9,4	74
XIII	H	$FeCl_4$	106—107	$C_{14}H_{13}Cl_4FeS$	34,6	8,0	34,5	7,8	85
V	C_6H_5	Cl	142—144	$C_{20}H_{17}ClS$	11,2	9,7	10,9	9,9	51
VIII	C_6H_5	ClO_4	213—215	$C_{20}H_{17}ClO_4S$	9,2	8,1	9,2	8,3	59
XI	C_6H_5	I	209—210	$C_{20}H_{17}IS$	—	7,4	—	7,7	94
VI	H	Cl	101—103	$C_{15}H_{15}ClS$	13,6	12,3	13,5	12,2	60
IX	H	ClO_4	162—163	$C_{15}H_{15}ClO_4S$	10,8	9,7	10,9	9,8	64
XIV	H	$FeCl_4$	113—114	$C_{15}H_{15}Cl_4FeS$	33,4	7,7	33,4	7,5	71
XII	H	I	159—160	$C_{15}H_{15}IS$[c]	—	8,9	—	9,1	95
XX	CH_3	ClO_4	186—187	$C_{15}H_{15}ClO_4S$	10,8	9,9	10,9	9,8	60
XXI	$CH_2C_6H_5$	ClO_4	160—161	$C_{21}H_{19}ClO_4S$	8,9	7,8	8,8	8,0	54
XXII	CH_3	ClO_4	203—205	$C_{16}H_{17}ClO_4S$	10,1	9,5	10,5	9,4	56
XXIII	$CH_2C_6H_5$	ClO_4	156—158	$C_{22}H_{21}ClO_4S$	8,5	7,8	8,4	7,6	52

---

a) The perchlorates and tetrachloroferrates were recrystallized from glacial acetic acid, the iodides were reprecipitated from chloroform or nitromethane solution by the addition of ether, and the chlorides were reprecipitated from chloroform or acetic anhydride solutions by the addition of absolute ether. b) Found: I 37.1%. Calculated: I 37.3%. c) Found: I 35.8%. Calculated: I 35.8%.

TABLE 2. 5,6-Trimethylene-γ-thiopyrans and 5,6,7,8-Tetrahydro-γ-thiochromenes

Compound	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	S	C	H	S	
XVI	52—53	$C_{21}H_{20}S$	83,4	6,8	10,3	82,8	6,6	10,5	81
XVII	49—51	$C_{16}H_{18}S$	79,5	7,1	13,4	79,2	7,5	13,2	73
XVIII	58—60	$C_{22}H_{22}S$	83,3	7,2	10,2	83,0	7,0	10,1	90
XXIV	53—54	$C_{14}H_{14}S$	78,2	6,4	15,0	78,5	6,6	15,0	88
XXV	49—51	$C_{15}H_{16}S$	78,8	7,0	14,0	78,9	7,1	14,1	90

TABLE 3. Electronic Absorption Spectra of Sulfides XVI and XVIII

Compound	λ_{max}, nm (hexane)	log ε
XVI	237, 299	4,43; 3,32
XVIII	238, 289	4,50; 3,45

The C-4 unsubstituted salts (VII and IX) seem of particular preparative interest, inasmuch as the synthesis of 2,4-disubstituted two-ring sulfides XV-XVIII and salts XX-XXIII, which cannot be obtained by other methods, is possible from them.

Lithium aluminum hydride reduces salts VII and IX to thiopyrans XXIV or XXV. Sulfides XV, XVI, and XXIV (Table 2) are members of the previously unknown homologous series of two-ring sulfides with the 5,6-trimethylene-γ-thiopyran structure. The structure of sulfides XV-XVIII, XXIV, and XXV was confirmed by conversion to perchlorates XX-XXIII, VII, and IX and by alternative synthesis of the known [2] 2,4-diphenyl-5,6,7,8-tetrahydro-γ-thiochromene (XXIX). The UV spectra of sulfides XVI and XVIII (Table 3) are similar to the spectrum of unsubstituted γ-thiopyran [3].

The thiapyrylium ion is characterized from the IR spectral data in the literature by three bands at 1390-1410, 1470-1500, and 1560-1590 cm^{-1} [1, 4]. The presence of aromatic substituents in the investigated salts hinders assignment of the bands at 1470-1500 cm^{-1}. This band does not change its position and intensity on passing from thiopyrans XV-XIX, XXIV, and XXV to the corresponding thiapyrylium salts, V, VII-XI, XIII, and XX-XXIII and appears at 1495 ± 5 cm^{-1}, so that one should apparently assign it to aromatic absorption. The thiapyrylium salts are readily distinguished from the corresponding thiopyrans by the very intense absorption at 1390-1405 and 1560-1570 cm^{-1}. The band at 1560-1570 cm^{-1} is usually split, and a shoulder at 1540 cm^{-1} appears on the principal band. The spectra of perchlorates VII-IX and XX-XXIII are characterized by the presence of intense bands at 620-625 and 1085-1090 cm^{-1}, which should be assigned to the absorption of ClO_4^- ions.

