When alternatively the Henry solution was added to the nitrous acid solution, the yield was decreased to 22%, m. p. 202°.

Summary

1. The system formaldehyde–ammonia has been re-examined. The results agree with those of Duden and Scharf, and designate cyclotrimethylenetriamine as the intermediate in the eventual formation of hexamine.

2. The formaldehyde–ammonia solution prepared by Henry is found essentially to behave as cyclotrimethylenetriamine and not as trimethylolamine, which he suggested.

3. The final stages of the hexamine synthesis from cyclotrimethylenetriamine are non-reversible in alkaline solution.


[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Hydrogenolysis of Alkyl Halides by Lithium Aluminum Hydride[1]

BY J. ENOCH JOHNSON, RONALD H. BLIZZARD AND HOMER W. CARHART

Lithium aluminum hydride is an excellent reducing agent for many types of organic compounds.[2,3] It has also been used successfully for the determination of active hydrogen.[4] The reactions using this reagent are ordinarily carried out conveniently in ethyl ether solution and usually proceed rapidly and to completion. The reaction of lithium aluminum hydride with alkyl halides is more sluggish and in some instances does not occur in a reasonable time in refluxing ethyl ether. This difficulty may be overcome by the use of solvents such as tetrahydrofuran which permit the employment of higher temperatures. The reactions have been further accelerated and yields improved by a new procedure using lithium hydride which also greatly decreases the amount of lithium aluminum hydride necessary to complete the reaction.

Experimental results indicate that not all four hydrogen atoms show the same reactivity toward alkyl halides, and that the reaction probably proceeds in at least two steps, as represented by the equations

$$LiAlH_4 + RX \longrightarrow RH + LiX + AlH_3$$
$$AlH_3 + 3RX \longrightarrow AlX_3 + 3RH$$
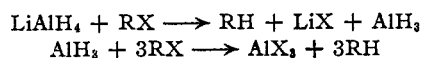
Of these steps, the first is presumed to be much more rapid than the second.

As may be seen from the data in Table I, when the molar ratio of reagent to the more active halides was greater than one the reactions proceeded rapidly and to completion. When the ratio was approximately 0.25 (the calculated value to replace all four hydrogens), the reactions were sluggish. The stepwise course of the reaction would account for the fact that more than one hydrogen per mole of reagent is consumed and that all four hydrogens are not replaced in a reasonable time.

Since aluminum hydride reacts with lithium hydride in ether to produce lithium aluminum hy-

dride,[5] it was considered reasonable that alkyl halides could be hydrogenated by means of lithium hydride with only a small amount of lithium aluminum hydride present. This hydrogenolysis was found to proceed rapidly and to completion. Under these conditions the reaction may be represented as

$$RX + LiH \xrightarrow{\text{LiAlH}_4} RH + LiX$$

It is evident that lithium aluminum hydride acts as a hydrogen carrier, as shown by the fact that no reaction was found to occur with lithium hydride alone. The use of lithium hydride greatly reduces the amount of lithium aluminum hydride necessary and minimizes the possibility of the formation of aluminum halide.

In general, it was found that alkyl bromides react more readily than alkyl chlorides with lithium aluminum hydride. Primary halides react more readily than secondary halides which in turn are more reactive than tertiary halides. Alicyclic and aromatic halides proved very unreactive.

The reaction of 1,2-dibromoöctane with lithium aluminum hydride to give a moderate amount of olefin was surprising, since, with the exception of a trace of olefin in the reaction product of bromocyclohexane, olefins were not observed in the reaction products of the other alkyl halides. No attempt was made to identify this olefin.

Experimental

In order to accelerate the reaction of lithium aluminum hydride with alkyl halides, it was necessary to use temperatures higher than that of refluxing ethyl ether. This temperature should be kept below 100°, the incipient decomposition point of the reagent. Tetrahydrofuran was found to be an excellent reaction medium because it is a good solvent for the reagent,[2] it is miscible with water and has a desirable boiling point. Diisopropyl ether, although having the proper boiling point, was found to be a poor solvent for the reagent. Di-n-butyl ether, in which the reagent is suitably soluble, requires an externally controlled temperature for the reaction, and in one instance of its use, there was a sudden rise in temperature of the reaction mixture with consequent decomposition of reagent.

The following serves as an example of the method used.

(1) The opinions contained herein are the authors' and are not to be construed as official or reflecting the views of the Department of the Navy.

(2) Finholt, Bond and Schlesinger, THIS JOURNAL, 69, 1199 (1947).

(3) Nystrom and Brown, ibid., 69, 1197, 2548 (1947).

