THIOPYRANS (REVIEW)

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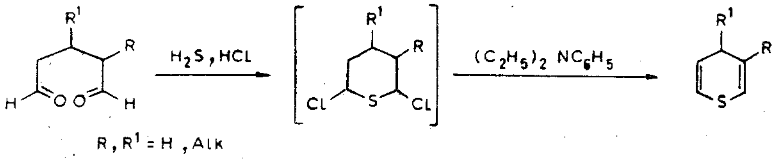
Information on methods for the preparation of and on the physical and chemical properties of monocyclic thiopyrans, as well as their spectral characteristics, is correlated.

One of the new fields of the chemistry of heterocyclic compounds is the chemistry of thiopyrans. The first attempts to synthesize the simplest 4H-thiopyrans were undertaken in 1886 [1, 2], but these studies did not undergo further development, apparently because of the long-standing concept of the instability of such systems [3]. Only in 1961, when information regarding the synthesis and some properties of 2,4,6-triphenyl-4H-thiopyran appeared [4], did this class of compounds become the subject of systematic study.

PREPARATION OF THIOPYRANS

Thiopyrans from Glutaraldehyde and Its Substituted Derivatives

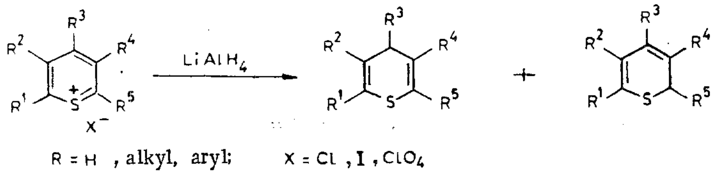
The simplest 4H-thiopyran was synthesized in 1962 by the action of hydrogen sulfide and hydrogen chloride on glutaraldehyde and subsequent heating of the mixture in vacuo in the presence of diethylaniline [5]. This reaction was extended to the synthesis of substituted thiopyrans and their analogs [6-12].



Thiopyrans from Thiapyrylium Salts

Depending on their structure, thiapyrylium salts are reduced by $LiAlH_4$ to give mixtures of 4H- and 2H-thiopyrans in various ratios [4, 10, 13-15].

Thus, a mixture of 2H- and 4H-thiopyrans in a ratio of 1 : 9 was obtained from 2,4,6-triphenylthiapyrylium iodide [16, 17]. 2,4,6-Triphenyl-4H-thiopyran containing the 2H-isomer was obtained by reduction of 2,4,6-triphenylthiapyrylium perchlorate (I) [4].



As in the reaction with $LiAlH_4$, the addition of Grignard reagents to thiapyrylium salts gives mixtures of 4H- and 2H-thiopyrans. As in the case of pyrylium salts [18-20], the direction of attack of the nucleophile depends on the nature of both reagents. A mixture of the corresponding 2H- and 4H-thiopyrans in a ratio of 3 : 1 is formed in the reaction of methyl- or ethylmagnesium bromide with I (or the tetrafluoroborate) [13].

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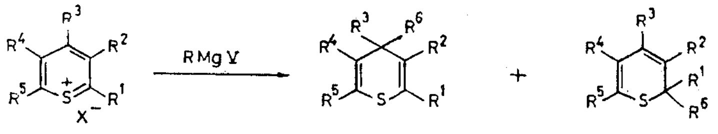
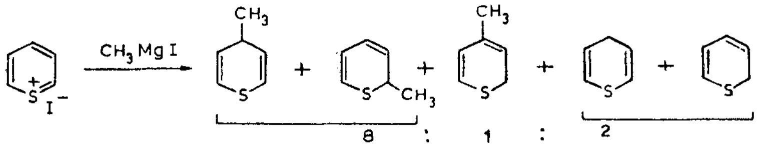
A mixture of isomers (56% 4H-thiopyran and 17% 2H-thiopyran) was also obtained from benzylmagnesium chloride and perchlorate I [21, 22], while reaction with 2,4,6-triphenylthiapyrylium iodide gives only the 4H-thiopyran [23]. The formation of only the 4H-thiopyran has also been noted in other cases [13-15].



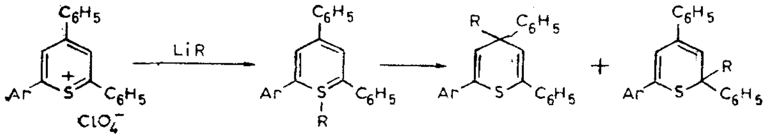
R^1, R^6 = alkyl, aryl; R^2, R^4 = H, alkyl, aryl; R^3, R^5 = H, aryl; X = Cl, I, ClO_4, BF_4; Y = Cl, Br, I.

If the thiapyrylium salt does not contain a substituent in the 4-position, only 4H-thiopyrans are obtained by the action of a Grignard reagent [14]. In the reaction of thiapyrylium iodide with methylmagnesium iodide [10], 4-methyl-2H-thiopyran and 2H- and 4H-thiopyrans [10] are detected along with the expected 4-methyl-4H- and 2-methyl-2H-thiopyrans. 4-Methyl-4H-thiopyran apparently isomerizes under the reaction conditions to give 4-methyl-2H-thiopyran [6]. In addition, the thiapyrylium cation undergoes reduction due to transfer of a hydride ion.



