

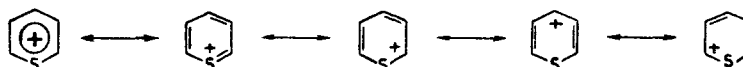
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and T. M. Konovalova

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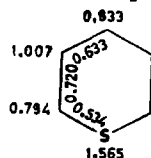
The literature data touching upon the synthesis of thiapyrylium salts and the stability of the thiapyrylium cation as compared with its isoelectronic analogs, as well as the nucleophilic, oxidation, anion-exchange, and other reactions of the salts with substituted and unsubstituted thiapyrylium cations are examined in this review.

Thiapyrylium salts became accessible almost a half century later than, and up to now have been less extensively studied than their isoelectronic analogs, pyrylium salts.

The thiapyrylium cation, like the pyrylium cation, is described as a resonance hybrid of a thionium and three carbonium structures [1-5].



The limiting structures reflect the principal properties of the thiapyrylium cation – its aromatic character and its ability to react with nucleophilic reagents ( $\text{H}_2\text{O}$ ,  $\text{H}_2\text{S}$ , amines, Grignard reagents, etc.) to give 2-, 4- or 6-substituted thiopyrans and also with organolithium compounds to give 1-substituted 1-thiabenzenes [6-12].

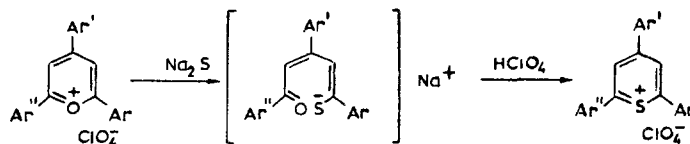


It should be noted that the electron densities and bond orders had been calculated and conclusions regarding the direction of nucleophilic reactions had been drawn [3, 4] for the unsubstituted thiapyrylium cation prior to its synthesis. In the opinion of Kontecky and Zahradnik, the relatively high delocalization energy (46 kcal/mole) and the bond orders [4] indicate the aromatic character of the thiapyrylium cation.

## SYNTHESIS OF THIAPYRYLIUM SALTS

### From Pyrylium Salts

In 1954, Wizinger and Ulrich [13, 14] established the possibility of conversion of pyrylium perchlorates to thiapyrylium perchlorates by the successive action of sodium sulfide and perchloric acid:



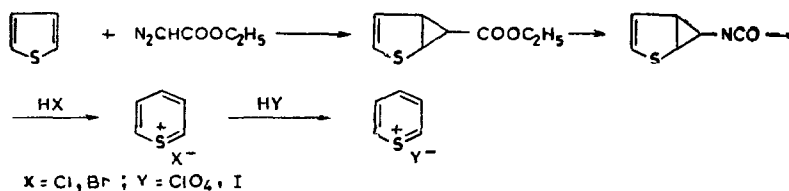
Pyrylium salts are also capable of undergoing similar transformations with other anions ( $\text{I}^-$ ,  $\text{BF}_4^-$ , etc.) [15]. The Wizinger reaction was one of the important methods for the preparation of salts with a thiapyrylium cation [6-12, 16-19]; however, it is evidently not a general reaction [13, 14, 20].

### From Thiophene

An unsubstituted thiapyrylium cation was synthesized for the first time by expansion of the thiophene ring [21]:

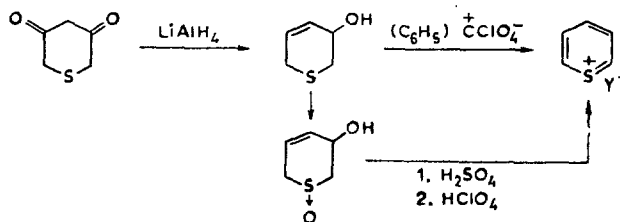
N. G. Chernyshevskii Saratov State University. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 2, pp. 147-161, February, 1975. Original article submitted November 12, 1973.

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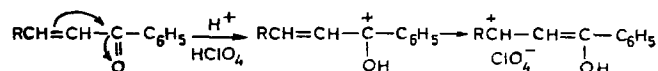
### From 3,5-Diketotetrahydrothiopyran

The same thiapyrylium salts are also formed as a result of a number of transformations of 3,5-diketotetrahydrothiopyran [2]:



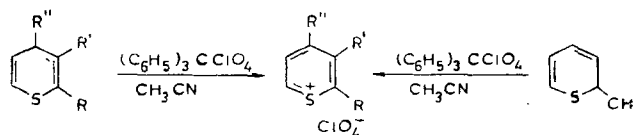
### From Thiopyrans and 1,5-Diketones. Disproportionation of Thiopyrans

