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BENZINDOLES.

24.* REDUCTION OF NITRO-2,3-DIMETHYL[4,5]- AND NITRO-2,3-DIMETHYL[6,7]BENZINDOLES

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The reduction of nitro-2,3-dimethyl[4,5]- and -[6,7]benzindoles was studied; Benzindoles were obtained with an amino group in the benzene ring. Individual isomers can be separated as the acyl derivatives.

Indole derivatives with an amino group in the benzene ring are of interest as intermediates for the synthesis of medicinals and colorants [2]. The synthesis of nitrobenzindoles with the nitro group in the benzene ring [3] offers the possibility of synthesizing previously unknown aminobenzindoles.

The present work describes the synthesis of some angular aminobenzindoles by reduction of nitrobenzindoles containing the nitro group in the benzene ring, with hydrazine hydrate in the presence of Raney nickel. We showed previously [3] that in the nitration of 2,3-dimethyl[6,7]benzindole, 9-nitro-2,3-dimethyl[6,7]benzindole (I) is formed in the 50% yield. This compound was quantitatively reduced to 9-amino-2,3-dimethyl[6,7]benzindole (II), which was purified by vacuum sublimation. The hydrochloride of II (III) was also obtained.

The 4- and 7-nitro derivatives (IV, V) obtained by nitration of 2,3-dimethyl[4,5]benzindole [3] were reduced after preacylation at the pyrrole nitrogen. Acylation was used to separate the mixture of IV and V because the chromatographic separation of these substances that we previously described is laborious on a preparative scale.

Acylation was carried out with acetic anhydride in the presence of potassium acetate. The yield of the mixture of 1-acetyl-4-nitro- and 1-acetyl-7-nitro-2,3-dimethyl[4,5]benzindoles (VI, VII) was 95%. VII was easily separated by recrystallization of the mixture from alcohol. The other isomer was obtained chromatographically pure after two recrystallizations of evaporated mother liquor from alcohol. Removal of the protective acetyl group was shown to form V by the reaction of VII with alcoholic potassium hydroxide.

Reduction of both acylated and unacylated nitration products (V-VII) with hydrazine hydrate in the presence of Raney nickel also proceeds in good yields (75-95%). In this reaction the acetyl group is retained at the pyrrole nitrogen. Compounds VIII-X were obtained by this method. 7-Amino-2,3-dimethyl[4,5]benzindole (X) was obtained as the hydrochloride.

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*For Communication 23, see [1].

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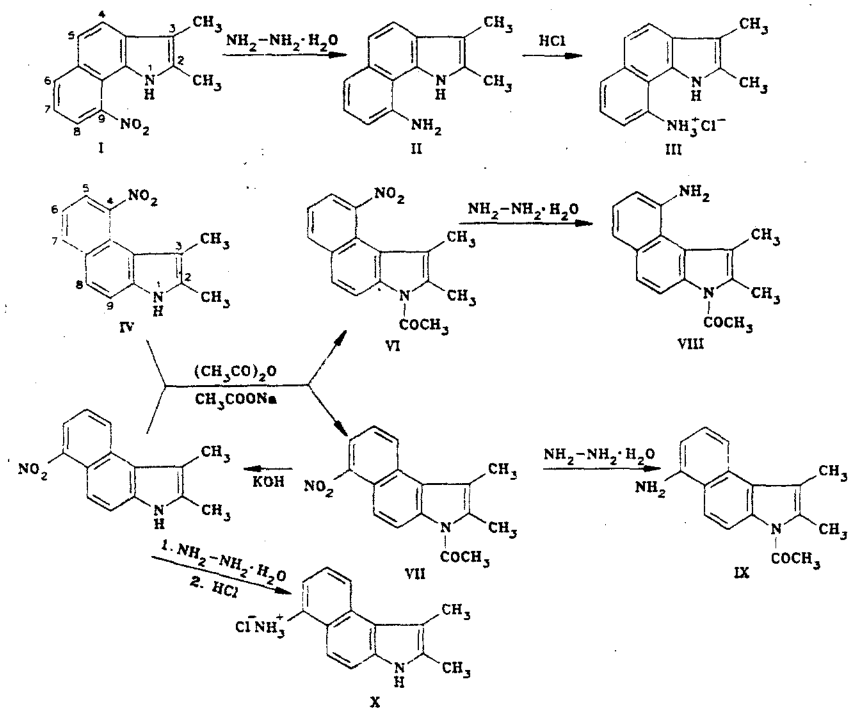

The structures of the synthesized compounds were confirmed by elemental analysis and IR and PMR spectra.

