# SYNTHESIS OF NEW UNSATURATED MESOTETRAARYLPORPHYRINS

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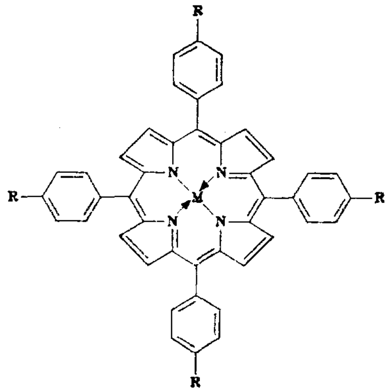
A method has been developed for the preparation of tetra(4'-vinylphenyl)porphyrin by the condensation of 4-β-halogenethylbenzaldehyde with pyrrole and dehydrohalogenation of the obtained tetra(4'-halogenethylphenyl) porphyrins.

The reaction of pyrrole with 4-allylhydroxy- and 4-propargylhydroxybenzaldehydes, and the O-alkylation of 5,10,15,20-tetra(4'-hydroxyphenyl)porphyrin with allyl and propargyl bromides gave 5,10,15,20-tetra(4'-allylhydroxyphenyl)porphyrin. The Cu(II)-, Ni(II)-, Co(II)- and Fe(III)Cl-complexes of these porphyrins have been synthesized.

In most cases the reaction between the functional groups of the polymers and the porphyrins is used to obtain polymeric catalysts with the attached metal—porphyrin complexes [2, 4]. The introduction of porphyrin fragments into the polymer chain is also achieved by the copolymerization of the porphyrin and other monomers [1, 3, 5]. Data in the literature on the synthesis of unsaturated derivatives of synthetic porphyrins that can undergo polymerization are limited. We have therefore undertaken to develop methods for the preparation of some tetraarylporphyrins and their metal complexes, containing substituents with double and triple bonds; since they appear to be promising for the synthesis of the above-mentioned systems, they are of interest themselves.

The present study was undertaken with the objective of developing procedures for the synthesis and investigation of the properties of monomeric porphyrins: 5, 10, 15, 20-tetra-(4'-vinylphenyl)porphyrin(III), 5,10,15,20-tetra(4'-allylhydroxyphenyl)porphyrin (VIII), 5,10,15,20-tetra(4'-propargylhydroxyphenyl)porphyrin (IX), and of their Cu(II)-, Ni(II)-Co(II)-, and Fe(III)Cl complexes:



I–XI

I $R=CH_2CH_2Cl$; II $R=CH_2CH_2Br$; III $R=-CH=CH_2$; IV—VII $R=-CH=CH_2$, VIII, X $R=OCH_2CH=CH_2$; IX, XI $R=OCH_2C\equiv CH$; I—III, VIII, IX $M=2H$, IV $M=Cu$, V $M=Ni$, VI, X, XI $M=CO$, VII $M=FeCl$

The approach selected for the synthesis of the porphyrin III consists of two stages. The condensation of pyrrole with 4-β-chloroethyl- and 4-β-bromoethylbenzaldehyde in boiling propionic acid leads to the 5,10,15,20-tetra(4'-β-halogenethylphenyl)porphyrins I and II with yields of 19 and 22% respectively. The subsequent dehydrohalogenation of compounds I and II proceeds easily in the presence of potassium hydroxide in DMFA at 40-50°C to give the compound III with high yields (more than 95%). The proposed method eliminates polymerization processes that take place when the substance III is prepared by the condensation of 4-vinylbenzaldehyde with pyrrole.

