BENZINDOLES.

XIV.* SYNTHESIS OF ANGULAR TETRAHYDRO[4,5]- AND TETRAHYDRO[6,7]BENZINDOLES

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The previously undescribed tetrahydro[4,5]- and tetrahydro[6,7]benzindoles and some of their derivatives were synthesized by Fischer cyclization of pyruvic acid 5- and 6-tetralinylhydrazones. A linear isomer — tetrahydro[5,6]benzindole —and its derivatives were obtained only in a mixture with tetrahydro[4,5]-benzindole. The geometrical isomers of the pyruvic acid hydrazones were isolated and characterized. A method for the separation of the mixtures of 5- and 6-aminotetralins was developed. The structures of the isolated compounds were confirmed by the PMR and IR spectral data.

Naphthalene derivatives are most often used for the synthesis of angular benzindoles. Very little study has been devoted to the Fischer cyclization of the corresponding 1,2,3,4-tetrahydronaphthalene derivatives whereas it seemed of interest to obtain angular benzindoles in the form of their hydrogenated analogs from them. In addition, one might have anticipated the isolation of derivatives of the difficult-to-obtain linear [5,6]benzindole in the cyclization of pyruvic acid 6-tetralinylhydrazones.

Although 5- and 6-aminotetralines (I and II) have been described [2], we found it was necessary to develop a preparative method for their synthesis. We found that it is expedient to reduce the difficult-to-separate mixture of 5- and 6-nitro derivatives (III and IV) [3] to aminotetralins with hydrazine hydrate in the presence of Raney nickel rather than by hydrogenation in an autoclave [2] and proposed a complex method for the separation of isomeric I and II by means of crystallization, fractional alkalization, and column chromatography. The yield of pure II was 35%, and the yield of isomer I was 20% based on the tetralin. To avoid pronounced resinification the diazotization of the aminotetralin hydrochlorides should be carried out in dilute aqueous solutions. Subsequent reduction with stannous chloride by the usual method leads to tetralinylhydrazines V and VI; VI was obtained for the first time in this research. Pyruvic acid 5- and 6-tetralinylhydrazones (VII and VIII) are obtained in the form of a mixture of geometrical isomers, which we were able to separate by column chromatography on silica gel. The regularities that we noted during a study of the syn—anti isomerism of the naphthylhydrazones of pyruvic acid and its esters by IR and UV spectroscopy [4] are also observed in this case (Table 2).

The conversion of hydrazones VII and VIII to tetrahydrobenzindole derivatives by the action of concentrated sulfuric acid in glacial acetic acid gives markedly contaminated 2-carboxytetrahydro[4,5]- and -[6,7]benzindoles (XII-XIV). Of the large number of cyclizing agents in the Fischer reaction that we tested, a 45% solution of sulfuric acid in methanol and alcohol saturated with gaseous hydrogen chloride were found to be the most suitable.

In the case of hydrazone VII cyclization proceeded unambiguously to give 2-carbomethoxy-6,7,8,9-tetrahydro[6,7]benzindole (IX), whereas in the case of hydrazone VIII we observed the formation of two products that give spots with close R_f values during thin-layer chromatography (TLC). Treatment of the reaction product with ether gave an individual substance (26%), to which we assigned indole ester structure X on the basis of IR, UV, and PMR spectral data. Since the tetrahydrobenzindole derivatives are essentially dialkylindoles, the fre-

*See [1] for communication XIII.

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TABLE 1. Tetralinylhydrazones of Pyruvic Acid and Its Esters

