ments, 97% of the α protons had been exchanged for deuterium, as determined by nmr spectroscopy.

1,5-Pentanediol-2,2,4,4-d_4 was obtained in 75% yield by the reduction of labeled dimethyl glutarate with lithium aluminum hydride (1.3 moles per mole of ester) followed by hydrolysis with 5% sodium hydroxide. The deuterium content was found by nmr spectroscopy to be 95%.

1,5-Dibromopentane-2,2,4,4-d_4.—Phosphorus tribromide (3 g per gram of diol) was placed in a three-necked flask equipped with a condenser and a dropping funnel. The labeled diol was added dropwise, and the resulting solution was heated on a steam bath overnight. Water (1 ml per gram of diol) was added, and the layers were separated. The aqueous layer was extracted four times with methylene chloride, and the combined organic portions were neutralized with aqueous sodium carbonate. 1,5-Dibromopentane-2,2,4,4-d_4 (87%) was isolated by distillation at reduced pressure. No loss of deuterium occurred during these manipulations.

Thiane-3,3,5,5-d_4.—To a refluxing solution of 2.0 g of sodium sulfide nonahydrate in 25 ml of 50% ethanol were added 2.3 g of 1,5-dibromopentane-2,2,4,4-d_4 and, simultaneously but separately, an additional 2.0 g of sodium sulfide in 25 ml of 50% ethanol. After the solution had refluxed for 2 hr, the ethanol was removed by careful distillation and the residue was steam distilled. The aqueous distillate was extracted with methylene chloride, and thiane-3,3,5,5-d_4 was obtained upon evaporation of the solvent.

Thiane-3,3,5,5-d_4 1-Oxide.—A mixture of 0.29 g of the deuterated sulfide and 0.32 g of 30% hydrogen peroxide was shaken in a sealed tube until only one layer was present. After standing overnight, the solution was extracted three times with methylene chloride. The combined organic portions were dried with magnesium sulfate. The crystalline sulfoxide that was obtained after removal of the drying agent and the solvent under anhydrous conditions possessed the characteristic band at 1020–1060 cm^{-1}. Sulfone bands were absent. Pentamethylene-3,3,5,5-d_4 sulfone could be obtained by the same method, with the use of 0.64 g of hydrogen peroxide. These products were identical with the known, unlabeled compounds.

Acknowledgments.—We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant 487-G1), and to the National Science Foundation for support for this work. We are indebted to Dr. J. T. Gerig for furnishing a copy of his program for the analysis of the exchange of two AB systems.

Thermal Decomposition of Quaternary Ammonium Hydroxides. Synthesis and Properties of Tri($^{2}H_{3}$-methyl)amine

JOHN TANAKA,[1a] JAMES E. DUNNING,[1b] AND JAMES C. CARTER

Department of Chemistry, University of Pittsburgh,
Pittsburgh, Pennsylvania

Received February 7, 1966

Completely deuterated trimethylamine was desired for infrared studies on boron hydride–amine adducts. One general synthesis for tertiary amines involves thermal decomposition of quaternary ammonium hydroxides. For example pyrolysis of ethyltrimethylammonium hydroxide yields ethylene and trimethylamine. If the methyl groups are deuterated, it would seem that deuterated trimethylamine could be synthesized by this route. However, both Shiner and Smith[2] and Cope, LeBel, Moore, and Moore[3] have shown hydrogens on α carbons to undergo exchange. The elimination, however, was shown not to proceed by way of a *cis*-ylide mechanism. An E2 elimination of the *trans* hydrogen on the β carbon was established as the mechanism of choice for most compounds undergoing the Hofmann elimination. Cope, *et al.*, clearly demonstrated that exchange of the α protons occurs with the water "pool" prior to elimination. In showing this Cope and co-workers were unable to parallel the results obtained by Weygand, Daniel, and Simon[4] on the exchange of tritium during the pyrolysis of β-tritiated ethyltrimethylammonium hydroxide carried out by blowing high-velocity steam through the melt. Doering and Hoffmann[5] found that tetramethylammonium deuterioxide in deuterium oxide solution is enriched only to the extent of 1.13 atom % deuterium in 358 hr at 100°. Because of this slow exchange rate and the relatively low vacuum generally used for Hofmann eliminations (6 mm by Cope, *et al.*), it seemed reasonable to try the elimination under high-vacuum conditions with the hope that the water "pool" can be reduced to a sufficiently low level to eliminate exchange.

