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SYNTHESIS AND CERTAIN PROPERTIES OF ACETYLENYLINDOLES

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UDC 542.953:547.754:547.538.241:541.69

A group of new acetylenic derivatives of indole was synthesized by condensation of 2- and 3-iodoindoles with terminal acetylenes. 3-Iodoindole unsubstituted at the heteroatom is distinguished by an increased tendency to undergo deiodination under the reaction conditions. Chemical transformations of the synthesized acetylenic derivatives were carried out, proceeding with both the retention of and with the participation of the triple bond. In the intramolecular cyclization of vicinal, functionally substituted indolylacetylenes, a tendency is manifested to form six-membered heterocycles. A primary pharmacological investigation of the compounds obtained was carried out. Most of them are slightly toxic, several of the compounds display in high doses indications of neurotropic activity.

Many natural and synthetic compounds of the indole series find application as effective medicinal preparations [1]. Because of the high reactivity of the acetylenic grouping, acetylenylindoles are promising intermediates in the synthesis of various indole derivatives, including biologically active compounds. It is probable that indolylacetylenes may also possess direct biological activity (see, for example, [2]). Therefore, in the present work, new acetylenic derivatives of indole were prepared, their chemical transformations were performed, and primary biological tests were carried out.

Acetylenylindoles were obtained by condensation of iodoindoles with terminal acetylenes in the presence of $Pd[PPh_3]_2Cl_2$–CuI or with copper acetylenides [3-5].

The catalytic condensation of 3-iodoindoles unsubstituted at the nitrogen atom, as in the case of the analogous 3-iodopyrroles [6], was accompanied, and in many cases was also suppressed, by the competing reaction of reductive dehalogenation. Thus, iodide (Ia) when heated with phenylacetylene (II) and a catalyst in pyridine in the presence of K_2CO_3, and iodoacetylenylindole (Ib) – with 2-methylbutyn-3-ol (III) in Et_2NH, were converted into deiodination products (IVa, b) in a 80-90% yield

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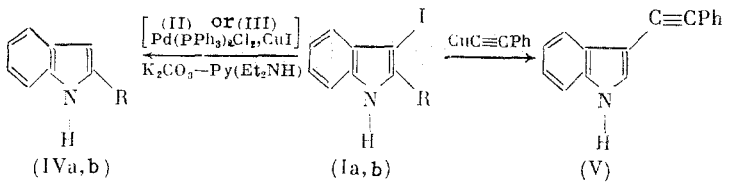
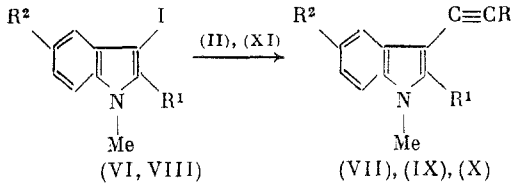


R = H (a), C≡CCMe$_2$OH (b).

The contribution of the deiodination reaction decreased when instead of the terminal acetylene, the corresponding copper acetylenide was used in the absence of the catalyst. Thus, by using this method, it was possible to obtain acetylene (V) from iodide (Ia) in 34% yield.

Alkylation of indoles at the nitrogen atom sharply alters the ratio of competing processes in favor of the condensation. In contrast to (Ia), 3-iodo-1-methylindole (VI) reacted with phenylacetylene (II) to form phenylethynylindole (VII) in a yield of 63%

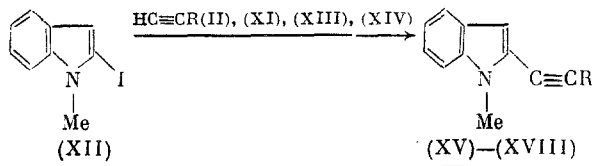


R = Ph (VII), (IX); CH$_2$N(CH$_2$)$_2$O (X); R^1 = H (VI), (VII); COOMe (VIII)—(X);

R^2 = H (VI), (VII); OMe (VIII)—(X).

Introduction of an electron-acceptor substituent into the α-position impedes the dehalogenation side-reaction. The ester of 3-iodo-1-methylindole-2-carboxylic acid (VIII) was condensed without any complications not only with (II), but also with the less active propargylmorpholine (XI) (yield 79-88%).

