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# STABLE HETEROARENIUM IONS - VIII[1,2]
# SOME TRANSFORMATIONS OF ALKYLTHIOPHENIUM IONS AND NEW SYNTHESIS OF 2-t-BUTYLTHIOPHENE

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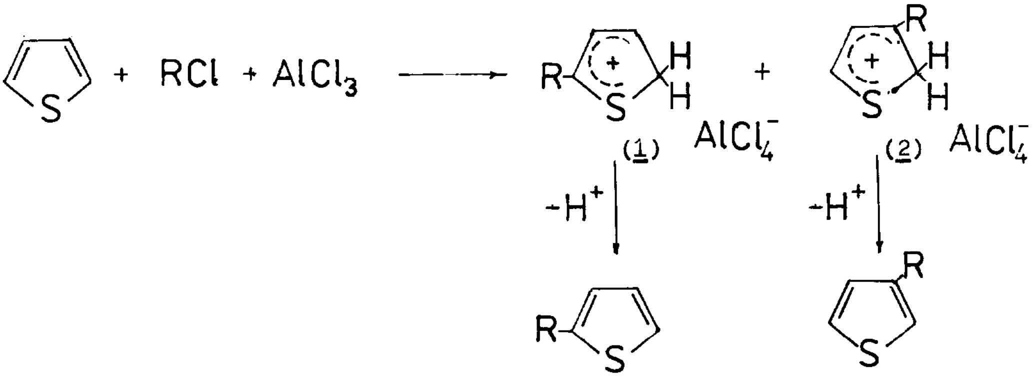
Abstract - The ratio of isomeric σ-complexes formed from thiophene, t-butyl chloride and $AlCl_3$ was found to be changed while keeping at room temperature within 1-2 days. This allows to obtain after deprotonation 2-t-butylthiophene containing only 3% of 3-isomer. Transformations of σ-complexes formed by protonation of individual 2- and 3-t-butylthiophenes in the presence of $AlCl_3$ have been studied and there was found that isomerization and disproportionation took place during their storage resulting in mixtures of 2- and 3-t-butylthiophenes (the ratio 97:3) which contained considerable quantities of 2,4-di-t-butylthiophene. Deprotonation of t-butylthiophenium ions in the presence of acetone leads to the formation of respective t-butylsubstituted dimethyldithienylmethanes.

As it was shown in one of our previous papers[3] the action of alkyl halides (t-BuCl, i-PrCl, EtBr, MeBr) on thiophene in the presence of equimolar amount of $AlCl_3$ using $CH_2Cl_2$, $ClCH_2CH_2Cl$ or an excess of the alkyl halide as solvents results in the formation of monoalkylthiophenes practically free of admixture of di- and polysubstituted derivatives. In the case of isopropylation it was demonstrated that in conditions used there were formed mixtures of σ-complexes (1 and 2) stable at room temperature which gave after deprotonation corresponding 2- and 3-alkylthiophenes (3 and 4)[3] (Scheme 1).



Scheme 1

## DISPROPORTIONATION OF t-BUTYLTHIOPHENIUM IONS

It has been found now that in contrast to isopropylation in the case of t-butylation the ratio of σ-complexes (1, 2) estimated by PMR spectrum after keeping the reaction mixture at room temperature within one day differs considerably from the ratio of 2- and 3-t-butylthiophenes (3, 4) in preparative experiments carried out at -70° C in conditions described in the paper[3]. It should be noted that the data[3] are well reproducible: the interaction of t-butyl chloride with thiophene at -70° C in the presence of 1 mole of $AlCl_3$ gives readily the mixture of σ-complexes transformed after deprotonation by water into the mixture of 2- and 3-t-butylthiophenes (85:15) contained 3% of 2,4- and 2,5-di-t-butylthiophenes (~1:4). Keeping the reaction mixture at temperatures below -20° C does not practically change the ratio of the products mentioned. However after two days at room temperature there was obtained the product which contained 96% of mono-t-butylthiophenes (the ratio of 2- and 3-isomers 97:3) and 4% of disubstituted derivatives, the ratio of 2,4- and 2,5-isomers being in this case 99:1. So keeping at room temperature can be used for the preparation of 2-t-butylthiophene containing only 3% of 3-isomer.

