

temperature, and 21 ml (0.15 mole) of triethylamine and 19.65 g (0.1 mole) of glycyglycine ethyl ester hydrochloride were added. After this, the temperature was raised to 50-60°C, and the mixture was stirred for 12-15 h. At the end of the reaction (monitoring by TLC) the solvent was evaporated *in vacuo*, and the p-nitrophenol was extracted from the residue with ether. Ethyl acetate (500 ml) was added to the residue, and the triethylamine salt was removed by filtration. The filtrate was passed through a column filled with neutral aluminum oxide, the ethyl acetate was evaporated, and the resulting yellow oil crystallized in air. The yield of dipeptide IV, with mp 105-106°C, was 12.1 g (65%).

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PYRROLES FROM KETOXIMES AND ACETYLENE.

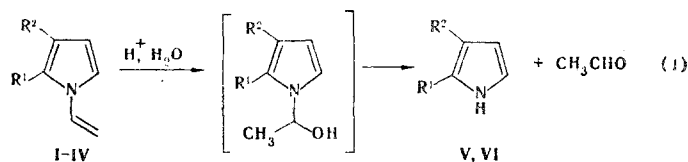
24.* ACIDIC HYDROLYSIS OF 1-VINYLPYRROLES

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The hydrolysis of 2-methyl-, 2-phenyl-, and 3-methyl-2-phenyl-1-vinylpyrroles and 1-vinyl-4,5,6,7-tetrahydroindole in the presence of HCl, H₂SO₄, NH₂OH·HCl, acetic acid, and H₂O₂ in aqueous, aqueous dioxane, and aqueous alcohol solutions leads to oligomers with complex structures and compositions, viz., products of acidic catalytic and oxidative condensation of the starting compounds and the resulting pyrroles both with one another and with the liberated acetaldehyde. 2-Phenylpyrrole was obtained in 52% yield from 1-vinyl-2-phenylpyrrole by hydrolysis in a dilute (~0.5%) solution [water-dioxane (5:9)] with excess NH₂OH·HCl, which ties up the acetaldehyde.

The literature contains no information regarding the transformations of 1-vinylpyrroles in aqueous acidic media, although without such information it is impossible to skillfully use these monomers and intermediates, which have now become accessible [2]. One might have assumed that 1-vinylpyrroles would be hydrolyzed in the same way as 1-vinylindole [3], 9-alkenyl-carbazoles [4-7], 10-vinylphenothiazine [8], and 1-vinylactams [9], i.e., via the scheme



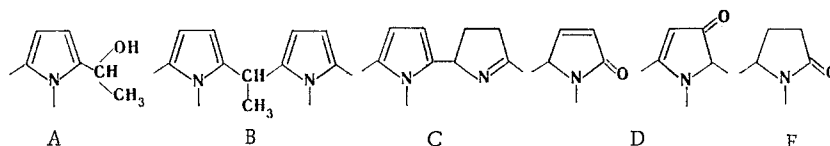
I R¹=Me, R²=H; II, V R¹-R²=(CH₂)₄; III, VI R¹=Ph, R²=H; IV R¹=Ph, R²=Me

However, studies have shown that this scheme can be realized for 1-vinylpyrroles only in dilute solutions under the condition of tying up the liberated acetaldehyde (by means of

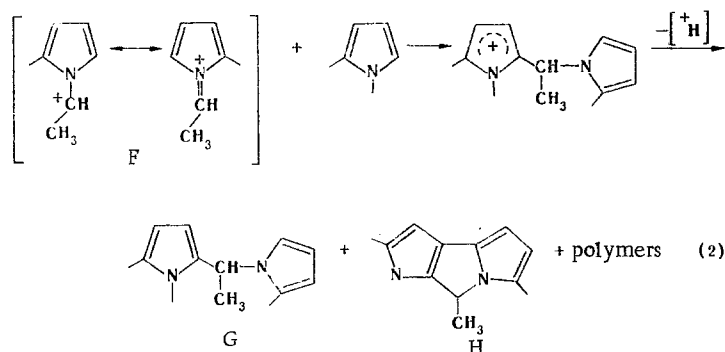
*See [1] for Communication 23.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 12, pp. 1631-1639, December, 1982. Original article submitted April 28, 1982.

hydroxylamine, for example). Under ordinary conditions, however, complex acidic catalytic and oxidative processes involving condensation of the starting compounds and resulting pyrroles both with acetaldehyde and with one another occur. As a result, mixtures of deeply colored oligomeric products, the compositions of which change as a function of the hydrolysis and isolation conditions, are formed. On the basis of the literature data [10-12], as well as the spectral (IR, PMR, and EPR) characteristics and the results of elementary analysis, it may be assumed that they contain 1-hydroxyethyl (A), 1,1-di(2-pyrryl)ethane (B), 2-pyrrylpyrroline (C), pyrrolinone (D), and pyrrolidinone (E) fragments.