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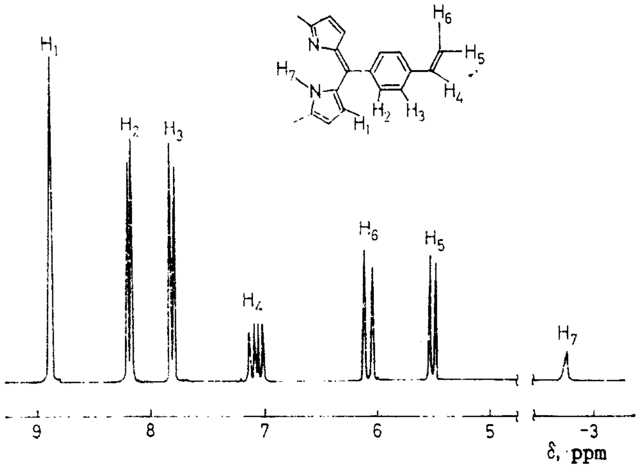

Fig. 1. PMR spectrum of 5,10,15,20-tetra(4'-vinylphenyl)porphyrin.

The metal complexes of porphyrins IV-VII were obtained by heating of compound III in solutions of the acetates of the corresponding metals (in acetic acid, propionic acid, or a mixture of acetic acid and chloroform). The yields were 70-95%. The synthesized porphyrin compounds were purified by column chromatography.

The composition and structure of the obtained porphyrins was confirmed by elemental analysis and by electron, IR, and PMR spectra. Compared to the spectrum of tetraphenylporphyrin (TPP), the IR spectrum of compound III shows some significant changes. The intensive band of the nonpolanar deformation vibrations $\delta_{(CH)}$ of the monosubstituted benzene ring in the region 700 $cm^{-1}$ has disappeared completely [6]. Absorption bands appear that are characteristic for the end-standing vinyl group: bands of the nonplanar deformation vibrations $\delta_{(=CH_2)}$ and $\delta_{(=CH)}$ at 913 and 995 $cm^{-1}$, of the valence vibration $\nu_{(C=C)}$ of the double bond, conjugated with the aromatic ring at 1626 $cm^{-1}$, and the valence vibration $\nu_{(=CH_2)}$ at 3080 $cm^{-1}$ [7]. The spectrum does not contain bands in the region 2800-3000 $cm^{-1}$ which are characteristic for the valence vibrations of the alkyl group; this indicates that the dehydrohalogenation of the β-halogenethyl groups takes place in all 4' positions of the phenyl rings.

The absorption bands characteristic for the end-standing vinyl group in the IR spectra of the metal complexes of III were found in the same regions of the spectrum as in the case of the metal-free porphyrin. As expected, the spectra of the metal complexes did not contain the valence vibration band $\nu_{(NH)}$ at 3220 $cm^{-1}$.

The PMR spectra of the porphyrin III (Fig. 1) shows the signals of the protons of the vinyl group at 7.05, 6.06, and 5.48 ppm with the expected chemical shifts. The ratio of the integral intensities of the protons of the vinyl groups and the protons of the pyrrole fragments indicates the presence of four vinyl group in the molecule.

The electron spectrum of compound III is similar to the spectrum of TPP and belongs to the etio-type [8]; this indicates a weak influence of the vinyl groups, conjugated with the aromatic rings, on the chromophoric system of the macroring.

The synthesis of porphyrins VIII and IX was achieved by two different approaches. In order to perform Rosenmund's reaction by the alkylation of 4-hydroxybenzaldehyde with allyl or propargyl halides, we prepared the starting 4-allylhydroxy- and 4-propargylhydroxybenzaldehydes [9, 10]. The reaction of the latter with pyrrole in boiling propionic acid for 1.5 h gives the porphyrins VIII and IX in satisfactory yields which are characteristic for this condensation (20%).

The other approach consisted in the conversion of tetra(4'-methoxyphenyl)porphyrin (T(4'-MeO)PP) to tetra(4'-hydroxyphenyl)porphyrin (T(4'-HO)PP) by the procedure described in [11], followed by the O-alkylation with allyl or propargyl bromides in DMFA in the presence of potassium carbonate. The porphyrin yields at this stage are high and are equal to 80% for compound VIII and 82% for compound IX. A comparison of the physicochemical parameters of the porphyrins VIII and IX, obtained by the described methods, showed that they were identical.

