[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, GONZAGA UNIVERSITY AND ST. PROCOPIUS COLLEGE]

Catalytic Behavior of 2-Amino-2-methyl-1-propanol Vapor over Alumina[1]

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When 2-amino-2-methyl-1-propanol vapor was passed through alumina at 300° the products formed, namely, ammonia, isobutyleneimine, isobutylidene, isobutylamine, diisobutylamine and 2,2,5,5-tetramethyl-3,6-dihydroxypiperazine indicate that under these experimental conditions deamination, amination, dehydrogenation and hydrogenation occur as well as dehydration.

Introduction

The amino alcohols have gained industrial prominence within the last few years, especially as emulsifying agents, corrosion inhibitors and intermediates in organic synthesis. One of the most versatile of these is 2-amino-2-methyl-1-propanol which was synthesized by Hass and Vanderbilt[3] and later made commercially available with the development of an industrially feasible process.[4]

We wish to report the unique behavior of this compound under catalytic dehydrating conditions. When 2-amino-2-methyl-1-propanol (I) vapor was passed over alumina at 300°, both ammonia and water were obtained along with isobutyleneimine (IV), diisobutylamine (VII) and a crystalline solid $C_8H_{18}O_2N_2$ which appears to be the dimer of α-aminoisobutyraldehyde, namely, 2,2,5,5-tetramethyl-3,6-dihydroxypiperazine (IX). The imine (IV), undoubtedly formed by deamination through the intermediate isobutyraldehyde, was identified by catalytic hydrogenation to isobutylamine (V) and hydrolysis to isobutyraldehyde. The imine (IV) was also probably hydrogenated in the alumina tower to isobutylamine (V), the hydrogen being supplied from the dehydrogenation of I to VIII and condensation of the amine (V) and imine (IV) or aldehyde (III) would result in the formation of isobutylidene isobutylamine (VI), which could then be further hydrogenated to diisobutylamine (VII). In several experiments which resulted in a very low yield of diisobutylamine a substance corresponding in physical properties and analyses to VI was obtained. This lends support to the above mechanism. Apparently, dehydration, deamination, amination, hydrogenation, and dehydrogenation take place simultaneously on the alumina column under these experimental conditions. The reactions are portrayed in Fig. 1.

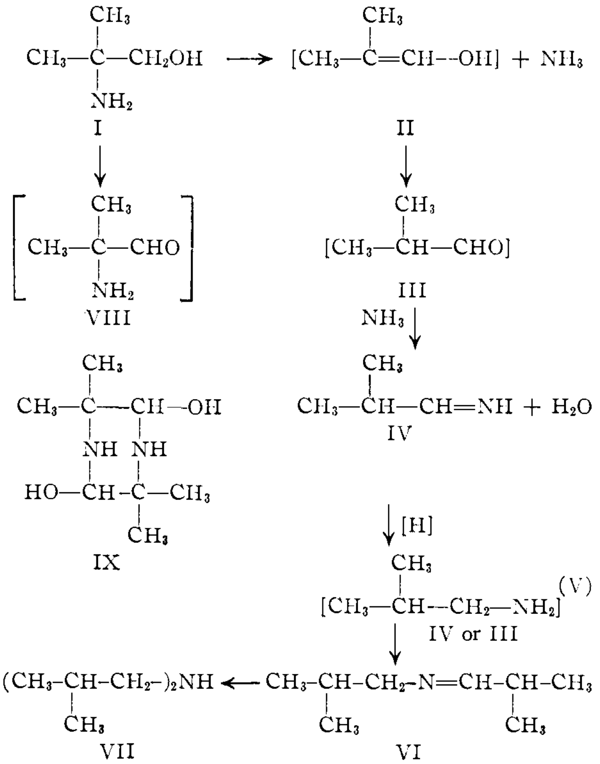

Fig. 1.

Experimental

2-Amino-2-methyl-1-propanol.—A quantity of this substance was generously supplied by the Commercial Solvents Corporation. It was further purified by distillation and fractional freezing. Material with a b.p. range of 164–166° was used throughout.

Apparatus and Procedure.—The dehydration apparatus was similar to those described previously,[5] but with a column (2.2 × 100 cm.) packed with activated alumina.[6] A temperature of 300° was maintained by electrical heating and measured with an iron-constantan resistance thermometer. The vapors from the reaction chamber were passed through a condenser and collected in a distilling flask. Gaseous products were collected in a dilute hydrochloric acid trap followed by one containing aqueous sodium hydroxide.