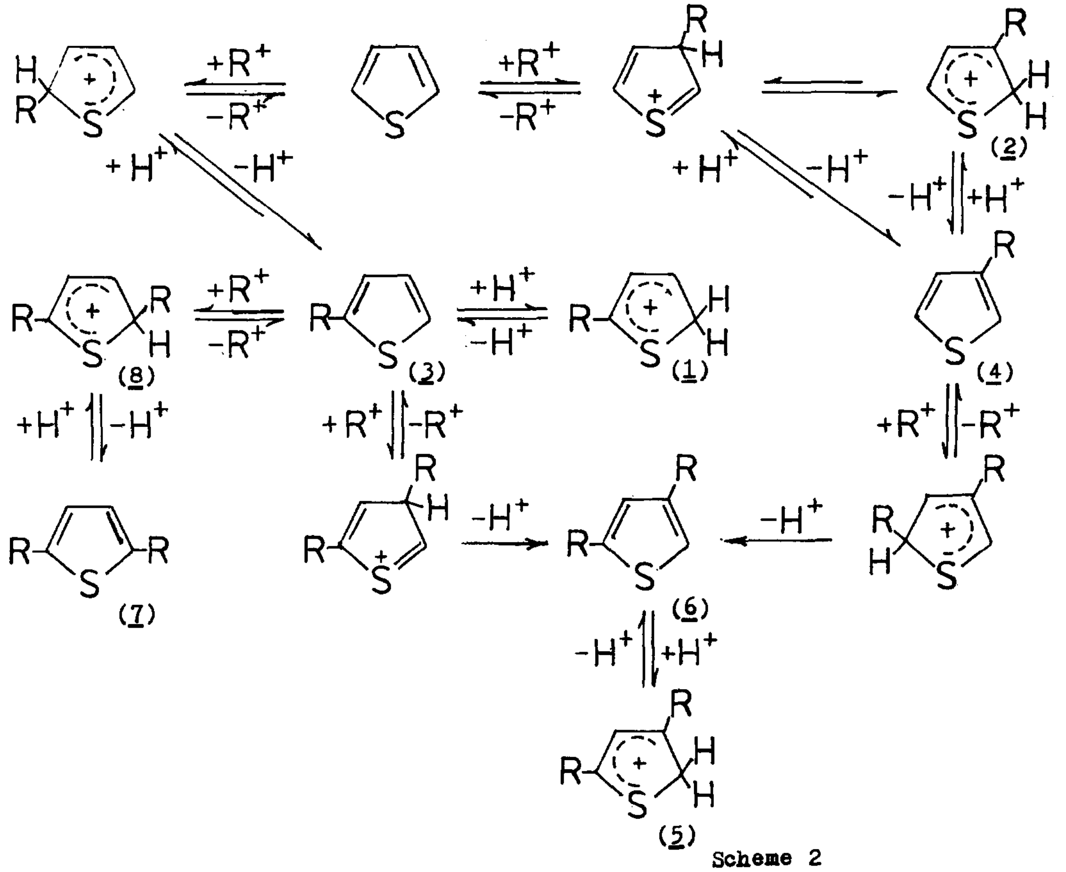
To clarify the process leading to the increase of 2-isomer content in reaction mixtures which are formed during t-butylation of thiophene in above conditions there were studied the transformations of σ-complex (2, R = t-Bu) obtained by protonation of 3-t-butylthiophene (PMR spectrum of the σ-complex is given in the Table 1). While keeping the latter at room temperature the isomeric σ-complex (1, R = t-Bu) is formed as well as σ-complex (5, R = t-Bu) corresponding to 2,4-di-t-butylthiophene (6, R = t-Bu). The ratios of the products (according to g.l.c data obtained after deprotonation) are given in the Table 2. It should be noted that already after one day the ratio of 2- and 3-t-butylthiophenes is close to that in the mixture formed by t-butylation of thiophene in the presence of 1 mole $AlCl_3$ at -70° C[3] and after 3 days this ratio reaches 97:3 as in the experiments above. One can suppose that t-butylation at -70° C gives kinetically controlled mixture of 2- and 3-isomers (~85:15) whereas keeping the reaction mixture at room temperature results in thermodynamically controlled ratio (97:3). The results obtained by keeping σ-complex (1, R = t-Bu) prepared by protonation of pure 2-t-butylthiophene (Table 2) are in agreement with above assumption. These transformations depend on disproportionation of monosubstituted derivatives and can be illustrated by Scheme 2. All neutral compounds in this Scheme have been detected by g.l.c. and stable σ-complexes (1, 2, 5) - by PMR. Differences in the content of dialkylated products (see Table 2) are apparently due to different rates of transformation of the ions (1, 2) into (5) which includes practically irreversible formation of 2,4-di-t-butylthiophene (6).