The formation of thiapyrylium salts from 2H- and 4H-thiopyrans is possible by means of splitting out of a hydride ion. Just as in the salt formation of 1,5-diketones, the problem of hydride-ion acceptors during the salt formation of thiopyrans seems of great interest and has a common solution. The formation of pyrylium salts by reaction of 1,5-diketones with protic and aprotic acids (perchloric acid, sulfuric acid, ferric chloride, stannic chloride, and phosphorus oxychloride) has been considered to be (for example, see [23, 24]) a redox process in which the acid acts as an oxidizing agent. However, it was found that pyrylium salts can also be generated by the action of polyphosphoric acid, to which the role of an oxidizing agent cannot be ascribed, on 1,5-diketones. It was later found that the yields of salts are lower in acetic acid or in ether than in acetic anhydride. It was found that acetic anhydride reacts with perchloric acid to give acetyl perchlorate ( $\text{CH}_3\text{CO}^+\cdot\text{ClO}_4^-$ ), which acts not only as an anion donor but also as a hydride-ion acceptor (for example, see [25-27]). The role of the acetyl cation as a hydride-ion acceptor is confirmed by the detection of acetaldehyde in the reaction mixture [25]. Chalcones, which are added to the reaction mixture in the preparation of salts from 1,5-diketones, pyrans, and thiopyrans [27-29], also may act as hydride-ion acceptors. It is assumed that in this case the carbonyl group of the chalcone is protonated to give a stable hydroxyallyl cation, which acts as a hydride-ion acceptor [27]:

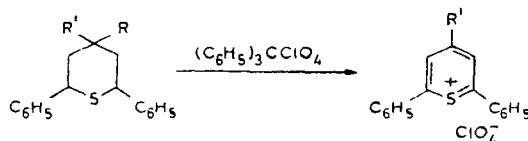


The yields of pyrylium salts reach 95% in the reaction of perchloric acid [27] or boron trifluoride [28] with 1,5-diketones when an equimolecular amount of the chalcone is present, whereas the yields do not exceed 40% when the chalcone is absent.

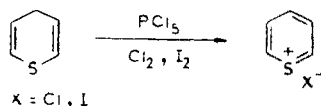
Triphenylmethyl perchlorate [29-33] and tert-butyl chloride [27], which readily give carbonium ions that act as hydride-ion acceptors, are widely used as reagents to obtain pyrylium and thiapyrylium salts from diketones [28-33], pyrans, and thiopyrans [24, 34-36].



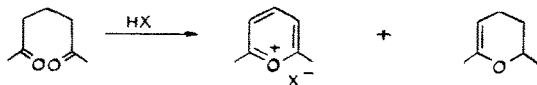
Triphenyl perchlorate is not only a hydride-ion acceptor but also a strong dehydrating agent, as evidenced by its ability to convert thiacyclohexanes to thiapyrylium salts [20].



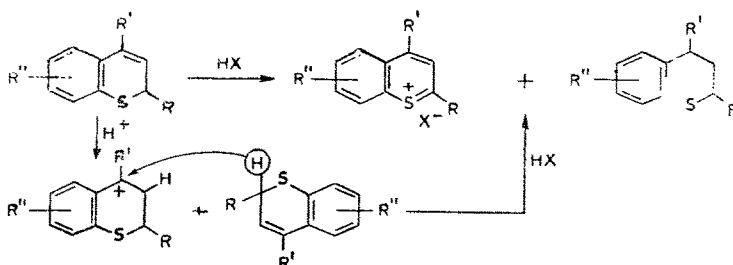
Thiapyrylium halides are formed in high yields in the reaction of  $\text{PCl}_5$ ,  $\text{Cl}_2$ , and  $\text{I}_2$  with 4H-thiopyrans [34, 37, 38]. In contrast to chlorine and iodine, bromine adds to double bonds [38].



The problem of the nature of the hydride-ion acceptors during the salt formation of 1,5-diketones, pyrans, and thiopyrans by reaction with protic acids in ether, acetic acid, and other solvents has remained unclear. Balaban [27] has proposed that in this case the formation of pyrylium salts may occur through disproportionation of the diketone to a pyrylium salt and a dihydropyran:

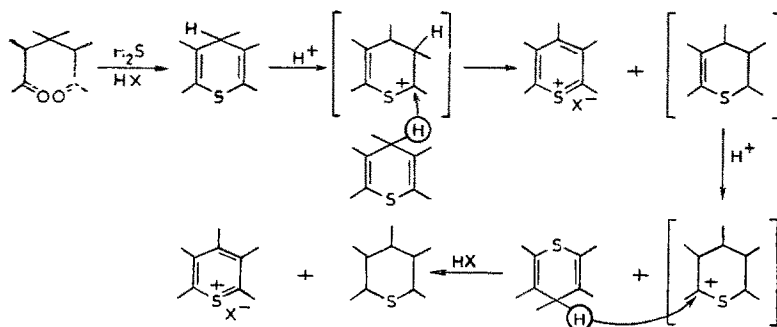


The disproportionation of 2H-chromenes and thiochromenes with intermolecular transfer of a hydride ion was observed in the reaction of perchloric and polyphosphoric acids [39, 40]:



The formation of thiapyrylium salts and thiacyclohexanes was observed in a study of the reaction of 1,5-diketones with hydrogen sulfide and protic acids, as well as with  $\text{P}_4\text{S}_{10}$  [41-47]. It was found that 2H- or 4H-thiopyrans are formed in most cases in the reaction of hydrogen sulfide and protic acids in 2-3 h, whereas mixtures of thiapyrylium salts and thiacyclohexanes are formed when the reaction is carried out for longer times (more than 24 h). These results constitute evidence for the ability of the 4H- and 2H-thiopyrans initially formed from the 1,5-diketones to undergo disproportionation with intermolecular transfer of a hydride ion [44-48]. The behavior of thiopyrans with respect to protic acids was studied in order to substantiate this ability [45]. The reaction of 4H-thiopyrans with hydrogen chloride and perchloric and trifluoroacetic acids gave mixtures of the corresponding thiapyrylium salts and thiacyclohexanes.

