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1,3-DIHYDROBENZO[*c*]THIENYLIUM (THIOPHTHALYLIUM) SALTS. (REVIEW)

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Methods of preparation, chemical reactions, the structures and reactivity of thiophthalylium ions are reviewed.

Keywords: thiophthalylium salts, methods of preparation, structure, stability, reactivity, electrophilic properties.

Thiophthalylium ions (1,3-dihydrobenzo[*c*]thienylium or benzo[*c*]thiophenium ions) are devoid of extended conjugation but are nevertheless highly stable and can be isolated as pure compounds as a variety of salts. Such salts are suitable models in theoretical organic chemistry for the study of the general properties of carbenium ions and the principles of the mechanisms of ionic reactions. The preparative value of thiophthalylium salts lies in their great reactivity relative to various nucleophilic reagents as a result of which they have exceptional value in the construction of a variety of functionally substituted derivatives of heterocyclic systems of thiophthalane which are difficult to obtain and which may include compounds with practically useful properties. Some aspects of the practical use of such compounds have been summarized in a review [1].

The field of chemistry of thiophthalylium salts is relatively new and has been less studied than the chemistry of their directly isoelectronic analogs, the phthalylium salts, the synthetic possibilities of which were cited in a review [2]. The first report of the possibility that thiophthalylium salts were intermediates in some reactions of thiophthalanes appeared only in 1971 [3], but a year later these ions were isolated as pure compounds in the form of stable salts [4].

1. PREPARATION

Depending on the nature of the substituent at the electrophilic carbon atom, the basic methods of preparation of thiophthalylium salts include heterolytic scission of a polarized C–bond, transfer of a hydride ion from a neutral molecule to an electrophilic acceptor, and addition of an electrophile to an unsaturated functional group.

A universal method for the synthesis of 1-arylthiophthalylium salts **1** is the ionization of 1-hydroxythiophthalanes **2** under the action of protonic acids or Lewis acids [5-13]. Compounds **2** may be readily obtained by the Grignard reaction from the corresponding 3,3-disubstituted 2-thiophthalides **3**, methods of synthesis of which has been cited in many papers [5, 13-17].

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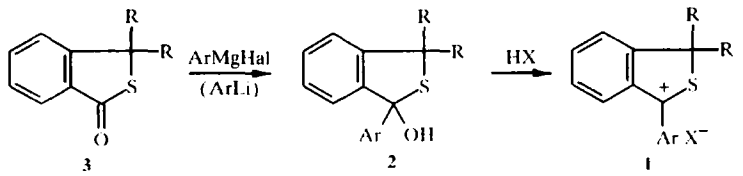
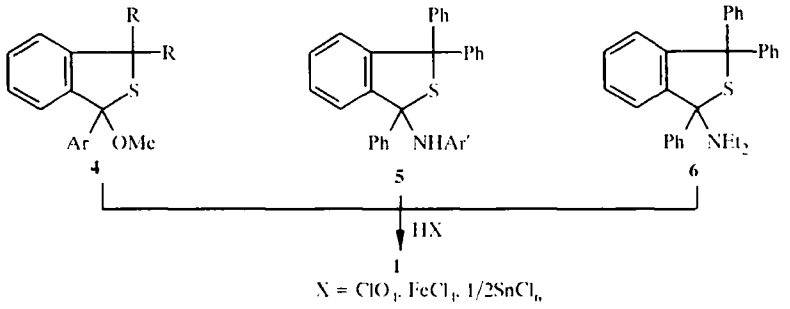


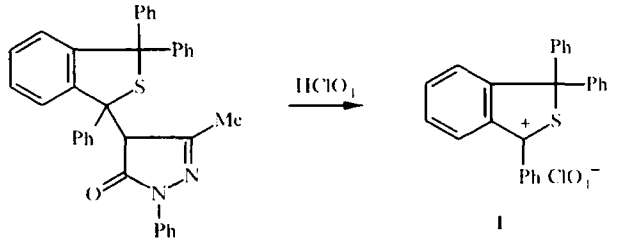
1–3 R = Me, Ph, C_6H_4Me-*m*;

1, 2 Ar = Ph, C_6H_4Me-*p*,-*m*,-*o*; C_6H_4OMe-*p*,-*m*,-*o*; C_6H_4OEt-*p*; C_6H_4F-*p*,-*m*; C_6H_4Cl-*p*,-*m*; C_6H_4Br-*p*,-*m*; $C_6H_4NMe_2$-*p*; $C_6H_4NEt_2$-*p*; $C_6H_2Me_3$-*p*,-*o*. 1 X = ClO_4, $FeCl_4$, 1/2$SnCl_6$

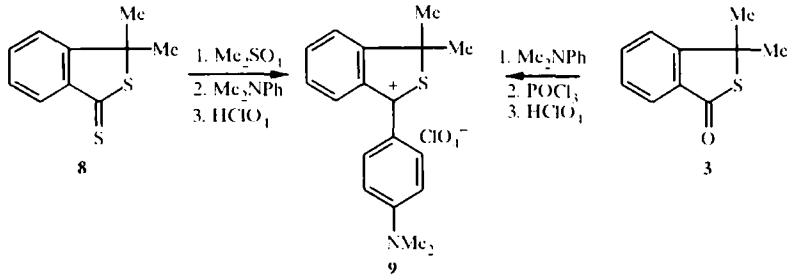
1-Arylthiophthalylium salts **1** were formed in high yield by ionization of ethers of hydroxythiophthalanes **4** [13, 18], arylamino- (**5**) [19] and dialkylaminothiophthalanes (**6**) [13]:



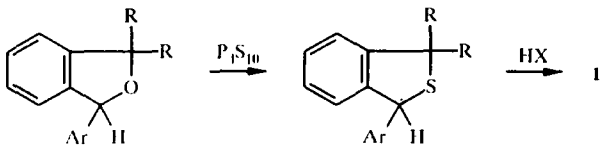
Heterolytic fission in some derivatives of the thiophthalane series with strongly polarized $C_{(1)}$–C bonds occurs in acid media, e.g., compound **7**:



1-(*p*-Dimethylaminophenyl)-3,3-dimethylthiophthalylium perchlorate (**9**) was obtained by the condensation of 1,2-dithio- (**8**) and 2-thio- (**3**) phthalides with dimethylaniline in the presence of $HClO_4$ [9]:



1-Arylthiophthalylium salts **1** were also obtained from the corresponding phthalanes **10** *via* the 1-H-thiophthalanes **11** by oxidation with either $FeCl_3$ or $HClO_4$ [4, 5, 18, 20]:

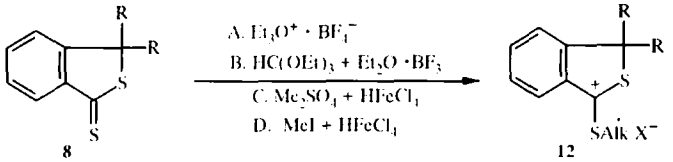


10 **11**

1, 10, 11 R = Me, Ph; Ar = Ph, C_6H_4Me-*p*; **1** X = $FeCl_4$, ClO_4

1-Arylthiophthalylium tetrachloroferrates readily exchanged the $FeCl_4$ ion for ClO_4 by boiling with 57% $HClO_4$ [6-9].

