

## NOTES

## The Hofmann Degradation of Glutaramide

BY SAMUEL R. ASPINALL

Although the Hofmann degradation has been used widely to prepare simple monoamines, its

and redistilled. It was finally obtained as a pure, water-white liquid boiling at 131° (uncor.) at 760 mm. by fractionation through a Vigreux column from a fresh piece of sodium. The yield was 56 g. (75% of theoretical). The amine was further identified as the derivatives tabulated below.

TABLE I  
DERIVATIVES OF TRIMETHYLENEDIAMINE

Derivative	Formula	M. p. ° C.	Recrystn. solvent	Nitrogen, %		
				Calcd.	Found, I	Kjeld. II
Dipicrate	(HPic.NH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	250 <sup>a</sup>	H <sub>2</sub> O	21.05	21.10	21.00
Diphenylcar- bonamido-	(C <sub>6</sub> H <sub>5</sub> NHCONHCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	215 <sup>b</sup>	aq. EtOH	17.94	17.97	18.04
Dibenzoyl-	(C <sub>6</sub> H <sub>5</sub> CONHCH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	140 <sup>c</sup>	aq. EtOH	9.93	9.90	9.69

<sup>a</sup> (uncor.) With decomposition. <sup>b</sup> (cor.). <sup>c</sup> (cor.) Literature 147-8° (*Ber.* 21, 2365 (1888)).

use to prepare diamines has been exploited but little. Urea, and presumably oxamide, yield elementary nitrogen when treated with alkaline hypobromite; while the use of malonamide is excluded because the anticipated product, methylenediamine, is unknown in the pure condition. Van Dam<sup>1</sup> states that bromine reacts on succinamide to yield a dibromo compound, but treatment of the latter with potassium or barium hydroxide fails to yield ethylenediamine, ammonia being the sole volatile product. The only records of the conversion of a diamide to a diamine by the Hofmann degradation are contained in German Patent No. 232,072 and an investigation by Von Braun and Lemke<sup>2</sup> which state that sodium hypohalite converts adipamide to tetramethylenediamine.

When a sample of trimethylenediamine was needed recently in this Laboratory it was found possible to prepare it easily and in good yield by the Hofmann degradation of glutaramide.

## Experimental

One mole (130 g.) of pure glutaramide (prepared by ammonolysis of the ester in the usual way) was dissolved at 0° in a solution of 2 moles (320 g.) of bromine and 10 moles (660 g.) of 85% of potassium hydroxide in 3 liters of water. The solution was allowed to come to room temperature, heated at 60° for two hours, acidified with hydrochloric acid and evaporated to a small volume. The large mass of inorganic salt was filtered, washed with acetone and the filtrates evaporated to a paste. An excess of crude potassium hydroxide was mixed into the paste and a water solution of the amine was distilled, dried over metallic sodium

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## The Reductive Alkylation of Hindered Aromatic Amines. II

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In continuing a study of the reductive alkylation of hindered aromatic amines,<sup>2</sup> two additional halogenated amines have been examined for dehalogenation accompanying alkylation.<sup>2a</sup>

When 4-iodo-2,6-dibromoaniline was refluxed with zinc, hydrochloric acid and formaldehyde in glacial acetic acid, all of the halogen was removed and the amine was smoothly methylated to give N,N-dimethylaniline. While this removal from the para position showed iodine to be more reactive than bromine in these reactions, chlorine was found to be far less reactive. Under these same conditions, the reductive alkylation of 2,4-dichloro-1,3-diaminobenzene produced the tetramethyl derivative, no chlorine having been removed by the amalgamated zinc and hydrochloric acid.

## Experimental

Reductive Alkylation of 2,6-Dibromo-4-iodoaniline.—After a mixture of 15 g. of 2,6-dibromo-4-iodoaniline.<sup>3</sup> 200

(1) Present address: Monsanto Chemical Co., Dayton, Ohio.

(2) (a) Emerson, Dorf and Deutschman, *THIS JOURNAL*, 62, 2159 (1940); (b) Emerson, Neumann and Moundres, *ibid.*, 63, 972 (1941)

(3) Sudborough and Lakhmalani, *J. Chem. Soc.*, 111, 41 (1917).

(1) Van Dam, *Rec. trav. chim.*, 15, 102 (1896).

(2) Von Braun and Lemke, *Ber.*, 55, 3526 (1922).