The amino alcohol was distilled directly into the reaction chamber. In a typical experiment 500 g. of material was passed over alumina at 300° over a period of 10 hours. The condensate amounted to 350 g. of "imine" layer along with 100 ml. of an aqueous ammoniacal layer. Separation into the constituent fractions was effected by fractional distillation in a packed column rated at 10 theoretical plates at total reflux. The products are listed in Table I.

TABLE I

PRODUCTS FROM THE REACTION OF 2-AMINO-2-METHYL-1-PROPANOL VAPOR (500 G.) OVER ALUMINA AT 300°

Fraction	Principal constituent	Wt., g.	Physical constants "best" sample B.p., °C.	$n^{20}D$
1	Isobutyleneimine	135	78–80	1.4020
2	Isobutylideneisobutylamine	50	129	1.4134
3	Diisobutylamine	43	142	
4	2,2,5,5-Tetramethyl-3,6-dihydroxypiperazine	11	Solid, m.p. 86°	

Identification of Fraction 1.—The first fraction was identified as isobutyleneimine by hydrolysis to isobutyraldehyde and catalytic hydrogenation to isobutylamine.

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[1] A portion of this work was abstracted from the M.S. thesis of D. M. Clarke to the Graduate School of Gonzaga University.

[2] Blockson Chemical Co., Joliet, Ill.

[3] H. Hass and B. Vanderbilt, U. S. Patent 2,139,122 (1938).

[4] M. Senkus, U. S. Patent 2,363,465 (1944).

[5] V. I. Komarewsky and J. T. Stringer, THIS JOURNAL, **63**, 921 (1941); L. Berg, G. L. Sumner, Jr., and C. W. Montgomery, *Ind. Eng. Chem.*, **38**, 734 (1946).

[6] Alcoa grade F-10 (8–14 mesh) generously supplied by the Aluminum Company of America.

To one gram of the imine in 2 ml. of water was added one drop of 10% hydrochloric acid followed by an acidified solution of 2,4-dinitrophenylhydrazine in methanol. The precipitate of isobutyraldehyde 2,4-dinitrophenylhydrazone was purified by recrystallization from chloroform and gave m.p. 179°. The recorded[7] m.p. for this derivative is 182°.

Isobutyleneimine (43.5 g., 0.61 mole) containing 4.4 g. of nickel catalyst (U.O.P.) was hydrogenated in a glass insert tube in a rocker type bomb at 130° and 800 p.s.i. showing a total consumption of 0.65 mole of hydrogen. After cooling, the material was filtered and fractionated in a packed column to give 38 g. (85%) of isobutylamine, b.p. 70°, $n^{20}\text{D}$ 1.3970 and $d^{24}{}_4$ 0.7343. The accepted[8] constants for isobutylamine are b.p. 69°, $n^{17}\text{D}$ 1.3988 and $d^{25}{}_4$ 0.724.

One gram of the isobutylamine was treated with benzenesulfonyl chloride and the resultant sulfonamide gave a melting point of 54°. The recorded[9] m.p. for N-isobutylbenzenesulfonamide is 53°.

Identification of Fraction 2.—In several experiments, in which a low yield of diisobutylamine was realized, a fraction boiling at 129° was obtained. Since it showed evidence of unsaturation and gave analyses corresponding to $C_8H_{17}N$ it was tentatively assumed to be isobutylideneisobutylamine (VI). This was further confirmed from the boiling point (129°) and refractive index ($n^{20}\text{D}$ 1.4134), which correspond favorably with the literature values of b.p. 130–131°[10] and $n^{21.5}\text{D}$ 1.4135[11] for VI.

Anal. Calcd. for $C_8H_{17}N$: C, 75.60; H, 13.47; N, 11.01. Found: C, 75.46; H, 13.68; N, 11.20.