TABLE 4. Action of Protic Acids on Saturated Solutions of 1,5-Diketones I-III

Starting compound	Solvent	Acid	Reaction time,* h, at 20°C	Reaction product (yield, %)
I	CH_3COOH	HCl	6,5 (48)	IV (52)
II	CH_3COOH	HCl	6,5 (72)	V (51)
III	CH_3COOH	HCl	5,0 (18)	VI (60)
I	CH_3COOH	$HClO_4$	6,5	VII (65)
II	CH_3COOH	$HClO_4$	7,0	VIII (59)
III	CH_3COOH	$HClO_4$	6,5	IX (64)
I	$(C_2H_5)_2O$	HCl	6,0 (40)	IV (64)
II	$(C_2H_5)_2O$	HCl	20,0 (48)	V (56)
III	$(C_2H_5)_2O$	HCl	6,0 (24)	VI (53)

---

*The time required for H_2S/HCl cosaturation is indicated in the experiments with hydrogen chloride, and the length of time the mixture was held at 20° is given in parentheses.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer, while the electronic spectra were recorded with an SF-4A spectrophotometer.

The 2-mono- and 2,4-disubstituted 5,6-trimethylenethiapyrylium and 5,6,7,8-tetrahydrothiochromylium chlorides and perchlorates (IV-IX) (Table 1) were obtained as described in [1] in acetic acid with the appropriate mineral acids. The experiments in ether were carried out similarly. The 1,5-diketones were introduced in 0.05-mole amounts into 70-100 ml of the solvent (Table 4). When acetic acid was used as the solvent, salts IV-IX were crystallized by the addition of ether; perchlorates VII-IX crystallized in better fashion than chlorides IV-VI. The hygroscopic chlorides were precipitated by the addition of absolute ether. The use of ether as the solvent considerably facilitated isolation of salts IV-IX. The reaction was followed by means of thin-layer chromatography (TLC) on aluminum oxide [cyclohexane—chloroform—ether (2:2:1)].

5,6-Trimethylenethiapyrylium and 5,6,7,8-tetrahydrothiochromylium iodides and tetrachloroferrates (X-XIV, Table 1) were obtained by exchange reactions by the method in [5].

Action of Grignard Reagents on Perchlorates VII and IX. The 2,4-disubstituted 5,6-trimethylene-γ-thiopyrans and 5,6,7,8-tetrahydro-γ-thiochromenes (XV-XIX) (Table 2) were obtained from perchlorates VII or IX and the appropriate organomagnesium compounds as described in [6]. Sulfides XVI-XVIII were crystallized by cooling solutions of them in ether—alcohol (4:1). Sulfide XV was isolated as an oil and characterized as perchlorate XX. Sulfide XIX was identified by a mixed-melting point determination with a genuine sample of 2,4-diphenyl-5,6,7,8-tetrahydro-γ-thiochromene [2].

Reaction of Lithium Aluminum Hydride with Perchlorates VII and IX. 2-Phenyl-5,6-trimethylene-γ-thiopyran (XXIV) (Table III). A 0.01-mole sample of perchlorate VII was added in portions in the course of an hour to 0.02 mole of lithium aluminum hydride in 150 ml of absolute ether, after which the mixture was stirred at 20° for ~1 h and then refluxed for 3 h. The ether layer was decanted, and the residue was washed with ether. The ether extracts were combined, washed with water, and dried with anhydrous magnesium sulfate. The ether was evaporated, and the residue was crystallized by cooling below 0°. Workup gave 2 g (88%) of XXIV.

2-Phenyl-5,6,7,8-tetrahydro-γ-thiochromene (XXV) was similarly obtained from perchlorate IX (Table 3).

Reaction of Perchloric Acid with Sulfides XV-XVIII, XXIV, and XXV. Perchlorates XX-XXIII, VII, and IX (Table 1) were obtained by reaction of sulfides XV-XVIII, XXIV, and XXV with a fivefold to sixfold excess of 70% perchloric acid in acetic acid solution as described in [6].

Chromatography on Al_2O_3 with isooctane established that saturated sulfides are formed along with salts XX-XXIII, VII, and IX; we will report this separately.

LITERATURE CITED

1. V. G. Kharchenko, M. E. Stankevich, N. M. Kupranets, V. I. Kleimenova, and S. K. Klimenko, Zh. Organ. Khim., 8, 193 (1972).

2. V. G. Kharchenko, S. K. Klimenko, V. I. Kleimenova, N. M. Kupranets, and A. R. Yakoreva, Khim. Geterotsikl. Soedin., No. 3, 73 (1971).
3. J. Strating, J. H. Keiyer, E. Molenaar, and J. Brandsma, Angew. Chem., 74, 469 (1962).
4. V. G. Kharchenko, M. E. Stankevich, A. R. Yakoreva, A. A. Rassudova, and N. M. Yartseva, Khim. Geterotsikl. Soedin., 916 (1972).
5. S. K. Klimenko and V. G. Kharchenko, Khim. Geterotsikl. Soedin., No. 3, 85 (1971).
6. V. G. Kharchenko, A. A. Rassudova, T. I. Krupina, S. K. Klimenko, and T. P. Chepurnenkova, Khim. Geterotsikl. Soedin., 338 (1970).