Table 1. PMR spectra of alkylsubstituted 2H-thiophenium ions

| Cation[a] | Chemical shifts, δ | | | | | | | J constants |
|---|---|---|---|---|---|---|---|---|
| | 2H | 3H | 4H | 5H | 2-Me | 3-Me | 5-Me | |
| 1, R = t-Bu | 5.29[b] | 8.97 dt | 8.00 dt | - | - | - | 1.63 s | $J_{23}$ 1.3, $J_{24}$ 0.9, $J_{34}$ 5.5 Hz |
| 2, R = t-Bu | 5.14[b] | - | 7.95 d | 10.83 dt | - | 1.52 s | - | $J_{25}$ 2, $J_{45}$ 4 Hz |
| 5, R = t-Bu | 4.96[b] | - | 7.67 s | - | - | 1.48 s | 1.60 s | |
| 9 | 5.37 m | - | 7.54 s | - | 1.99 d | 1.46 s | 3.16 d | $J_{2Me-2H}$ 7.6, $J_{5Me-2H}$ 3.5 Hz |
| 5, R = Me | 5.03 m | - | 7.53 s | - | - | 2.72 d | 3.18 d | $J_{3Me-4H}$ 1, $J_{5Me-4H}$ 1.2 Hz |

[a] Solvents: $CH_2Cl_2$ for 1, 2 and 5, R = t-Bu; $ClCH_2CH_2Cl$ for 5, R = Me and 9.

[b] From the spectrum in $CD_2Cl_2$, broadened signal.



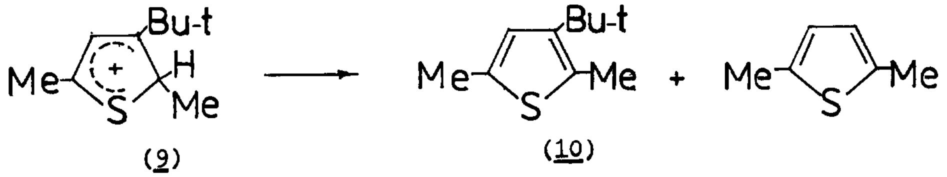
Scheme 2

Table 2. Transformations of σ-complexes (1, 2, R = t-Bu) by storage (r.t.)

| Starting σ-complex | Duration of storage, h. | Ratio of products[a] 2- : 3- | mono- : di- |
|---|---|---|---|
| 1 | 0 | 99.9 : 0.1 | - |
| | 2 | 99.6 : 0.4 | 98 : 2[b] |
| | 24 | 97 : 3 | 94 : 6 |
| | 100 | 97 : 3 | 89 : 11 |
| | 200 | 97 : 3 | 80 : 20 |
| | 400 | 97 : 3 | 60 : 40 |
| 2 | 0 | 7 : 93 | - |
| | 1 | 9 : 91 | 93 : 7[c] |
| | 5 | 37 : 63 | 85 : 15 |
| | 24 | 81 : 19 | 80 : 20 |
| | 72 | 97 : 3 | 76 : 24 |
| | 150 | 97 : 3 | 67 : 33 |

[a] Samples were analysed by g.l.c. after treatment with water. All samples except starting mixtures contained besides t-butylthiophenes (3, 4) traces (~1%) of thiophene. [b] The ratio of 2,5- (7) and 2,4-di-t-butylthiophenes (6) 72:28, at longer storage the content of 7 ~1%. [c] The content of 2,5-di-t-butylthiophene (7) ~1%, in subsequent samples 7 was not detected.

It may be supposed that disproportionation of β-substituted derivative (4) starts with presented in the Scheme 2 dealkylation of σ-complex (2, R = t-Bu) which takes place after 1,2 proton shift from position 2 into position 3. We have observed a similar loss of t-butyl group from the β-position in deprotonation conditions of σ-complex (9) obtained by the action of HCl and $AlCl_3$ on 2,5-dimethyl-3-t-butylthiophene (10): in deprotonation products there were detected not only starting trialkylthiophene (10) but also considerable amount of 2,5-dimethylthiophene (7, R = Me), the ratio 10 : 7 being ~2:1[†] (Scheme 3).



