CHEMISTRY OF THIOPHENIUM IONS

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Data are reviewed for the generation and reaction of 2H-thiophenium ions which are cationic thiophene σ-complexes.

In principle, the attack of an electrophilic fragment on a heteroaromatic molecule can be directed to a carbon or to a heteroatom. Up to comparatively recent times the latter seems to have been preferred. In particular, it was commonly thought that the widely known acidophobocity of five membered heterocycles with one hetero atom was due to protonation of the heteroatom accompanied by loss of aromaticity and tarring as typified by the acid polymerization of 1,3-dienes [1]. However, results obtained from studying the structures of products of the acid oligomerization of five membered heteroatomatic compounds (including thiophene [2]) were impossible to explain without invoking C-protonated species. With the advent of the PMR method in 1959 experiments were carried out for directly studying the structure of various protonated compounds including pyrrole [3-5] and these unambiguously pointed to C-protonation. Similar data was obtained later for thiophene and homologs [6] and for tert-butylfurans [7]. In this way it became apparent that protonation of five membered heterocyclics containing one hetero atom occurs at the rinng α-carbon.

For compounds with group VI elements as heteroatom it is at least theoretically possible for addition of an electrophile to occur at the unbonded electron pair which does not have to lead to loss of aromaticity. For furans, formation of such cations has never been shown experimentally to the best of our knowledge. However, for thiophenes, in parallel with studies of their protonation, such a reaction course was revealed in the synthesis of S-alkylthiophenium salts. The S-alkylation of thiophene compounds was carried out using methyl iodide in the presence of perchlorate [8] or silver tetrafluoroborate [9, 10], trimethyloxonium tetrafluoroborate [8], or methylfluorosulfonate ("magic methyl") [10]. Recent reviews report little data concerning S-alkylthiophenium salts [11, 12] and this leads to the proposal that the difference in the mode of attack in the cases of protonation and alkylation are related to the hardness or softness of the reagent and the reaction center. It must be mentioned that the S-alkylthiophenium salts are inferior in stability to their C-alkyl isomers, e.g., they are converted to the latter upon UV irradiation [13]. There are also data to show that S-alkylthiophenium ions are intermediates in the gas phase C-methylation of thiophene [14].

The subject of this review is a correlation of the literature and of specific data concerning the generation and reactions of thiophenium ions with a geminal substituent at the α-carbon atom. Moreover, we have restricted it to cations having at least one geminal hydrogen atom.

GENERATION OF THIOPHENIUM IONS

In early experiments, traditional methods were used to generate C-protonation products, i.e. excess HF, $HF-BF_3$ and $HF-SbF_5$ [6, 15-17], or fluorosulfonic acid and its mixture with Lewis acids [13, 15-17] which also served as solvent. The thiophenium ions were fully characterized by PMR spectroscopy [6], which served as a reference series for subsequent spectral assignments [18-22] (Table 1).

Acylation of thiophene and its homologs has been studied in conditions which are not usually used for this series but which are standard for benzenes (the action of acid chlorides in the presence of aluminum chloride in 1,2-dichloroethane or methylene chloride). Unexpectedly, we discovered formation of thiophenium ions as products of C-protonation of the starting

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TABLE 1. PMR Spectra of 2-R-3-R^1-4-R^2-5-R^3-2H-Thiophenium Ions*