TABLE 1. Electronic Absorption Spectra of Tetraarylporphyrins

| Compound | Absorption bands, $\lambda_{max}$, nm ($\varepsilon \cdot 10^{-3}$) | | | | |
|---|---|---|---|---|---|
| | soret | IV | III | II | I |
| TPP | 420 (415,2) | 520 (19) | 550 (8,3) | 600 (6,03) | 655 (5,58) |
| T(4'-MeO)PP | 426 (403) | 523 (14,6) | 561 (10) | 598 (4,8) | 660 (6,7) |
| VIII | 425 (450) | 523 (17,2) | 560 (11,7) | 600 (5,5) | 665 (6,9) |
| IX | 425 (442,9) | 525 (18,0) | 560 (11,1) | 600 (5,53) | 650 (5,88) |

In the IR spectra of compounds VIII and IX the intensive band in the region 700 $cm^{-1}$ had disappeared, which is present in TPP and which is characteristic for the monosubstituted benzene ring [6]. An intensive band in the region 800 $cm^{-1}$ appears instead which is characteristic for out-of-plane deformation vibrations $\delta_{CH}$ of para-disubstituted benzene rings [12]. In comparison with the spectrum of TPP, additional bands appear in the regions of asymmetrical and symmetrical valence vibrations of the ether groups related to the aromatic ring: at 1245, 1028 $cm^{-1}$ for compound VIII and 1235, 1030 $cm^{-1}$ for compound IX. The spectrum of compound VIII also contains absorption bands which are characteristic for the end-standing vinyl group at $\delta_{=CH_2}$ 911, $\delta_{CH}$ 995, and $\nu_{C=C}$ 1655 $cm^{-1}$, and the spectrum of compound IX at $\nu_{C\equiv C}$ and $\nu_{\equiv CH}$ at 2125 and 3308 $cm^{-1}$, which indicate the presence of an end-standing acetylene group.

In the PMR spectra of compounds VIII and IX the protons of the pyrrole fragments appear as singlets at 8.8 ppm. The doublets at 8.07 and 7.22 ppm in the case of VIII and at 8.1 and 7.3 ppm in the case of IX with the same chemical shifts $J_{o,m}$ = 9 Hz indicate the presence of 1,4-disubstituted benzene rings. The protons of the NH groups appear in both cases at ≅2.8 ppm; this is characteristic for porphyrins [8]. Besides this, in the spectrum of compound VIII the presence of allyl-hydroxy groups is confirmed by the appearance of multiplets at 6.1, 5.55, and 5.35 ppm, and of a doublet at 4.72 ppm with J = 6 Hz; the spectrum of compound IX contains a doublet at 4.9 ppm and a triplet of 2.6 ppm with J = 2 Hz, indicating the presence of a propargylhydroxy group.

The electron absorption spectra of porphyrins VIII and IX, and of TPP and T(4'-MeO)PP are collected in Table 1. The data in Table 1 show certain changes in the spectrum which manifest themselves in an increase in the extinction coefficient of bands I and III in the transition from TPP to its 4-hydroxy-derivatives. In particular, the first band of the 4-substituted derivatives becomes more intensive than the second band, thus disturbing the etio-type of the TPP spectrum [8]. The changes in the spectrum agree with the conclusions reached in [13], where it has been demonstrated that electron donor substituents in the position 4 of the phenyl ring lead to an increase in the intensity of these bands; this is yet another confirmation for the formation of the desired compounds.

The cobalt complexes X and XI are obtained with high yields by the reaction of porphyrins VIII and IX with cobalt acetate in boiling propionic acid.

Preliminary results obtained in the radical copolymerization with styrene show that the synthesized porphyrin monomers V-VII (with the exception of the cobalt complex VI) are highly reactive; thus, they represent effective cross-linking agents and can be used for the preparation of structurized polymeric systems, including metal-porphyrin fragments.