Attack of the intermediate carbimmonium ion (F) at the double bond (cationic vinyl polymerization) or at the pyrrole ring with corresponding intra- and intermolecular transformations should also play an appreciable role in the formation of the structures of the products of acidic hydrolysis of 1-vinylpyrroles, particularly when insufficient water is present:



As one should have expected, 1-vinylpyrroles I and II with alkyl substituents in the ring proved to be the least resistant to acidic hydrolysis. They are readily hydrolyzed by dilute acids at room temperature. Thus if 1-vinyl-4,5,6,7-tetrahydroindole (II) is stirred without heating with a 1% aqueous solution of HCl, only ~65% of the starting substance can be recovered after 1 h. At 65°C the same pyrrole is converted completely after 2.5 h to an orange-red resinous substance, whereas no more than 1-1.5 h is required for this at 90-96°C with 0.6-1% HCl.

According to the IR spectra (Fig. 1), fragments with conjugated double bonds, carbonyl groups, and NH and OH groups (a broad intense doublet at 1650-1700 cm^{-1} with maxima at 1640 and 1690 cm^{-1} and a very broad intense band at 3000-3600 cm^{-1} with a maximum at 3400 cm^{-1}) predominate in the reaction products, and the cyclohexane rings (2850 and 2930 cm^{-1}) are also retained. The elementary compositions of the substances obtained (9-14% oxygen) are in agreement with the high percentages of carbonyl and hydroxy groups recorded by the IR spectra. Several overlapped quartets (3.6-4.3 ppm) and doublets (1.5-1.7 ppm) of CH-CH₃ groupings (A, B, G, and H fragments), as well as weak signals of N-vinyl (5.0-5.2 ppm) and pyrrole (5.6-6.3 ppm) protons, can be isolated in the PMR spectra. The broad diffuse lines indicate the polymeric structures of the resulting compounds and that the groupings listed above are situated in different environments. The narrow intense signal in the EPR spectra ($\sim 1 \cdot 10^{18}$ spins/g, $\Delta H = 0.8-1.0$ mT) constitutes evidence for the presence of a developed polyconjugation chain in the compounds.

The formation of 4,5,6,7-tetrahydroindole (V) in ~5% yield from its vinyl derivative II was observed only when hydrolysis was carried out in excess acidified NH₂OH·HCl. A special experiment showed that pyrrole V itself is unstable under acidic catalytic hydrolysis conditions: At 65°C in 1% aqueous HCl solution it underwent 66% conversion to a brown-red resin after 2.5 h. In the presence of acetaldehyde under the same conditions the degree of conversion of pyrrole V to a polymer was 90%.

Replacement of the 1-vinyl group in the pyrrole ring by an ethyl group substantially increases the resistance of the molecule to acidic hydrolysis. Thus whereas in the presence

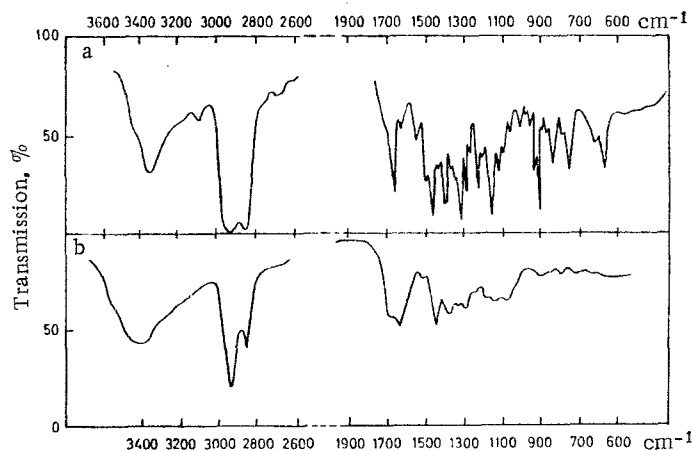


Fig. 1. IR spectra of the products of hydrolysis of 1-vinyl-4,5,6,7-tetrahydroindole II: a) 0.6% HCl, H₂O-dioxane (1:1), 96°C, 1.5 h; b) 1% HCl, water, 90°C, 1 h.

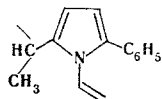
of 1% HCl at 65°C pyrrole II undergoes complete polymerization after 2.5 h, 1-ethyl-4,5,6,7-tetrahydroindole under the same conditions remains virtually completely unchanged. This fact confirms the active participation of the N-vinyl group (the carbonium center generable from it) in hydrolysis processes (see the initial scheme in this article). The rapid conversion of pyrrole II to solid condensation products when it is heated with 33% hydrogen peroxide constitutes evidence that purely oxidative transformations that lead to structures of the D and E type also make a substantial contribution to them.

