The Displacement of Ammonia from Benzylamine by Benzylamide Anion

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In the course of another investigation[1] largely reported earlier, ethyl 1-phenylpyrrolidine-2,5-dicarboxylate was heated with benzylamine in which sodium hydride had been dissolved. A red-purple color developed and, when the reaction mixture was worked up, a considerable quantity of a base hydrochloride sparingly soluble in water was isolated. This was identified as dibenzylamine hydrochloride. The same compound was isolated when sodium hydride was dissolved in benzylamine and the resulting solution was heated (initially to reflux). Liberation of ammonia was grossly observable.

The obvious interpretation of this reaction is as a displacement of amide anion by benzylamide anion in the sense

$$C_6H_5CH_2NH_2 + C_6H_5CH_2\bar{N}H \longrightarrow (C_6H_5CH_2)_2NH + \bar{N}H_2$$

Such a displacement has not previously been reported to our knowledge[2] although readily assimilated to current theories.

In order to determine the approximate requirements of the reaction, sodium hydride was dissolved in benzylamine while volatile base was swept out by nitrogen and collected for titration. As the temperature was raised, color became evident at about 50° and evolution of ammonia at about 65°. After 3.5 hr. at 85°, ammonia equivalent to 20% of the starting benzylamine had been collected. From the reaction mixture dibenzylamine hydrochloride equivalent to 75% of the evolved ammonia was obtained. Traces of other bases were present but were not investigated further.

Since in the above experiment oxygen was not rigidly excluded (an unknown volume of nitrogen of unknown purity had been employed) a second experiment was performed in a vessel previously evacuated and in which the pressure could be determined. The result was entirely comparable to that in the first experiment although the amount of oxygen that could have been present was insignificant (less than 10^{-6} mole).

Attempts to produce directed reactions using aniline and methylaniline with benzyldimethylamine (expecting the formation of benzylaniline or benzylmethylaniline with release of dimethylamine) were unsuccessful. These reactions evidently do not take place under conditions comparable to the benzylamine sodium hydride reaction.

Experimental

The apparatus consisted of a 100-ml. three-necked flask equipped with a gas inlet tube, dropping funnel, and condenser. The condenser was packed with glass wool and led through a gas inlet tube to another three-necked flask containing 100 ml. of distilled water colored with Methyl Red–Methylene Blue indicator and, initially, 0.6 cc. of 2.07 *N* hydrochloric acid. More acid was added to this receiving flask from a burette as required. The apparatus was flushed with nitrogen (passed over sulfuric acid) and 34 ml. (0.32 mole) of benzylamine was admitted. While the dropping funnel was replaced by a thermometer dipping into the liquid, 2 g. of 52% sodium hydride in mineral oil was added. There was an immediate transient evolution of gas but no color at this time. The temperature was raised by a heating mantle and nitrogen passed through in a gentle stream. The solution became pinkish at 47°, cherry red at 65°, and deep magenta at 77°. One milliliter of acid had been neutralized in the receiver after 30 min. at 75–77°. The temperature was raised to about 85° and maintained in the range of 83–88° for 3.5 hr., the evolved ammonia being titrated at intervals. The rate of evolution of ammonia rose to a maximum of 0.5 meq./min. after about 30 min. at 85° and then slowly diminished. A total of 26 ml. of the standard acid had been neutralized after 3.5 hr. At that point 10 ml. of water was added to the reaction mixture. This caused some evolution of gas and a 5° rise in temperature, while the color vanished. Sweeping with nitrogen was continued for an hour at the end of which time a total of 30.4 ml. of standard acid had been neutralized in the receiver. The reaction flask was then cooled and the contents partitioned between ether and water. The washed ethereal layers were dried over potassium carbonate and evaporated. After removal of benzylamine by distillation *in vacuo*, 14 g. of residual yellow oil remained. This was redissolved in ether and extracted with successive inadequate amounts of dilute hydrochloric acid. From the acid extracts a total of 11 g. of dibenzylamine hydrochloride was isolated and also 0.5 g. of benzylamine hydrochloride. The neutral fraction weighed 2.3 g. and had an odor of benzaldehyde.

A second experiment using the same quantities was performed in a flask initially containing the sodium hydride suspension and evacuated to 0.04-mm. pressure. On addition of the benzylamine, only a portion of the expected hydrogen was released (20%) and the rest was not evolved until the bath temperature reached 60°. At this point color appeared and further observations were virtually identical to those in the first experiment. The neutral portion of the reaction mixture, after removal of benzylamine and dibenzylamine, was found to contain 0.7 g. of benzaldehyde and about the same amount of toluene (identified as 2,4-dinitrotoluene). This latter could have been formed by debenzylative reduction during solution of the sodium hydride in benzylamine. The amount of aldehyde appears too small to be directly related to the main reaction product.

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(1) S. W. Blackman and R. Baltzly, *J. Org. Chem.*, **26**, 2750 (1961).

(2) *Cf.* W. Krabbe, G. Grünwald, E. Polzin, and W. Menzel, *Ber.*, **74**, 1343 (1941). These authors observed a "red" color in reactions of alkali metals and amides in ether with benzylamine. In one reaction they established the presence of ammonia but did not investigate other final products, principal interest being in the colors. These latter seem more characteristic of carbanions than of amide anions and may have no intimate connection with the reaction here reported.