According to the PMR spectra (Table 1), the substituent in II and III is located at position 9 in the benzene ring condensed with indole, whereas in VI, VII, and IX it is in positions 4 and 7. This follows from comparison of the multiplet nature of the signals and the aromatic proton chemical shifts with the PMR spectra of the previously studied nitro derivatives of the angular 2,3-dimethyl[4,5]- and -[6,7]benzindoles [3]; it also follows from comparison with theoretical estimates of the multiplet nature and order of succession of each proton signal for all possible cases of amino substitution for proton in the benzene ring condensed with indole. It should be noted that in the PMR spectrum of IX further spin-spin coupling of 4-H and 8-H protons through five bonds was established ($J_{4,8}$ = 0.5 Hz); this is analogous to the coupling in the nitro derivatives of 2,3-dimethyl[4,5]- and -[6,7]benzindoles [3] and in substituted naphthalenes [4].

EXPERIMENTAL

PMR spectra were obtained on a Varian HA-100D spectrometer in DMSO-D_6 at 31.5°, with HMDS internal standard. IR spectra were obtained on a UR-10 instrument. For chromatography Silufol UV-254 plates were used; eluents were benzene (1) and 4:1 benzene-acetone (2).

9-Amino-2,3-dimethyl[6,7]benzindole (II). Compound I, 1.55 g (6.5 mmole), was dissolved in 60 ml of 96% alcohol, 0.88 g (17.0 mmole) of hydrazine hydrate was added, the mixture was heated to 50°, 1.5 g of Raney nickel was added, and the mixture was stirred for 20 min.* The catalyst was filtered off and the filtrate was evaporated in vacuum. Yield 1.37 g (99%), mp 178-179, (sublimation in vacuum). IR spectrum ($CHCl_3$): 3440 (NH), 3020, 1570 cm^{-1} (NH_2). Found, %: C 80.0, H 6.8, N 13.7. $C_{14}H_{14}N_2$. Calculated, %: C 79.9, H 6.7, N 13.8.

9-Amino-2,3-dimethyl[6,7]benzindole Hydrochloride (III). Compound II purified by vacuum sublimation, 1.55 g (7.4 mmole), was dissolved in 20 ml of absolute ether and the solution was filtered. To the filtrate with cooling to 0° was added 5.5 ml of 5% alcoholic hydrogen chloride dropwise. The precipitate was filtered off and dried in air. Yield 1.48 g (81%), mp 260° (decomposes). IR spectrum (KBr): 3285 (NH), 3000-2700 cm^{-1} (NH_3^+). Found, %: C 67.9, H 6.1, Cl 14.3, N 11.5. $C_{14}H_{15}ClN_2$. Calculated, %: C 68.1, H 6.1, Cl 14.4, N 11.4.

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*All reduction tests were carried out in a stream of nitrogen.

TABLE 1. PMR Spectra of Compounds II, III, VI, VIII, and IX

Compound	Chemical shift, δ, ppm, and SSCC (J, Hz)										
	$COCH_3$	1-H	CH_3 (2)	CH_3 (3)	ABS-system protons		6-H	7-H	8-H	9-H	NH, NH_2, $\overset{+}{N}H_3$
					4-H	5-H					
II	—	10,46	2,35	2,16	7,39	7,21	7,15	6,99	6,75	—	5,11
					$J_{4,5}=8,2$; $J_{6,7}=J_{7,8}=7,1$; $J_{6,8}=1,6$						
III	—	11,46	2,40	2,20	7,64	7,42	7,88	7,29	7,57	—	7,40
					$J_{4,5}=8,4$; $J_{7,8}=J_{8,9}=7,6$; $J_{7,9}=1,2$						
					8-H	9-H	4-H	5-H	6-H	7-H	
VI	2,75	—	2,50	2,00	7,80	8,36	—	8,26	7,53	8,07	—
					$J_{8,9}=9,0$; $J_{5,6}=J_{7,6}=7,7$; $J_{5,7}=1,1$						
VII	2,73	—	2,61	2,53	7,96	8,40	8,77	7,65	8,09	—	—
					$J_{8,5}=9,0$; $J_{4,5}=J_{5,6}=7,9$; $J_{4,6}=1,1$; $J_{4,8}=0,5$						
IX	2,68	—	2,49	2,46	7,70	8,10	7,69	7,20	6,65	—	3,37
					$J_{8,9}=9,0$; $J_{4,5}=J_{5,6}=8,0$; $J_{4,6}=10$; $J_{4,8}=0,5$						