Identification of Fraction 3.—The yellow oil boiling at 142°, which did not show evidence of unsaturation was identified as diisobutylamine from its derivatives, namely, the benzenesulfonamide, m.p. 55°, phenylthiourea, m.p. 114° and the oxalate, m.p. 244°. The literature[12] values for the melting points of these three derivatives are 55°,[9] 113°[9] and 245–248°,[12] respectively. The boiling point of diisobutylamine is listed as 139°.[9]

Isolation of 2,2,5,5-Tetramethyl-3,6-dihydroxypiperazine (IX).—From the higher boiling fractions, 150–180°, 11 g. of a white crystalline substance separated upon standing and was purified by washing with benzene. It gave a melting point of 86°, was miscible with alkalies, sparingly soluble in water and evolved a gas, presumably carbon monoxide, with dilute acids. The substance did not react with benzenesulfonyl chloride nor show evidence of unsaturation with bromine. Since it gave molecular weight values (Rast) between 180–200 and analyses corresponding to $C_8H_{18}O_2N_2$, the substance appears to be the dimer of the amino aldehyde, 2-amino-2-methyl-1-propanal, 2,2,5,5-tetramethyl-3,6-dihydroxypiperazine (IX).

Anal. Calcd. for $C_8H_{18}O_2N_2$: C, 55.14; H, 10.41. Found: C, 55.10; H, 10.46.

Identification of Ammonia.—The hydrochloric acid solution in the first trap was treated with an excess of sodium hydroxide, a benzenesulfonamide, m.p. 154–155°, and a phenylthiourea, m.p. 149°, were prepared from the ammoniacal smelling gas. The literature melting point values for benzenesulfonamide, 153°,[13] and phenyl thiourea, 154°,[14] indicated that ammonia was the sole gaseous product of the reaction. No gaseous products were detected in the alkali trap.

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(8) I. M. Heilbron and B. M. Bunbury, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1936, p. 412.

(9) Reference 7, p. 234.

(10) M. A. Berg, *Bull. soc. chim.* (*Paris*), [3] **7**, 545 (1892).

(11) M. Delépine, *Ann. chim. phys.*, [8] **25**, 559 (1912).

(12) Reference 8, Vol. 1, p. 553.

(13) Reference 7, p. 232.

(14) Reference 8, Vol. 3, p. 461.

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Restricted Rotation About the Aliphatic Carbon–Carbon Bond

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Ethyl triphenylcarbinyl ketone, ethyl and methyl diphenyl-*o*-tolylcarbinyl ketone and ethyl and methyl phenyl-di-*o*-tolylcarbinyl ketone were prepared. All except the methyl diphenyl-*o*-tolylcarbinyl ketone were synthesized through intermediate triarylcarbinols, triarylchloromethanes, triarylacetic acids and triarylacetyl chlorides. By the action of ethylmagnesium bromide and carbon dioxide, the ethyl and methyl diphenyl-di-*o*-tolylcarbinyl ketones were converted to α-methyl-β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid and β-keto-γ-phenyl-γ,γ-di-*o*-tolylbutyric acid, respectively. The former by the action of phosphorus pentachloride did not yield the corresponding β-chlorocrotonic acid, but instead the β-keto acid chloride. Diazomethane and this acid resulted merely in esterification to the β-keto acid ester.

The concept of restricted rotation has been effectively demonstrated by chemical resolution of properly substituted biphenyls,[2] aryl olefins[3] and aryl amines.[4] To date, however, the only evidence for restricted rotation about the aliphatic carbon–carbon bond has been furnished by thermodynamic data[5] and by physical data on dipole moments,[6] X-ray spectra,[7] Raman spectra,[8] and electron diffraction.[9]

As a logical extension from the biphenyls I, in which the hindrance centers about an aromatic–aromatic bond, and the aryl olefins II, in which the hindrance centers about an aromatic-aliphatic bond, it did not appear impossible that certain triarylcarbinyl III-a and trialkylcarbinyl III-b olefins might be resolvable because of the restriction of rotation about the aliphatic–aliphatic single bond attached to bulky tertiary groups.

Although the structure IIIa contains aromatic groups, the β,γ-pivotal bond is not attached to an

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(1) Allied Chemical and Dye Corporation Fellow, 1941–1943. Part of the experimental work on the diphenyl-*o*-tolyl derivatives and all of the work on the di-*o*-tolylphenyl derivatives was performed by R. S. Voris in partial fulfillment of requirements for the Degree of Doctor of Philosophy, 1943.

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(3) (a) H. Gilman, "Organic Chemistry," Vol. I, John Wiley and Sons, Inc., New York, N. Y., Second Edition, 1943, p. 377; (b) R. Adams and J. W. Mecorney, THIS JOURNAL, **67**, 798 (1945).

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(7) J. D. McCullough, *ibid.*, **62**, 480 (1940).

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(9) Y. Morino and M. Iwasaki, *J. Chem. Phys.*, **17**, 216 (1949).