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Reinvestigation of the Preparation of Dicarboxylic Acids

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A SURVEY of the literature pertaining to the preparation of dicarboxylic acids from diols via nitrile hydrolysis, or to the preparation of the necessary intermediates results in considerable confusion with respect to optimum conditions and methods. Furthermore, many references are

lacking in specific details such as method used, time, temperature, etc.

1,6-Hexanedioic acid from tetramethylene glycol, 1,7-heptanedioic acid from pentamethylene glycol, 1,8-octanedioic acid from hexamethylene glycol, and 1,12-dodecanedioic acid from decamethylene glycol have been prepared. From the results obtained, specific conditions were formulated for the steps involved. Many of these are considerably simpler than those reported in literature.

Table I. Conversion of Diols to Dibromides^a

Glycol Used	Reflux Time ^b	% Yield of Dibromide	B.P., °C.
Tetramethylene	1 Hour	89.0-91.3	196-197
Pentamethylene	2 Hours	83.0-86.0	90 (8)
Hexamethylene	1 Hour	86.8-87.0	110 (8)
Decamethylene	1 Hour	89.3-90.8	141 (4)

^aThe preparation of the dibromides was carried out using sodium bromide-sulfuric acid since it was found that this was the simplest method and gave the best yields. The ratios were 1 mole diol:5.3 moles acid:4.1 moles sodium bromide:360 ml. water. The acid was added dropwise over a period of 1 hour to the mixture of glycol-sodium bromide-water. The crude product was extracted with ether, the extracts washed with water, aqueous sodium bicarbonate, and aqueous sodium thiosulfate, then dried over sodium sulfate.

^bThis is the time of reflux after addition of sulfuric acid was completed. Gentle reflux was maintained during the addition of the acid.

Table II. Conversion of Dibromides to Dicyanides^a

Dibromide Used	Reflux Time	% Yield of Dicyanide	B.P.
Tetramethylene	2 Hours	89.8-91.6	156-158 (7)
Pentamethylene	3 Hours	89.5-91.3	152-153 (3.5)
Hexamethylene	2 Hours	92.2-94.6	153-154 (2.5)
Decamethylene	2 Hours	90.0-92.0	183 (3)

^aThe following ratios were used: 1.0 mole dibromide:2.1 moles potassium cyanide:360 ml. water:1060 ml. 95% ethanol. The crude product was obtained by distilling off most of the solvent, extracting the residue with benzene, and washing the benzene extracts with aqueous sodium hydroxide and water.

CONCLUSION

The preparation of the dibromides and dicyanides can be carried out using methods and conditions that are less complicated than many suggested in literature. Stirring is necessary in the first two steps to avoid dangerous bumping.

Table III. Hydrolysis of Dicyanides^a

Dicyanide Used	Acid Formed	% Yield of Acid	M.P.
Tetramethylene	1,6-Hexanedioic	96.2-97.3	151-152
Pentamethylene	1,7-Heptanedioic	94.1-95.5	103-104
Hexamethylene	1,8-Octanedioic	93.1-93.4	139-140
Decamethylene	1,12-Dodecanedioic	98.1-98.9	128-128.5

^aCarried out as suggested in literature by refluxing a mixture of 1 mole dicyanide and 420 grams conc. hydrochloric acid for 3 hours.

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