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Abstract

Full Text

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L. Kh. FREIDLIN, Academician A. A. BALANDIN, and T. A. SLADKOVA

PREPARATION OF *n*-XYLYLENEDIAMINE BY CATALYTIC REDUCTION OF TEREPHTHALIC ACID DINITRILE

n-Xylylenediamine is of interest for the synthesis of high-molecular-weight polyamides. It was first obtained by Lüthström ([1]) by Gabriel' s method in the form of the hydrochloride by heating *n*-xylylenediphthalimide with acetic acid and concentrated hydrochloric acid. I. P. Losev and co-workers ([2]) obtained *n*-xylylenediamine by Hoben' s method from *n*-xylylene dichloride through the complex compound with hexamethylenetetramine. A. M. Sladkov and S. V. Vitt ([3]) described the synthesis of *n*-xylylenediamine from *n*-phenylenediacetic acid and hydrazoic acid by the Schmidt reaction. Catalytic methods for the preparation of *n*-xylylenediamine have not been described in the literature.

In the present work, the preparation of *n*-xylylenediamine by catalytic hydrogenation of the industrially available dinitrile of terephthalic acid was studied. Hydrogenation was carried out in a rotating autoclave of 0.15 l capacity in a dioxane medium in the presence of ammonia, which was fed from a weighed small cylinder into the cooled autoclave in an amount of 15–20% by weight of the dinitrile. The constants of the dinitrile corresponded to the literature data*. Raney nickel, cobalt, and iron were used as catalysts. The catalysts were prepared by exhaustive leaching of 50% alloys of nickel with aluminum and cobalt with aluminum, as well as of a 30% alloy of iron with aluminum, with a 10% solution of caustic soda at 90–100°. The initial hydrogen pressure was 90–100 atm. Hydrogen absorption began at 80–85°. During the experiment, hydrogen, as it was consumed, was fed into the autoclave. The total duration of hydrogen absorption was 2–2.5 hr. The discharged reaction products were separated from the catalyst by filtration and, after removal of the dioxane, were subjected to fractionation in vacuo in a stream of nitrogen.

As a result of the distillation, two fractions and a residue were obtained. The amount of fraction I did not exceed 5% of the weight of the reaction products. It was a transparent liquid with b.p. 82°/3.5 mm and 92°/5 mm, $d_4^{20} = 0.9406$, $n_D^{21.5} = 1.4925$. MR 40.80. $NC \cdot C_6H_4 \cdot CH_2NH_2$, calculated 40.98.

The main part of the hydrogenation products was fraction II, with b.p. 113°/3.5 mm and 122°/5.5 mm, which solidified to a white crystalline mass. Determination of the content of *n*-xylylenediamine in fraction II was carried out by titration of an accurately weighed sample with hydrochloric acid in the presence of

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methyl orange. For the titration of 0.1357 g of diamine, 19.30 ml of 0.0993 N HCl were consumed. Theoretically, for $H_2N \cdot H_2C \cdot C_6H_4 \cdot CH_2 \cdot NH_2$, 20.0 ml are required.

The *n*-xylylenediamine obtained is readily soluble in water, alcohol, pyridine, and dioxane. The dibenzoyl derivative after recrystalli-

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* We take this opportunity to express our gratitude to B. V. Suvorov for the sample of dinitrile provided.

···from dioxane melts at 198°. According to the literature data (1), mp 194°.

Found, %: N 8.40
$C_{22}H_{20}O_2N_2$. Calculated, %: N 8.14

When 10% alcoholic solutions of *n*-xylylenediamine and succinic acid were mixed, white crystals precipitated; after washing with hot alcohol they melted at 231–232°, while according to the literature data (2) mp 230°.

Found, %: C 56.76; H 7.09; N 11.07
$C_{12}H_{18}N_2O_4$. Calculated, %: C 56.69; H 7.09; N 11.03

Cyclohexenyldiamines were not isolated. Apparently, addition of hydrogen takes place only at the nitrile group, while the aromatic nucleus is not hydrogenated owing to blocking of the active surface of the catalyst by amines and nitrile.

Table 1 gives the experimental conditions and the yields of amines obtained. From these data it is evident that the greatest influence on the yield of *n*-xylylenediamine

Table 1

Dinitrile, mol	Dioxane, ml	Ammonia, mol	Catalyst and its wt., g	Initial hydrogen pressure, atm	Maximum experimental temperature, °C	Yield of amine fraction, wt. %	Composition of amine fraction, wt. % I	Composition of amine fraction, wt. % II
0.195	60	0.2	Ni, 10	80	100	68.2	1.4	66.8
0.195	35	0.47	Ni, 6	80	135	51.0	3.8	47.2
0.195	55	0.35	Ni, 5	130	80	28.5	0.0	28.5
0.195	45	1.15	Ni, 6	95	100	70.0	5.0	6.5
0.156	50	0.65	Co, 5	85	105	68.2	1.5	66.7

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Note. I —*n*-cyanobenzylamine, II —*n*-xylylenediamine.

is exerted by the experimental temperature. At 80° the yield of *n*-xylylenediamine is only 28.5%; when the temperature is raised to 100° its yield reaches 66.8%, and at 135° the yield decreases to 47.2%. Doubling the amount of catalyst does not change the yield of diamine.

In the experiment with an iron catalyst it was not possible to isolate the amine fraction, although during the experiment 23% of the theoretically required hydrogen was absorbed. After distillation of dioxane from the reaction products, a viscous brownish-red mass remained in the flask together with unreacted dinitrile.

The data obtained show that *n*-xylylenediamine can be obtained in high yield by the method of catalytic hydrogenation of terephthalic acid dinitrile.

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Note: Figure translations are in progress. See original paper for figures.

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