Chemistry of Heterocyclic Compounds, Vol. 33, No. 11, 1997

TRICHLOROMETHYLATION AND tert-BUTYLATION OF 2,4-DISUBSTITUTED THIOPHENES: ELECTROPHILIC SUBSTITUTION REACTIONS WITH STERICALLY HINDERED REAROMATIZATION STAGES*

L. I. Belen'kii, G. P. Gromova, B. V. Lichitskii, and M. M. Krayushkin

The interaction of 2,4-disubstituted thiophenes with $AlCl_3$ and CCl_4 or tert-BuCl proceeds through cationic σ-complexes corresponding to electrophilic substitution; the deprotonation of these complexes to form 2,3,5-trisubstituted products is sterically hindered, since this stage (rearomatization) involves a change in hybridization of the $C_{(2)}$ atom from sp^3 to sp^2, which leads to an increase of repulsion between the substituent R in position 3 and the bulky trichloromethyl or tert-butyl group that has entered into position 2 and is coplanar with R. It has been concluded tentatively that in the case of 2,4-alkylthiophenes that have even one hydrogen atom on the α-C atom of the substituent, deprotonation of the σ-complexes that are formed leads to the corresponding 3-alkylidene-5-R-2-dichloromethylene-2,3-dihydrothiophenes or 2-alkylidene-4-R-5-dichloromethylene-2,5-dihydrothiophenes, which then readily undergo oligomerization, as is also observed for such compounds under conditions of trichloromethylation. The hydrogen chloride that is evolved forms a stable 2H-thiophenium ion with the unreacted 2,4-dialkylthiophene. In the example of 2-tert-butyl-4-methylthiophene, formation of the stable 2,5-di-tert-butyl-3-methylthiophenium ion is observed; upon treatment with water, this ion does not lose a proton, but rather a tert-butyl group, thus being converted to the original 2,4-dialkylthiophene.

In a recent publication [1], we showed that electrophilic trichloromethylation can be used successfully in the preparative synthesis of not only o,o'-disubstituted benzotrichlorides, but also products formed from m-xylene and pseudocumene, in which the CCl_3 group is shielded by one methyl group. It was subsequently found that 2,4-dichlorothiophene is smoothly trichloromethylated by the action of carbon tetrachloride in the presence of aluminum chloride, with either methylene chloride or excess CCl_4 as the solvent, giving a high yield of 3,5-dichloro-2-trichloromethylthiophene [2]. Under the indicated conditions, 2,5-dichlorothiophene is partially isomerized, so that in this case a mixture of 2,5-dichloro-3-trichloromethylthiophene and 3,5-dichloro-2-trichloromethylthiophene is formed. We also investigated the electrophilic trichloromethylation of 3-chlorothiophene, 3-bromothiophene, and 3,4-dibromothiophene [3]. Here it was shown that the reaction is directed to position 2 and is accompanied by partial formation of the corresponding substituted bis(2-thienyl)chloromethanes. The trichloromethylation of β-bromothiophenes is complicated by exchange of bromine for chlorine under the conditions of reaction. In the cases under consideration, steric shielding of the trichloromethyl group by a chlorine or bromine atom minimizes the undesirable reaction of "cross-linking" to form the corresponding derivatives of dithienyldichloromethane.

Since the van der Waals radius of the chlorine atom is close to that of the methyl group, it appeared logical to extend the trichloromethylation to dialkylthiophenes. However, an attempt to carry out this reaction under analogous conditions with 2,4-dialkylthiophenes [4] proved to be successful only in the case of 2,4-di-tert-butylthiophene (I). For the other objects of

*Devoted to the bright memory of I. N. Goncharova.

N. D. Zelinskii Institute of Organic Chemistry, Russian Academy of Sciences, Moscow 117913. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1477-1485, November, 1997. Original article submitted May 30, 1997.

 0009-3122/97/3311-1276$18.00

TABLE 1. PMR Spectra of 3,5-Dialkyl-2H-thiophenium Ions V* and XVIII, and 3,5-Di-tert-butyl-α,α-dichloro-2-thenyl Tetrachloroaluminate VI

Ion	Chemical shift δ, ppm								Solvent†
	2-H	2,4-Bu	4-H	3-CH	3-Me	5-CH	5-CH_2	5-Me	
Va	5.03	—	7.55	—	1.37	—	—	1.50	A
	5.15	—	7.72	—	1.52	—	—	1.67	B
	Overlap	—	7.67	—	1.48	—	—	1.60	C
Vb	5.10	—	7.62	3.33	1.40	—	—	1.55	C
Vc	5.04	—	7.62	—	2.71	3.72	—	1.50	A
XVIII	4.85	1.22	7.47	—	2.62	—	—	1.46	B
VI	—	—	7.70	—	1.35	—	—	1.55	C

