6-Nitro-7-oxo-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine, Sodium Salt (VIIIb). A solution of the diazonium salt of 5-amino-1,2,4-triazole (1.7 g, 20 mmoles), nitromalonic diester (4.4 g, 20 mmoles) and Na_2CO_3 (3.2 g) was mixed in ethanol (50%, 20 ml). Stirring for 1 h at 0°C and 2 h at 20°C and filtration gave triazine VIIIb (1.25 g, 60%) with mp >300°C (from [2], mp >300°C).

2-Methyl-6-nitro-7-oxo-4,7-dihydro-1,2,4-triazolo-[5,1-c][1,2,4]triazine, sodium salt (VIIIc) was obtained by the method described above in 55% yield with mp 282-284°C (from [2], mp 282-284°C).

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REACTION OF 3,4-DIAMINOFURAZAN WITH CARBONYL COMPOUNDS AND THEIR METAL COMPLEXES

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It is shown that when 3,4-diaminofuranzan reacts with formic acid under various conditions there is, along with the mono- and diformylation, an intermolecular reaction leading to a polymeric compound. The diamine under consideration forms a monoazomethine with salicylaldehyde but a bis(azomethine) complex with the salicylaldehydate of divalent nickel.

It is known that as a consequence of the extremely low basicity of the NH_2 groups in aminofurazans [1, 2], the latter have substantial difficulty in reacting with carbonyl-containing compounds [1].

In the present paper, we report on an attempt to obtain imidazo[d,c]furazan (II) and azomethines from 3,4-diaminofurazan (I) with salicylaldehyde (III). These products are of interest as potentially biologically active substances [1] and as ligands for complex formation [4].

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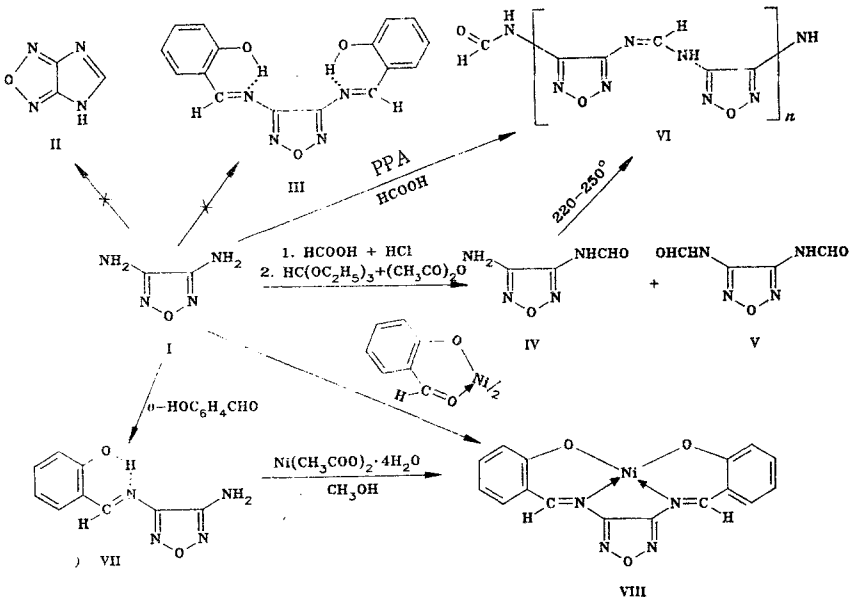

When 3,4-diaminofurazan reacts with formic acid in the presence of a catalytic amount of concentrated HCl or with an o-formic ester in acetic anhydride under the conditions usually used for the annelation of an imidazol ring from ortho-diamines [5, 6], the bicyclic compound, II, is not obtained; only mixtures of the mono- and diformyl derivatives, IV and V, respectively, are formed. Carrying out the condensation of diamine I with HCOOH in polyphosphoric acid (PPA) leads to high-melting polymers, probably having structure VI. The analogous polymer VI was evolved when it was attempted to cyclize the monoformyl derivative, IV, to imidazo-[d,c]furazan with PPA or by high-temperature dehydration. In addition to bands which are characteristic of the furazan ring (~1620-1630 cm^{-1}), carbonyl absorption bands appear in the 1690-1700 cm^{-1} region of the IR spectra of compounds IV-VI; the azomethine group of polymer VI absorbs at 1635 cm^{-1}.

Consequently, even under rigorous conditions the cyclization takes place as an inter- rather than an intramolecular process. In our opinion, this result is explained not only by the low basicity of the amino groups in diaminofurazan I, but also by their spatial arrangement which impedes the participation of both amine groupings in reactions with carbonyl compounds to form five-membered heterocycles [1].

