<u>Condensation of N-Chloroacetamidoacetone (IX) with 2,5,6-Triamino-4-hydroxypyrimidine (XI)</u>. With stirring, to a mixture of 0.63 g of (IX) and 0.5 g of sulfate (XI) in 8 ml of water was gradually added 2.5 ml of Et₃N and the mixture was stirred for another 12 h at 20°. To the reaction mixture was added 10% KOH solution until all of the precipitate had dissolved, after which the solution was heated for 10 min at 100°, acidified with AcOH to pH 6-6.5, and the precipitate was filtered, washed in succession with water, acetone, and ether, and dried at 100° in vacuo. We obtained 0.31 g (84%) of 7-methylpterin (X), decomposition point > 360°, R_f 0.47 (i-PrOH-H₂O-NH₄OH, 7:2:1, fluorescent spot in UV light). In its R_f, UV, IR, and PMR spectra the obtained 7-methylpterin coincided with an authentic specimen [6].

Acetamidoacetone (Ia) itself does not react with sulfate (XI) under the above indicated conditions.

CONCLUSIONS

1. The bromination of acetamidoacetone and 1-benzamido-2-butanone in $CHCl_3$ or AcOH respectively gives 1-bromo-3-acetamidoacetone and 1-benzamido-3-bromo-2-butanone.

2. The reaction of 1-bromo-3-acetamidoacetone and 1-benzamido-3-bromo-2-butanone with thioacetic acid salts respectively gives 1-acetamido-3-acetylmercaptoacetone and 1-benzamido-3-acetylmercapto-2-butanone, while reaction with piperidine gives 1-acetamido-1-piperidinoacetone and 1-benzamido-1-piperidino-2-butanone.

3. N-Chloroacetamidoacetone was obtained by the chlorination of acetamidoacetone with sulfuryl chlor-ide.

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ELECTROPHILIC CYCLIZATION OF 2-GERANYLTHIOPHENE

AND ITS 5-CARBOXY DERIVATIVE*

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The electrophilic cyclization of 1,5-polyenes, containing either an olefinic or acetylenic fragment (terminator) in the homoallylic position to the terminal multiple bond, is accompanied by the formation of a fivemembered ring, which is used to build hydrindan and perhydrocyclopentanophenanthrene skeletons [2-4]. Recently, it was shown that the thiophene ring can be used in an analogous cyclization, which leads to the formation of cyclohexano[b]thiophene derivatives [5, 6]. In order to have access to compounds of the hydrindan series and, in the final analysis, to perhydrocyclopentanophenanthrenes we studied the electrophilic cyclization of the previously unknown 2-geranylthiophene (Ia) and the corresponding 5-carboxylic acid (Ib), containing the thienyl group as the terminator in the allylic position to the terminal double bond, which were obtained in respective yields of 90 and 80% by the following scheme:



*See [1] for preliminary communication. † Deceased.

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Sub- strate	Cyclization conditions				Products.	Viold
	agent/solvent	agent/substrate (moles)	т., ℃	time, min	ratio	<i>%</i>
(Ia) (Ia) (Ib) (Ib) (Ib) (Ib)	$\begin{array}{l} H_2SO_4/EtNO_2\\ SnCl_4/MeNO_2\\ CF_3CO_2H/CH_2Cl_2\\ H_2SO_4/EtNO_2\\ H_2SO_4/EtNO_2\\ SnCl_4/CH_2Cl_2 \end{array}$	5,0 1,0 2,5 5,0 5,0 3,0	$ \begin{vmatrix} -40 \\ 16 \\ 40 \\ 0 \\ 0 \\ 20 \end{vmatrix} $	30 30 90 30 5 72 h	(IV) (IV) (IIa) + (IIIa), 4:1 (IIb) + (IIIb), 7:3 (IVb) + (Vb), 2:1	80 66 64 60 62 59

TABLE 1. Conditions and Results of Cyclizing Geranylthiophenes(I)

TABLE 2. Chemical Shifts of Signals of Methyl Groups of Hydrindanothiophenes (IVa), (IVb), and (V), ppm

Compound	a-CH₃ at C ⁸	e-CH ₃ at C ⁸	$\begin{array}{c} CH_{3}\\ at C^{4} \end{array}$	
(IVa) (IVb) (V)	0,93 0,92 0,96	1,09 1,08 1,02	$ \begin{array}{c c} 1,39\\ 1,40\\ 1,28 \end{array} $	

To cyclize (I) we used anhydrous H_2SO_4 , $SnCl_4$, and CF_3COOH under the conditions given in Table 1.