Another route more certain of success is the pyrolysis of completely deuterated tetramethylammonium deuterioxide. As Musker[6] has recently reported, this reaction yields trimethylamine and dimethyl ether as the two major products. It should be noted that Hofmann[7] originally reported trimethylamine and methyl alcohol as products of this reaction. An additional possibility is that tetramethylammonium deuterioxide might lend itself to direct deuteration in case the deuterium exchange reaction studied by Doering exhibits a very favorable anti-Arrhenius temperature dependence.

Results and Discussion

Pyrolysis of ethyltri($^{2}H_{3}$-methyl)ammonium deuterioxide under high vacuum yields tri($^{2}H_{3}$-methyl)amine and ethylene. When the methyl groups of the original quaternary ammonium salt were 97% deuterated, the trimethylamine obtained contained 94% deuterium. Pyrolysis of the quaternary ammonium hydroxide instead of the deuteroxide yielded trimethylamine containing only 86.5% deuterium. In each case the ethylene obtained was found to contain strong CD stretching bands in the infrared, at times exceeding the intensity of the CH stretching bands. Thermal decomposition of tetra($^{2}H_{3}$-methyl)ammonium deuterioxide as a dry solid yielded trimethylamine, which contained 99.0% deuterium according to its mass spectrum. The infrared spectrum corroborates the mass spectral data. Deuterated dimethyl ether was obtained as the second major product. In contrast to Chablay,[8] who states that the

---

(1) (a) Postdoctoral Fellow, Space Program. (b) Participant in Undergraduate Honors Research Program.

(2) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4195 (1958).

(3) A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *ibid.*, **83**, 3861 (1961).

(4) F. Weygand, H. Daniel, and H. Simon, *Ber.*, **91**, 1691 (1958).

(5) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).

(6) W. K. Musker, *ibid.*, **86**, 960 (1964).

(7) A. W. Hofmann, *Ber.*, **14**, 494 (1881).

(8) E. Chablay, *Ann. Chim.* (Paris), [9] **1**, 477 (1914).

reaction of methyl iodide with solid ammonia at −80° to yield tetramethylammonium iodide is very rapid, we found the reaction to be very slow at −83° and not quantitative after 48 hr at −63°.

The following physical properties were determined on a sample of 99.0% deuterated trimethylamine. The molecular weights of two samples measured by vapor density were 68.5 and 67.8 compared with the calculated value for completely deuterated trimethylamine of 68.2. The melting point was determined by the plunger technique of Stock[9] to be −114.90, −114.94, and −114.88° for an average value of −114.9°. The vapor pressure may be described by the equation log $P_{\mathrm{mm}} = 7.760 - 1333/T$ over the temperature range of −84 to −8°. Measured data at several temperatures are compared in Table I with values calculated using the above equation. The extrapolated boiling point is 0.0° (760 mm) The heat of vaporization as determined using the Clausius–Clapeyron equation is 6.09 ± 0.03 kcal/mole and the Trouton constant is 22.3 compared to 21.8 for $(CH_3)_3N$. The infrared spectrum of deuterated trimethylamine was taken over the range of 4000 to 250 cm^{-1} in the gas phase and as a solid film at −190°. Major bands are given in Table II.

TABLE I

VAPOR PRESSURE OF $(CD_3)_3N$

Temp, °C	−83.9	−64.0	−45.6	−36.3	−23.4
Vapor pressure (calcd), mm	5.2	24.4	80.0	136	265
Vapor pressure (obsd), mm	5.3	23.7	80.6	137	261

Temp, °C	−15.8	−12.4	−8.3	0.0
Vapor pressure (calcd), mm	380	445	533	760
Vapor pressure (obsd), mm	384	448	531	...