(4) Krynitsky, Johnson and Carhart, ibid., 70, 486 (1948).

(5) H. I. Schlesinger, from an unpublished report to the Naval Research Laboratory.

TABLE I

Compound	Solvent	Reflux, hr.	Moles LiAlH₄/ Mole RX	Moles LiH/ Mole RX	Product	Yield, %
1-Bromoöctane	Et₂O	1	0.25	2.0	n-Octane	40
1-Bromoöctane	Et₂O	3	.25	2.0	n-Octane	72
1-Bromoöctane	Bu₂O	1ᵃ	.28	0	n-Octane	32
1-Bromoöctane	Bu₂O	3ᵃ	.28	0	n-Octane	64
1-Bromoöctane	THFᵇ	0.5	.13	1.5	n-Octane	96
1-Bromoöctane	THF	1	.03	1.5	n-Octane	95
1-Bromoöctane	THF	1	.36	0	n-Octane	61
1-Bromoöctane	THF	1	.8	0	n-Octane	96
1-Bromoöctane	THF	2	0	1.5	.....	0
1-Chlorododecane	THF	2.5	.8	0	n-Dodecane	80
1-Chlorododecane	THF	5	.8	0	n-Dodecane	86
1-Chlorododecane	THF	0.5	1.25	0	n-Dodecane	98
3-(Bromomethyl)-heptane	THF	1	0.25	2.0	3-Methylheptane	98
3-(Chloromethyl)-heptane	THF	1	.17	2.0	3-Methylheptane	52
3-(Chloromethyl)-heptane	THF	3	.4	3.0	3-Methylheptane	96
3-(Chloromethyl)-heptane	Et₂O	3	.25	2.0	.....	0
Benzyl chloride	THF	1	.13	1.5	Toluene	98
2-Bromoheptane	THF	1	.8	0	n-Heptane	76
2-Bromoheptane	THF	1	.13	1.5	n-Heptane	92
Bromocyclohexane	THF	1	1.25	0	Cyclohexaneᶜ	10
Chlorocyclohexane	THF	1	0.13	1.5	.....	0
5-Chloro-5-n-butylnonane	THF	1	.4	3.0	.....	0
p-Bromotoluene	THF	1	.25	1.75	Toluene	4
p-Bromotoluene	THF	3	.25	2.0	Toluene	14
1,2-Dibromoöctane	THF	1	.25	3.0	n-Octaneᵈ	80

ᵃ Reaction maintained at 85°.   ᵇ Tetrahydrofuran.   ᶜ Contained a trace of olefin.   ᵈ In addition to the n-octane the reaction product contained 14% olefin calculated as octene.

Variations in conditions from this procedure are given in Table I. In all cases, from 0.3 to 1.0 mole of alkyl halide was used.

Hydrogenolysis of 1-Bromoöctane.—A mixture of 0.13 mole (5 g.) of lithium aluminum hydride[6] and 1.5 moles (12 g.) of lithium hydride (100 mesh) was placed in a one-liter three-necked flask equipped with a Hershberg stirrer and a reflux condenser fitted with a calcium chloride tube. A thermometer was inserted through the center stopper parallel to the stirrer shaft. The flask was cooled and 300 ml. of tetrahydrofuran was added, with stirring. The solution was heated to reflux. One mole (193 g.) of 1-bromoöctane was added dropwise from a dropping funnel at such a rate as to maintain moderate reflux without external heating (approximately forty-five minutes). The mixture was refluxed for another hour, then cooled to 10°. A mixture of approximately 100 ml. of tetrahydrofuran/water, 60/40 by volume, was added very cautiously with stirring, keeping the temperature below 20°. The mixture was transferred slowly with stirring into a two-liter beaker containing 80 ml. of sulfuric acid in ice and water. The product layer was separated, washed twice with one-liter portions of water, dried over anhydrous potassium carbonate

and distilled through a 60-plate Stedman column. A 96% yield of n-octane, b. p. 125° (uncor.), n^{20}D 1.3975, was obtained.

In some cases, e.g., 3-(chloromethyl)-heptane, it was necessary to continue heating throughout the addition of the alkyl halide in order to maintain a steady reflux. In the case of the normal paraffins it was found possible to eliminate the distillation procedure by means of several additional water washes followed by washing with cold concentrated sulfuric acid.

Summary

The hydrogenolysis of several alkyl halides by lithium aluminum hydride has been accomplished by use of more stringent conditions than required for reduction of many organic compounds with this reagent. This hydrogenolysis may be carried out by means of lithium hydride with a small amount of lithium aluminum hydride as the hydrogen carrier.

(6) From Metal Hydrides, Inc., Beverly, Mass.