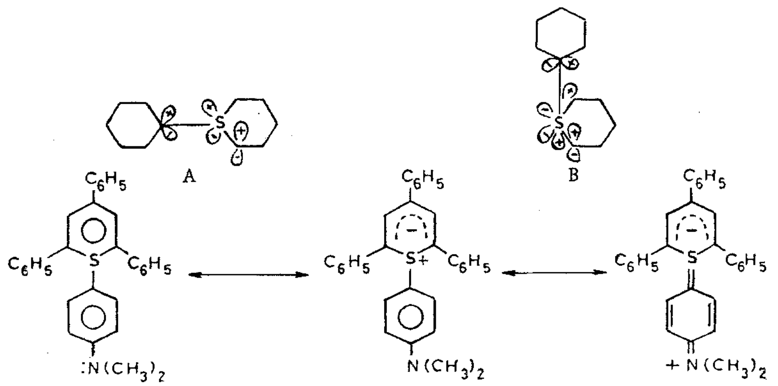
Thiopyrans from 1-Substituted 1-Thiabenzenes and 1-Thiabenzene S-Oxides

In contrast to Grignard reagents, organolithium compounds on reaction with thiapyrylium salts attack the sulfur atoms to give one alkyl- or 1-aryl-1-thiabenzenes [4, 13, 24-29]. 1-Alkyl-1-thiabenzenes are extremely unstable and are readily converted to 2H- or 4H-thiopyrans [13]. 4-Butyl-2,4,6-triphenyl-4H- and 2-cyclopentadienyl-2,4,6-triphenyl-2H-thiopyrans, respectively, are formed in the reaction of butyl- and cyclopentadienyllithium with perchlorate I [13].

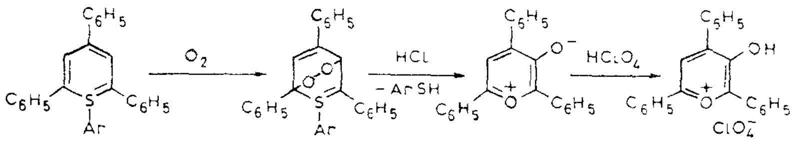


R = aryl, cyclopentadienyl, alkyl

1-Arylthiabenzenes are relatively stable and can be stored in an inert medium for weeks and even months, but in light at room temperature they are isomerized to 4H-thiopyrans [4, 13, 16, 17, 24-29]. 1-Phenyl-1-thiabenzene, which does not change on prolonged storage in light and in the presence of oxygen, is distinguished by high stability [16, 26]. The decrease in the stability of substituted 1-aryl-1-thiabenzenes as compared with unsubstituted compounds [24] is explained by steric factors [16], which disrupt the conjugation in the thiabenzene ring. The high stability of 1-(p-dimethylaminophenyl)-2,4,6-triphenyl-1-thiabenzene (II) has been noted [28]. A peak corresponding to splitting out of a p-dimethylaminophenylmercaptide ion is observed in its mass spectrum. Cleavage of the S—Ar bond is characteristic for other 1-arylthiabenzenes. The high stability of 1-thiabenzene II may be explained by the considerable contribution of the ylid structure of bent conformer B [28].

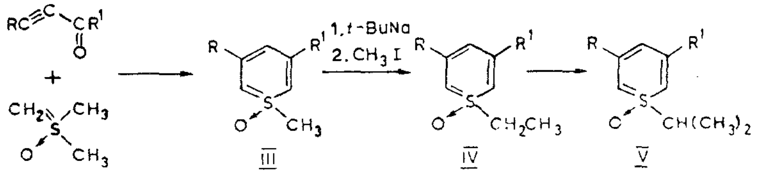


A continuous π orbital of aromatic rings conjugated through sulfur can be constructed for each conformer (A and B) while retaining the aromatic character of the thiabenzene ring. Participation in the conjugation of the $3p_z$ orbital of sulfur in the case of conformer A and of one $3d_x$ orbital of sulfur in conformer B is considered probable. Thus, the stability of 1-arylthiabenzenes is associated with the presence of a continuous conjugation chain including thiabenzene with retention of its aromatic character. This concept makes it possible to explain the unsuccessful attempts to obtain 1-alkyl-1-thiabenzenes [13] and 1-phenylethynyl-2,4,6-triphenyl-1-thiabenzenes [28]. In the latter case, a mixture of 4-phenylethynyl-4H- and 2-phenylethynyl-2H-2,4,6-triphenylthiopyrans in a ratio of 7 : 4 was obtained by the action of phenylethynyllithium on perchlorate I. The structure of the 1-arylthiabenzenes is confirmed by their cleavage (by the successive action of oxygen and hydrogen chloride in ether) to give an ylid and an aryl mercaptan [13, 24, 28].



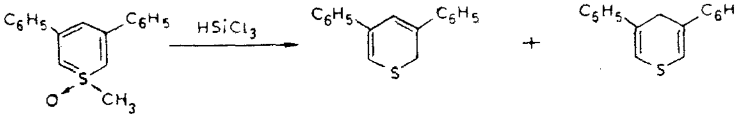
$Ar = C_6H_5$, p-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$(CH_3)_2NC_6H_4$

Extremely stable 1-thiabenzene S-oxides (III) were obtained by reaction of substituted α,β-acetylenic ketons with dimethyloxosulfonium methylide [30-32]. The hydrogen atoms of the $S-CH_3$ group in III are exchanged by deuterium on refluxing in CH_3OD-D_2O containing NaOD, but are replaced by methyl groups on treatment with butyllithium and subsequent reaction with methyl iodide to give thiabenzene S-oxides IV and V [32].



R, R^1 = alkyl, phenyl

In contrast to 1-arylthiabenzenes, S-oxides III are not isomerized to thiopyrans in light and by heating but give a mixture of 2H- and 4H-thiopyrans in a ratio of 3 : 2 on reduction with trichlorosilane in refluxing benzene [31]. Their reduction with lithium aluminum hydride did not give definite results [32].

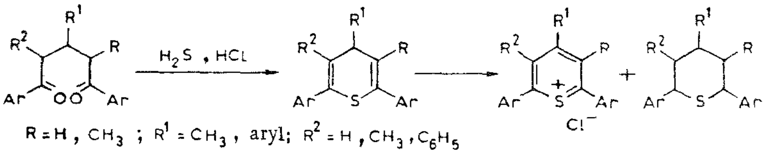


The formation of an extremely unstable 1-methyl-3,5-diphenylthiabenzene was proved spectroscopically by careful hydrolysis of 1-methyl-3,5-diphenylthiapyrylium tetrafluoroborate [31].