TABLE II

INFRARED SPECTRUM OF $(CD_3)_3N$[a]

Gas, 30 mm, 10-cm Cell

2220 (s), 2175 (s), 2020 (s), 1225 (s), 1065 (m), 1015 (sh), 1000 (m), 885 (m), 875 (m), 860 (sh), 750 (m), 740 (s), 725 (sh)

Solid at −190°

2410 (w), 2265 (w), 2215 (s), 2200 (w), 2170 (m), 2160 (ms), 2125 (m), 2105 (w), 2030 (m), 2015 (s), 1952 (m), 1213 (s), 1195 (m), 1095 (w), 1070 (s), 1060 (s), 1050 (w), 1013 (s), 935 (w), 874 (s), 744 (s), 605 (w), 470 (w), 353 (m), 320 (m)

[a] s, strong; m, moderate; w, weak; sh, shoulder.

When ethyltrimethylammonium deuterioxide was heated in deuterium oxide in sealed tubes, it was found that temperatures at least 100° higher were required for decomposition than when the "dry" base was pyrolized. The degree of deuteration of the ethylene evolved was essentially the same from both methods of decomposition. Thermal decomposition of tetramethylammonium deuterioxide in the "dry" state at 135 to 140° yielded trimethylamine and methyl ether. Decomposition in aqueous solution required 250 to 270° and in this case methyl alcohol was isolated in yields slightly greater than half the molar amount of trimethylamine obtained. Dimethyl ether was isolated in barely detectable quantities. No exchange was observed for the quaternary ammonium ion remaining in solution after the heating periods. This is in contrast to the results of Cope, *et al.*,[3] who found exchange in the recovered quaternary salt during "dry" pyrolysis. This, then, is definite evidence that the rate of exchange during a "dry" pyrolysis is much greater than the rate found in solution and that there is some factor setting apart the Cope observed exchange and the Doering observed exchange. This difference may be ascribed to two principal factors. Differences in concentration of the reacting species certainly affect the rates of the reactions concerned. The second factor is the effectiveness of the base utilized. In this example the differences in effective base strength of the hydroxide ion in solution and in the solid must be considered. The base strength arguments lead to the suggestion that elimination could take place even more easily if a stronger base were available. Since it is impossible to have a stronger base than the hydroxide ion in aqueous solution and since direct comparisons of base strengths in other solvents are at best suspect, the comparison could best be made on the solid. An example of a stronger base than the hydroxide ion is the amide ion. Parry and Schumacher[10] have provided experimental results concerning the decomposition of tetramethylammonium amide. They found the solid to detonate violently upon removing the solvent ammonia at low temperatures. Although the products were not identified, it is highly likely that a reaction similar to the decomposition of tetramethylammonium hydroxide occurred. In the case of the amide the violent reaction at low temperatures is apparently the result of the presence of a more effective base than the hydroxide ion and lends support to the importance of base strength in the rate of the elimination reaction.

The difference between the observations of Hofmann[7] and Musker results from different experimental conditions as confirmed above. We found, as did Musker, that pyrolysis of the "dry" hydroxide yields primarily dimethyl ether. We also found, as did Hofmann, that decomposition of an aqueous solution of tetramethylammonium hydroxide yields primarily methyl alcohol. The extremely small quantities of dimethyl ether that we observed in this case would certainly have escaped detection under Hofmann's experimental conditions.[11] The product differences when the decomposition of tetramethylammonium hydroxide is carried out in solid and in solution might be rationalized in the following way. In the solution the hydroxide ion effects a simple substitution reaction on the methyl carbon to form methyl alcohol and trimethylamine. In the solid phase this same reaction initially occurs, but the methyl alcohol is formed on or in a solid adjacent to other hydroxide ions. The equilibrium to form methoxide ion and water is established. The

---

[9] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[10] R. W. Parry and H. Schumacher, private communication.

[11] Although Hofmann does not provide detailed description of his experimental techniques, the quaternary hydroxide was not dried under high vacuum and was presumably pyrolyzed as a concentrated solution.

methoxide ion, being a stronger base but more importantly a stronger nucleophile than the hydroxide ion, then substitutes on a methyl carbon to form dimethyl ether and trimethylamine. Although we have little more experimental evidence than Musker did for his "carbene" mechanism, we feel that the above proposal is a more satisfying explanation than Musker's proposal.