This conclusion is confirmed by the unusual reaction of diaminofurazan with salicylaldehyde. Unlike o-phenylenediamine [7], diamine I forms only monoazomethine VII with this aldehyde. Carrying out this condensation in the presence of HCl or $ZnCl_2$, which is known [8] to facilitate the formation of azomethines, still does not lead to the diazomethine. Therefore, we carried out a template synthesis [9], introducing the nickel complex of salicylaldehyde into the reaction with compound I. It turned out that as a result of this change (I → VIII), both amino groups of 3,4-diaminofurazan react to form an innercomplex compound (ICC) that is similar in properties to salicyliminato ICC's of aliphatic and aromatic diamines [7]. In the IR spectrum of ICC VIII, one finds the total furazan and azomethine absorption at 1580-1630 cm^{-1} and the absence of NH_2 group frequencies. The complex is diamagnetic. The composition and the properties adduced agree with structure VIII that we have proposed for the nickel ICC being considered.

The participation of both amino groups of compound I in the synthesis of ICC VIII can be explained by the activation of the carbonyl groups in the salicylaldehydate by the metal. We note also that the formation of ICC VIII is facilitated by the chelate effect [10] that is responsible also for the formation of compound VIII from monoazomethine VII and nickel acetate. Reaction VII → VIII obviously starts with the hydrolysis of monoazomethine VII under the conditions of the synthesis to the diamine and aldehyde, followed by the formation of nickel salicylaldehydate that then reacts with liberated diamine just as in the I → VIII transformation.

Thus, the reaction of 3,4-diaminofurazan with carbonyl compounds is substantially activated by carrying out the reaction in a transition metal matrix.

EXPERIMENTAL

The IR spectra of the samples were taken on a Specord-71 spectrometer in petrolatum. The magnetic properties of the complex compounds were measured by the Faraday comparative method at 293 K [11].

3-Amino-4-formylaminofurazan (IV). Boil a solution of 1 g (10 mmoles) of diaminofurazan I [3] in 3 ml of concentrated HCOOH for 3 h and allow to stand at romm temperature. On the following day, filter off the solid precipitating out when the reaction mixture is diluted twofold. Yield 0.89 g, mp 160-164°C. Recrystallize twice from ethanol to obtain 0.72 g of coarse, colorless crystals with mp 169-170°C. IR spectrum: 1700 (CHO), 3075, 3195, 3375 cm^{-1} (NH_2). Found: C 28.0; H 3.1; N 44.1%. Calculated for $C_3H_4N_4O_2$: C 28.1; H 3.1; N 43.8%.

3,4-Di(formylamino)furazan (V). A. After separation of the monoformyl derivative, IV, neutralize the formic acid solution with ammonia, evaporated to a small volume (~1.5 ml), and filter off the solid that precipitates. Unite it with the residue after evaporation of the alcoholic mother liquor remaining from the recrystallization of compound IV, and crystallize from alcohol and acetonitrile to give 0.12 g of the diformyl derivative in the form of colorless, needle-like crystals with mp 140°C. IR spectrum: 1615-1620 (furazan ring), 3205 (NH), 1690 cm^{-1} (CHO). Found: C 30.6; H 2.6; N 36.2%. Calculated for $C_4H_4N_4O_3$: C 30.8; H 2.6; N 3.5%.

B. When diaminofurazan reacts with HCOOH in the presence of two drops of concentrated HCl under the conditions stated above for the synthesis of the monoformyl derivative, IV, there first precipitates from the reaction mixture a solid (0.2 g, mp 130-133°C) consisting primarily of the diformyl derivative, V, but when the filtrate, neutralized with ammonia, is evaporated, compound IV is evolved (0.8 g, mp 160-163°C), contaminated with diformylamine V. After subsequent recrystallization from the above-mentioned solvents, pure samples of compounds IV (mp 169-170°C) and V (mp 140°C) are obtained.

C. Heat a mixture of 1 g (10 mmoles) of 3,4-diaminofurazan, 5 ml of acetic anhydride, and 5 ml of ethyl orthoformate for 5 h at the boiling point. After evaporation of the solution to 5 ml cool it, filter off the precipitate, and pass it through a layer of Al_2O_3 (eluent, ethyl acetate) and recrystallize it from a large quantity (100 ml) of benzene or toluene. mp 134-135°C (incipient liquifaction at 112°C). From the elementary analysis, the precipitate is a mixture of mono- and diformyl derivatives, IV and V, containing more than 50% of compound V.

