PYRROLOINDOLES.

14.* SYNTHESIS OF DIMETHYL SUBSTITUTED PYRROLO[2,3-e]INDOLE, INDOLO[4,5-e]INDOLE, AND SOME DITETRAHYDROCARBAZOLOCARBAZOLES

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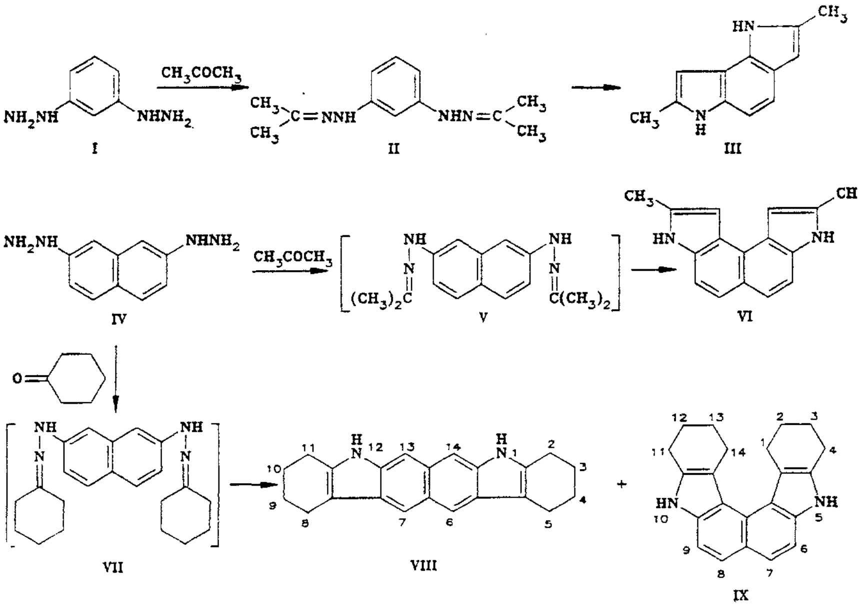
Cyclization of the m-phenylen- and 2,7-naphthylendihydrazones of acetone leads to formation of dimethyl substituted, angular pyrrolo- and indoloindoles. Cyclization of the 2,7-naphthylendihydrazone of cyclohexanone gives the linear 1H,12H-2,3,4,5,8,9,10,11-octahydrocarbazolo[3,4-d]carbazole. A further impurity of an angular ditetrahydrocarbazolocarbazole is also formed.

We have previously reported [2, 3] the synthesis of unsubstituted 1H,6H-pyrrolo[2,3-e]-indole and 3H,8H-indolo[4,5-e]indole.

With the aim of studying the effect of a substituent on the formation of pyrroloindoles and indoloindoles we have carried out the cyclization of acetone and cyclohexanone hydrazones.

The m-phenylen- (II) and 2,7-naphthalendihydrazones (V) of acetone, obtained by condensation of acetone with the dihydrazines I and IV, respectively, prove to be unstable and immediately undergo cyclization. For indolization of dihydrazone II better results were obtained using zinc chloride in cumene as cyclizing agent. Ethyl polyphosphate proved best for dihydrazone V.

Cyclization of acetone hydrazones II and V leads to 2,7-dimethyl-1H,6H-pyrrolo[2,3-e]-indole (III) and 2,9-dimethyl-3H,8H-indolo[4,5-e]indole (VI).



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*For Communication 13 see [1].

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

Compound	Chemical shift (in acetone-d_6), δ, ppm							Spin-spin coupling, J, Hz
	1-H	2-H	3-H	4-H	5-H	6-H	CH_3, s	
II[*1]	—	6,40	—	6,80 . . . 6,90			1,87; 1,95	—
III[*2]	9,93 br.s	—	6,09 d	7,08 d	6,93 d	9,93 br.s	2,45	$J_{13}=2,0$; $J_{45}=8,5$; $J_{68}=2,1$
VI	6,94 dd	—	10,2 br.s	7,30 dd	7,48 d	—	2,54	$J_{13}=2,0$; $J_{45}=8,8$; $J_{14}=0,8$
VIII[*3]	9,8 br.s	1,7 . . . 3,0				7,28 s	—	—
IX[*4]	1,7	3,0			9,9 br.s	7,15 d	—	$J_{67}=8,8$

[*1] 7.83 ppm (br. s, NH).

[*2] 6.27 ppm (d, 8-H).

[*3] 7.26 ppm (s, 14-H).

[*4] 7.35 ppm (d, 7-H).

To investigate the possible cyclization of linear indoloindoles we have attempted to cyclize cyclohexanone 2,7-naphthylendihydrazone (VII). Because of the steric effect of the linear cyclohexane ring, formation of a linear structure appears to be more likely. Synthesis of the bistetrahydrocarbazole VIII was brought about in a single stage using a mixture of concentrated acetic and sulfuric acids [4] without separation of the dihydrazone VII. The cyclization product appears to be the linear carbazole VIII and the angular isomer IX is formed as a side product (PMR spectral data, Table 1).

EXPERIMENTAL

IR Spectra were recorded on a UR-20 instrument in Vaseline mull, UV spectra on a Specord spectrophotometer using ethanol solvent, and molecular weights were determined mass spectrometrically using an MX-1303 with direct introduction of the sample into the ionization source and ionization energy of 50 eV. PMR Spectra were measured on a Varian CFT-20 (80 MHz) instrument using TMS as internal standard. The reaction course, compound purity, and R_f were measured on Silufol UV-254. Preparative column chromatography was performed on 100-250 mesh silica gel.