Scheme 3

The Scheme 2 includes isomerization of 2,5-di-t-butylthiophene (7, R = t-Bu) into 2,4-isomer (6, R = t-Bu) which probably proceeds through the ion (8). Such process was earlier observed by Wynberg and Wiersum[5] who used $AlCl_3$ in $CS_2$. These authors obtained also data in favour of intermolecular transfer of t-butyl group. In the same paper[5] there was shown that 2,4-di-t-butylthiophene can be formed from 3-t-butylthiophene under the action of $AlCl_3$. However the authors[5] have not observed the formation of 2,4-di-t-butylthiophene (6, R = t-Bu) from 2-t-butylthiophene (3, R = t-Bu) as well as mutual transformations of mono-t-butylthiophenes (3, 4, R = t-Bu). The differences of our results from the data[5] are probably due to insufficient concentration of $\sigma$-complexes (1, 2) in the latter case: Wynberg and Wiersum did not used any proton acid and only traces of HCl might be formed by hydrolysis of $AlCl_3$.

In the case of isopropylation of thiophene there was also observed a small but definite change in the ratio of 2- and 3-isomers from 69:31 to 72:28 while keeping the reaction mixture during a week at room temperature. At the same time some increase in amount of disubstituted derivatives (from 1.5 to 3%) was also noted. Thus one can suppose that reactions described in the Scheme 2 take place not only for R = t-Bu but also for other alkyls though their rates are considerably lower. In particular transformation of $\sigma$-complex of the type (8) into its isomer (5) proceeds even when R = Me. So in PMR spectrum of $\sigma$-complex (8, R = Me) prepared from 2,5-dimethylthiophene[6] and stored in a sealed tube at room temperature for several months there appeared additional signals corresponding to $\sigma$-complex (5, R = Me) - the product of protonation of 2,4-dimethylthiophene. These signals became predominate (~90%) in the spectrum of the sample stored for 10 year and deprotonation of the mixture gave 2,4-dimethylthiophene as the main product (g.l.c.).

## BEHAVIOUR OF ALKYLTHIOPHENIUM IONS IN THE PRESENCE OF SOME NUCLEOPHILIC ORGANIC COMPOUNDS

Supposing that isomeric $\sigma$-complexes (1, 2) should have different reactivity as electrophiles an attempt was made to change the ratios of 2- and 3-alkylthiophenes formed by alkylation of thiophene with alkyl halides in the presence of $AlCl_3$. For the purpose neutral benzene and some of its derivatives were added to the reaction mixtures. However these attempts were unsuccessful. Even the transfer of t-butyl and isopropyl groups from $\sigma$-complexes (1, 2) to other aromatics was a minor reaction: it took no place at temperatures between -70° and -20° C

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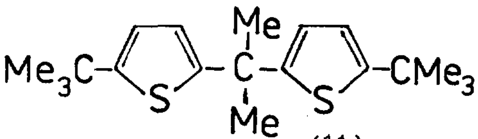
[†] Gol'dfarb and Korsakova[4] observed the substitution of t-butyl group for acetyl group and the formation of 2,5-dialkyl-3-acetylthiophenes by acetylation of 2,5-dimethyl-3-t-butylthiophene (10) and some other similar compounds. Such facts may be not neccessarily the result of direct attack of acyl into substituted position 3 but (taking into account our data above) in the reaction conditions protonation and dealkylation may take place followed by the introduction of acyl group into one of free positions of formed 2,5-dimethylthiophene.

and only long keeping at room temperature or boiling in methylene chloride resulted in the formation of respective alkylaromatic compounds but in ~1% yields. Simultaneously there was observed the oligomerization of liberated thiophene and possibly alkylthiophene without participation of added aromatics: according to g.l.c. data high-boiling products formed were principally identical in experiments with benzene or toluene and reaction products of these aromatic compounds with σ-complexes were not detected. It is in agreement with the results of our experiments in which mesitylene was added to the mixture of σ-complexes (1, 2, R = t-Bu). Apparently owing to steric hindrances mesitylene does not form t-butylation products[7] and this caused stability of the σ-complexes in this case: there were not observed the formation of both t-butylmesitylene and high-boiling products which were obtained using benzene or toluene.

