A NEW APPROACH TO THE SYNTHESIS OF FUNCTIONALLY SUBSTITUTED DERIVATIVES OF TETRAARYLPORPHYRINS

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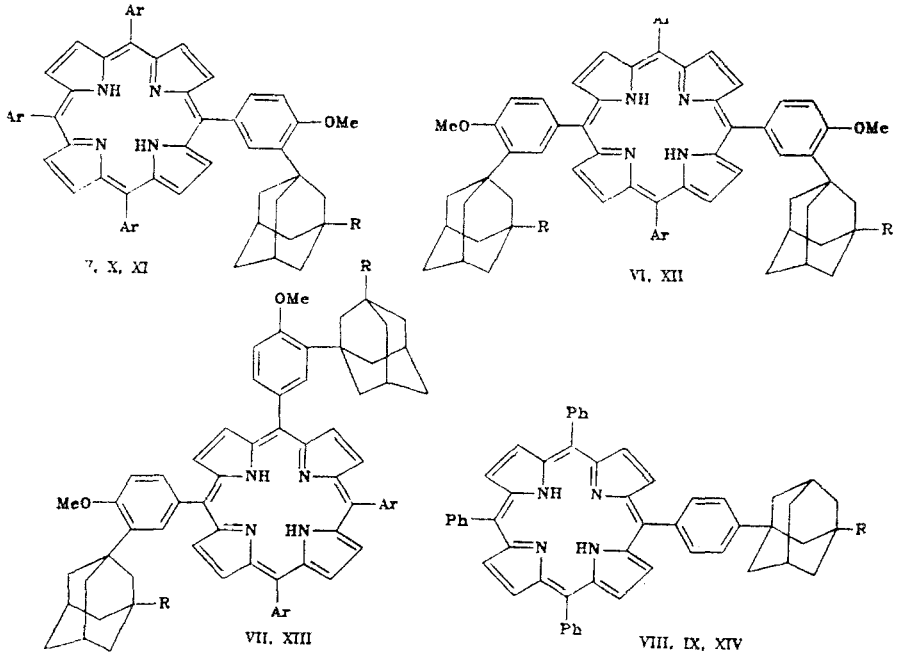
UDC 547.749

Usually, a mixture of two different aldehydes and pyrrole are used in a Rothemund cyclization reaction in order to synthesize *meso*-tetraarylporphyrins containing substituents on the aryl rings. In this case, a mixture of all six possible porphyrins are formed, and the yield of the monosubstituted product of greatest interest does not exceed 5-10% [1].

We have established that the symmetrical *meso*-tetraphenylporphyrins (I), *meso*-tetra(4-methoxyphenyl)porphyrin (II) in particular, are easily alkylated at room temperature in methanesulfonic acid by the adamantol derivatives 3-aminomethyl-1-hydroxyadamantane (III) and 1-hydroxy-3-carboxyadamantane (IV). While porphyrin I is alkylated in the *para* position of the phenyl ring, it is the *meso* position of the methoxyphenyl substituent that undergoes attack in the alkylation of porphyrin II. An insignificant amount of polyalkylation of the porphyrins also occurs in the reaction (see scheme below).

A mixture of 500 mg (0.65 mmole) of porphyrin II and 150 mg (0.83 mmoles) of adamantane III in 10 ml of MsOH is stirred for 2 h and poured into water, neutralized with aqueous ammonia, the material extracted with chloroform, and chromatographed on a column with silica gel in a 85:5:10 chloroform/methanol/acetone system. After the separation of 63 mg (12%) of the starting porphyrin II, 243 mg (42%) of porphyrin V and 155 mg (22%) of a mixture of isomers VI and VII are obtained.