2-Iodo-1-methylindole (XII) is considerably more stable than its isomer (VI) [3], and readily enters into condensation with various terminal acetylenes, including the diyne (XIII). The formation of deiodination products was not observed

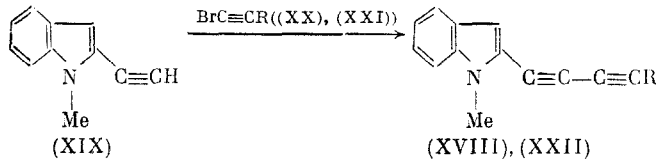


R = Ph (XV), (II); CH$_2$N(CH$_2$)$_2$O (XVI), (XI); CH$_2$N(CH$_2$)$_4$ (XVII), (XIV);

C≡CCMe$_2$OH (XVIII), (XIII).

Several indole compounds were obtained from the synthesized acetylenic derivatives.

A general and possibly more simple path than acetylenic condensation to 2-alkadiynylindoles is the Caldo–Chodkiewicz reaction [7]. 1-Methyl-2-ethynylindole (XIX) [3] readily reacted with 1-bromo-3-methylbut-1-yn-3-ol (XX) and 1-bromo-3-morpholinoprop-1-yne (XXI) under standard conditions to form diynes (XVIII) and (XXII), respectively, in yields of >80%



R = CMe$_2$OH (XVIII, XX); CH$_2$N(CH$_2$)$_2$O (XXII), (XXI).

TABLE 1. Acetylynolindoles

Compound	Time, h, method*	Yield, %	Mp, °C (solvent)	Empirical formula
(VII)	9,5 B	62,9	84–85 (petr. ether)	$C_{17}H_{13}N$
(IX)	7,5 † B	88,4	192,5–193 (EtOAc)	$C_{20}H_{17}NO_3$
(X)	47,5	73,1	97–98 (petr. ether)	$C_{19}H_{22}N_2O_4$
(XV)	13 B	91,3	134–134,5 (hexane)	$C_{17}H_{13}N$
(XVI)	16,5 B	80,4	123–124 (hexane)	$C_{16}H_{18}N_2O$
(XVII)	18,5 B	83,3	103–104 (hexane)	$C_{17}H_{20}N_2$
(XVIII)	8, B (5, C)	84,4 (80,4)	96–97 (petr. ether)	$C_{16}H_{15}NO$
(XXII)	5 C	84,0	75–76 (petr. ether)	$C_{16}H_{18}N_2O$
(V)	3,5 A	34,2	158–159 (C_6H_6) [12]	$C_{16}H_{11}N$
(XXIII)	24 D	91,7	120–121 (petr. ether)	$C_{21}H_{27}N_3O_2$
(XXV)	24 D	86,7	46–47 (petr. ether)	$C_{19}H_{25}N_3O$
(XXVI)	24 D	67,9	74,5–75,5 (hexane)	$C_{22}H_{29}N_3O$
(XXIV)	32 D	85,7	81–82 ‡ (hexane)	$C_{23}H_{27}N_3O_2$

*Condensatdion with Cu(I) acetylenides (method A); catalytic the Chodkewicz–Caldo reaction (method C); the aminomethyla-

†In Et_3N at 85-90°C.

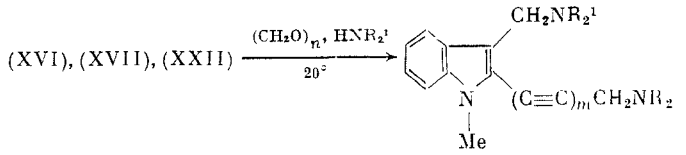
‡Compound (XXIV) exists in two crystalline modifications; the