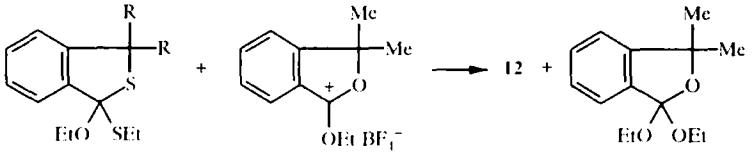
A basic method for the synthesis of 1-alkylthiosubstituted thiophthalylium salts **12** is alkylation of the very accessible 1,2-dithiophthalides **8** [15, 16, 21] with triethyloxonium tetrafluoroborate [15, 22, 23], a mixture of ethyl orthoformate and boron trifluoride etherate [12, 13, 24], dimethyl sulfate [13, 15, 16], or iodomethane [15]. In the last two cases the thiophthalylium salts formed were isolated as tetrachloroferrates by treating the reaction mixture with $HFeCl_4$:



8 **12**

8, 12 R = Me, Ph; C_6H_4Me-*p*, -*m*, C_6H_4Cl-*p*;
Alk = Me, Et; **12** X = BF_4, $FeCl_4$

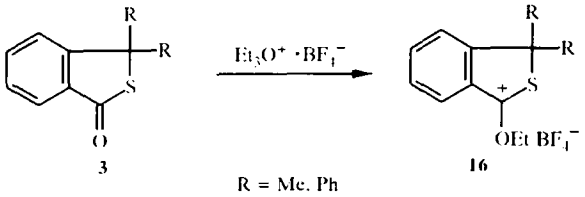
The tetrafluoroborates **12** (R = Me, Ph; Alk = Et; X = BF_4) were obtained in quantitative yield together with the ether **13** by the exchange reaction between the thioethers **14** and the phthalylium salt **15** [25]:



14 **15** **13**

The corresponding tetrachloroferrates **12** (X = $FeCl_4$) were obtained by the treatment of the tetrafluoroborates **12** (X = BF_4) with $HFeCl_4$ [15].

Thiophthalylium salts **16** with an ethoxy group in position 1 were obtained by the alkylation of 2-thiophthalides **3** with triethyloxonium tetrafluoroborate [15]:

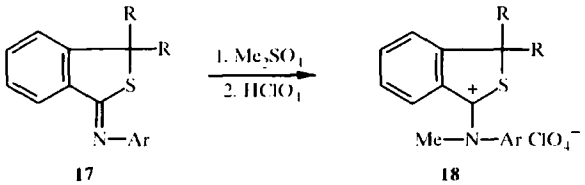


3 **16**

R = Me, Ph

The thiolactones **3** were not alkylated by dimethyl sulfate or iodomethane [15].

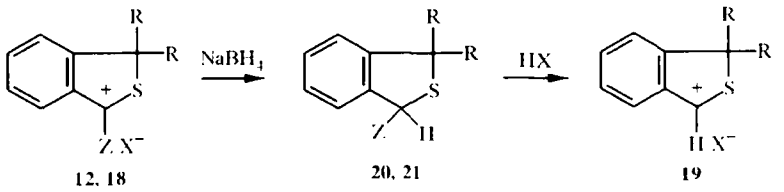
1-Methylarylthiophthalylium perchlorates **18** were obtained by alkylation of 1-aryliminothiophthalanes **17** with dimethyl sulfate followed by treatment of the reaction mixture with $HClO_4$ [26, 27]:



17 **18**

17, 18 R = Ph; Ar = Ph, C_6H_4Me-*p*

The following scheme was proposed to prepare unsubstituted thiophthalylium salts **19**. Salts **12** and **18**, containing a heterosubstituent (Z) were reduced and heterolytic scission of the exocyclic carbon-heteroatom bond in the products of hydride ion addition **20** and **21** gave the required products [27-29]:

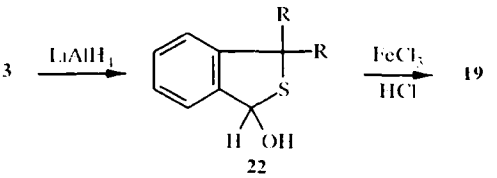


12, **18** **20**, **21** **19**

12, **20** Z = SEt; **18**, **21** Z = NMeAr; **12** X = BF_4; **18** X = ClO_4; **19** X = ClO_4, $FeCl_4$;

12, **18**–**21** R = Ph, C_6H_4Me-*p*, C_6H_4Cl-*p*

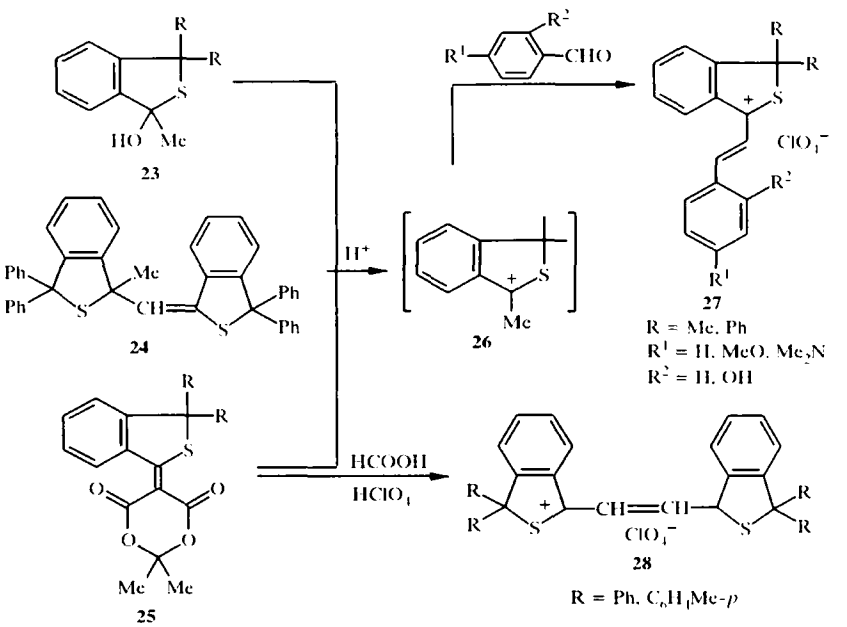
A tetrachloroferrate **19** (R = Me, X = $FeCl_4$) was synthesized by treating compound **22**, a product of the reduction of the 2-thiophthalide **3** (R = Me), with $HFeCl_4$ [15]:



22

However this method has limited use since reduction of 3,3-diaryl-substituted 2-thiophthalides **3** (R = Ar) does not lead to the corresponding 1-H-1-hydroxythiophthalanes **22** (R = Ar) [15].

It has been shown by spectroscopy that ionization of 1-methyl-substituted hydroxythiophthalanes **23** [10, 18], acid scission of dimers of their methylene bases **24** [30], and hydrolysis and decarboxylation of thiophthalylidene derivatives of isopropyl malonate **25** [31, 32] gave the 1-methylthiophthalylium ion **26**, but no stable salt was isolated. The ions **26**, generated *in situ* condensed readily with aromatic aldehydes to form 1-styrylthiophthalylium salts **27** [10, 30, 31]. Heating of the derivatives **25** with conc. HCOOH in $HClO_4$ gave the symmetrical trimethylcyanines **28** [31, 32]:



Reactions of 1-alkylthio-substituted **12** and unsubstituted **19** thiophthalylium salts with compounds containing activated benzene ring or active methyl group led to modification of the substituent at position 1. These methods arise from the chemical properties of thiophthalylium salts which are examined below.

