Decomposition of *trans*-2-Phenylcyclohexyl-3,3,6,6-d_4-trimethylammonium Hydroxide (V).—A solution of 1.00 g. of *trans*-2-phenylcyclohexyl-3,3,6,6-d_4-trimethylammonium iodide in 3.0 ml. of water and 6.0 ml. of methanol was stirred for 24 hours with freshly prepared silver oxide obtained from 0.970 g. of silver nitrate. The solution was filtered and the precipitate was washed until the filtrate was neutral. The filtrate was concentrated at 1.0 mm. at room temperature. The flask containing the quaternary base was attached to a series of two traps, the first cooled in Dry Ice–acetone, the second in liquid nitrogen. The pressure was reduced to 1 mm. and the flask was heated slowly to 60°, at which point decomposition began. The temperature was raised slowly to 80° over a period of 20 minutes. The pressure was then reduced to 0.05 mm. and the temperature was raised to 120° to distil all the olefin into the trap. The material in the Dry Ice–acetone trap was dissolved in 5 ml. of pentane. Gas chromatography of the pentane solution on 1,2,3-tris-(2-cyanoethoxy)-propane[17] showed that there was no 3-phenylcyclohexene in

the solution. The pentane solution was washed with 10% hydrochloric acid[18] and water and dried over Drierite. The bulk of the pentane was removed by distillation and the residue was purified by gas chromatography on Silicone oil[17] to obtain 376 mg. (81%) of 1-phenylcyclohexene-3,3,6,6-d_4, n^{25}D 1.5651, λ_{max} 247 mμ (ϵ 11,390); deuterium analysis: 3.86 atoms of deuterium per molecule; mass spectrograph analysis: less than 1% dideuterated species, 4.8% trideuterated species and 94.3% tetradeuterated species.

(17) Gas chromatography columns were 8-mm. Pyrex tubes of 190-cm. length containing 30% by weight of liquid phase absorbant. The liquid phase absorbants employed were: Dow–Corning Silicone oil no. 550 on 60–80 mesh firebrick support (column temperature 170–180°) and 1,2,3-tris-(2-cyanoethoxy)-propane on 48–80 mesh firebrick support (column temperature 180°). Helium at 15 p.s.i. was the carrier gas and thermistors were employed for detecting sample peaks.

(18) Preliminary experiments showed that 3-phenylcyclohexene is not isomerized to 1-phenylcyclohexene by brief shaking of a pentane solution of the olefin with cold 10% hydrochloric acid.


Mechanism of the Hofmann Elimination Reaction: Evidence that an Ylide Intermediate is not Involved in Simple Compounds[1]

BY ARTHUR C. COPE, NORMAN A. LEBEL,[2] PHYLIS T. MOORE[3] AND WILLIAM R. MOORE

The trimethylamine produced at the outset of pyrolyses of cyclohexylmethyl-β-d-trimethylammonium hydroxide (I) and ethyl-β-d_3-trimethylammonium hydroxide (II) has been shown to be deuterium-free. As the pyrolyses progressed, the trimethylamine evolved contained an increasing amount of deuterium as a result of isotope exchange (with the DOH formed) in the methyl groups of the quaternary ammonium hydroxides. Pyrolysis of II at *ca.* 170° while sweeping with a large excess of steam produced deuterium-free trimethylamine. The reaction of cyclohexylmethyl-β-d-trimethylammonium bromide and of octyl-β-d_2-trimethylammonium bromide with phenyllithium in ether resulted in the incorporation of deuterium in the trimethylamine that was formed (evidence for the ylide mechanism of this elimination, sometimes called the Wittig reaction).
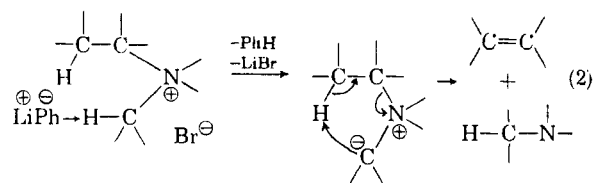
The Hofmann elimination reaction, the thermal decomposition of a quaternary ammonium hydroxide which gives an olefin and a tertiary amine, generally has been considered to be an E2 elimination.[4] Thus the mechanism has been depicted as involving removal of a β-proton by hydroxide ion with simultaneous expulsion of the (forming) tertiary amine (eq. 1). This mechanism now has

