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HIGH-TEMPERATURE CATALYTIC SYNTHESIS OF QUINOLINO[1,2-*a*]BENZIMIDAZOLE AND SOME OF ITS TRANSFORMATIONS

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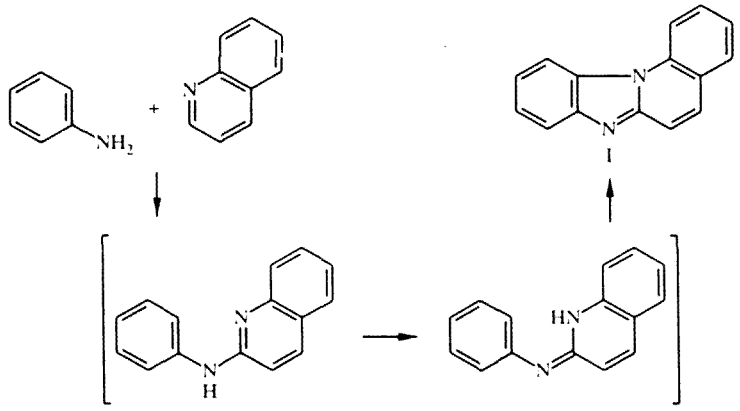
The possibility of synthesis of quinoline[1,2-a]benzimidazole from aniline and quinoline on a dehydrogenating mark K-16 catalyst at 560-580°C was demonstrated. It was established that in the nitration of quinolino[1,2-a]benzimidazole, a 10-nitro-derivative is formed, whereas in the reaction with ADCE, tetramethoxycarbonylquinolino[1,2-a]pyrido[2',1'-b]benzimidazole is formed.

We have developed a method of synthesizing pyrido[1,2-*a*]benzimidazole based on the conversions of α-phenylaminopyridine or α-cyclohexylidenaminopyridine on an industrial catalyst, and it was suggested that the concluding step of these conversions is heterocyclization of the imine form of the α-N-aryl-substituted azine [1].

To obtain information on the possibility of the formation of an analogous condensed system under conditions of heterogeneous catalysis, we undertook an attempt to synthesize quinolino[1,2-*a*]benzimidazole — the benzannelated analog of pyrido[1,2-*a*]benzimidazole.

A mixture of equimolar amounts of aniline and quinoline in benzene was passed through a layer of the catalyst mark K-16 at 560-580°C. From the cytolysate, which contained a complex mixture of various substances, quinolino[1,2-*a*]benzimidazole (I) was isolated chromatographically with a negligible yield (~0.3%). Probably in this case phenylamination of quinoline at the β-position occurs first, and the concluding step is heterocyclization of 1,2-dihydroquinolidene-2-aniline. Naturally, in the preparative respect this method of synthesis of the polynuclear heterocyclic system I is unsuitable, but the results obtained may be useful in studying catalytic reactions of this type.



In the PMR spectrum of compound I (see Table 1), the signal of the 11-H proton is shifted by 0.71 ppm in the weak-field direction in comparison with the chemical shift of the 9H proton in pyrido[1,2-*a*]benzimidazole [1], which is evidently due to the anisotropy of the 1,2-annelated aromatic ring. The weakly polar position of the signal of the 1-H proton is associated

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TABLE 1. Parameters of the PMR Spectra of Quinolino[1,2-*a*]benzimidazoles and Quinolino[1,2-*a*]pyrido[2′,1′-*b*]benzimidazoline

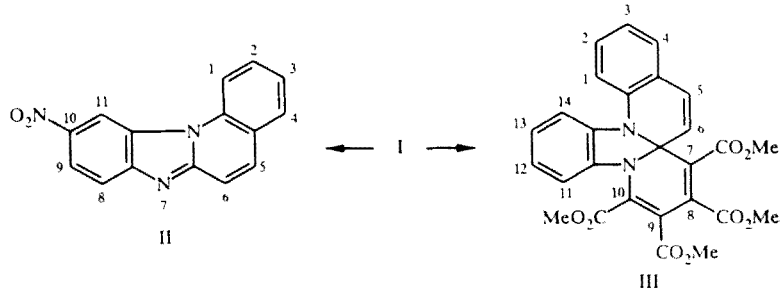
Compound	Chemical shifts of protons, δ, ppm (J, Hz)						
	1-H	2-H	3-H	4-H	5-H	6-H	8-H
I	8,40 (7,0, 1,5)	7,38 (7,0)	7,42 (7,0)	7,81 (7,0)	7,69 (9,0)	7,49	7,80 (8,0, 1,5)
II	8,87 (8,5, 1,0)	7,99 (7,0, 1,5)	7,69 (7,0, 1,0)	8,16 (7,5, 1,5)	8,06 (9,0)	7,79	8,20 (9,0)
III*	6,71 (9,0, 1,0)	6,95 (8,0, 9,0)	7,05 (8,0, 1,0)	6,13 (8,0)	6,57 (1,0)	6,04	—

Compound	9-H	10-H	11-H	12-H	13-H	14-H
I	7,38 (8,5)	7,67 (8,0)	8,54			
II	8,44 (9,0, 2,2)	—	9,47 (2,2)			
III*	—	—	8,15 (8,0, 1,0)	7,20 (8,0, 8,0)	8,26 (8,0, 1,0)	8,29 (8,0, 1,0)

*δ_{OCH_3} 2.79, 3.67, 3.70, 4.05 mp.

with the anisotropic effect of the aromatic system and the nitrogen atom. 1,2-Benzannelation of the pyrido[1,2-*a*]benzimidazole system virtually does not change the nature of the UV spectrum [1]; it only increases the intensity of the absorption bands in the region of 250-300 nm by ~0.2.

