

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  $\text{cm}^{-1}$  (C=O). Found: C 67.4; H 7.8; N 8.6%;  $M^+$  483.  $\text{C}_{27}\text{H}_{37}\text{N}_3\text{O}_5$ . 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  $[\text{C}_{(6)}-\text{C}_{(12)}]$  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 radical 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 vanadylporphyrins. 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  $\text{Pf}-\text{CH}_2\text{X}$ , in which  $\text{X} = \text{NH}_2$ ,  $\text{NHAlk}$ ,  $\text{NAlk}_2$ , or  $\text{OAlk}$  [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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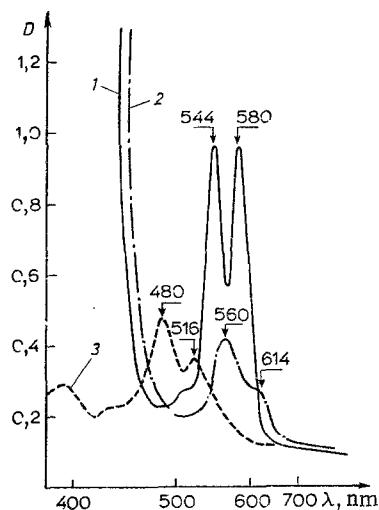
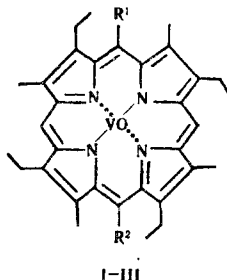


Fig. 1. Absorption spectra of the compounds obtained: 1) II; 2) III; 3) vanadyl complex of 5,15-dihexyl-5,15-dihydroetioporphyrin.



I  $R^1=R^2=H$ ; II  $R^1=C_6H_{13}$ ,  $R^2=H$ ; III  $R^1=R^2=C_6H_{13}$

The principal products of the reaction with hexyl bromide are 5-hexylvanadyletioporphyrin (II,  $R_f$  0.5, red-brown) and the 5,15-dihexyl derivative (III,  $R_f$  0.75, green, 8-10% yield). In the electronic spectrum of II one observes a bathochromic shift of the absorption as compared with the spectrum of I, whereas the ratio of the intensities of the  $\alpha$  and  $\beta$  bands is close to 1.0 (see Fig. 1); this is usually characteristic for such substances. The presence of a meso substituent is also confirmed by the spectrum of the free base obtained by the demetallization of II by means of concentrated sulfuric acid; it has a phyllo type of spectrum.

The principal fragment ion in the mass spectrum of porphyrin II is the ion with  $m/z$  556, which corresponds to fragmentation of the meso substituent at the  $\beta$  bond relative to the conjugated system of the porphyrin ring. The mass spectrum also reveals the existence of a product of fragmentation at the  $\alpha$  bond with simultaneous transfer of one hydrogen atom to the conjugated system ( $m/z$  543); this is also characteristic for the mass-spectrometric behavior of meso-alkylporphyrins [6].

The product of more profound meso-alkylation of vanadyletioporphyrins can, with respect to its spectral properties (see Fig. 1), chromatographic mobility, and the character of its fragmentation in mass spectrometry (see the experimental section), with confidence be assigned the 5,15-dihexylvanadyletioporphyrin (III) structure. We were unable to obtain products with a larger number of meso substituents by the described method.

meso-Alkylation is accompanied by the formation of a number of side products. The products, which are more polar than III, are green and have  $R_f$  values of 0.15 and 0.6 (the latter compound is not formed in all experiments). Their overall yields amount to 10-15%. Their electronic spectra constitute evidence for the existence of a complete system of conjugation over the porphyrin ring, whereas the mass spectra are distinguished by a large number of fragments and are not amenable to unambiguous interpretation.