As compared with 2- and 2,3-dialkyl-1-vinylpyrroles, 1-vinyl-2-phenylpyrroles III and IV are appreciably more resistant to acidic hydrolysis. Without heating they remain virtually unchanged upon prolonged contact (15 h) with a 0.4-1.3% aqueous solution of HCl. However, they undergo complete condensation to solid deeply colored resins with red tones at 96°C in the same solutions after 1.5 h. Their IR spectra (Fig. 2a) contain several bands in common with the spectra of 2-phenyl- and 1-vinyl-2-phenylpyrroles, although the complete frequency set of these compounds is lacking.

The new absorption regions indicate the development in the products of condensation of the aliphatic fragments (1370, 1452, 2855, and 2965 cm⁻¹; evidently CH-CH₃ in the A, B, G, and H structures) of a conjugated carbonyl group (1690 cm⁻¹; structures of the D and E type), an NH group, and, possibly, an OH group (3300 cm⁻¹). The PMR spectra of these compounds contain a strong broad unresolved signal at 6.7-7.5 ppm, which belongs to phenyl and pyrrole protons, and weak poorly resolved multiplets at 5.6 ppm (CH-CH₃) and at 1.4-1.7 ppm (CH-CH₃). The poor resolution of the signals is explained by different environments of the fragments and the presence of oligomers.

A comparison of the IR and PMR spectra and the results of elementary analysis of the products of hydrolytic condensation of pyrroles III and V leads to the conclusion that 1-vinyl-2-phenyl-3-methylpyrrole (IV) under comparable conditions undergoes more profound (than pyrrole III) oxidative hydrolysis: One observes a larger amount of oxygen in the products, more intense bands of carbonyl groups in the IR spectrum (Fig. 2b), and broader and more complex signals in the PMR spectrum. This is in agreement with the known fact of the facilitation of the protonation of the pyrrole ring when alkyl substituents are introduced into it (protonation accelerates the oxidation and polycondensation of pyrroles [10-12]).

According to the IR and PMR spectroscopic data, the hydrolysis products obtained at a lower HCl concentration (0.8%) contain the fragment depicted below:



Evidence for this is provided by the characteristic absorption bands [13] (Fig. 2c) and signals of the protons [14] of the N-vinyl group and the CH-CH₃ groups (the presence of incom-

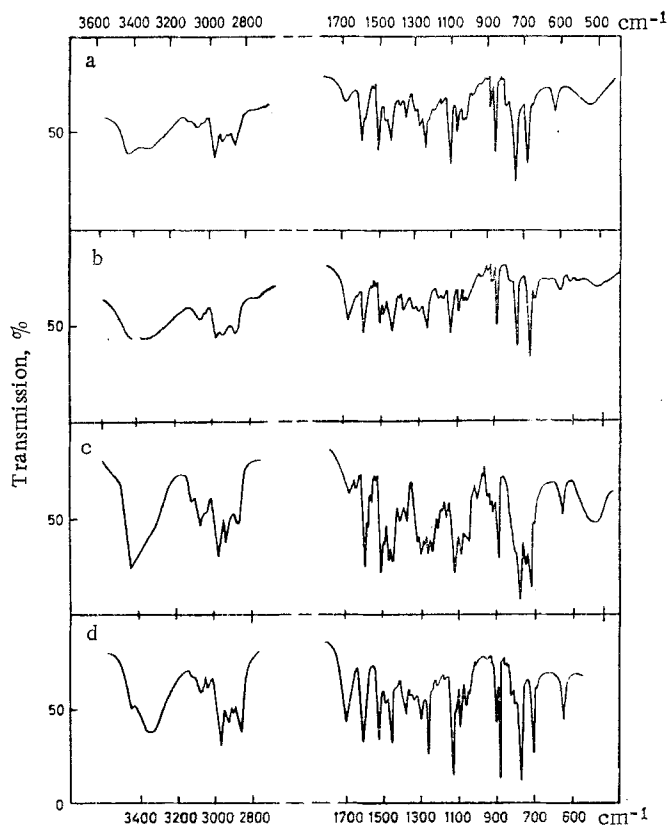


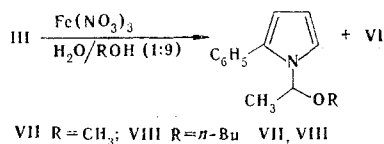
Fig. 2. IR spectra of the products of hydrolysis of 1-vinyl-2-phenylpyrroles (III, IV): a) pyrrole III, 1.3% HCl, water-dioxane (1:1), 96°C, 1.5 h; b) pyrrole IV (under the conditions in point a); c) pyrrole III, 0.8% HCl, water-dioxane (2.5:1), 96°C, 1.5 h; d) pyrrole III, 0.5% H₂SO₄, water-dioxane (1:5), 96°C, 1.5 H.