$$ \text{HO}^{\ominus} \quad \text{—C—C—} \quad \rightarrow \quad \text{HOH} + \rangle\text{C=C}\langle + \text{N—} \quad (1) $$
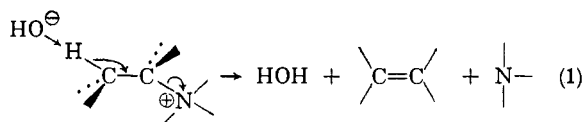
been supported by recent studies which exclude two-step (β-carbanion) and α-elimination processes in the systems investigated.[5,6]

Wittig and Polster found that trimethylalkylammonium bromides react with phenyllithium to give trimethylamine and an olefin, an over-all result similar to that of the Hofmann elimination.[7] They suggested that the mechanism involved initial formation of an ylide followed by intramolecular

proton transfer from the β-carbon atom with resultant collapse to the observed products (eq. 2). This *cis*-ylide elimination requires a 5-membered cyclic transition state which closely resembles

$$ \text{—C—C—} \quad \xrightarrow[\text{—LiBr}]{\text{—PhH}} \quad \text{—C—C—} \quad \rightarrow \quad \rangle\text{C=C}\langle + \quad (2) $$

the transition state for the thermal decomposition of an amine oxide.[4] In view of the fact that several Hofmann eliminations are known in which there cannot be a β-proton *trans* to the ammonium group and since isotopic exchange experiments[6,8] have established that ylides are formed under conditions similar to those employed for the Hofmann decomposition, an important question arises concerning the possibility that the Hofmann elimination, at least in part, follows the *cis*-ylide mechanism. Shiner and Smith noted that deuterium-free trimethylamine resulted from the decomposition of ethyl-β-d_3-trimethylammonium hydroxide in ethylene glycol at 130°.[6] This result indicates that in this solvent the elimination does not involve ylide intermediates. However, this conclusion cannot be extended to the normal Hofmann reaction, pyrolysis of the quaternary ammonium

(1) Supported in part by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-4542.

(2) Postdoctoral Fellow, 1957.

(3) Postdoctoral Research Associate, 1959–1960.

(4) A. C. Cope and E. R. Trumbull in "Organic Reactions," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., 1960.

(5) W. von E. Doering and H. Meislich, *J. Am. Chem. Soc.*, **74**, 2099 (1952).

(6) V. G. Shiner and M. L. Smith, *ibid.*, **80**, 4095 (1958).

(7) (a) G. Wittig and R. Polster, *Ann.*, **599**, 13 (1956). (b) G. Wittig and T. F. Burger, *ibid.*, **632**, 85 (1960).

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

hydroxide without solvent, since ylide formation may be dependent upon the environment. Indeed (while the present work was in progress), Weygand, Daniel and Simon reported that pyrolysis of β-tritiated ethyltrimethylammonium hydroxide at 150° in a stream of superheated steam gave trimethylamine with 7.8% of the tritium present in the starting material.[9] They concluded that the tritium was incorporated into the trimethylamine by way of the cis-ylide mechanism. When kinetic isotope effects and statistical factors are considered[10] this result, if correct, would mean that the cis-ylide mechanism must be the primary path for Hofmann elimination in the simplest possible system. However, in this paper evidence is presented which establishes that the cis-ylide mechanism is not important in Hofmann elimination in simple systems.