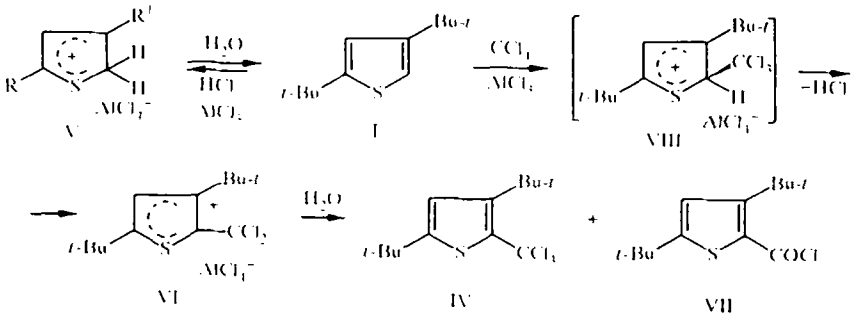
*Assignment of signals in the spectra of the ions Va-c is consistent with data for ions of the type of V (R = Me or Et and R^1 = t-Bu [4], and R = R^1 = Me or Et [6]).
†A = $ClCH_2CH_2Cl$ + $CDCl_3$; B = CD_2Cl_2; C = CH_2Cl_2 + $CDCl_3$.

investigation, namely 2,4-dimethyl-, 2,4-diethyl-, 4-isopropyl-2-ethyl-, 4-tert-butyl-2-methyl-, and 4-tert-butyl-2-ethylthiophene, and also for the compounds studied in the present work, namely 2-tert-butyl-4-methylthiophene (II) and 2,4-diisopropylthiophene (III), we were not successful in recovering any products of trichloromethylation. As was suggested in [4], the failure is due to a reaction that proceeds under comparatively mild conditions (~40°C with an equimolar amount or excess of aluminum chloride), the acidic oligomerization of these 2,4-dialkylthiophenes and possibly their "cross-linking" to form dithienyldichloromethanes. At lower temperatures, the 2,4-dialkylthiophenes did not react, and a considerable part of the original compound was recovered without change.

In the work reported here, we investigated in more detail the interaction of 2,4-dialkylthiophenes with carbon tetrachloride in the presence of aluminum chloride. We used NMR to investigate the reaction mixtures before they were treated with water.

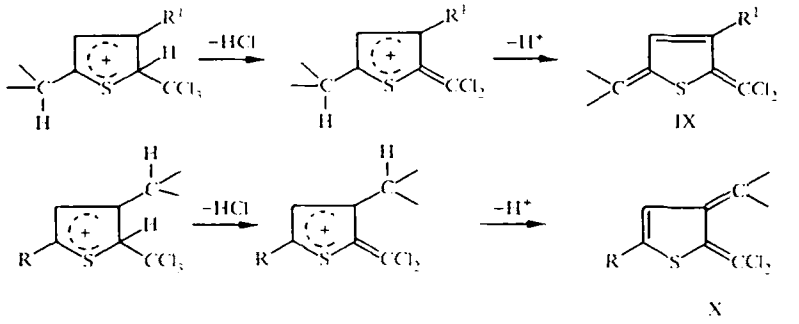
Previously [4], in the trichloromethylation of 2,4-di-tert-butyl-thiophene (I), after the usual treatment and vacuum distillation, we recovered the original compound I (33%) and 3,5-di-tert-butyl-2-trichloromethylthiophene (IV) (yield 50%), plus a still residue which, according to PMR data, contained the trichloride IV and bis(3,5-di-tert-butyl-2-thienyl)-dichloromethane in a ratio of about 6:1. We suggested that the reversion to the original compound I may be related to its protonation at the expense of the HCl evolved in the reaction (similar to what was observed previously in the acylation of thiophene and its homologs [5]). Actually, in contrast to the products from trichloromethylation of 2,4-dichlorothiophene, which even before treatment with water did not contain any 3,5-dichloro-2H-thiophenium ion, we found in a study of the PMR and ^{13}C NMR spectra of the reaction mixture obtained from 2,4-di-tert-butylthiophene I, CCl_4, and $AlCl_3$, that we did register the formation of the product of protonation of the original thiophene I, namely the σ-complex (Va). Moreover, as shown in a special experiment, this σ-complex can be formed under conditions of trichloromethylation not only at the expense of the hydrogen chloride that is evolved, but also at the expense of traces of hydrogen chloride in the aluminum chloride and traces of moisture in the medium and the apparatus. The target compound, the trichloride IV, prior to decomposition of the reaction mixture with water, exists in the form of a complex with $AlCl_3$ (VI). After decomposition of the mixture, the σ-complex Va is converted to 2,4-di-tert-butylthiophene I, and the 3,5-di-tert-butyl-α,α-dichloro-2-thenyl tetrachloroaluminate VI is converted to the trichloride IV with admixture of the acid chloride of 3,5-di-tert-butyl-2-thiophenecarboxylic acid (VII).

In an investigation of the PMR and ^{13}C NMR spectra of reaction mixtures obtained by the action of CCl_4-$AlCl_3$ on 4-tert-butyl-2-ethylthiophene, and also the PMR spectra of mixtures obtained from the 2,4-dialkylthiophenes II and III (in all these cases, we were unable to detect any products of trichloromethylation), we established the formation of the corresponding products of protonation, σ-complexes of the type of V (Vb-d). The characteristics of the PMR spectra of compounds Va-c are listed in Table 1, and those of the ^{13}C NMR spectra in Table 2. The PMR spectrum of compound Vd matched the spectrum reported previously in [4].