Octahydrobenzo-4H-thiopyrans [49, 50] undergo a similar disproportionation on reaction with ferric chloride, perchloric acid, and hydrogen chloride. Thus the carbonium ions that arise on protonation of the  $\pi$  bonds of thiopyrans and dihydrothiopyran are hydride-ion acceptors in the salt formation of 4H-thiopyrans with protic acids, as a result of which thiacyclohexanes are formed along with thiapyrylium salts [44-48].



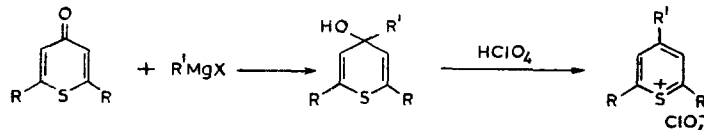
2,6-Diphenyl-3,5-dimethyl-4H-thiopyran undergoes disproportionation under the influence of perchloric and trifluoroacetic acids [43, 47]. 1,5-Diketones react with phosphorus pentasulfide in pyridine to give only 4H-thiopyrans [51], whereas thiapyrylium salts are formed in high yield [52] in hydrocarbons (toluene, xylene, etc.) or when the reagents are simply mixed in equimolar amounts and heated to 90-100°

This dependence of the degree of transformation of 1,5-diketones with  $P_4S_{10}$  on the nature of the solvent is explained by the fact that the acidic products of the conversion of phosphorus pentasulfide are tied up in pyridine, and weak-base catalysis evidently takes place. In the reaction of 1,5-diketones with  $P_4S_{10}$  in toluene and xylene, the products of conversion of  $P_4S_{10}$  – strong thio- and dithiophosphoric acids – act as catalysts and reagents of acidic character. As a result, a mixture of thiapyrylium salts (probably phosphates and thio- and dithio-phosphates) is formed [52, 53].

In the case of 1,3,5-triphenyl-2-methyl- and 1,3,5-triphenyl-2,4-dimethyl-1,5-pentanediones, the corresponding 4H-thiopyrans are detected in the reaction mixture along with thiapyrylium salts [51, 52].

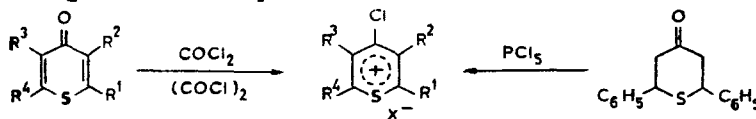
### From Thiopyrones and Thiopyranthiones

Thiopyrones undergo nucleophilic reactions with Grignard reagents to give hydroxyl-containing thiopyrans, which react with perchloric acid or triphenylmethyl perchlorate to give thiapyrylium salts [14, 20]:



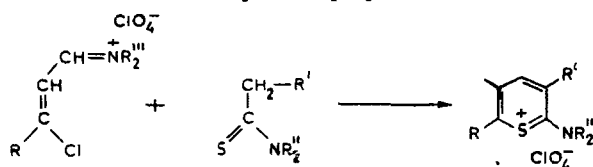
The reactions of thiopyrones with oxalyl chloride [54], phosgene, and thionyl chloride [55] give 4-chlorothiapyrylium chlorides. 2,6-Diphenyl-1-thia-4-cyclohexanone reacts with phosphorus pentachloride to give a mixture of 2,6-diphenyl-4-chloro- and 2,6-diphenyl-3,4-dichlorothiapyrylium salts [54, 55].

Thiapyrylium chlorides are very hygroscopic, and they are therefore usually not isolated but are converted as a result of exchange reactions to perchlorates and other stable salts.



2H-Thiopyrones, 4H-thiopyrones, and 2H-thiopyran-2-thiones are readily reduced by aluminum hydride [34, 37] and lithium aluminum hydride [56] to the corresponding pseudobases – 2H- or 4H-thiopyranols. The latter react with perchloric and hydriodic acids to give thiapyrylium salts.