Preparation of Materials.—Two compounds have been studied in detail in this work: cyclohexyl-methyl-β-d-trimethylammonium hydroxide (I) and ethyl-β-d_3-trimethylammonium hydroxide (II). The former represents a system in which E2 elimination is hindered by dialkyl substitution on the β-carbon atom; hence an ylide mechanism should be relatively favored. The latter is the simplest system that can undergo Hofmann elimi ti-nation.
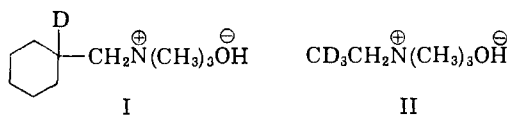
Hexahydrobenzoic-α-d acid[11] was treated with thionyl chloride and the resulting acid chloride was converted to the dimethylamide. Reduction with lithium aluminum hydride furnished cyclohexylmethyl-β-d-dimethylamine which was methylated with methyl iodide. The resultant cyclohexylmethyl-β-d-trimethylammonium iodide was converted to the quaternary ammonium hydroxide I which was shown to consist of at least 98% of the monodeuterated species.[12]

Tetradeuterioacetic acid was converted through the acid chloride to the dimethylamide. Reduction of the amide with lithium aluminum hydride followed by reaction of the tertiary amine with methyl iodide gave ethyl-β-d_3-trimethylammonium iodide. Treatment of the quaternary iodide with silver oxide gave the quaternary hydroxide II which was shown to consist of 99% of the d_3-species.[12]

Results of Pyrolyses.—A preliminary pyrolysis of I showed that the trimethylamine formed did contain deuterium, but that during the decomposition deuterium from the DOH formed by elimination was being exchanged into the α-methyl groups
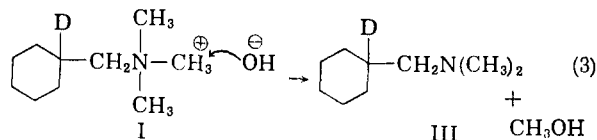
of the quaternary hydroxide. This exchange was demonstrated by the isolation of cyclohexyl-methyldimethylamine (III), formed by the competing displacement reaction (eq. 3), which contained more deuterium (1.28 atoms of deuterium

per molecule) than the quaternary hydroxide that was pyrolyzed (0.99 atom of deuterium per molecule). Thus it became clear that it would be necessary to perform pyrolyses in a manner which would permit a determination of the extent of exchange. This result was accomplished by collecting the products of a pyrolysis, as they were formed, in several fractions. Clearly at the outset of a pyrolysis no exchange can occur since the "solvent" contains no DOH. However, if the cis-ylide mechanism is operative, from the outset of a pyrolysis the trimethylamine formed must contain deuterium.

The decomposition of I was performed in the usual way but the products were collected in a series of fractions. Each fraction was analyzed by gas chromatography. The trimethylamine and the cyclohexylmethyldimethylamine (III) were collected and analyzed for deuterium by mass spectrometry.[13] The results (Table I, Experimental section) showed that the *trimethylamine formed at the beginning of a decomposition did not contain a significant amount of deuterium* (less than 0.3% of monodeuteriotrimethylamine) *and therefore that less than 0.3% elimination occurred by way of an ylide mechanism.* As the reaction proceeded, the trimethylamine contained an increasing amount of deuterium (up to 19% monodeuterioamine). However (as is shown in Table I), the cyclohexyl-methyldimethylamine was found to contain, within experimental error, *an equivalent amount of deuterium.*[14]

These results establish that the deuterium found in the trimethylamine results solely from exchange in the quaternary hydroxide. Therefore, in this system elimination does not occur by way of an ylide mechanism.

Pyrolysis of β-d_3-ethyltrimethylammonium hydroxide under normal Hofmann conditions employing the fractionation technique described above showed that the *trimethylamine formed at the outset of the decomposition did not contain deuterium* (less than 0.2% monodeuterioamine; Table II) *and therefore that less than 0.2% elimination occurred by way of an ylide mechanism.* Again, as the reaction progressed, the trimethylamine was found to contain an increasing amount of deuterium. In this system, elimination predominates so greatly over displacement that it was not feasible to

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

(10) With a kinetic isotope effect, k_H/k_T, of 5 (probably a low estimate since k_H/k_D is about 4 in a similar reaction; ref. 6) coupled with the statistical factor (2 hydrogen atoms for each tritium atom), if *all* elimination followed the cis-ylide path, about 9% of the tritium would be found in the trimethylamine.

