RELATIVE STABILITIES OF HETARENIUM IONS: FACTORS CONTROLLING POSITIONAL SELECTIVITIES OF ELECTROPHILIC SUBSTITUTION AND ACID-INDUCED TRANSFORMATIONS OF PYRROLE, FURAN AND THIOPHENE DERIVATIVES[#]

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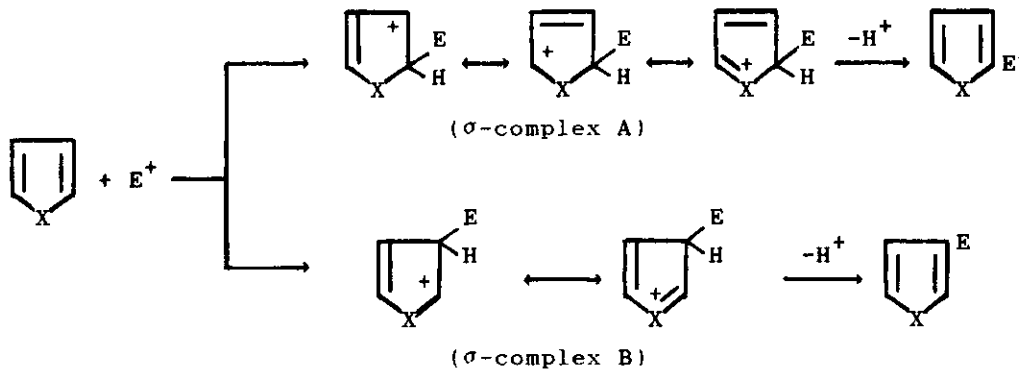
Abstract - Positional selectivity in electrophilic substitution reactions of pyrrole, thiophene and furan derivatives including methods of orientation control as well as stability and some transformations of hetarenium ions are reviewed.

INTRODUCTION

Electrophilic substitution is apparently the most important reaction type of five-membered heteroaromatic compounds with one heteroatom giving as products various substituted derivatives, such reactions of thiophenes being used frequently as model ones owing, in particular, to availability and relatively high stability of thiophene compounds. This review is devoted mainly to positional selectivity and methods of the orientation control in electrophilic substitution of five-membered heteroaromatics as well as the stability and some transformations of hetarenium ions. The consideration has to be limited with pyrrole, furan and thiophene since there is no neccessary data for other five-membered heterocycles with one heteroatom. It is well known that the effect of heteroatom is manifested in enhanced

[#] *Dedicated to Professor A.R.Katritzky on the occasion of his 65th birthday.*

reactivity of α-positions which is usually interpreted as the result of higher stability of respective σ-complex (A) owing to better conditions for charge delocalization as compared with its β-isomer (B) (Scheme 1).



Scheme 1

Reactivity and Positional Selectivity

Both reactivities and positional selectivities of the three parent compounds in electrophilic substitution reactions are now investigated quantitatively.[1] It is important to emphasize enormous differences in reactivities which fall in the row pyrrole >> furan > thiophene on *ca.* 10 orders of magnitude (if the relative reactivity of thiophene is accepted to be equal to 1 the reactivities of pyrrole and furan are equal depending on the reaction to 10^7-10^9 and 10-10^2 respectively).[1] The differences in positional selectivities are not so high (for example on acetylation the differences in α:β-ratios between the most selective furan and low selective pyrrole are "only" 3 orders of magnitude[1]). However α:β-ratios change in the sequence furan > thiophene > pyrrole which does not correlate with the row of reactivities.

We have offered a hypothesis[2] that the differences between these three heterocycles in their abilities to the formation of β-substituted derivatives are based on relative stabilities of onium states of respective elements the sequence of which (N^+ > S^+ > O^+) correlates well with experimental data

on the abilities of pyrrole, thiophene and furan to the formation of β-substituted derivatives. In fact it is quite naturally to suppose that for the ions B in which the positive charge is distributed between only two atoms, i.e. heteroatom and one of carbon atoms, the stability is more dependent on heteroatom effect than for ions A since in the latter almost all ring atoms except geminal C-atom take part in the charge delocalization. Quantum-chemical calculations (CNDO/2)[3] (Table 1) support the hypothesis: while localization energies values ($\Delta\Lambda_{\alpha}^{+}$ and $\Delta\Lambda_{\beta}^{+}$) are in a qualitative agreement with the reactivity row (N > O > S), the differences of localization energies for α- and β-positions ($\Delta\Lambda_{\alpha-\beta}^{+}$) are consistent with the sequense mentioned for positional selectivities (O > S > N).