Compound	Isomer	R	Form	mp, °C	Found, %			Empirical formula	Calc. %			Yield, %
					C	H	N		C	H	N	
VII	5-	H	syn	163—165	66,8	6,9	11,9	$C_{13}H_{16}N_2O_2$	67,3	7,0	12,1	22
		H	anti	177—178	67,1	7,1	12,3	$C_{13}H_{16}N_2O_2$	67,3	7,0	12,1	50
		CH_3	syn	90—91	68,3	7,3	11,4	$C_{14}H_{18}N_2O_2$	68,8	7,4	11,0	40
		CH_3	anti	111—112	68,4	7,4	11,3	$C_{14}H_{18}N_2O_2$	68,8	7,4	11,0	20
		C_3H_7	syn	56—57	70,3	8,1	10,3	$C_{16}H_{22}N_2O_2$	70,1	8,0	10,0	44
		C_3H_7	anti	116—117	70,2	8,1	10,0	$C_{16}H_{22}N_2O_2$	70,1	8,0	10,0	9
VIII	6-	H	syn	148—150	66,8	6,9	11,7	$C_{13}H_{16}N_2O_2$	67,3	7,0	12,1	6
		H	anti	166—167	66,8	6,9	11,7	$C_{13}H_{16}N_2O_2$	67,3	7,0	12,1	62
		CH_3	syn	78—79	68,3	7,2	11,3	$C_{14}H_{18}N_2O_2$	68,8	7,4	11,0	5
		CH_3	anti	114—115	68,4	7,3	11,2	$C_{14}H_{18}N_2O_2$	68,8	7,4	11,0	57
		C_3H_7	syn	36—37	70,1	7,9	10,0	$C_{16}H_{22}N_2O_2$	70,1	8,0	10,2	3
		C_3H_7	anti	116—117	70,3	8,2	10,0	$C_{16}H_{22}N_2O_2$	70,1	8,0	10,2	30

TABLE 2. Tetralinylhydrazones of Pyruvic Acid and Its Esters

Compound	Isomer	R	Form	IR spectra, cm^{-1} (in mineral oil)						UV spectrum (in ethanol)		PMR spectrum, δ, ppm		
				$\nu_{C=O}$	$\Delta\nu_{C=O}$	$A \cdot 10^{-3}$, liter · mole · cm^{-2}	ν_{NH}	$\Delta\nu_{NH}$	$A \cdot 10^{-3}$, liter · mole · cm^{-2}	λ_{max}, nm	$\varepsilon \cdot 10^{-3}$	NH	CH_3	R
VII	5-	H	syn	1660	36		3280	86		340	12,2	11,84	2,16	—
										240	9,0			
		H	anti	1696		4,52	3366		0,150	318 i	13,6	7,48	2,04	—
										230	11,0			
		CH_3	syn	1640	10	0,75	3240	110	0,287	359 sh	11,0	11,97	2,06	3,71
										243	7,4			
		CH_3	anti	1650		3,2	3350		0,157	323	11,8	7,07	2,04	3,76
										237	8,2			
		C_3H_7	syn	1638	12	0,785	3236	116	0,262	357	10,2	11,98	2,06	—
										245	6,4			
		C_3H_7	anti	1650		2,8	3352		0,206	323	12,0	7,24	1,96	—
										237	8,0			
VII	6-	H	syn	1660	40		3275	65		344	16,4	11,70	2,13	—
										245 sh	9,0			
		H	anti	1700		3,11	3340		0,277	330	16,4	7,57	2,03	—
										230	9,0			
		CH_3	syn	1648	2	0,718	3236	100	0,212	356	11,6	11,90	2,04	3,70
										244	6,4			
		CH_3	anti	1650		3,0	3346		0,083	335	13,5	7,52	1,96	3,70
										238	7,0			
		C_3H_7	syn	1648	2	0,712	3232	100	0,210	357	15,0	11,89	2,05	—
		C_3H_7	anti	1650		2,76	3332		0,098	334	13,0	7,20	2,00	—
										237	6,4			

quencies of the bands of the vibrations of the NH group in the IR spectra of both angular isomers are virtually identical. The PMR spectra of the compounds in CCl_4, acetone, and dimethyl sulfoxide (DMSO) give the greatest amount of information regarding the structures of the compounds obtained (Table 3). The multiplicity of the signals of the protons of the pyrrole ring is similar to the multiplicity of the signals of the same protons in benzindoles [5], but the signals are shifted to the strong-field region because of a decrease in the overall aromatic character of the system and differ only slightly from one another in both isomers. The signals of the protons of the benzene ring constituted a characteristic AB quartet, which is also shifted to stronger field as compared with the analogous shifts of benzindoles; the previously found index from which one can distinguish between [4,5]- and [6,7]benzindoles XIX and XVIII is also noted in this case — the $\delta_{6-H} - \delta_{7-H}$ difference (30 Hz) for [4,5]tetrahydrobenzindole derivatives (XVI) is less than the $\delta_{4-H} - \delta_{5-H}$ difference (60 Hz) for [6,7]isomeric esters, acids, and unsubstituted tetrahydrobenzindoles. The protons of the hydrogenated ring give two multiplets at 2.60-3.00 ppm (for the 9-H and 11-H protons) and 1.55-1.95 ppm (for the 9-H and 10-H protons).