 $\mathbf{R} = \mathbf{H}$ (a), COOH (b).

The obtained results testify to the important effect exerted by the nature of the electrophilic agent on the cyclization process. Thus, for (Ia) the best result was obtained with H_2SO_4 , whereas CF₃COOH leads only to thienyl-substituted monocyclic products (IIa) and (IIIa). The insertion of the electronegative carboxy group into the thiophene ring changes the order in the efficiency of the cyclizing agents, and tricyclic compounds (IVb) and (Vb) can be obtained when using SnCl₄. The use of H_2SO_4 (0°C, 5 min) gives only a mixture of the transformation products of the geranyl portion of the molecule, namely (IIb) and (IIIb), while increasing the reaction time up to 30 min leads to the pure β -isomer (IIIb) without forming the tricyclic compounds. Treatment of the mixture of neryl- and geranylthiophenes (7:3) with H_2SO_4 gave only (IVa), which testifies to the insensitivity of the reaction to the geometry of the double bond next to the terminator. An interesting fact of some change in the stereochemistry of the tricyclic products as a function of the nature of the substituent in the thienyl ring was established on the example of cyclizing acid (Ib). Here, together with the desired (IVb), was obtained trans-isomer (V). The last two results enabled us to analyze the later discussed theory regarding the reaction mechanism observed by us.

The structure of the obtained compounds and the composition of the mixed cyclization products were determined employing PMR and GLC. The structure of cyclogeranyl derivatives (IIa)-(IIIb) unequivocally follows from the PMR spectral data, which have the signals of the fragments Me_2C and MeC = C. In addition, partial cyclization is confirmed by the fact that a part of the spectrum, relating to the aromatic protons, remains unchanged when compared with the same portion in the spectra of the starting compounds.

The PMR spectra of the tricyclic products (IVa), (IVb), and (V) testify to the fact that their molecules contain, besides a geminal dimethyl group, also an angular methyl group, in which connection the chemical shift value of the latter (Table 2) enables making a reliable decision as to the manner in which rings A and B are coupled in these compounds.

Thus, the singlet signal of $C^4 - CH_3$ in the spectra of (IVa) and (IVb) is located downfield when compared with the corresponding signal in the spectrum of (V), while the difference in the chemical shift values of the protons of the gem-dimethyl group for this pair of products is greater than the corresponding difference for compound (V). Consequently, in harmony with the data given in [7, 8], hydrindanothiophenes (IVa) and (IVb) were assigned a cis-, while (V) was assigned a trans-coupling of rings A and B.

The stereochemistry of the coupling of the rings in compounds (IVa) and (IVb) was proved independently by converting them to the known [9] cis-bicyclolactone of geranylacetic acid (VIII).



For this purpose hydrindanothiophene (IVa) was converted to acid (IVb), the reductive desulfurization of which with Li in NH₃ at 25° [10] gave in satisfactory yield a mixture of acids (VI), which, based on the PMR spectral data, contained 80% of the isomer with an exocyclic double bond. A quantitative estimate of the composition of the mixed (VI) acids was made on the basis of comparing the integral intensities of the doublet signal of the α -methylene protons for the isomer with an exocyclic C = C bond (δ 2.87 ppm, J = 7.5 Hz) and the singlet signal of the CH₃O group (δ 3.59 ppm) of the corresponding methyl esters, which were obtained from the (VI) acids by treatment with CH₂N₂. Their ozonolysis led to the previously unknown hydrindanone (VII), which by treatment with CH₃CO₃H at 50° was converted in 70% yield to δ -lactone (VIII).

The observed course of the cyclization of the (I) compounds can be interpreted in the following manner. Apparently, the primary process is the formation of α -cyclogeranyl derivatives (IIa) and (IIb), which corresponds to the former data on the electrophilic cyclization of analogous compounds on the type of pseudoionone, geraniol and its ethers, and geranoic acid [11-14]. Previously it was shown that the closure of ring B for the α -cyclogeranyl derivatives leads mainly to the cis-A/B products, whereas the β -isomers give products with a trans-compling of the A/B rings [15, 16]. On the basis of these rules it may be assumed that the formation of the tricyclic derivative (IVa), with a cis-coupling of the rings, proceeds via cyclization of the α -isomer (IIa). When the electron-acceptor carboxyl grouping is present in the (Ib) molecule, the electrophilic cyclization involving the thiophene nucleus is sharply hindered. As a result, a substantial portion of the α -cyclogeranyl product (IIb) succeeds in isomerizing to the β -isomer (IIIb), the subsequent cyclization of which gives trans-isomer (V).