pletely hydrolyzed starting N-vinylpyrroles is excluded, since the entire set of their frequencies is not present in the IR spectrum). The broadening of the signals of the protons of the phenyl and pyrrole rings, as well as of the vinyl and ethylidene groups, indicates that they evidently are present in the compositions of the various oligomeric compounds that include fragments A-H. However, the decreased intensity of the two bands at 1684 and 1690 cm⁻¹ and the lower percentage of oxygen are in agreement with the smaller contribution of the oxidized structures (D, E). Correspondingly, in the case of the solid products of hydrolysis of pyrrole III obtained at an even lower acidity (0.4% HCl, 96°C, 1.5 h) the IR spectrum and the results of elementary analysis established a further decrease in the percentages of the oxidized structures (one band of medium intensity at ~1680 cm⁻¹), although doublet and triplet splitting of the principal bands, which constitutes evidence for different environments of the structural elements, is also retained in this case. Analysis by thin-layer chromatography (TLC) of the reaction mixture obtained under milder conditions [pyrrole III, 0.4% HCl, water-dioxane (1:1), room temperature, 15 days] demonstrates the presence in it, in addition to pyrroles III (in preponderance) and VI (traces), of at least seven different products, which confirms the complexity of the acidic catalytic hydrolysis of 1-vinylpyrroles.

The nature of the acid affects the degree and character of the hydrolysis of 1-vinylpyrroles. Thus, according to the IR spectrum, pyrrole and benzene rings are not observed in the products of hydrolysis of pyrrole III obtained in the presence of 0.5% H₂SO₄ (96°C, 1.5 h), and this indicates profound polycondensation and oxidative (intense absorption at 1680 cm⁻¹) transformations with the participation of these fragments. The complex absorption at 1500-1700 cm⁻¹ (maxima at 1520, 1604, 1652, and 1680 cm⁻¹) is probably associated with the presence in the polymer of blocks of polyconjugation with the carbonyl groups. At the same time, 2% acetic acid under the same conditions has virtually no effect on this pyrrole, where-

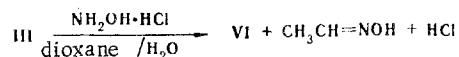
as only traces of 2-phenylpyrrole (VI) are formed after 12 days when it is in contact with 7% acetic acid (at room temperature).

It is known [5] that ferric nitrate at room temperature catalyzes the hydrolytic decomposition of 9-vinylcarbazole in aqueous methanol (1:9) to carbazole and acetaldehyde or (at a higher concentration) causes its dimerization to trans-1,2-dicarbazylcyclobutane. However, pyrrole III under these conditions undergoes very little hydrolysis (the yield of pyrrole VI is ~10%) and primarily adds alcohol to give 1-(1-alkoxyethyl)-2-phenylpyrroles (VII, VIII) in 76-85% yields.



2-Phenylpyrrole (VI) in the presence of HCl reacts with acetaldehyde exothermally to give substances, the appearance and spectra (IR and PMR) of which change qualitatively as a function of the condensation conditions and the methods used to isolate them. Thus when the reaction and removal of the solvent (ethanol) are carried out without heating (with ~1% HCl), one can obtain dark-red crystals, which even upon gentle heating (40-50°C) in order to dry them undergo irreversible changes (they melt, darken, and resinify). A red-brown resin is formed from 2-phenylpyrrole and acetaldehyde at 96°C [water-dioxane (1:3), 0.5% HCl, 1.5 h].

We were able to obtain 2-phenylpyrrole (VI) in 52% yield only by hydrolyzing pyrrole III in a dilute aqueous dioxane solution of hydroxylamine hydrochloride (80°C, 2 h), which ties up the acetaldehyde that is formed. The course of the hydrolysis can be followed by titrating the liberated acid (Fig. 3). It is known [11] that protonated pyrrole under the influence of hydroxylamine is capable of undergoing ring opening to give succinaldehyde oxime. However, the oximation of 2-phenylpyrrole was not observed when it was heated (90°C, 1 h) with excess NH₂OH·HCl in aqueous dioxane solution (homogeneous conditions). The liberation of acid in the hydrolysis of pyrrole III with hydroxylamine hydrochloride can be ascribed entirely to oximation of the acetaldehyde formed in the reaction.



It is apparent from Fig. 3 that the course of the hydrolysis is affected not only by the temperature of the process but also by the initial acidity of the solution. One's attention is directed to the extremal character of curves 1 and 2, which indicates gradual tying up of the liberated acid by the hydrolysis products. Dimers of the C type, which form salts with strong acids [10-12], are evidently responsible for this.

