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FISCHER INDOLIZATION OF 1-ARYL-4-OXO-4,5,6,7-TETRAHYDROINDAZOLES

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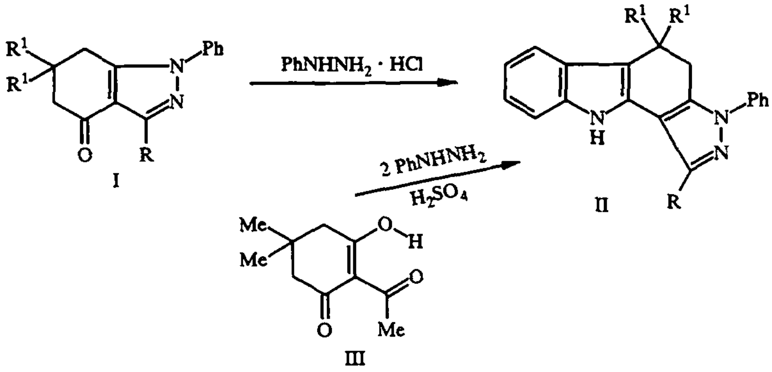
In view of the cardiotonic activity of pyrido[2,3-*c*]- and pyrano[2,3-*c*]-carbazoles [1], in continuing the studies in [2] on synthesis of condensed systems based on 4,5,6,7-tetrahydroindazole derivatives in reactions of indolization of 1-phenyl-4-oxo-4,5,6,7-tetrahydroindazoles (I), we synthesized pyrazolo[4,5-*c*]carbazoles (II).



I, II a R = Me, R¹ = H; b R = R¹ = Me; c R = H, R¹ = Me

The indolization reactions were conducted by boiling equimolar amounts of 4-oxo-4,5,6,7-tetrahydroindazoles with phenylhydrazine hydrochloride in glacial acetic acid. It was also shown that the reaction of 2-acetyldimedone (III) with an excess of phenylhydrazine in the presence of H_2SO_4 yields pyrazolo[4,5-*c*]carbazole IIb. The structure of pyrazolocarbazoles II was confirmed by the data from the IR and PMR spectra. In the IR spectra of compounds II, there was no absorption in the 1800-1600 cm^{-1} region, while the absorption band of the carbazole NH fragment was located in the 3280-3200 cm^{-1} region. The PMR spectra of these compounds were characterized by low-field absorption of carbazole NH protons whose resonance signals were observed at 8.29 (IIa), 8.28 (IIb), and 11.36 ppm (IIc).

1-(2-Pyridyl)-4-oxo-4,5,6,7-tetrahydroindazoles [3] did not react with phenylhydrazine in the conditions indicated above.

1-Methyl- (IIa), 1,5,5-Trimethyl- (IIb), and 5,5-Dimethyl- (IIc) 3-Phenyl-4,5-10H-pyrazolo[4,5-*c*]-carbazoles. Here 5 mmole of the corresponding indazole I and 0.73 g (5 mmole) of phenylhydrazine hydrochloride were boiled in 25 ml of glacial acetic acid for 4 h in the case of Ia, for 6 h for Ib, and for 10 h for Ic. It was cooled, diluted with 50 ml of water, and the sediment formed was recrystallized: from ethanol for IIa, from DMF–water for IIb and IIc.

IIa. Yield of 47%. mp = 186-187°C. Found, %: C 80.22; H 5.73; N 14.02. $C_{20}H_{17}N_3$. Calculated, %: C 80.24; H 5.72; N 14.03. IR spectrum (1800-1500 and 3050-3600 cm^{-1} regions), ν, cm^{-1}: 1598, 1580, 1550, 1515, 1505; 3250. PMR spectrum ($CDCl_3$): 2.51 (3H, s, CH_3); 3.02 (4H, m, CH_2CH_2); 7.11-7.45 (9H, m, C_6H_5, C_6H_4); 8.29 ppm (1H, br. s, NH).

IIb. Yield of 37%. mp = 203-205°C. Found, %: C 80.56; H 6.54; N 12.75. $C_{22}H_{21}N_3$. Calculated, %: C 80.70; H 6.46; N 12.83. IR spectrum, ν, cm^{-1}: 1590, 1550, 1504; 3280. PMR spectrum ($CDCl_3$): 1.44 (6H, s, $2CH_3$); 2.58 (3H, s, CH_3); 2.91 (2H, s, CH_2); 7.09-7.76 (9H, m, C_6H_5, C_6H_4); 8.28 ppm (1H, br. s, NH).

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IIc. Yield of 64%, sublimated beginning at 245°C. Found, %: C 80.36; H 6.10; N 13.33. $C_{21}H_{19}N_3$. Calculated, %: C 80.48; H 6.11; N 13.41. IR spectrum, ν, cm^{-1}: 1600, 1580, 1550; 3200. PMR spectrum (DMSO-D_6):. 1.41 (6H, s, $2CH_3$); 2.97 (2H, s, CH_2); 6.90-7.60 (9H, m, C_6H_5, C_6H_4); 7.89 (1H, s, =CH−); 11.36 ppm (1H, br. s, NH).

Compound IIb was also obtained from 1.10 g (6 mmole) of 2-acetyldimedone and 1.35 ml (12 mmole) of phenylhydrazine in 10 ml of glacial acetic acid. The mixture was boiled for 1 h, 0.3 ml of conc. H_2SO_4 was added, and it was boiled for another 1.5 h. It was cooled, 30 ml of water was added, and the precipitated sediment was recrystallized from DMF−water, yielding 0.70 g (35%) of compound IIb. mp = 203-205°C. Depression of the melting point with the sample obtained from Ib did not occur.

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