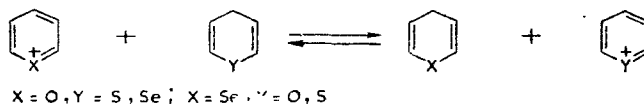
Of the other methods for the preparation of thiapyrylium salts that are of interest, one should note the reaction of  $\beta$ -chlorovinylmethineammonium perchlorate with substituted thioacetamides, which proceeds under the influence of triethylamine in acetic anhydride [57]:



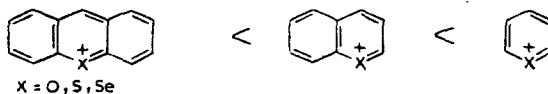
## PROPERTIES OF THIAPIRYLIUM SALTS

### Relative Stability of the Thiapyrylium Cation

The relative stabilities of thiapyrylium, pyrylium, selenapyrylium cations and their benzo and dibenzo derivatives have been studied qualitatively by means of investigations of equilibrium reactions of the type:



It was found that the reaction of pyrylium and selenapyrylium cations with thiopyran proceeds quantitatively to give thiapyrylium perchlorate, whereas the reactions of the pyrylium cation with selenopyran and the selenapyrylium cation with pyran lead to approximately equal amounts of pyrylium and selenapyrylium salts [5]. These results attest to the higher stability of the thiapyrylium cation as compared with the pyrylium and selenapyrylium cations. The qualitatively estimated stabilities increase in the following order for the same heteroatom in series of the corresponding benzo and dibenzo derivatives:



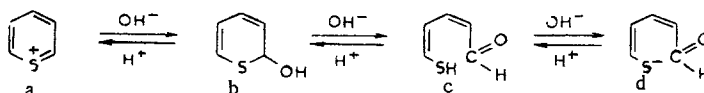
However, quantitative investigations of the stabilities of benzo- and dibenzothiapyrylium cations by measurements of the constants of the equilibrium  $R^+ + H_2O \rightleftharpoons ROH + H^+$  by a spectrophotometric method provide evidence for the greater stability of the xanthylium cation as compared with the chromylium cation [58].

The conclusion regarding the greater stability in each series of the cation that includes a sulfur atom as compared with cations that include oxygen and selenium atoms is confirmed by the results of quantitative investigations [58] (Table 1).

The thiapyrylium cation is more stable than the isoelectronic carbocyclic tropylium cation [59] ( $pK_{R^+} + 4.7$ ). The reasons for the increase in the stability of sulfur-containing cations is evidently the fact that the system is a conjugate base that has  $\pi$ -electron bonds of considerably lower energy than those in the hydrocarbon system of tropylium [59].

### Hydrolysis of Thiapyrylium Salts

An analysis of the products of hydrolysis of thiapyrylium perchlorate by UV spectroscopy showed that up to pH 6 the thiapyrylium cation remains unchanged, hydrolysis commences gradually only at higher pH values, and the bands characteristic for the thiapyrylium cation ( $\lambda_{max}$  245 and 284 nm in 70 % perchloric acid [60]) disappear and two new bands appear at 235 and 395 nm [36, 60, 61]. At pH 9, the thiapyrylium salt is hydrolyzed completely, and gradual establishment of equilibrium between the tautomeric forms is observed at pH 6-11. No changes whatsoever are observed in the spectrum above pH 11 [36, 60]. It should be noted that Pettit and co-workers [59] present a  $pK_{R^+}$  value of 8.7 for the thiapyrylium cation  $\rightleftharpoons$  pseudo-base equilibrium, whereas Degani and Fochi consider this result to be unreliable [60]. In contrast to pyrylium perchlorate, the hydrolysis of thiapyrylium perchlorate is completely reversible [61]. The band at 395 nm that appears in the UV spectrum of the product of hydrolysis of thiapyrylium perchlorate is ascribed to the absorption of anion d, which arises in strongly alkaline media from 1-formyl-4-mercapto-1,3-butadiene (c) [61]. It is interesting to note the data that reflect the effect of a heteroatom during the hydrolysis of chromylium and thiachromylium perchlorates. Oxygen-containing chromylium pseudobases have  $pK_{R^+} = 1.86$ , which is considerably lower than the value (3.15) for the thiachromylium pseudobase; this evidently should be explained by the different degree of participation of the electrons of the heteroatoms in conjugation [62].



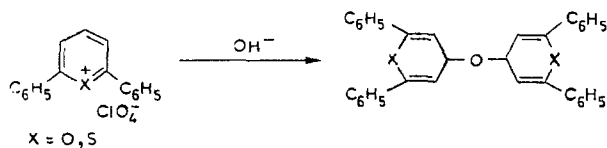
Electron-donor substituents in the aromatic ring of the benzothiapyrylium ion stabilize the thiapyrylium cation, whereas electron-acceptor substituents destabilize it [63].

TABLE 1.  $pK_{R^+}$  Values for Heterocyclic Cations That Include an Oxygen, Sulfur, or Selenium Atom [58]

	$pK_{R^+}$ (X=O)	$pK_{R^+}$ (X=S)	$pK_{R^+}$ (X=Se)
		> +6	
	-1.96	+3.15	+1.20
		+2.17	
	-0.83	-0.21	-1.67
	-5.96	-1.67	-4.28

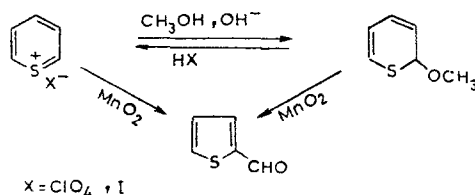
In the hydrolysis of thiachromylum perchlorate one might have expected the formation of 4-hydroxy-4H-thiochromene (a  $\gamma$ -pseudobase). The results of experimental studies attest to the formation of only 2-hydroxy-2H-thiochromene (an  $\alpha$ -pseudobase) [63].