2. STRUCTURE

The formation of thiophthalylium ions by the action of acids on 1-hydroxythiophthalanes **2** was established by analysis of the electronic spectra of the latter in neutral and acidic solutions [18]. Transfer to acid solution was accompanied by a bathochromic shift of the absorption maxima and an increase in their intensities. The absorption spectra of hydroxythiophthalanes, taken in acid solution, coincided with the spectra of the corresponding thiophthalylium salts **1**, the elemental analysis of which showed unambiguously that ionization of the hydroxythiophthalanes occurs simultaneously with dehydration: ROH + $H^+ \rightarrow R^+ + H_2O$. Thus the hydroxythiophthalanes show properties of carbynol bases and the cations formed from them under the action of acids have the character of conjugated carbenium ions.

1-Arylthiophthalylium ions **1** absorb in the visible region of the spectrum and they are characterized by two absorption maxima of different intensities. The position of the less intense maximum in the 350-360 nm region is practically independent of the nature of the substituents at $C_{(1)}$ and $C_{(3)}$ [6, 9] but is only affected by the nature of the heteroatom. For example, in the oxygen analogs (phthalylium ions) this maximum is found in the 290-300 nm [33-35], and in the nitrogen analogs (isoindolinium ions) it is found in the 280-295 nm region [36-38]. The appearance and position of this maximum in the spectra of thiophthalylium ions is connected with the presence of a carbenium-sulfonium group conjugated with the annelated benzene ring [9, 18].

The position of the more intense long wavelength maximum in the spectra of 1-arylthiophthalylium ions **1** depends on both the nature of heteroatom and the nature of the substituent in the heterocycle, particularly at position 1 [9]. Replacement of the sulfur atom in the heterocycle by a nitrogen or oxygen atom causes a bathochromic shift of this band by ~ 69 and ~ 22 nm respectively [9]. The bathochromic shift is greater the greater the ability of the substituent at $C_{(1)}$ to enter into conjugation [11, 18]. An increase in the conjugated chain by the introduction of an ethylidene chromophore in position 1 (ions **27**) leads to a considerable bathochromic shift (70-92 nm) of the long wavelength maximum [10]. The intensity of λ_{max} changes in parallel with changes in the electron donor properties of the substituent in 1-Ar [9, 11]. The influence of structure factors on the long wavelength maximum indicates that its appearance and position in the spectra is caused by conjugation of the 1-aryl substituent with the carbenium-sulfonium group. Substituents at $C_{(3)}$, isolated from this group by an sp^3-hybridized carbon atom, have little effect on the position of the long wavelength band.

The long wavelength band is extinguished by replacement of the 1-aryl substituent in thiophthalylium ions by the heterosubstituents AlkS, AlkO, and AlkArN (**12**, **16**, **18**) [15, 22, 27]. The effect of the exocyclic heteroatom in these salts on the position and intensity of λ_{max} has the same trend as the effect of a heteroatom in the ring.

In the spectra of 1-H-thiophthalylium ions **19** the absorption maximum associated with oscillating charge in the thiophthalylium unit is found at 340 nm [27, 29].

The change from the covalent structure of the thiophthalanes to the ions shows up in the ^1H NMR spectra as a weak field shift of the signals of all proton containing groups which is typical for carbenium ions [49]. The shift of the proton signals for groups in position 1 is caused by conjugation of this group with the carbenium center, whereas for the proton signals of groups at position 3 it is caused by the presence of the electron acceptor group $-S^+=$ in the cations which decreases the electron density at $C_{(3)}$. The size of the shift of the signals for proton containing groups for the oxygen [9, 33] and nitrogen [50] analogs of thiophthalylium ions is in complete agreement with the change in electron acceptor properties of the groups $-N^+= < -S^+= < -O^+=$ [51].

The presence of formal positive charges on the carbon and sulfur atoms in thiophthalylium ions has been confirmed by quantum-chemical calculations [12].

It was established by the dynamic ^1H NMR spectroscopic method [18] that in the spectra of 1-diakylaminophenyl)thiophthalylium ions **1** (Ar = *p*-$Me_2NC_6H_4$, *p*-$Et_2NC_6H_4$) the magnetic equivalence of the

TABLE 1. Values of the Long Wavelength Absorption Maxima and pK_R for 3,3-R_2-1-Ar-Thiophthalylium, -Phthalylium, and 2-Phenylisoindolinium Ions.

R	Ar	Thiophthalylium			Phthalylium			Isoindolinium		
		λ_{max}, nm	$pK_{R^+(a)}$	Ref.	λ_{max}, nm	$pK_{R^+(a)}$	Ref.	λ_{max}, nm	$pK_{R^+(a)}$	Ref.
1	2	3	4	5	6	7	8	9	10	11
Me	Ph	360	-0.72	[5]	340	-1.77	[39]	292	+10.35	[47]
Me	*p*-MeC_6H_4	396	+0.22	[6]	362	-0.83	[39]	300	+10.83	[47]
Me	*m*-MeC_6H_4	364	-0.41	[6]	342	-1.48	[40]	295	+10.53	[47]
Me	*o*-MeC_6H_4	359	+0.34	[9]	338	-0.31	[33]			
Me	*p*-$MeOC_6H_4$	439	+1.22	[6]	390	+0.56	[39]	335	+11.30	[47]
Me	*m*-$MeOC_6H_4$	360	-0.74	[9]	338	-2.12	[41]	295	+11.01	[47]
Me	*o*-$MeOC_6H_4$	357	+0.76	[9]	332	-0.98	[33]			
Me	*p*-$EtOC_6H_4$	441	+1.23	[6]	392	+0.58	[33]			
Me	*p*-FC_6H_4	369	-0.61	[9]	350	-1.68	[42]			
Me	*m*-FC_6H_4	358	-1.60	[9]	332	-2.86	[42]			
Me	*p*-ClC_6H_4	380	-1.24	[6]	359	-2.18	[43]	300	+9.60	[47]
Me	*m*-ClC_6H_4	358	-1.63	[9]	333	-2.96	[43]	295	+9.24	[47]
Me	*p*-BrC_6H_4	382	-1.34	[6]	365	-2.37	[44]			
Me	*m*-BrC_6H_4	357	-1.81	[9]	334	-2.98	[44]			

TABLE 1 (continued)

1	2	3	4	5	6	7	8	9	10	11
Me	*p*-$Me_2NC_6H_4$	523, 554	+5.42 (+4.58)	[9]	464, 492	+4.94 (+4.50)	[9]	450	+12.70	[47]
Me	*p*-$Et_2NC_6H_4$	524, 556	+5.60 (+5.85)	[9]	466, 495	+5.14 (+5.74)	[9]			
Ph	Ph	375	-3.15	[5]	347	-3.74	[45]	305	+7.30	[37]
Ph	*p*-MeC_6H_4	397	-2.18	[11]	376	-2.74	[35]	315	+7.66	[37]
Ph	*m*-MeC_6H_4	376	-2.52	[11]	350	-3.21	[35]	305	+6.48	[48]
Ph	*p*-$MeOC_6H_4$	468	-0.83	[11]	414	-1.06	[35]	365	+8.20	[37]
Ph	*m*-FC_6H_4	368	-4.33	[11]						
Ph	*p*-$Me_2NC_6H_4$	532, 567	+3.07 (+3.05)	[11]	476, 509	+2.98 (+3.17)	[46]	475	+9.30	[37]
Ph	*p*-$Et_2NC_6H_4$	533, 569	+3.39 (+4.24)	[11]	478, 511	+3.33 (+4.40)	[46]			
m-MeC_6H_4	Ph	376	-2.95	[18]						
m-MeC_6H_4	*p*-$Me_2C_6H_4$	533, 568	+3.30 (+3.21)	[18]	474, 504	+3.15 (+3.31)	[18]			