Found / Calculated, %			PMR spectrum ($CDCl_3$, ppm)	IR spectrum, ($CHCl_2$, ν, cm^{-1})	
C	H	N		C≡C	others
88.34 / 88.28	5.58 / 5.67	6.08 / 6.05	3.30 (CH_3–N), 6.87 (2-H), 7.0–7.8 m (4,5,6,7-H and arom. H)	2220	–
75.10 / 75.22	5.38 / 5.36	4.51 / 4.39	[$(CD_3)_2CO$]: 3.90 (CH_3N), 3.99 and 4.03 (CH_3O), 7.0–7.5 m (4,6,7-H and arom. H)	2220	1720 (C=O)
66.50 / 66.65	6.45 / 6.48	8.25 / 8.18	–	2225	1710 (C=O)
88.34 / 88.28	5.71 / 5.67	6.13 / 6.05	3.56 (NCH_3), 6.76 (3-H), 7.0–7.6 m (4,5,6,7-H and arom. H)	2222	–
75.70 / 75.56	7.01 / 7.13	11.0 / 11.01	2.52 m (CH_2NCH_2), 3.48 (–CH_2–), 3.69 m (CH_3N and CH_2OCH_2), 6.63 (3-H), 6.9–7.5 m (4,5,6,7-H)	2241	–
80.59 / 80.91	7.87 / 7.99	11.08 / 11.10	1.2–1.7 m [$(CH_2)_3$], 2.55 m (CH_2NCH_2), 3.54 (≡C–CH_2), 3.73 (CH_3N), 6.64 (3-H), 7.0–7.5 m (4,5,6,7-H)	2230	–
80.92 / 80.98	6.62 / 6.37	5.86 / 5.90	1.49 [$C(CH_3)_2$], 2.46 (OH), 3.63 (NCH_3), 6.75 (3-H), 6.8–7.5 m (4,5,6,7-H)	2170 2240	3600 (OH)
77.61 / 77.67	6.54 / 6.52	10.03 / 10.06	2.62 m (CH_2NCH_2), 3.50 (≡C–CH_2), 3.79 (CH_3N), 6.88 (3-H), 7.2–7.3 m (5,6,7-H), 7.54 d (4-H)	2160 2230	–
88.47 / 88.45	5.16 / 5.10	6.28 / 6.45	7.1–7.9 m (2,4,5,6,7-H and arom. H) 8.10 (NH)	2220	3485 (NH)
71.50 / 71.36	7.88 / 7.70	11.70 / 11.89	CCl_4: 2.2–2.7 m (CH_2NCH_2 of the two morpholine rings), 3.4–3.6 m (–CH_2–; ≡CCH_2; CH_2OCH_2 of the two morpholine rings), 3.63 (CH_2–N), 6.8–7.0 m (5,6,7-H), 7.56 d (4-H)	2225	–
73.08 / 73.28	7.99 / 8.09	13.48 / 13.49	2.26 [$(CH_3)_2$], 2.65–2.70 m (CH_2NCH_2), 3.66 m and 3.69 (CH_2–, ≡CCH_2–), 3.77 (CH_3–N), 3.75–3.80 m (CH_2OCH_2), 7.1–7.3 m (5,6,7-H), 7.69 d (4-H)	2230	–
75.20 / 75.18	8.30 / 8.32	11.79 / 11.95	1.2–1.8 m (β-, β_1'-, γ-, –CH_2 of piperidene), 2.3–2.7 m (CH_2NCH_2 of piperidine and morpholine), 3.5–3.7 m (≡CCH_2, –CH_2–, CH_2OCH_2), 3.72 (CH_3N), 7.0–7.2 m (5,6,7-H), 7.83 d (4-H)	2230	–
73.13 / 73.18	7.22 / 7.21	10.93 / 11.13	2.3–2.6 m (CH_2NCH_2 of the two morpholine rings), 3.42 (–CH_2–), 3.5–3.8 m (≡CCH_2, CH_3–N, CH_2OCH_2), 7.0–7.2 (5,6,7-H), 7.72 d (4-H)	2160	–

condensation in the presence of $(Ph_3P)_2PdCl_2$–CuI (method B);
tion method (D).

second modification has mp 99.5-100°C.

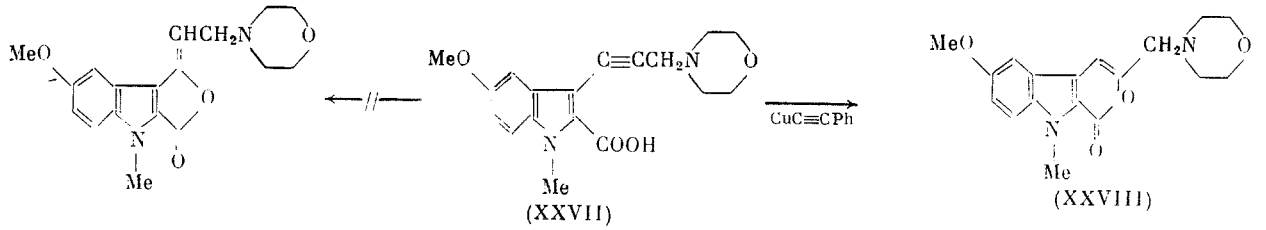
Diamines (XXIII)-(XXVI) were synthesized from indoles (XVI), (XVII), and (XXII) by taking advantage of their high activity in the aminomethylation reaction