Table 1

Localization energies (kcal/mol) relative to benzene[a]

Molecule	$\Delta\Lambda_{\alpha}^{+}$	$\Delta\Lambda_{\beta}^{+}$	$\Delta\Lambda_{\alpha-\beta}^{+}$
Pyrrole	-24.7	-22.3	-2.4
Furan	-24.4	-3.1	-21.3
Thiophene[b]	-19.3	-1.4	-17.9
Selenophene[b]	-18.5	-3.0	-15.5

[a] For benzene $\Delta\Lambda^{+}$ = 0.4542 a.u.

[b] Taking into account d-AO's.

Considering the distribution of electron density in σ-complexes one can see (cf.[3]) that π-charges localized on heteroatoms are really greater for ions B and changes for the latter in the sequence (N > S > O) which coinsides with the abilities of respective elements to exist in onium states and is inverse to the row of positional selectivities (Table 2). It is interesting to note that the calculation predicts for selenophene about the same

reactivity but lower positional selectivity than for thiophene.

Table 2

π-Charges on Heteroatoms (% of whole π-charge)

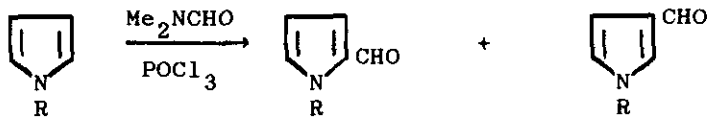
Molecule	π-Charges on heteroatom	
	Cation A	Cation B
Pyrrole	41	67
Furan	30.5	53
Thiophene	31	61
Selenophene	34.5	64

Positional Selectivities in Electrophilic Substitution Reactions of Pyrrole, Furan and Thiophene Derivatives

Mentioned peculiarities display quite clearly in reactions of substituted five-membered heteroaromatics. High positional selectivity of electrophilic substitution of furan and thiophene prevents a preferential introduction of electrophiles into position 3 of their derivatives having electron-releasing substituents in the position 2. The same is true for 2-substituted pyrrole analogs.

However, for *N*-substituted pyrroles there is an unique possibility to change the nature of heteroatom and its orientation mode (Scheme 2). In particular, for *N*-alkylpyrroles the formation of β-aldehydes in Vilsmeier formilation rises from *N*-methyl- to *N*-*tert*-butylpyrrole.[4] This trend could be interpreted as the result of steric effect of *N*-alkyl group but in the case of *N*-phenylsulfonylpyrrole having also bulky *N*-substituent only 2-aldehyde is formed.[5] One can suppose that the enhancement of electron-releasing ability of *N*-alkyl group going from methyl to *tert*-butyl results in progressive stabilization of ring nitrogen onium state which is favorable for β-sub-

stitution (enamine type of electrophilic substitution). In the case of electron-withdrawing group at ring nitrogen atom the onium state is destabilized and *N*-phenylsulfonylpyrrole behaves like thiophene or furan giving only the 2-substituted derivative.

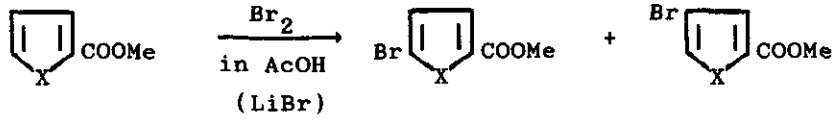


R =	α-isomer only		-
Et	11.5	:	1
i-Pr	1.9	:	1
t-Bu	1	:	14
SO_2Ph	α-isomer only		-

Scheme 2

Unfortunatelly, it is difficult to generalize this conclusion for other reactions since 2-substituted pyrroles rearrange smoothly into 3-isomers under usual conditions of most electrophilic substitution reactions which are carried out in the presence of Lewis or Broensted acids.

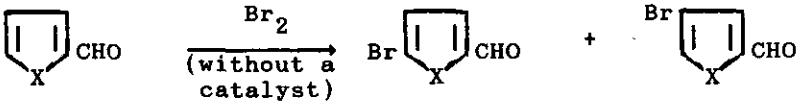
For compounds bearing an electron-withdrawing groups in the position 2 there is a possibility of a competition between α-orienting heteroatom effect and "meta"-orienting effect of the substituent. The results of this competition are very different for pyrrole, thiophene and furan derivatives. These differences can be illustrated on bromination of respective methyl 2-carboxylates.[6] In these cases thiophene and furan esters give only 5-substituted derivatives while pyrrole ester gives a mixture with 4-brominated product as the main component (Scheme 3).