## EXPERIMENTAL

The IR spectra of the compounds were recorded on an UR-20 spectrometer as suspensions in liquid petrolatum or as KBr tablets. The electronic spectra were taken on a Specord UV-vis spectrophotometer in chloroform (c = $10^{-6}$-$10^{-5}$ M). The PMR spectrum of compound III was obtained on a Bruker WM-250 instrument in $CDCl_3$, with TMS as an internal standard. The PMR spectra of compounds VIII and IX were taken on a Perkin-ELmer 12RB spectrometer (60 MHz) in $CDCl_3$, with HMDS as internal standard. Thin-layer chromatography was performed on Silufol UV-254 foils, column chromatography on alumina, Brockmann activity II.

4-β-Bromoethylbenzaldehyde was synthesized by the procedure given in [14]. 4-Allylhydroxy benzaldehyde, 4-propargylhydroxybenzaldehyde, TPP, T(4'-MeO)PP, and T(4'-OH)PP were obtained by the procedures described in [9-11, 15, 16].

4-β-Chloroethylbenzaldehyde was obtained under the conditions given in [14] by the reaction of equimolar amounts of β-chloroethylbenzene and α,α-dichloromethylmethyl ether in the presence of titanium tetrachloride with a yield of 48%. Found: C 63.8; H 5.5; Cl 21.5%. $C_9H_9ClO$. Theory: C 64.1; H 5.3; Cl 21.0%.

5,10,15,20-Tetra(4'-β-halogenethylphenyl)porphyrins (I, II). A mixture of 60 mmole 4-β-halogenethylbenzaldehyde and 4 g (60 mmole) pyrrole is added to 250 ml boiling proprionic acid and refluxed for 20 min. The reaction mixture is cooled to 20°C, the precipitate formed is filtered off, washed with methanol, water, and again with methanol, and dried in air. The substance is dissolved in 30 ml chloroform and chromatographed on a column (h = 50 cm, d = 3 cm) packed with alumina, by using chloroform as the eluent. After evaporation of the solvent to dryness the corresponding porphyrin remains.

5,10,15,20-Tetra(4'-β-chloroethylphenyl)porphyrin (I), yield 19%. $R_f$ 0.64 (chloroform-$CCl_4$ 1:1); electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 423 (458), 520 (19.1), 555 (9.5), 600 (5.7), 650 nm (5.3). Found: C 72.0; H 5.0; Cl 16.9; N 6.5%. $C_{52}H_{42}Cl_4N_4$. Theory: C 72.2; H 4.9; Cl 16.4; N 6.5%.

5,10,15,20-Tetra(4'-β-bromoethylphenyl)porphyrin (II), yield 21%. $R_f$ 0.58 (chloroform-$CCl_4$ 1:1). Electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 422 (305.2), 520 (13.3), 558 (7.1), 598 (4.9), 660 nm (4.5). Found: C 59.4; H 4.3; Br 30.3; N 5.3%. $C_{52}H_{42}Br_4N_4$. Theory: C 59.9; H 4.1; Br 30.7; N 5.4%.

5,10,15,20-Tetra(4'-vinylphenyl)porphyrin (III). A solution of 3 mmole of compound I or II in 150 ml DMFA, heated to 50°C, is treated under stirring with a solution of 8 g potassium hydroxide in 30 ml methanol and kept at this temperature for 7 h. The precipitate formed is filtered off, washed with water and ethanol, and dried in air. The substance is dissolved in 20 ml chloroform and chromatographed on 100 g alumina by using chloroform as the eluent, to isolate compound III after evaporation of the solvent. Yield 95%. $R_f$ 0.71 (chloroform-$CCl_4$ 1:3). IR spectrum: 913, 3080 $(=CH_2)$, 995 $(-CH=)$, 1626 $cm^{-1}$ $(C=C)$. Electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 425 (454.4), 520 (18.5), 560 (11.9), 600 (5.52), 650 nm (4.87). PMR spectrum: 8.87 (8H, s, 1-H); 8.16 (8H, d, 2-H, $J_{2-H,3-H}$ = 7.8 Hz); 7.8 (8H, d, 3-H); 7.05 (4H d.d, 4-H); 6.06 (4H, d, 6-H, $J_{4-H,6-H}$ = 17.6 Hz); 5.48 (4H, d, 5-H, $J_{5-H,4-H}$ = 10.7 Hz); −2.76 ppm (2H, s 7-H). Found: C 86.5; H 5.5, N 8.0%. $C_{52}H_{38}N_4$. Theory: C 86.9; H 5.3; N 7.8%.