Thiopyrans from 1,5-Diketones

The formation of 2H- and 4H-thiopyrans in the reaction of 1,5-diketones with H_2S and P_4S_{10} [14, 15, 33-41] is more general in character, although some 1,5-diketones are readily condensed under these conditions to give carbocyclic compounds [42-46].

The nature of the solvent has a great effect on the degree of conversion of 1,5-diketones with hydrogen sulfide under the influence of hydrogen chloride [14, 15]. Thus, mainly 4H-thiopyrans are obtained in methanol, while mixtures of thiacyclohexanes and thiapyrylium chlorides are obtained in acetic acid [34, 35, 40].

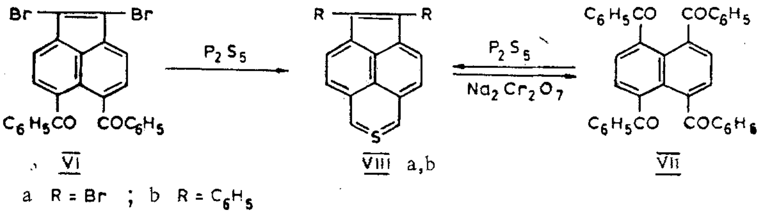


$R = H, CH_3$; $R^1 = CH_3$, aryl; $R^2 = H, CH_3, C_6H_5$

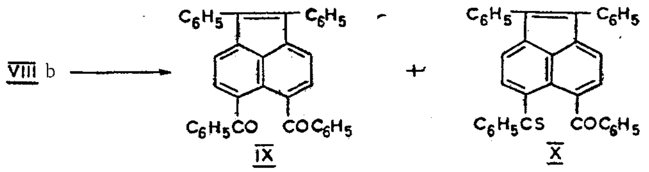
On brief standing, the reaction mixture also contains thiopyrans. After 48 or more hours, depending on the structure of the 1,5-diketone, the reaction products at 20° are the corresponding thiapyrylium chloride and thiacyclohexane [34, 36, 40]. The degree of conversion of diketones with hydrogen sulfide under acid catalysis conditions is also determined by the degree of their substituted character and the character of the substituent [36, 41]. 1,5-Diphenyl-1,5-pentanedione and the 3-methyl derivative react in methanol with H_2S and HCl to give mixtures of thiapyrylium salts and thiacyclohexanes. 1,2,4,5-Tetraphenyl-1,5-pentanedione does not react with the same reagents in either methanol or acetic acid [14]. 1,5-Diaryl-1,5-pentanediones containing substituents in the 2- and 4- or 2-, 3-, or 4-positions react with hydrogen sulfide and hydrogen chloride in both methanol and acetic acid to give thiopyrans.

1,5-Diketones react with P_4S_{10} to give 4H-thiopyrans in pyridine [38]. In the absence of a solvent, the reaction proceeds in the same way as the reaction of 1,5-diketones with hydrogen sulfide and hydrogen chloride in acetic acid [47]. Tetra- and pentasubstituted 1,5-pentanediones do not react with P_4S_{10} in pyridine [38]. The state of the electron density on the carbonyl carbon atom and the weakly basic character of the catalyst, which does not sufficiently promote either enolization of the ketones or cyclodehydration of the initially formed unstable gem-hydroxythiols, are apparently manifested in this case [38].

New thianaphthene systems (VIII) with a tetravalent sulfur atom are obtained by the action of phosphosphorus pentasulfide in pyridine on 1,2-dibromo-5,6-dibenzoylacenaphthene (VI) and 1,4,5,8-tetrabenzoylnaphthalene (VII) [48-51].



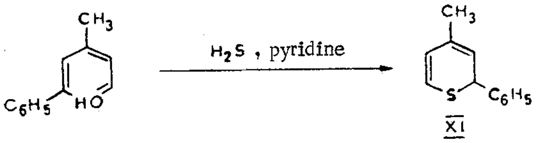
Starting tetraketone VII is formed in the oxidation of thiopyran VIIIb with sodium dichromate, while a mixture of diketone IX and monothiodiketone X is obtained by the action of CrO_3 in pyridine. Monothiodiketone X reacts with hydrogen chloride in ether to reform thiopyran VIIIb:



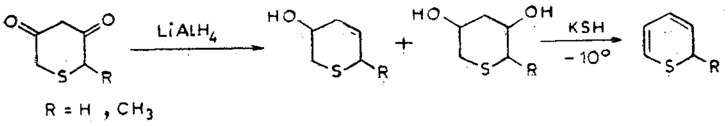
Specific Methods for the Preparation of 2H-Thiopyrans

The above-described methods lead to 4H-thiopyrans or to a mixture of the latter with 2H-thiopyrans. Individual reactions that give only 2H-thiopyrans are known.

