Synthesis of Adiponitrile from Tetrahydrofurane.

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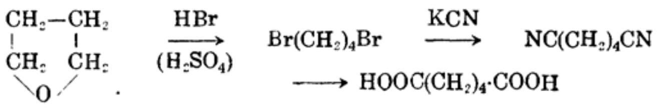
This paper is the 6th report on the studies of furfural and its related compounds(1).

In the previous reports(2), an attempt was described to prepare butadiene by the catalytic dehydration of tetrahydrofurane, which was obtained from furfural. In the present report an attempt was described to prepare adiponitrile and adipic acid, which have recently obtained an industrial significance as the intermediates for synthetic fibre, from tetrahydrofurane by the following schema:



There are some literatures on the bromination of tetrahydrofurane into tetramethylene dibromide, using HBr in acetic acid(3), fuming hydrobromic acid(4) and dry hydrogen bromide gas(5). In the present investigation tetrahydrofurane has been brominated with hydrobromic acid in the presence of sulphuric acid, following the method described in " Organic Syntheses ". The yield of tetramethylene dibromide was about 64% of the theoretical. The mixture of hydrobromic acid and sulphuric acid was prepared by mixing commercial 45% hydrobromic acid and sulphuric acid or by the reduction of the mixture of bromine and water with sulphurous anhydride, both giving similar results.

There is only an old report on the preparations of adiponitrile from tetramethylene dibromide(6). Tetramethylene dibromide was heated with aqueous ethanol solution of potassium cyanide and adiponitrile was obtained in the yield of about 75-78%. The reaction of tetramethylene dibromide with aqueous solution of potassium cyanide gives unsatisfactory results, probably due to the low solubility in the aqueous layer. Although the formation of isomers containing isonitril group $CN\cdot(CH_2)_4\cdot$

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(1) M. Katuno: *J. Soc. Chem. Ind., Japan,* **46** (1943), 25 B, 180 B, 184 B, 210 B, 214 B.

(2) M. Katuno: ibid., **46** (1943), 210 B, 214 B.

(3) R. Paur: *Bull. Sac. Chem.* (5), **5** (1938), 1053.

(4) Demjanow· *J. Russ. Phys. Chem. Ges.* **24** (1892), 349; Beilsteins Handb. d. Org. Chem. **17** (1933) SIO.

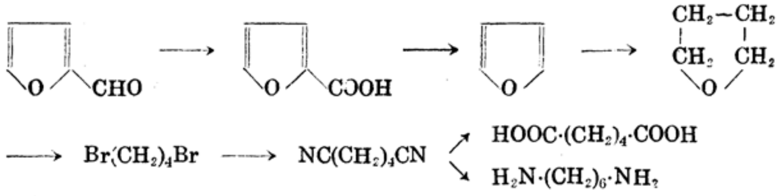
(5) S. Fried & R. D. Kleene: *J. Amer. Chem. Soc.* **62** (1940), 3258; **63** (1941), 2691.

(6) Henry: Zentr, 1901, 11, 807; Beilsteins Handb. d. Org. Chem. Bd. **2** (1920), S 635.

CN and $CN \cdot (CH_2)_4 \cdot NC$, in small amounts as byproducts is to be expected, they were not identified in the present investigation.

The hydrolysis of adiponitrile into adipic acid proceeds almost quantitatively by the ordinary method of heating the solution with sulphuric acid.

The hydrogenation of adiponitrile into hexamethylene diamine, on which there are several recent patents and literatures, was not attempted in the present investigation. Although adipic acid and hexamethylene diammine are obtained from phenol, they can also be obtained from furfural by the following rout.



Experimental 1. *Tetramethylene dibromide from tetrahydrofurane*: 471 g. of commercial 45% hydrobromic acid (contained 43% of HBr by titration) was mixed with 125 g. of 97% sulphuric acid under cooling. 72 g. (1.0 mol) of tetrahydrofurane (bp. 66.0-67.0°C; $d_4^{20} = 0.8884$; $n_D^{20} = 1.4073$), which was obtained from furfural in the previous reports(7), was mixed with the above acid and heated at about 100°C for about 7 hrs. with reflux condenser under occasional shaking. After cooling, lower layer of tetramethylene dibromide was pipetted out (yield 136 g.). The upper aqueous layer was distilled using 20 cm. Widmer column. Only a negligible amount of tetrahydrofurane fraction was recovered, and from the subsequent fraction boiling between 95°-125°C (125 g.), which separates into two layers, 36 g. of lower layer of tetramethylene dibromide was separated. The yield of tetramethylene dibromide was 172 g. (0.797 mol or 79.7% of theoretical), and it was redistilled under reduced pressure, and 138 g. of crude tetramethylene dibromide (0.639 mol or 63.9% of the theoretical) boiling at 90°C/23 mm.-92°C/22mm. was obtained.

Similar results were obtained by using the mixture of hydrobromic acid, water and sulphuric acid which was prepared by the reduction of the mixture of bromine and water with sulphurous anhydride.

The crude tetramethylene dibromide, obtained from three experiments, was purified by redistillation, and a colourless, heavy liquid with stimulative smell was obtained. Bp. = 83°C/18mm.-86°C/19mm. $d_4^{20} = 1.8080$; $n_D^{20} = 1.5175$; $MR_D = 36.21$(found); 36.20(calcd. for $C_4H_8Br_2$). Anal. C:

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(7) M. Katuno: *J. Soc. Chem. Ind. Japan*: **46** (1943), 214 B, 210 B.

