ANGULAR CONDENSED HETEROCYCLIC DERIVATIVES OF α-NAPHTHOL

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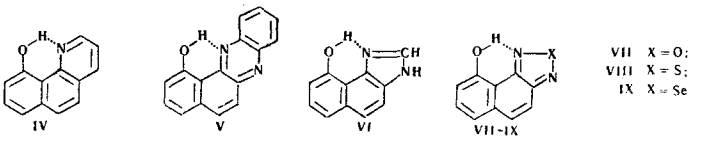
In order to study the intramolecular hydrogen bond, angular condensed heterocyclic derivatives of naphthalene containing a hydroxyl group in the peri position with respect to the nitrogen atom of the heterocycle have been synthesized.

Intramolecular hydrogen bonds with the participation of a heterocyclic nitrogen atom have been studied far less than intermolecular hydrogen bonds. The information available in the literature relates predominantly to compounds with a five-membered chelate ring in which the hydrogen bond is considerably weakened because of the distances between the proton donor and acceptor. In a classical example of this type – 8-hydroxyquinoline (I), the existence of an intramolecular hydrogen bond is completely contradicted by NMR spectra [1], although this itself contradicts the conclusions drawn on the basis of IR spectroscopy [2, 3].

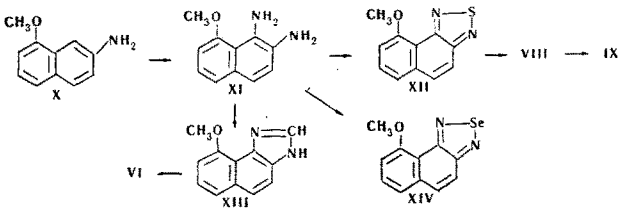
The 2-(3-pyridyl)indan-1,3-dione (II), 2-(o-hydroxyphenyl)benzoxazole (IIIa), and 2-(o-hydroxyphenyl)benzimidazole (IIIb) with the nitrogen atom in the six-membered ring that have been described in the literature [4-6] possess a relatively flexible configuration permitting the angles to be distorted in the formation of a H-bond, which may mask the influence of the nature of the heterocycle.

To elucidate the possibility of the formation and the strength of an intramolecular hydrogen bond in dependence on the structure of the heterocycle, it is necessary to study models with a more rigid spatial configuration. Angular condensed derivatives of α-naphthol containing the hydroxy group in the peri position with respect to the heterocyclic nitrogen atom may be regarded as suitable materials. Of such substances, only compounds IV [7] and V [8] containing pyridine and pyrazine rings are known.

Naphthols with the nitrogen of a five-membered heterocycle in the peri position with respect to the hydroxyl group have not been reported in the literature. The present paper is devoted to their synthesis. For comparison with the hydroxybenzoquinoline IV and the hydroxybenzophenazine V, we took derivatives with an imidazole ring (VI) and with 1,2,5-X-diazole (X = O, S, Se) rings (VII-IX). The basicity of the first is similar to that of pyridine [9], and the others are electronic analogs of pyrazine just as furan, thiophene, and selenophene are electronic analogs of benzene [10].



The hydroxy compounds IV-IX were synthesized from disubstituted naphthalene derivatives by grafting the heterocycle to one nucleus with subsequent hydrolysis of the substituent in the peri position of the other nucleus or by replacing a substituent in this position by a hydroxyl group. The hydroxybenzoquinoline IV and the hydroxybenzophenazine V were obtained, respectively, from 1-naphthylamine-8-sulfonic acid [7] and from 2-naphthol-8-sulfonic acid [8]. 9-Hydroxynaphtho[1,2-c]-[1,2,5]-oxadiazole VII (X = O) was prepared from 8-acetylamino-2-naphthol as we have described previously [11]. The starting material for the synthesis of the hydroxy derivatives VI, VIII, and IX was 8-methoxy-2-naphthylamine X, which, by coupling with a p-nitrobenzene-diazonium salt and reduction of the azo dye with stannous chloride, was converted into the hydrochloride of 8-methoxy-1,2-naphthylenediamine XI and then by reaction with thionylaniline into the thiadiazole XII, by treatment with formic acid into the imidazole XIII, and by treatment with selenium dioxide into the selenadiazole XIV. On being heated with hydrobromic acid, the first two were converted into the naphthols VI and VIII, but the seleandiazole XIV, just like the methoxypiazselenoles [12] decomposed with the evolution of hydrogen selenide. To obtain the hydroxy compound IX we used the reduction of the thiadiazole VIII with subsequent cyclization of the resulting 8-hydroxy-1,2-naphthylenediamine. Attempts to synthesize the latter directly from 7-amino-1-naphthol or its O-acetyl derivative encountered difficulties at the stage of the reduction of the azo compound.



A separate communication will be devoted to a study of the hydrogen bonds in the compounds obtained.

EXPERIMENTAL

8-Methoxy-1,2-naphthylenediamine (XI). To a boiling suspension of 4 g (12.4 mM) of the azo dye 8-methoxy-1-(4-nitrophenylazo)-2-naphthylamine (XV) in 20 ml of water was added a solution of 21 g of stannous chloride in 52 ml of conc. HCl and, after an hour, 25 ml of conc. HCl, and the mixture was boiled for another 30 min. The colorless solution was filtered hot and cooled to 0°C. The light gray crystalline precipitate was separated off, dried on a Büchner funnel, and washed with a large amount of ether. This gave about 4 g of the hydrochloride of the diamine XI.