The hydrolysis of thiapyrylium salts initially gives pseudobases, which, depending on the reaction conditions, undergo secondary transformations of different types [36, 60, 63-66]. Under strongly alkaline conditions, the pseudobases are converted to open desmotropic forms, which are reconverted to thiapyrylium salts in acidic media. In aqueous solutions or in organic solvents the pseudobases are capable of undergoing spontaneous conversion to ethers [63]. 2,6-Diphenylthiapyrylium and 2,6-diphenylpyrylium perchlorates react with a half equimolecular amount of water under the influence of organic bases (pyridine, hexamethylenetetramine) or under the influence of sodium bicarbonate with excess water to give tetraphenyldipyranyl or tetraphenyldithiapyranyl ethers [64].

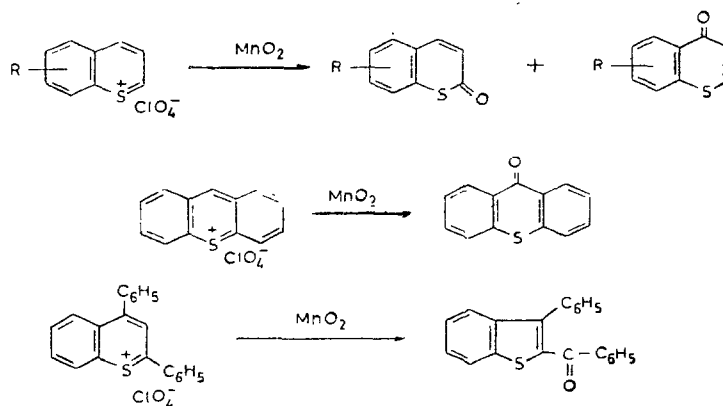


The available data regarding the reversibility of this reaction are contradictory [63, 64].

$\alpha, \alpha'$ -Dithiochromenyl ether, which, according to the data in [63], is readily converted to a benzothiapirylium salt in acidic media, is readily formed by hydrolysis of benzothiapyrylium perchlorate with 0.1 N sodium carbonate solution.

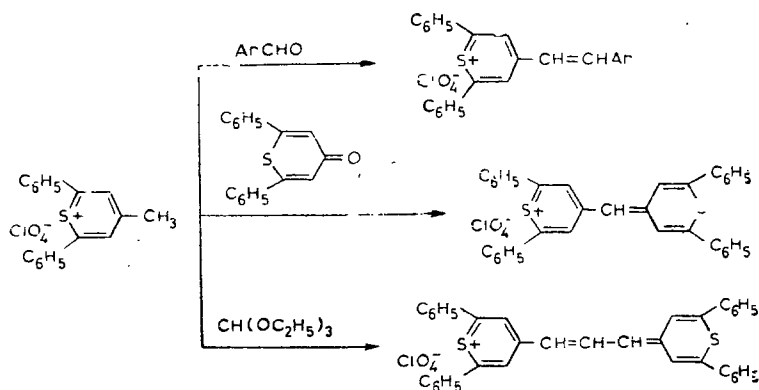


The solvolysis of thiapyrylium perchlorate and iodide in methanol under the influence of sodium bicarbonate leads to 2-methoxy-2H-thiopyran [36], which is converted by perchloric acid to the starting thiapyrylium perchlorate, whereas 2-formylthiophene is formed by oxidation with manganese dioxide. Thiapyrylium iodide is also converted to 2-formylthiophene by refluxing with manganese dioxide in chloroform [36, 60]. It was found that under similar conditions thiachromylum perchlorates form thiocoumarins (75-93%) and thiochromanones [65, 66], thiaxanthylum perchlorate forms thioxanthone [66], and only 2,6-diphenylthiachromylum perchlorate undergoes a transformation similar to that of thiapyrylium perchlorate [66] upon oxidation with manganese dioxide.

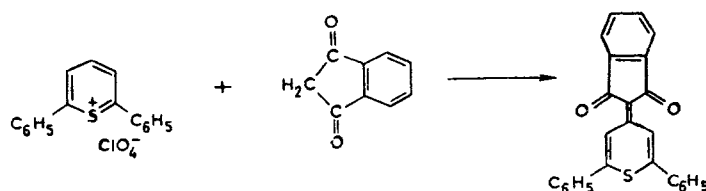


### Condensation of Thiapyrylium Salts

Thiapyrylium salts containing a methyl group in the 2 or 4 position, like the pyrylium salts, under the influence of acetic anhydride condense with aldehydes, ketones, and thiopyrones to give methine cyanine salts [14, 20, 67].

