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Aromatic dihydrazines can be prepared by reducing diazo compounds [1]. Aliphatic dihydrazines are prepared by reacting alkylene dihalogenides with hydrazine [2, 3] or by the acid hydrolysis of bis-sydnones [4]. After unsuccessfully attempting to prepare an aliphatic-aromatic dihydrazine by reacting p-xylylenedichloride with excess hydrazine, we succeeded in synthesizing it by hydrolyzing p-xylene-bis-sydnone, which was obtained from p-xylylenediamine by the following scheme, in acid:

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By carrying out the condensation of the diamine with the formaldehyde and hydrocyanic acid in a weakly basic medium and also by having changed the order of adding the components during the nitrozation, the yield of the dihydrazines was substantially increased. Thus, tetramethylenedihydrazine was obtained earlier in a 30% yield [4]; we obtained this dihydrazine in a 47.5% yield by changing the conditions of the synthesis. We obtained p-xylylenedihydrazine in a 15% yield by the method in [4], but in a 63% yield under the modified conditions. Compounds (I), (II), and (III) were isolated and characterized for the first time.

## EXPERIMENTAL METHOD

The starting p-xylylenediamine was obtained by the method in [5].

The Preparation of N.N'-Dinitroso-p-xylene-bis-glycine (I). Concentrated hydrochloric acid, 0.45 mole, was slowly added to a solution of 31.3 g of p-xylyenediamine in 50 ml of water while cooling the flask externally (the reaction remained weakly basic), and then 31 g of KCN was added at room temperature along with enough water to dissolve the components completely. Forty grams of a 34% aqueous formaldehyde solution was slowly added at 17-20°C to the solution obtained. The mixture was kept at room temperature for another hour, a solution of 52 g of KOH in a small amount of water was added, and it was heated for 5 h on a boiling water bath — the last two h with a vacuum aspirator attached to ensure the complete removal of ammonia. After cooling, the reaction mixture was transferred to a beaker, and 0.8 mole of concentrated hydrochloric acid was added slowly until a slightly basic reaction was obtained. Then a concentrated aqueous solution of 32 g of NaNO<sub>2</sub> was added dropwise at  $-50^{\circ}$ C, and concentrated HCl was slowly added at -5 to  $-10^{\circ}$ C until the mixture was strongly acidic. The suspension that formed stood overnight in a refrigerator. In the morning the precipitate was filtered off, recrystallized from water, and dried in a vacuum desiccator over  $P_2O_5$ . Compound (I) was obtained as fine yellowish crystals, 45 g (63%)

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of theoretical), mp 152-156°C. Found %: C 46.84, 47.01; H 4.85, 4.83; N 17.99, 18.09;  $C_{12}H_{14}O_6N_4$ . Calculated %: C 46.45; H 4.51; N 18.06. The Lieberman reaction for the nitroso group was positive [6]. IR spectrum (cm<sup>-1</sup>): 1700 vs (C = O group); 1420-1310 gr (N = O group).

<u>The Preparation of p-Xylylene-bis-sydnone (II)</u>. Compound (I), 43.5 g, was kept in the dark for 24 h with 150 ml of freshly distilled  $(Ac)_2O$ . Another 150 ml of  $(Ac)_2O$  was added and the mixture was heated for 6 h on a boiling water bath using a reflux condenser. After cooling, the residue which precipitated out was isolated, the filtrate was evaporated, and the residue was added to the main portion of the product. After recrystallizing it from hot water and drying it in a vacuum desiccator over  $P_2O_5$  (in the dark), 32 g of (II) (85% of theoretical) was obtained, mp 230 to 233°C (decomp.). Found %: C 52.83, 52.87; H 4.05, 4.11; N 20.48, 20.43.  $C_{12}H_{10}N_4O_4$ . Calculated %: C 52.55; H 3.65; N 20.43. IR spectrum (cm<sup>-1</sup>): 1742 vs (CO-group in sydnones [4]), 311 s (CH-bond of the sydnone rings).

<u>The Preparation of p-Xylylenedihydrazine Dihydrochloride (III)</u>. Compound (II), 7.8 g, was heated with 100 ml of concentrated HCl for 3 h using a reflux condenser on a boiling water bath. The evolution of  $CO_2$  was observed as well as precipitation. The precipitate was filtered off, washed with absolute ethanol, and dried in a vacuum desiccator over CaCl<sub>2</sub>. Compound (III), 5.45 g (85% of theoretical) was obtained, mp 246 to 248° (decomp.). Found %: N 22.59, 22.58; Cl 30.11, 29.83.  $C_8H_{16}N_4Cl_2$ . Calculated %: N 23.43; Cl 29.72. IR spectrum (cm<sup>-1</sup>): 3100 vs (NH-group). The bands which correspond to the absorption by syndnones were absent.

A solution of the p-xylylenedihydrazine base, which was used for further conversions, was obtained by treating the dihydrochloride (III) with 2 equiv of  $CH_3ONa$  in absolute methanol after filtering the NaCl precipitate off.

## CONCLUSIONS

1. The feasibility of preparing the aliphatic-aromatic p-xylylene-dihydrazine by the well known method used to synthetize aliphatic dihydrazines was demonstrated.

2. p-Xylylenedihydrazine dihydrochloride, p-xylylene-bis-sydnone, and N, N'-dinitroso-p-xylylenebis-glycine were prepared and characterized for the first time.

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