9-Methoxynaphtho[1,2-c]-[1,2,5]-thiazole (XII). To the hydrochloride of the diamine XI obtained from 1.22 g (3.8 mM) of the azo dye XV were added 6 ml of thionylaniline and 24 ml of pyridine; the temperature rose to 37°C and the solid matter gradually dissolved. After being stirred at 30°C for 20 min, the solution was poured into 50 ml of water and acidified with 5% HCl. The product that deposited (1.3 g) was filtered off, washed with water, dried, dissolved in chloroform, and passed through a layer of alumina*; yield of XII was 0.84 g (51.2%). Colorless crystals with a violet fluorescence in UV light, mp 157-158°C (from benzene – hexane). Found %: C 61.17; H 3.86; N 12.91; S 14.58. $C_{11}H_8N_2OS$. Calculated %: C 61.11; H 3.73; N 12.96; S 14.82.

9-Hydroxynaphtho[1,2-c]-[1,2,5]-thiadiazole (VIII). A solution of 2.2 g (10 mM) of XII in 40 ml of acetic acid was mixed with 40 ml of 40% HBr, and the mixture was boiled for 8 hr. After cooling, 100 ml of water was added and the precipitate was filtered off, washed with water dissolved in 5% caustic soda solution, and reprecipitated with conc. HCl. The yield of compound VIII was 1.88 g (91.3%), mp 112.5-113.5°C (from ethanol). Lustrous yellow needles and plates readily soluble in dilute alkali, benzene, and chloroform. Found %: C 59.32; H 2.98; N 14.14; S 16.04. $C_{10}H_6N_2OS$. Calculated %: C 59.41; H 2.99; N 13.86; S 15.85.

9-Methoxynaphtho[1,2-c]-[1,2,5]-selenadiazole (XIV). To a solution in 70 ml of water of the hydrochloride of the diamine XI obtained from 1.29 g (4 mM) of the azo dye XV was added at room temperature a solution of 1 g of selenium dioxide in 30 ml of water. After 30 min, the precipitate was separated off, washed with water, dried, and chromatographed on alumina, chloroform eluting 0.26 g (24.5%) of compound XIV; yellow crystals, mp 184-185°C (from chloroform–hexane). Found %: C 50.46; H 3.34; N 10.87. $C_{11}H_8N_2OSe$. Calculated %: C 50.20; H 3.06; N 10.65.

9-Hydroxynaphtho[1,2-c]-[1,2,5]-selenadiazole (IX). Over 40 min, with boiling, 7 g of zinc dust was added to a suspension of 1.88 g (9.3 mM) of VIII in 65 ml of 10% HCl, and the mixture was boiled until the starting material had dissolved. The hot solution was filtered and the filtrate was mixed with a solution of 2 g of selenium dioxide in 20 ml of water and brought to the boil. After cooling, 2 g of a dark substance separated out which was passed in benzene solution through a layer of silica, giving 0.61 g (30%) of compound IX. Bright yellow needles readily soluble in dilute alkalis and sparingly soluble in chloroform and acetone; mp 170-171°C (from hexane). Found %: C 48.15; H 2.50; N 11.18; Se 31.84. $C_{10}H_6N_2OSe$. Calculated %: C 48.20; H 2.43; N 11.25; Se 31.70.

9-Methoxynaphtho[1,2-d]imidazole (XIII). A mixture of the hydrochloride of the diamine XI obtained from 4 g (12.4 mM) of the azo dye XV and 50 ml of 80% formic acid was boiled for 2 hr and cooled. The precipitate (2.01 g) was filtered off, treated with sodium bicarbonate solution, washed with water, dried, and passed in chloroform solution through a column of alumina, giving 1.2 g (48.8%) of XIII in the form of colorless needles, mp 180.5-181.5°C (from benzene). Found %: C 72.57; H 5.23; N 14.37. $C_{12}H_{10}N_2O$. Calculated %: C 72.71; H 5.09; N 14.13.

9-Hydroxynaphtho[1,2-d]imidazole (VI). A solution of 0.85 g (4.3 mM) of XIII in 17 ml of 40% HBr was boiled for 30 hr and evaporated in vacuum. The residue was stirred in 50 ml of water and neutralized with saturated sodium bicarbonate solution. The precipitate was filtered off, washed with water, dried in the air, and chromatographed on silica,

*In all cases, alumina of activity grade II was used for chromatography.

0.56 g (71%) of the hydroxy compound VI being eluted with ethyl acetate. After crystallization from a large amount of chloroform, mp 230-233°C (decomp.). The substance rapidly darkened on being dissolved in alkali, on being heated with various solvents, and also on alumina. Found %: C 71.52; H 4.55. $C_{11}H_8N_2O$. Calculated %: C 71.73; H 4.38.

1-Hydroxybenzo[*a*]phenazine (V). A suspension of 7.2 g (30 mM) of 1-amino-2-naphthol-8-sulfonic acid in 200 ml of 0.25% HCl was treated gradually with 5 g of sodium nitrite, and the mixture was heated to 40-45°C. The excess of nitrous acid was decomposed with sulfanilic acid, and the reaction mixture was cooled to 10°C and treated with a solution of 3.3 g (30 mM) of o-phenylenediamine in dil. HCl. The precipitate of benzo[*a*]phenazine-1-sulfonic acid (4.75 g) was separated off and fused with 10 g of saturated potassium hydroxide solution and 12 g of solid potassium hydroxide in an open crucible at 210-225°C for 1 hr, 30 min. After cooling, the melt was treated with 400 ml of water, and the solid matter was filtered off, washed, dried, and passed through a column of alumina, 1.46 g (39%) of V being eluted with chlor form. Orange needles, mp 215.5-216.5 (from benzene); according to the literature [9]: mp 210°C (from nitrobenzene). Found %: N 11.57. $C_{16}H_{10}N_2O$. Calculated %: N 11.38.

10-Hydroxybenzo[h]quinoline (IV): mp 103.5-104.5°C (from hexane); according to the literature [7]: mp 104-105°C (from toluene).

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