Experimental Section

Standard vacuum line techniques were used throughout this work.[12] Infrared spectra were taken on a Beckman IR-10. Melting points were taken using a device similar to that described by Stock[9] and temperatures for the melting points and the vapor pressure data were measured by vapor pressure thermometers also described by Stock.[9]

Chemicals.—The CD_3Br (97% deuterated) was generously provided by Professor R. C. Taylor of the University of Michigan. The CD_3I was prepared by the method of Cotton, *et al.*[13] The ND_3 was prepared by the method described by Brauer.[14] Anhydrous ammonia from Matheson was dried over sodium. The $C_2H_5NH_2$ and CH_3Br were from Matheson and CH_3I was from Fisher Scientific. All three were used as obtained. The D_2O was obtained from Diaprep, Inc., Atlanta, Ga., and contained 99.8% deuterium. The Ag_2O was prepared as described by Cope, *et al.*[15]

Ethyltrimethylammonium Deuterioxide.—In a typical experiment 15.6 mmoles of CD_3Br and 5.1 mmoles of $C_2H_5NH_2$ were condensed in a reaction tube containing 32 mequiv of Ag_2O and approximately 10 ml of D_2O and the mixture was stirred for 4 days. After the slurry was filtered to remove Ag_2O and AgBr, the solvent D_2O was removed under vacuum and the white solid obtained was pumped on for several hours using a Hg diffusion pump during which time only traces of water were obtained. A heater was placed around the tube and the temperature was raised to 200° in 1.5 hr while continuously pumping through liquid nitrogen traps. The temperature was maintained at 200° for an additional 0.5 hr and the products were separated by distillation in the vacuum line. The $(CD_3)_3N$ was purified using P_4O_{10}. The reaction yielded 3.92 mmoles of $(CD_3)_3N$ and 4.1 mmoles of ethylene, 77 and 80%, respectively, based on $C_2H_5NH_2$ used. The percentage of hydrogen present was estimated by sealing known gaseous volumes of the amine and benzene into an nmr tube and comparing the integrated proton resonance of the amine with that of the reference C_6H_6. Using CD_3Br containing 3.1 ± 0.6% H, $[C_2H_5N(CD_3)_3^+][OH^-]$ was prepared and on pyrolysis yielded $(CD_3)_3N$ containing 13.5 ± 1% H. $[C_2H_5N(CD_3)_3^+][OD^-]$, prepared by exchanging the above $[C_2H_5N(CD_3)_3^+][OH^-]$ with D_2O as the final step, yielded $(CD_3)N$ containing 6.0 ± 0.6% H. $(CD_3)_3N$ obtained from $[C_2H_5N(CD_3)_3^+][OD^-]$ prepared entirely in D_2O using the same CD_3Br as above contained 5.5 ± 0.6% H. Yields of $(CD_3)_3N$ varied from 63 to 77% and of C_2H_4 from 66 to 87%, both based on $C_2H_5NH_2$ used. CD_3I was also used in place of CD_3Br with no apparent disadvantages.

Tetramethylammonium Deuterioxide.—The reactions were conducted in a manner similar to that described above. In a typical experiment 126 mmoles of CD_3I, 42 mmoles of ND_3, and 500 mequiv of Ag_2O were allowed to react for 3 days in *ca.* 40 ml of D_2O. The Ag_2O and AgI were removed by filtering and the D_2O by distilling at room temperature under vacuum. Pyrolysis of the resulting solid was accomplished by heating it under high vacuum to 200° in 1.5 hr and maintaining that temperature for 2.5 hr. This yielded 10.6 mmoles of $(CD_3)_3N$ (33% based on CD_3I used) and 5.14 mmoles of $(CD_3)_2O$. No methanol was observed. The $(CD_3)_3N$ was shown to contain 99.0% deuterium by its mass spectrum.

Reaction of CD_3I with Anhydrous Ammonia at −85 to −50°.—In a typical reaction 9.54 mmoles of CD_3I and 56.8 mmoles of NH_3 were condensed in a reaction tube; the tube was surrounded with a chloroform slush (−63.5°) for 48 hr. At this time the NH_3 was removed, measured, and returned to the tube. The gas volume of ammonia indicated that reaction was nearly complete. However, the system was maintained at −63° for an additional 15 hr. The ammonia was removed, excess Ag_2O in D_2O added, and after stirring overnight the D_2O removed under vacuum at 0°. The remaining $[(CD_3)_4N^+][OD^-]$ was pyrolyzed as described above and was found to yield 37% $(CD_3)_3N$ based on CD_3I used. A similar reaction using ND_3 instead of NH_3 gave a product of identical deuterium content indicating that no exchange occurs between the N–H and C–D bonds.

