QUINOLINE DERIVATIVES

IV.* SYNTHESIS OF TETRAHYDROQUINOLINO- AND QUINOLINOPYRAZINES

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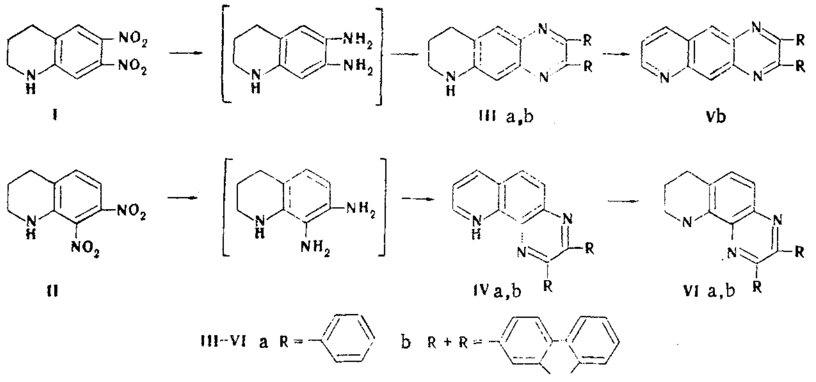
A number of difficult-to-obtain heterocyclic compounds – tetrahydroquinolino- and quinolinopyrazines – were synthesized from o-dinitrotetrahydroquinolines. The UV spectra of the synthesized compounds were studied.

The present communication is devoted to the synthesis and some physicochemical properties of pyrazine structures obtained from 1,2,3,4-tetrahydroquinoline (THQ). The latter are of interest in that they consist of fused tetrahydroquinoline and pyrazine rings, each of which enters into the composition of substances that are abundant in nature.

The pyrazine structures were synthesized by condensation of aromatic o-diamines with α-dicarbonyl compounds [2]. The starting materials were the previously described [1] 6,7- (I) and 7,8-dinitro-THQ (II), which were reduced with hydrazine hydrate in alcohol in the presence of Raney nickel to the corresponding diamines. In view of the extreme instability of the latter, the reduction was carried out under nitrogen without isolation of the diamines in the free state, and the reaction mixture was treated with benzil or phenanthrenequinone. The substances obtained were purified by chromatography.

The synthesized pyrazinotetrahydroquinolines were dehydrogenated to the corresponding pyrazinoquinolines (V and VI) in quantitative yield:



All of the compounds obtained are high-melting crystalline substances that are only slightly soluble in organic solvents.

The pyrazinoquinolines have clearly expressed fluorescence like other pyrazine derivatives. Solutions of these compounds in chloroform fluoresce with blue light.

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*See [1] for communication III.

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An absorption band in the long-wave portion of the spectrum ($\lambda_{max} \sim 400$ nm), which indicates the presence of a system of markedly conjugated bonds in molecules of these compounds, is observed in the electronic absorption spectra of tetrahydroquinolinopyrazines. The bathochromic shift in the maxima of the absorption bands of IV as compared with III indicates an additional increase in the conjugated character of the system of IV; this is confirmed in the literature regarding the effect of o- and m-substituents in the benzene ring [3]. The intramolecular hydrogen bond that arises between the NH group of the piperidine ring and the electron pair of the pyrazine nitrogen also apparently makes a definite contribution to the increase in the conjugated character of structure IV as compared with structure III. The latter was confirmed by the presence of an absorption band at 3400-3490 cm^{-1} in the IR spectrum of IV and retention of this band during a study of the concentration dependence.

As compared with the corresponding analogs – indolinopyrazines – the maxima of the absorption curves of the tetrahydroquinolopyrazines are less intense and are shifted hypsochromically. This decrease in the conjugated character of the system is apparently associated with removal of the electron pair of the nitrogen of the piperidine ring from conjugation due to its ability to take on the position of a half-chair. The character of the UV spectra of the dehydrogenated compounds – pyrazinoquinolines – is similar to that of the UV spectra of the corresponding pyrazinoindoles [4].

EXPERIMENTAL

6,7-Dinitro-THQ (I) and 7,8-dinitro-THQ (II) were obtained by the method in [1].

2,3-Diphenyl-6,7,8,9-tetrahydropyridino[2,3-g]quinoxaline (IIIa). A 10-ml sample of hydrazine hydrate and 1 g of Raney nickel were added to 2 g (8.9 mmole) of 6,7-dinitro-THQ in 200 ml of ethanol, and the mixture was heated at 60° until it became colorless, after which it was filtered under nitrogen to remove the catalyst. The filtrate was added to a solution of 2 g (9.6 mmole) of benzil in 25 ml of benzene, and the mixture was allowed to stand for 12 h. It was then evaporated, and ether was added to the residual oil. The precipitate was separated and washed thoroughly with ether. The ether extracts were evaporated, and the residue was purified by preparative chromatography on activity-III (Brockmann classification) aluminum oxide with benzene–ethyl acetate (3 : 1) and chloroform as the eluent to give 0.1 g of a dark-orange powder with mp 134° (ethanol). Found: C 81.8; H 5.7%. $C_{23}H_{19}N_3$. Calculated: C 81.9; H 5.7%. UV spectrum [in dimethyl sulfoxide (DMSO)], λ_{max}, nm ($\log \varepsilon$): 260 (4.85), 397 (3.31).

