yellow crystals with R_f 0.53 [benzene—acetone (3:1)] and mp 250-251°C. IR spectrum: 1720, 1700, 1670 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 206 (4.45), 232 (4.40), 253 (4.52), 289.8 (4.26), and 314 nm (4.30). Found: C 67.6; H 5.4; N 9.5%; M^+ 282. $C_{16}H_{14}N_2O_3$. Calculated: C 68.1; H 5.0; N 9.9%; M 282.

1-(p-Chlorophenylazo)-3H,6H-pyrrolo[3,2-e]indole (XVI). This compound was obtained by the reaction of 0.2 g (1.3 mmole) of X with a solution of 3.9 mmole of p-chlorobenzenediazonium chloride by a procedure similar to that used to obtain XII. Workup of the reaction mixture gave 0.29 g (78%) of crude product. The compound was purified with a column (elution with benzene) to give red crystals with mp 183-184°C and R_f 0.58 (benzene). IR spectrum: 3460, 3400 (NH); 1400 cm^{-1} (N=N). UV spectrum, λ_{max} (log ε): 207.5 (4.49), 270 (4.03, 322 (3.95), and 242 nm (4.53). Found: N 18.9%; M^+ 294.5. $C_{16}H_{11}ClN_4$. Calculated: N 19.0%; M 294.5.

1-(p-Nitrophenylazo)-3H,6H-pyrrolo[3,2-e]indole (XVII). This compound was obtained by the reaction of 0.2 g (1.3 mmole) of X with a solution of 3.9 mmole of p-nitrobenzenediazonium chloride by a procedure similar to that used to obtain VII. Workup of the reaction mixture gave 0.35 g (89%) of a crude product, which was purified with a column [elution with benzene—ether (6:1)] to give a product with mp 285-286°C and R_f [benzene—ether (3:1)]. IR spectrum: 3445, 3385 (NH); 1400 cm^{-1} (N=N). UV spectrum, λ_{max} (log ε): 208 (4.49), 268 (3.96), 339 (3.96), 204.5 (3.96), and 253 nm (4.54). Found: N 22.6%; M^+ 305. $C_{16}H_{11}N_5O_2$. Calculated: N 23.0%; M 305.

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SYNTHESIS OF BIS(DIETHYLAMINOETHYL) 1,2-DIMETHYL-8-OXOINDENO[2,1-b]PYRROLE-3,5-DICARBOXYLATE

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UDC 547.567'759.3'665'29.02'26'298.7.07:543.422'51

An 8-oxoindeno[2,1-b] derivative, viz., the heteroanalog of the antivirus preparation thilorone, was synthesized from 6-ethoxycarbonyl-1,2-naphthoquinone through a series of intermediate steps.

The antivirus preparations thilorone [1] and fluorenal [2] have been found in the fluorenone series. One of them, viz., fluorenal, has found application in medical practice.

In this connection, we have realized the synthesis of the previously unknown bis(diethylaminoethyl) 1,2-dimethyl-8-oxoindeno[2,1-b]pyrrole-3,5-dicarboxylate (X), viz., the heteroanalog of the antiviral preparation thilorone, from 6-ethoxycarbonyl-1,2-naphthoquinone (I) via the scheme:

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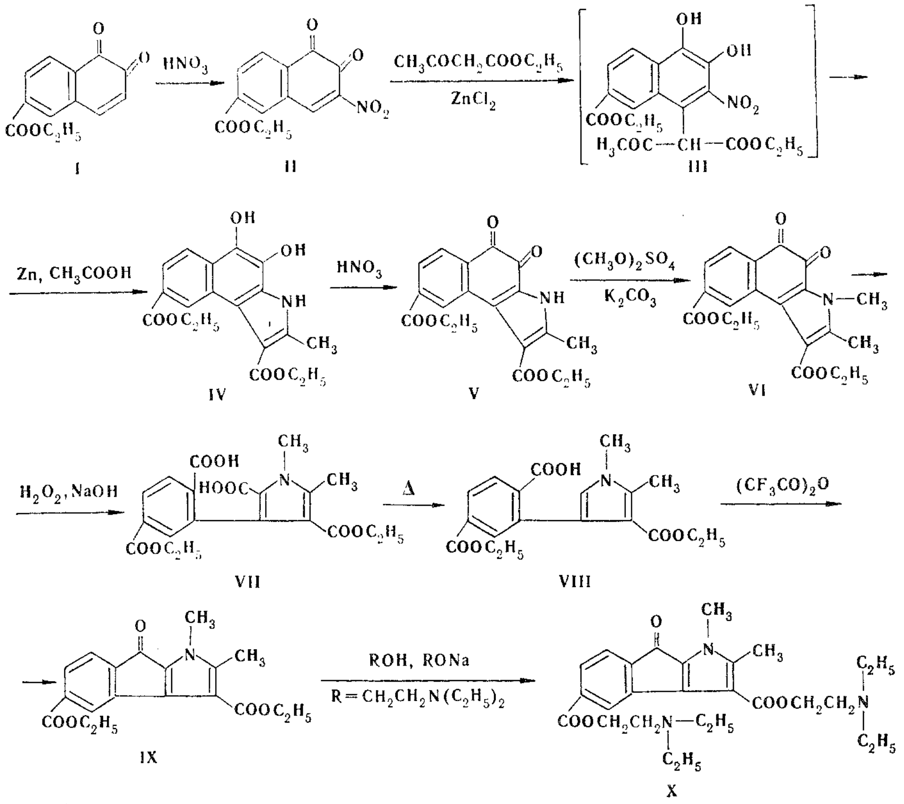