We were unable to isolate hydrogenated 2-carbomethoxy[5,6]benzindole (XI) in individual form: Mixtures of 2-carbomethoxy derivatives of angular and linear tetrahydrobenzindoles X

TABLE 3. Chemical Shifts (δ, ppm) and Spin–Spin Coupling Constants (Hz) of Tetrahydrobenzindoles

Isomer	Compound	R	Solvent	δ							Notes
				NH	2-H	3-H	4-H	5-H	Δδ(4-H)–(5-H)	$J_{4,5}$	
	XV	H	CCl_4	7,49	6,83	6,28	7,21	6,61	60,6	8,1	$J_{1,2}=2,5$;
	IX	$COOCH_3$	CCl_4	8,65	3,77	6,97	7,27	6,63	63,7	8,0	$J_{1,3}=2,0$;
			Acetone	10,27	3,76	7,03	7,34	6,70	63,7	8,0	$J_{2,3}=3,2$
6,7	XII	COOH	Acetone	10,14		7,07	7,33	6,69	63,6	8,1	
							4-H	7-H		$J_{4,7}$	
	XVII	H	DMSO	10,77	7,10	6,18	6,98	7,11	—	0,5	$J_{1,2}=2,4$;
			Acetone	9,73	7,09	6,21	7,01	7,06	—	0,5	$J_{1,3}=1,8$;
5,6	XI	$COOCH_3$	Acetone	10,33	3,78	6,98	7,13	7,24	—	0,5	$J_{2,5}=3,2$;
			DMSO	11,47	3,80	6,95	7,10	7,20	—		$J_{3,7}=0,9$
	XIV	COOH	Acetone	10,35		6,98	7,14	7,24		0,5	
			DMSO	11,33		6,95	7,11	7,19			
							6-H	7-H	Δδ (6-H)–(7-H)	$J_{6,7}$	
	XVI	H	CCl_4	7,62	6,84	6,24	6,64	6,88	24,0	8,5	$J_{1,2}=2,6$;
			DMSO	10,72	7,09	6,27	6,69	7,05	35,5	8,6	$J_{1,3}=2,4$;
			Acetone	9,73	7,11	6,31	6,68	7,03	35,0	8,4	$J_{2,3}=3,2$
4,5	X	$COOCH_3$	CCl_4	8,89	3,84	6,98	6,80	7,05	25,1	8,5	
			DMSO	11,66	3,78	7,02	6,87	7,13	26,7	8,4	
			Acetone	10,51	3,79	7,04	6,90	7,18	28,3	8,5	
	XIII	COOH	Acetone	10,58		7,06	6,90	7,18	28,5	8,5	
			DMSO	11,54		7,04	6,90	7,15	25,0	8,4	

and XI with different melting points (134-137 and 140-153°C, etc.) were obtained by column chromatography on aluminum oxide. Two sets of signals that are close to the chemical shifts related to the protons of the hydrogenated ring, the quartet of an AB system of the angular isomer, and signals of 4-H and 7-H protons of the linear isomer, which are singlets broadened by spin–spin coupling with $J_{4,7} \sim 0.5$ Hz can be isolated in the PMR spectra of these mixtures. A $J_{4,7}$ constant of the same order of magnitude (0.6-0.8 Hz) was previously observed in the spectra of some substituted indoles [6].

