

REARRANGEMENT IN THE SERIES OF ARYL-SUBSTITUTED DIHYDROTHIOPHENOCYCLOALKANONES AND THE INFLUENCE OF CARBOXYLIC ACID CHLORIDES ON THIS PROCESS

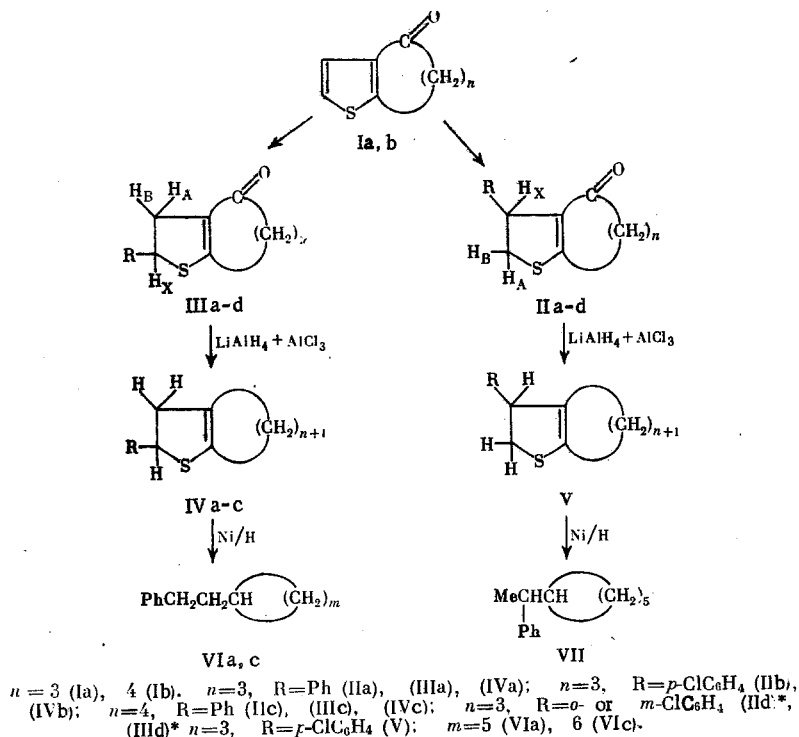
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We have already shown [1] that by the action of monoethyl oxalate acid chloride (AC) in the presence of AlCl_3 on a solution of thiophenocycloalkanones (Ia) and (Ib) in benzene (see scheme below), besides the ester of benzoylpropionic acid, compounds (IIa) and (IIc) are formed, which can formally be regarded as adducts of these compounds with benzene. Further study of this process showed that AC in a specific way influences the formation of compounds (II), apparently independent of it, but the nature of this action is not yet clear. In the present article, we give new experimental data related to this problem, although they do not completely solve the problem.

We should note that during a more thorough study of the reaction products, we detected small amounts of compounds (IIIa) and (IIIc), isomeric with the adducts (IIa) and (IIc). In a series of the experiments without AC the formation of a mixture of compounds (IIIa) and (IIa) was also observed, but with a considerable predominance of (IIIa). In the absence of AC, the reaction of ketone (Ia) with chlorobenzene leads to compound (IIIb); isomer (IIb) could not be isolated in this case. In the presence of acetyl chloride in the initial mixture, the direction of the process changed in favor of isomer (IIb); isomer (IIIb) was isolated in a small amount only.

Scheme 1

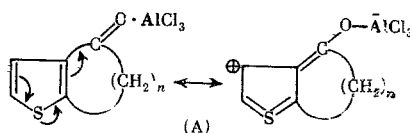


*Adducts isomeric with compounds (IIb) and (IIIb) with chlorine atoms in the o or m position (see below).

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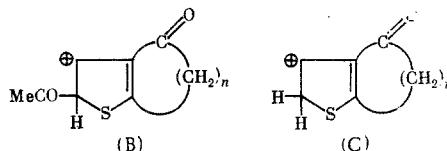
Thus, in the mixture of aryl-substituted 2,3-dihydrothiophenocycloalkanones, the isomer with the substituting group in position 2 predominates if the reaction takes place in the absence of AC; in the presence of AC, the main product is 3-substituted isomer. Hence, the nature of AC does not influence the direction of the process.

