ing, from the cuprammonium viscosity data for both the mercaptalated and non-mercaptalated hydrolyzed celluloses, were in good agreement throughout with those calculated from the sulfur analytical data, except for the very early stages of the hydrolysis, wherein the sulfur data gave lower results.

4. The mercaptalated hydrolyzed celluloses showed a low copper number, varying from 1.8 to 5.5. The copper numbers of the non-mercaptalated hydrolyzed celluloses varied from 5.0 to 28.4. The copper number ratios for these two series of products showed an apparent regularity.

5. A determination has been made of the viscosity changes taking place at 16° in a 5% cellulose solution in fuming hydrochloric acid with increasing time of hydrolysis.

COLUMBUS, OHIO RECEIVED JANUARY 22, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE CITY COLLEGE, COLLEGE OF THE CITY OF NEW YORK]

Alkanolamines. IV. Reducing Properties of the Amino Alcohols

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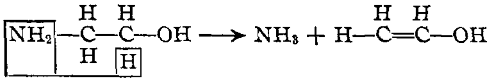
The ability of the ethanolamines to reduce organic compounds and aqueous solutions of silver, lead and mercury salts, has been the subject of recent investigations.[1,2] It was thought of interest to determine the ability of other amino alcohols to act as reducing agents and to compare their action with that of the ethanol compounds. A list of the alcohols studied may be obtained by reference to Tables I and II. In addition to these, pentanolamine, diethylaminoethyl alcohol and the cyclic amines morpholine and phenylmorpholine were investigated.

While it has been proposed[1] that in these reactions the amino alcohol is decomposed into ammonia and an aldehyde, no mechanism for such a decomposition has been given. The presence of ammonia in many of these reactions is detected readily. The decomposition may very well parallel that of the esters of amino acids wherein ammonia is liberated and an unsaturated, nitrogen-free compound results. Accordingly, we would have for monoethanolamine



$$\boxed{NH_2}-\underset{H}{\overset{H}{C}}-\underset{\boxed{H}}{\overset{H}{C}}-OH \longrightarrow NH_3 + H-\overset{H}{C}=\overset{H}{C}-OH$$

Ammonia and acetaldehyde (enol form) are here seen to be the end-products. The mechanism appears plausible and the presence of aldehyde has been proved.

The fact that morpholine reduces aqueous solutions of certain metal salts to a slight degree, led to the carrying out of a series of reactions with this material, and also with phenylmorpholine. In all cases studied the morpholines failed to effect reduction of organic compounds.

An interesting observation was made in comparing the reducing ability of alcohols containing a tertiary amine group. Whereas triethanolamine, as well as triisopropanolamine, proved to be good reducing agents, diethylaminoethyl alcohol was extremely weak in action. More interesting, was the fact that the latter compound reduced solely to the azoxy state, a result not duplicated by any other amino alcohol studied.

All of the reductions were carried out upon either nitrobenzene or *m*-chloronitrobenzene; both in the presence and absence of added alkali. Alkalinity of medium, length of heating, temperature of refluxing and the molar ratio of the reactants materially affect the yields and nature of the end-products.

TABLE I

Amino alcohol	Yield of reduction products, % 3,3'-Dichloroazobenzene	*m*-Chloroaniline
Monoethanolamine	30–40	60–70
Monopropanolamine	15–18	30–35
Monoisopropanolamine	20–25	60–70
Monoisobutanolamine	12–14	20–22

TABLE II

Amino alcohol	NaOH	Approximate yield, % Azobenzene	Aniline
Monoethanolamine	None	10	12
Diethanolamine	None	27	10
Diethanolamine	5 g.	50	5
Triethanolamine	None	10	7
Triethanolamine	5 g.	55	Trace
Monoisopropanolamine	None	20	25
Monoisopropanolamine	5 g.	60	Trace
Diisopropanolamine	None	25	Trace
Triisopropanolamine	None	12	5
Monopropanolamine	None	5	Trace
Monoisobutanolamine	None	Trace	Trace

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[1] M. Meltsner, C. Wohlberg and M. J. Kleiner, THIS JOURNAL, **57**, 2554 (1935).

[2] M. Meltsner, L. Greenstein, G. Gross and M. Cohen, *ibid.*, **59**, 2660 (1937).