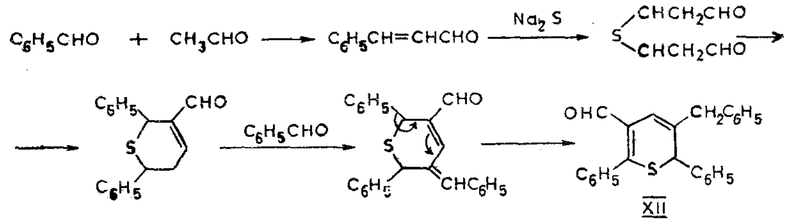
2H-Thiopyran XI is obtained by the action of hydrogen sulfide on a substituted pentadienal under basic catalysis conditions [52, 53]:



2H-Thiopyran [11] and 2-methyl-2H-thiopyran [9, 11, 12] were obtained from 1-thia-3,5-cyclohexanedione:

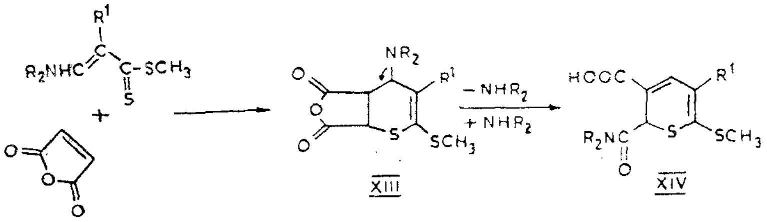


The formation of 2H-thiopyran XII in 15% yield by refluxing benzaldehyde with sodium sulfide in alcohol solution was unexpected [54, 55]. The ethanol is apparently oxidized to acetaldehyde, which condenses with benzaldehyde:

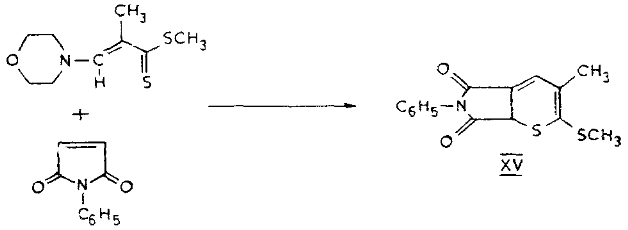


p-Tolualdehyde reacts like benzaldehyde with sodium sulfide in alcohol [54].

Dithioacrylates react with maleic anhydride in benzene to give adducts XIII, which are immediately converted to 2H-thiopyran XIV [56].

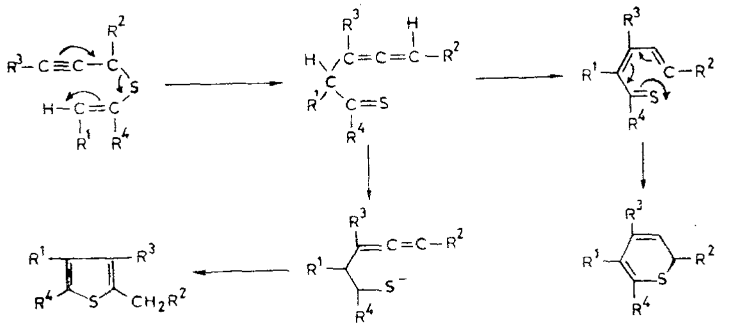


The intermediate formation of adduct XIII is confirmed by the synthesis of its nitrogen analog (XV) [56].



The thermal cyclization of propargyl vinyl sulfides in hexametapol or dimethyl sulfoxide (DMSO) in the presence of amines, which gives a mixture of 2H-thiopyrans and thiophenes, is of great interest [57-59]. If there is an alkyl substituent in the 4-position of the thiopyran, a certain amount of 4-alkylidenedihydrothiopyran is formed.

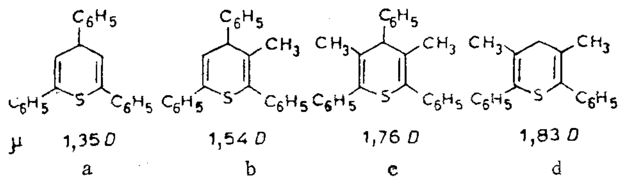
4-Ethyl-4H-thiopyran is more greatly inclined to give an "exo" isomer than 4-methyl-4H-thiopyran. When benzene, alkanes, and aliphatic alcohols are used as the solvent in this reaction, vinyl propargyl sulfides are resinified on heating without a catalyst, while mixtures of the corresponding thiopyrans and thiophenes in low yields are formed in the presence of amines. The yield of thiophenes increases in DMSO as the basicity of the amine increases, and the yield of thiopyrans increases with the same amines in hexametapol. Only thiopyrans are formed in high yield in pure hexametapol [59].



PROPERTIES OF THIOPYRANS AND THEIR DERIVATIVES

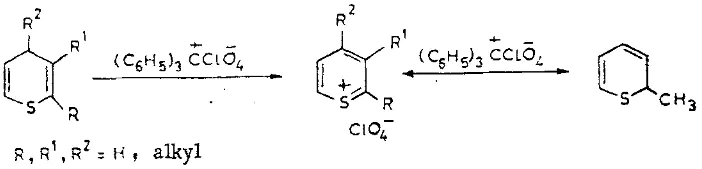
The simplest 2H- and 4H-thiopyrans and their monoalkyl-substituted derivatives change rapidly in air and can be stored for a long time only in the solid state at temperatures below −28° in a nitrogen atmosphere [5, 7, 59]. The more substituents in the thiopyran ring, the more stable the compounds are. 2,4,6-Triaryl- and tetra- and pentaalkyl(aryl)thiopyrans are stable, but they darken in light in the presence of air oxygen and "deliquesce." 2,6-Diaryl-4-alkyl-substituted compounds are less stable than 2,4,6-triarylthiopyrans [14, 15, 39].

The dipole moment of 2,4,6-triphenyl-4H-thiopyran is 1.35 D [60]. The dipole moment increases by 0.2 and 0.4 D, respectively, on successive replacement of the hydrogen atoms in the 3- and 5-positions by a CH_3 group. If dipole moments of 0, 0.4, and 0.4 D are adopted for the $C_{sp^2} \rightleftharpoons H$, $H \rightleftharpoons C_{sp^3}$, and $CH_3 \rightleftharpoons C_{sp^2}$ bonds, respectively, it can be shown that the contribution to the total dipole moment of each CH_3 group in the 3- and 5-positions of thiopyrans a-c will be 0.2 D [60].

