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MACROCYCLIC FORMAZANS – DERIVATIVES OF [1,11,4,5,7,8]-DIOXA-TETRAAZACYCLOTETRADECYNE

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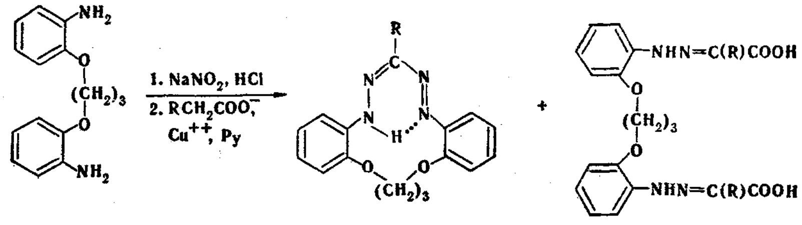
Quadridentate 14-membered macrocycles attract attention, as shown by research into the metal chelates of macrocyclic ligands of the [N_4] [1-3] and [N_2S_2] [4] types. In some cases these metal chelates were obtained by a condensation reaction [1, 4], and in others they were obtained by nucleophilic substitution of halogen in ortho-halogenoazoarenes [2, 3]. The free ligands were not synthesized. We have synthesized metal-free [1, 11, 4, 5, 7, 8]-dioxa-tetraazacyclotetradecynes of the [N_2O_2] type containing the formazan group in the inner coordination contour, i.e., the so-called crown formazans. This synthesis was realized by the double azo coupling of bisdiazotized bis(2-aminophenoxy)-1,3-propane [5] with cyanoacetic, acetoacetic, or malonic acids in pyridine in the presence of copper (II) ions:



I–II a R=H; b R=COCH$_3$; c R=CN Ia–c IIa–c

The obtained crown formazans (Ia–c) have a chelate structure, as shown by the absence of the NH band in the IR spectra and by the presence of the NH signal in the downfield region of the PMR spectra. In the absence of copper the main products are the dihydrazones (IIa–c).

EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument in the region of 400-800 cm^{-1} in hexachlorobutadiene and in the region of 1900-400 cm^{-1} in Vaseline oil. The PMR spectra were recorded on an XL-100-12 instrument with TMS as internal standard. The reaction products were separated by column chromatography on silica gel.

16,17-Dihydro-5H,7H,15H-dibenzo[b,i][1,11,4,5,7,8]-dioxatetraazacyclotetradecyne (Ia). A 2.58-g sample (0.01 mole) of 1,3-bis(2-aminophenoxy)propane in solution in 20 ml of water and 5 ml of concentrated hydrochloric acid at –5°C was diazotized with a solution of 1.38 g (0.02 mole) of sodium nitrite in 8 ml of water for 1 h 30 min. The filtered mixture was added dropwise with stirring to a solution of 1.04 g (0.01 mole) of malonic acid in 20 ml of water, 20 g of sodium acetate trihydrate, 200 ml of pyridine, and 1 g of copper(II) sulfate pentahydrate. The mixture was stirred at –5°C for 1 h 30 min. The reaction mass

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was then filtered, the filter was washed with 15 ml of pyridine, and the precipitate was rejected. The filtrate was added to 400 ml of water and ice and 10 ml of concentrated hydrochloric acid. The solution was extracted with benzene (4 × 100 ml), and the benzene extract was evaporated to 25 ml and chromatographed on a column with benzene as eluent. A dark-red oil was obtained. The yield was 0.2 g (7%). IR spectrum: 1597 (C=C arom.), 1502 (C=N of formazan), 1462 cm^{-1} (C–H). Found %: C 64.3; H 5.2; N 18.3. $C_{16}H_{16}N_4O_2$. Calculated %: C 64.8; H 5.4; N 18.9.

16,17-Dihydro-7-acetyl-5H,15H-dibenzo[b,i][1,11,4,5,7,8]-dioxatetraazacyclotetradecyne (Ib). A 2.58-g sample (0.01 mole) of 1,3-bis(2-aminophenoxy)propane was diazotized as for compound (Ia). The filtered solution was added dropwise with stirring to a solution of 1.02 g (0.01 mole) of acetoacetic acid (obtained by the method in [6]) in 250 ml of pyridine with 1 g of copper(II) sulfate pentahydrate and 20 ml of water. The obtained mixture was stirred at –5°C for 1 h 30 min. After the reaction the whole mass was poured into a beaker containing 400 ml of water and 50 ml of concentrated hydrochloric acid. After 4 h the precipitate was filtered off, washed on the filter with water, and reprecipitated from 100 ml of benzene with 150 ml of petroleum ether. We obtained 1 g of the product in the form of a finely crystalline dark-red powder, which was separated by column chromatography on silica gel with a 4:1 mixture of methylene chloride and chloroform as eluent. From the evaporated solution we isolated a substance with R_f 0.16; mp 161-162°C. The yield was 0.2 g (6%). IR spectrum: 1663 (C=O), 1605 (C=C arom.), 1520 (C=N of formazan), 1470 cm^{-1} (C–H). Found %: C 63.8; H 5.4; N 16.1. $C_{18}H_{18}N_4O_3$. Calculated %: C 63.9; H 5.4; N 16.6.

16,17-Dihydro-7-cyano-5H,15H-dibenzo[b,i][1,11,4,5,7,8]-dioxatetraazacyclotetradecyne (Ic). A 1.29-g sample (5 mmole) of 1,3-bis(2-aminophenoxy)propane wad diazotized as for compound (Ia). The filtered solution was added dropwise with stirring to a solution of 0.57 g (5 mmole) of cyanoacetic ester in 5 ml of 20% sodium hydroxide solution (which had previously been neutralized with 1.5 ml of concentrated hydrochloric acid in 10 ml of water), 200 ml of pyridine, 0.5 g of copper(II) sulfate pentahydrate, and 20 ml of water. The obtained mixture was stirred at –5°C for 1 h 30 min. After the reaction the whole mass was added to a beaker containing 300 ml of water and 20 ml of concentrated hydrochloric acid. The precipitate was filtered off, washed on the filter with water, and dried in a drying cabinet at 60°C. A 0.9-g yield of the dark-red technical product was obtained. Further purification was realized by column chromatography on silica gel with benzene as eluent. After distillation of the benzene we obtained dark-red crystals with a greenish luster; mp 250-251°C. The yield was 0.6 g (41%). IR spectrum: 2222 (C≡N), 1593 (C=C arom.), 1507 (C=N of formazan), 1465 cm^{-1} (C–H). PMR spectrum, δ 15.90 m (NH); 4.29 (4H, α-CH_2); 2.36 ppm (2H, β-CH_2). Mass spectrum: m/e 321. Mol.wt. 321.34. Found %: C 63.0; H 5.1; N 21.7. $C_{17}H_{15}N_5O_2$. Calculated %: C 63.5; H 4.7; N 21.8.

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