(11) C. C. Price, E. L. Eliel and R. J. Convery, *J. Org. Chem.*, **22**, 347 (1957).

(12) Analysis by mass spectrometry; see the Experimental section for the procedures employed.

(13) The methylenecyclohexane produced was found to be deuterium-free (less than 0.4% monodeuterio olefin) except for the last fraction which contained a small amount of monodeuterated olefin (Table I).

(14) A statistical correction must be made for the comparison since in the formation of cyclohexylmethyldimethylamine one methyl group is lost.

attempt deuterium analysis of the trace of ethyl-dimethylamine formed by displacement. However, the extent of exchange was determined by analyzing the quaternary hydroxide obtained by stopping the reaction before the pyrolysis was complete. All of the deuterium in the trimethylamine could be accounted for on the basis of exchange in the quaternary ammonium hydroxide.[15]

As noted earlier, Weygand and co-workers reported that pyrolysis of β-tritiated ethyltrimethylammonium hydroxide gave 7.8% of tritiated trimethylamine when a stream of superheated (150°) steam was passed through the pyrolysis flask in an attempt to sweep out (and dilute) TOH as it was formed.[16] They believed that exchange had been eliminated in this experiment and on the basis of this assumption they concluded that the tritiated trimethylamine resulted from an ylide mechanism.[17] Although our results reported above excluded ylide elimination in this system, it appeared to be highly desirable to repeat the superheated steam experiment with II.

High velocity steam with a measured inlet temperature of 170° was swept through the melt of II while an external heating bath (160°) was simultaneously applied to the pyrolysis flask. The decomposition was stopped at 65% completion. *The trimethylamine, collected in a single fraction, contained no deuterium* (less than 0.3%) of the monodeuterioamine. The recovered quaternary hydroxide contained the same amount of deuterium as the starting material. Therefore, it has been established that exchange can be eliminated by rapid sweeping with steam and that when this is done the results conclusively demonstrate that the *cis*-ylide mechanism does not apply to the elimination reaction occurring during pyrolysis of ethyl-β-d_2-trimethylammonium hydroxide. The same conclusion must also apply to the non-deuterated quaternary hydroxide.

It is clear that in the systems we have investigated, elimination does not occur by way of either a *cis*-ylide (intramolecular) or intermolecular[18] ylide mechanism. It seems reasonable to conclude that elimination from a quaternary ammonium hydroxide will not follow the *cis*-ylide path unless the geometry of the system precludes normal *trans* elimination. Currently, we are investigating such systems in which *cis* elimination appears to be favored over *trans* elimination, because of steric factors.

Although the normal Hofmann decomposition does not involve ylides, we have verified that ylides are intermediates in the reaction of alkyltrimethylammonium bromides with phenyllithium as sug-

gested by Wittig. Treatment of cyclohexyl-methyl-β-d-trimethylammonium bromide containing 0.99 atom of deuterium per molecule with an equivalent of phenyllithium in ether gave trimethylamine (as the picrate) containing 1.01 ± 0.03 atoms of deuterium per molecule and methyl-enecyclohexane containing 0.00 atom of deuterium per molecule. Similarly, octyl-β-d_2-trimethyl-ammonium bromide containing 1.58 ± 0.03 atoms of deuterium per molecule gave trimethylamine containing 0.76 ± 0.03 atom of deuterium per molecule and 1-octene-2-d containing 0.85 ± 0.03 atom of deuterium per molecule. These data clearly establish that an ylide mechanism for elimination must operate in these systems in the Wittig reaction.[19]

Experimental[20]