From the above data we can assume, as already stated in [1], that in the absence of AC a hetarenium cation (C) is formed, which as the result of electrophilic attack forms 3-phenyl-substituted thiophenocycloalkanones. Of the two systems, benzene and thiophenocycloalkanone, present in the reaction mixture, benzene, clearly, initiates the formation of the protonating agent, in this case HAlCl_4 . In fact, under these conditions, thiophenocycloalkanone is deactivated as an aromatic system.



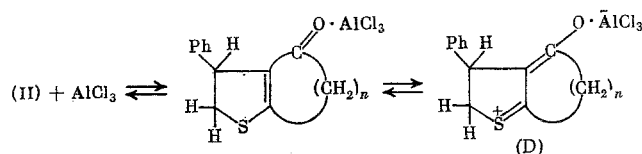
The fact that in the canonical form this corresponds to a structure of a ring with a tetravalent sulfur does not contradict existing assumptions, as compounds of this type are known (see [2]).

In complex (A), the positive charge, as in the case of the hetarenium ion, is localized at position 3, and therefore the formation of compounds (II) can be described also without taking into account the assumption on the participation of the σ complex in the process. However, it appears that we have to take into account the fact that the acylium salt $\text{R}^+\text{COAlCl}_4$ formed at the beginning can serve as a "supplier" of an acylium cation stronger than a proton, which, in parallel with the attack on benzene, reacts with thiophenocycloalkanone (I) to form a σ complex (B). The latter, under the action of acid HAlCl_4 , formed during the acylation of benzene (see above – the formation of benzoylpropionic acid), is apparently able to be converted into complex (C). In this connection, we should note that complexes of type (B), but with a different counterion, have been described [3]

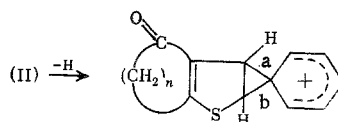


The most interesting of the above phenomena is the formation of mixtures of aryl-substituted isomers with a predominance of one of them, depending on the reaction conditions (with or without AC). In any interpretation of the process, we have to take into account the fact that the positive charge in the initially formed system is localized at position 3. For this reason, the 3 position is first always occupied by phenyl. It follows that 2-aryl-substituted derivatives are formed from 3-substituted ones as the result of a rearrangement. We confirmed this experimentally. On boiling with AlCl_3 in an excess of benzene, isomer (IIa) is transformed into the 2-substituted isomer (IIIa) in a 60% yield. Under similar conditions, isomerization in an opposite direction is observed, although the isomer is formed in a smaller amount.

The problem of the mechanism of the rearrangement should not be considered as conclusively solved, but we believe that most probable pattern of the relationships existing here is the following. The complexes of the ketones studied with AlCl_3 in a solution, clearly exist in the form of an equilibrium system



Thus, it becomes possible for an intermolecular transfer of the hydride ion with the formation of a phenonium cation



Aluminum chloride or the polarized complex (D) can serve as acceptor of the hydride ion. According to [4], in intermediate forms carrying the phenonium cation, the positive charge may be concentrated in the

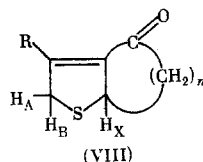
TABLE 1. Parameters of PMR Spectra of 2,3-Dihydrothiophenocycloalkanones (II) and (III)

Adduct	Solvent	H _A	H _B	H _X	H _{arom}	H _{aliph}	J _{AB}	J _{AX}	J _{BX}	J _{X, CH₂}	J _{ACH₂}
(IIa)	CCl ₄	3,00	3,67	4,45	7,12	2,00÷2,50	11,5	10,0	3,0	1,0	—
(IIc)	CCl ₄	2,88	3,62	4,58	7,12	1,75÷2,43	11,5	10,0	3,5	1,0	—
(IIb)	CDCl ₃	3,03	3,75	4,52	7,23	1,60÷2,80	11,5	9,7	3,0	2,5	—
(IIId)	CDCl ₃	2,95	3,75	4,97	6,05÷7,25	1,72÷2,78	11,5	10,0	3,5	3,0	—
(IIIa)	CCl ₄	3,07	3,33	4,82	6,92÷7,38	1,75÷2,67	16,0	9,1	8,4	—	2,0
(IIIc)	CCl ₄	3,29	3,48	4,75	6,88÷7,55	1,47÷2,85	16,0	9,1	8,3	—	3,0
(IIId)	CCl ₄	3,02	3,33	4,82	7,18	1,80÷2,18	16,0	9,9	7,5	—	2,0
(IIIb)	CCl ₄	3,16	3,38	5,10	6,68÷7,76	1,65÷2,75	16,5	9,4	5,8	—	2,0