EXPERIMENTAL

The PMR spectra of solutions of CCl₄ were recorded with Tesla BS-487C spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard. The IR spectra were recorded with a UR-20 spectrometer. The EPR spectrum was obtained with a THN-252 spectrometer (Tomson, France). Potentiometric titration was carried out with a Universal pH meter of the OP-204/1 type at 20°C. Chromatographic analysis was performed with a Khrom-4 chromatograph (the detector was a catharometer, the column was 2.5-m long and had a diameter of 3 mm, the solid phase was Chromaton N-AW-DMCS, the liquid phase was 15% DS-550 silicone, the thermostat temperature was 170°C, and the carrier gas was helium) and in a thin layer [Silufol UV-254, elution with hexane-ether (3:1)].

Pyrroles I and V were synthesized by the method in [15], II was synthesized by the method in [16], III and VI were obtained by the method in [14], and 1-ethyl-4,5,6,7-tetrahydroindole and 1-ethyl-2-phenylpyrrole were prepared by the method in [17].

Hydrolysis of 1-Vinyl-2-methylpyrrole (I). A mixture of 0.5 g (4.7 mmole) of pyrrole I, 1 ml of water, 1 ml of dioxane, and 0.1 ml of concentrated HCl was maintained at room temperature for 22 h with periodic shaking. The mixture was then neutralized with aqueous KOH solution and extracted with ether, and the ether extracts were washed with water and dried with

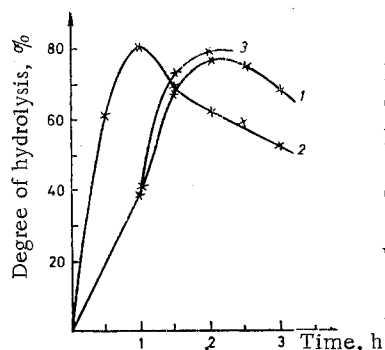


Fig. 3. Change in the percentage of HCl in the hydrolysate in the hydrolysis of 1-vinyl-2-phenylpyrrole (III) in the presence of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (100% corresponds to the liberation of one equivalent of HCl per mole of pyrrole III) at 80°C (1, 3) and 90°C (2). The following equivalent amounts of HCl were contained in 25 ml of 0.5 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ used for the hydrolysis: $1.48\cdot 10^{-4}$ (1, 2) and $1.85\cdot 10^{-4}$ (3).

potassium carbonate. The ether was removed to give 0.3 g of a viscous yellow-brown liquid, which, according to GLC and the IR spectrum, contained, in addition to resinous substances, starting vinylpyrrole I; however, 2-methylpyrrole was absent.

Hydrolysis of 1-Vinyl-4,5,6,7-tetrahydroindole (II). A) A 0.8-g (5.4 mmole) sample of pyrrole II was heated with 4 ml of 1% aqueous HCl solution at 65°C for 2.5 h. The mixture immediately turned violet and became viscous, and the odor of acetaldehyde developed. Work-up gave 0.68 g of a brown-red resin (soluble in ether, acetone, methanol, ethanol, butanol, benzene, dioxane, CCl_4 , and CHCl_3 , but insoluble in petroleum ether). Neither starting pyrrole II nor 4,5,6,7-tetrahydroindole was detected in the hydrolysis products by GLC.

B) A mixture of 0.55 g (3.7 mmole) of pyrrole II, 1 ml of H_2O , and 1 ml of dioxane was heated at 96°C for 1.5 h in the presence of 0.6% HCl. The reaction mixture (lilac-colored) was extracted with ether, and the ether was removed to give 0.5 g of a nonhomogeneous orange-red product consisting of a liquid and a resin that was insoluble in it. According to the IR spectrum, the liquid contained starting pyrrole II; the IR spectrum of the resin is reproduced in Fig. 1a. The PMR spectrum of the liquid contained broad signals of pyrrole protons (5.67 and 6.22 ppm), weak signals of the β protons of two different $\text{N}-\text{CH}=\text{CH}_2$ groups shifted ~ 6 Hz relative to one another (5.2 and 5.0 ppm), and intense H_2O singlet (3.55 ppm), broad and very intense signals of the CH_2 groups of the cyclohexane ring (2.42 and 1.55 ppm), somewhat overlapped CHCH_3 quartets at 3.6–4.3 ppm, and broad doublets of CH_3 groups (1.6 ppm) overlapped with a strong-field CH_2 signal. Found: C 70.3; H 7.2; N 8.2%.