Elemental analytical data for C, H, and N agreed with that calculated.

Acetone m-Phenylendihydrazone (II). A solution of I (8 g, 40 mmole) in water (150 ml) was adjusted to pH 3 with sodium acetate and acetone (8 g, 100 mmole) added. After 2 h the mixture was extracted with benzene, dried with Na_2SO_4, filtered, solvent evaporated and the solid filtered off to give the dihydrazone II (6 g, 75%) with R_f 0.67 (benzene-acetone 3:1). IR Spectrum: 3520, 3220 (NH), 1590, 1510 cm^{-1} (C=N). UV Spectrum, λ_{max} (log ε): 231 sh (4.12), 272 (4.48), 317 sh nm (3.73).

2,7-Dimethyl-1H,6H-pyrrolo[2,3-e]indole (III, $C_{12}H_{12}N_2$). $ZnCl_2$ (15 g) was added to a solution of dihydrazone II (6 g) in cumene (15 ml) and refluxed for 1 h. The solution was evaporated, the solid filtered off, washed with water, and purified on a column (eluent-benzene). Yield of III 0.48 g (10%) with mp 95-96°C and R_f 0.66 (benzene-acetone 3:1). IR Spectrum: 3360 cm^{-1} (NH). UV Spectrum, λ_{max} (log ε): 206 sh (4.26), 236 (4.62), 270 sh (4.04), 279 (4.08), 296 sh nm (3.86).

2,9-Dimethyl-3H-8H-indolo[4,5-e]indole (VI, $C_{16}H_{14}N_2$). A solution of 2,7-naphthylendihydrazine IV (0.94 g, 5 mmole) in acetone (16 g) was refluxed for 30 min. The solution was evaporated and ethyl polyphosphate (40 g) added. After stirring for 30 min at 80-85°C the product was cooled and poured into water. The aqueous solution was extracted with ether and the ether extracts washed with water and dried with Na_2SO_4. The solvent was evaporated and the residue column purified using benzene to give VI (0.02 g, 2%) with mp 310-311°C and R_f 0.81 (benzene-acetone 5:2). UV Spectrum, λ_{max}: 201, 232, 255 sh, 266, 275, 304, 310, and 325 nm. Found: M^+ 234. Calculated: M 234.

1H-12H-2,3,4,5,8,9,10,11-Octahydrocarbazolo[3,4-d]carbazole (VIII, $C_{22}H_{22}N_2$). A solution of the naphthylendihydrazine (0.94 g, 15 mmole) in glacial acetic (30 ml) was added in a fine stream to cyclohexanone (1.8 g, 15 mmole) in glacial acetic acid (5 ml). A mixture of glacial acetic acid and concentrated sulfuric acid (5.0:0.5) was then added and the product stirred for 30 min at 70°C. After cooling, the reaction mixture was poured into water, the solid filtered off and washed with water and dried to give a yield of 1.5 g (96%). Column chromatography using ether eluent gave VIII as colorless crystals with mp 258°C (decomp.) and R_f 0.6 (benzene-acetone 3:2). IR Spectrum: 3350 cm^{-1} (NH). UV Spectrum, λ_{max} (log ε): 205 (5.21), 207 sh (5.15), 235 (4.39), 242 (4.35), 248 (4.32), 253 (4.27), 260 (4.19), 290 nm (4.18). Found: M^+ 314. Calculated M 314.

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QUANTUM-CHEMICAL INVESTIGATION OF THE FACTORS WHICH DETERMINE STABILITY OF THE 3,5-DIMETHYL-1H-PYRAZOLE-4-DIAZONIUM ION

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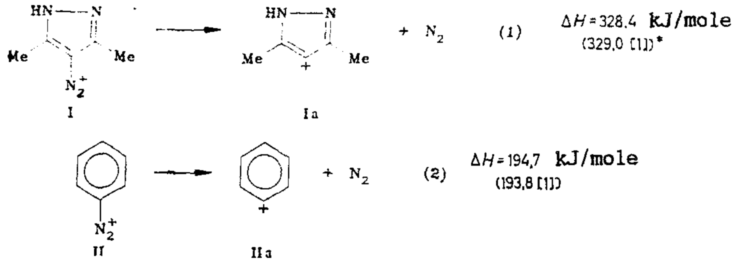
It was shown by MNDO calculations that the stability of the 3,5-dimethyl-1H-pyrazole-4-diazonium ion to decomposition with the elimination of nitrogen is due to the destabilization of the formed carbocation, which has a triplet ground electronic state.

Compared with benzenediazonium chloride, 3,5-dimethyl-1H-pyrazole-4-diazonium chloride has unusual stability [1]. The relative stability of the diazonium cations (I) and (II) can be compared by means of the data from calculation of the enthalpy of the dissociation reactions (1) and (2) (by the MNDO method [2]), which represent the main path in the decomposition of the diazonium ions:



In connection with the fact that the energy profile of the decomposition reactions (1) and (2) is characterized by a monotonic increase of the energy with increase in the length of the C–N_2 bond [1], the enthalpies of reactions (1) and (2) can provide a measure not only of the thermodynamic stability but also of the kinetic stability of the

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*Our calculated heats of formation [$\Delta H_f(I) = 1028.5$; $\Delta H_f(II) = 1024.2$; $\Delta H_f(Ia) = 1323.5$ kJ/mole] differ somewhat from the data given in [1].

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