three-membered ring, and consequently, distributed over all the atoms of the benzene ring. This lowers the energy level of the transition form, which leads to acceleration of the process. It can easily be seen that cleavage of the *a* bond during attack by the hydride ion leads to a 2-substituted isomer, and cleavage at the *b* bond to the 3-substituted isomer. The rearrangement of ketone (IIIa) can take place similarly.

At present it is impossible to answer the question as to the nature of the influence of AC on the isomerization of aryl-substituted dihydrothiophenocycloalkanones. It is, however, clear that in the presence of AC, a large part of AlCl₃ is bound into a complex, and thus there is insufficient free AlCl₃ in the mixture to effect the isomerization.

Of the seven structures possible for the reaction products, from the PMR data (Table 1), we can exclude, as in the case of R = Ph [1], those in which the H atoms are attached to double-bonded C atoms of the heterocyclic ring, and also structure (VIII) in which the spin-spin bond of the proton H_X with H_A and H_B would be considerably weaker, i.e., J_{AX} and J_{BX} would have considerably lower values than those listed in Table 2.



Thus, the compounds studied have structure (II) or (III). The position of substituent R in (II) and (III) was established by PMR spectra of compounds (VI) and (VII) obtained from (II) and (III) by reactions shown in Scheme 1 (the PMR spectra are listed in the experimental part).

The conclusions from the PMR spectra are also confirmed by the ¹³C NMR spectra (for n = 3), in which the splittings of the lines of vinyl C atoms with ¹J_{C,H} are missing, and there are four triplets with ¹J_{C,H} = 129-146 Hz, indicating the presence of four CH₂ groups in dihydrothiophenocycloalkanones (see Table 2).

Isomers (II) and (III) differ in the following spectral characteristics: in the ¹³C NMR spectra, the spin-spin coupling constants ¹J_{HA} and ¹J_{HB} in (II) are 11-14 Hz higher than in (III), while J_{HX} is by 6-11 Hz lower than in isomer (II). Moreover, the δ CH_X is lower for (II), while δ =CS is higher for (II). In the PMR spectra of isomer (II), a greater difference in the chemical shifts of H_A and H_B is observed, namely, 0.67-0.80 ppm, compared to 0.19-0.31 ppm for isomer (III). In the spectra of (II) there are also much greater differences in the values of J_{AX} and J_{BX}.

As already mentioned, in the adducts of thiophenocycloalkanones with chlorobenzene, chlorine is present in different positions. The *p* position of the chlorine atom in substituent R in isomers (IIb) and (IIIb) (see Table 2) follows from the presence of two *o*- and two *m*-C atoms equivalent in pairs in the ¹³C NMR spectra, and also from the transformation of the aromatic protons singlet in the PMR spectrum (with a width of 0.6 Hz) into a spectrum of an AB spin system (J_{AB} = 8.7 Hz) with broadened components, when Eu(fod)₃ is added to (IIIb). The observed shift in pairs into the weaker field of the two *o* and two *m* protons is possible only if chlorine is present in the *p* position.

For compounds (IIId) and (IIIId) (see Tables 1, 2), a nonequivalency of all the aromatic ¹³C nuclei in the ¹³C NMR spectrum is observed, while in the PMR spectrum, there is a complex multiplet of aromatic protons. This indicates the presence of chlorine in the *o* or *m* position.