C) A 3.1-g (21 mmole) sample of pyrrole II was heated with 10 ml of 1% aqueous HCl solution at 90°C for 1 h, after which the mixture was extracted with ether, and the extract was dried with Na_2SO_4 (according to the GLC data, the starting pyrrole was not present in the extract). Removal of the ether gave 2.1 g of an orange-red solid substance. IR spectrum, cm^{-1} : 720 (w), 790 (w), 920 (w), 1060 (m), 1140 (m), 1290 (m), 1313 (m), 1440 (s), 1520 (w), 1628 (s), 1680 (s), 2860 (s), 2935 (vs), and 3400 (vs) (all of the bands were broad and poorly resolved with split maxima; see Fig. 1b). The part of the reaction mixture that was insoluble in hot octane (with mp $260\text{--}270^\circ\text{C}$ after drying *in vacuo*) had an intense signal in its EPR spectrum ($3.3\cdot 10^{18}$ spins/g, $\Delta H = 0.95$ mT). The results of its elementary analysis (C 74.2; H 7.8; N 8.9%) indicated the presence of oxygen in its composition, in agreement with the presence of an intense band of a conjugated carbonyl group in its IR spectrum (1680 cm^{-1}).

D) A mixture of 1 g (6.8 mmole) of pyrrole II, 2.1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$, 10 ml of H_2O , and 0.03 ml of concentrated HCl was shaken at 60°C (pronounced resinification was observed). It was found by GLC that the ether extract contained 0.08 g of starting pyrrole and 0.04 g ($\sim 5\%$) 4,5,6,7-tetrahydroindole (VI); the principal substance (0.8 g) was a deeply colored resin.

E) A 3-g (20 mmole) sample of pyrrole II was heated with 10 ml of 33% H_2O_2 at $60\text{--}70^\circ\text{C}$ for 3 h, after which the mixture was extracted with ether. The extract was dried with KOH and distilled *in vacuo*, as a result of which 1.9 g of the starting pyrrole was recovered, and 1.3 g of resinous residue was obtained.

Hydrolysis of 4,5,6,7-Tetrahydroindole (V). A 0.94-g (7.8 mmole) sample of pyrrole VI was heated with 4.7 ml of 1% aqueous HCl solution at 65°C for 2.5 h. The mixture immediately turned pink, after which it reddened and gradually darkened. A saturated aqueous solution of K_2CO_3 was added, and the mixture was extracted with ether to give 0.78 g of a brown-red substance containing 0.31 g of the starting pyrrole (66% conversion).

Condensation of 4,5,6,7-Tetrahydroindole (V) with Acetaldehyde. A mixture of 1.2 g (9.9 mmole) of pyrrole VI, 6 ml of 1% aqueous HCl solution, and 0.34 g (7.7 mmole) of acetalde-

hyde was heated at 65°C for 2.5 h (the solution darkened when the acetaldehyde was added, and solid condensation products developed). At the end of the experiment the mixture was violet-brown, and there was a gray precipitate on the bottom of the reaction vessel. A saturated aqueous solution of potassium carbonate was added, and the mixture was extracted with ether to give 1.3 g of a solid substance (acicular crystals and a resin), from which 0.12 g of the starting pyrrole was isolated (90% conversion).

Hydrolysis of 1-Ethyl-4,5,6,7-tetrahydroindole. A 0.53-g (3.6 mmole) sample of 1-ethyl-4,5,6,7-tetrahydroindole was heated with 2.5 ml of a 1% aqueous solution of HCl at 65°C for 2.5 h. At the end of the experiment the mixture took on a red-brown color, although, according to GLC, it did not contain other volatile substances in addition to the starting substance. A 0.42-g sample of the starting pyrrole was isolated by extraction with ether, removal of the ether by distillation, and vacuum distillation of the residue.

Hydrolysis of 1-Vinyl-2-phenylpyrrole (III). A) A mixture of 1.2 g (7.1 mmole) of pyrrole III, 2 ml of H₂O, 2 ml of dioxane, and 0.2 ml of concentrated HCl (v.1.3% HCl of the reaction mass) was stirred at 96°C for 1.5 h. After 5 min, the mixture took on a lilac color, and the color continued to deepen. Extraction with ether gave 0.8 g of a brown-red compound with mp 58-68°C that was soluble in ether, acetone, chloroform, CCl₄, benzene, dioxane, dichloroethane, nitrobenzene, dimethyl sulfoxide (DMSO), and cyclohexanone but insoluble in ethanol, hexane, and isopropyl alcohol. After reprecipitation from CHCl₃ by the addition of hexane and removal of the solvents by heating *in vacuo* to constant weight, the substance had mp 120-150°C. Found: C 82.7; H 6.3; Cl 0.6; N 8.2%. IR spectrum - Fig. 2a.