X =	$k_{rel.}$ (for pos.5)		
NH	5.9×10^8	23 :	77
O	1.2×10^2	α-isomer only	-
S	1.0	α-isomer only	-

Scheme 3

As to aldehydes having a stronger electron-withdrawing group, furfural gives 5-bromide as the only product[7] while for 2-thiophenecarbaldehyde a small amount of 4-bromide has been detected besides 5-isomer as the main product.[8] From 2-pyrrolecarbaldehyde only traces of 5-substituted derivative are formed and 4-isomer is the almost sole product.[9] It should be emphasized however that *N*-*p*-nitrophenyl-2-pyrrolecarbaldehyde is brominated only in the position 5 and this is apparently the result of mentioned effect of electron-withdrawing *N*-substituent[10] (Scheme 4).



X =			
NH	traces		main product
O	α-isomer only		-
S	97	:	3
N-$C_6H_4NO_2$-*p*	α-isomer only		-

Scheme 4

Data available for thiophene derivatives[6,8,11-14] show that the ratios of 4- and 5-substituted isomers depend on electron-withdrawing ability of the existing 2-substituent as well on the nature of the electrophilic reagent.

It should be mentioned that none of usual electron-withdrawing substituents allows to obtain a 4-substituted derivative exclusively and only at nitration of 2-nitrothiophene[13] and dimethyl 2-thienyl sulfonium perchlorate[14] 4-substituted derivatives are the main products (the 4-/5-ratio *ca.* 60:40).

Control of Orientation

The orientation of electrophilic substitution reactions of 2-substituted pyrroles, thiophenes and furans can be changed using enhancing electron-withdrawing ability of usual substituents by complex formation with proton or Lewis acids. The effect could be predicted qualitatively by quantum-chemical calculations[15,16] as well as ^{1}H and ^{13}C nmr spectra of α-carbonyl compounds of furan and thiophene and their complexes.[17-19] Basing on ^{13}C nmr spectra of benzene analogs this effect was estimated in terms of Braun σ_p^+ constants of modified substituents (Table 3).[20]

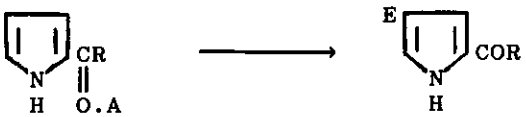
Table 3

σ_p^+ Values of Modified Substituents

Substituent	$CN.AlCl_3$	$MeOCO.AlCl_3$	$PhCO.AlCl_3$	$MeCO.AlCl_3$	$NO_2.AlCl_3$	$CHO.AlCl_3$
σ_p^+	1.2	1.2	1.3	1.5	1.6	1.9
Substituent	$PhCO.AlBr_3$	$MeCO.BCl_3$	$MeCO.SbCl_5$	$CHO.AlBr_3$	$CHO.H^+$	$CHO.SbCl_5$
σ_p^+	1.3	1.6	0.9	1.9	1.9	1.0

Taking into account mentioned high ability of pyrroles to the formation of β-substituted derivatives it is quite natural that complex formation of practically any 2-acylpyrrole, alkyl pyrrole-2-carboxylate or -thiocarboxylate with strong Lewis acids leads to the substitution in the position 4 only (Scheme 5).[21-29] It is interesting to note that the complex of *N*-*p*-nitrophenyl-2-pyrrolecarbaldehyde with $AlCl_3$ gives on bromination also 4-bro-

mide.[10]



A = $AlCl_3$, $AlBr_3$, $GaCl_3$

R = alkyl, alkoxy or alkylthio group

E = Br, Ac, CHO, Alk

Scheme 5

The modification of substituents by complex formation with aluminum chloride[30-35] or protonation[17,32-38] allows very high positional selectivity to be achieved for 2-acylthiophenes: the admixtures of 5-isomers for complexes with $AlCl_3$ or true protonated forms (complexes with $HSbCl_6$) don't exceed several percents (Table 4).