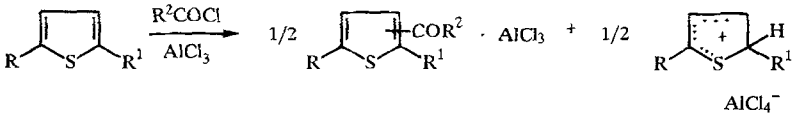
R	R^1	R^2	R^3	Chemical shift, δ, ppm								Literature
				2H	3H	4H	5H	R	R^1	R^2	R^3	
H	H	H	H	5,40	9,33	8,23	11,27	—	—	—	—	[6]
H	H	H	Me	5,27	8,93	7,95	—	—	—	—	3,32	[6]
H	Me	H	H	5,22	—	7,87	10,83	—	2,87	—	—	[6]
Me	H	H	Me	5,47	8,80	7,77	—	1,98	—	—	3,27	[6]
H	Me	H	Me	5,03	—	7,53	—	—	2,72	—	3,18	[19]
H	H	H	*t*-Bu	5,29	8,97	8,00	—	—	—	—	1,63	[19]
H	*t*-Bu	H	H	5,14	—	7,95	10,83	—	1,52	—	—	[19]
H	*t*-Bu	H	*t*-Bu	4, 96	—	7,67	—	—	1,48	—	1,60	[19]
Me	*t*-Bu	H	Me	5,37	—	7,54	—	1,99	1,46	—	3,16	[19]
H	H	H	Et	5,29	8,92	7,93	—	—	—	—	3,63 1,64	[21]
H	Et	H	Et	5,12	—	7,64	—	—	3,07 1,56	—	3,47 1,40	[21]
Et	H	H	Et	5,42	8,83	7,80	—	2,42 1,26	—	—	3,60 1,62	[21]
Et	Et	H	Et	5,24	—	7,60	—	2,64 1,13	2,92 1,47	—	3,49 1,47	[21]
H	H	H	MeS	5,03	8,30	7,64	—	—	—	—	3,18	[18]
Me	H	H	MeS	5,33	8,14	7,47	—	1,82	—	—	3,16	[18]
MeS	H	H	MeS	6,30	7,89	7,38	—	1,92	—	—	3,15	[18]
H	MeS	H	MeS	4,88	—	7,22	—	—	2,77	—	2,98	[20]
H	EtS	H	EtS	4,88	—	7,17	—	—	3,25 1,45	—	3,44 1,57	[20]
H	EtS	EtS	EtS	5,03	—	—	—	—	3,22 1,53	2,87 1,28	3,44 1,60	[20]
H	Cl	H	Cl	5,12	—	7,67	—	—	—	—	—	[22]

*Chemical shifts varied little with solvent, spectra were recorded in HF [6], CH_2Cl_2 (CD_2Cl_2) [18,, 19, 21, 22], or CF_3COOH [20]; spin-spin coupling $J_{3,4}$ = 5.0-5.6, $J_{2,5}$ = 2.4-2.5, $J_{4,5}$ = 4.5 Hz.

TABLE 2. Ratio of 2- and 3- Alkylthiophenes Formed on Alkylation of Thiophene in the Presence of an Equimolar Amount of $AlCl_3$ [27]

Reagent	MeBr	EtBr	*i*-PrCl	*t*-BuCl
Temperature, °C	-10	-20	-70	-70
Ratio of 2- and 3- isomers	73 : 27	65 : 35	60 : 40	83 : 17

materials [18]. These cations are stable under aculation conditions, being produced in the absence of any excess of protonic acid. The hydrogen chloride liberated upon acylation is practically consumed (acylthiophenes being obtained in about 50% yields along with equimolar amounts of the relevant thiophenium ions):



a R=R^1=H; b R=Me, R^1=H; c R=R^1=Me

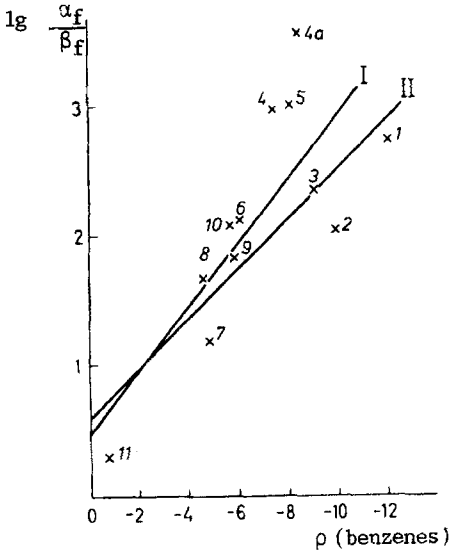
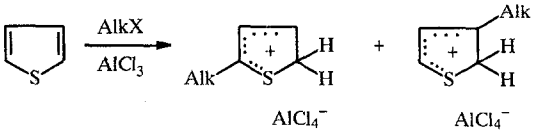


Fig. 1. Attempted correlation of log α_f/β_f and ρ. 1) Bromination (Br_2), 2) chlorination (Cl_2), 3) acetylation, 4) protodedeuteration (aq. H_2SO_4), 4a) protodedeuteration (CF_3COOH), 5) protodetritiation (aq. H_2SO_4), 6) bromination (Br^+), 7) iododeborination, 8) protodesilylation, 9) solvolysis of α-arylethyl-p-nitrobenzoates, 10) solvolysis of α-arylethylacetates, 11) pyrolysis of α-arylethylacetates. For all points (line I): $\log \alpha_f/\beta_f = -0.24\,\rho + 0.45$ ($r = 0.763$, $s = 0.595$). Without points 4, 4a, and 5 (line II): $\log \alpha_f/\beta_f = -0.19\,\rho + 0.55$ ($r = 0.889$, $s = 0.348$).