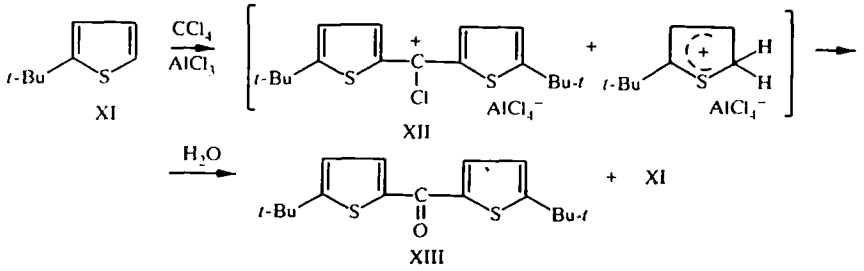
V a)R = R^1 = t-Bu; b)R = R^1 = i-Pr; c)R = t-Bu, R^1 = Me; d)R = Et, R^1 = t-Bu

Deprotonation of the σ-complex (VIII) that is formed in the trichloromethylation of di-tert-butylthiophene I, and also the subsequent formation of the trichloride IV, encounter specific steric hindrance, since these reactions require a change of hybridization of the $C_{(2)}$ atom from sp^3 to sp^2, which should lead to a coplanar system (or one tending toward coplanarity) with an ortho position of the tert-butyl group and the trichloromethyl group, which is similar in bulk to the tert-butyl group. It maybe that dehydrochlorination of the cation VIII taking place before treatment of the mixture with water, plus conversion of VIII to the resonance-stabilized ion VI, will remove part of the strain energy. When we consider that the above-noted hindrances for compound I are retained in the case of 4-tert-butyl-2-ethylthiophene and the 2,4-dialkylthiophenes II and III when a proton is split off from the geminal site, we can assume that such dehydrochlorination will also take place for these dialkylthiophenes. However, the ion of the type of VI that is formed in this case when the mixture is treated with water is capable of splitting off a proton from the substituent in position 5 (Et or i-Pr) or position 3 (Me or i-Pr), which has at least one hydrogen atom on a carbon bonded to the thiophene ring. When such deprotonation occurs, it should form the unstable 2-alkylidene-4-R^1-5-dichloromethylene-2,5-dihydrothiophenes (IX) or 3-alkylidene-5-R-2-dichloromethylidene-2,3-dihydrothiophenes (X), which may also be sources of products of oligomerization:



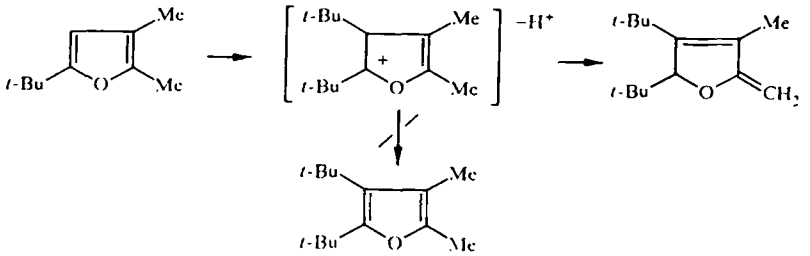
Products of oligomerization of compounds of the type of IX and X may be responsible for the poorly resolved upfield PMR peaks that are added to the signals of the ion V, these peaks appearing in the spectra of the reaction mixtures after several days of holding at room temperature (for example, signals at ~4.5, 2.8-3.0, ~2.2, and 0.8-0.9 ppm that appear in the mixtures obtained from 4-tert-butyl-2-ethylthiophene). However, we have not been able to interpret these signals.

The formation of unsaturated compounds similar to IX and X — which have no aromaticity and are readily subject to oligomerization — is a possibility that is not restricted to the case of the 2,4-dialkylthiophenes. Any alkylthiophenes with a suitable position of the substituents may undergo similar conversions under conditions of trichloromethylation. Thus, the only identifiable products in the reaction mixtures in the attempted trichloromethylation of 2,5-dimethylthiophene and 2-methylthiophene were the corresponding 2H-thiophenium ions, which were converted upon treatment with water to the original alkylthiophenes; these were accompanied by considerable amounts of oligomerized products. At the same time, 2-tert-butylthiophene (XI) is converted smoothly to the corresponding product of "cross-linking" (XII) and the 5-tert-butyl-2H-thiophenium ion (Ve, R = t-Bu, R^1 = H), which upon hydrolysis give bis(5-tert-butyl-2-thienyl) ketone (XIII) and the original thiophene XI.



With the aim of obtaining additional information on trichloromethylation in the thiophene series, we undertook the synthesis of certain thiophene derivatives in which the substituents do not contain any hydrogen atom on a carbon bonded to the thiophene ring; this must exclude the possibility of dehydrochlorination to form analogs of compounds IX and X, namely 5-tert-butyl-2-methoxythiophene (XIV) and 5-tert-butyl-2-(methylthio)thiophene (XV). The ether XIV was obtained smoothly by tert-butylation of 2-methoxythiophene; however, we were unable to bring this product into the trichloromethylation reaction. The failure can be explained on the basis that under the particular conditions we were using, the substrate exists in the form of an $n\nu$ complex with aluminum chloride, in which, as evidenced by the ^{13}C NMR data, the thiophene ring is strongly deactivated, as both of the free positions of the ring are sterically shielded by bulky substituents—the $MeO \cdot AlCl_3$ grouping and the tert-butyl group. The sulfide XV was obtained by tert-butylation of 2-(methylthio)thiophene in the form of a mixture with the isomeric 4-tert-butyl-2-(methylthio)thiophene (XVI) and 3-tert-butyl-2-(methylthio)thiophene (XVII) in a ratio of approximately 3.5:2:1. An attempt to obtain the individual sulfide XV from this mixture by means of C-protonation, as had been done in obtaining 2,4-di-tert-butyl-thiophene [11], was unsuccessful. We were likewise unsuccessful in carrying out the trichloromethylation of the mixture of sulfides XV-XVII; for at least two of the main components, this can be explained by the same factors described above for the ether XIV.