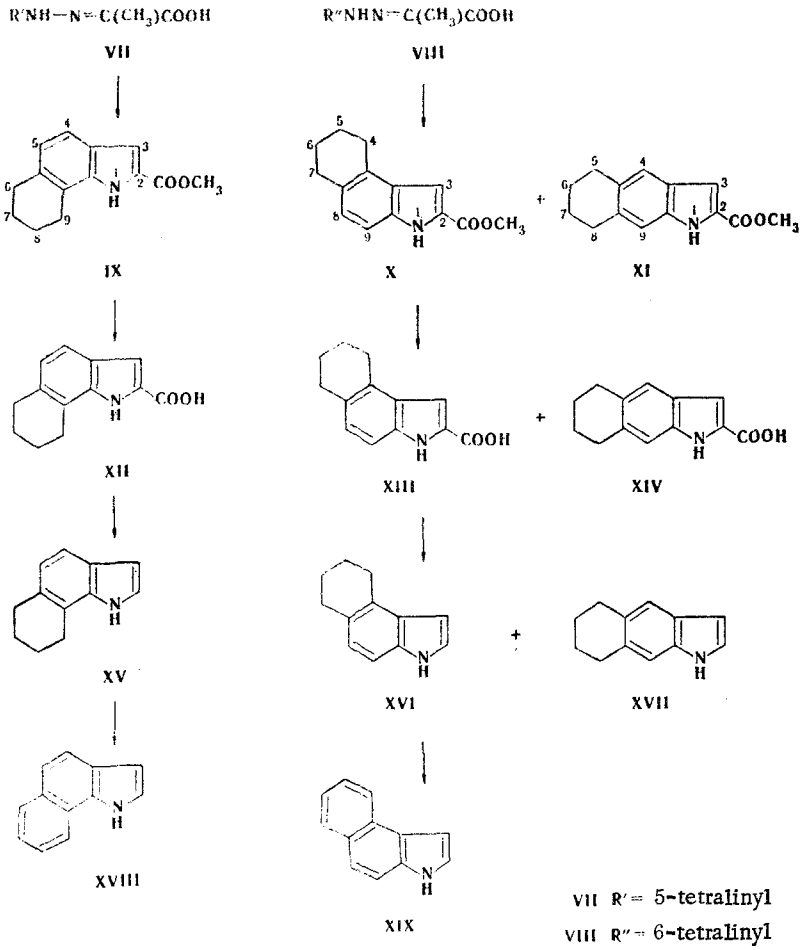
It follows from the PMR data that hydrazone VIII undergoes cyclization via two pathways to approximately the same extent. We were also unable to separate isomeric indoles XVI and XVII in the form of the corresponding 2-carboxylic acids, obtained by alkaline hydrolysis of a mixture of the esters. It should be noted that the use of a 5% solution of concentrated H_2SO_4 in glacial acetic acid as the cyclizing agent gives an almost quantitative yield of a mixture of 2-carboxy[4,5]- (XIII) and 2-carboxy[5,6]tetrahydrobenzindoles (XIV).

Decarboxylation at 220-240°C leads to angular tetrahydrobenzindoles XV and XVI in 75-85% yields. A mixture of acids XIII and XIV was similarly decarboxylated. All attempts to separate tetrahydrobenzindoles XVI and XVII by column chromatography and preparative TLC gave negative results. Dehydrogenation of a mixture of XVI and XVII with dichlorodicyanoquinone gave the angular isomer, i.e., [4,5]benzindole (XIX), which, according to the PMR data, was identical to the benzindole previously characterized in [5].

EXPERIMENTAL

The IR spectra of the compounds were obtained with a UR-10 spectrometer. The UV spectra of ethanol solutions of the compounds were obtained with a Shimadzu MRS-50α spectrophotometer. The PMR spectra were recorded with a Varian HA-100D spectrometer with HMDS as the internal standard. Thin-layer chromatography was carried out on Silufol UV-254 plates in $CHCl_3$ (B) and petroleum ether–ether (1:1) (C) systems.

5- and 6-Aminotetralins (I and II). A mixture of 40 g (0.225 mole) of 5- and 6-nitrotetralins [2, 3] III and IV [bp 147-167°C (7 mm)], 28 g (0.56 mole) of 99.5% hydrazine hydrate, and 300 ml of 96% alcohol was heated with stirring at 38-40°C for 4-5 h, after which a suspension of 4 g of Raney nickel in 100 ml of alcohol was added, and the mixture was stirred for another 2 h. It was then cooled, and the catalyst was removed by filtration and washed with alcohol. The solvent was removed from the filtrate by distillation, and the residue was vacuum distilled. The fraction (75-95%) with bp 106°C (2 mm) (130°C (7 mm) [3])