The proposed route for forming thiophenium ions was confirmed in model experiments using HCl and $AlCl_3$ in the same solvents [18] and was later used several times for generation of such ions both by us [19-22] and by other workers [23-25] PMR Spectroscopy showed that cations, obtained from thiophene, 2-methyl- and 2,5-dimethylthiophenes and also 2-(methylthio)- and 2-methyl-5-(methylthio)thiophenes, are stable in solution at room temperature with no evident decomposition over times from several days to several months [18]. The stability of the 2,5-dimethyl-2H-thiophenium ion is particularly high and is converted to the 3,5-dimethyl isomer only after several years at room temperature [19]. This stability and the ease of formation is significantly affected by the nature of the counterion. Hence according to [6], thiophene and alkylthiophenes form in HF cations which are stable only at $-40°C$ but in $HF-BF_3$ the same cations are stable even at $-20°C$. A comment in this study that the 2,5-dimethyl-2H-thiophenium ion, generated in HF in the presence of SbF_5, is stable even at 60°C has received little attention. Naturally, the substituent in the thiophene ring also has a large influence. Hence 2,4-bis-(alkylthio)thiophenes are converted to the corresponding stable thiophenium ions in trifluoroacetic acid [25] or in inert solvent by the action of HCl in the presence of $SnCl_4$ [26]. Protonation in trifluoroacetic acid is also observed for isomers of cyclopentadithiophenes [15].

The high stability of the thiophenium ions allows them to be generated in a fundamentally novel way by alkylation of thiophene with alkyl halides in the presence of an equimolar amount of aluminum chloride [27]. Due to low selectivity, the alkylation products are themselves a mixture of 5-alkyl-2H- and 3-alkyl-2H-thiophenium ions which can be deprotonated to the corresponding mixtures of 2- and 3-alkylthiophenes (Table 2). It is important to point out that the stability of the thiophenium ions, allowing use of equimolar and not the usual catalytic amount of $AlCl_3$, stops the alkylation at the mono substitution stage even if the alkyl halide is used as solvent [27]:



The reaction of thiophene with alkyl halides in the presence of $AlCl_3$ must initially lead to ions which have hydrogen and an alkyl group at a geminal position, i.e., "normal" alkylation σ-complexes. Evidently the latter then isomerizes with proton migration to change to more stable ions with two hydrogen atoms in the geminal position. Our attempts to bring about a similar generation of stable thiophenium ions in halogenation and sulfenylation conditions with subsequent formation of monohalothiophenes and sulfides of the thiophene series [28] have been unsuccessful. This is evidently due to the readier migration of Hal^+ and RS^+ cations when compared with a proton. As shown below, migration of alkyl cations from a geminal position also occurs but significantly more slowly than proton migration. The effect of the inherent stability of α-C-protonation products on the occurrence of some reactions of the thiophenes will be discussed in a subsequent section.

TABLE 3. Comparison of the Rates of Nitration and Hydrogen Exchange in Some Aromatic Hydrocarbons and Thiophene

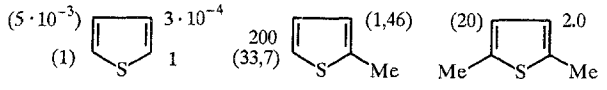
Compound	log k_2^0 (nitration)	log k_0 (H/D exchange)
Benzene	0,45	-11,00
Toluene (meta- position)	0,26	-11,42
Toluene (para- position)	1,82	-7,95
para-Xylene	1,65	-8,44
Thiophene	1,68	-2,39
Naphthalene (α-position)	1,85	-6,75
Naphthalene (β-position)	0,85	-8,11