5,10,15,20-Tetra(4'-vinylphenyl)porphyrinatocopper (IV). The solution of 0.5 g (0.7 mmole) of compound III in 80 ml chloroform is treated with a solution of 0.4 g (2 mmole) copper acetate in 50 ml acetic acid and refluxed with stirring for 4 h. After cooling the precipitated crystals are filtered off, washed with water and methanol, and dried. Yield 0.52 g (96.3%). Electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 421 (471.2), 545 nm (23.3). Found: C 79.7; H 4.3; Cu 8.5; N 7.5%. $C_{52}H_{36}CuN_4$. Theory: C 80.0; H 4.6; Cu 8.1; N 7.3%.

5,10,15,20-Tetra(4'-vinylphenyl)porphyrinatonickel (V) is obtained under the same conditions form 0.5 g (0.7 mmole) of compound III and 0.4 g (1.6 mmole) nickel acetate. Yield 0.52 g (96.4%). Electron spectrum (in DMFA), $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 427 (267), 535 nm (19.2). Found: C 80.6; H 4.7; N 7.6; Ni 8.1%. $C_{52}H_{36}N_4Ni$. Theory: C 80.5; H 4.7; N 7.2; Ni 7.6%.

5,10,15,20-Tetra(4'-vinylphenyl)porphyrinatocobalt (VI) is obtained under the same conditions from 0.4 g (0.55 mmole) of compound III and 2 g cobalt acetate. Yield 0.4 g (93%). Electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 435 (262), 533 nm (16.3). Found: C 80.8; H 5.2; Co 7.1; N 7.0%. $C_{52}H_{36}CoN_4$. Theory: C 80.5; H 4.7; Co 7.6; N 7.2%.

5,10,15,20-Tetra(4'-vinylphenyl)porphyrinatoiron Chloride (VII). The solution of 0.5 g (0.7 mmole) of compound III in 60 ml chloroform, containing 0.3 g sodium chloride, is treated with a filtered saturated hot solution of iron acetate, which is prepared by refluxing 10 g iron powder in 160 ml glacial acetic acid for 5 h. The reaction mixture is refluxed for 3 h, evaporated down to a volume of 50 ml, and cooled; the fine crystalline precipitate formed is filtered off, washed with methanol, repeatedly with water, and again with methanol, and dried in air. Yield 0.4 g (71.4%). Electron spectrum, $\lambda_{max}$ $(\varepsilon\cdot10^{-3})$: 426 (187), 520 nm (16.0). Found: C 77.3; H 4.5; Cl 4.7; Fe 6.9; N 6.9%. $C_{52}H_{36}ClFeN_4$. Theory: C 77.6; H 4.0; Cl 5.2; Fe 7.3; N 6.5%.