was collected. A 21.8-g sample of the mixture of amines I and II was dissolved in 260 ml of water, and the solution was acidified with 88 ml of concentrated HCl. The precipitated hydrochlorides were removed by filtration and crystallized from water to give 7.3 g (27%) of the hydrochloride of II. Fractional alkalization of the filtrate to pH 4-6 gave a mixture of aminotetralins enriched in the 5 isomer. The last fraction of aminotetralin was converted to the hydrochloride and crystallized to give the hydrochloride of I. Final alkalization to pH 10-12 gave a mixture of I and II, which was separated with a column filled with L 5/40μ silica gel (Czechoslovakian Socialist Republic) by elution with chloroform. A 228-g sample of the mixture of aminotetralins yielded 125 g (34.8%) of the hydrochloride of II, with mp 260°C (dec.), 67.5 g (18.8%) of the hydrochloride of I, with mp 236-237°C (dec.), and 62.7 g (17.5%) of a mixture of the hydrochlorides of I and II. A 57-g sample of this mixture was separated with a column filled with silica gel to give 35 g (61.2%) of amine I, 2 g (3.5%) of amine II, and 18 g (32%) of a mixture of amines I and II.

5-Tetralinylhydrazine (V). A 14.7-g (0.1 mole) sample of amine I was dissolved by heating in 1 liter of hydrochloric acid (2:1), the solution was cooled sharply and rapidly, and the finely crystalline precipitate of the hydrochloride of I was diazotized at 0-3°C with a solution of 7.6 g (0.11 mole) of $NaNO_2$ in 40 ml of water. A solution of 70 g (0.30 mole) of $SnCl_2 \cdot 2H_2O$ in 60 ml of concentrated HCl was added rapidly with vigorous stirring to the solution, and the resulting precipitate was stirred for another hour at 3-6°C. It was then separated, washed with a saturated solution of sodium chloride, and crystallized from 600-700 ml of 10% hydrochloric acid to give the hydrochloride of V with mp 187-189°C in 70% yield. Found, %: C 60.7; H 7.7; Cl 11.0; N 14.2. $C_{10}H_{14}N_2 \cdot 3HCl$. Calculated, %: C 60.4; H 7.5; Cl 11.3; N 14.1.

6-Tetralinylhydrazine (VI). The hydrochloride of hydrazine VI, with mp 205-206°C, was similarly obtained in 70% yield. Found, %: C 60.5; H 7.5; Cl 11.1; N 14.1. $C_{10}H_{14}N_2 \cdot HCl$. Calculated, %: C 60.4; H 7.5; Cl 11.3; N 14.1.

Pyruvic Acid 5-Tetralinylhydrazone (VII), syn (a) and anti (b) Forms. A 2-g (0.01 mole) sample of the hydrochloride of V was dissolved in 100 ml of water, and a solution of 0.9 g

(0.01 mole) of pyruvic acid in 2 ml of water was added with stirring at room temperature. After 30 min, the precipitate was filtered to give 8.8 g (94.6%) of hydrazone VII in the form of a mixture of geometrical isomers VIIa and VIIb with mp 176-177°C (from absolute ethanol). Found, %: C 67.5; H 7.0; N 12.0. $C_{13}H_{16}N_2O_2$. Calculated, %: C 67.2; H 6.9; N 12.1.

Two recrystallizations from absolute ethanol of 0.8 g of the mixture of syn and anti isomers VIIa and VIIb gave 0.5 g (62.5%) of anti form VIIb with mp 177-178°C, which was washed on the filter with ether—petroleum ether (1:1); the product had R_f 0.11 (system B). Found, %: C 67.1; H 7.1; N 12.3. $C_{13}H_{16}N_2O_2$. Calculated, %: C 67.3; H 7.0; N 12.1. The mixture of petroleum ether and ether from washing of the anti form was evaporated, and syn isomer VIIa was separated by column chromatography on silica gel from anti isomer VIIb [ether—petroleum ether (1:1)] to give 0.05 g (6.3%) of syn form VIIa with mp 163°C and R_f 0.43 (system B). Found, %: C 66.7; H 6.9; N 11.9. $C_{13}H_{16}N_2O_2$. Calculated, %: C 67.3; H 7.0; N 12.1.

Pyruvic Acid 6-Tetralinylhydrazone (VIII), syn (a) and anti (b) Forms. This compound was similarly obtained in 66% yield from the hydrochloride of VI in the form of a mixture of isomers VIIIa and VIIIb with mp 156-157°C (from absolute ether). Found, %: C 67.5; H 7.1; N 12.1. $C_{13}H_{16}N_2O_2$. Calculated, %: C 67.3; H 7.0; N 12.1.