EXPERIMENTAL

The ¹³C NMR spectra were run on the "Brucker WP-60" spectrometer (15.08 MHz) in a pulse regime, using Fourier transformation. The chemical shifts of ¹³C nuclei were obtained in experiments on ¹H-{¹³C}

TABLE 2. Parameters of ^{13}C NMR Spectra of 2,3-Dihydrothiopheno-cycloalkanones (II) and (III) at $n = 3$

Adduct	Sol-vent	$\delta\text{CH}_2(^1J_{\text{CH}})$	$\delta\text{CH}_X(^1J_{\text{CH}})$	$\delta\text{CH}_A\text{H}_B \times \times (^1J_{\text{CH}})$	$\delta\text{C}=\text{}$	$\delta\text{C}=\text{S}$	$\delta\text{C}=\text{O}$	δR
(IIa)	CCl_4	23,43 (130) 27,07 (130) 37,15 (131)	50,45 (140)	40,61 (144)	143,09	166,83	192,03	126,94; 127,13 128,76; 135,44
(IIb)	CDCl_3	23,43 (132) 27,01 (131) 37,03 (130)	49,78 (138)	40,37 (146)	141,64	167,19	191,84	128,40; 128,83 132,71; 132,02
(IIc)	CDCl_3	23,49 (131) 27,20 (130) 37,03 (130)	47,17 (135)	39,70 (145)	139,27	169,08	191,85	127,08; 127,37 128,34; 129,98 133,44
(IIId)	CCl_4	23,19 26,17 36,24	51,66	41,22	140,49	162,34	190,41	128,40; 128,71 130,71; 133,25
	CDCl_3	23,43 (131) 26,59 (129) 36,73 (130)	51,96 (144)	41,16 (132)	140,79	165,01	192,81	128,52; 129,07 130,83; 133,68
(IIIc)	CDCl_3	23,43 (131) 26,52 (130) 36,66 (130)	48,50 (146)	39,09 (134)	139,63	164,58	192,33	127,49; 127,73 128,94; 129,67 130,76; 133,13

NMR with a complete decoupling from protons with reference to TMS (internal standard; ± 0.06 ppm). The spin-spin coupling constants were measured from high-resolution spectra obtained under "gated decoupling" regime (± 0.9 Hz). The PMR spectra were run on the "Varian DA-60-IL" spectrometer (60 MHz), with TMS as an internal standard; (± 0.01 ppm). The $J_{\text{H,H}}$ constants given are accurate to within ± 0.2 Hz.

2-Phenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIIa). A 29.4-g portion of anhydrous AlCl_3 was added gradually at $5-10^\circ\text{C}$ to a solution of 12 g (0.079 mole) of (Ia) in 100 ml of benzene. The mixture was heated for 30 min at 70°C , and then poured onto a mixture of 150 g of ice with 20 ml of concentrated HCl. The organic layer was washed with dilute HCl, a solution of sodium carbonate, and water, and dried over MgSO_4 . By distillation, 14.76 g (81%) of a viscous oil, bp $188-195^\circ\text{C}$ (5 mm), were obtained, containing (GLC) 17% of (IIa) and 83% of (IIIa). A 14.7-g portion of the mixture of ketones was converted into a mixture of oximes (10.4 g, yield 66%), which on recrystallization from alcohol, gave 8.8 (85%) of oxime of ketone (IIIa), mp $188-189^\circ\text{C}$. Found: C 69.04; H 6.13; N 5.70; S 13.02%. $\text{C}_{14}\text{H}_{15}\text{NOS}$. Calculated: C 68.54; H 6.16; N 5.71; S 13.08%. By heating with dilute HCl, this oxime was converted into ketone (IIIa) (oil), yield 66%, bp $202-205^\circ\text{C}$ (7 mm); n_D^{20} 1.6375; mol. wt. 230 (here and forthwith, mass-spectrometrically). Found: C 72.87; H 6.05; S 13.92%. $\text{C}_{14}\text{H}_{14}\text{OS}$. Calculated: C 73.00; H 6.13; S 13.92%.

2-Phenyl-2,3,5,6,7,8-hexahydro-4H-cyclopenta[b]thiophen-4-one (IIIc). A 14.5-g (0.1 mole) portion of AlCl_3 was added with ice-cooling to a solution of 6 g (0.036 mole) of (Ib) in 50 ml of benzene. The mixture was heated for 30 min at 70°C , and poured onto a mixture of ice and HCl. From the organic layer, 9.12 g (60%) of an oil, bp $192-195^\circ\text{C}$ (5 mm) were isolated; n_D^{20} 1.6298; on storage, the oil partially crystallized. The product contained 15% of (IIc) and 85% of (IIIc) (GLC). After three recrystallizations from a mixture of hexane with toluene, a pure ketone (IIIc), mp $38-39^\circ\text{C}$, was obtained; mol. wt. 244. Found: C 73.64; H 6.62; S 13.10%. $\text{C}_{15}\text{H}_{16}\text{OS}$. Calculated: C 73.71; H 6.60; S 13.12%. Oxime of ketone (IIIc), mp $132-133^\circ\text{C}$ (from aqueous alcohol). Found: N 5.35%. $\text{C}_{15}\text{H}_{17}\text{NOS}$. Calculated: N 5.35%.

