2-(2-N-Phenylcarbamido-2-cyano)methylenetetrahydrofuran (XIV). A mixture of 1.7 g (9 mmoles) of compound IVb and 4 ml of butyrolactone acetal is boiled for 1 h, then cooled, and the precipitate is filtered and washed with alcohol. Yield, 1.3 g of compound XIV. The mother liquor is evaporated, and the residue is ground with ether. Yield, 0.4 g of compound XIV. Overall yield 1.7 g.

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STUDY OF REACTION OF 2,3,3-TRIMETHYL-3H-INDOLE WITH HALOACETIC ACID AMIDES. SYNTHESIS OF 1,2,3,9a-TETRAHYDRO-9H-IMIDAZO[1,2-a]INDOL-2-ONES

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In the reaction of 2,3,3-trimethyl-3H-indole with α-chloro- and α-iodoacetamides, 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium salts are formed, which by the action of bases convert into imidazo[1,2-a]indol-2-one and 1-carbamoyl-2-methylene-2,3-dihydroindole. The latter compound can by cyclized into imidazo[1,2-a]indol-2-one by the action of acetic acid.

The products of the reaction of 3H indoles with haloacetic acids and their derivatives have not been extensively described. Thus, the reactions of 2,3,3-trimethyl-3H-indole with α-bromoacetic acid and its ethyl ester are described in [1, 2]. In the view of the authors of [3], the cyclization products of 1-carboxymethyl derivatives of 3H-indoles are oxazolo-[3,2-a]indol-2-ones. There is a report [4] on the use of the 1-carbamoylmethyl derivatives of 3H-indoles for the synthesis of dyes, but there are no data on the preparation and structure of these compounds.

To carry out the synthesis of the new heterocyclic compounds belonging to the practically unexplored series of imidazo[1,2-a]indole derivatives, we studied the reaction of 3H-indoles Ia-c with haloacetic acid amides. The reaction of 2,3,3-trimethyl-3H-indole (Ia) with α-chloroacetamide proceeds at 100-150°C in aromatic hydrocarbons, nitrobenzene, or in the absence of solvent. The best results were obtained on heating indole Ia with an amide, at a molar ratio of 1:1.1, in the presence of a small amount of xylene at 140°C. Under these conditions, the main reaction product was 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride (IIa).

The structure of chloride IIa is confirmed mostly by the presence of a singlet of the 2-CH_3 group protons at 2.45 ppm in the PMR spectrum (in CF_3COOH), which is absent on recording the spectrum in D_2O because of deutero-exchange, characteristic of 2-methyl-3-H-indolium salts [5].

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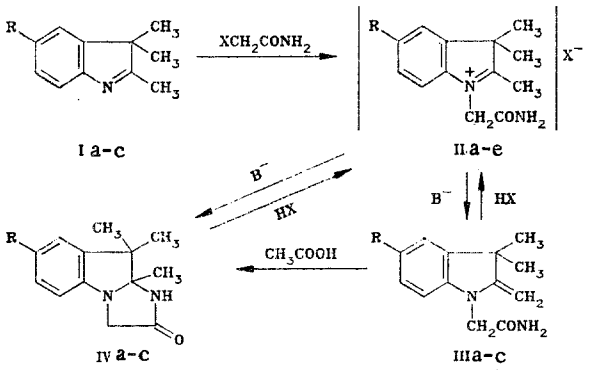

I—III, IV a R=H; b R=CH_3; c R=Br; II d R=H; e R=CH_3; a-c X=Cl; d-e X=I

Salts IIb,c were obtained similarly to chloride IIa. 1-Carbamoylmethyl-3H-indolium iodides IId,e were synthesized by heating 3H-indoles Ia,b with α-iodoacetamide in acetonitrile.

During the treatment of the aqueous solution of salts IIa,d with potassium hydroxide or sodium carbonate, the methylene base IIIa is formed mainly. A small proportion of the salt is converted into imidazo[1,2-a]indol-2-one (IVa), which was isolated in a pure state by column chromatography on aluminum oxide (acetone—hexane, 2:5, Rf 0.52). Later it was found that the methylene base IIIa can be easily cyclized into imidazo[1,2-a]indol-2-one (IVa) on heating in acetone in the presence of acetic acid. This method of cyclization was also used in the synthesis of 7-methyl- and 7-bromoimidazo[1,2-a]indol-2-ones (IVb,c).