The above method applied to 0.8 g of the mixture of VIIIa and VIIIb yielded 0.40 g (50.0%) of anti isomer VIIIb with mp 166-167°C and R_f 0.11 (system B). Found, %: C 66.8; H 6.9; N 12.1. $C_{13}H_{16}N_2O_2$. Calculated, %: C 67.3; H 7.0; N 12.1. Also obtained was 0.18 g (22.5%) of syn isomer VIIIa with mp 148-150°C and R_f 0.44 (system B). Found, %: C 66.8; H 6.9; N 11.7. $C_{13}H_{16}N_2O_2$. Calculated, %: C 63.7; H 7.0; N 12.1.

Esterification of Pyruvic Acid Tetralinylhydrazones and Isolation of the syn and anti Isomers (general method). A solution of 10 g (0.04 mole) of hydrazone VII (or VIII) in 200 ml of methanol (or n-propanol) was refluxed for 1-1.5 h with 5 ml of concentrated H_2SO_4, after which the mixture was cooled and poured over ice. The aqueous mixture was extracted with ether, and the ether extract was washed with water and dried. The solvent was removed from the extract by distillation, and the residue was transferred to a column filled with Al_2O_3 and eluted with ether—petroleum ether (1:1). The yields and melting points are presented in Table 1.

2-Carbomethoxy-6,7,8,9-tetrahydro[6,7]benzindole (IX). A solution of 4 g (0.017 mole) of hydrazone VII in 40 ml of methanol was refluxed with 10 ml of concentrated H_2SO_4 for 4-6 h, after which it was cooled, and the precipitate was separated and washed with water and methanol. The mother liquor was poured over ice, and the precipitate was removed by filtration. The combined mixture was applied to a column filled with Al_2O_3 and eluted with ether to give 1.9 g (50%) of indole IX with mp 191-192°C [alcohol—water (1:1)]. IR spectrum (KBr): 3350 and 1690 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 302 (13.6) and 242 nm (15.6). The product had R_f 0.30 (system C). Found, %: C 73.3; H 6.6; N 6.2. $C_{14}H_{15}N_2O_2$. Calculated, %: C 73.4; H 6.6; N 6.1.

2-Carbomethoxy-4,5,6,7-tetrahydro[4,5]- and -5,6,7,8-tetrahydro[5,6]benzindoles (X and XI). A) A stream of hydrogen chloride was passed through a solution of 4 g (0.017 mole) of hydrazone VIII in 80 ml of methanol at 20-25°C for 6 h, after which the precipitate was removed by filtration to give 2 g of a product with mp 166-176°C (50% aqueous alcohol). Work-up of the mother liquor by the usual method gave an additional 1.6 g of a mixture of esters X and XI with mp 127-153°C. The combined mixture was treated with ether, the insoluble portion was removed by filtration, and the solvent was removed from the filtrate by distillation to give 1 g (20%) of individual ester X with mp 186-187°C. IR spectrum: 3330 and 1690 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 302 (18.0) and 238 nm (17.0). The product had R_f 0.30 (system C). Found, %: C 73.1; H 6.7; N 6.0. $C_{14}H_{15}NO_2$. Calculated, %: C 73.4; H 6.6; N 6.1. Chromatography of the precipitate with a column filled with Al_2O_3 (elution with ether) gave 0.9 g (23%) of a mixture of esters X and XI with mp 134-137°C. IR spectrum: 3320 and 1690 cm^{-1}. Found, %: C 73.4; H 6.5; N 6.0.

B) Cyclization of hydrazone VIII under conditions similar to those in the cyclization of VII gave ester X, with mp 184-186°C, in 26% yield and a mixture of X and XI, with mp 127-148°C and R_f 0.30 (system C), in 20-25% yield.