The nitration of 6-ethoxycarbonyl-1,2-naphthoquinone (I), obtained by the method in [4], by means of nitric acid leads to the formation of 3-nitro-6-ethoxycarbonyl-1,2-naphthoquinone (II). Using the method in [5], by condensation of the latter with acetoacetic ester in the presence of zinc chloride (which we were the first to propose) we obtained 1,2-dihydroxy-3-nitro-4-(1-ethoxycarbonyl-2-oxopropyl)-6-ethoxycarbonylnaphthalene (III), which we did not identify, and which, after reduction of the nitro group by the action of zinc in acetic acid, underwent intramolecular cyclization. The resulting 1,8-diethoxycarbonyl-2-methyl-4,5-dihydroxy-3H-benz[e]indole (IV) was oxidized by means of nitric acid to give 1,8-diethoxycarbonyl-2-methyl-4,5-dioxo-4,5-dihydro-3H-benz[e]indole (V). Methylation of the latter by means of dimethyl sulfate led to N-methyl derivative VI, which, by oxidation with hydrogen peroxide in an alkaline medium, was converted to 1,2-dimethyl-3-ethoxycarbonyl-4-(2-carboxy-5'-ethoxycarbonylphenyl)-5-carboxypyrrole (VII). When the latter was heated to its melting point, the carbon group in the pyrrole ring was eliminated to give 1,2-dimethyl-3-ethoxycarbonyl-4-(2-carboxy-5-carbonylphenyl)pyrrole (VIII). Treatment of latter with trifluoroacetic anhydride resulted in intramolecular cyclization to give diethyl 1,2-dimethyl-8-oxoindeno-[2,1-b]pyrrole-3,5-dicarboxylate (IX). As a result of transesterification, the reaction of diethyl ester IX with diethylaminoethanol led to bis(diethylaminoethyl) 1,2-dimethyl-8-oxoindeno[2,1-b]pyrrole-3,5-dicarboxylate (X).

The IR spectra of benzindole V are characterized by an intense band of stretching vibrations of an NH group at 3180 cm^{-1}. The IR spectra of all of the synthesized compounds contain intense absorbtion bands with maxima at 1640-1740 cm^{-1}, which we assigned to stretching vibrations of ester and carbonyl groups.

The mass numbers found for I, II, V-X from their mass spectra were in agreement with the calculated molecular masses.

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with Perkin-Elmer spectrometer. The UV spectra of solutions in alcohol were recorded with a Perkin-Elmer 575 spectrophotometer. The mass spectra were obtained with a Varian MAT-112 spectrometer (70 eV) with direct introduction of the substances and the courses of the reactions were monitored by chromatography on Silufol UV-254 plates with chloroform as the solvent; the chromatograms were developed in UV light.

6-Ethoxycarbonyl-1,2-naphthoquinone (I). This compound, with mp 168-170°C (from dichloroethane), was obtained in 73% yield by oxidation of 1-bromo-2-hydroxy-6-carbonylnaphthalene by means of nitric acid in chlorobenzene [4]. Found: C 67.9; H 4.4%. Calculated: C 67.8; H 4.4%.