22.52%, 22.64% ; H: 3.83% ; 3.86% ; Calcd. for $C_4H_8Br_2$: C: 22.25% ; H: 3.73%.

2. Adiponitrile from tetramethylene dibromide: **Expt. 1.** A four-necked flask of 500 cc. content, equipped with a mercury-sealed stirrer, dropping funnel, thermometer and reflux condenser, was used. 19 g. of potassium cyanide (0.29 mol) was dissolved in 25 cc. of water, and 56 g. (about 70 cc.) of absolute alcohol was added. 21.6 g. of tetramethylene dibromide (0.10 mol) was dropped under stirring, and the temperature was raised to about 75°C. on the water bath with automatically controlled burner. The mixture was stirred for 4 hrs. at 75°C and then allowed to cool.

Ethanol was removed by distillation up to 90°C using 20 cm. Widmer column. Adiponitrile, which forms the upper layer, was separated, and the aqueous layer was extracted three times with ethyl acetate, and the extract was joined with the adiponitrile layer. The solvent was removed by distillation, and adiponitrile was distilled under reduced pressure. 8.1 g. (0.075 mol or 75% of the theoretical against tetramethylene dibromide) of crude adiponitrile boiling at 140–141°C/6mm. was obtained.

Expt. 2. The amount of ethanol used was decreased, and the separation of adiponitrile was slightly modified. 19 g. (0.29 mol) of potassium cyanide was dissolved in 25cc. of water and 30 cc. of ethanol was added, and heated to 75°C under stirring. 21.6 g. (0.10 mol) of tetramethylene dibromide was dropped in 10 min., and stirred for 5.5 hrs. at 75°C.

After cooling, 50 cc. of water was added to the product to dissolve the crystal separated, and thus adiponitrile formed the upper layer. The mixture was extracted four times with ethyl acetate, and the extract was distilled under ordinary pressure to remove ethyl acetate, and then under reduced pressure. 8.4 g. of crude adiponitrile (0.078 mol; or 78% of the theoretical) boiling at 173.5–140°C/5 mm. was obtained.

Expt. 3. The reaction was carried out without using ethanol. 21.6 g. (0.10 mol) of tetramethylene dibromide was dropped in the solution of 19 g. of potassium cyanide (0.29 mol) and 25 cc. of water, under stirring at 75°C, and stirring was continued for 6 hrs. Tetramethylene dibromide, which separates as lower layer, was recovered, and the aqueous layer was extracted three times with ethyl acetate, and the extract was joined with the tetramethylene dibromide layer. Ethyl acetate was distilled off, and tetramethylene dibromide was recovered by distillation under reduced pressure. Yield 17.1 g. (79%), boiling between 65–80°C/7.5 mm. Little formation of adiponitrile was observed.

Expt. 4. 95 g. of potassium cyanide (about 1.5 mol) was dissolved in 100 cc. of water and 79 g. (about 100 cc.) of absolute ethanol was added, and was stirred at 75°C. 108.0 g. (0.50 mol) of tetramethylene dibromide was dropped in about 10 minutes. The temperature of liquid was raised gradually to about 85°C and the boiling of the liquid began. The mixture then was cooled for a while and heated again to 75°C, and was stirred for about 6 hrs.

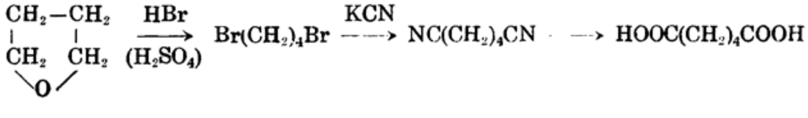
Ethanol was distilled off using 20 cm. Widmer column up to the temperature 90° C. The adiponitrile layer was separated, and the aqueous layer was extracted with ethyl acetate. The solvent was removed by distillation, and 28.8 g. of crude adiponitrile (0.267 mol or 53.4% of the theoretical) boiling between 145–160°C/8 mm. was obtained. Purification of adiponitrile: Crude adiponitrile was redistilled and the main fraction boiling at 165–166°C/16 mm. was obtained. It is a colourless, slightly viscous liquid. $d_4^{20} = 0.9396$; $n_D^{20} = 14390$; $MR_D = 30.91$ (obsd.); 29.54 (calcd. for $(CH_2)_4(CN)_2$). Anal. : C : 66.60% ; 66.76% ; H : 7.40% ; 7.77% ; Calcd. for $C_6H_8N_2$: C : 66.64% ; H : 7.46%.

3. Adipic acid from adiponitrile: 2.0 g. of adiponitrile was dissolved in 10 g. of 62% sulphuric acid, and heated at about 100°C. The liquid separated crystal after about 2 hrs. After heating more than 3.5 hrs., it was allowed to cool. The crystal of adipic acid was washed with a small amount of water, wiped with filter paper, and dried to constant weight by steam oven and evacuated desiccator. 2.7 g. (100% of the theoretical) of crude adipic acid was obtained. It was recrystallised twice from water after treating with charcoal, and 1.1 g. (41% of the theoretical) of pure adipic acid was obtained. It is a snowwhite crystal with mp. 149.0–149.5°/C (uncorr.).

Anal. C : 49.14% ; 48.95% ; H : 6.84% ; 6.94%. Calcd. for $C_6H_{10}O_4$: C : 49.31% ; H : 6.90%.

Summary.

The synthesis of adiponitrile and adipic acid from tetrahydrofurane, which was obtained from furfural, has been attempted, according to the following schema :



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