2-Carboxy-6,7,8,9-tetrahydro[6,7]benzindole (XII). A solution of 0.47 g (0.002 mole) of ester IX in 6 ml of 5% alcoholic KOH solution was refluxed for 15 min, after which it was poured into 70 ml of water, and the aqueous mixture was acidified with dilute hydrochloric acid. The resulting precipitate was separated to give 0.4 g (91%) of acid XII with mp 212-213°C (aqueous alcohol). IR spectrum (dioxane): 3273 and 1710 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 302 (9.6) and 293 nm (10.8). The product had R_f 0.24 (system C). Found,%: C 72.9; H 6.0; N 6.4. $C_{13}H_{13}NO_2$. Calculated, %: C 72.5; H 6.1; N 6.5.

2-Carboxy-4,5,6,7-tetrahydro[4,5]benzindole (XIII). Acid XIII, with mp 223-224°C (dec., from aqueous alcohol), was similarly obtained from X in 90-95% yield. IR spectrum (dioxane): 3275 and 1710 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 298 (10.8) and 225 nm (22.4). The product had R_f 0.25 (system C). Found, %: C 72.6; H 6.1; N 6.5. $C_{13}H_{13}NO_2$. Calculated, %: C 72.5; H 6.1; N 6.5.

2-Carboxy-4,5,6,7-tetrahydro[4,5]- and -5,6,7,8-tetrahydro[5,6]benzindoles (XIII and XIV). A) A mixture of acids XIII and XIV, with mp 202-204°C (from aqueous alcohol), was obtained in 90-95% yield from 0.3 g (0.001 mole) of a mixture of esters X and XI, with mp 140-143°C, by refluxing in 5 ml of 5% KOH solution (as in the preparation of XII). IR spectrum (dioxane): 3275 and 1710 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 302 (20.2) and 218 nm (21.5).

B) A solution of 5 g (0.002 mole) of a mixture of esters X and XI in 150 ml of glacial acetic acid and 5.5 ml of concentrated H_2SO_4 was heated gradually from 30 to 80°C for 30 min, after which it was worked up to give a mixture of acids XIII and XIV. A mixture of XIII and XIV with mp 201-202°C was obtained in 50-60% yield after purification on silica gel [elution with ether–petroleum ether (1:1)].

6,7,8,9-Tetrahydro[6,7]benzindole (XV). A 0.48-g (0.002 mole) sample of acid XII was decarboxylated at 210-220°C for 30 min. Chromatography on Al_2O_3 gave indole XV, with mp 89-90°C, in 75-85% yield. IR spectrum: 3400 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 238 (3.87), 281 (7.8), and 271 nm (9.8). The product had R_f 0.70 (system B) and 0.52 (system C). Found, %: C 84.4; H 7.8; N 8.3. $C_{12}H_{13}N$. Calculated, %: C 84.2; H 7.6; N 8.2.

4,5,6,7-Tetrahydro[4,5]benzindole (XVI). This compound, with mp 99-100°C, was similarly obtained in 75-85% yield. IR spectrum: 3390 cm^{-1}. UV spectrum, λ_{max} ($\varepsilon \cdot 10^{-3}$): 288 (4.0), 287 (7.0), and 272 nm (10). The product had Rf 0.69 (system B) and 0.54 (system C). Found, %: C 84.5; H 7.7; N 8.1. $C_{12}H_{13}N$. Calculated, %: C 84.2; H 7.6; N 8.2.

4,5,6,7-Tetrahydro[4,5]benzindole and 5,6,7,8-Tetrahydro[5,6]benzindoles (XVI and XVII). A mixture [0.3 g (75%)] of indoles XVI and XVII, with mp 38-39°C, was obtained from 0.5 g (0.002 mole) of a mixture of acids XIII and XIV with mp 202°C.

6,7-Benzindole (XVIII). A solution of 0.5 g (0.003 mole) of indole XV in 65 ml of xylene was refluxed for 13 h with 1.5 g of chloranil, after which the xylene was removed in vacuo, and the residue was chromatographed with a column filled with Al_2O_3 to give 0.1 g (20%) of indole XVIII with mp 174-176°C, which was identical to a genuine sample.

[4,5]Benzindole (XIX). A 0.5 g (0.003 mole) sample of a mixture of indoles XVI and XVII was stirred with 1.53 g of dicyanodichloroquinone in 60 ml of benzene at 15°C in a nitrogen atmosphere for 1 h. The precipitate was removed by filtration, and the filtrate was worked up to give 0.1 g (20%) of indole XIX with mp 33-35°C, which was identical to a genuine sample.

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