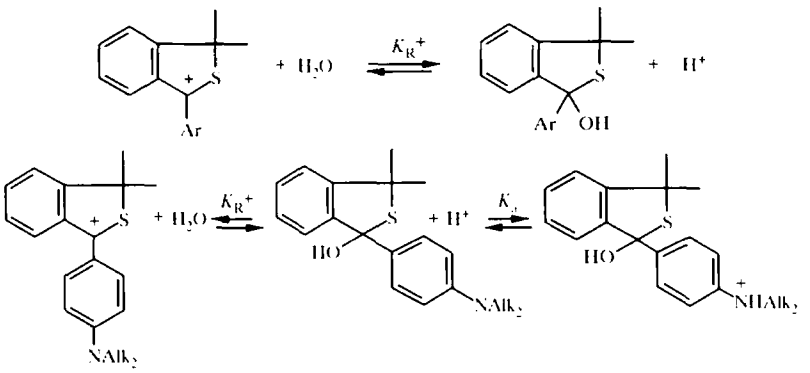
protons of the phenyl ring directly attached to the electrophilic carbon atom is lost as the temperature is lowered. The hindered rotation effect is characteristic of arylmethyl cations [52] and is caused by double bond character of the C^+–$C_6H_4NAlk_2$ and $C^+C_6H_4$–$NAlk_2$ groups as a result of p,π-conjugation of the cationic center with the 1-aryl substituent.

The intensity of the band in the aromatic ring vibration region is increased in the IR spectra of the thiophthalylium salts **1** in comparison with the spectra of the hydroxythiophthalanes **2** which indicates the conjugation of the annelated benzene ring with the carbenium-sulfonium unit [6].

The totality of the spectral data shows conclusively the presence of the carbenium-sulfonium unit in the thiophthalylium ions which is only possible if the cations have a cyclic structure. This conclusion is confirmed by the results of the studies of the stability of thiophthalylium ions, their reactivity, and chemical conversions.

3. STABILITY

Studies of acid-base processes involving 1-arylthiophthalylium ions **1** showed that the processes are not complicated by side reactions and are reversible [5, 9, 18, 20]. An equilibrium exists over a definite range of acidity which includes carbocations, ammonium ions (for compounds containing dialkylaminophenyl substituents) and the corresponding carbynol bases:



The reversibility of the hydrolysis 1-arylthiophthalylium salts permits the use of the acid-base equilibrium constants (pK_{R^+}, pK_a) as quantitative characteristics of the relative thermodynamic stability of the cations.

As an analysis of the values of pK_{R^+} shows (Table 1), thiophthalylium ions are more stable than their oxygen analogs but less stable than their nitrogen analogs which indicates the effectiveness of the heteroatom (O < S < N) in delocalization of the positive charge on C_{11} atom. The stabilizing effect of the heteroatom is determined by the nature of the substituent in position 3 and while the electron donating effect of the substituent at the carbenium center has a levelling effect [11].

Substituents in the heterocycle also take part in the stabilization of 1-arylthiophthalylium ions. Substituents in position 1, directly linked to the carbenium center, show the greatest effect and their effect is unequivocal: electron donor groups increase and electron acceptors decrease the stability of the cations in hydrolysis reactions. The influence of *meta* and *para* substituents in 1-Ar on the stability of the thiophthalylium ions is described by the Brown-Okamoto electrophilic σ^+ constants [9, 11]. The stabilizing effect of *ortho* substituents is not linked with steric interactions but has an electron character [53]. It has been shown [53, 54] that σ_p^+ constants most completely reflect the overall electron effect of any substituents in 1-Ar on the stability of thiophthalylium ions.

Substituents at position 3 have a smaller effect. Their influence has a purely inductive character and affects the carbenium center predominantly *via* the heteroatom [18].

The influence of substituents in the five-membered ring on the stability of the 1-arylthiophthalylium ions is additive [18]:

$$\lg K_{R^+} = 3.68\sigma^+_{R(1\text{-}Ar)} + 1.75\Sigma\sigma^*_{R(C_3)} + 1.68$$

The alkyl groups at the nitrogen atom provide the main contribution to the stability of the ammonium ions formed by protonation of hydroxythiophthalanes containing a dialkylaminophenyl substituent [9, 11]. The inductive influence of substituents at position 3 on the stability of the ammonium ions is 1.6 times smaller than that of the same substituent on the stability of carbenium ions [18].

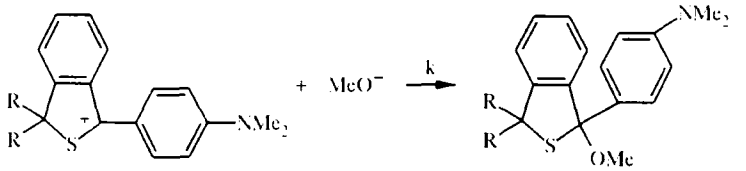
The stability of carbenium ions is decreased to a small extent and of ammonium ions to a great extent by increasing the temperature. The entropy factor is the principal contribution to the change in free energy for the hydrolysis of carbocations whereas the change in enthalpy is the principal factor for the hydrolysis of ammonium ions [55].

It is not possible to estimate quantitatively the stability of thiophthalylium ions **12**, **16**, and **18** containing heterosubstituents AlkS, AlkO, and AlkArN at the carbenium center because of the irreversible hydrolysis of these salts. However by comparison of the reaction conditions it is possible to establish [25, 27] that the influence of heteroatoms in the side chain on the stability of the cations is in the same order as the heteroatoms in the ring (O < S < N).

Prolonged heating in acetic acid of 3,3-dialkyl substituted phthalylium salts with a bulky substituent at position 1 (mesityl) caused destruction of the furan ring. In contrast thiophthalylium salts with an analogous structure are not affected under the same conditions which shows that the annelated sulfur-containing rings are more stable than the corresponding oxygen-containing rings [56].

4. REACTIVITY

The effect of structural factors and the polarity of the medium on the kinetic behavior of thiophthalylium ions and their oxygen analogs in reactions with sodium methoxide in methanol and its mixtures with acetonitrile have been studied by the established spray method [57]:



R = Me, Ph, C_6H_4Me-*m*

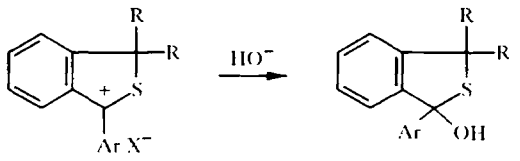
It was shown that reactivity of the heterocyclic systems was determined predominantly by the charge size δ^+ on the carbenium center and that structural units provided the principal contribution for its delocalization: the rate of the methoxylation reaction increased with increasing electron accepting properties of the substituent and on replacing sulfur by oxygen. Thiophthalylium ions were characterized by a high degree of delocalization of the positive charge on $C_{(1)}$ atom and by enthalpy control of the reactivity.

The rate of methoxylation of thiophthalylium ions decreased with increasing polarity of the medium, which is linked with distribution of the charge on formation of the activated complex and decreased tendency of the transition state to undergo electrostatic solvation in comparison with the starting reagents. An increase in the polarity of the medium leads to a weakened electrostatic interaction of the substituent with the reaction center of the cations. The effect of the dielectric permeability on the rate constant is described by the Scatchard equation.