2-p-Chlorophenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIId). A 14.7-g (0.1 mole) portion of AlCl_3 was added at $18-23^\circ\text{C}$ to a solution of 6 g (0.04 mole) of (Ia) in 57 ml of chlorobenzene. The mixture was boiled for 30 min and poured onto a mixture of ice and HCl. The organic layer was diluted with ether and washed with solutions of Na_2CO_3 and NaCl. By distillation, 9.1 g of an oil, bp $218-226^\circ\text{C}$ (5 mm) were isolated; this was a mixture of three compounds (GLC). Heating with NH_2OH in an aqueous-alcoholic solution yielded a mixture of oximes, which after recrystallization from alcohol, gave 2.02 g of the oxime of ketone (IIId), mp $176-177^\circ\text{C}$. Found: N 5.21%. $\text{C}_{14}\text{H}_{14}\text{ClNOS}$. Calculated: N 5.01%. From the mother liquor, the oxime of ketone (IIId), mp $174-175^\circ\text{C}$ (from alcohol) was isolated. Found: N 5.51. $\text{C}_{14}\text{H}_{14}\text{ClNOS}$. Calculated: N 5.01%. A mixture of these two oximes melted at $123-126^\circ\text{C}$. The suspension of 6.3 g of the oxime of ketone (IIId) in dilute HCl was boiled for 3 h to yield 5.84 g of ketone (IIId), mp $87-88^\circ\text{C}$ (from alcohol). Found: C 63.81; H 4.93; Cl 13.58; S 12.27%; mol. wt. 264.5. $\text{C}_{14}\text{H}_{13}\text{ClOS}$. Calculated: C 63.50; H 4.95; Cl 13.39; S 12.11%.

Action of AlCl_3 on 3-Phenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIa). A 5-g (0.04 mole) portion of AlCl_3 was gradually added at $20-25^\circ\text{C}$ to a stirred solution of 2 g (0.0087 mole) of ketone (IIa) in 20 ml of

benzene. The mixture was boiled for 30 min, and then poured onto ice with 5 ml of HCl. The organic layer was washed with solutions of NaCl and sodium carbonate, and dried over MgSO_4 . After distillation, 1.82 g of an oil was obtained, bp 190–193°C (3 mm), consisting of the initial ketone and a new compound (GLC). This mixture was boiled with an aqueous-alcoholic solution of NH_2OH . An oxime was obtained (yield, 60%) melting at 188–190°C; its mixture with the oxime of ketone (IIIa) melted at 188–190°C.

Action of AlCl_3 on 2-Phenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIIa). The experiment was carried out by a similar procedure. The reaction product contained, besides the initial ketone, 28% of (IIa), and an unidentified compound (GLC).

2-Phenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophene (IVa). To a suspension of 1.85 g (0.053 mole) of LiAlH_4 in 100 ml of absolute ether, 13 g of AlCl_3 were gradually added at 0°C, and then at 5–10°C, a solution of 6.5 g (0.03 mole) of ketone (IIIa) in 100 ml of absolute ether. The mixture was boiled for 30 min, cooled to 0°C, and at $\leq 10^\circ\text{C}$, 120 ml of dilute HCl were added. The ether layer was separated, and the aqueous layer extracted with ether. The extracts were treated with dilute HCl, washed twice with a saturated solution of NaCl, and dried over MgSO_4 . After distillation, 4.45 g (73%) of (IVa), bp 156–158°C (6 mm), were obtained; n_D^{20} 1.5965. Found: C 77.77; H 7.40; S 14.43%; mol. wt. 216. $\text{C}_{14}\text{H}_{16}\text{S}$. Calculated: C 77.72; H 7.46; S 14.82%. Compound (IVa) contained 1% of the initial ketone. IR spectrum of (IVa) (ν , cm^{-1}): 1710 (C=O), 1655 (C=C), 3000–3100, 1500 and 1600 (monosubstituted phenyl); the frequency of the OH bond is absent.