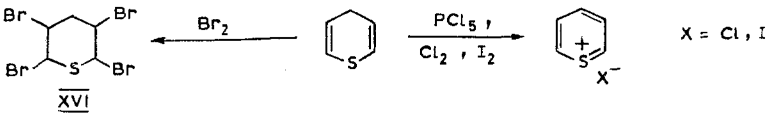


Salt Formation of Thiopyrans

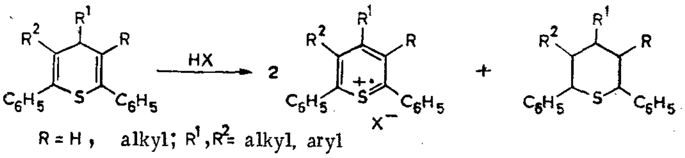
One of the basic properties of thiopyrans is their capacity under the influence of protic and nonprotic acids to undergo conversion to thiapyrylium salts with splitting out of a hydride ion. The thiopyran ring is fully converted to the thiapyrylium cation when a hydride-ion acceptor is present in the reaction mixture. Thus, the hydride-ion acceptor in the reaction of triphenylmethyl perchlorate is the triphenylmethyl cation [8-12].



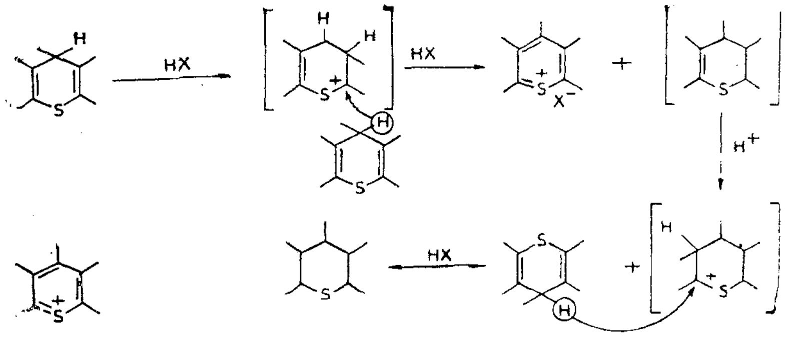
4H-thiopyrans are converted to thiapyrylium salts by the action of PCl_5, Cl_2, and I_2 [7, 8, 61]. In contrast to chlorine and iodine, bromine adds to the double bond of 4H-thiopyran [61].



Under the influence of protic acids (HCl, $HClO_4$, and CF_3COOH), substituted thiopyrans disproportionate with intermolecular hydride-ion transfer to give a mixture of the corresponding thiapyrylium salts and thiacyclohexanes [36, 37, 40, 41, 62-64].

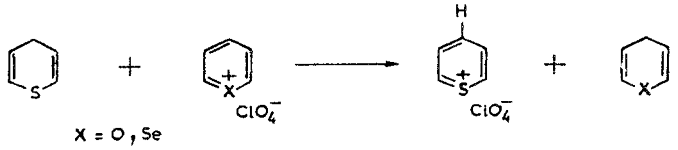


Similarly, sym-octahydrodibenzo-4H-thiopyrans disproportionate under the influence of ferric chloride, perchloric acid, and hydrogen chloride [63-64]. The formation of thiacyclohexanes along with thiapyrylium salts in the reaction of thiopyrans with protic acids attests to the fact that the carbonium ions that develop during protonation of the π bonds of the thiopyrans and dihydrothiopyrans are hydride-ion acceptors in the disproportionation [40, 62].



The carbonium ions are stabilized as a result of intermolecular hydride transfers.

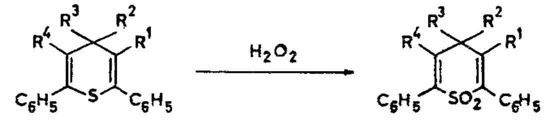
4H-Thiopyrans are distinguished by high mobility of the hydride ion. Thus, a hydride ion is transferred in the reaction of pyrylium and selenopyrylium perchlorates with 4H-thiopyran with the quantitative formation of thiapyrylium perchlorate and pyran or selenopyran [65, 66]:



Sulfones and Sulfoxides of Thiopyrans

Substituted and mono- and disubstituted H- and 4H-thiopyrans undergo profound transformations under the influence of oxidizing agents (hydrogen peroxide, peracids, and manganese dioxide). The nature of the oxidation products has not been studied [61].

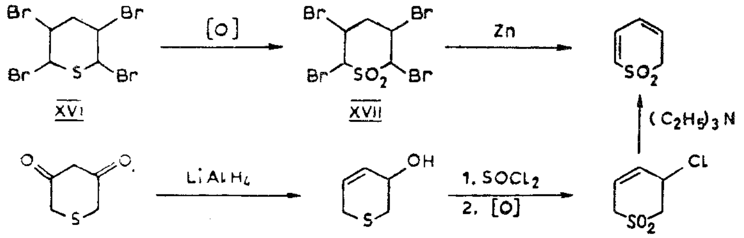
Tetra- and pentasubstituted 4H-thiopyrans are capable of undergoing oxidation to give sulfones [4, 13-15, 24, 37, 38].



R^1, R^3, R^4 = H, alkyl, aryl; R^2 = alkyl, aryl

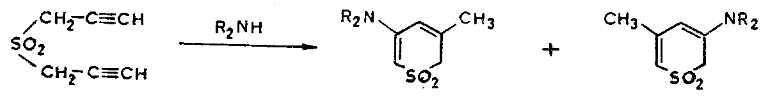
The different behavior of substituted 2H- and 4H-thiopyrans with respect to oxidation is well known. 2,4,6-Triphenyl-4-methyl-4H-thiopyran is smoothly oxidized by hydrogen peroxide to the sulfone, while the isomeric 2,4,6-triphenyl-2-methyl-2H-thiopyran forms a sulfoxide under the same conditions [13]. An attempt to oxidize the latter to the sulfone was unsuccessful [13]. 2H-Thiopyrans are apparently more stable than 4H-thiopyrans, and oxidation to the sulfone does not occur when two substituents are present in the 2-position because of steric factors.