The chemical properties of thiophthalylium salts are determined predominantly by their electrophilicity. Therefore reactions with a variety of nucleophilic reagents is characteristic for these salts. The nucleophilic attack not ever terminates by formation of addition products to $C_{(1)}$ atom of the cation. The stability of the addition products to further conversions is determined by the structure of the substrate (predominantly the nature of the substituent at the electrophilic center), the nature of the nucleophile, and the reaction conditions.

4.1. Reactions with O-Nucleophiles

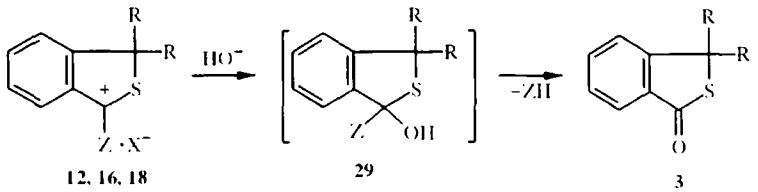
Hydrolysis of 1-arylthiophthalylium salts **1** leads to formation of addition products of the hydroxide ion – 1-hydroxythiophthalanes **2** [5-7, 13]. Depending on the reaction conditions replacement of the sulfur atom by oxygen with formation of 1-hydroxyphthalanes may also occur [7]:



1 **2**

1, 2 R = Me, Ph; Ar = Ph, C_6H_4Me-*p*,-*m*,-*o*; 1 X = ClO_4, $FeCl_4$, $1/2SnCl_6$

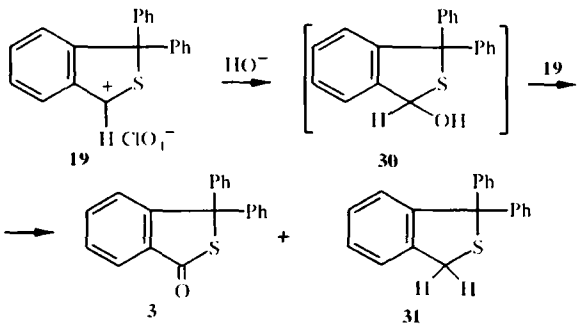
Hydrolysis of salts containing 1-alkylthio- (**12**) [13, 25], 1-alkoxy- (**16**) [25], and 1-methylarylamino- (**18**) [27] groups occurs irreversibly. Water reacts with these salts at the α-carbon atom to give unstable hydroxy compounds of type **29** which are stabilized by loss of a thiol, an alcohol, or methylaniline to give a 2-thiophthalide **3**:



12, 16, 18 **29** **3**

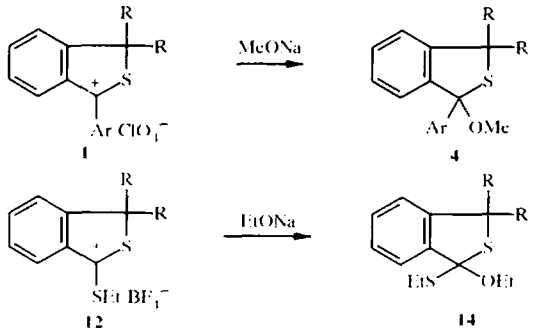
12 Z = SEt, X = BF_4; 16 Z = OEt, X = BF_4; 18 Z = NMeAr, X = ClO_4;
3, 12, 16, 18 R = Me, Ph, C_6H_4Me-*m*, C_6H_4Cl-*p*

The hydrolysis of unsubstituted thiophthalylium salts **19** occurs in a different way. The reaction occurs *via* formation of a pseudo-base **30** with subsequent transfer of a hydride ion to the cationic center of the original salt to give a mixture of a 2-thiophthalide **3** and a thiophthalane **31** [29]:



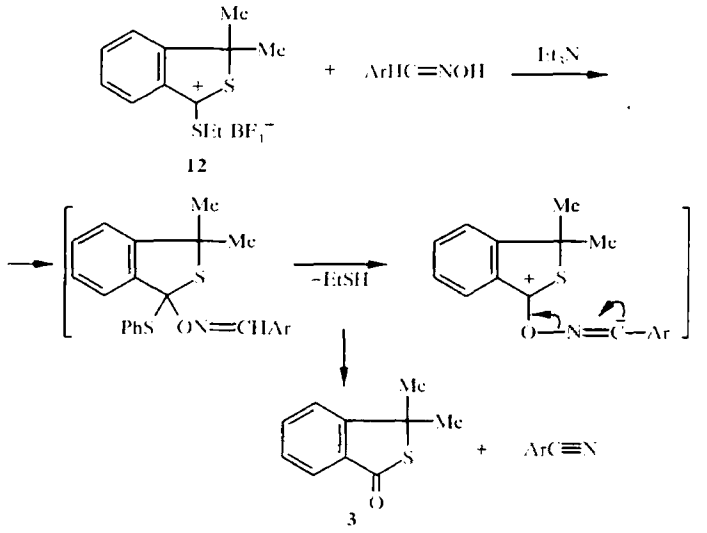
19 **30** **3** **31**

Thiophthalylium salts react with alkoxides to give ethers **4** [7, 13] and **14** [25] not depending on the substituent at the electrophilic center:



1, 4, 12, 14 R = Me, Ph; Ar = Ph, PhMe-*p*,-*m*,-*o*, C_6H_4OMe-*o*

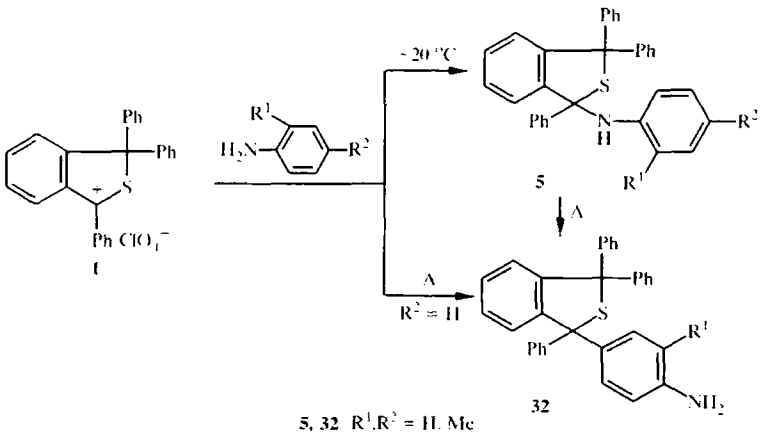
1-Ethylthio-3,3-dimethylthiophthalylium tetrafluoroborate **12** caused dehydration of aromatic oximes in the presence of triethylamine [58]:



Ar = Ph, OC_6H_4Me-*p*

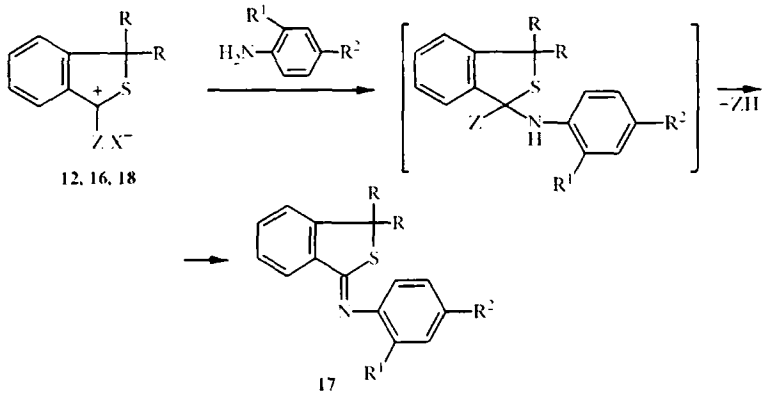
4.2. Reaction with N-Nucleophiles

1-Arylthiophthalylium salts **1** form the N-derivatives **5** and the C-derivatives **32** with primary aromatic amines at room temperature and on heating respectively [19]:



5, 32 R^1,R^2 = H, Me

When the Ar substituent at position 1 is replaced by a heterosubstituent Z, the final products of the reactions of the thiophthalylium salts **12**, **16**, and **18** with aniline, *p*- and *o*-toluidines are the 1-aryliminothiophthalanes **17** [23, 26, 27, 59]:

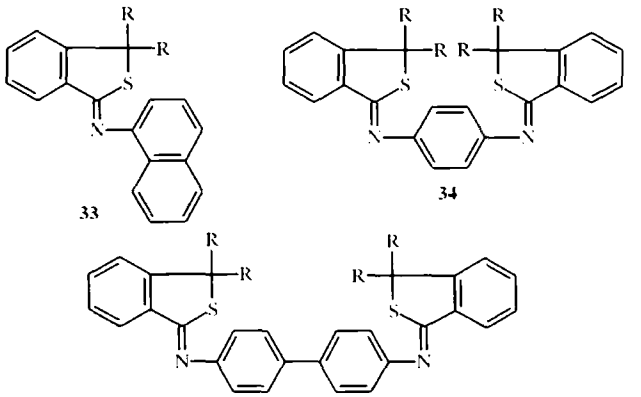


12, 16, 18

17

12 Z = SEt, X = BF_4; 16 Z = OC_2H_5, X = BF_4; 18 Z = NMeAr, X = ClO_4;
12, 16, 18 R = Ph, C_6H_4Me-*p*,-*m*; R^1, R^2 = H, Me

The reactions of salts **12** with α-naphthylamine, *p*-phenylenediamine, and benzidine occur analogously to give the corresponding iminothiophthalanes **33-35** [24]:



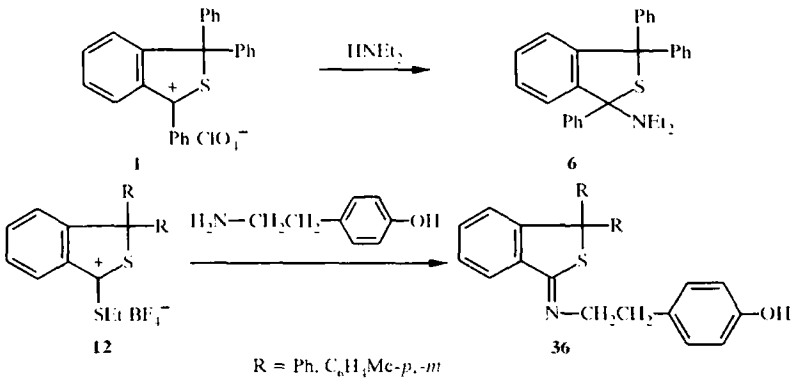
33

34

35

R = Ph, C_6H_4Me-*p*,-*m*

In the reactions of thiophthalylium salts with aliphatic amines the influence of the substituent at the electrophilic center on the structure of the end products is the same as in the case of aromatic amines [13, 24]:



1

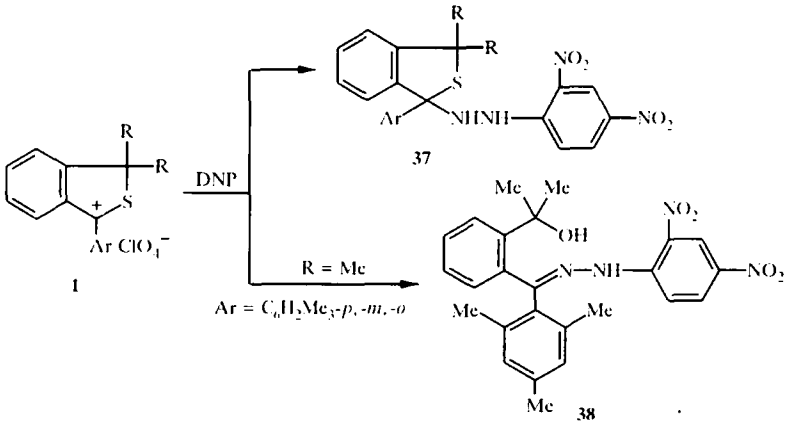
6

12

36

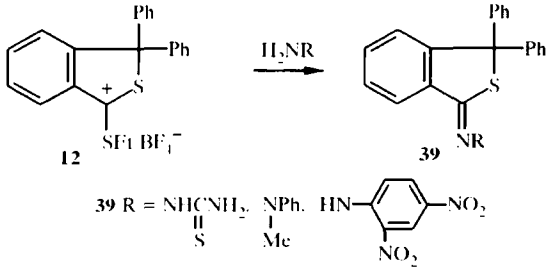
R = Ph, C_6H_4Me-*p*,-*m*

The structure of the reaction products of 1-arylthiophthalylium salts **1** with 2,4-dinitrophenylhydrazines depends on the spacial structure of the aryl substituent [8, 13]. The reaction normally gives hydrazinothiophthalanes **37**, but in the case of a bulky substituent (mesityl) ring opening occurs, the tertiary mercapto group is replaced by hydroxy group, and a hydrazone **38** is formed which does not contain sulfur:

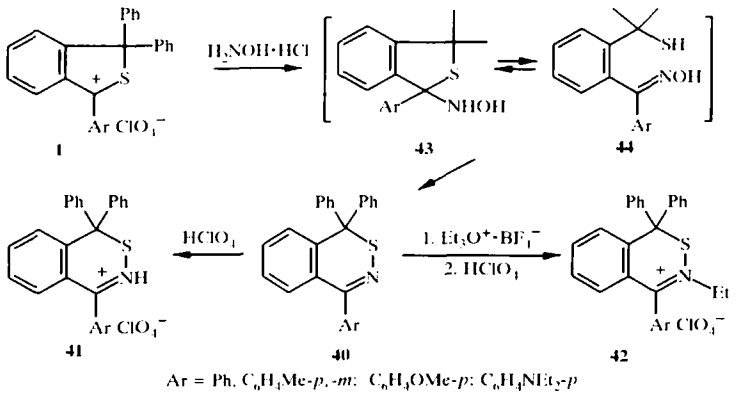


1, **37** R = Me, Ph; Ar = Ph, C_6H_4OMe-*p*,-*m*

The reaction of 1-ethylthio-substituted thiophthalylium salts **12** with hydrazine derivatives does not stop at the formation of addition products but continues to give hydrazonothiophthalanes **39** [60]:



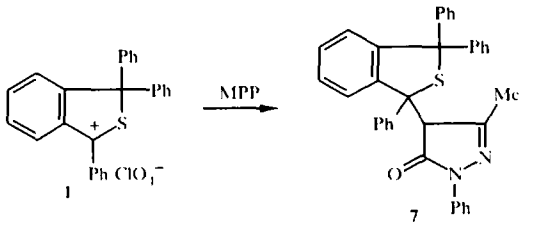
The reaction of triarylthiophthalylium salts **1** with hydroxylamine occurred *via* expansion of the heterocycle and formation of substituted 2,3-benzothiazines **40** which were isolated as unalkylated **41** or alkylated **42** salts [61-63]. The formation of the possible intermediates, hydroxyiminothiophthalane **43** and is open chain isomer, the mercaptooxime **44**, was not observed [18]. 3,3-Dialkylsubstituted thiophthalylium salts did not react with hydroxylamine [63].