Table 4

Bromination of 2-Thiophenecarbaldehyde and 2-Acetylthiophene Complexes with $AlCl_3$ and $HSbCl_6$

Substrate	Reagent	Ratio of 2,4- and 2,5-isomers
ThCHO.$AlCl_3$	$Br_2/AlCl_3$ in CH_2Cl_2	99 : 1
ThCOMe.$AlCl_3$	$Br_2/AlCl_3$ in CH_2Cl_2	99 : 1
ThCHO.$HSbCl_6$	$Br_2/AlCl_3$ in $(CH_2Cl)_2$	98 : 2
ThCOMe.$HSbCl_6$	$Br_2/AlCl_3$ in $(CH_2Cl)_2$	96 : 4

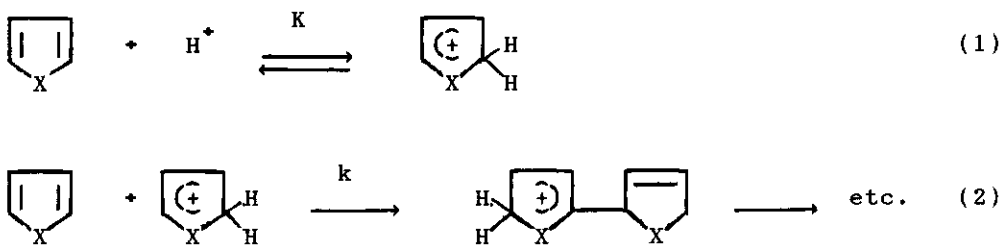
On the other hand, the synthesis of 4-substituted derivatives from 2-acylfurans is a very difficult problem. The only proved cases of the formation of such compounds as main products are those of bromination of complexes of aluminum chloride with furfural and 2-acetylfuran.[32] It is interesting to note that deactivation of heterocycle in 2-acylfurans on complex formation is greater than this in 2-acylthiophenes, the complexes of the latter become more reactive than furan analogs though for free carbonyl compounds

the inverse ratio is true.[32]

Some reactions of complexes of carbonyl compounds demanding drastic conditions are accompanied by side processes. Thus, on acylation of 2-acylthiophenes carried out at *ca.* 100°C in excess $AlCl_3$ without a solvent transacylation and deacylation take place to some extent[39,40] and one can conclude that the initial stages of these side reactions are *ipso*-acylation and *ipso*-protonation respectively, unstable thiophenium ions being formed undergo further transformations.

Generation of Hetarenium Ions and Their Stability

Many features of electrophilic substitutions of thiophene, pyrrole and furan themselves as well as their derivatives having electron releasing substituents are the results of easy formation and rather high stability of respective hetarenium ions, first of all those being the products of α-C-protonation of a five-membered heterocycle. The reversible formation of such σ-complexes (reaction 1) competes with well-known acid-promoted oligomerization (reaction 2), the latter being a practically irreversible reaction the first step of which is electrophilic substitution with hetarenium ion playing the role of electrophile (Scheme 6).



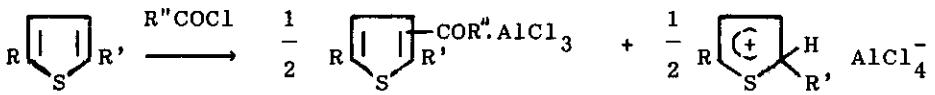
Scheme 6

Basing on relative basicities of three parent heterocycles which according to[41] falls in the row $K_{NH} : K_O : K_S \approx 10^9 : 1 : 1$ it is very simple to predict that pyrrole compounds should be protonated most easily. However the

real stability of σ-complexes depends on the rates of oligomerization which can be estimated using data[1] on various electrophilic substitution reactions as varying in the sequence as follows: $k_{NH} : k_O : k_S \approx 10^8 : 10^2 : 1$. Indeed, the row of stability of σ-complexes is NH > S > O, the hetarenium ions being quite stable at ordinary temperature for the first members of the series in the cases of pyrrole[42-45] and thiophene,[46-52] whereas in the case of furan they are stable for the sterically hindered di- and trialkyl-substituted compounds only.[53-56] It should be noted that several sterically hindered pyrrolium ions could be isolated as crystalline tetrafluoroborates,[45] whereas the generation of furanium ions from both 2-methyl- and 2,5-dimethylfurans demanded extraction of the latter from dilute solution in CCl_3F with the FSO_3H - SbF_5 mixture at -78 °C.[54] Taking into account rather high basicity of pyrroles (for 2,5-dimethylpyrrole pK_a = -1.0[41]) it is not surprizing that polyalkylated carbonyl compounds of pyrrole series undergo protonation not at CO group but at α-carbon atom.[57,58] A similar ring protonation is known also in furan series but it takes place for nitriles having strong activating amino group in the ring.[59] It is essentially to note that aminofurans are protonated not at NH_2 group but at α-carbon atom.[60] High "acidofoby" of furans and their relatively low aromaticity led to the development of some peculiar procedures for generation of furanium ions which use as starting compounds not heteroaromatic furans but other compounds. Thus, 3,5-dimethyl-2H-furanium ion was generated from mesityl oxide in FSO_3H - SbF_5 system,[54] several highly sterically hindered furanium ions were formed by protonation of t-butylated methylenedihydrofurans.[61] Numerous stable 3,5-substituted 2,2-dimethylfuranium salts were prepared from alkinyl-substituted aliphatic 1,2-diols or 5,5-dimethyl-2-furanones.[62-66]

