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THE REDUCTION OF URETHANS WITH LITHIUM ALUMINUM HYDRIDE

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The reduction of urethans with lithium aluminum hydride has not been reported but appears to be a promising method of synthesis of amines of unusual structure. Successful reductions of amides of fatty acids to amines have already been obtained (1). The use of urethans is of interest from two standpoints: first, urethans can usually be prepared more easily than formamides as intermediates in the synthesis of methylamines; second, by reaction of alcohols with isocyanates it is possible to obtain the urethans (*e.g.* N-perfluoralkyl type) of amines which have never been isolated.

In some instances (2), the reaction of an amide with lithium aluminum hydride has led to appreciable cleavage to liberate the original amine. Since the reduction of a urethan may very well proceed through the formation of a formamide, both the reduction to the formamide and the following step of reduction to the amine might be susceptible to the cleavage reaction which then could become predominant.

Therefore, in the present work, several representative urethans have been treated with lithium aluminum hydride to determine whether reduction or cleavage would result. The results are shown in Table I. It was found that not only were excellent yields of the methylated amines obtained, but in addition, a complete absence of cleavage was observed. The purity of the amines was estabished from their infrared spectra.

EXPERIMENTAL PART

Typical preparation of a urethan. A mixture of 129 g. of di-*n*-butylamine, 150 ml. of ether, and 250 ml. of water was cooled to 5° and 108.7 g. of ethyl chloroformate slowly was added. After one-half of the chloroformate had been added, a cold solution of 40 g. of sodium hydroxide in 60 ml. of water was added simultaneously with the remainder of the chloroformate. The mixture was stirred for an additional hour at 5°, the ether layer decanted, and the aqueous solution extracted with two 50-ml. portions of ether. The combined ether solutions were dried with magnesium sulfate, the ether distilled at atmospheric pressure, and the product distilled *in vacuo*. The urethans of aniline and methylaniline were prepared in identical fashion. The urethan of diphenylamine was prepared by refluxing a mixture of diphenylamine and the ethyl chloroformate in benzene solution. The physical properties of the urethans are listed in Table II.

Preparation of pure amines. Pure samples of di-*n*-butylamine, aniline, methylaniline, and dimethylaniline were obtained by fractional distillation of the corresponding Eastman Kodak products. Diphenylamine, m.p. 54–55°, was obtained by recrystallization of the commercial material from Skellysolve C.

The N,N-di-*n*-butylmethylamine obtained by reduction of the corresponding urethan was converted to the *picrate* by refluxing with a saturated methanolic solution of picric acid. The picrate was recrystallized from methanol to the constant m.p. 87.5–88.5° [lit. (3) m.p. 86–87.5°]. The pure amine was recovered from the picrate by the method of Weiner and Kaye (4).

TABLE I

AMINES OBTAINED BY REDUCTION OF ETHYL CARBAMATES

Product	Boiling Point, °C.	Mm.	Refractive Index (20°)	Yield, %
Methyl-di-*n*-butylamine	156–157	757	1.4172	85
Methylaniline	112–114	60	1.5697	86
Dimethylaniline	76.7–77.9	13	1.5585	96
Methyl-diphenylamine	148–149	12	1.6621	80

TABLE II

PROPERTIES OF SUBSTITUTED ETHYL CARBAMATES

Substituents	Boiling Point, °C.	Mm.	Yield, %
N,N-Di-*n*-butyl	82–83	3	92
N-Phenyl	148–149	13.5	81
N-Methyl-N-phenyl	79–80	1	92
N,N-Diphenyl	m.p. 72–73		15

Typical reduction of a urethan with lithium aluminum hydride. A solution of lithium aluminum hydride was prepared by placing 28.5 g. of the commercial hydride in a Soxhlet apparatus and extracting for two days with 1000 ml. of dry ether. The flask then was fitted with a stirrer and a reflux condenser and 90 g. of the N-methyl-N-phenylurethan was added at a rate to maintain a vigorous ether reflux. The mixture was stirred for an additional hour, the excess of lithium aluminum hydride destroyed by adding wet ether, and the ether layer decanted from the inorganic gel. Strong sodium hydroxide was added to the inorganic gel and the mixture was steam-distilled. The distillate was extracted with two 100-ml. portions of ether, and these ether extracts were added to the previously decanted ether layer. The combined ether solutions were dried with magnesium sulfate, the ether was removed at atmospheric pressure, and the product, 58.2 g. (96%), was distilled *in vacuo*, b.p. 76.9–77.9° (13 mm.). Identical procedures were used with the other urethans with the results shown in Table I.

Purity of the methylamines from the urethans. The purities of the reduction products were established from the infrared absorption spectra. Measurements were made in a Perkin-Elmer model 12C spectrometer. In each case, at least one wave length was found at which the methylamine had an absorption peak while the unsubstituted amine showed practically no absorption characteristics. With three of the amines (there is no simple method of purification of methyldiphenylamine), the spectrum of the reduction product was compared with a synthetic mixture of 2% starting amine and 98% methyl homolog to get an estimate (Table III) of the maximum amount of unalkylated amine which could be present. The maximum figure shown actually represents, in each case, the limit of impurity detectable

TABLE III

DETERMINATION OF THE PURITY OF THE REDUCTION PRODUCTS

Amine Mixture	Wave Length at Which Purity Was Established	Maximum % of Unsubstituted Amine
Aniline and methylaniline	3.05 μ	1
Methylaniline and dimethylaniline	2.94 μ	2
Dibutylamine and di-*n*-butyl-methylamine	8.80 μ	1
Diphenylamine and methyldiphenylamine	2.95 μ	—

by the analytical method. No positive evidence for the presence of the unalkylated amine was obtained. Comparison of the spectrum of the methyldiphenylamine with that of pure diphenylamine indicated a similar purity of 98% or better.

The commercial method of analysis (5) for methylaniline in dimethylaniline indicated less than 0.5 per cent of methylaniline in the product.

The N-methyldiphenylamine was converted to a crystalline compound by treatment with zinc chloride and hydrochloric acid (6). When the amine was regenerated by treatment with H_2O, the infrared spectra of the original sample and the regenerated material were found to be identical. This indicates a pure sample, but as diphenylamine also gives a derivative with the the same reagent, the purity of this amine was not as well established as the purities of the other reference materials in this work.

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SUMMARY

The reduction of urethans with lithium aluminum hydride is an excellent method of synthesis of methylamines in yields of 80% or better. No evidence of unalkylated amine could be found in the reduction products.

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REFERENCES

(1) BROWN, *Org. Reactions*, **6**, 479 (1951).
(2) NYSTROM AND BROWN, *J. Am. Chem. Soc.*, **70**, 3738 (1948).
(3) EMERSON AND URANECK, *J. Am. Chem. Soc.*, **63**, 749 (1941).
(4) WEINER AND KAYE, *J. Org. Chem.*, **14**, 868 (1949).
(5) DAVIS, *Allen's Commercial Organic Analysis*, Fifth Edition, P. Blakiston's Son and Co., Philadelphia, 1927, Volume 5, p. 581.
(6) CRAIG, *J. Am. Chem. Soc.*, **55**, 3723, (1933).