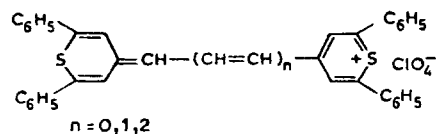


Thiapyrylium salts that do not contain substituents in the 2 and 4 positions undergo condensation (in acetic acid in the presence of sodium acetate) with indanedione, barbituric and rhodanic acids, methylphenylpyrazolone [20], thiazolidones [67], etc.



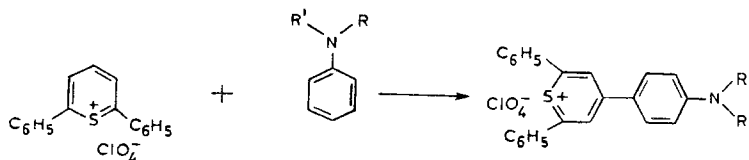
The reactions with thiazolidones give high yields when solutions of the reagents in acetonitrile or dimethylformamide are simply refluxed [67].

Under similar conditions, 2,6-diphenylthiapyrylium perchlorate undergoes condensation with malonic, glutamic, and piperidylidene carboxylic acids. The process is accompanied by "dual" dehydrogenation and decarboxylation. As a result, mono-, tri-, and pentamethine cyanines, respectively, are formed [20]:

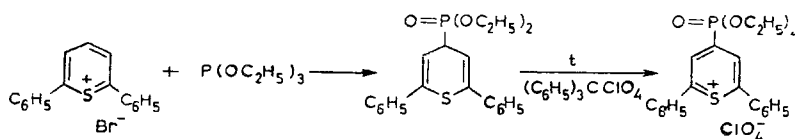


The same monomethine cyanine was also obtained by condensation of 2,6-diphenyl- and 2,6-diphenyl-4-methylthiapyrylium perchlorates in the presence of sodium acetate [20].

Thiapyrylium salts that are unsubstituted in the 2 or 4 positions are capable of undergoing reaction with nucleophilic reagents (aniline, dimethylaniline, N-methyldiphenylamine, and antipyrine) [20]; this reaction is similar to pyrylation [68]:

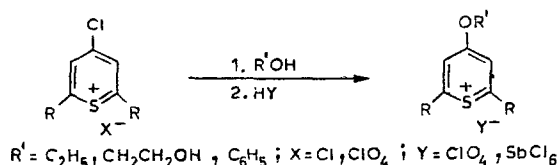


2,6-Diphenylthiapyrylium bromide, like the pyrylium and chromylium salts [69], undergoes the Ar-buzov rearrangement [70] with triethyl phosphite. The product of the reaction is thiapyranylphosphonic acid, which is converted to the perchlorate of a thiapyryliumphosphonic acid ester on refluxing with trityl perchlorate.

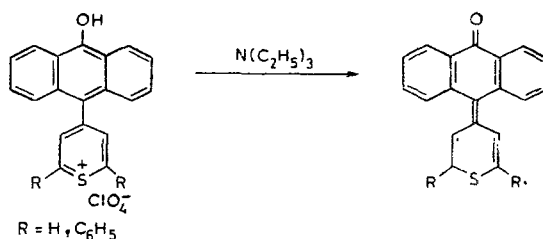


Thiapyrylium salts containing chlorine, bromine, alkoxy, or thioalkyl groups in the 2 or 4 position readily undergo exchange reactions [55, 71-73]. Thus mono- and diatomic alcohols and phenols react with

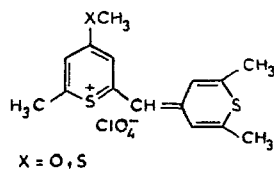
4-chloro- or 4-bromothiapyrylium perchlorate or chloride when solutions of them in polar aprotic solvents (nitromethane, acetonitrile, etc.) are simply heated [55, 71, 72].



In the reaction of 4-chlorothiapyrylium and 4-chloro-2,6-diphenylthiapyrylium chlorides under the same conditions with anthrone, as a result of subsequent treatment of the reaction product with perchloric acid one obtains a salt that is converted to a "quinonemethidine" on reaction with triethylamine [55]. Similar reactions are characteristic for 4-chloropyrylium and chromylium chlorides [55].



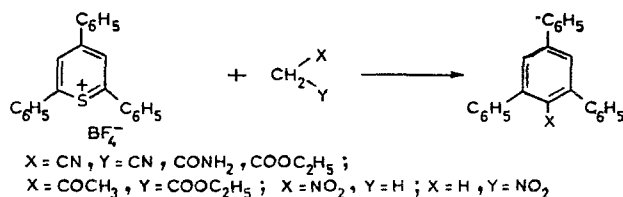
2,6-Dimethyl-4-methoxy- and -4-methylthiothiapyrylium perchlorates readily undergo self-condensation to give monomethine cyanines [73]:



The action of sodium benzoylacetate in refluxing ethanol on 2,6-diphenyl-4-methylthio- and 2,4-diphenyl-2-methylthiothiapyrylium iodides gives 4- or 2-phenacylidene thiopyrans, respectively [72]:



Nucleophilic reactions of pyrylium salts that are accompanied by facile replacement of the ring oxygen by nitrogen and carbon to give more stable hetero- or carbocyclic compounds are well known (for example, see [74-76]). Thiapyrylium salts are considerably more stable compounds, and until recently it was assumed that they are incapable of exchanging a sulfur atom for a carbon atom in reactions with nitromethane, acetylacetone, and malonic ester and that they exchange a sulfur atom for a nitrogen atom very slowly and with difficulty [74]. Information regarding the ability of thiapyrylium salts to react with these reagents to give carbocyclic compounds recently appeared [77, 78]. Thus, in the case of the reaction of 2,4,6-triphenylthiapyrylium tetrafluoroborate with nitromethane in the presence of alkali, 2,4,6-triphenyl-1-nitrobenzene is formed, whereas 1,3,5-triphenylbenzene is formed in the presence of an acid [77]. 2,4,6-Triphenylthiapyrylium tetrafluoroborate reacts with compounds having an active methylene group under the influence of potassium tert-butoxide in butyl alcohol to give substituted triphenylbenzenes [77].



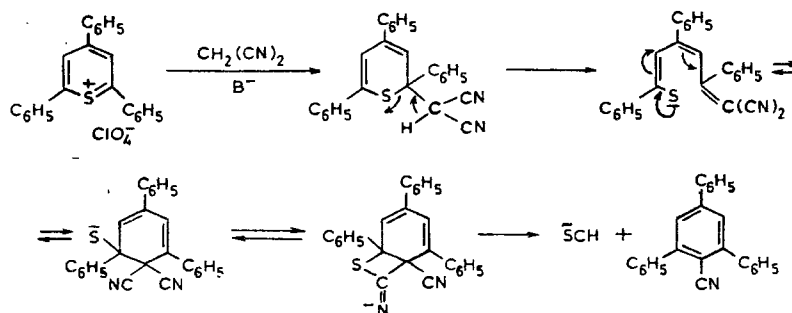
The reaction of malonic acid dinitrile with 2,4,6-triphenyl- and 2,4,6-tri(p-methoxyphenyl)thiapyrylium perchlorate in the presence of ethyldiisopropylamine proceeds similarly [78]. In the latter case, the



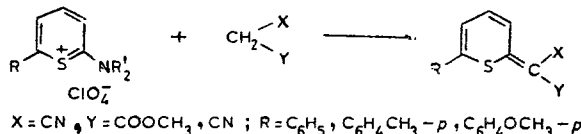
TABLE 2.  $\pi$ -Electron Densities ( $q_r$ ), Hyperdelocalizabilities ( $S_r$ ), and Localization Energies ( $L_r$ ) for the 2,4,6-Triphenylthiapyrylium Cation [77]

	s	$\alpha$	$\beta$	$\gamma$
$q_r$	1,603	0,857	1,008	0,887
$S_r$	1,423	1,893	1,021	1,809
$L_r(-\beta)$	2,452	2,085	2,421	2,396

thiocyanate ion is detected in the reaction products [78], and this in some measure sheds light on its mechanism. A study of the reaction showed that the attack of the nucleophile is described only to the  $\alpha$  position of the cation, despite the fact that the  $\pi$ -electron densities ( $q_r$ ) in the 2,4,6-triphenylthiapyrylium cation calculated by the Hückel method indicate that the maximum positive charge is concentrated on the sulfur atom (Table 2) [77]. However, the reactivity indexes, as well as the hyperdelocalizabilities ( $S_r$ ) and the localization energies ( $L_r$ ), confirm that nucleophilic attack is directed exclusively to the carbon atom in the  $\alpha$  position [77].



Thiapyrylium perchlorates containing a dialkylamino group in the 2 position react with nucleophilic reagents in the presence of triethylamine with retention of the sulfur atom in the ring [57].



The thiapyrylium cation is considerably more stable than the pyrylium cation. It is distinguished by greater delocalization of the positive charge and by the ability to give charge-transfer complexes with olefins in which the thiapyrylium cation acts as an electron acceptor [79-81]. Two absorption bands in the visible region of the UV spectrum are observed for the thiapyrylium cation-olefin system; these bands are explained by the existence of two closely situated vacant orbitals and electron transitions from the higher occupied level of the olefin to the lower and second lower vacant levels of the thiapyrylium cation [81].