Proton abstraction not from the geminal site but from the alkyl substituent is apparently favored by the absence of the steric hindrance that might appear upon transition to a product of the type of IV with the ortho position of the bulky groups t-Bu (or Me, i-Pr) and CCl_3. This sort of situation has been described for the tert-butylation of 5-tert-butyl-2,3-dimethylfuran, which leads not to 4,5-di-tert-butyl-2,3-dimethylfuran, but rather to 4,5-di-tert-butyl-3-methyl-2-methylene-2,5-dihydrofuran [12].



In view of the closeness in volume of the trichloromethyl and tert-butyl groups, we cannot eliminate the possibility that steric hindrance is manifested in the rearomatization stage in tert-butylation. Thus, an attempt at tert-butylation of 2-tert-butyl-4-methythiophene II resulted in recovery of the original compound. However, in the ^1H and ^{13}C NMR spectra of the reaction mixture before decomposition with water, we detected signals pertaining to the σ-complex (XVIII) that is formed in the tert-butylation of compound II (see Tables 1 and 2) and also signals pertaining to the thiophenium ion Vc, the product of α-C-protonation of the original thiophene II. The formation of this ion could take place at the expense of traces of water and hydrogen chloride in the solvent that was used (CH_2Cl_2 or CD_2Cl_2) and in the aluminum chloride. However, in spite of precautionary measures that were taken, we were unable to obtain the ions Vc and XVIII in a ratio lower than 4:3. The main source of HCl is probably the tert-butyl chloride. It is known that at moderate temperatures (beginning at 61°C, according to some reports), there is a reversible decomposition of tert-butyl chloride to isobutylene and hydrogen chloride [13-15]. The dehydrochlorination of tert-butyl chloride under the action of $AlCl_3$, leading to a mixture of various chlorinated hydrocarbons, is an extremely vigorous reaction even at 0°C [16, 17]. In our case, apparently,

TABLE 2. ^{13}C NMR Spectra of 3,5-Dialkyl-2H-thiophenium Ions V and XVIII,* and 3,5-Di-tert-butyl-α,α-dichloro-2-thenyl Tetrachloroaluminate VI†

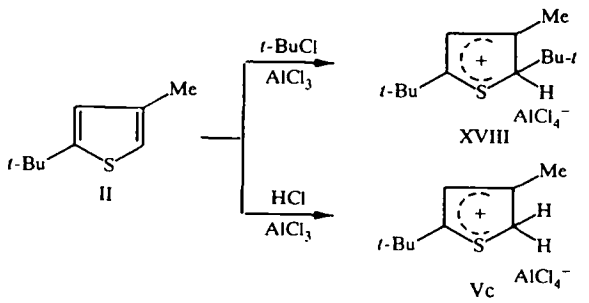
Ion	Chemical shift δ, ppm											Solvent‡
	2-C	3-C	4-C	5-C	2-CMe	2-Me	3-CMe	3-Me	5-CMe	5-Me	CCl_2	
Va	55.9	200.5	134.7	210.7	—	—	39.9	29.2	43.1	30.7	—	A
Vb	56.6		137.2		—	—	40.0	30.2	32.8	12.5	—	B
Vc	59.2	198.8	139.1	245.5	—	—	—	41.6	44.4	30.4	—	B
XVIII	87.0	200.3	140.4	248.0	24.9	22.5	—	36.2	44.4	30.0	—	B
VI	146.2	159.7	139.1	183.3	—	—	38.3	29.5	41.6	29.8	219.9	C

*In assigning the signals, we used data on 2,3,4,5-tetramethyl-2H- and 2,2,3,4,5-pentamethylthiophenium ions [7], and also on the 2,5-dimethyl-2H-thiophenium ion [8]. We were unable to identify the signals of the $C_{(3)}$ and $C_{(5)}$ atoms of the ion V (R = Et, R^1 = t-Bu).

†In assigning the signals, we used data for 2-thienyl (dialkyl)carbocations [9] and α,α-dichlorobenzyl tetrachloroaluminate [10].

‡A) = $ClCH_2CH_2Cl$ + $CDCl_3$; B) = CD_2Cl_2; C) CH_2Cl_2 + CD_2Cl_2.

owing to steric hindrance, the formation of the σ-complex XVIII proceeds rather slowly, and the dehydrochlorination of tert-butyl chloride competes successfully.