EXPERIMENTAL

The IR spectra were obtained on a UR-20 instrument as CCl_4 solutions. The UV spectra of the alcohol solutions were obtained on a Specord UV-VIS spectrophotometer, the PMR spectra were obtained on a Tesla BS-497 spectrometer (100 MHz) in CCl_4 solution and using TMS as the internal standard, the mass spectra were measured on a Varian CH-6 instrument, and the GLC was run on an LKhM-7a instrument equipped with a katharometer and a 200 \times 0.3 cm steel column packed with 5% SE-30 deposited on Chezasorb AW-HMDS, and using helium as the carrier gas.

<u>2-Geranylthiophene (Ia)</u>. With stirring, in an argon atmosphere, to a solution of 4.2 g (50 mmoles) of thiophene in 20 ml of THF at -20° were added 3.2 g (50 mmoles) of BuLi (1.5 N solution in hexane) and, after 2 h, 11 g (50 mmoles) of geranyl bromide [17]. The mixture was stirred for 1 h at -20° , let stand overnight at 25°, treated with water, and extracted with ether. The extract was washed with water, dried over Na₂SO₄, and evaporated in vacuo. The residue (10.7 g) was chromatographed on 20 g of SiO₂. Elution with hexane gave 10 g (89%) of oily (Ia) with bp 106-107° (1 mm), n_D^{23} 1.5232, which based on the GLC (175°), is pure. Ultraviolet spectrum λ_{max} , nm): 234 (ϵ 8800), 284 (ϵ 745). PMR spectrum (δ , ppm): 1.56 s (3H, CH₃), 1.65-1.66 d (6H, 2CH₃), 1.97-2.30 m (4H, CH₂), 3.45 d (2H, CH₂, J = 7 Hz), 5.03 s (1H, CH), 5.37 t (1H, CH, J = 7 Hz), 6.80 m (3H, C₄H₃S). Mass spectrum (m/e): M⁺ 220 (32), 151 (84), 135 (34), 123 (75), 97 (100), 69 (64), 67 (43), 55 (57), 41 (66). Found: C 76.32; H 9.28; S 14.37%. C₁₄H₂₀S. Calculated: C 76.27; H 9.15; S 14.54%.

<u>2-Geranylthiophene-5-carboxylic Acid (Ib).</u> With stirring, in an argon atmosphere, to a solution of 2.2 g (10 mmoles) of (Ia) in 20 ml of ether at 5° was added 0.65 g (10 mmoles) of BuLi (1N solution in hexane) and after 1 h the mixture was poured on finely crushed dry ice. After removal of the CO_2 , the obtained salt was extracted with water, acidified with 5% HCl solution, and extracted with ether. The ether solution was worked up in the usual manner to give 2.1 g (79%) of oily (Ib) with R_f 0.57 (Silufol, 1:1 hexane-ether). Infrared spectrum: 1715 cm⁻¹. Ultraviolet spectrum (λ_{max} , nm): 257 (ε 7800), 280 (ε 10,200). Mass spectrum (m/e): M⁺ 264 (10), 141 (13), 123 (32), 97 (12), 69 (100), 41 (74). Found: C 68.31; H 7.67; S 11.93%. $C_{15}H_{20}O_2S$. Calculated: C 68.24; H 7.58; S 12.12%.

Treatment of an ether solution of acid (Ib) with CH_2N_2 gave in quantitative yield the methyl ester, which, based on the GLC (215°), is pure. PMR spectrum (δ , ppm): 1.56 s (3H, CH₃), 1.69 s (6H, 2CH₃), 2.06 s (4H, 2CH₂), 3.48 d (2H, CH₂, J = 7 Hz), 3.76 s (3H, CH₃), 5.03 s (1H, CH), 5.53 t (1H, CH, J = 7 Hz), 6.69 d (1H, C₄H₂S, J = 4 Hz), 7.50 d (1H, C₄H₂S, J = 4 Hz).