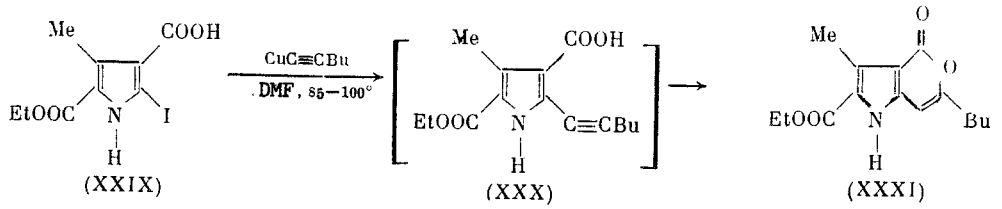
$R—R=R^1—R^1=CH_2CH_2OCH_2CH_2$, $m = 1$ (XXIII); $m = 2$ (XXIV);
$R—R=CH_2CH_2OCH_2CH_2$, $R^1 = Me$, $m = 1$ (XXV); $R—R=(CH_2)_5$,
$R^1—R^1=CH_2CH_2OCH_2CH_2$, $m = 1$ (XXVI).

It is known that various condensed heterocyclic compounds can be obtained by intramolecular cyclization of vicinal functionally substituted aryl- and hetarylacetylenes [8, 4].

Acetylenylindolecarboxylic acid (XXVII), obtained by hydrolysis of ester (X) with aqueous KOH at 20°C was cyclized in the presence of PhC≡CCu in boiling pyridine

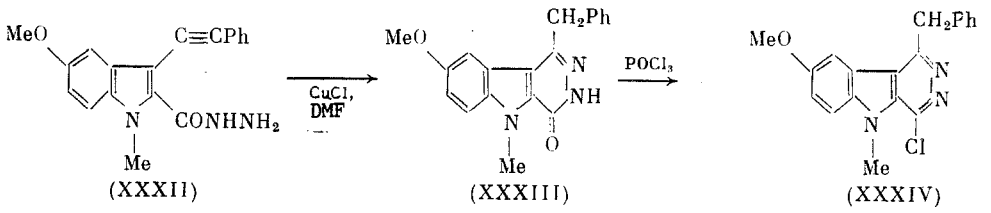


The structure of the cyclization product as 9-methyl-6-methoxy-3-morpholinomethyl-1-oxopropano[3,4-b]indole (XXVIII) (66%) follows unequivocally from the PMR spectrum data in which the aliphatic CH_2 group and the ethylenic proton are manifested in the form of singlets at 3.44 and 6.81 ppm, but not in the form of a doublet or triplet, as in the case of the isomeric five-membered lactone. The same reaction path was also observed in the cyclocondensation of the iodo-acid (XXIX) containing a noncondensed pyrrole ring with BuC≡CCu (which is equivalent to the cyclization of acetylenylpyrrolecarboxylic acid (XXX) [8])



These results conform well with the data on the cyclization of analogous acids in the pyrazole and thiophene series [8, 9]. The tendency to form a condensed system of five- and six-membered rings may possibly comprise a general pattern, determining the direction of this reaction for the derivatives of five-membered heterocycles.