The structure of the 2,5-di-tert-butyl-3-methyl-2H-thiophenium ion XVIII that is formed in the alkylation of compound II is favorable for splitting out $t\text{-}Bu^+$ from position 2. This sort of splitting takes place so readily that the tert-butyl group has been proposed as a protective group in regioselective synthesis of aromatic compounds [18]. In contrast, deprotonation of the σ-complex XVIII, from either the geminal site or the methyl group, is extremely unfavorable, since in the first case steric hindrance would have to appear, and in the second case the aromaticity would have to be eliminated, this being much less favorable than for the less-aromatic furan analog [12] (see above). Let us note in this connection that previously, in the deprotonation of the 2,5-dimethyl-3-tert-butyl-2H-thiophenium ion, the product of protonation of 2,5-dimethyl-3-tert-butylthiophene, we had observed even partial splitting off of the tert-butyl group located in the β-position of the thiophene ring [6]. We can assume that such splitting, leading to 2,5-dimethylthiophene (in which, in contrast to 2,5-dimethyl-3-tert-butylthiophene, there is no steric repulsion between the substituents in positions 2 and 3), will be preceded by a hydride 1,2-shift from the geminal site.

The data we have set forth in this paper provide a means for understanding certain features of trichloromethylation and tert-butylation of 2,4-dialkylthiophenes as reactions of electrophilic substitution with steric hindrance in the rearomatization stage. In the future, we hope that we will be able to obtain a more complete picture of the circle of such reactions, the requirements on structure of the participating compounds, and the nature of the products that are formed.

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken in a Bruker AC-200 radiofrequency spectrometer. The solvents that were used are indicated below.

2-tert-Butyl-4-methylthiophene (II). To 11.35 g (85 mmoles) of anhydrous $AlCl_3$, a solution of 6.4 g (5 ml, 57 mmoles) of 3-thiophenaldehyde in 80 ml of dry CH_2Cl_2 was added gradually while stirring. To this solution, a solution of 5.27 g (6.2 ml, 57 mmoles) of tert-butyl chloride in 20 ml of dry CH_2Cl_2 was added dropwise. The mixture was refluxed with stirring for 1 h and then held for ~16 h at room temperature, after which it was poured onto ice with hydrochloric acid. The organic layer was separated off, and the aqueous layer was extracted with CH_2Cl_2. The extract, combined with the organic layer, was washed with water, sodium carbonate solution, and again with water, after which it was dried over magnesium sulfate. After removing the solvent by vacuum distillation, recovered 5.2 g (yield 54%) of 5-tert-butyl-3-thiophenaldehyde, bp 94-105°C/5 mm Hg. PMR spectrum ($CDCl_3$), ppm: 9.68 (1H, s, CHO); 7.82 (1H, s, 2-H); 7.13 (1H, s, 4-H); 1.25 (3H, s, 3-Me). These characteristics of the aldehyde are in agreement with values reported in the literature [19]. In addition, a lower-boiling fraction was recovered (73-94°C/5 mm Hg) in amount of 1.25 g (13%); this was also used for reduction.

To a solution of 3.75 g (3.75 ml, 75 mmoles) of hydrazine hydrate in 20 ml of diethylene glycol, a solution of 6.3 g (37.5 mmoles) of 5-tert-butyl-3-thiophenaldehyde in 20 ml of diethylene glycol was added dropwise; the mixture was heated for 5 min on a water bath, after which a solution of 8.4 g (150 mmoles)* in 10 ml of water was added. The reaction mass was heated to boiling and held at the boiling point (~100°C) for 1 h; evolution of nitrogen was observed during this time. The product was steam-distilled, and the distillate was extracted with ether. The extract was washed with water and dried with magnesium sulfate, and the ether was driven off. By vacuum distillation of the residue, recovered 2.7 g (yield 47%) of 2-tert-butyl-4-methylthiophene (II), bp 94-100°C/40 mm Hg. PMR spectrum ($CDCl_3$), ppm: 6.73 (1H, s, 5-H); 6.70 (1H, s, 3-H); 2.25 (3H, s, 4-Me); 1.42 (9H, 2-CMe_3). Found, %: C 69.88; 70.15; H 9.13; 9.29; S 20.76; 20.60. $C_9H_{14}S$. Calculated, %: C 70.07; H 9.15; S 20.78.

2,4-Diisopropylthiophene (III). To a suspension of 2.41 g (18 mmoles) of anhydrous $AlCl_3$ in 10 ml of dry CH_2Cl_2 containing 1.25 g (1.5 ml, 16 mmoles) of isopropyl chloride, held at −70°C with mixing, there was added a solution consisting of 10 ml of dry CH_2Cl_2 and 2.0 g (16 mmoles) of a mixture (~70:30) of 2- and 3-isopropylthiophene, obtained by isopropylation of thiophene by a procedure given in [20]. The reaction mass was held 5 h at −70°C, then ~16 h at room temperature, refluxed 5 h, and again held ~16 h at room temperature, after which it was treated with aqueous acetone (1:1) and then excess water. The organic layer was separated off, and the aqueous layer was extracted with CH_2Cl_2. The extract, combined with the organic layer, was washed with water, KOH solution, and again with water, after which it was dried over magnesium sulfate. After removing the solvent, vacuum distillation of the residue gave 1.0 g (yield 37.5%) of a fraction with bp 130-140°C/70 mm Hg, which contained, according to the PMR spectrum, ~85% of compound III and ~15% of 2,3-diisopropylthiophene (IIIa). When refluxing of the reaction mixture was eliminated, the yield of the analogous fraction increased to 54%, but the content of the desired 2,4-isomer III in this fraction was considerably lower, and the fraction also contained unidentified impurities. Previously, compound III had been synthesized by a similar method but with a lower yield, starting with monoisopropyl-2H-thiophenium ions [21].