V, X, XI

VI, XII

VII, XIII

VIII, IX, XIV

V—VIII R = CH_2NH_2; IX, X R = COOH; XI—XIV R = CH_2NHAc, Ar = C_6H_4OMe-*p*

Porphyrin VIII is obtained in an analogous manner from porphyrin I. Carboxyporphyrins IX and X are synthesized in 40-45% yields by the alklylation of porphyrins I and II with carboxylic acid IV. N-Acetyl derivatives XI-XIV are obtained by the acylation of the corresponding aminoporphyrins V-VIII in Ac_2O. Porphyrins XII and

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0009-3122/91/2710-1153 $12.50

XIII are separated into the individual isomers by PTLC [preparative thin-layer chromatography] on silica gel plates. The structures of the compounds prepared were shown by means of PMR and confirmed by mass spectra obtained in a Finnigan MAT90 instrument with ionizing electrons of 70-eV energy and a source temperature of 200°C. Despite the presence of labile substituents and the high temperature of vaporization of the samples, the latter were characterized by the maximum intensity of the molecular ion peaks.

Thus, we propose a simple and accessible method of introducing one or two functional groups into tetraarylporphyrin molecules that allows them to be used for further chemical transformations.

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RECYCLIZATION OF METHYL-4-HYDROXY-2-(*o*-HYDROXYPHENYLAMINO)-5-OXO-2,5-DIHYDROPYRROLE-2-CARBOXYLATE INTO THE AMIDE OF (2-OXO-3,4-DIHYDRO-2H-1,4-BENZOXAZIN-3-YLIDENE)PYRUVIC ACID

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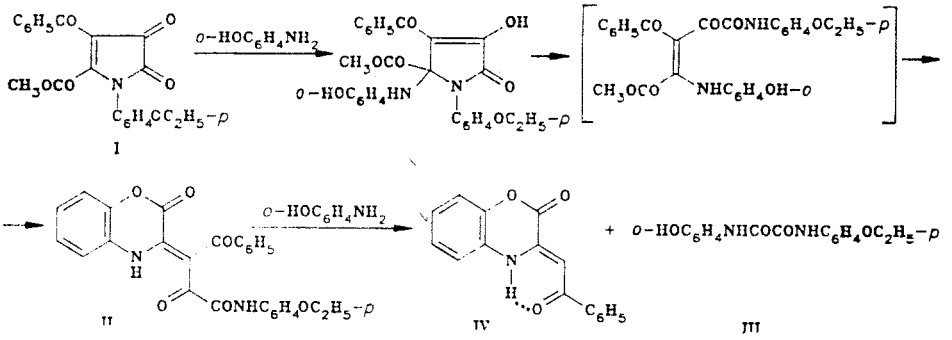
UDC 547.867.05'745

We have established that methyl-3-benzoyl-4-hydroxy-2-(*o*-hydroxyphenylamino)-5-oxo-1-(*p*-ethoxyphenyl)-2,5-dihydropyrrole-2-carboxylate, prepared by the reaction of methyl 4-benzoyl-2,3-dioxo-1-(*p*-ethoxyphenyl-2,3-dihydro-1H-pyrrole-5-carboxylate (I) with *o*-aminophenol, undergoes recyclization when attempts are made to recrystallize it, forming the *p*-ethoxyanilide of 3-(2-oxo-3,4-dihydro-2H-1,4-benzoxazin-3-ylidene)benzoylpyruvic acid (II). On heating compound (II) with an excess of *o*-aminophenol, aminolysis of the oxamide residue occurs forming N-*o*-hydroxyphenyl-N′-*p*-ethoxyphenyloxamide (III), and 3-phenyl-3,4-dihydro-2H-1,4-benzoxazin-2-one (IV), identified by comparison with an authentic sample [1].



Compounds III and IV are also formed on boiling compound I with an excess of *o*-aminophenol.

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A. M. Gorkii State University, Perm. Perm Pharmaceutical Institute. Institute of Organic Chemistry, Urals Branch, Russian Academy of Sciences. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, p. 1429, October, 1991. Original article submitted September 11, 1990; revision submitted March 28, 1991.

 0009-3122/91/2710-1154$12.50