B) The hydrolysis of 1 g (5.9 mmole) of pyrrole III by means of 5 ml of H₂O, 2 ml of dioxane, and 0.8% HCl and heating at 96°C for 1.5 h gave 1.2 g of a substance with mp 45-57°C. Found: C 85.3; H 6.3; N 8.5%. With respect to its principal bands, the IR spectrum was identical to the IR spectrum of the compounds from the preceding experiment except for a strong band at 1642 cm⁻¹ (the CH₂=CH-N groups of 1-vinylpyrroles [13]). PMR spectrum (80 MHz, CCl₄, hexamethyldisiloxane): broad signals at 6.8-7.3, 5.9-6.0, and 1.4-1.7 ppm (signals of pyrrole III were present at 6.8-7.2 and 6.1 ppm).

C) A mixture of 0.55 g (3.3 mmole) of pyrrole III, 1 ml of water, and 1 ml of dioxane was heated with stirring at 96°C in the presence of 0.4% HCl for 1.5 h. Workup gave 0.5 g of a dark-brown resin. With respect to the principal bands in the IR spectrum, this product was identical to the preceding product; however, many of the bands were split into doublets and triplets.

D) A mixture of 1.2 g (7.1 mmole) of pyrrole III, 2 ml of water, and 10 ml of dioxane was heated at 96°C in the presence of 0.5% H₂SO₄ for 1.5 h. Workup gave 1.1 g of a brown resin. The IR spectrum is presented in Fig. 2d.

E) A mixture of 1.2 g (7.1 mmole) of pyrrole III, 2 ml of water, 2 ml of dioxane, and 0.2 ml of concentrated HCl (v.1.3% HCl of the reaction mass) was stirred at room temperature for 15 h. Extraction with ether and removal of the solvent gave 1.1 g of a red-orange liquid, the IR and PMR spectra of which were in agreement with starting pyrrole III.

F) A mixture containing 0.5 g (2.9 mmole) of pyrrole III, 1 ml of water, 1 ml of dioxane, and 0.4% HCl was maintained at room temperature for 15 days. Workup gave 0.4 g of a dark-red liquid, which, according to data from TLC and the IR spectra (as compared with the spectra of genuine samples) contained primarily starting pyrrole III, a small amount of 2-phenylpyrrole, and seven unidentified substances.

G) A mixture of 1 g (5.9 mmole) of pyrrole III, 2 ml of water, and 2 ml of dioxane was heated at 96°C in the presence of 2% acetic acid for 1.5 h. Workup gave 0.85 g of orange liquid, which, according to the IR spectrum, was the starting pyrrole.

H) A 1.04-g (6.2 mmole) sample of pyrrole III was maintained at room temperature for 12 days in the presence of 7% acetic acid, 5 ml of water, and 1 ml of dioxane. The mixture was then extracted with ether, and the ether was removed to give 0.9 g of a yellow-brown liquid, which was found to be starting pyrrole III with traces of 2-phenylpyrrole (TLC).

I) A mixture of 6 g (35.5 mmole) of pyrrole III, 0.6 g of Fe(NO₃)₃, 238 ml of butanol, and 26 ml of water was heated at 50°C for 20 h. Workup gave 5 g of a mixture consisting (according to GLC) of pyrrole III (5%), 1-(1-butoxyethyl)-2-phenylpyrrole [17] (85%), and 2-phenylpyrrole (10%).

J) A mixture of 2 g (11.8 mmole) of pyrrole III, 0.2 g of $\text{Fe}(\text{NO}_3)_3$, 80 ml of methanol, and 8 ml of water was stirred at room temperature. The substance was extracted with ether, and the methanol was washed out with water. The ether extracts were dried with magnesium sulfate, the ether was removed by distillation, and the residue was fractionated *in vacuo* to give 1.8 g (76%) of 1-(1-methoxyethyl)-2-phenylpyrrole [17].

K) A mixture of 3.3 g (19.5 mmole) of pyrrole III, 0.5 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ (250 ml) and 450 ml of dioxane was heated at 80°C for 2 h, after which it was extracted with ether, and the dioxane was washed out with water. The ether extracts were dried with potassium carbonate, and the ether was removed by distillation to give 1.7 g of a dark-claret-colored crystalline substance, which, according to GLC data, contained 85% 2-phenylpyrrole (52% yield), 1% starting pyrrole III, and two unidentified substances (14%).

L) A mixture of 1 g (5.9 mmole) of pyrrole III, 2.1 g of $\text{NH}_2\text{OH}\cdot\text{HCl}$, and 10 ml of water was shaken at 60°C for 1 h. According to GLC data, the organic layer contained 97% starting pyrrole III, 0.1% 2-phenylpyrrole, and 2.9% of an unidentified substance. Distillation yielded 0.7 g of starting pyrrole III.