Compound III. PMR spectrum ($CDCl_3$), ppm: 6.76 (2H, br.s, 3-H and 5-H); 3.25 (1H, m, 2-C<u>H</u>Me_2); 2.95 (1H, m, 4-C<u>H</u>Me_2); 1.35 (6H, t, 2-CH<u>Me</u>$_2$, J = 7 Hz; 1.26 (6H, t, 4-CH<u>Me</u>$_2$, J = 7 Hz). ^{13}C NMR spectrum ($CDCl_3$), ppm: 153.1 ($C_{(4)}$): 149.3 ($C_{(2)}$); 122.1 ($C_{(3)}$); 115.1 ($C_{(5)}$); 30.1 and 29.9 (<u>C</u>HMe_2); 24.8 and 23.6 (CH_3).

Compound IIIa. PMR spectrum ($CDCl_3$), ppm: 7.00 (1H, br.d, J = ~5 Hz, 5-H); 6.62 (1H, br.d, J = ~5 Hz, 4-H); 3.33 (1H, m, 5-C<u>H</u>Me_2); 3.08 (1H, m, 4-C<u>H</u>Me_2), 1.35 and 1.26 (signals are superposed on signals of CH<u>Me</u>$_2$ group of isomer III). ^{13}C NMR spectrum ($CDCl_3$), ppm: 148.3 ($C_{(2)}$); 142.0 ($C_{(3)}$); 120.4 ($C_{(5)}$); 118.4 ($C_{(4)}$); 27.8 and 27.5 (<u>C</u>HMe_2); 25.4 and 24.1 (CH_3).

5-tert-Butyl-2-methoxythiophene (XIV). To a suspension of 9.3 g (70 mmoles) of $AlCl_3$ in 15 ml of CH_2Cl_2, two solutions were added simultaneously—a solution of 7.2 g (63 mmoles) of 2-methoxythiophene (XXII) in 15 ml of CH_2Cl_2, and 5.9 g (63 mmoles) of tert-butyl chloride in 8 ml of CH_2Cl_2; these solutions were added while holding the temperature of the reaction mixture between −65° and −70°C. The mixture was held 1 h in this same temperature interval and then held 2 days at ~20°C. After the usual workup by distillation, recovered 7 g (yield 56%) of product

*As in Russian original; solute not identified—Translator.

XIV, bp 125-130°C (60 mm Hg). PMR spectrum ($CDCl_3$), ppm: 6.48 (1H, d, J = ~4 Hz, 4-H); 6.03 (1H, d, J = ~4 Hz, 3-H); 3.90 (3H, s, MeO); 1.40. ^{13}C NMR spectrum ($CDCl_3$), ppm: 163.8 ($C_{(2)}$); 143.5 ($C_{(5)}$); 117.9 ($C_{(4)}$); 102.7 ($C_{(3)}$); 60.1 (MeO); 34.3 ($\underline{C}Me_3$); 32.3 ($C\underline{C}H_3$). The parameters of the NMR spectra of compound XIV correspond to those given in the literature [23]. For a solution of the complex XIV·$AlCl_3$ (obtained by mixing equimolar quantities of the components in a neutral solution, then holding until the $AlCl_3$ was dissolved): PMR spectrum ($CDCl_3$), ppm: 6.87 (1H, d, J = ~4 Hz, 4-H); 6.59 (1H, d, J = ~4 Hz, 3-H); 4.65 (3H, s, MeO); 1.40 (9H, s, CMe_3). ^{13}C NMR spectrum ($CDCl_3$), ppm: 154.5 ($C_{(5)}$); 151.7 $C_{(2)}$); 119.0 ($C_{(4)}$); 118.1 ($C_{(3)}$); 74.3 (MeO); 34.8 ($\underline{C}Me_3$); 31.9 ($C\underline{C}H_3$).

tert-Butylation of 2-(Methylthio)thiophene. To a suspension of 22.5 g (0.17 mole) of anhydrous $AlCl_3$ in 45 ml of CH_2Cl_2, held at −70°C while mixing, a solution of 15.7 g (0.17 mole) of tert-butyl chloride in 15 ml of CH_2Cl_2 was added; then, a solution of 10.9 g (0.08 mole) of 2-(methylthio)thiophene [24] was added dropwise. The mixture was held 1 h at −70°C and then left for 2 days at ~20°C. Next, the reaction mass was poured onto ice, the organic layer was separated off, and the aqueous layer was extracted with methylene chloride. The extract, combined with the organic layer, was washed with water, a 1% KOH solution, and again with water, after which it was dried over $MgSO_4$. After driving off the solvent, the residue was vacuum-distilled, recovering 10.6 g (yield 68%) of a fraction with bp 125-170°C/40 mm Hg, which contained, according to the PMR data, 5-tert-butyl-2-(methylthio)thiophene (XV), 4-tert-butyl-2-(methylthio)thiophene (XVI), and 3-tert-butyl-2-(methylthio)thiophene (XVII) in a ratio of approximately 3.5:2:1. Redistillation gave a sample for analysis with bp 132°C/30 mm Hg. Found, %: C 58.65; 58.71; H 7.59; 7.69; S 33.76; 33.61. $C_9H_{14}S_2$. Calculated, %: C 58.01; H 7.57; S 34.41.

Sulfide XV. PMR spectrum ($CDCl_3$), ppm: 6.94 (1H, d, J = ~4.5 Hz, 4-H); 6.70 (1H, d, J = ~4.5 Hz, 3-H); 2.50 (3H, s, MeS); 1.40 (9H, s, CMe_3).