3-Nitro-6-ethoxycarbonyl-1,2-naphthoquinone (II). A suspension of 2.3 g (0.01 mmole) of I in 20 ml of nitric acid (sp. gr. 1.35) was heated with stirring on a boiling-water bath for 15-20 min, after which the mixture was cooled, and the resulting precipitated orange crystals were removed by filtration, washed successively with nitric acid and water, and dried to give 2.0 g (72%) of II with mp 203-204°C (from acetone). IR spectrum: 1690 (C=O); 1530, 4120 cm^{-1} (NO_2). UV spectrum, λ_{max} (log ε): 207 (4.42), 245 (3.32), 265 (4.30), and 420 nm (3.04) (shoulder). Found: C 56.8; H 3.5; N 5.2%; M^+ 275. $C_{13}H_9NO_6$. Calculated: C 56.7; H 3.3; N 5.1%.

1,8-Diethoxycarbonyl-4,5-dihydro-3H-benz[e]indole (V). A mixture of 2.75 g (0.01 mole) of II, 2.8 g (0.02 mole) of anhydrous zinc chloride, and 2.6 g (0.02 mole) of acetoacetic ester in 40 ml of dioxane was refluxed for 5-10 min, after which heating was discontinued, and the reaction mixture was allowed to stand for 20 min, after which it was diluted with water and extracted with chloroform. The chloroform was evaporated *in vacuo*, the residue (III) was dissolved in 100 ml of acetic acid, and the solution was heated to the boiling point. A 5-g sample of zinc dust was then added in portions in the course of 20 min, and the mixture was then refluxed until the reaction mixture lost its color completely. The hot solution was filtered to remove the sediment, 1 ml of nitric acid (sp. gr. 1.35) was added to the filtrate, and the mixture was stirred for 2-3 min. The resulting dark-red mass was diluted with 100 ml of water, and the precipitate was removed by filtration, washed with water, and dried to give 2.5 g (70.42%) of V with mp 218-219°C (from acetic acid). IR spectrum: 3180 (NH), 1720 and 1640 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 212 (4.53), 247 (4.34), 274 (4.48), 350 shoulder (3.67), 384 (3.81), and 460 nm shoulder (3.19). Found: C 64.1; H 4.7; N 3.9%; M^+ 355. $C_{19}H_{17}NO_6$. Calculated: C 64.2; H 4.8; N 3.9%.

1,8-Diethoxycarbonyl-2,3-dimethyl-4,5-dioxo-4,5-dihydrobenz[e]indole (VI). A 5.04-g (0.04 mmole) sample of dimethyl sulfate and 5.56 g (0.04 mole) of anhydrous potassium carbonate were added to a refluxing solution of 3.55 g (0.01 mole) of 3H-benz[e]indole V in a mixture of dioxane (50 ml) with acetone (50 ml), and the reaction mixture was refluxed for 15 min. The hot solution was filtered, and the solvent was removed by evaporation to a small volume. The residue was treated with 10 ml of methanol, and the precipitated orange crystals were removed by filtration and washed with isopropyl alcohol to give 3 g (84%) of VI with mp 121-123°C. IR spectrum: 1710 and 1640 cm^{-1} (C=O). UV spectrum, λ_{max} (log ε): 214 (4.49), 249 (4.35), 274 (4.47), 340 shoulder (3.60), and 384 nm (3.83). Found: C 65.0; H 5.1; N 3.8%; M^+ 369. Calculated: C 65.0; H 5.2; N 3.8%.

1,2-Dimethyl-3-ethoxycarbonyl-4-(2-carboxy-5-ethoxycarbonyl)-5-carboxypyrrole (VII). A 22-ml sample of 2 N sodium hydroxide solution was added all at once to a suspension of 3.69 g (0.01 mole) of N-methyl derivative VI in 125 ml of methanol at room temperature, after which 15.5 ml of 33% hydrogen peroxide was then added. The reaction mixture was stirred for 30 min, after which 250 ml of water was added to the resulting colorless solution, and the mixture was acidified to pH 5.0 by means of dilute hydrochloric acid. The precipitate was removed by filtration, washed with water, and dried to give 2.8 g (69%) of VII with mp 182-183°C (from methanol). IR spectrum: 1720 and 1690 cm^{-1} (C=O). Found: C 59.5; H 5.2; N 3.4%; M^+ 403. $C_{20}H_{21}NO_8$. Calculated: C 59.5; H 5.3; N 3.5%.