Characteristic signals in the PMR spectra (in $CDCl_3$) of imidazoindolones IVa-c are three singlets of the 10,10,10a-CH_3 groups in the 1.12-1.48 ppm region. The methylene protons of the imidazolidine ring resonate in the form of an AB-quadruplet with a geminal SSCC [spin-spin coupling constant] of 16.3-16.5 Hz in the 3.55-3.90 ppm region. In the IR spectra of compounds IVa-c, the absorption band of the C=O group is observed at 1700 cm^{-1}, which is characteristic of five-membered ring lactams [6]. The absorption maxima in the UV spectrum of imidazo[1,2-a]indol-2-one [λ_{max} (log ε) 209 (4.08), 234 (4.31), 284 nm (3.30)] are specific for indoline derivatives [7].

By the action of hydrochloric or trifluoroacetic acid on imidazo[1,2-a]indol-2-ones IVa-c, a heterolytic cleavage of the nitrogen—carbon bond in the imidazolidine ring takes place with the formation of 1-carbamoylmethyl-3H-indolium salts. Thus, the PMR spectrum of compound IVa in trifluoroacetic acid is not different from the spectrum of salt IIa in the same solvent. When hydrogen chloride is passed through the ethanolic solution of imidazo-[1,2-a]indol-2-one IVa, a crystalline compound separates out, which is identical with salt IIa. By the action of sodium carbonate, salts IIa convert into the methylene base IIIa. Thus, by using acids and bases it is easy to carry interconversions of 1-carbamoylmethyl-3H-indolium salts, 1-carbamoylmethyl-2-methylene-2,3-dihydroindoles, and 1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-ones.

EXPERIMENTAL

The PMR spectra were run on a Tesla BS-487-C apparatus (80 MHz), with HMDS as internal standard. The IR spectra were obtained on a UR-20 spectrophotometer in KBr tablets. The UV spectra were run on a Specord UV-vis spectrophotometer. The course of the reaction and the purity of the compounds obtained were controlled by TLC on aluminum oxide in the acetone—hexane, 2:5, system.

1-Carbamoylmethyl-2,3,3-trimethyl-3H-indolium Chloride (IIa). A mixture of 47.8 g (0.3 mole) of compound Ia, 30.85 g (0.33 mole) of α-chloroacetamide, and 20 ml of xylene is heated at 140°C for 2.5 h. The mixture is cooled, the crystalline compound is filtered, washed with acetone, and crystallized from ethanol. Yield 51.5 g (68%) of chloride IIa, mp 260-261°C. IR spectrum: 3100-3300 (NH_2), 1680 (C=O), 1630 cm^{-1} ($C=N^+$). UV spectrum (in ethanol), λ_{max} (log ε): 209 (4.10), 235 (3.78), 277 nm (3.45). PMR spectrum (in CF_3COOH): 1.26 (6H, s, 3,3-CH_3), 2.45 (3H, s, 2-CH_3), 5.15 (2H, s, NCH_2), 6.96-7.55 ppm (4H, m, 4-H, 5-H, 6-H, 7-H); (in D_2O): 1.69 (6H, s, 3,3-CH_3), 5.53 (2H, s, NCH_2), 7.60-7.96 ppm (4H, m, 4-H, 5-H, 6-H, 7-H). Found, %: Cl 13.8, N 10.8. $C_{13}H_{17}ClN_2O$. Calculated, %: Cl 14.0, N 11.1.

1-Carbamoylmethyl-2,3,3,5-tetramethyl-3H-indolium chloride (IIb) is obtained from 17.3 g (0.1 mole) of 2,3,3,5-tetramethyl-3H-indole and 10.3 g (0.11 mole) of α-chloroacetamide in 10 ml xylene in the same way as described above for the preparation of chloride IIa. Yield 20.4 g (66%), mp 261-262°C (from ethanol). Found, %: Cl 13.2. $C_{14}H_{19}ClN_2O$. Calculated, %: Cl 13.3.