In connection with the fact that the oxidation of the simplest thiopyrans leads to disruption of the heteroring, a number of indirect methods for the preparation of their sulfones and sulfoxides have been developed [61, 67-76]. The sulfone of 2H-thiopyran was obtained as the result of oxidation and subsequent dehalogenation with zinc dust of 2,3,5,6-tetrabromothiacyclohexane (XVI) [61] and also from 1-thia-3,5-cyclohexanedione [68].



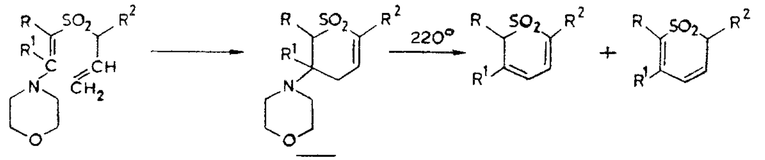
Only the corresponding sulfoxide is readily formed in the oxidation of sulfide XVI with hydrogen peroxide. Oxidation to sulfone XVII proceeds with greater difficulty [61]. Only the sulfone of 4H-thiopyran, which is apparently isomerized under these conditions to the sulfone of 2H-thiopyran [61, 68], could arise initially as a result of debromination of sulfone XVI.

The synthesis of 2H-thiopyran S,S-dioxides from dipropargyl sulfone by the action of secondary amines is of great interest [71]:



Under the same conditions, dipropargyl sulfoxides form products of the addition of the secondary amines, which are not cyclized [71].

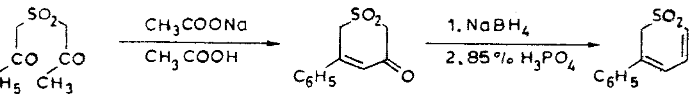
2H-Thiopyran S,S-dioxides are also formed in the cyclization of allylsulfonyl enamines under the influence of triethylamine and subsequent deamination at 220° of cyclization product XVIII [69, 70, 72-76].



XVIII

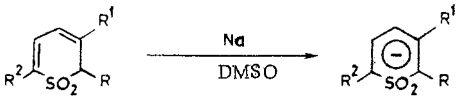
R,R²=H, alkyl; R′= alkyl, aryl

Certain difficulties have arisen in the solution of the problem of the position of the double bond in the thiopyran ring [61, 67, 68]. In this connection, the synthesis and spectral characteristics of 3-phenyl-2H-thiopyran S,S-dioxide (XIX), in the ring of which the position of the double bonds was predetermined by the structure of the starting diketone [69], seemed of great interest:

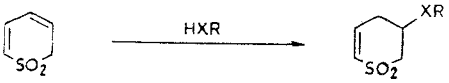


XX XIX

The properties of sulfones of 2H-thiopyrans [67, 68, 72, 73] have been studied most completely. The high lability of the hydrogen atoms of the α-methylene group, as attested to by their complete deuterium exchange in the absence of basic catalysts [77], was established. S,S-Dioxide anions are formed on treatment of sulfones of 2H-thiopyrans with sodium or sodium methoxide in DMSO [72]. The PMR spectra confirm the benzoid character of the system. The direct observation of an anion attests to extensive π-electron delocalization [72]:

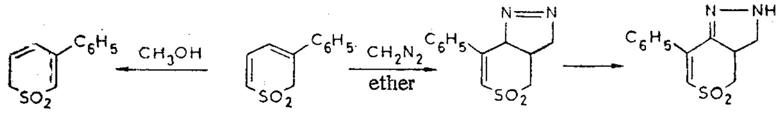


Like α,β-unsaturated acyclic sulfones, the sulfones of 2H-thiopyrans add weakly basic nucleophiles on refluxing in chloroform or benzene [67, 68, 70].



XR = $(C_2H_5)_2N$; NHC_4H_9-*n* ; HNC_6H_{11} ; morpholino; pyrrolidino; $S(C_2H_5)_2$; SC_6H_5 ; $SC_6H_4CH_3$-*p* ; SC_6H_4Br

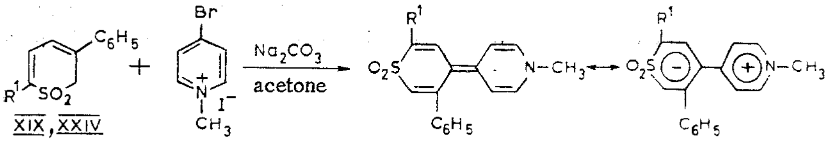
Despite the obvious lability of the hydrogen atoms of 2H-thiopyran S,S-dioxides, the action of diazomethane does not result in alkylation in the 2-position but rather in addition of the reagent to give 1-pyrazoline XXI, which is isomerized to 2-pyrazoline XXII on refluxing in methanol [73].



XXIII XIX XXI XXII

The formation of 1-pyrazoline XXI suggests isomerization of sulfone XIX to 5-phenyl-2H-thiopyran S,S-dioxide (XXIII) [73]. It was found that this sort of isomerization is observed when a methanol solution of sulfone XIX is simply stored. As a result, the possibility of attack by dipolar reagent CH_2N_2 at the "end" of the diene system of sulfone XXIII, which is apparently more reactive than sulfone XIX, appears.

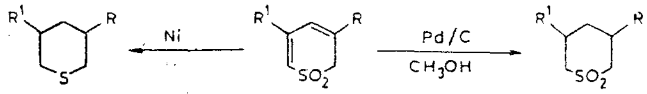
Condensation of sulfone XIX and 3-phenyl-6-methyl-2H-thiopyran S,S-dioxide (XXIV) with 1-methyl-4-bromopyridinium iodide gives compounds of the XXV type [76].