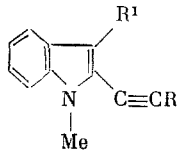
The tendency to undergo cyclization with a six-membered ring closure was also shown by indolecarboxylic acid derivatives, such as hydrazides. Thus, hydrazide (XXXII) in DMF in the presence of CuCl at 140-145°C underwent cyclization to oxopyridazino[4,5-b]indole (XXXIII)



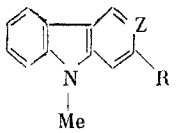
The reaction was accompanied by strong resinification, which impeded the isolation and purification of the product. Compound (XXXIII) was therefore obtained in a yield of only 25%. The data on the PMR and IR spectra of (XXXIII) ruled out a two-condensed five-

membered heterocyclic ring structure for it, but it was not possible to determine from the spectra whether the diazine or diazepine ring structure is formed. To determine the ring size, compound (XXXIII) was heated in $POCl_3$. Diazepinones isomerize by the action of $POCl_3$ with ring contraction to N-aminolactams [10], and pyridazinones are converted into chlorodiazines [11]. The formation of 1-chloropyridazino[4,5-b]indole (XXXIV) from (XXXIII) confirmed the pyridazine structure of this cyclization product.

Compounds (IX), (X), (XV)-(XVII), (XXII)-(XXIV), (XXVI), (XXVIII), (XXXI), (XXXII), and also the previously synthesized (XXXV)-(XLI) [3-6] were subjected to primary pharmacological tests for neurotropic activity

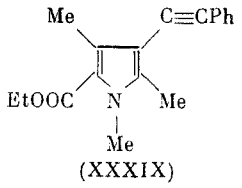


(XXXV), (XXXVI)

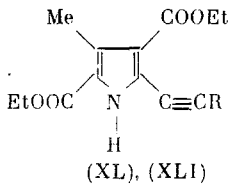


(XXXVII), (XXXVIII)

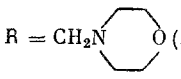
R = CMe_2OH, R^1 = H (XXXV); R = Ph, R^1 = CH=NOH (XXXVI); R = Ph, Z = N → O (XXXVII); R = Bu, Z = N (XXXVIII).



(XXXIX)



(XL), (XLI)

R =  (XL); CMe_2OH (XLI).

In experiments on white mice using intraperitoneal administration, a standard set of tests was applied to determine the maximal-diurnal toxicity (LD_{50}) and the character of the influence of the preparations on the central nervous system. The influence of the compounds on the thermoregulation, movement coordination on a revolving rod, duration of a medicated sleep, orientational reactions, convulsions induced by Corazol and a maximal electrical shock, the pain sensitivity threshold during electrical irritation, blepharoptosis developing after the introduction of reserpine were studied in doses corresponding to 1/5 of LD_{50}.

It was found that compounds (XXV) and (XXXVIII) are moderately toxic (the LD_{50} are within 200-250 mg/kg), and the remainder are slightly toxic; their LD_{50} are equal to 550-900 mg/kg or exceed 1000 mg/kg). Several of the compounds display indications of a depressant effect on the central nervous system. Thus, in doses equal to 1/5 of the LD_{50}, compounds (IX), (X), (XV), (XXIV), (XXXV), (XXXVII), (XXXVIII) decrease the body temperature of mice by 1.5-3°C, (XXXV) and (XXXVII) disturb the ability to stand on a revolving rod, compounds (XXIV), (XXVIII), (XXXVII), and (XXXVIII) inhibit the orientational reactions, (IX), (XXIII), and (XXIV) increase the duration of a chloral hydrate induced sleep. Compounds (X) and (XXXVII) increase slightly and for a short time the electrical pain sensitivity threshold, and (XV), (XXXI), and (XI), on the contrary, decrease it. None of the compounds studied has anticonvulsant or antireserpine activity.

EXPERIMENTAL

The PMR spectra were run on a Varian XL-200 spectrometer and the IR spectra on a UR-20 spectrophotometer.

1-Methyl-2-phenylethynylindole (XV). A mixture of 2.6 g of (XII) [3], 1.5 g of (II), 40 mg of $(PPh_3)_2PdCl_2$ and 20 mg of CuI in 30 ml of Et_2NH was heated in an Ar atmosphere for 13 h at 50°C up to the disappearance of (XII) (TLC control: Silufol; hexane–benzene, 1:1). The mixture was poured into 500 ml of ether, filtered through Al_2O_3 (30 × 20 mm) and the solvent was distilled off. The residue was recrystallized from hexane; the yield of (XV) was 2.1 g (see Table 1).

Compounds (XVI)-(XVIII) were prepared in a similar manner from (XII); (VII) from (VI); (IX), (X) from (VIII) (Table 1).