STABILITY OF THIOPHENIUM IONS AND SOME HYDROGEN ISOTOPIC EXCHANGE PROPERTIES FOR THIOPHENES

The high stability of σ-complexes, formed on protonation of the thiophene α-position and including those bearing a substituent, is shown in some properties of acid catalyzed hydrogen isotope exchange where similar cationns are actual intermediates [29]. The reported quantitative data shows that hydrogen isotopic exchange in thiophenes is higher than for other reactions when comparing the activity of the α- with the β-positions. In fact this is shown more clearly when treated graphically (Fig. 1) where we have attempted to correlate the log α_f/β_f and ρ values for various reactions of electrophilic substitution of thiophene and some solvolysis and pyrolysis reactions in the side chain. We obtained the log α_f/β_f values as the difference values quoted by Marino [30] when correlating the "extended selectivity relationship" for ln α_f-ρ and ln β_f-ρ, where αf and β_f are benzene partial rate factors relative to the α- and β-positions and ρ- the reaction constants for benzene. The values for protodedeuteration of benzene in aqueous sulfuric acid (-7.5) and in CF_3COOH (-8.5) are taken from [31] and data for deuterium exchange of thiophene in CF_3COOH (point 4a) from [32]. The remaining values are taken from the review [30].

As can be seen, points 4, 4a, and 5 corresponding to hydrogen exchange deviate markedly from the rest. The ratio α_f/β_f is increased by approximately one order of magnitude compared with a value which might be expected from the reaction constant ρ.

The relative increase in the case of hydrogen exchange for the activity of the α- when compared to the β-position is also clearly revealed when comparing the partial rate factors relative to the thiophene α-position for the isotopic exchange of hydrogen [33, 34] and acetylation [35, 36] for the same thiophene compounds. Acetylation partial rate factors are given in brackets. For thiophene itself there were more significant differences in the α- and β-position activities towards hydrogen exchange than for acetylation even though the latter reaction would be expected to be more selective (in the benzene series ρ for hydrogen exchange is -7.5 and for acetylation -9.1). In the isotopic exchange of hydrogen with acid, position 5 in 2-methylthiophene is 100 times more reactive than the 3 position in 2,5-dimethylthiophene. By contrast, for acetylation these positions are practically the same in activity [36].

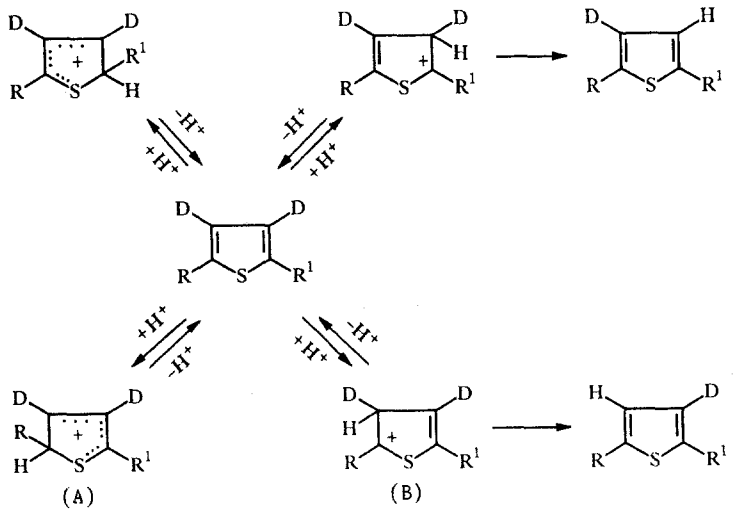


A particular problem arises when using the isotopic exchange of hydrogen for reckoning the β-position activity of α,α-disubstituted thiophenes e.g., the above 2,5-dimethylthiophene and also 5-(alkylthio)-2-methyl- and 2,5-bis-(alkylthio)thiophenes (partial rate factors are given in [34] relative to the α-position of unsubstituted thiophene).

It might be expected that in acid medium such compounds undergo mainly α-C-protonation to the more stable σ-complexes which cannot directly be converted to products of β-hydrogen atom isotopic exchange. In fact, exchange of the latter occurs only through the small equilibrium concentration of the isomeric σ-complexes arising from β-position protonation.