2-Phenyl-2,3,5,6,7,8-4H-cyclohepta[b]thiophene (IVc). This was obtained similarly to (IVa), yield 76%. The product contained a small amount of the initial ketone (IIIc), bp 170–173°C (5 mm); n_D^{20} 1.5932. Found: C 77.61; H 7.74; S 14.14%; mol. wt. 230. $\text{C}_{15}\text{H}_{18}\text{S}$. Calculated: C 78.26; H 7.88; S 13.92%.

2-p-Chlorophenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophene (IVb). Compound (IVb) was obtained by the reduction of ketone (IIb) with LiAlH_4 in absolute ether in the presence of AlCl_3 . Yield 95%, bp 186–190°C (5 mm); n_D^{20} 1.5990. Found: C 67.00; H 6.18; Cl 13.84; S 12.52%. $\text{C}_{14}\text{H}_{15}\text{ClS}$. Calculated: C 67.05; H 6.03; Cl 14.4; S 12.81%.

β -Cyclohexylethylbenzene (VIa). A 15-g portion of Raney nickel catalyst (stored under CH_3OH) was added to a solution of 3.06 g (0.014 mole) of (IVa) in 75 ml of hot CH_3OH . The suspension was stirred at 55–60°C to a negative reaction for S (12 h); nickel was filtered and washed several times with CH_3OH . Distillation of the filtrates yielded 1.84 g (69%) of (VIa), bp 105–107°C (5 mm); n_D^{20} 1.5158; d_4^{20} 0.924. Found: C 89.54; H 10.71%. $\text{C}_{14}\text{H}_{20}$. Calculated: C 89.29; H 10.70%; compare [5]. Compound (VIa) was obtained also by treating a solution of (IVb) in CH_3OH with Raney nickel catalyst; yield 78%, bp 120–122°C (7 mm); n_D^{20} 1.5139; d_4^{20} 0.925. According to GLC data, the product contained an admixture of an unidentified compound. PMR spectrum (δ , ppm): 0.55–2.05 m (6CH_2), 2.22–2.28 m ($=\text{CCH}_2$, CH), 6.72–7.30 m (C_6H_5).

β -Cycloheptylethylbenzene (VIb). This compound was obtained from (IVc) similarly to (VIa), yield 75%, bp 150–152°C (10 mm); n_D^{20} 1.5195; mol. wt. 202. Found: C 88.87; H 11.09%. $\text{C}_{15}\text{H}_{22}$. Calculated: C 89.04; H 10.96%. PMR spectrum (δ , ppm): 0.95–2.22 m (7CH_2), 2.22–1.80 m ($=\text{CCH}_2$, CH), 6.78–7.30 m (C_6H_5).

3-p-Chlorophenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIb) and 3-o (or m)-Chlorophenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophen-4-one (IIc). To a solution of 6 g (0.039 mole) of (Ia) in 57 ml of chlorobenzene, 14.7 g of AlCl_3 was gradually added at 8–12°C, and then at 3–5°C, a solution of 6 g (0.076 mole) of CH_3COCl in 50 ml of chlorobenzene. The mixture was stirred for 30 min at 20°C and for 30 min at the boiling point, cooled and poured onto ice with HCl. After the usual treatment, p-chloroacetophenone was isolated in a yield of 43.5%, bp 88–98°C (5 mm); n_D^{20} 1.5585. Semicarbazone, mp 202–204°C (alcohol) compare [6]. Besides p-chloroacetophenone, 8.9 g (85%) of ketones, bp 210–220°C (3 mm) were obtained, whose crystallization from alcohol gave 5.35 g of ketone (IIb), mp 121–122°C. Found: C 63.62; H 4.90; Cl 13.33; S 12.06%. $\text{C}_{14}\text{H}_{13}\text{ClOS}$. Calculated: C 63.50; H 4.95; Cl 13.39; S 12.11%. Oxime, mp 151–152°C (alcohol). Found: N 5.05%. $\text{C}_{14}\text{H}_{14}\text{ClNOS}$. Calculated: N 5.01%. From the mother liquor, 0.8 g of ketone (IIb) and 1.5 g of ketone (IIc), mp 128–130°C, were isolated. Found: C 63.51; H 5.01; Cl 13.38; S 12.10%. $\text{C}_{14}\text{H}_{13}\text{ClOS}$. Calculated: C 63.50; H 4.95; Cl 13.39; S 12.11%.