<u>4,8,8-Trimethyl-4,4a,5,6,7,7a-hexahydro-8H-cis-indeno[b]thiophene (IVa)</u>. With stirring, in an argon atmosphere, to a solution of 9.8 g (0.1 mole) of 100% H₂SO₄ in 50 ml of nitroethane at -40° was added 4.4 g (20 mmoles) of (Ia) and after 10 min the mixture was poured into an ice solution of Na₂CO₃ and extracted with ether. The extract was washed with water, dried over Na₂SO₄, evaporated in vacuo, and the residue (4.3 g) was filtered through a bed of 10 g of SiO₂. Elution with hexane gave 3.5 g (80%) of oily (IVa) with bp 105-106° (1 mm), n²⁰_D 1.5427, which based on the GLC (175°), is pure. Ultraviolet spectrum (λ_{max} , nm): 228 (ϵ 4120), 247 (ϵ 3080). PMR spectrum (δ , ppm): 0.93 s (3H, CH₃), 1.09 s (3H, CH₃), 2.16 t (1H, CH, J = 8 Hz), 2.39 d (2H, CH₂ J = 8 Hz), 6.55 d (1H, C₄H₂S, J = 4 Hz), 6.89 d (1H, C₄H₂S, J = 4 Hz). Mass spectrum (m/e): M⁺ 220 (57), 205 (100), 177 (35), 149 (51), 135 (63), 97 (64), 91 (48), 69 (67), 56 (45), 41 (60), 39 (51). Found: C 76.44; H 9.20; S 14.41%. C₁₄H₂₀S. Calculated: C 76.27; H 9.15; S 14.54%.

With stirring, in an argon atmosphere, to a solution of 0.59 g (2.3 mmoles) of SnCl_4 in 10 ml of MeNO_2 at 16° was added a solution of 0.54 g (2.4 mmoles) of (Ia) in 3 ml of MeNO_2 and after 30 min the mixture was treated with 5% NaHCO₃ solution and extracted with ether. The extract was washed with water, dried over Na₂SO₄, evaporated in vacuo, and the residue (0.48 g) was filtered through a bed of 5 g of SiO₂. Elution with hexane gave 0.36 g (66%) of (IVa), which, based on the GLC (175°), is pure.

<u>Mixture of 2, 6, 6, -Trimethyl-1-(2-methylenothienyl)-2-cyclohexene (IIa) and 2, 6, 6-Trimethyl-1-(2-methylenothienyl)-1-cyclohexene (IIIa)</u>. With stirring, in an argon atmosphere, to a solution of 0.76 g (6.7 mmoles) of CF₃COOH in 3 ml of CH₂Cl₂ was added a solution of 0.59 g (2.7 mmoles) of (Ia). The mixture was refluxed for 1.5 h, after which it was poured into water and extracted with ether. The extract was worked up in the usual manner to give 0.58 g of product, which was chromatographed on 10 g of SiO₂. Elution with hexane gave 0.38 g (64%) of an oily substance with R_f 0.72 (SiO₂, hexane), which, based on the GLC (172°) and PMR spectral data, is a mixture of (IIa) and (IIIa) in a 4:1 ratio. PMR spectrum of the mixture (δ , ppm): 0.86, 0.87, 0.90, 0.91 s (CH₃), 1.52, 1.53, 1.55 s (CH₃), 1.87 m (CH₂), 2.83 t (CH₂), 3.44 s (CH₂), 5.1 s (CH), 6.80 m (C₄-H₃S).

2,6,6-Trimethyl-1-(5-carboxythienyl-2-methyleno)-1-cyclohexene (IIIb). With stirring, in an argon atmosphere, to a solution of 0.74 g (7.5 mmoles) of 100% H₂SO₄ in 15 ml of nitropropane at -30° was added 0.40 g (1.5 mmoles) of (Ib) and after 30 min the mixture was poured into 5% NaHCO₃ solution, acidified with 5% HCl solution, and extracted with ether. The extract was washed with water, dried over Na₂SO₄, and evaporated in vacuo to give 0.38 g of oily product, the recrystallization of which from hexane gave 0.24 g (60%) of (IIIb) as colorless needles with mp 140-141°.

Treatment of an ether solution of (IIIb) with CH_2N_2 gave in quantitative yield the methyl ester with R_f 0.5 (SiO₂, 2:1 hexane ether). Infrared spectrum: 1720 cm⁻¹. Ultraviolet spectrum (λ_{max} , nm): 255 (ϵ 6800), 280 (ϵ 10,900). PMR spectrum (δ , ppm): 0.99 s (6H, 2CH₃), 1.64 s (3H, CH₃), 2.03 d (2H, CH₂), 3.56 d (2H, CH₂), 3.80 s (3H, CH₃), 6.67 d (1H, C₄H₂S, J = 4 Hz), 7.49 d (1H, C₄H₂S, J = 4 Hz). Mass spectrum of acid (m/e): M⁺ 264 (54), 249 (95), 141 (100), 123 (90). Found: C 68.18; H 7.75; S 11.85%. C₁₅H₂₀O₂S. Calculated: C 68.24; H 7.58; S 12.12%.