Sulfide XVI. PMR spectrum ($CDCl_3$), ppm: 7.10 (1H, br.s, 5-H); 6.95 (1H, br.s, 3-H); 2.55 (3H, s, MeS); 1.32 (9H, s, CMe_3).

Sulfide XVII. PMR spectrum ($CDCl_3$), ppm: 7.23 (1H, d, J = ~5.5 Hz, 5-H); 7.00 (1H, d, J = ~5.5 Hz, 4-H); 2.50 (3H, s, MeS); 1.50 (9H, s, CMe_3).

Interaction of 2,4-Dialkylthiophenes with CCl_4 and $AlCl_3$. To 0.67 g (5 mmoles) of anhydrous $AlCl_3$ in 10 ml of CH_2Cl_2, held at ~20°C with stirring, a solution of 0.77 g (0.5 ml, 5 mmoles) of CCl_4 in 10 ml of CH_2Cl_2 was added. The resulting suspension was held 10-15 min; then, at ~20°C with stirring, a solution of 4.8 mmoles of the 2,4-dialkylthiophene in 5 ml of CH_2Cl_2 was added dropwise with stirring over the course of 1 h, after which a sample of the solution was drawn for recording of the NMR spectrum. After holding at room temperature for 1-2 h in the case of compound I or three days for the other 2,4-dialkylthiophenes, the mixture was poured onto ice. The organic layer was separated off, the aqueous layer was extracted with methylene chloride, and the combined extract was washed with water, 1% NaOH solution, and again with water, after which it was dried over $CaCl_2$, the solvent was driven off, and the NMR spectra of the residue was taken. In all cases, we found the original 2,4-dialkylthiophenes. After trichloromethylation of di-tert-butylthiophene I, distillation gave a mixture with bp 140-150°C/1 mm Hg, containing the trichloride IV and the acid chloride VII in a ~3:1 ratio (according to PMR data), together with a small quantity of the original compound I.

3,5-Di-tert-butyl-2-trichloromethylthiophene (IV). PMR spectrum ($CDCl_3$), ppm: 6.91 (1H, s, 4-H); 1.55 (9H, s, 5-CMe_3); 1.37 (9H, s, 3-CMe_3). ^{13}C NMR spectrum ($CDCl_3$), ppm: 154.9 ($C_{(3)}$); 148.8 $C_{(5)}$); 137.5 ($C_{(2)}$), 127.2 ($C_{(4)}$), 92.8 (CCl_3), 36.2 and 35.3 ($\underline{C}Me_3$), 32.9 and 32.2 (CH_3).

Acid Chloride of 3,5-Di-tert-butylthiophene-2-carboxylic Acid (VII). PMR spectrum ($CDCl_3$), ppm: ($CDCl_3$): 6.98 (1H, s, 4-H); 1.63 (9H, s, 5-CMe_3); 1.40 (9H, s, 3-CMe_3). ^{13}C NMR spectrum ($CDCl_3$), ppm: 168.7 (CO), 163.2 ($C_{(3)}$), 157.9 $C_{(5)}$), 128.3 ($C_{(2)}$), 126.5 ($C_{(4)}$), 35.4 and 34.5 ($\underline{C}Me_3$), 31.4 and 29.5 (CH_3).

Reaction of 2-tert-Butylthiophene with CCl_3 and $AlCl_3$. *A*. To a suspension of 4.0 g (29 mmoles) of anhydrous $AlCl_3$ in 50 ml of CH_2Cl_2 and 2.9 ml (4.6 g, 30 mmoles) of CCl_4, a solution of 4.0 g (28 mmoles) of 2-tert-butythiophene [6] in 20 ml of CH_2Cl_2 was added dropwise at ~20°C. The resulting mixture was held 1 h at this same temperature, after which it was poured onto ice with hydrochloric acid and then treated the same as in the preceding experiment. After removing the solvent, obtained 3.5 g (yield 41%) of bis(5-tert-butyl-2-thienyl) ketone (XIII), mp 132-133°C (from hexane). An analytical sample with mp 136°C was obtained by recrystallization of compound XIII from aqueous alcohol. PMR spectrum ($CDCl_3$), ppm: 7.72 (2H, d, J = ~4.5 Hz, 3- and 3'-H); 6.93 (2H, d, J = ~4.5 Hz, 4- and 4'-H); 1.42 (18H, s, 2CMe_3). ^{13}C NMR spectrum ($CDCl_3$), ppm: 178.7 (CO); 166.5 ($C_{(5)}$ and $C_{(5')}$); 139.8 ($C_{(2)}$ and $C_{(2')}$); 133.1 ($C_{(3)}$ and $C_{(3')}$); 122.7 ($C_{(4)}$ and $C_{(4')}$); 35.2 ($\underline{C}Me_3$); 32.2 (CH_3). Found, %: C 66.84; 67.23; H 7.48; 7.52; S 20.63; 20.68. $C_{17}H_{22}S_2O$. Calculated, %: C 66.62; H 7.24; S 20.92.