Thus "alkylation" with alkylthiophenium ions was not observed though similar reaction takes place during oligomerization of thiophene and 2-methylthiophene in the presence of proton or aproton acids (see for example[8–11]). In conditions considered above, i.e. in the presence of neutral aromatic compounds, σ-complexes (1, 2) were sufficiently stable and at the same time proved to be inactive as electrophiles, this in our opinion could be explained as a result of both delocalization and considerable compensation of positive charge of thiophenium cations in ion-pairs.

"Alkylation" did not take place also with unsaturated compounds such as methyl acrylate and butyl vinyl ether. However the interaction of the latter with σ-complex (1, R = Me) obtained by protonation of 2-methylthiophene in the presence of $AlCl_3$ according to[6] resulted in the mixture of products identical with that formed by t-butylation of thiophene. Apparently in this case σ-complex (1, R = Me) is destroyed due to the transfer of HCl and $AlCl_3$ on vinyl butyl ether molecule, the latter after cleavage and subsequent isomerization generating t-butyl cation.

Similar deprotonation of alkylthiophenium ions under the action of acetone may be accompanied by linking of two alkylthiophene molecules with isopropylidene bridge. One of such products, 2,2-bis-(5-t-butylthienyl-2)propane (11), was isolated from the mixture obtained by treatment of σ-complexes (1, 2, R = t-Bu) with acetone.



(11)

## EXPERIMENTAL[†]

Analytical procedures

G.l.c. analyses were carried out using LKhM-8MD chromatograph with flame-ionization detector and nitrogen as carrier gas. A capillary pyrex column (50 m x 0.25 mm, Carbowax 40M/KF) was prepared according to[12]. It was found practically impossible to select an internal standard inert in reaction conditions especially in the presence of more than equimolar amount of $AlCl_3$. In particular n-undecane having suitable retention volume reacts with $AlCl_3$ at temperatures over 0° C giving complex mixture of hydrocarbons which is formed probably as the result of its isomerization, condensation (via dehydrogenation), cleavage and cyclization (cf.[13]). The addition of an internal standard after decomposition of aliquot volume of reaction mixture also met some difficulties. Therefore only ratios but not yields of products are presented in Table 2.

PMR spectra were performed on Varian DA-60-IL (60 MHz) and Tesla BS-497 (100 MHz) spectrometers, $^{13}C$ NMR decoupled and gated spectra of 11 – on Bruker WM-250 (62.89 MHz) spectrometer using tetrametylsilane or solvent ($CH_2Cl_2$ or $ClCH_2CH_2Cl$) as internal standards.

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[†] With the participation of I.A.Bessonova and L.G.Chagelishvili (Buchukuri).

## Preparation of some starting alkylthiophenes

3-t-Butylthiophene (cf.[14]). To 35.7 g of 2- and 3-t-butylthiophene mixture (85:15) in 150 ml of glacial AcOH bromine (52 g in 50 ml AcOH) was added at 8-10° C during 1 hour 45 min. After stirring at r.t. for 3 hours the reaction mixture was poured in water and extracted with $CH_2Cl_2$. The extract was washed with 5% KOH solution and water. Rectification gave 5-bromo-2-t-butylthiophene (38 g), b.p. 98-100°/18 mm and a fraction (16.4 g), b.p. 142-160°/18 mm which contained (g.l.c.) dibromo-t-butylthiophenes with the admixture of 5-bromo-2-t-butylthiophene. To the latter fraction in 50 ml of dry ether 140 ml of 1.5N n-BuLi in ether was added at -70° C. The mixture was stirred at -70° C for 1 hour and poured onto ice, the ether layer was separated, the aqueous layer extracted with ether. The combined extract was dried with $MgSO_4$. Distillation gave 5.5 g of a mixture of 2- and 3-t-butylthiophenes (30:70), b.p. 161-172°/760 mm. This mixture (5.2 g) in AcOH (40 ml) was brominated with bromine (10.2 g) in AcOH (15 ml) as described above. A fraction was obtained by rectification (b.p. 140-141°/22 mm, 4.85 g) which contained mainly 2,5-dibromo-2-t-butylthiophene with the admixture of 4,5-dibromo-2-t-butylthiophene (~3%) and 5-bromo-2-t-butylthiophene (~3%). Debromination of the fraction with 55 ml of 1.5N n-BuLi in ether at -70° C (see above) resulted in 1.05 g of 3-t-butylthiophene, b.p. 162-164°/760 mm which contained 7% of 2-isomer.