Polymer VI. A. Pour 1 ml of 98% HCOOH with stirring into a mixture of 1 g (10 mmoles) of diamine I and 10 g PPA, heat to 60-70°C, and continue to heat, gradually raising the temperature. At 120°C, the reaction mixture foams strongly. After holding the mixture at this temperature for 1 h, cool it and pour it into water. Separate the solid which precipitates and wash it with water, alcohol, and acetone — to obtain 0.63 g of polymer in the form of a yellow, finely crystalline substance, difficulty soluble in the majority of organic solvents and water. mp >340°C. IR spectrum: 1620 (furazan ring), 1635 (C=N, azomethine), 1700 (a low-intensity band, C=O), 3325 cm^{-1} (a broad band, NH). Found: C 31.4; H 2.5; N 55.2%. Calculated for polymer VI with n = 10-20: C 32.1; H 2.4; N 51.6%.

B. Heat 0.64 g (5 mmoles) of 3-amino-4-formylamino furazan in a sealed tube in a silicone oil bath. At 170-175°C, a melt forms which foams violently when the bath temperature is raised to 220-225°C, forming the yellow, crystalline polymer. Digest it with alcohol, then acetone. Yield 0.38 g, mp >340°C. A similar polymer forms when monoformyl derivative II is heated in PPA at 120-130°C.

3-Salicylideneamino-4-aminofurazan (VIII). Add 4.88 g (40 mmoles) of salicylaldehyde in 20 ml of ethanol to a solution of 2 g (20 mmoles) of 3,4-diaminofurazan, I, in 20 ml of the same solvent. Boil the mixture 30 min, evaporate to a volume of 20 ml, cool, and filter off the solid that has precipitated. Light yellow, needle-like crystals are obtained chromatographically pure (silica gel) after recrystallization from toluene. Yield 75%, mp 191-192°C. IR spectrum: 1620 (furazan ring), 1645 (C=N, azomethine), 3305, 3385 cm^{-1} (NH_2). Found: C 52.6; H 4.11; N 27.3%. Calculated for $C_9H_8N_4O_2$: C 52.9; H 3.9; N 27.4%.

(3,4-Bissalicylideneaminofurazan)nickel (VIII). A. Add 2.44 g (20 mmoles) of salicylaldehyde in 10 ml of methanol to a boiling solution of 2.48 g (10 mmoles) of nickel acetate tetrahydrate in 20 ml of the same solvent. Boil the solution for 20 min, during which time

the color characteristic of nickel salicyladehydrate appears. Then add in sequence 1.12 g (20 mmoles) of KOH in 15 ml of methanol and 1 g (10 mmoles) of 3,4-diaminofurazan in 10 ml of methanol. After boiling the solution for 10 h, filter off the precipitated complex compound, wash it repeatedly with hot methanol, and dry it in vacuum at 120°C. Yield 2.95 g (82%), black crystals with mp 350°C. IR spectrum: 1615 (C=N, azomethine), 1630 cm^{-1} (furazan ring). Found: C 52.8; H 2.7; N 15.5; Ni 16.5%. Calculated for $C_{16}H_{10}N_4NiO_3$: C 52.6; H 2.8; N 15.4; Ni 16.1%.

B. Dissolve 0.5 g (2.5 mmoles) of azomethine VII in 30 ml of methanol and add 0.26 g (1.25 mmoles) of nickel acetate tetrahydrate in 10 ml of the same solvent. After boiling the solution for 4 h, filter off the black crystals, wash three times with methanol, and dry in vacuum at 120°C.

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CROWN ETHERS BOUND TO SULFANILAMIDE PREPARATIONS

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Complexes with a 1:2 composition were obtained by the reaction of 8-crown-6 ethers with 4-aminobenzenesulfonamide and 4-aminobenzensulfoguanidine. Crown ethers containing a sulfanilyl group were obtained in the reaction of azacrown ethers with 4-acetylaminobenzenesulfonyl chloride.

Interest has recently arisen in crown ethers containing pharmacophoric groups [1, 2]. To change the hydrophilic-hydrophobic properties of sulfanilamide preparations (SFAP), we carried out reaction of 4-aminobenzenesulfonamide, 4-aminobenzenesulfoguanidine, 2-(4-aminobenzenesolfonamido)thiazole, 4-aminobenzenesulfonylurea, 2-(4-aminobenzenesulfonamido)-4,6-dimethylpyridimidine, 2-(4-aminobenzenesulfonamido)-3-methoxypyrazine, 3-(4-aminobenzenesulfonamido)-6-methoxypyridazine, and 6-(4-aminobenzenesulfonamido)-2,4-dimethoxypyrimidine with 15-crown-5 and 18-crown-6 ethers in solvents that ensure the dissolution of the starting materials. In the literature, spectral data are given on the complexation of 18-crown-6 ethers with SFAP, including 3-(4-aminobenzenesulfonamido)-6-methoxypyradizine and 6-(4-aminobenzenesulfononamido)-2,4-dimethoxypyrimidine [3], but preparatively, we succeeded only

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