3-Phenylethynylindole (V). A mixture of 2.2 g of (Ia) and 3.5 g of copper phenylacetylenide in 30 ml of pyridine was heated in an Ar atmosphere at 115°C for 3.5 h. The mixture was then diluted with 50 ml of ether and filtered through a shallow SiO_2 layer. After the removal of the solvent, and recrystallization from petroleum ether, 0.67 g of (V) was obtained (Table 1).

1-Methyl-2-(5-morpholinopenta-1,3-diynyl)indole (XXII). A 0.1 g portion of $NH_2OH \cdot H_2SO_4$, 2 ml of $EtNH_2$, and 40 mg of CuCl were added at 0°C in an Ar atmosphere to 1.4 g of (XIX) [3] in 10 ml of THF, and then 2.2 g of (XXI) in 6 ml of THF was gradually added. The reaction mixture was stirred for 30 min at 3-10°C and for 5 h at 30-35°C. Chromatography on SiO_2 in ether and recrystallization from hexane gave 2.1 g of (XXII) (Table 1).

Compound (XVIII) was synthesized in a similar manner.

1-Methyl-3-morpholinomethyl-2-(3-morpholinopropynyl)indole (XXIII). A 0.5-ml portion of formalin and 1.3 g of (XVI) were added at 5°C to 0.5 g of morpholine in 5 ml of AcOH. The mixture was stirred to room temperature, and was allowed to stand for 24 h. The reaction mixture was diluted with ether, washed with a solution of 6 g of KOH in 7 ml of water, dried over K_2CO_3, and the solvent was distilled off under vacuum. After recrystallization from petroleum ether, 1.7 g of (XXIII) was obtained (Table 1).

Compound (XXIV) was obtained in a similar manner from (XXII), (XXV) from (XVI), and (XXVI) from (XVII) (Table 1).

9-Methyl-6-methoxy-3-morpholinomethyl-1-oxopyrano[3,4-b]indole (XXVIII). A mixture of 1.45 g of (XXVII), obtained in a yield of 96.2% by hydrolysis of (X) with a 30% aqueous solution of KOH at 20°C, 0.54 g of CuC≡CPh and 0.2 g of CuI in 25 ml of pyridine was heated at 115°C in an inert atmosphere for 10 min, then was diluted with 300 ml of ether and filtered. After evaporation of the solvent, the residue in ether was purified on Al_2O_3 and recrystallized from a mixture of benzene and petroleum ether (1:10). Yield 0.95 g (65.5%) of (XXVIII), mp 127-128°C (from petroleum ether). Found, %: C 65.56, H 6.15, N 8.60. $C_{18}H_{20}N_2O_4$. Calculated, %: C 65.84, H 6.14, N 8.53. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1700 (C=O). PMR spectrum ($CDCl_3$, δ, ppm): 2.56 m (CH_2NCH_2), 3.44 ($-CH_2-$), 3.71 m (CH_2OCH_2), 3.87 (CH_3N), 4.16 (CH_3O), 6.81 (4-H), 7.1-7.3 m (5,7,8-H).

Ethyl Ester of 3-n-Butyl-7-methyl-1-oxopyrano[4,3-b]pyrrole-6-carboxylic Acid (XXXI). A 1.6-g portion of acid (XXIX), obtained in a yield of 17.6% by hydrolysis of the diethyl ester of 5-iodo-3-methylpyrrole-2,4-dicarboxylic acid [13] with concentrated H_2SO_4 at 20°C, with subsequent purification via the sodium salt, and 0.9 g of CuC≡CBu were heated in 20 ml of DMF in an Ar atmosphere for 14.5 h at 85-100°C. After cooling, the mixture was diluted with 500 ml of ether, was then filtered, and the ether solution was washed with aqueous NH_3, water, and dried over Na_2SO_4. A 1-g portion of (XXXI) was recrystallized from benzene, to give 0.77 g (56.2%) of pure compound, mp 122-123.5°C. Found, %: C 65.05, H 6.95, N 5.23. $C_{15}H_{19}NO_4$. Calculated, %: C 64.97, H 6.91, N 5.05%. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1670, 1700 (C=O), 3290 br, 3440 (NH). PMR spectrum ($CDCl_3$, δ, ppm): 0.91 t [$(CH_2)_3CH_3$], 1.39 m (γ-CH_2, CH_3CH_2O), 1.63 m (β-CH_2), 2.50 t (α-CH_2), 2.66 (7-CH_3), 4.37 q (CH_3CH_2O), 6.18 (4-H), 9.38 br (NH).