The PMR spectra of thiapyrylium, pyrylium, and pyridinium cations attest to considerable peculiarity of the electronic structure of the thiapyrylium cation [79]. The PMR spectra of trifluoroacetic acid solutions are characterized by the following chemical shifts ( $\delta$ ):

thiapyrylium cation	$\alpha$ -H 10.20	$\beta$ -H 9.11	$\gamma$ -H 9.11
pyrylium cation	9.70	8.53	9.36
pyridinium cation	8.81	8.82	8.60

The spectrum of the thiapyrylium cation differs from the spectra of its isoelectronic analogs with respect to the resonance of the  $\alpha$ -hydrogen atoms at too weak a field ( $\delta$  10.20) and coincidence of the shifts of the signals of the  $\beta$ - and  $\gamma$ -hydrogen atoms ( $\delta$  9.11). The first difference is explained by the effect of magnetic anisotropy of the sulfur atom, and the second difference is evidently a consequence of the considerable decrease in the electron density of the  $\beta$ -carbon atom of the thiapyrylium cation due to its migration to the sulfur atom. The decrease in the electron density on the  $\beta$ -carbon atom can be explained by overlapping of the 2p orbitals of the  $\alpha$ -carbon atoms with the 3d-unsubstituted orbitals of the sulfur atom [(p-d)  $\pi$ ] [79]:



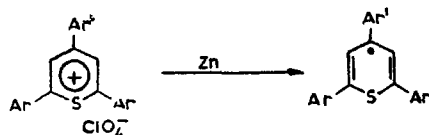
Calculations by the Hückel MO method provide evidence that the charges on the  $C_3$  and  $C_4$  atoms differ less when 3d orbitals are included in the basis than when the 3d orbitals are disregarded and that the order of the bonds of the  $\alpha$ -carbon atoms with the sulfur atom also increases [79]. The considerable increase in

the order of the sulfur atom- $\alpha$ -carbon atom bond as a consequence of the inclusion of the 3d orbitals may serve as an explanation of the high stability of the thiapyrylium cation.

### Photooxidation and Other Reactions of Thiapyrylium Salts

The results of photooxidation of 2,4,6-triphenylthiapyrylium perchlorate at room temperature in methanol attest to the considerable contribution of carbonium structures to the ground state of the thiapyrylium cation. It is assumed that the cation in the excited triplet state reacts with oxygen in the ground valence state to give an intermediate hydroperoxide, which undergoes secondary transformations leading to the formation of a mixture of benzyl alcohol, phenol, and benzaldehyde [82].

As in the case of the reduction of 2,4,6-triphenylpyrylium salts [84] with magnesium, zinc, copper, and silver, the formation of a 2,4,6-triphenylthiapyryl radical is observed in the reduction of 2,4,6-triphenylthiapyrylium perchlorate with zinc in cyclohexane [83]:



### Exchange of Anions of Thiapyrylium Salts

The synthesis of thiapyrylium salts with different anions is of interest in connection with the study of the effect of the nature of an anion on the direction of nucleophilic reactions [9, 12, 86] and the stabilities of the salts [55, 71] and in connection with the practical application of thiapyrylium salts [57, 85-89]. Thiapyrylium perchlorates, which are capable of exchanging the  $\text{ClO}_4^-$  anion for other anions under the influence of acids and salts (KI in acetone,  $\text{HBF}_4$ ,  $\text{FeCl}_3$ , etc.), are the most widely known. The mixtures of thiapyrylium phosphates and thio- and dithiophosphates that are formed in the reaction of 1,5-diketones with phosphorus pentasulfide are capable of undergoing exchange reactions with perchloric acid, potassium iodide, and ferric chloride [52, 53, 90].

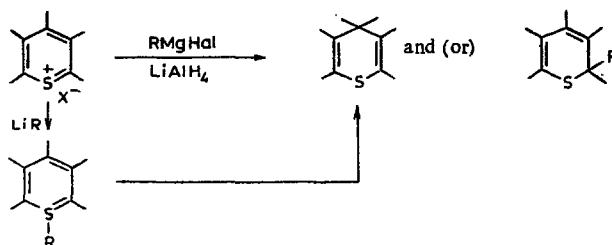
Exchange reactions of 2,4,6-triphenylthiapyrylium iodide, periodide, and tetrafluoroborate with various salts (potassium nitrate, bromide, chloride, and iodide, and silver cyanide and tetrafluoroborate), perchloric acid, and halogens to give the corresponding salts and salts with mixed anions are well known [15].

The possibility of the application of thiapyrylium salts as dyes for polymers and photosensitizers in photography is indicated in the patent literature. Thiapyrylium salts increase the sensitization zone to 720 nm and improve the sharpness, transparency, and contrast of the image [85-89].

### Nucleophilic Reactions of Thiapyrylium Salts

Some characteristic nucleophilic reactions of thiapyrylium salts are reduction with lithium aluminum hydride [9, 12, 16, 17, 53, 60, 91] and reaction with Grignard reagents [17-19, 53, 60, 91, 92] and organolithium compounds [6-12].

In the case of reactions with Grignard reagents and lithium aluminum hydride the reagent attacks and adds at the 2 and 4 positions [9, 12, 17-19, 53, 60, 91, 92]. Organolithium compounds [6-12] react with thiapyrylium salts at the sulfur atom. In the first case, depending on the number and character of substituting groups in the cation, 2H- or 4H-thiopyrans or mixtures of them are formed. In the second case, 1-substituted thiabenzenes of low stability are formed. The latter are converted to 2H- or 4H-thiopyrans under the usual conditions [6-12].



All of these reactions are valuable methods for the preparation of thiopyrans.

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