When CD_3I was treated with an excess of ND_3 or NH_3 at −85° to −80°, the reaction was only about 80% complete after 10 days. The trimethylamine yields ranged from 34 to 37% based on CD_3I.

Observations on Exchange of D into CH_3 Groups.—The rate of exchange of deuterium from solvent D_2O into CH_3 groups of $[(CH_3)_4N^+]$ and $[C_2H_5N(CH_3)_3^+]$ was observed qualitatively. Samples were heated in sealed glass tubes or stainless steel cylinders. The containers were opened to the vacuum lines and volatile products examined by infrared techniques. Methyl alcohol was identified by its retention time in a gas chromatograph. The quaternary salts were then precipitated as tetraphenylborates and their infrared spectra taken in pressed KBr disks to determine if C–D bands were present.

Heating a 0.6 *M* solution of $[(CH_3)_4N^+][ID^-]$ in D_2O to 130° or 142° for 1 hr resulted in essentially no decomposition. After 4 hr at 130°, no CD stretching band could be observed in the $[(CH_3)_4N^+][B(C_6H_5)_4^-]$ precipitate. One hour at 180° yielded approximately 2% of the possible trimethylamine which had a weak CD band (approximately 3% as intense as the CH band). After 1.5 hr at 250–270°, 65% of the total trimethylamine was recovered and found to have ν_{C-H} and ν_{C-D} peaks of comparable intensity. Methyl alcohol was also recovered in essentially the same yield with similar ν_{C-H} and ν_{C-D} intensities. A 0.3 *M* solution of $[C_2H_5N(CH_3)_3^+]$-$[OD^-]$ in D_2O decomposed less than 10% after 27.5 hr at 150°, 40% after 21 hr at 170°, and 65% after 1 hr at 240–280°. Both the trimethylamine and the ethylene isolated contained moderately strong ν_{C-D} bands.

Purification of Deuterated Trimethylamine for Physical Property Measurements.—The trimethylamine obtained from the pyrolysis of tetramethylammonium deuteroxide was collected in a −126° trap after passing through a −63° trap. The material in the trap was redistilled from −63°. A volume of gaseous hydrochloric acid equivalent to that of the product was added. After allowing to stand for several hours, the volatiles were condensed into a reaction tube containing quinoline. Several milliliters of distilled water were added to the solid amine hydrochloride the solution was frozen in liquid nitrogen. While the trap containing the solution was kept immersed in liquid nitrogen, 5 to 10 pellets of KOH were added. The trap was then evacuated, isolated from the rest of the line, and allowed to warm to room temperature. The trimethylamine was distilled from the basic solution through a trap cooled to −63° to a trap cooled with liquid nitrogen. After this distillation was repeated, the product was condensed into a tube containing P_4O_{10}. After standing for 2–8 hr, the purified trimethylamine was distilled once more through a −63° trap.

The deuterated dimethyl ether was removed from the quinoline tube by distilling through a −63° trap. After redistillation the CO_2 present was largely removed by allowing the gas mixture to stand overnight in a tube containing potassium hydroxide.

Acknowledgment.—The authors gratefully acknowledge the support of this research by the American Cancer Society and the Research Corporation. We appreciate the cooperation of Mr. Jack Sharkey, U. S. Bureau of Mines, Pittsburgh, Pennsylvania, in obtaining and interpreting mass spectral data, and Professor R. C. Taylor of the University of Michigan who provided samples of CD_3Br.

---

[12] R. T. Sanderson, "Vacuum Line Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

[13] F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).

[14] G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Ferdinand Enke Verlag, Stuttgart, 1960, p 136.

[15] A. C. Cope, N. A. LeBel, H. H. Lee, and W. R. Moore, *J. Am. Chem. Soc.*, **79**, 4720 (1957).