B. In an analogous experiment performed with 5 ml of $ClCH_2CH_2Cl$ as the solvent, and without treating the reaction mass with water, from 0.2 g (1.4 mmoles) of the thiophene XI, obtained a mixture containing bis(5-tert-butyl-2-thienyl)chloromethyl tetrachloroaluminate XII and 5-tert-butyl-2H-thiophenium tetrachloroaluminate in a ratio ~1:2 (according to PMR data). PMR spectrum of salt XII ($ClCH_2CH_2Cl$ + $CDCl_3$) ppm: 8.43 (2H, d, J = ~4.5 Hz, 3- and 3'-H); 7.50 (2H, d, J = 4.5 Hz, 4- and 4'-H); 1.45 (18H, s, $2CMe_3$).

PMR spectrum of salt Ve ($ClCH_2CH_2Cl$ + $CDCl_3$), ppm: 8.85 (H, d, J = ~4.5 Hz, 3-H); 7.91 (1H, d, J = ~4.5 Hz, 4-H); 5.20 (2H, s, two 2-H); 1.55 (9H, s, $3CMe_3$). The spectra given for the ion Vd is in agreement with data reported in [6].

Interaction of 2-tert-Butyl-4-methylthiophene with tert-Butyl Chloride and $AlCl_3$. To a suspension of 1.4 g (10.5 mmoles) of anhydrous $AlCl_3$ in 10 ml of CH_2Cl_2 containing 0.98 g (10.5 mmoles) of tert-butyl chloride, a solution of 1.3 g (8.5 mmoles) of 2-tert-butyl-4-methylthiophene II in 5 ml of CH_2Cl_2 was added at ~20°C while stirring; during this time, the temperature of the mixture increased by 5-6°C. The mixture was held ~1 h without heating, after which it was poured onto ice and then subjected to the usual workup. Distillation gave only the original compound II. In an analogous experiment, from 40 mg (0.26 mmole) of the thiophene II, 24 mg (0.26 mmole) of t-BuCl, and 87.5 mg (0.65 mmole) of $AlCl_3$ in 0.5 ml of CD_2Cl_2, the reaction mixture was not treated with water; as shown by the NMR spectra (Tables 1 and 2), it contained 2,5-di-tert-butyl-3-methyl-2H-thiophenium tetrachloroaluminate XVIII and 5-tert-butyl-3-methyl-2H-thiophene Vc.

REFERENCES

1. L. I. Belen'kii, D. B. Brokhovetskii, and M. M. Krayushkin, Chem. Scripta, **29**, 81 (1989).
2. L. I. Belen'kii, G. P. Gromova, and M. M. Krayushkin, Gazz. Chim. Ital., **120**, 365 (1990).
3. G. P. Gromova, L. I. Belen'kii, and M. M. Krayushkin, Khim. Geterotsikl. Soedin., No. 8, 1046 (1993).
4. L. I. Belen'kii, G. P. Gromova, and M. M. Krayushkin, Khim. Geterotsikl. Soedin., No. 8, 1040 (1993).
5. L. I. Belen'kii, A. P. Yakubov, and Ya. L. Gol'dfarb, Zh. Org. Khim., **11**, 424 (1975).
6. L. I. Belen'kii and A. P. Yakubov, Tetrahedron, **40**, 2471 (1984).
7. H. Hogeveen, R. M. Kellog, and K. A. Kuindersma, Tetrahedron Lett., No. 40, 3929 (1973).
8. Yu. I. Lyakhovetskii, Candidate's Dissertation, Institute of Heteroorganic Compounds, Moscow (1982), p. 26.
9. G. A. Olah, A. L. Berrier, and G. K. S. Prakash, J. Org. Chem., **47**, 3903 (1982).
10. U. S. Rachenla, T. Daniel, P. R. Rajamohanan, and N. P. Ayyangar, J. Am. Chem. Soc., **111**, 7659 (1989).
11. M. M. Krayushkin, A. A. Loktionov, and L. I. Belen'kii, Khim. Geterotsikl. Soedin., No. 8, 1037 (1988).
12. U. E. Wiersum and H. Wynberg, Tetrahedron Lett., No. 31, 2951 (1967).
13. D. Brearley, G. B. Kistiakovsky, and C. H. Stauffer, J. Am. Chem. Soc., **58**, 43 (1936).
14. G. B. Kistiakovsky and C. H. Stauffer, J. Am. Chem. Soc., **59**, 165 (1937).
15. K. E. Howlett, J. Chem. Soc., No. 6, 1409 (1951).
16. H. H. Schlubach and V. Franzen, Annalen, **583**, 93 (1953).
17. F. E. Condon, J. Org. Chem., **21**, 761 (1956).
18. M. Tashiro, Synthesis, No. 12, 921 (1979).
19. L. Lunazzi, A. Mangini, G. Placucci, P. Spagnolo, and M. Tiecco, J. Chem. Soc., Perkin Trans. II, No. 2, 192 (1972).
20. L. I. Belen'kii, A. P. Yakubov, and I. A. Bessonova, Zh. Org. Chim., **13**, 364 (1977).
21. L. I. Belen'kii and A. P. Yakubov, Tetrahedron, **42**, 759 (1986).
22. J. Sice, J. Am. Chem. Soc., **75**, 3697 (1953).
23. H. Hinrichs and P. Margaretha, Chem. Ber., **125**, 2311 (1992).
24. Ya. L. Gol'dfarb, M. A. Kalik, and M. L. Kirmalova, Zh. Org. Khim., **29**, 2034 (1959).