The second group of side products is orange and consists of three chromatographically homogeneous substances with  $R_f$  0.80-0.95, which are formed in an overall yield of 5-10%. The ratios of the amounts of substances in this group and the parameters of their electronic spectra change as a function of the length of the alkyl bromide introduced into the reaction. These compounds have spectral properties that constitute evidence for disruption of the conjugation system in the porphyrin ring: They do not have any strong absorption  $>530$  nm and display principal bands at 480 and 520 nm. These spectral peculiarities are characteristic for vanadyl complexes of 5,15-dialkyl-5,15-dihydroporphyrins that are formed in the process of reductive alkylation, inasmuch as for the corresponding vanadyl complex of the 5,15-dimethyl derivative the major absorption bands are found at 478 and 510 nm [7]. Moreover, their IR spectra contain a strong band at  $1600\text{ cm}^{-1}$ , which is characteristic for these compounds [7].

The chromatographic nonhomogeneity of the 5,15-dialkyl-5,15-dihydrovanadyletioporphyrins formed in meso alkylation is probably associated with the existence of various stereoisomers in their composition. The electronic and mass spectra of the chromatographically homogeneous compounds isolated from the mixture are very similar and differ only in minor details. Thus the compositions of the products of the reaction of porphyrin I with alkyl bromides in the presence of silver metal fit almost completely within the framework of the most frequently encountered mechanism of radical substitution in the aromatic ring [8]. The principal reaction product (meso-alkyl-substituted I) is the result of splitting out of a hydrogen atom from the  $\sigma$  complex, which, in turn, is formed by attack of the radical on the aromatic system of the starting vanadyletioporphyrin. The formation of 5,15-dialkylporphyrin is the result of processes that take place in the same sequence with the vanadyl complex of the meso-alkyletioporphyrin complex. The absence of products of a higher degree of substitution is evidently associated with steric hindrance to attack by the rather bulky alkyl radical on the vanadyl-5,15-dialkyletioporphyrin.

5,15-Dialkyl-5,15-dihydroporphyrins are side products that are formed as a result of the addition of a second radical to the  $\sigma$  complex. Covalently bonded dimers of porphyrins, the formation of which one might have conceived of as proceeding through a step involving the detachment of a hydrogen atom by the attacking alkyl radical from the alkyl substituents of the porphyrin ring with subsequent dimerization of the resulting radicals, were not detected in the reaction products.

#### EXPERIMENTAL

The electronic spectra of solutions of the compounds in chloroform were recorded at 350-800 nm with a Specord UV-vis spectrophotometer. The low-resolution mass spectra were obtained with a Varian MAT-311 spectrometer at an ionizing-electron energy of 70 eV; the vaporization and ionization-chamber temperatures were  $200^\circ\text{C}$ . Preparative thin-layer chromatography (TLC) was carried out on  $20 \times 20$  cm Silufol UV-254 plates in benzene.

5-Hexylvanadyletioporphyrin (II). A mixture of 230 mg (0.4 mmole) of the vanadyl complex of etioporphyrin, 2.2 g (0.02 mole) of finely dispersed silver metal, and 25 ml of hexyl bromide was heated in an argon atmosphere at  $170\text{--}180^\circ\text{C}$  for 80 h, after which the mixture was cooled, the precipitate was removed by filtration, the hexyl bromide was removed by distillation *in vacuo*, and the products were separated by TLC on silica gel. This procedure gave 64.7 mg (29.6%) of product, UV spectrum,  $\lambda_{\text{max}}$ : 420, 544, and 580 nm. Mass spectrum,  $m/z$  (%): 627 (100), 556 (39), 541 (13), 526 (19), 511 (8), 496 (6). Found: C 72.3; H 7.9%.  $\text{C}_{38}\text{H}_{48}\text{N}_4\text{O}_2\text{V}$ . Calculated: C 72.7; H 7.6%. Mass spectrum of III,  $m/z$ : 711, 640, 627, 626, 556, and 543.