Mixture of 2, 6, 6-Trimethyl-1-(5-carboxythienyl-2-methyleno)-2-cyclohexene (IIb) and 2, 6, 6-Trimethyl-2-(5-carboxythienyl-2-methyleno)-1-cyclohexene (IIb). With stirring, in an argon atmosphere, to a solution of 0.53 g (5.4 mmoles) of 100% H₂SO₄ in 10 ml of nitropropane at -30° was added 0.29 g (1.1 mmoles) of (Ib) and after 5 min the mixture was worked up as in the preceding experiment. We obtained 0.18 g (62%) of substance, which crystallized from petroleum ether as colorless plates with mp 104-106°. Based on the PMR spectral data, the product is a mixture of (IIb) and (IIIb) in a 7:3 ratio.

<u>4,8,8-Trimethyl-4,4a,5,6,7,7a-hexahydro-8H-cis-indeno[b]thiophene-2-carboxylic Acid (IVb).</u> With stirring, in an argon atmosphere, to a solution of 3.59 g (13.6 mmoles) of (VII) in 20 ml of ether at 10° was added 12 ml of 1.4 N BuLi solution (26.2 mmoles) in hexane and after 1 h the mixture was poured on finely crushed dry ice. After evaporation of the CO_2 , the obtained salt was extracted with water, acidified with 5% HCl solution, and extracted with ether. The ether solution was worked up in the usual manner to give 2.71 g (63%) of (IVb) as colorless crystals with mp 200-202° (aqueous methanol).

Treatment of an ether solution of (IVb) with CH_2N_2 gave in quantitative yield the methyl ester with R_f 0.5 (SiO₂, 2:1 hexane-ether). Infrared spectrum: 1715 cm⁻¹. Ultraviolet spectrum (λ_{max} , nm): 250 (ϵ 8200),

294 (ϵ 10,600). PMR spectrum (δ , ppm): 0.92 s (3H, CH₃), 1.08 s (3H, CH₃), 1.38 s (3H, CH₃), 1.40–1.70 m (6H, 3CH₂), 2.15 t (1H, CH, J = 9 Hz), 2.74 d (2H, CH₂, J = 9 Hz), 3.76 s (3H, CH₃), 7.33 s (1H, C₄HS). Mass spectrum of acid (m/e): M⁺ 264 (20), 249 (100), 221 (8), 135 (31), 69 (18), 41 (15). Found: C 68.04; H 7.45; S 12.30%. C₁₅H₂₀O₂S. Calculated: C 68.24; H 7.58; S 12.12%.

Mixture of 4,8,8-Trimethyl-4,4a,5,6,7,7a-hexahydro-8H-cis-indeno[b]thiophene-2-carboxylic Acid (IVb) and 4,8,8-Trimethyl-4,4a,5,6,7,7a-hexahydro-8H-trans-indeno[b]thiophene-2-carboxylic Acid (V). With stirring, in an argon atmosphere, to a solution of 2.36 g (9.1 mmoles) of SnCl₄ in 30 ml of CH₂Cl₂ at 16° was added a solution of 0.8 g (3.0 mmoles) of (Ib) in 5 ml of CH₂Cl₂ and after 72 h the mixture was treated with 5% NaHCO₃ solution and ice, acidified with 5% HCl solution, and extracted with ether. From the extract we obtained 0.71 g (89%) of a mixture, which, based on the GLC (210°) data for the methyl esters, consisted of (IIIb) and a tricyclic product in a 1:2 ratio. Recrystallization of the mixture from hexane gave 0.52 g of product as colorless prisms with mp 201-203°, which, based on the PMR spectral data, is a mixture of (IVb) and (V) in a 2:1 ratio. Treatment of the indicated mixture of acids with ethereal CH₂N₂ solution gave their methyl esters. PMR spectrum (δ , ppm): 0.92, 0.96, 1.02, 1.08 s (CH₃), 1.28, 1.38 s (CH₃), 2.15 t (CH, J = 9 Hz), 2.74 d (CH₂, J = 9 Hz), 3.73 s⁻(CH₃), 7.33, 7.38 (C₄HS).