XIX, XXIV XXV

XIX $R^1 = H$; XXIV $R^1 = CH_3$

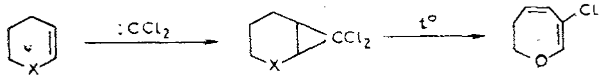
The sulfones of 2H-thiopyrans are reduced to the corresponding sulfones of thiacyclohexane by catalytic hydrogenation on palladium [69], and the sulfo groups are also reduced on nickel [71].



$R = C_6H_5$, $R^1 = H$; $R^1 = CH_3$, R = piperidino, $N(CH_3)_2$, morpholino

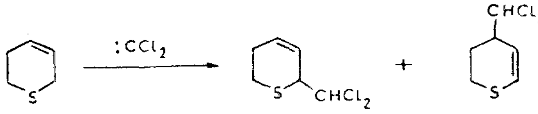
Reaction with Dichlorocarbene

This reaction of dihydropyran (or dihydrothiopyran) has generated a great deal of interest in connection with the ability of the resulting adducts to undergo conversion to an oxepine on refluxing in quinoline [78-80]:

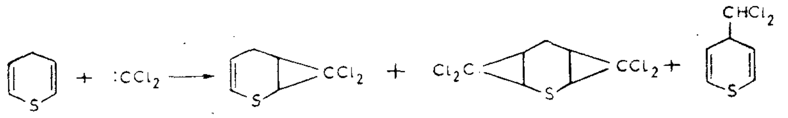


X = O, S

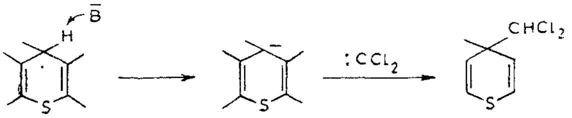
In contrast to Δ^2-dihydrothiopyran, Δ^3-dihydrothiopyran forms 2- and 4-dichloromethyldihydrothiopyrans [80]:



A similar difference with respect to dichlorocarbene is manifested by 4H- and 2H-benzothiopyrans [81]. The 3p orbitals of the sulfur atom in Δ^2-dihydrothiopyran and 4H-benzothiopyran apparently interact with the π bond and activate it; this promotes addition of dichlorocarbene [80]. This notion is confirmed by the ability of 4-methoxy-2H-benzothiopyran, in which the double bond is polarized due to p-π conjugation of the free electron pairs of oxygen and the π bond, to give an adduct with dichlorocarbene [77]. Dimroth has extended this reaction to pyrans and thiopyrans [82]. It was found that 4H-thiopyran is capable of adding dichlorocarbene at one and two double bonds to give mono- and diadducts. In addition, the reaction mixture contains 4-dichloromethyl-4H-thiopyran.



The possibility of the formation of a carbanion that undergoes attack by dichlorocarbene evidently shows up under basic catalysis conditions due to splitting out of a proton in the 4-position.

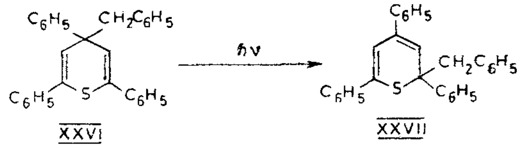


The formation of dichloromethyl-substituted compounds in the reaction of dichlorocarbene with 2H-benzothiopyran and Δ^3-dihydrothiopyran can be similarly explained [81].

2,4,6-Triphenyl-4H-pyran adds dichlorocarbene only at one double bond [82]. An attempt to accomplish conversion of the monoadducts of pyran and thiopyran to an oxepine and a thiepine in analogy with the pyran adduct was unsuccessful [82].

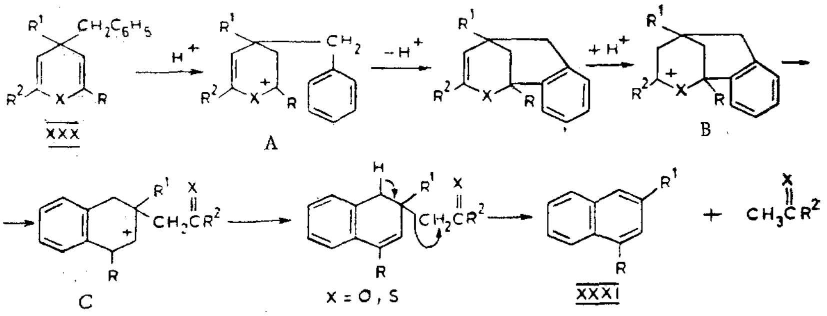
Isomerization and Other Transformations of Thiopyrans

When a solution of 2,4,6-triphenyl-4-benzyl-4H-thiopyran (XXVI) in hexane is subjected to UV irradiation in a nitrogen atmosphere it is isomerized to 2,4,6-triphenyl-2-benzyl-2H-thiopyran (XXVII) [21, 22, 83]. The structure of isomer XXVII is confirmed by conversion to 1,3,5-triphenyl-3-benzylpentane by desulfuration over Raney nickel. Tetraphenylbenzene is formed when 2H-thiopyran XXVII is heated with sodium ethylene glycoxide.



2,4,6-Triphenyl-4-benzyl- and 2,6-diphenyl-4-(p-tolyl)-4-benzyl-4H-pyrans are similarly isomerized [83, 84].