3-p-Chlorophenyl-2,3,4,5,6,7-hexahydrobenzo[b]thiophene (V). By the action of 2.5 g of LiAlH_4 and 15 g of AlCl_3 on 10.64 g of (IIb), under conditions similar to those for (IVb), 7.14 g of (V), bp 187–190°C (5 mm), were obtained; n_D^{20} 1.6049. Found: C 67.06; H 5.86; Cl 14.05; S 12.70%. $\text{C}_{14}\text{H}_{15}\text{ClS}$. Calculated: C 67.05; H 6.03; Cl 14.14; S 12.81%. The data of IR spectrum showed that the product did not contain CO and CHOH groups.

α -Cyclohexylethylbenzene (VII). Compound (VII) was obtained from (V) in the same way as (IVa); yield 78%, bp 118–120°C (6 mm); n_D^{20} 1.5195; d_4^{20} 0.9407; compare [1]. Found: C 89.16; H 10.77%. $\text{C}_{14}\text{H}_{20}$. Calculated: C 89.29; H 10.70%. PMR spectrum (δ , ppm): 1.15 d (CH_3 , $J = 7.0$ Hz), 2.35 dq. (CH , $J = 7.0$ Hz), 0.75–2.00 m (5CH_2 , CH), 6.77–7.40 m (C_6H_5).

CONCLUSIONS

1. The primary products of the reaction of thiophenocycloalkanones with benzene or chlorobenzene in the presence of AlCl_3 are 3-aryl-substituted 2,3-dihydrothiophenocycloalkanones.
2. 2- and 3-Substituted compounds of this type isomerize into one another by the action of AlCl_3 .

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ELECTROREDUCTION IN THE SERIES OF THIOPHENE DERIVATIVES

II.* ELECTROSYNTHESIS OF 2,5-DIHYDROTHIOPHENE-2-CARBOXYLIC ACIDS

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In recent years, great attention is being paid [2-4] to the development of methods for the preparation of dihydro derivatives of thiophene because of the interesting possibilities of using them in synthesis [2, 5]. In particular, methods of electrochemical synthesis, by carrying out both anodic [6] and cathodic [1] processes, are very promising. Previous studies [1] on the conditions of electrolysis of thiophene-2-carboxylic acid on mercury led to the development of an original method for the preparation of its 2,5-dihydro derivative. It was necessary to clarify the influence of the introduction of substituents into the thiophene ring on the process of the electrochemical hydrogenation, and on the position of the double bond in the dihydro products, since the stability of this bond is very dependent on the nature of its substitution.

For the electrochemical reduction, we chose thiophenecarboxylic acids (II), obtained by hypobromite oxidation of the corresponding acetothienones (I). Compounds (Ia) [7] and (Ib) [8] were synthesized by known methods, while (Ic) was obtained by reductive dechlorination of 5-methyl-4-chloromethyl-2-acetothienone [9] by the method given in [8].

Thiophenecarboxylic acids (II) were electrolyzed under previously found optimal conditions [1], i.e., at a discharge potential of Li on the background of a 2 M aqueous solution of LiOH. It was found that the reduction of these compounds leads to a high material yield (~90%) of the corresponding 2,5-dihydro acids (III), converted into the corresponding methyl esters (IV). Thus, the introduction of methyl substituents into the thiophene ring does not affect the direction of the electrochemical process.

It was therefore interesting to study the reduction of a more complex compound, and we choose a functionally substituted dicarboxylic acid (X) for this purpose. We therefore synthesized the intermediate thiophenecarboxaldehyde (IX) by the condensation of Li salt (V) with iodoacetal (VII), obtained from the chloride (VI) by the Finkelstein reaction, starting from the known [10] chloroaldehyde (VIII). The oxidation of the

*Article I, see [1].

†Deceased.