5-Bromo-1-carbamoyl-2,3,3-trimethyl-3H-indolium Chloride (IIc). A mixture of 11.2 g (0.05 mole) of 5-bromo-2,3,3-trimethyl-3H-indole, 5.6 g (0.06 mole) of α-chloroacetamide and 8 ml of xylene is heated at 140°C for 4.5 h. The mixture is cooled, the crystalline compound is filtered, washed with acetone, and crystallized from ethanol. Yield 8.5 g (51%) of chloride IIc, mp 243-244°C. PMR spectrum (in CF_3COOH): 1.34 (6H, s, 3,3-CH_3), 2.51 (3H, s, 2-CH_3), 5.23 (2H, s, NCH_2), 6.93-7.63 ppm (3H, m, 4-H, 6-H, 7-H). Found, %: N 8.6. $C_{13}H_{16}BrClN_2O$. Calculated, %: N 8.5.

1-Carbamoylmethyl-2,3,3-trimethyl-3H-indolium Iodide (IId). A mixture of 1.59 g (0.01 mole) of 2,3,3-trimethyl-3H-indole and 1.85 g (0.01 mole) of α-iodoacetamide is boiled in 3 ml of acetonitrile for 1.5 h. A crystalline compound separates and is filtered and crystallized from ethanol. Yield 1.17 g (34%) of iodide IId, mp 225-226°C. PMR spectrum (in CF_3·COOH) of compound IId corresponds to the spectrum of chloride IIa. Found, %: N 8.2. $C_{13}H_{17}IN_2O$. Calculated, %: N 8.1.

1-Carbamoylmethyl-2,3,3,5-tetramethyl-3H-indolium iodide (IIe) is obtained as described above for iodide IId from 1.73 g (0.01 mole) of 2,3,3,5-tetramethyl-3H-indole and 1.85 g (0.01 mole) of α-iodoacetamide. Yield 2.21 g (62%), mp 247-248°C (from ethanol). Found, %: N 8.0. $C_{14}H_{19}IN_2O$. Calculated, %: N 7.8.

3,3-Dimethyl-1-carbamoylmethyl-2-methylene-2,3-dihydroindole (IIIa). A solution of 25.3 g (0.1 mole) of chloride IIa in 200 ml of water is treated with sodium carbonate and extracted with 100 ml of ether. The ether solution is separated and left to stand for 3 h. The crystalline compound that separates is filtered, dried, and purified by reprecipitation from an acetone solution by hexane. Yield 18.9 g (88%) of the methylene base IIIa, mp 104-105°C. IR spectrum: 3300-3430 (NH_2), 1670 cm^{-1} (C=O). PMR spectrum ($CDCl_3$): 1.36 (6H, s, 3,3-CH_3), 3.96 (2H, C=CH_2), 4.06 (2H, s, NCH_2), 5.85 (1H, br, NH), 6.30 (1H, br., NH), 6.43-7.18 ppm (4H, m, 5-H, 6-H, 7-H, 8-H). Found, %: N 13.3. $C_{13}H_{16}N_2O$. Calculated, %: N 13.0.

9,9,9a-Trimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one (IVa). A. A solution of potassium hydroxide is added to a solution of 2.53 g (0.01 mole) of 1-carbamoylmethyl-2,3,3-trimethyl-3H-indole in 20 ml of water up to an alkaline reaction. The compound that separates out is extracted with ether, the solvent is distilled off, and from the residue the first fraction with R_f 0.6 is isolated on a column with aluminum oxide [acetone–hexane (3:5)]. After the distillation of the solvent, 0.15 g (7%) of imidazo 1,2-a indol-2-one IVa, mp 188-189°C (from ethanol) are obtained. PMR spectrum (in $CDCl_3$): 1.14 (3H, s, 9-CH_3), 1.35 (3H, s, 9-CH_3), 1.48 (3H, s, 9a-CH_3), 3.71, 3.84 (2H, AB-syst., NCH_3, J_{AB} = 16.3 Hz), 6.45-7.26 (4H, m, 5-H, 6-H, 7-H, 8-H), 8.38 ppm (1H, br., NH). Found, %: C 72.4, H 7.7, N 12.8. $C_{13}H_{16}N_2O$. Calculated, %: C 72.2, H 7.5, N 13.0.