The high stability of hetarenium ions results in unusual procedures of their generation. Thus, while studying acylation of thiophene and its homologs under conditions unusual for the series but standard for benzene

derivatives (the action of acid chlorides in the presence of aluminum chloride in 1,2-dichloroethane or methylene chloride as solvents) we have found unexpectedly the formation of thiophenium ions being the *C*-protonation products of starting compounds[48] (Scheme 7). The thiophenium ions proved to be stable in acylation conditions, they were formed in the absence of any proton acid excess using the hydrogen chloride eliminating on acylation, HCl being consumed practically completely (acylthiophenes were obtained in *ca.* 50% yields and besides equimolar quantities of thiophenium ions mentioned were formed).



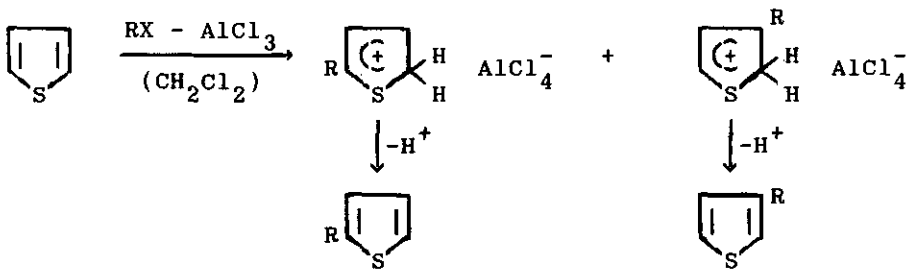
a R = R'= H; b R = Me, R'= H; c R = R'= Me

Scheme 7

The route of thiophenium ions formation under consideration has been confirmed in model experiments using HCl and $AlCl_3$ in the same solvents[48] and exploited repeatedly later by us[49,51,52,67] and other investigators as well[68-70] for generation of such ions. The cations obtained from thiophene, 2-methyl- and 2,5-dimethylthiophenes as well as from 2-methylthio- and 2-methyl-5-(methylthio)thiophenes are stored in solutions at room temperature without visible changes (PMR data) for a long time (from several days to several weeks).[48] Especially high stability was revealed by 2,5-dimethyl-2*H*-thiophenium ion which was transformed into isomeric 3,5-dimethyl-2*H*-thiophenium ion only after storage at room temperature during several years.[51] The stability of considered cations and their easy formation are substantionally governed by the nature of the counter ion. Thus, thiophene and alkylthiophenes form in HF cations which are stable at temperatures lower -40 °C only, in the HF-BF_3 system the same cations are stable already untill -20 °C and 2,5-dimethyl-2*H*-thiophenium ion generated in the HF-SbF_5 system is sufficiently stable even at +60 °C.[46] The nature of substituents

in thiophene nucleus affects the stability of thiophenium ions to the great extent: 2,4-bis-(alkylthio)thiophenes are transformed to respective stable thiophenium ions in trifluoroacetic acid[49] or in an inert solvent under the action of HCl in the presence of $SnCl_4$.[50] Protonation in trifluoroacetic acid was observed also for isomeric cyclopentadithiophenes.[71]

The high stability of thiophenium ions made it possible to use for their generation an in principle novel method, i.e. alkylation of thiophene with alkyl halides in the presence of an equimolar amount of aluminum chloride (Scheme 8).[72] Owing to the low selectivity of alkylation its products are mixtures of 5-alkyl-2*H*- and 3-alkyl-2*H*-thiophenium ions, deprotonation of which leads to respective mixtures of 2- and 3-alkylthiophenes (Table 5). It is essentially to note that the stability of thiophenium ions allows alkylation to be stopped on the stage of monosubstitution if an equimolar but not common catalytic amount of $AlCl_3$ is used even when alkyl halide plays a role of a solvent.[72]



