Tetrahedron Letters, No. 7, pp. 5-7, 1959. Pergamon Press Ltd. Printed in Great Britain.

THE PREPARATION OF N-DISUBSTITUTED FORMAMIDES

M. B. Frankel, Aerojet General Corporation Research Laboratories, Azusa, California and

H. Feuer and J. Bank, Dept. of Chemistry, Purdue University, Lafayette, Indiana

(Received 1 June 1959)

THE conversion of primary amines to isocyanides on treatment with chloroform and base is well known and is used qualitatively to distinguish between primary and secondary amines.[1] When diethylene triamine was heated with chloroform and base, the product was found to be void of a free secondary amino group, as evidenced from the infrared spectrum. Since a literature search revealed that the reaction between a secondary amine, chloroform and base had not been investigated, a study of this reaction was initiated. Our preliminary findings indicate that secondary amines are converted to substituted formamides under the conditions of the carbylamine reaction. On refluxing dibutylamine, diisobutylamine and diethylamine with chloroform in an aqueous methanolic sodium hydroxide solution, dibutylformamide, diisobutylformamide and diethylformamide were obtained in yields of 65,35 and 40%, respectively. These amides were

---

[1] J. Houben, Die Methoden der organischen Chemie Vol. 4, (3rd. Ed.) p. 587. Georg Thieme Verlag, Leipzig (1941).

identified by comparison of their physical constants with those reported in the literature.

Recently, Saunders and Murray[2] communicated a similar reaction in which secondary amines were converted to amides on treatment with chloroform and potassium t-butoxide in benzene. We are in agreement with these investigators on the course of the reaction, which might entail the following steps:

$$CHCl_3 \xrightarrow{OH^-} CCl_3^- + H_2O$$

$$CCl_3^- \longrightarrow CCl_2 + Cl^-$$

$$R_2NH + CCl_2 \longrightarrow R_2N^+HCCl_2^- \longrightarrow R_2NCHCl_2$$

$$R_2NCHCl_2 \xrightarrow{H_2O} R_2NCHO + 2HCl$$

The first two steps are well substantiated by the investigations of Hine.[3]

The following example typifies our reaction conditions:

To a solution of 129.2 g (1.0 mole) redistilled dibutylamine in 160 ml of chloroform was added a solution of 160 g (4.0 moles) of sodium hydroxide in 1 l. of methanol in 1.5 hr. The exothermic reaction caused the methanol to reflux and sodium chloride to precipitate. After the addition

---

[2] M. Saunders and R. W. Murray, *Tetrahedron* **6**, 88 (1959).

[3] J. Hine, *J. Amer. Chem. Soc.* **72**, 2438 (1950).

was complete, the reaction mixture was refluxed for 24 hr cooled and filtered. Concentrating the filtrate and distilling in vacuo gave 19.9 g (15.40%) unreacted dibutylamine and 102.0 g (65.1%) dibutylformamide, b.p. 63° at 0.1 mm; n_D^{25} 1.4419, (lit. value[4] n_D^{25} 1.4416).

Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 68,69; H, 12.13; N, 8.75.

---

[4] H. G. Mandel and A. J. Hill, J. Amer. Chem. Soc. **76**, 3978 (1954).