1,2-Dimethyl-3-ethoxycarbonyl-4-(2-carboxy-5-ethoxycarbonyl)pyrrole (VIII). A 1-g (2.5 mmole) sample of dicarboxylic acid VII was heated to the melting point and maintained at this temperature until the evolution of bubbles of carbon dioxide gas ceased. The reaction mixture was then cooled and treated with 5 ml of methanol and 5 ml of water, and the resulting precipitate was removed by filtration, washed with water, and dried to give 0.6 g (67%) of VIII with mp 170-171°C [from benzene–petroleum ether (1:1)]. IR spectrum: 1740 and 1720 cm^{-1} (C=O). Found: C 63.4; H 5.7; N 3.7%; M^+ 359. $C_{19}H_{21}NO_6$. Calculated: C 63.5; H 5.9; N 3.9%.

Diethyl 1,2-Dimethyl-8-oxoindeno[2,1-b]pyrrole-3,5-dicarboxylate (IX). A 3.6-ml sample of trifluoroacetic anhydride was added to a solution of 3.6 g (0.01 mole) of VIII in 80 ml of benzene, and the reaction solution was allowed to stand at room temperature for 20 h. The solvent was then removed by evaporation to dryness, and the residue was treated with 15-20 ml of methanol to give 3.19 g (93%) of IX with mp 166-167°C [from acetone–methanol (1:1)]. IR spectrum: 1710 and 1690 cm^{-1} (C=O). Found: C 66.5; H 5.6; N 3.8%; M^+ 341. $C_{19}H_{19}NO_5$. Calculated: C 66.8; H 5.6; N 4.1%.

Bis(diethylaminoethyl) 1,2-Dimethyl-8-oxoindeno[2,1-b]pyrrole-3,5-dicarboxylate (X). A 12-ml sample of a 10% solution of sodium diethylaminoethoxide in diethylaminoethanol was added to a solution of 3.41 g (0.01 mole) of IX in 90 ml of benzene, and the reaction solution was refluxed for 1 h, after which the benzene was evaporated *in vacuo*, and the residue was extracted with ether. The ether was then evaporated until the mixture had a small volume, and the resulting crystals were removed by filtration and washed with ether to give 2.1 g (43%) of orange crystals of X with mp 95-96°C (from acetone). IR spectrum: 1710 and 1690 cm^{-1} (C=O). Found: C 67.4; H 7.8; N 8.6%; M^+ 483. $C_{27}H_{37}N_3O_5$. Calculated: C 67.1; H 7.7; N 8.7%.

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RADICAL meso-ALKYLATION OF VANADYLETIOPORPHYRIN

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The possibility of the meso-alkylation of vanadyletioporphyrin (25-30% yields) by its reaction with alkyl bromides [$C_{(6)}$-$C_{(12)}$] in the presence of finely dispersed silver metal at 150-180°C in an argon atmosphere with the formation of 5,15-dialkylvanadyletioporphyrins and 5,15-dialkyl-5,15-dihydrovanadyletioporphyrins as side products is demonstrated.

The radial alkylation of vanadyletioporphyrin (I) is of interest as a convenient direct method for the production of a large number of meso-alkyl derivatives of vanadyl complexes of octaalkylporphyrins that are of independent preparative significance and may serve as compounds that, to some degree, model the structure of porphyrins that are contained in geological substances such as in fractions of petroleum vanadylprophyrins. Moreover, we regard radical alkylation as one of the possible routes for the formation of the molecular compositions of petroleum vanadylporphyrins, considering the substantial role of radical processes in the thermal and thermocatalytic transformations of petroleum in the catagenetic stage [1].

Information regarding the production of meso-alkyl-substituted porphyrins directly from octaalkylporphyrins is limited. The direct alkylation of the palladium complex of octaethylporphyrin by means of methyl fluorosulfonate to give the product in 37% yield has been described [2]. The formation of a meso-methylporphyrin was also observed in the thermolysis of porphyrins with the general formula $Pf-CH_2X$, in which X = NH_2, NHAlk, $NAlk_2$, or OAlk [3, 4]. The literature contains no information regarding the production, by a direct method, of meso-alkyl-substituted porphyrins with a meso substituent that is longer than that of a single carbon atom.

We have demonstrated the possibility of the formation of meso-alkyl-substituted vanadylporphyrins in 25-30% yields by the reaction of porphyrin I with hexyl, nonyl, and dodecyl bromides in the presence of finely dispersed silver at 150-180°C in an argon atmosphere [5]. The results of the reactions were similar in all cases. The yields of the meso-alkylvanadyletioporphyrins are increased somewhat when the silver is added to the reaction mixtures in a stepwise manner.

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