1-Methyl-5-methoxy-3-phenylethynylindole-2-carboxylic Acid Hydrazide (XXXII). A 6.4-g portion of (IX) and 47 ml of $NH_2NH_2 \cdot H_2O$ in 80 ml of absolute ethanol was boiled under reflux condenser for 26 h. The mixture was then cooled, and the precipitate that separated out (6 g) was recrystallized from ethyl acetate. Yield, 5.4 g (83.7%) (XXXII), mp 163-164°C (from ethanol). Found, %: C 71.30, H 5.33, N 13.12. $C_{19}H_{17}N_3O$. Calculated, %: C 71.46, H 5.37, N 12.94. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1760 (C=O), 2205 (C≡C), 3324, 3405 (NH and NH_2). PMR spectrum ($CDCl_3$, δ, ppm): 3.89 (CH_3N), 4.09 (CH_3O), 4.13 (NH_2), 7.0-7.6 m (3,6,7-H, Ph), 8.67 (NH).

4-Benzyl-9-methyl-6-methoxy-1-oxopyridazino[4,5-b]indole (XXXIII). A mixture of 1.6 g of (XXXII) and 0.25 g of CuCl in 15 ml of DMF was heated in an Ar current at the boiling point for 1 h. The mixture was then diluted with 500 ml of ether, the ether solution was washed with aqueous NH_3 and water, and dried over Na_2SO_4. Chromatography on Al_2O_3 (anhydrous) in ether gave 0.9 g (56.3%) of (XXXIII). After additional purification by recrystallization from ethyl acetate, the yield of (XXXIII) was 0.4 g (25.0%), mp 237-238°C. Found, %: C 71.58, H 5.45, N 13.17. $C_{19}H_{17}N_3O_2$. Calculated, %: C 71.46, H 5.37, N 13.16. IR spectrum ($CHCl_3$, ν, cm^{-1}): 1110 (C-O-), 1660 (C=O), 3402 (NH). PMR spectrum ($CDCl_3$, δ, ppm): 3.72 (CH_3-N), 4.33 (CH_3O), 4.48 ($-CH_2-$), 7.2-7.4 m (5,7,8-H; Ph), 10.34 (NH).

4-Benzyl-9-methyl-6-methoxy-1-chloropyridazino[4,5-b]indole (XXXIV). A 0.9-g portion of (XXXIII) in 5 ml of $POCl_3$ was boiled for 45 min. The mixture was then poured into 100 ml of ice water, extracted with $CHCl_3$, and the extract was dried over Na_2SO_4. After evaporation of the solvent and crystallization of the residue (0.9 g) from methanol, 0.6 g (63.1%) of (XXXIV) was obtained, mp 205-206°C. Found, %: C 67.32, H 4.78, Cl 10.48. $C_{19}H_{16}ClN_3O$. Calculated, %: C 67.56, H 4.77, Cl 10.49. PMR spectrum ($CDCl_3$, δ, ppm): 3.74 (CH_3N), 4.23 (CH_3O), 4.81 ($-CH_2-$), 7.2-7.5 m (5,7,8-H; Ph).

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ONE-ELECTRON TRANSFER IN THE VINYLATION OF 4,5,6,7-TETRAHYDROINDOLE WITH ACETYLENES IN THE SYSTEM KOH–DMSO

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It has been shown by EPR, using 2-methyl-2-nitrosopropane as a radical trap, that vinylation of 4,5,6,7-tetrahydroindole with phenylacetylene in the system KOH–DMSO involves the formation of the 4,5,6,7-tetrahydroindolyl radical by transfer of an electron from the 4,5,6,7-tetrahydroindole anion to the acetylene.

The Favorskii vinylation reaction is a classical example of ionic nucleophilic addition to the triple bond [1]. In numerous examples of this reaction involving attack of O-, N-, and S-nucleophiles, no evidence was found for the involvement of one-electron transfer, except for the reaction of the salts KCNS and KI with propiolate and acetylenedicarboxylate esters, in which paramagnetic species were detected [2].

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