5,10,15,20-Tetra(4'-allylhydroxyphenyl)porphyrin (VIII). The mixture of 6.7 g (0.1 mole) pyrrole and 16.2 g (0.1 mole) 4-allylhydroxybenzaldehyde is added with stirring to 300 ml boiling propionic acid, and the solution refluxed for 1.5 h. A part of the solvent is evaporated until the formation of crystals starts. The mixture is cooled to 20°C, the precipitate formed is filtered off, washed with methanol, warm water, and again with methanol. The dry substance is dissolved in 50 ml chloroform and passed through a column (h = 100 cm, d = 3 cm) packed with alumina, using chloroform as the eluent. Yield after removal of the chloroform 3.1 g (19%). $R_f$ 0.61 (chloroform-benzene 3:2). IR spectrum: $\nu_{C=O}$ 1245, $\nu_{O-C}$ 1028, $\delta_{=CH_2}$ 911, $\delta_{CH=}$ 955, $\nu_{C=C}$ 1655 $cm^{-1}$. PMR spectrum: 8.8 (8H, s, pyrrole); 8.07 (8H, d, $H_o$, $J_{o,m}$ = 9 Hz); 7.22 (8H, d, $H_m$); 5-6.4 (12H, m, vinyl); 4.83 (8H, d, $CH_2$), −2.8 ppm (2H, s, NH). Electron spectrum, $\lambda_{max}$ ($\varepsilon \cdot 10^{-3}$): 425 (450), 523 (17.2), 560 (11.7), 600 (5.5), 665 nm (6.9). Found: C 80.3; H 5.7; N 6.8%. $C_{56}H_{46}N_4O_4$. Theory: C 80.2; H 5.5; N 6.7%.

5,10,15,20-Tetra(4'-propargylhydroxyphenyl)porphyrin (IX). The solution of 6.7 g (0.1 mole) pyrrole and 16 g (0.1 mole) 4-propargylhydroxybenzaldehyde in 20 ml xylene is added with stirring to 400 ml of boiling propionic acid; the mixture is refluxed for 1.5 h and allowed to stand overnight. The crystals formed are filtered off, washed with ethanol, warm water, and again with ethanol, and dried in air. The dry substance is dissolved in 20 ml chloroform and passed through a column (h = 50 cm, d = 3 cm) packed with alumina, using chloroform as the eluent. Yield after removal of the solvent 4.1 g (20%). $R_f$ 0.45 (chloroform-benzene 3:2). IR spectrum: $\nu_{C-O}$ 1235, $\nu_{O-C}$ 1030, $\nu_{C\equiv C}$ 2125, $\nu_{\equiv CH}$ 3308 $cm^{-1}$. PMR spectrum: 8.8 (8H, s, pyrrole); 8.1 (8H, d, $H_o$), 7.28 (8H, d, $H_m$, $J_{o,m}$ = 9 Hz), 4.88 (8H, d, $CH_2$); 2.6 (4H, t, ≡CH), −2.8 ppm (2H, s, H). Electron spectrum $\lambda_{max}$ ($\varepsilon \cdot 10^{-3}$): 425 (443), 525 (18), 560 (11.1), 600 (5.53), 650 nm (5.88). Found: C 81.1; H 5.0; N 6.9%. $C_{56}H_{38}N_4O_4$. Theory: C 80.9; H 4.6; N 6.7%.

General Method for the Synthesis of Unsaturated Derivatives of Tetraphenylporphyrin (VIII, IX) by O-Alkylation of 5,10,15,20-Tetra(4'-hydroxyphenyl)porphyrin. The mixture of 3 g (4 mmole) 5,10,15,20-tetra(4'-hydroxyphenyl)porphyrin, 24 g potassium carbonate, and 8.8 mmole allyl bromide or propargyl bromide in 200 ml DMFA is refluxed for 1 h. The reaction mixture is poured into 1 liter of water, refluxed for 30 min, and the precipitate formed filtered off. The dried substance is dissolved in 20 ml chloroform and chromatographed on a a column (h = 50 cm, d = 3 cm) packed with alumina, by using chloroform as the eluent. After evaporation of the solvent and treatment of the residue with 50 ml ethanol the porphyrins VIII and IX are obtained with yields of 80 and 82% respectively.

5,10,15,20-Tetra(4'-allylhydroxyphenyl)porphyrinatocobalt (X). 0.55 g (0.65 mmole) of compound VIII and 2 g cobalt acetate is refluxed in 250 ml propionic acid for 1.5 h. After removal of the solvent, the residue is treated with 50 ml water; the precipitate formed is filtered off and washed with water. The dried reaction product is dissolved in 15 ml chloroform and chromatographed on a column (h = 50 cm, d = 2 cm) packed with alumina, with chloroform as the eluent. The solvent is evaporated to dryness. Yield 0.5 g (86%). Electron spectrum, $\lambda_{max}$ ($\varepsilon \cdot 10^{-3}$): 415 (241.9), 532 nm (15.2). Found: C 75.2; H 5.3; Co 6.4; N 6.3%. $C_{56}H_{44}CoN_4O_4$. Theory: C 75.1; H 4.9; Co 6.6; N 6.2%.