4,4,8-Trimethyl-cis-1-hydrindanone (VII). A mixture of 1.49 g (5.6 mmoles) of (IVb), 0.27 g (38.9 mgatoms) of Li shavings, and 50 ml of NH₃ was kept in a sealed glass ampul for 10 h at 25°, decomposed with NH_4Cl , the NH_3 was evaporated, and the residue was treated in succession with water and ether. The aqueous layer was acidified with 5% HCl solution and extracted with ether. The ether extract was washed with water, dried over $MgSO_4$, evaporated in vacuo, and the residue (1.28 g) was chromatographed on 20 g of SiO_2 . Gradient elution with a hexane – ether mixture, containing up to 15% ether, gave 0.71 g (53%) of a mixture of olefins (VI). A solution of 0.55 g (2.3 mmoles) of the indicated mixture in 15 ml of ethyl acetate was subjected at -40° to exhaustive oxidation with an $O_3 - O_2$ (mixture containing up to 4% O_3), after which it was washed with water, evaporated in vacuo, and the residue (0.39 g) was chromatographed on 10 g of SiO₂. Gradient elution with a hexane-ether mixture, containing up to 10% ether, gave 0.18 g (53%) of pure (based on GLC at 140°) ketone (VII) as a colorless oil, Rf 0.5 (Silufol, 2:1 hexane-ether). Infrared spectrum: 1740 cm⁻¹. PMR spectrum (ô, ppm): 0.86 (3H, CH₃), 1.05 (3H, CH₃), 1.11 3H, CH₃), 1.20-2.50 m (11H, 5CH₂, CH). Mass spectrum (m/e): M⁺ 180 (27), 165 (11), 136 (29), 109 (100), 97 (58), 69 (45), 68 (45), 55 (49), 41 (87). Found: C 79.90; H 11.06%. $C_{12}H_{20}O$. Calculated: C 80.00; H 11.11%. The 2,4-dinitrophenylhydrazone was obtained as light orange crystals with mp 144-145° (from alcohol). Ultraviolet spectrum (λ_{max} , nm): 234 (ϵ 18,000), 270 (ϵ 10,800), 365 (£ 23,000). Found: C 60.09; H 6.27; N 15.44%. C₁₈H₂₄N₄O₄. Calculated: C 60.00; H 6.67; N 15.55%.

5,5,9-Trimethyl-cis-hexahydro-2-chromanone (VIII). A solution of 20 mg (0.11 mmole) of (VII) and 54 mg (0.5 mmole) of 70% AcO₂H in 1 ml of CH_2Cl_2 was kept in a sealed ampul for 35 h at 50°, diluted with ether, washed in succession with 5% NaHCO₃ solution and water, dried over Na₂SO₄, and the solvent was removed in vacuo to give 15 mg (69%) of lactone (VIII), which, based on the GLC (175°) data and spectral characteristics (IR, PMR), was identical with an authentic [9] specimen.

CONCLUSIONS

An allylic thienyl group can serve as a terminator of electrophilic cyclization, which in this case proceeds by a stepwise scheme.

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OXIDATION OF DISUBSTITUTED SILICON-CONTAINING PHENOLS

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Despite the substantial number of papers devoted to the oxidation of phenols, the reactivity of disubstituted phenols with organosilicon substituents in the aromatic ring and the products formed by their oxidation have received little study. Only some information exists on the reactivity of disubstituted silicon-containing phenols when reacted with organomercury compounds [1].

The oxidation of disubstituted silicon-containing phenols (I), which are analogs of the 2,4- and 2,6-ditert-butylphenols, by alkaline potassium ferricyanide was studied in the present paper. The effect of O_2 on this process was also studied.



Phenoxyl radicals, generated by the one-electron oxidation of dialkylphenols with free o- or p-positions, usually dimerize with the formation of C-C or C-O bonds. Thus, from 2,4-dialkylphenols are formed dimers with a C-C bond between the o-C atoms of the phenoxyls [2], while from 2,6-dialkylphenols are formed dimers with a C-C bond between the p-C atoms. Here coupling at the C-C bonds leads to substituted dipheno-quinones, while coupling at the C-O bonds leads to polyphenyl ethers [3-5].

When phenol (Ia) is oxidized in an inert atmosphere, the first to be formed is dihydroxydiphenyl (IIa), which is then converted to two products. These products correspond to the dihydroxydiphenyl dimers, contain organosilicon fragments, and their IR spectra have a band that is characteristic for the OH group (3550 cm^{-1}). As a whole, their structure could not be ascertained. The oxidation of (Ia) in the presence of O₂ leads to spiroketals (IIIa) and (IVa), and also to a small amount of the oxidation products of dihydroxydiphenyl (IIa).



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