Table I gives a comparison of the products and yields obtained in the reduction of *m*-chloronitrobenzene with certain of the amino alcohols in the presence of anhydrous sodium carbonate.

Table II summarizes some of the results obtained in the reduction of nitrobenzene.

Experimental

Reduction of *m*-Chloronitrobenzene with Monopropanolamine.—One-sixth mole of *m*-chloronitrobenzene was mixed with one-third mole of anhydrous sodium carbonate in a 3-necked round-bottomed flask, fitted with mechanical stirrer, reflux condenser and dropping funnel. The mixture was heated with a small flame until the chloronitrobenzene had melted completely. Stirring was then started and one-sixth mole of monopropanolamine gradually added through the dropping funnel. The mixture was then heated with a small flame for approximately six hours.

After completion of reaction, the flask contents were steam distilled until distillate came over clear. The distillate was made acid with hydrochloric acid and extracted with ether (ethyl) to remove unreacted chloronitrobenzene. It was then made alkaline with sodium hydroxide; whereupon a light colored oil separated out and the whole was extracted with ether and the extract dried over sodium hydroxide pellets. Upon removal of the ether and fractionation of residue, a light orange liquid boiling at 229–231° was obtained. Conversion to the hydrochloride completed the identification of *m*-chloroaniline; yield 35%.

The residue in the steam distillation flask was treated with strong hydrochloric acid to decompose the excess carbonate and filtered. The solid residue was extracted with hot benzene and the extract evaporated to dryness, yielding a mass of dark red, impure crystals. Upon recrystallization from ethyl alcohol, light orange crystals melting at 101° were obtained. This corresponds to the azo compound. A mixed melting point with an authentic sample of 3,3′-dichloroazobenzene showed no depression; yield about 15%.

Reduction of Nitrobenzene with Monoisopropanolamine.—Three moles of the amino alcohol were mixed with one mole of nitrobenzene and the mixture refluxed in an oil-bath at 180° for five hours. The mixture was then steam distilled. An oil and a light red solid collect in the distillate. The solid was filtered off and upon examination proved to be azobenzene; yield 20%. The filtrate was treated as described for the steam distillate in the experiment above. A colorless oil boiling at 185° was finally obtained. Conversion to the hydrochloride completed its identification as aniline; yield 25%.

Discussion

From the results of these experiments, it appears that the reducing ability of an amino alcohol depends upon the relative positions of the amino and hydroxyl groups. When these groups are separated by two carbon atoms, the alcohol exhibits the greatest reducing power. Thus the ethanolamines and isopropanolamines are the best reducing agents among those amino alcohols thus far studied. This ability is diminished markedly with propanolamine where the hydroxyl and amino groups are separated by three carbon atoms, and this diminished activity is even more marked with pentanolamine.[3] It is of interest to note here, that fatty aromatic amines have been shown to exhibit greatest physiological activity when the phenyl and amine groups are also separated by two carbon atoms and this activity diminishes as the distance between the two groups increases.[4]

When the reductions were carried out in the presence of anhydrous sodium carbonate, dehydration of the amino alcohol also occurred. Upon steam distillation of the reaction mixtures, typical imine odors were evident and it was possible, in certain of the experiments with monoethanolamine, to isolate a small amount of ethyl imine. With pentanolamine, ring closure was effected quite readily and all reductions involving this amino alcohol were characterized by the odor of piperidine.

Inspection of Table II reveals that when nitrobenzene was reduced in the presence of sodium hydroxide, the yield of azo compound was materially increased, while the yield of aniline, in most cases, was reduced sharply.

Summary

1. A study of the reducing ability of a number of amino alcohols has been effected.

2. When the amino and hydroxyl groups are separated by two carbon atoms, the reducing ability appears to be greatest.

3. Decomposition of the alcohol into ammonia and an aldehyde occurs during reduction.

4. In certain instances, ring closure, through dehydration, takes place when reduction is carried out in the presence of anhydrous sodium carbonate.

5. Diethyl aminoethyl alcohol reduces solely to the azoxy state.

6. Morpholines do not reduce organic compounds.

NEW YORK, N. Y. RECEIVED MARCH 7, 1938

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[3] Monoisobutanolamine appears to be an exception to this generalization, but other factors may be involved here, *e. g.*, alkalinity.

[4] Barger and Dale, *J. Physiol.*, **41**, 19 (1910).