Isotopic hydrogen exchange can be successfully used to assess the relative activities of thiophene β-positions only in examples where there exist two positions in the same molecules e.g. 2-alkyl-5-(alkylthio)thiophene. When comparing two

different compounds, the results may depend on the characteristics of each of their equilibrium positions between the more (A) and less (B) stable σ-complexes. Of these, only the latter (as already discussed) can be directly converted to a product of isotopic β-hydrogen atom exchange. In particular, the closeness of the observed [34] rates of exchange for 2,5-dimethyl- and 2,5-di(methylthio)thiophenes probably does not indicate equal thermodynamic stability for the σ-complexes (B, R = R′ = Me and R = R′ = MeS). In a number of cases it is evidently due to a balancing between differences in the relative β-position reactivities and differences in the equilibrium concentrations of σ-complexes (B).

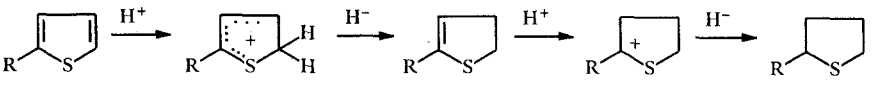


The effect of the stability of the products of α-C-protonation may also be revealed by comparing the hydrogen isotopic exchange rates for thiophene and for other series. Hence, "standardized" values of log k_O for hydrogen exchange in aqueous H_2SO_4, extrapolated to $H_O = 0$ at 100°C, and log k_2 for nitration in aqueous H_2SO_4 at 25°C ($H_O = 6.6$) [37] for benzenes and naphthalenes show complementary changes but thiophene behaves anomalously (Table 3).

A marked increase in hydrogen exchange (up to 6 orders) on changing from p-xylene to toluene which nitrates at almost the same rate may be explained in two ways. First, a particularly facile protonation of the thiophene ring which significantly accelerates the isotopic hydrogen exchange. Alternatively, under nitration conditions of concentrated sulfuric acid a more or less significant part of the thiophene molecules exist protonated and cannot undergo electrophilic substitution without deprotonation. We have shown a similar effect in the acylation of thiophene and homologs by acetyl chloride and chloroacetic acid in the presence of aluminum chloride [18]. Using a similar rationale associating the thiophene as the stable 2H-thiophenium ion, we can explain the lower activity of thiophene when compared with benzene for alkylation in liquid hydrogen fluoride (previously found by Weinmayr [38]).

GENERATION OF THIOPHENIUM IONS AND IONIC HYDROGENATIONN OF THIOPHENES

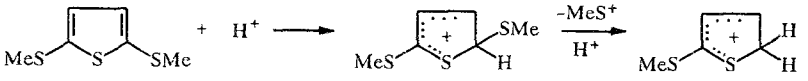
The ease of C-protonation of thiophenes suggested that compounds of this series can undergo ionic hydrogenation since the mechanism of this reaction includes the consecutive addition of protons and hydride ions. In fact, ionic hydration of thiophenes was realized in conditions standard for this reaction, i.e., the action of triethylsilane in trifluoroacetic acid [39-41]. This reaction allows ready conversion of a wide range of thiophenes to the corresponding tetrahydrothiophenes according to the scheme:



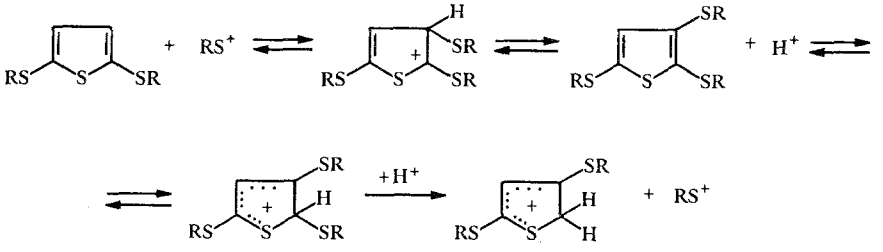
However, some compounds (e.g., 2,5-diphenylthiophene) do not reduce under standard conditions. As has been shown [42, 43], generation of stable thiophenium ions and their reaction with triethylsilane makes possible a sharp acceleration of the process and loss of the restriction noted above. Ionic hydrogenation in the system triethylsilane–HCl–$AlCl_3$ can be carried out using catalytic amounts of aluminum chloride [43].

DISPROPORTIONATION OF THIOPHENIUM IONS AND ITS USE IN ORGANIC SYNTHESIS

As noted above, the stability of thiophenium ions depends markedly on the nature of the substituents. The formation of the thiophenium ions is reversible. Moreover, not only protons but also other electrophilic fragments at a geminal position can be split off. In fact, this type of process has been observed for 2,5-di(methylthio)-2H-thiophenium ion [18] which, in contrast to 2-(methylthio)- and 2-methyl-5-(methylthio)-2H-thiophenium ions, is stable only at low temperatures with separation of the MeS group (probably as a cation) above −40°C.