2-t-Butylthiophene. To the solution of 5-bromo-2-t-butylthiophene (14.1 g in 30 ml of dry ether) 1.5N ether solution of n-BuLi (95 ml) was added at -70° C, in 1 hour the reaction mixture was poured onto ice and extracted with ether. The extract was dried with $MgSO_4$. Distillation gave 3.44 g of 2-t-butylthiophene, b.p. 160-161°/760 mm containing only 0.1% of 3-isomer.

2,4-Dimethylthiophene. Reduction of 5.08 g of 2,4-thiophenedicarbaldehyde[15] with $NH_2NH_2.H_2O$ (40 ml) and KOH (20 g) in diethylene glycol (100 ml) gave 2,4-dimethylthiophene in 76% yield, b.p. 138-141°/760 mm (cf.[16]).

## Generation and transformations of alkylthiophenium ions

t-Butylthiophenium ions (via alkylation of thiophene)
a) To intensively stirred suspension of anhydrous $AlCl_3$ (15.5 g) in $CH_2Cl_2$ (25 ml) t-butyl chloride (10.75 g) in $CH_2Cl_2$ (12 ml) and thiophene (9.75 g) in $CH_2Cl_2$ (20 ml) were added in 20 min. keeping the temperature from -70° to -65° C. The mixture became homogeneous during additional stirring at -70° C for 1 hour. PMR spectrum of the reaction mixture after 1 day keeping at r.t. contained the signals of 5-t-butyl-2H-thiophenium ion (1, R = t-Bu) presented in Table 1 as well as 5H signal of 3-t-butyl-2H-thiophenium ion (2, R = t-Bu), the content of the latter was according to integral curve no greater than 5%, other signals of 2 were overlapped by the spectrum of the ion 1. After 2 days keeping at r.t. the mixture was poured onto ice. Organic layer was separated, aqueous layer extracted with $CH_2Cl_2$ (3 x 20 ml). Combined extract was washed with water, 1% KOH solution, again with water. Subsequent distillation gave two main fractions:
1. b.p. 165-170°/760 mm, 11.4 g contained 98% of mono-t-butylthiophenes (the ratio of 2- and 3-isomers 97:3) and 1.5% of di-t-butylthiophenes (the ratio of 2,5- and 2,4-isomers 1:99); 2. b.p. 60-85°/10 mm, 2.2 g contained mono- and di-t-butylthiophenes in the ratio 73:27. The overall yield of mono-t-butylthiophenes was 79% and that of di-t-butylthiophenes 3.5%.
b) The mixture of σ-complexes (1 and 2, R = t-Bu) was prepared as in exp. a) and after its keeping at r.t. for 15 hours benzene or toluene were added. This resulted in formation of ~1% of t-butylbenzene or the mixture of t-butyltoluenes respectively as well as of complex mixture of not identified products with high retention times which in both cases were very similar (g.l.c.). In one of such experiments the mixture obtained from 3.9 g of thiophene gave after treatment with acetone (5 ml, -30° C, 15 min.) and excess of water an extract. Two fractions were obtained from this extract: 1. b.p. 54-100°/10 mm, 1.86 g (the mixture of mono- and di-t-butylthiophenes) and 2. b.p. 150-160°/0.3 mm, 1.7 g which gave after recristallization from MeOH 1 g of 2,2-di-(5-t-butyl-2-thienyl)propane (11), m.p. 70-71°. Found: C 71.61, 71.62; H 8.99, 8.87; S 19.79, 19.50%; M 320 (MS). Calc. for $C_{19}H_{28}S_2$: C 71.20, H 8.80, S 20.00%; M 320.54. PMR ($CCl_4$), δ: 1.26 /s, 18H, $(CH_3)_3C$/; 1.66 /s, 6H, $(CH_3)_2C$/; 6.42 (s, 4H, $H_{thiophene}$). $^{13}C$ NMR ($CDCl_3$), δ: 32.56 /q, $(\underline{C}H_3)_3C$/; 33.09 /q, $(\underline{C}H_3)_2C$/; 34.36 /s, $(CH_3)_3\underline{C}$/; 40.26 /s, $(CH_3)_2\underline{C}$/; 120.17 (d, $4C_{thiophene}$); 122.17 (d, $3C_{thiophene}$); 152.07 (s, $5C_{thioph.}$); 155.14 (s, $2C_{thiophene}$).
c) The σ-complex mixture (obtained from thiophene and t-BuCl in the presence of $AlCl_3$) when treated with acetone (1 equiv.) at -70° C gave besides mono- and di-t-butylthiophenes the mixture of di-(t-butylthienyl-propanes (~10%) which contained 70% of 11. At -30° C the yield of the latters (6 isomers) increased to 65% but the content of 11 in the mixture decreased to 45%.