Hydrolysis of 1-Vinyl-2-phenylpyrrole with a Solution of Hydroxylamine Hydrochloride. A 100-ml conical flask equipped with a magnetic stirrer and a reflux condenser was charged with 0.3442 g (2.0 mmole) of pyrrole III in 40 ml of dioxane and 25 ml of an acidified 0.5 N solution of hydroxylamine hydrochloride, in the titration of which 0.42 ml of 0.44 N NaOH solution was consumed. The reaction mixture was stirred in a sealed system at 80°C for 1 h. At the end of the reaction the mixture was titrated with 2.25 ml of a 0.44 N solution of NaOH. The calculations were made from the formula

$$X = \frac{0,001 \cdot M \cdot n \cdot (a - a_1) \cdot 100}{g}$$

where X is the degree of conversion of pyrrole III (in percent), M is the molecular weight of pyrrole III, n is the normality of the NaOH solution, a is the volume of the NaOH solution consumed in the titration of the HCl (in milliliters), a_1 is the volume of the NaOH solution consumed in the titration of the HCl in a blank experiment (in milliliters), and g is the weight of the sample of pyrrole III (in grams).

The degree of conversion of pyrrole III with respect to the liberated acetaldehyde was 39.5%.

Experiments were carried out similarly at 80 and 90°C (with 0.296 N NaOH) for 1-3 h.

Verification of the Possibility of Oximation of 2-Phenylpyrrole (VI). A mixture of 0.2710 g (1.89 mmole) of 2-phenylpyrrole, 25 ml of an acidified 0.5 N aqueous solution of $\text{NH}_2\text{OH}\cdot\text{HCl}$, and 40 ml of dioxane (a homogeneous mixture) was heated at 91°C for 1 h. A 1.6-ml sample of a 0.204 N solution of NaOH was consumed in titration of the mixture, and the same amount was consumed in a blank experiment (without 2-phenylpyrrole).

Hydrolysis of 1-Vinyl-3-methyl-2-phenylpyrrole (IV). A resin with mp 60-66°C was obtained under the conditions of hydrolysis of pyrrole III (experiment 1). Found: C 77.2; H 6.5; N 7.0%. The IR spectrum is presented in Fig. 2b. The PMR spectrum contained a broad poorly resolved signal at 6.7-7.5 ppm, a weak unresolved multiplet centered at 5.6 ppm, and a broad multiplet at 1-2.5 ppm with maxima at 2.0, 1.5, and 1.0 ppm (CH_3 groups). This was also confirmed by the presence of chlorine (~1%) in the hydrolysis products.

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9-ALKENYLCARBAZOLES.

10.* ¹³C NMR SPECTRA OF 9-VINYL- AND cis- AND trans-9-PROPENYLCARBAZOLES

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The ¹³C NMR spectra of a number of ring-substituted 9-vinylcarbazoles and cis- and trans-9-propenylcarbazoles were studied. It was found that the C_β chemical shifts of the vinyl atoms of these compounds correlate satisfactorily with the σ_p constants of the substituents in the 3 and 6 position of the carbazolyl rings; the slopes of the straight lines increase in the order 5.84, 7.68, 9.56. The inductive and conjugation components of the effect of the substituents on the chemical shifts of the C_β atoms were evaluated. It follows from the results obtained that the effects of p-π conjugation are realized not only in the relatively planar isomers but also in the nonplanar cis isomers of 9-alkenylcarbazoles.

Previously by means of ¹³C NMR spectroscopy for the study of the effects of p-π conjugation in 9-vinylcarbazole (Ia) and its derivatives with electron-acceptor substituents in the heterocyclic fragment (Ic-e) we evaluated the effect of substituents on the shielding of vinyl C_β atoms [2]. In the present paper we present the results of an NMR spectral study of a series of substituted (in the 3 and 6 positions of the carbazolyl ring) cis (IIa-d) and trans (IIIa-d) isomers of 9-propenylcarbazoles. We also recorded the spectrum of 3-methyl-9-vinylcarbazole (Ib) in order to expand the series of substituted vinylcarbazoles I. The results are examined in conjunction with the data in [2] in order to compare the effects of transmission of the effects of the X and Y substituents on the C=C group in all three series of alkenylcarbazoles I-III.

Compounds I-III constitute two conformationally different groups. The trans isomers (III) are isosteric (relative to the mutual orientation of the planes of the carbazolyl ring and the C=C bond) with respect to I. The existence of two conformations with angles of deviation from coplanarity of the ring and the C=C bond of 2.6 and 14° has been established for vinylcarbazole Ia by x-ray diffraction analysis [3]. Thus there is a small degree of noncoplanarity as a result of repulsion of the cis proton of the methylene group and the ring 1-H and 8-H protons. Taking into account the known indeterminacy in the application of the crystallographic parameters of the substances to their solutions, one may tentatively adopt

*See [1] for Communication 9.

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