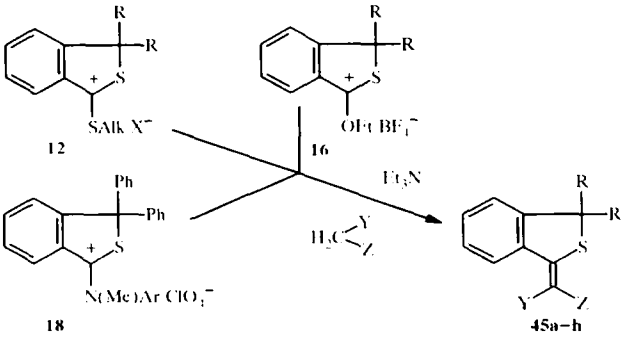
Ar = Ph, C_6H_4Me-*p*,-*m*; C_6H_4OMe-*p*; $C_6H_4NEt_2$-*p*

4.3. Reactions with C-Nucleophiles

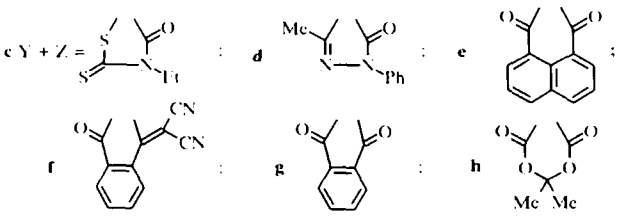
Reaction of 1,3,3-triphenylthiophthalylium perchlorate with methylphenylpyrazolone (MPP) leads to addition of the reagent at the electrophilic center with retention of the heterocycle [13]:



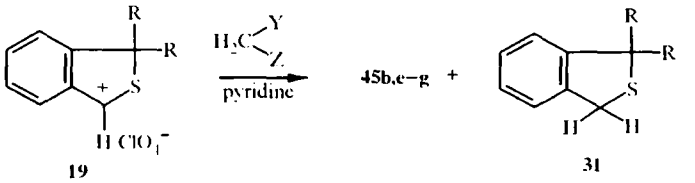
Despite the variety of structures and properties of the CH acids used in reactions with the thiophthalylium salts **12**, **16**, and **18**, containing heterosubstituents, isolation of the initial products of addition of the nucleophiles was not achieved [18, 22, 26, 27, 31, 59, 64, 65]. In all cases elimination of the substituent occurred to give the derivatives **45** which contain the thiophthalylidene unit.



12, **16**, **45** R = Me, Ph, C_6H_4Me-*p*, C_6H_4Cl-*p*;
12 Alk = Me, Et; X = ClO_4, $FeCl_4$; **18** Ar = Ph, C_6H_4Me-*p*;
45 a Y = CN, Z = COOEt; **b** Y = Z = CN;

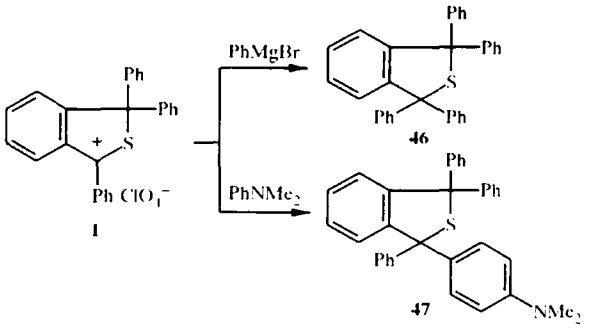


Reaction of unsubstituted thiophthalylium salts **19** with CH-acids occurred like hydrolysis (section 4.1) by a classical hydride transfer mechanism for bases mixed with the corresponding cations to give a mixture of compounds **31** and **45** [29].

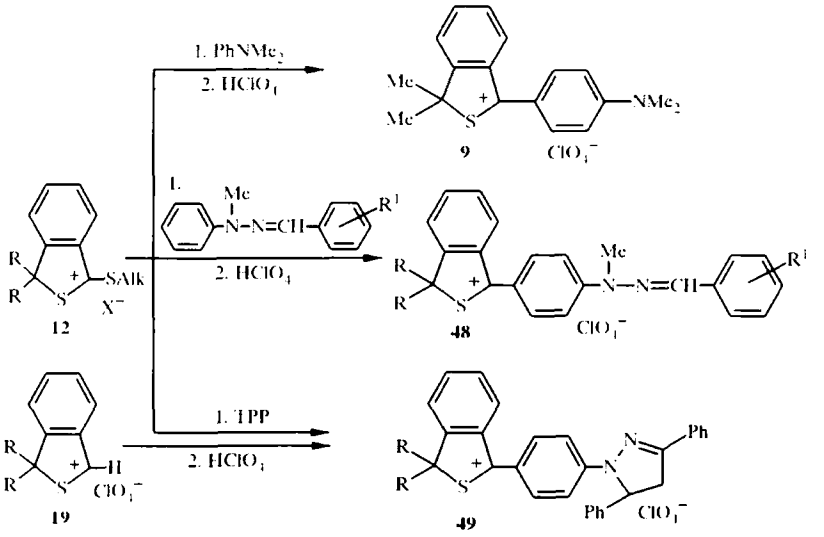


19, **31**, **45** R = Ph, C_6H_4Me-*p*

1-Arylthiophthalylium salts react with Grignard reagents and dimethylaniline to give stable products of the carbon nucleophiles addition **46** and **47** [13]:

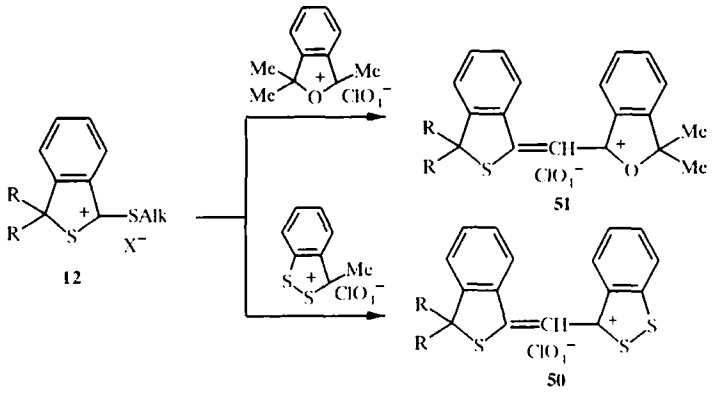


In contrast, the reaction of the 1-alkyl-substituted thiophthalylium salts **12** with activated aromatic compounds (dimethylaniline [9], N-methylphenylhydrazones of aromatic aldehydes [66], triphenylpyrazoline - TPP [12]) occurs with elimination of the thiol and, under conditions of general acid catalysis, formation of thiophthalylium salts **9**, **48**, **49** with modification of the substituent at position 1 is occurred. The unsubstituted salt **19** reacted with TPP to give the salt **49** [12].