Scheme 8

Table 5

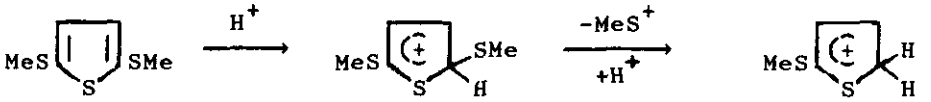
Monoalkylation of Thiophene Using Equimolar Amounts of $AlCl_3$

RX	t °C	yield, % (glc yield)	α :β ratio
t-BuCl	-70	73	83 : 17
i-PrCl	-70	51 (65)	60 : 40
EtBr	-20	(45)	65 : 35
MeBr	-10	(6)	73 : 27

The interaction of thiophene with alkyl halides in the presence of $AlCl_3$ should give initially the ions possessing alkyl group and hydrogen atom at the nodal center, i.e. "normal" σ-complexes of alkylation. The latter undergo evidently an isomerization including proton migration which results in more stable ions with two hydrogen atoms in the nodal center. We failed in our attempts to carry out analogous generations of stable thiophenium ions in conditions of halogenation and sulfenylation with subsequent preparation of monohalothiophenes and sulfides of thiophene series[73] which caused apparently by an easier migration of Hal^+ and RS^+ cations as compared with the proton. As it will be shown below the migration of alkyl cations from the nodal center also takes place, however it is substantially slower than that of protons.

Some Transformations of Stable Hetarenium Ions

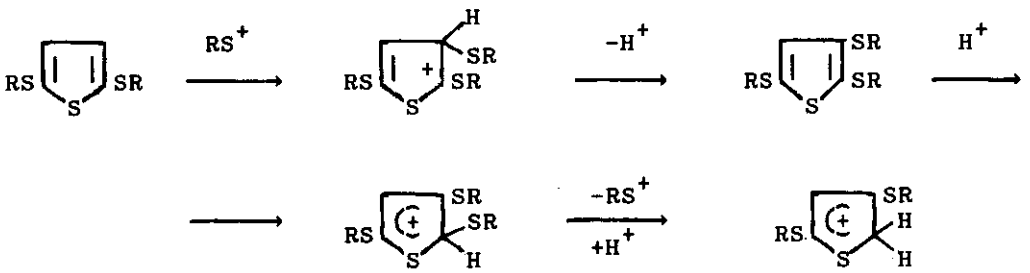
This Section deals mainly with thiophenium ions since their transformations are studied in more details than those of pyrrole and furan analogs. As it was pointed out above, stabilities of thiophenium ions vary to the large extent depending on the character of substituents. The formation of thiophenium ions is a reversible process, not only protons but also other electrophilic species being able to eliminate from the geminal center. The process of such kind was observed in the case of 2,5-di(methylthio)-2*H*-thiophenium ion[48] which in contrast to 2-methylthio- and 2-methyl-5-methylthio-2*H*-thiophenium ions is stable only at low temperatures eliminating MeS group (probably in the cation form) above -40 °C (Scheme 9).



Scheme 9

At HCl deficiency or when protonation is carried out in trifluoroacetic acid the reaction mixture contains some quantity of bis-sulfide which un-

dergoes electrophilic sulfenylation. The reaction proceeds as intermolecular disproportionation resulting in complex mixture of products main of which is 2,4-bis-sulfide (*ca.* 50% yield) and can be used for preparative isomerization of 2,5-bis-sulfides to hardly accessible 2,4-isomers.[49] The reaction driving forse is the formation of 2,4-bis-(alkylthio)-2*H*-thiophenium ions the structure of which provides especially favourable conditions for the positive charge delocalization (Scheme 10). The key role of thermodynamic stabilities of thiophenium ions in the transformations of bis-sulfides under consideration has been corroborated by quantum chemical calculations.[74] Apparently similar mechanism governs the isomerization of 3-indolyl sulfides to 2-isomers.[75,76]