1-Acetyl-4-nitro- and 1-Acetyl-7-nitro-2,3-dimethyl[4,5]benzindoles (VI, VII). The mixture of isomers obtained by nitration of 2,3-dimethyl[4,5]benzindole [3] [1.0 g (4.12 mmole)] was heated with 1.5 g (15.3 mmole) of potassium acetate in 25 ml of acetic anhydride at 130° for 3 h 30 min. The mixture was cooled to 20°, 25 ml of water was added, and the precipitate was filtered off, washed with water until the washings were neutral, and air-dried. Yield 1.17 g (95%) of a mixture of VI and VII. Recrystallization of the mixture from 125 ml of absolute alcohol gave 0.46 g (40%) of orange crystals of VII, mp 152-153°, R_f 0.57 (1). IR spectrum (KBr): 1713 ($COCH_3$), 1525, 1375 cm^{-1} (NO_2). Found, %: C 68.1, H 5.1, N 10.2. $C_{16}H_{14}N_2O_3$. Calculated, %: C 68.1, H 5.0, N 9.9. The mother liquor was evaporated and the residue was recrystallized from 30 ml of absolute ether to give 0.26 g (22%) of orange crystals of VI, mp 114-116°, R_f 0.69 (1). IR spectrum (KBr): 1717 ($COCH_3$), 1525, 1370 cm^{-1} (NO_2). Found, %: C 68.1, H 4.9, N 10.1. $C_{16}H_{14}N_2O_3$. Calculated, %: C 68.1, H 5.0, N 9.9.

7-Amino-1-acetyl-2,3-dimethyl[4,5]benzindole (IX). Compound VII, 0.44 g (1.55 mmole), was dissolved in 220 ml of 96% alcohol at 50°, and 0.18 ml (3.8 mmole) of hydrazine hydrate and 1.5 g of Raney nickel were added. The mixture was heated at 50° for 15 min, then filtered into 250 ml of water containing ice. The precipitate was filtered off, washed with water, and air-dried. Yield 0.36 G (97%), mp 188-189° (from methanol), R_f 0.36 (2). IR spectrum (KBr): 3380, 1590, 1640, 1605, 1540 (NH_2), 1700 cm^{-1} (C=O). Found, %: C 75.9, H 6.3, N 11.0. $C_{16}H_{16}N_2O$. Calculated, %: C 76.2, H 6.4, N 11.1.

4-Amino-1-acetyl-2,3-dimethyl[4,5]benzindole (VIII). Compound VI, 0.30 g (1.05 mmole), was dissolved in 100 ml of 96% alcohol at 30°, and 0.12 ml (2.5 mmole) of hydrazine hydrate and 1.2 g of Raney nickel were added. The mixture was heated for 15 min at 50°, then filtered into 150 ml of water containing ice. The precipitate was separated, washed with water, and air-dried. Yield 0.17 g. Extraction of the aqueous filtrate with ether (3•50 ml) and evaporation of the extract gave another 0.065 g. Over all yield, 89%. Recrystallization of 0.24 g of compound VIII from methanol gave 0.08 g of colorless crystals, mp 124-125°, R_f 0.60 (2). IR spectrum (KBr): 3360, 1590, 1560 (NH_2), 1690 cm^{-1} (C=O). Found, %: C 76.0, H 6.4, N 11.0. $C_{16}H_{16}N_2O$. Calculated, %: C 76.2, H 6.4, N 11.1.

7-Nitro-2,3-dimethyl[4,5]benzindole (V). Compound VII, 0.1 g (0.35 mmole), was dissolved in 10 ml of 5% alcoholic potassium hydroxide. The mixture was stirred for 1 h at 20°, then neutralized with conc. HCl, poured into 20 ml of water, and extracted with ethyl ether (3•20 ml). The combined ether extracts were washed with 60 ml of water, dried over magnesium sulfate, and evaporated in vacuum. Yield 0.07 g (95%), mp 164-166° (from benzene). IR spectrum (KBr): 3412 (NH), 1528, 1360, 1326 cm^{-1} (NO_2). Found, %: C 70.0, H 5.1, N 11.8. $C_{14}H_{12}N_2O_2$. Calculated, %: C 70.0, H 5.0, N 11.7.