Quinolino[1,2-*a*]benzimidazole I has not been studied from the standpoint of chemical conversions. We nitrated it and condensed it with acetylenedicarboxylic ester. The nitration of quinolino[1,2-*a*]benzimidazole I with a nitrating mixture, just like the nitration of pyrido[1,2-*a*]benzimidazole [2], proceeds at the $C_{(10)}$ position of the benzimidazole ring, i.e., analogously to the nitration of benzimidazole.



II III

10-Nitroquinolino[1,2-*a*]benzimidazole (II) is formed with a quantitative yield. The position of the nitro group in compound II was established according to the position and multiplicity of the signals of the 8-, 9-, 10-, and 11-H protons in its PMR spectrum (see Table 1), considering the increments of the chemical shifts for the nitro group [3]. Compound II, just like pyrido[1,2-*a*]benzimidazole, adds two molecules of acetylenedicarboxylic ester [4] at the C=N bond of the benzimidazole fragment at 20°C in benzene. 7,8,9,10-Tetramethoxycarbonylquinolino[1,2-*a*]pyrido[2′,1′-*b*]benzimidazoline (III) was isolated from the reaction mixture with a yield of 28%. The PMR spectrum of compound III is characterized by the presence of a four-spin system of protons of the phenylene fragment of 11-, 12-, 13-, and 14-H with SSCC $J_{11.12} = J_{12.13} = J_{13.14} = 8$ Hz and $J_{11.13} = J_{12.14} = 1$ Hz. The values of the SSCC are close to the analogous constants in the adduct of acetylenedicarboxylic ester with pyrido[1,2-*a*]benzimidazole. In the UV spectrum of the adduct III, in comparison with the spectrum of compound I, a broad long-wave absorption band with maximum at 475 nm appears.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WM-400 spectrometer in $CDCl_3$, internal standard TMS. The UV spectra were obtained on a Specord UV-vis spectrometer in ethanol. The mass spectra were recorded on an MX 1303 instrument with a system of direct introduction of the sample into the ion source with ionizing voltage 70 eV. The IR spectra were obtained on a UR-20 instrument in KBr tablets. For column chromatography we used aluminum oxide, II degree of activity according to Brockman; Alufol plates were used for thin-layer chromatography. The developer was iodine vapors.

Quinolino[1,2-*a*]benzimidazole (I). A mixture of 51.5 g (0.55 mole) of aniline and 65.5 g (0.55 mole) of quinoline was passed through a quartz reactor with 50 ml of the catalyst K-16 at 560-580°C at a constant rate for 3 h. Then the reactor was washed with 100 ml of benzene at 450°C. The residue (2.7 g) after benzene, aniline, and quinoline were distilled off from the cytolysate (under vacuum) was chromatographed on a column (30 × 1 cm). Using ether we eluted 0.2-0.3 g (0.2-0.3%) of compound I, colorless crystals, mp 101-102°C (from ether). Lit. [5] mp 102-103°C. UV spectrum, λ_{max} (log ε): 208 (4.40), 240 (4.40), 251 (4.44), 261 (4.38), 270 (4.36), 336 (4.00), 357 (3.94), 376 nm (3.70). Mass spectrum: M^+ 218. Found, %: C 83.0, H 4.2, N 12.7. $C_{15}H_{10}N_2$. Calculated, %: C 82.6, H 4.6, N 12.8.

10-Nitroquinolino[1,2-*a*]benzimidazole (II). To a nitrating mixture of 2.4 g conc. sulfuric acid and 15 g nitric acid (1.37 g/cm^3) at 0°C we added 0.35 g (1.6 mmoles) of compound I over 0.5 h. After 1 h the temperature was raised to 20°C, and the mixture was exposed for another 0.5 h. It was poured out into 100 ml of water and alkalinized with a saturated soda solution to pH 10-11. The precipitate was filtered off and dried. We obtained 0.4 g (95%) of compound II, yellow crystals, R_f 0.39 (toluene–chloroform, 1:1), mp 342-344°C (from toluene). Lit. [5] mp 243°C (from nitrobenzene). IR spectrum: 1526 and 1340 cm^{-1} (NO_2). Mass spectrum: M^+ 263. Found, %: C 68.6, H 3.3, N 16.3. $C_{15}H_9N_3O_2$. Calculated, %: C 68.4, H 3.4, N 16.0.

7,8,9,10-Tetramethoxycarbonylquinolino[1,2-*a*]pyrido[2′,1′-*b*]benzimidazoline (III). A solution of 0.1 g (0.45 mmole) of compound I and 0.19 g (1.34 mmole) acetylenedicarboxylic ester in 15 ml of benzene was mixed for 9 h at 20°C. The residue after the benzene was distilled off was chromatographed on a column (30 × 1 cm); the eluent was a mixture of ether–heptane, 2:1. First 0.01 g (10%) of compound I was eluted, then 0.06 g (28.3%) of compound III, red crystals, mp 190-193°C (from ether), R_f 0.20 (ethyl acetate–alcohol, 3:1). IR spectrum: 1740 and 1775 cm^{-1} (CO). UV spectrum, λ_{max} (log ε): 220 (4.34), 256 (4.20), 288 (4.10), 340 (3.83), 475 nm (3.42). Mass spectrum: M^+ 502. Found, %: C 64.7, H 4.0, N 5.9. $C_{27}H_{22}N_2O_8$. Calculated, %: C 64.5, H 4.4, N 5.6.

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