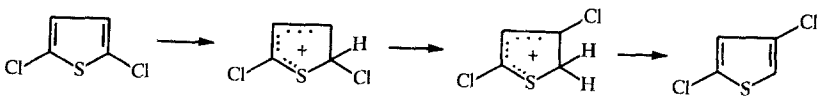
With insufficient HCl or when protonated in trifluoroacetic acid, there is found in the reaction medium some bis-sulfide which undergoes electrophilic sulfenylation. The reaction occurs via intermolecular disproportionation and gives a range of products, chief of which is the 2,4-isomers [20]. The driving force of the reaction is the formation of 2,4-bis-(alkylthio)thiophenium ions, the structure of which ensures especially favorable conditions for delocalization of the positive charge:



The deciding role of the thermodynamic stability of the thiophenium ions in the discussed reaction of bis-sulfides is confirmed by quantum chemical calculations [44].

Disproportionation is also observed for alkylthophenes with the tert-butyl group migrating most readily. In particular, this allows the conversion of a mixture of 2- and 3-isomers (83:17) prepared by tert-butylation of thiophene in the presence of an equimolar amount of $AlCl_3$ to 2-tert-butylthiophene containing only 3% of the 3-isomer by holding the mixture of the thiophenium ions at room temperature for 1-2 days [19]. 2,4-Di-tert-butylthiophene obtained as a one of the disproportionation products (as the corresponding σ-complex) is naturally more convenient to produce as a mixture of 2,4- and 2,5-isomers by, for example, tert-butylation of thiophene in the presence of $SnCl_4$ [45]. Similar conversion of the products of isopropylation and ethylation requires either an increased temperature (80°C) or a very prolonged reaction at room temperature [21]. In the case of the unsymmetrical 2-methyl- and 2-ethyl-5-tert-butylthiophenes a similar migration at room temperature is shown only for the tert-butyl group. This can be used to synthesize the difficult to obtain 2-alkyl-4-tert-butylthiophenes [46].

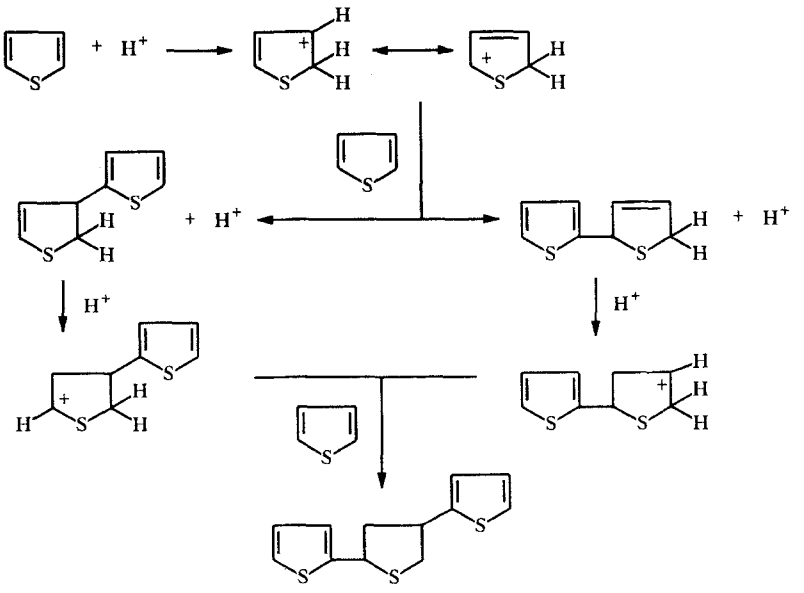
Disproportionation is observed also for unstable halothiophenium ions as shown by NMR only at temperatures less than −30°C. Hence Japanese workers have seen the disproportionation of 2,5-dibromo-2H-thiophenium ion [47]. We have used a similar process as a preparative method for converting 2,5-dichlorothiophene to the 2,4-isomer [22].