B. A 2 ml portion of acetic acid is added to a solution of 2.16 g (0.01 mole) of the methylene base IIIa in 6 ml of acetone, and the mixture is boiled for 10 min. It is then cooled, poured into water, and the compound that separates is filtered and crystallized from ethanol. Yield 1.7 g (78%) of compound IVa, which is identical to the sample obtained in experiment A.

7,9,9,9a-Tetramethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one (IVb). A solution of 2.67 g (0.01 mole) of chloride IIb in water is treated with sodium carbonate and extracted with ether. The solvent is distilled, and the residue dissolved in 8 ml of acetone. A 2 ml portion of acetic acid is added, and the mixture is boiled for 10 min. It is then cooled, poured into water, and the compound separating out is filtered and crystallized from ethanol. The yield of compound IVb is 1.7 g (74%), mp 205-206°C. PMR spectrum ($CDCl_3$): 1.12 (3H, s, 9-CH_3), 1.33 (3H, s, 9-CH_3), 1.45 (3H, s, 9a-CH_3), 2.24 (3H, s, 7-CH_3), 3.67, 3.81 (2H, AB-syst., NCH_2, J_{AB} = 16.3 Hz), 6.49-7.00 (3H, m, 5-H, 6-H, 8-H), 8.25 ppm (1H, br., NH). Found, %: 12.0. $C_{14}H_{18}N_2O$. Calculated, %: N 12.2.

7-Brom-9,9,9a-trimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one (IVc) was obtained in a similar way as described above for compound IVb from 3.32 g (0.01 mole) of chloride IIc. Yield 2.21 g (75%), mp 221-222°C (from ethanol). PMR spectrum ($CDCl_3$): 1.14 (3H, s, 9-CH_3), 1.13 (3H, s, 9-CH_3), 1.47 (3H, s, 9a-CH_3), 3.64, 3.82 (2H, AB-syst., N=CH_2,

J_{AB} = 16.5 Hz), 6.48-7.30 (3H, m, 5-H, 6-H, 8-H), 8.06 ppm (1H, br., NH). Found, %: N 9.8. $C_{19}H_{15}BrN_2O$. Calculated, %: N 9.5.

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PORPHYRINS.

20.* INTERACTION OF 2-FORMYL-5,10,15,20-TETRAPHENYLPORPHYRIN WITH CH ACIDS

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The reactions of 2-formyl-5,10,15-20-tetraphenylporphyrin (Ia) with nitromethane and of its Cu complex (Ib) with nitromethane, malonic acid, and its esters have been investigated. On interacting porphyrins (Ia,b) with nitromethane in AcOH/$BuNH_2$ the 2-(2-nitrovinyl)porphyrins (IIa,b) were formed, in liquid NH_3 the nitroalcohols (IIIa,b) were formed, and in DMF/$BuNH_2$ the dinitro derivatives (IVa,b) were formed. The interaction of porphyrin (Ib) with malonic acid and its esters led to the corresponding condensation products in high yield.

The substance 5,10,15,20-tetraphenylporphyrin is one of the simplest and most widely investigated porphyrins in numerous catalytic processes. With the aim of designing accessible catalysts containing immobilized metalloporphyrin we have effected the synthesis of functionally substituted derivatives of tetraphenylporphyrin which may be used for immobilization on various carriers.

We consider the following route the most promising for obtaining functional derivatives of tetraphenylporphyrin. First, a formyl group was introduced into the tetraphenylporphyrin in the β-pyrrole position, and then various reactions were effected on it which led to a compound with an active functional group such as carboxyl. Such compounds may readily be used for covalent addition to various carriers.

The introduction of a formyl group into the tetraphenylporphyrin molecule by the Vilsmeier reaction has been investigated in sufficient detail and occurs in practically quantitative yield. It was shown in [2, 3] that 2-formyl-5,10,15,20-tetraphenylporphyrin (Ia) interacted readily with phosphoranes by the Wittig reaction forming derivatives of acrylic acid. It was established in the present study that porphyrin (Ia) and its Cu complex (Ib) reacted readily with CH acids with the formation of various functionally substituted derivatives of tetraphenylporphyrin.

*For Communication 19 see [1].

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