11,12,13,14-Tetrahydropyridino[2,3-b]dibenzo[h,j]phenazine (IIIb). A solution of 2 g (9.6 mmole) of phenanthrenequinone in 50 ml of benzene was added to 2 g (8.9 mmole) of 6,7-dinitro-THQ after reduction under the conditions of the preceding experiment. The resulting precipitate was separated and purified by means of preparative chromatography as in the preparation of IIIa to give 0.2 g of a light-brown powder with mp 240° (toluene). Found: C 82.8; H 5.1%. $C_{23}H_{17}N_3$. Calculated: C 82.4; H 5.1%. UV spectrum (in DMSO), λ_{max}, nm ($\log \varepsilon$): 256 (4.63), 317 (4.29), 380 (3.57), 462 (3.70).

2,3-Diphenyl-7,8,9,10-tetrahydropyridino[3,2-h]quinoxaline (IVa) and 12,13,14,15-Tetrahydropyridino[2,3-a]dibenzo[h,j]phenazine (IVb). Compound IVa was similarly obtained from 2 g (8.9 mmole) of 7,8-dinitro- THQ and 2 g (9.6 mmole) of benzil in 25 ml of benzene or 2 g (9.6 mmole) of phenanthrenequinone in 50 ml of benzene. The resulting precipitate was purified by preparative chromatography with a column (d = 20 mm, v = 30 ml) filled with aluminum oxide with elution by benzene to give 0.4 g of light-yellow needles of IVa with mp 168° (ethanol). Found: C 81.8; H 5.7%. $C_{23}H_{19}N_3$. Calculated: C 81.9; H 5.7%. UV spectrum (in carbon tetrachloride), λ_{max}, nm ($\log \varepsilon$): 314 (4.65), 453 (3.23). Also obtained was 0.8 g of IVb as dark-raspberry needles with mp 228.5° [hexane–benzene (1 : 1)]. Found: C 82.0; H 5.1%. $C_{23}H_{17}N_3$. Calculated: C 82.4; H 5.1%. UV spectrum (in carbon tetrachloride), λ_{max}, nm ($\log \varepsilon$): 257 (4.80), 335 (4.64), 378 (3.75), 399 (3.81), 483 (3.26).

Pyridino[2,3-b]dibenzo[h,j]phenazine (Vb). A solution of 1.64 g (6.7 mmole) of chloranil in 100 ml of absolute p-xylene was added to a solution of 1 g (3 mmole) of IIIb in 200 ml of the same solvent, and the mixture was refluxed for several hours until the starting material had been consumed (as monitored by thin-layer chromatography). The solvent was then evaporated, and the residue was removed by filtration and purified by column chromatography (elution with ether) to give 0.98 g (100%) of a light-yellow powder with mp 240° (hexane). Found: C 83.4; H 4.0%. $C_{23}H_{13}N_3$. Calculated: C 83.4; H 4.0%. UV spectrum (in DMSO), λ_{max}, nm ($\log \varepsilon$): 280 (4.19).

2,3-Diphenylpyridino[3,2-h]quinoxaline (VIa). This compound [0.98 g (100%)] was similarly obtained from 1 g (3 mmole) of 2,3-diphenyl-7,8,9,10-tetrahydropyridino[3,2-h]quinoxaline. Purification was carried out by column chromatography with benzene – ethanol (16 : 1) to give a product with mp 250° (ethanol). Found: C 82.5; H 4.5%. $C_{23}H_{15}N_3$. Calculated: C 82.8; H 4.5%. UV spectrum (in DMSO), λ_{max}, nm (log ε): 297 (4.40), 356 (3.93), 367 (3.97), 414 (1.90).

Pyridino[2,3-a]dibenzo[h,f]phenazine (VIb). This compound was obtained in quantitative yield as in the preceding experiment from IVb. The yellow-green powder had mp 284° (ethanol). Found: C 83.0; H 4.0%. $C_{23}H_{13}N_3$. Calculated: C 83.4; H 4.0%. UV spectrum (in DMSO), λ_{max}, nm (log ε): 256 (4.73), 296 (4.42), 307 (4.56), 364 (3.90), 383 (4.20), 405 (4.38).

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