Demetallization of II. Several milligrams of II were dissolved in concentrated  $\text{H}_2\text{SO}_4$ , and the solution was allowed to stand in a dark place for 3-4 h. The mixture was then poured over ice, and the aqueous mixture was neutralized to pH 4-5 by means of  $\text{NaHCO}_3$  and extracted with chloroform. The chloroform solution was washed with 5% sodium acetate solution, dried over anhydrous sodium sulfate, and evaporated *in vacuo*. The mixture was separated by TLC in a benzene-chloroform system (1:1). The fraction that was more polar and fluoresced in UV light (365 nm) was collected and additionally purified by TLC to give the product in 10% yield. UV spectrum,  $\lambda_{\text{max}}$ : 415, 512, 540, 580, and 645 nm.

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## DIAZO CARBONYL DERIVATIVES OF HETEROCYCLES.

### 1. DIAZOACETYL DERIVATIVES OF PYRIDINE AND THEIR TRANSFORMATIONS

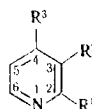
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Isomeric o-carbomethoxydiazoacetylpyridines were obtained. It is shown that, under the influence of acids on  $\beta$ -diazoacetyl derivatives of pyridine, the corresponding azaisochroman-1,4-diones are formed. The formation of azaisochroman-1,4-diones does not occur in the case of  $\alpha$ - and  $\gamma$ -diazoacetylpyridines.

Reactions involving intramolecular cyclization of  $\alpha$ -diazo ketones, which take place under the influence of acids, are finding application in the preparation of many heterocyclic systems that are difficult to obtain [1]. Reactions of this type proceed most readily in the case of o-substituted diazoacetophenones [2]. Thus, for example, o-carbomethoxydiazoacetophenone is readily converted to isochroman-1,4-dione under the influence of mineral acids [3, 4]. Such reactions have not yet been described for heterocyclic analogs.

In order to study the possibility and peculiarities of intramolecular cyclization of heterocyclic diazo ketones under the influence of acidic agents we obtained four isomeric o-carbomethoxydiazoacetylpyridines Ia-g and studied their acidic transformations.



Ia-d

a  $R^1 = \text{COCHN}_2$ ,  $R^2 = \text{COOCH}_3$ ,  $R^3 = \text{H}$ ; b  $R^1 = \text{COOCH}_3$ ,  $R^2 = \text{COCHN}_2$ ,  $R^3 = \text{H}$ ; c  $R^1 = \text{H}$ ,  $R^2 = \text{COCHN}_2$ ,  $R^3 = \text{COOCH}_3$ ; d  $R^1 = \text{H}$ ,  $R^2 = \text{COOCH}_3$ ,  $R^3 = \text{COCHN}_2$

Isomeric diazo ketones Ia-d were obtained by acylation of diazomethane by means of the chlorides of the corresponding acids. Intense absorption bands at 2084-2110 of an  $\text{N} \equiv \text{N}$  group and at 1725-1735 and 1600-1625  $\text{cm}^{-1}$  (ester and keto groups, respectively) are observed in the IR spectra of the diazo ketones (Table 1). Weak bands of stretching vibrations of  $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  bonds of the pyridine ring are observed at 1555-1600  $\text{cm}^{-1}$ . Singlets of three protons of a methyl group at 3.93-4.08 ppm and singlets of methylidyne protons at 5.6-6.08 ppm, as well as signals of three protons at 7.3-9.1 ppm, which are characteristic for 2,3- and 3,4-disubstituted pyridines, show up in the PMR spectra. The mass spectra of diazo ketones Ia-d (Table 2) do not contain  $\text{M}^{+}$  molecular-ion peaks, but intense ion peaks\* are observed at 177  $[(\text{M} - \text{N}_2)^+]$  and 164  $[(\text{M} - \text{CHN}_2)^+]$ . The subsequent fragmentation pathway is elimination of  $\text{CH}_3$ ,  $\text{COOCH}_3$ , and  $(\text{CO} + \text{CH}_3)$  fragments, which leads to the appearance of ions at

\*Here and subsequently, the m/z values are given for the ion peaks.

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