7-Amino-2,3-dimethyl[4,5]benzindole Hydrochloride (X). To a solution of 0.23 g (0.9 mmole) of compound V in 30 ml of 96% alcohol was added 0.11 ml (1.4 mmole) of hydrazine hydrate. The solution was heated to 45° and 1 g of Raney nickel was added. After 30 min the catalyst was filtered off in a stream of nitrogen. The filtrate was evaporated and dried in vacuum. The residue was dissolved in 30 ml of dry ether and cooled to 0°, and 7 ml of 5% ethereal hydrogen chloride was added dropwise. The precipitate was filtered off, washed on the filter with dry ether, and dried in vacuum over calcium chloride. Yield 0.18 g (75%), mp 260° (with decomposition). IR spectrum (KBr): 3307 (NH), 3320-2100 cm^{-1} (NH_3^+). Found, %: C 68.0, H 6.3, Cl 14.2, N 11.2. $C_{14}H_{14}N_2 \cdot HCl$. Calculated, %: C 68.1, H 6.1, Cl 14.3, N 11.3.

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SYNTHESIS OF 1-SUBSTITUTED 1,2,3,9a-TETRAHYDRO-9H-IMIDAZO[1,2-a]INDOL-2-ONES

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1-R-9,9,9a-Trimethyl-1,2,3,9a-tetrahydro-9H-imidazo[1,2-*α*]indol-2-ones and the corresponding 2-methylene-2,3-dihydroindoles were obtained by the reaction of 2,3,3-trimethyl-3H-indole with a number of N-substituted chloroacetic acid amides and subsequent reaction of the resulting quaternary salts with bases. The kinetics of intramolecular cyclization of 1-(N-alkylcarbamoylethyl)-2-methylene-2,3-dihydroindoles under the influence of acetic acid were studied. Under the influence of strong protic acids 1-R-imidazo[1,2-*α*]indol-2-ones undergo decyclization and are converted to 3H-indolium salts.

As we have already reported [1], the reaction of 2,3,3-trimethyl-3H-indole (I) with α-chloroacetamide with subsequent treatment of 1-carbamoylmethyl-3H-indolium chloride (IIa) with bases leads to the formation of imidazo[1,2-*α*]indol-2-one (IIIa) or the corresponding 2-methylene-2,3-dihydroindole (IVa). It seemed of interest to us to study the alkylation of I with N-substituted chloroacetamides and to determine the effect of substituents attached to the nitrogen atom of the carbamoyl group on the formation of the imidazolidine ring.

The reaction of 3H-indole I with chloroacetic acid alkyl-, cyclohexyl-, allyl-, and benzylamides yielded salts IIb-h, which, without isolation, were subjected to the action of potassium hydroxide at 40°C; this procedure gave mixtures of imidazo[1,2-*α*]indol-2-ones (IIIb-h) and methylene bases IVb-h. The degree of conversion of 1-(N-benzylcarbamoylmethyl)-3H-indolium chloride (IIh) to the corresponding imidazo[1,2-*α*]indol-2-one under the indicated conditions reaches 90%, as compared with 3-5% in the case of 1-(N-cyclohexylcarbamoylmethyl)-3H-indolium chloride (IIf). For the separation of III and IV ether or benzene solutions of the mixtures were treated with 2-3% hydrochloric acid; IIIb-h remain primarily in the organic solvent, while methylene bases IVb-h pass into the acidic layer in the form of indolium salts IIb-h. Perchlorates IIi-k crystallize out when the calculated amount of perchloric acid is added to ethanol solutions of imidazo[1,2-*α*]indolones IIIb-d.

Opening of the imidazolidine ring of 1-methyl-imidazo[1,2-*α*]indol-2-one (IIIb) by strong protic acids is confirmed by the fact that in the PMR spectrum of a solution in CF_3COOH, instead of a singlet of a $CONCH_3$ group, one observes a doublet at 2.65 ppm with a spin—spin coupling constant (SSCC) of 4.7 Hz, which is peculiar to the methyl protons of the $CONHCH_3$

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