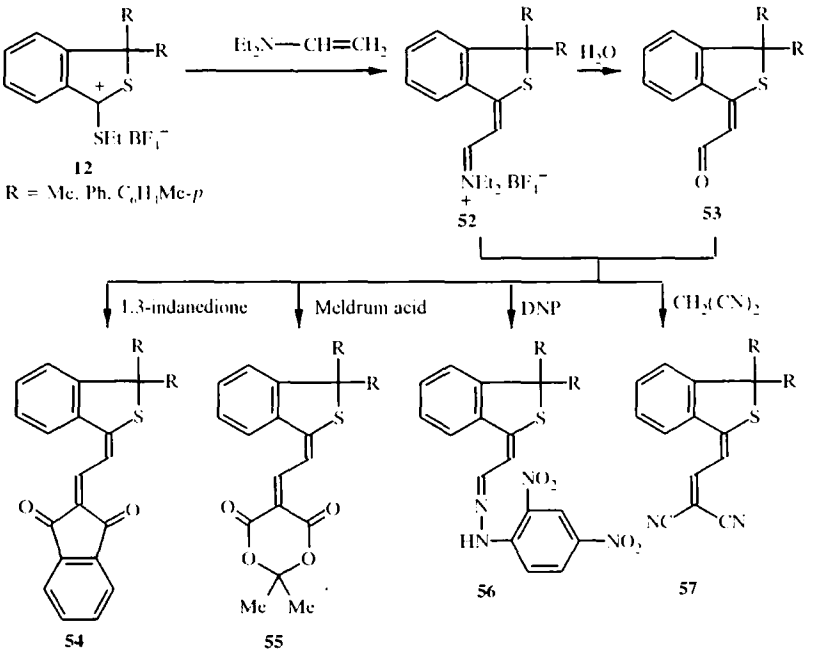
12, **18**, **48**, **49** R = Me, Ph, C_6H_4Me-*p*,-*m*; **48** R^1 = H, OMe-*p*, Br-*p*;
12 Alk = Me, Et; **12** X = BF_4, $MeSO_4$

Thiophthalylium salts containing 1-alkylthio groups **12** readily condense with heterocyclic salts containing a methyl group at an electrophilic carbon atom to give monomethinecyanine dyes **50** and **51** [67, 68].

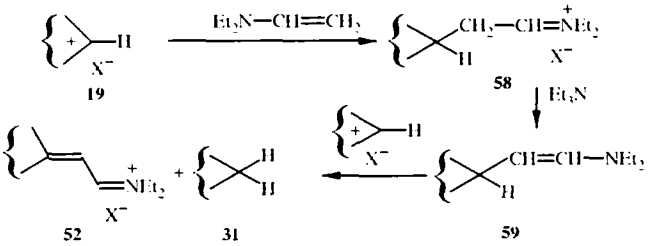


12, **50**, **51** R = Me, Ph, C_6H_4Me-*p*; **12** Alk = Me, Et; X = BF_4, $FeCl_4$

The thiophthalylium salts **12** reacted at the β-carbon atom with diethylaminoethene, generated *in situ* by oxidation of triethylamine with iodine, to give salts **52** with an iminium structure [29, 64]. These salts, and the aldehydes formed from them by hydrolysis **53**, are very active in reactions with nucleophiles as their interactions with CH-acids and dinitrophenylhydrazone demonstrate.

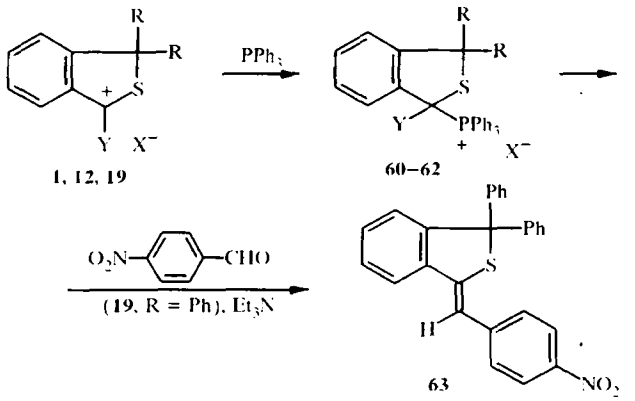


The reaction of the unsubstituted thiophthalylium salt **19** (R = Ph, X = ClO_4) with diethylaminoethene did not stop at the stage of the salt **58** but gave two products: the iminium salt **52** and the thiophthalane **31** [29]. This occurs because the hydrobase **59**, formed from the salt **58**, is able to reduce the initial salt **19** to the thiophthalane **31** and is itself oxidized to the iminium salt **52**.



4.4. Reactions with P-Nucleophiles

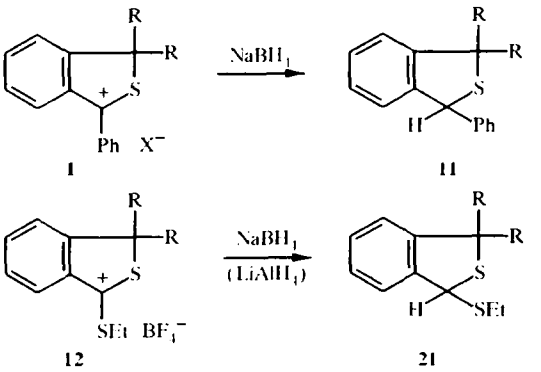
Thiophthalylium salts form stable thiophthalylphosphonium salts **60-62** not depending on the substituent at the electrophilic center [13, 18, 29]. The salt **62**, unsubstituted at $C_{(1)}$, readily underwent the Wittig reaction with aromatic aldehydes to give arylidenethiophthalanes of type **63** [29].



1, 60 Y = Ph, X = $FeCl_4$; 12, 61 Y = SMe, SEt, X = $FeCl_4$, BF_4;
19, 62 Y = H, X = ClO_4

4.5. Effect of the Hydride Ion

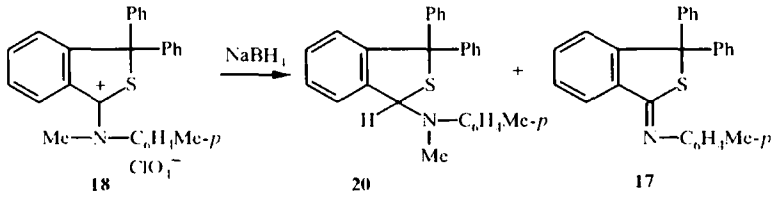
The reduction ($NaBH_4$, $LiAlH_4$) of thiophthalylium salts containing 1-Ar (**1**) [5, 6, 18] and 1-EtS (**12**) groups [25, 29] gave the corresponding 1-H-thiophthalanes **11** and **21**.



1, 11 R = Me, Ph; X = $FeCl_4$, ClO_4; 12, 21 R = Ph, C_6H_4Me-*p*, C_6H_4Cl-*p*

Attempts to reduce salts **1** with 3,3-dimethyl-1-phenylphthalane and 3,3-dimethyl-1,2-diphenylisoindoline, which have a hydride-mobile hydrogen atom, were unsuccessful [6].

Salt **18** containing an N(Alk)Ar group at position 1 shows two-fold reactivity: reductive dealkylation occurred along with addition of the hydride ion to $C_{(1)}$ to give a mixture of the 1-H-thiophthalane **20** and the aryliminothiophthalane **17** [69]:



18 20 17

To summarize the results of studies of the electrophilic activity of thiophthalylium salts three basic directions of the transformation of the primary products of the addition of the proton nucleophiles to the electrophilic center of the cation can be separated: removal of the substituent at position 1 in the case of salts with heterosubstituents, hydride transfer for unsubstituted salts, and recyclization for triarylsubstituted thiophthalylium salts.

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