3-t-Butyl-2H-thiophenium ion (2, R = t-Bu). The suspension of $AlCl_3$ (0.48 g) in $CH_2Cl_2$ (2 ml) was saturated with dry HCl gas at -70° C and the solution of 3-t-butylthiophene (0.51 g) in $CH_2Cl_2$ (2 ml) was added dropwise in HCl stream. The mixture was kept at -70° C with periodic shaking for 20 min. (until the dissolution of $AlCl_3$), resulting solution was warmed to r.t. and than the samples were taken for PMR (see Table 1) and g.l.c. (the results of g.l.c. analyses of the mixtures after treatment the samples with water are given in Table 2).

5-t-Butyl-2H-thiophenium ion (1, R = t-Bu). The ion 1 was obtained similarly to 2 from 2-t-butylthiophene (1.08 g) and $AlCl_3$ (0.97 g) in $CH_2Cl_2$ (8 ml) saturated with dry HCl at -70° C. The results of g.l.c. analyses of the mixtures obtained at storage are given in Table 2.

Isopropylthiophenium ions (1 and 2, R = i-Pr). The mixture of 5- (1) and 3-isopropyl-2H-thiophenium (2) tetrachloroaluminates was obtained as described in[3] from thiophene (10 g), i-PrCl (9.35 g) and $AlCl_3$ (15.9 g) in $CH_2Cl_2$ (60 ml). After keeping at r.t. during 2 days and treatment with ice-water and KOH solution as described above a fraction was obtained (b.p. 150-155°/760 mm, 9.61 g) which contained 99% of monoisopropylthiophenes (the ratio of 2- and 3-isomers 70:30) and 1% of diisopropylthiophene mixture (g.l.c.). In similar experiment equimolar amount of benzene was added to the mixture of σ-complexes (1 and 2, R = i-Pr), the formation of isopropylbenzene (~0.3%) was detected after keeping for 4 days at r.t.

2,5-Dimethyl-3-t-butyl-2H-thiophenium ion (9). 2,5-Dimethyl-3-t-butylthiophene (0.76 g) was added dropwise to the suspension of $AlCl_3$ (0.61 g) in 1,2-dichloroethane (4.5 ml) saturated with dry HCl at -40° C, the mixture was kept for 2 hours at -40° C, then warmed to r.t. and PMR spectrum was recorded which was practically unchanged when the sample was stored for 2 month (see in Table 1). After treatment with acetone and water there was obtained a mixture contained 2,5-dimethyl-3-t-butylthiophene (10) and 2,5-dimethylthiophene in the ratio ~2:1 (g.l.c., stainless-steel column, 3 x 2000 mm, 5% SE-30 on Chromosorb P, 80° C).

Interaction of 5-methyl-2H-thiophenium tetrachloroaluminate (1, R = Me) with vinyl butyl ether. Vinyl butyl ether (3.5 g in 10 ml $CH_2Cl_2$) was added at -40°C to the solution of σ-complex (1, R = Me) obtained as described above from 2-methylthiophene (3.3 g), $AlCl_3$ (11.2 g) and HCl gas in $CH_2Cl_2$ (45 ml). The mixture was stirred at r.t. for 20 hours and then poured onto ice-water. Organic layer was separated, the aqueous extracted with $CH_2Cl_2$ (3 x 25 ml). Combined extract was washed with 1% KOH solution, then with water and distilled. A fraction (b.p. 65-72°/10 mm, 0.7 g) was collected which contained (g.l.c.) two isomeric 2-methyl-t-butylthiophenes in the ratio 1:7. Similar mixture was obtained from 2-methylthiophene and t-BuCl in the presence of $AlCl_3$.

3,5-Dimethyl-2H-thiophenium ion (5, R = Me). The ion was prepared by protonation of 2,4-dimethylthiophene in $ClCH_2CH_2Cl$ as in the case of ion 9. PMR data are presented in Table 1.

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