5,10,15,20-Tetra(4'-proparygylhydroxyphenyl)porphyrinatocobalt (XI) is obtained analogously to compound X with a yield of 90%. Electronic spectrum, $\lambda_{max}$ ($\varepsilon \cdot 10^{-3}$): 416 (183.3), 536 nm (14.7). Found: C 75.3; H 4.4; Co 6.1; N 6.1%. $C_{56}H_{36}CoN_4O_4$. Theory: C 75.8; H 4.1; Co 6.6; N 6.3%.

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# 1,2,3,9a-TETRAHYDRO-9H-IMIDAZO[1,2-a]INDOLES

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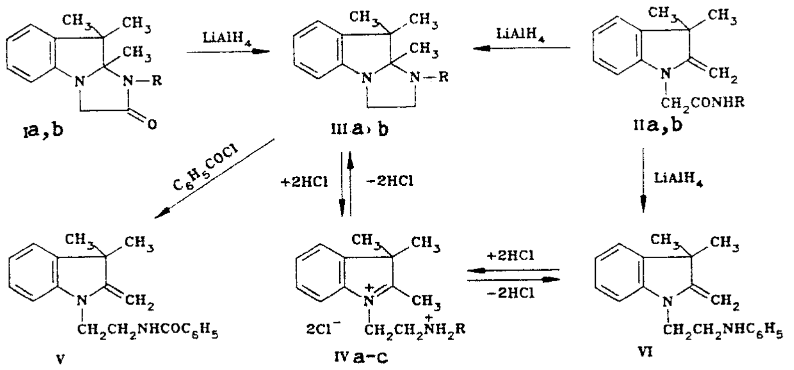
When derivatives of 1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one or 1-carbamoylmethyl-2-methylene-2,3-dihydroindole are reacted with lithium aluminum hydride, derivatives of 1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indole are formed. Under the same conditions 1-(N-phenylcarbamoylmethyl)-2-methylene-2,3-dihydroindole is not cyclized to an imidazo[1,2-a]indole. When treated with proton acids imidazo[1,2-a]indoles are converted to 3H-indolium salts. Opening of the imidazolidine ring is also found when imidazo[1,2-a]indole is acylated with benzoyl chloride.

It has been reported previously [1] that when 1-carbamoylmethyl-2,3,3-trimethyl-3H-indolium chloride is treated with bases an intramolecular nucleophilic addition of the amide nitrogen to the α-carbon atom of the indole ring takes place with the formation of 1,2,3,9a-tetrahydro-9H-imidazo[1,2-a]indol-2-one (Ia). In this reaction a certain fraction of the initial salt does not undergo cyclization but is converted to the methylene base IIa. It was of interest to carry out the reduction of the carbonyl group of imidazolidines Ia,b and 1-carbamoylmethyl-2-methylene-2,3-dihydroindoles IIa,b to a methylene group using lithium aluminum hydride and to study the cyclic chain conversions of the hydrogenated compounds obtained when they were treated with acids and bases.

The tricyclic compounds Ia,b react with lithium aluminum hydride extremely slowly and the yields of imidazolidines IIIa,b after heating for 36 h in tetrahydrofuran do not exceed 20%. Under similar conditions reduction of the carbonyl group of the methylene base IIa is complete within 1.5-2 h.



I, III, IV a $R=H$, b $R=CH_2C_6H_5$; II a $R=H$, b $R=C_6H_5$; IV c $R=C_6H_5$

In this case addition of the nitrogen atom to the enamine double bond takes place and the final reaction product is imidazolidine IIIa. This cyclization can be grouped with those reactions typical of enamine compounds [2, 3].

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