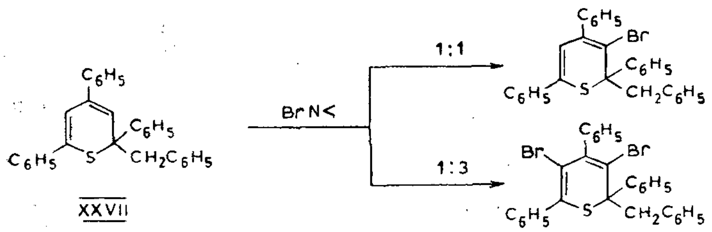
The conversion of 2,4,6-triphenyl-4-benzyl-4H-thiopyran and pyran by heating to 90° with 70% perchloric acid is different in character. In this case, two parallel processes – elimination of a benzyl group to give 2,4,6-triphenylthiapyrylium or 2,4,6-triphenylpyrylium perchlorate and a substituted naphthalene and thioacetophenone – are observed [21, 22]. Dimroth proposes the following mechanism for the conversion of 4-benzyl-4H-thiopyran and pyrans to 1,3-diphenylnaphthalenes [21, 22]:



According to the data in [21, 22], 2-benzyl-2H-pyrans and 2-benzyl-2H-thiopyrans do not form substituted naphthalenes with perchloric acid.

Halogenation of Thiopyrans

2H-Thiopyran XXVII undergoes radical substitution by the action of N-bromosuccinimide (NBS) in the presence of benzoyl peroxide to give mono- or dibromo-substituted 2H-thiopyrans, depending on the reagent ratio [23]. More than two bromine atoms cannot be introduced into the thiopyran molecule under these conditions [23].



Similar bromination products are formed by the action of NBS on 4-benzyl-4H-thiopyran (XXVI), but the reaction proceeds less smoothly, and only 3-bromo-4-benzyl-4H-thiopyran could be isolated preparatively. The halogenation of 2H- and 4H-pyrans with NBS proceeds similarly [23].

The chlorination of 2H- and 4H-thiopyrans XXVI and XXVII with N-chlorosuccinimide (NCS) or CCl_3SO_2Cl leads to a very complex mixture of reaction products, in which 3-chloro-2,4,6-triphenyl-2-benzyl-2H-thiopyran was detected only by spectral methods [23].

2,3,5,6-Tetrabromotetrahydrothiopyran is formed in 75% yield by the action of a solution of bromine in chloroform at −35° on 4H-thiopyran in the same solvent. Under similar conditions at −40°, thiapyrylium chloride is formed with chlorine. 4H-Thiopyran does not react with iodine under the same conditions, but the iodine color in the aqueous acetone solution vanishes in the course of 1 h, and thiopyrylium iodide is formed. It should be noted that 4H-thiopyran did not give a thiapyrylium bromide with bromine in aqueous acetone solution, but the product of the addition of bromine and resinification products were formed in small amounts [61].

Spectral Characteristics of Thiopyrans

There are only disconnected data on the electronic and IR spectra of unsubstituted and substituted

TABLE 1. UV Spectra of Thiopyrans

Thiopyran	λ_{max}, nm	log ε
4H-Thiopyran [5, 6, 11]	236-238, 278	3.7, 3.4
2,4,6-Triphenyl-4H-thiopyran [11, 13, 38, 60]	234 (235), 312 (350)	4.5 (4.46), 3.4 (3.20)
2,4,6-Triphenyl-3-methyl-4H-thiopyran [60]	224, 310	4.2, 3.3
2,4,6-Triphenyl-3,5-dimethyl-4H-thiopyran [60]	222, 282	4.3, 3.2
2,6-Diphenyl-3,5-dimethyl-4H-thiopyran [60]	220, 280	4.5, 3.7
2,3,5,6-Tetraphenyl-4H-thiopyran [60]	226, 250-290	4.57, 4.25
2,4,6-Triphenyl-4-benzyl-4H-thiopyran [21, 23]	233, 237	4.48, 4.45
2,4,4,6-Tetraphenyl-4H-thiopyran [13, 23]	235	4.29
2,4,6-Triphenyl-4-methyl-4H-thiopyran [13]	235	4.4
2H-Thiopyran [10, 57]	231, 324	3.36, 3.29
3,5-Diphenyl-2H-Thiopyran [31, 32]	270, 304	4.49, 3.69
2,4,6-Triphenyl-2-methyl-2H-thiopyran [13]	257, 347	4.32, 3.75

2H- and 4H-thiopyrans in the literature [5, 6, 11, 13, 38, 51, 57, 60]. The electronic spectrum of unsubstituted 4H-thiopyran contains λ_{max} bands at 236-238 nm (log ε 3.7) and 278 nm (log ε 3.4) [5, 6, 11]. The following bands are presented for the most thoroughly studied compound, 2,4,6-triphenyl-4H-thiopyran: 235 nm (log ε 4.46), 350 nm (log ε 3.25) [13], 234 nm (log ε 3.95), and 312 nm (log ε 3.30) (in hexane) [60]. The second band undergoes a bathochromic shift. Substituents in the 3- and 5-positions have the greatest effect on the position of the bands in the electronic spectra of 4H-thiopyrans; substituents in the 4-position have virtually no effect on the UV spectra [13, 23, 26, 38, 60] (Table 1).

Judging from the data presented in [11, 57], the electronic spectrum of 2H-thiopyran differs only slightly from the spectrum of 4H-thiopyran.

Two bands in the region of absorption of C=C bonds are observed in the IR spectra of 2H- and 4H-thiopyrans [5, 14, 15, 38]. A shift in the absorption bands in the spectrum of 2H-thiopyran ($\nu_{C=C}$ 1535, 1565 cm^{-1}) [11, 57] as compared with the IR spectrum of 4H-thiopyran [5, 6, 11] ($\nu_{C=C}$ 1600, 1640 cm^{-1}) in the longwave region is observed.

Resonance signals at δ 5.9 ppm (2-H, 6-H), 5.5 ppm (3-H, 5-H), and 2.8 ppm (4-H) are observed in the PMR spectra of 4H-thiopyrans; signals at 5.59 ppm (4-, 5-, and 6-H), 5.10-5.60 ppm (3-H), and 3.00-3.19 ppm (2-H) are observed in the spectra of 2H-thiopyrans [10, 59, 82, 85, 86].

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