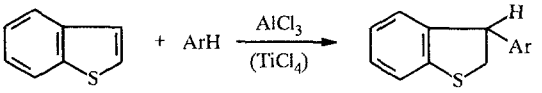
As shown by quantum chemical calculations [48], the basic factor determining the mode of disproportionation of halothiophenium ions is their relative thermodynamic stability.

THIOPHENIUM IONS AS ELECTROPHILES

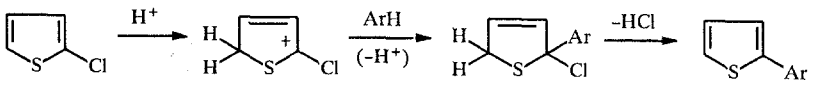
There is considerable interest in reactions in which thiophenium ions behave as electrophilic reagents. One of these is the acid oligomerization of thiophenes. This reaction was studied as far back as 1950 [2] and led to a determination of the structure of the so-called trimer (this was later confirmed by x-ray analysis [49]). The authors proposed the reaction scheme which quite clearly demonstrated the characteristic reactivity of thiophenium ions:



A related reaction is observed with unsymmetrical linking of 2-arylthiophenes on a cation exchange resin [50] to give 5,5-diaryl-2,3-bithiophenes. Other aromatic compounds can behave as the substrate. Hence reaction of benzo[b]thiophene with different benzenes in the presence of $AlCl_3$ or $TiCl_4$ occurs, in the authors opinion [51], via C-protonation to give aryl 2,3-dihydrobenzothiophenes which are the products of the formal addition of an aromatic molecule to the thiophene double bond:



Arylthiophenes are readily obtained by using chlorothiophene which serves as a unique "alkylating" agent [25].



Via a similar process 3,5,4′-trichloro-2,2-bithiophene is found to be the single side product of the isomerization of 2,5-dichlorothiophene discussed above [22]

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INDOLE FULGIDES

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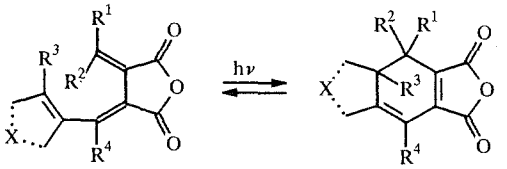
The syntheses and photochemical properties of fulgides derived from indole and indoline are reviewed.

Aryl and heteryl derivatives of bismethylenesuccinic anhydride with the general formula I were first synthesized at the beginning of the present century by the German chemist, Stobbe [1]. These crystals were termed fulgides in light of their appearance from the Latin root *fulgere* meaning "shining, sparkling." Fulgides have photochromic properties, that is, are capable of reversibly altering their color upon the action of light due to an electrocyclic conrotatory closure of the hexatriene ring and formation of deeply colored products II [2].

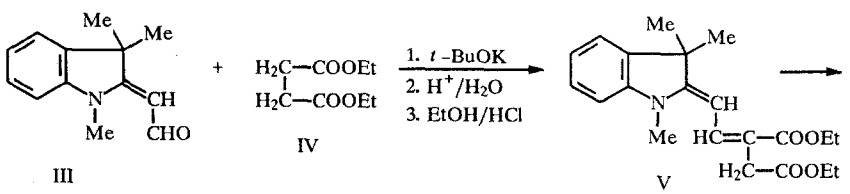


I II

Photochromic compounds have found use for the storage and treatment of optical information, in laser technology, and light filters with variable optical density [3]. Fulgides, in contrast to many other photochromic compounds such as spiropyrans [4], have high photochromic stability, which permits their use in durable photochromic materials [2]. Special interest is found in fulgides with heteryl fragments. Thus, derivatives of bismethylenesuccinic anhydride containing thiophene, furan, or pyrrole rings have been reported [2]. In recent years, we have synthesized and studied fulgide derivatives of indole and indoline. The results of these studies are summarized in this review.

1. INDOLINE FULGIDES

Indoline fulgides with the general formula VI were obtained in a search for new photochromic compounds in our previous work [5, 6] according to Stobbe's method. Diethyl succinate IV was condensed with Fischer's aldehyde III in the presence of potassium tert-butylate with subsequent esterification in ethanol saturated with hydrogen chloride. Diester V was used in reactions with carbonyl compounds such as benzaldehyde, 4-fluorobenzaldehyde, 4-ethoxybenzaldehyde, 1,2-dimethyl-3-formylindole, and Fischer's aldehyde.



III IV V

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