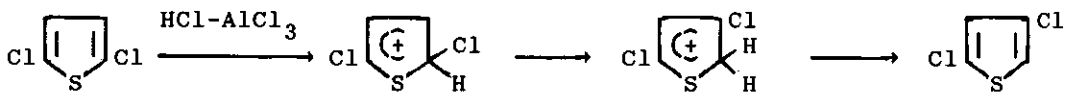


Scheme 10

Alkylthiophenium ions also undergo disproportionation. *tert*-butyl group has one of the highest migration abilities. This allows, in particular, the 83:17 mixture of 2- and 3-isomers formed by *tert*-butylation of thiophene in the presence of an equimolar $AlCl_3$ amount to be transformed to 2-*tert*-butylthiophene, containing only minor admixture (3%) of 3-isomer using simple storage of thiophenium ions mixture at room temperature during 1-2 days.[51] 2,4-Di-*tert*-butylthiophene (in the form of respective σ-complex) is obtained as one of the disproportionation products, it can be, naturally, prepared more conveniently from 2,4- and 2,5-isomers mixture obtained e.g. by thiophene *tert*-butylation in the presence of $SnCl_4$.[77] Analogous transformation of isopropylation and ethylation products needs either higher tempera-

ture (up to 80°C) or very long storage at room temperature.[52] In the cases of unsymmetrically substituted 2-methyl- and 2-ethyl-4-*tert*-butylthiophenes similar migration at room temperature undergo *tert*-butyl group only and this behaviour can be used for the synthesis of hardly accessible 2-alkyl-4-*tert*-butylthiophenes.[78]

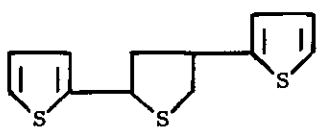
Disproportionation has been observed also for unstable halothiophenium ions which can be checked by nmr spectra at temperatures below -30 °C. Thus, disproportionation of 2,5-dibromo-2*H*-thiophenium ion has been marked in.[79] A similar process has been used for preparative synthesis of 2,4-dichlorothiophene from its 2,5-isomer (Scheme 11).[67] Relative thermodynamic stabilities of halo-substituted thiophenium ions were shown by quantum chemical calculations to be the main factors governing the disproportionation route.[80]



Scheme 11

Hetarenium Ions as Electrophiles

Transformations are of considerable interest in which hetarenium ions play the role of electrophilic agents. One of such processes is acid oligomerization of pyrrole, furan, thiophene and their substituted derivatives. This reaction has been studied for thiophene as early as in 1950, the authors[81] succeeded in structure determination of so-called trimer (1).



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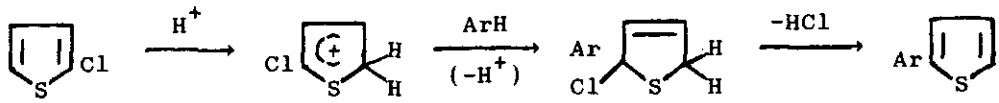
Later the structure (1) was confirmed by X-ray diffraction method.[82] Basing on the structure the reaction scheme was offered in[81] which involved the

formation and further transformations of 2*H*-thiophenium ion (cf. Scheme 6) quite clearly demonstrating the ability of thiophenium ions to operate as electrophiles. Analogous role can be played by furan, however oligomerization of the latter and its derivatives is accompanied frequently by hydrolytic opening of the heterocycle.[83,84] The peculiarity of pyrroles as compared with thiophene is that their oligomerization sometimes includes β-protonated species.[85]

Related transformations of preparative value have been observed by non-symmetrical coupling of 2-arylthiophenes on cation exchange resin[86] leading to 5,5'-diaryl-2,3'-bithiophenes. The substrate role can be played by another aromatic compound. Thus, interaction of benzo[b]thiophene with various benzene derivatives in the presence of $AlCl_3$ or $TiCl_4$ proceeds *via* *C*-protonation and gives aryl-substituted 2,3-dihydrobenzothiophenes, i.e. products of formal addition of an aromatic molecule to the double bond of thiophene cycle.[87] *Arylthiophenes can be readily obtained using 2-chlorothiophene* which plays a role of a peculiar "alkylating" agent (Scheme 12).[70] An analogous process results in 3,5,4-trichloro-2,2-bithiophene which is a single by-product of 2,5-dichlorothiophene isomeriza- tion discussed above.[67]



Scheme 12

Some other data concerning the effect of stability of thiophenium ions in such reactions as hydrogen isotope exchange and ionic hydrogenation have been discussed in review.[88]

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