Cyclohexylmethyl-β-d-trimethylammonium Iodide.—Hexahydrobenzoic-α-d-acid, b.p. 89°(1.8 mm.), was prepared in 65% yield from diethyl 1,1-cyclohexanedicarboxylate by the procedure of Price, Eliel and Convery.[11] Treatment of the acid with thionyl chloride afforded hexahydrobenzoyl-α-d-chloride, b.p. 78–79° (20 mm.), n^{25}D 1.4663 (92%), that was converted to the dimethylamide, b.p. 83° (1.6 mm.), n^{25}D 1.4788 (86%), by treatment with dimethylamine. Reduction of the amide with lithium aluminum hydride furnished cyclohexylmethyl-β-d-trimethylamine (III), b.p. 87° (47 mm.), n^{25}D 1.4444 (95%). The tertiary amine was converted to cyclohexylmethyl-β-d-trimethylammonium iodide, m.p. 229.0–229.2° (lit.[21] m.p. 226.5–227.5° for the undeuterated analog), in 88% yield with methyl iodide. Deuterium analysis (combustion) of the quaternary iodide indicated 0.99 ± 0.03 atom of deuterium per molecule. Analysis (mass spectrometry) of III and a sample of the same amine prepared by reduction of the quaternary iodide with lithium aluminum hydride indicated for both at least 98% of the monodeuterioamine (less than 2% non-deuterated III).

Ethyl-β-d_2-trimethylammonium Iodide.—Trideuterio-acetyl chloride was obtained in 92% yield by distillation of a mixture of tetradeuterioacetic acid[22] and benzoyl chloride. Treatment of the acid chloride with dimethylamine afforded N,N-dimethylacetamide-α-d_3, b.p. 98–101° (8 mm.), n^{25}D 1.4348, 73% yield. Analysis by mass spectrometry showed that the dimethylamide consisted of 98.4 ± 0.5% d_3 and 1.3 ± 0.5% d_2 species. Reduction of the dimethylamide with lithium aluminum hydride in ether, decomposition of the excess hydride, removal of the solids by filtration and distillation of the filtrate furnished an ether solution of ethyl-β-d_3-dimethylamine. The ether solution was treated with methyl iodide to give ethyl-β-d_3-trimethylammonium iodide in 61% yield (from the dimethylamine); dithiourea adduct, m.p. 138–140° (lit.[8] m.p. 139.5–141.0°). A sample of the quaternary iodide was converted to the quaternary hydroxide which then was converted back to the iodide by treatment with hydroiodic acid. Reduction of the recovered quaternary iodide with lithium aluminum hydride in tetrahydrofuran followed by isolation by gas chromatography (silicone oil, room temperature) afforded ethyl-β-d_3-dimethylamine. Analysis by mass spectrometry showed that the amine consisted of at least 98% of the d_3-

(15) More deuterium was found in the recovered quaternary ammonium hydroxide than in the trimethylamine. This result was expected since the deuterium content of a trimethylamine fraction is averaged over the period of time during which it was collected.

(16) It must be emphasized that the percentages reported in the tritium experiments cannot be compared directly with the values reported in this paper for the deuterium experiments. The tritium experiments must be corrected for both a large kinetic isotope effect and a statistical factor (see footnote 10), whereas the deuterium experiments require no corrections and give directly the upper limit of elimination by way of an ylide mechanism.

(17) The results which follow suggest that exchange occurred under the conditions that they employed.

(18) An ylide could serve as the base in E2 elimination.

(19) Since the experiments reported in this paragraph (performed before a mass spectrometer was available for deuterium analysis) employed combustion analysis for deuterium, which gives the *average* number of deuterium atoms per molecule, the relative importance of the intramolecular ylide mechanism proposed by Wittig and an intermolecular ylide mechanism cannot be determined here. Both mechanisms would give an average of one deuterium atom per molecule of trimethylamine, but the intramolecular mechanism must give only the d_1-amine whereas the intermolecular mechanism would give a rather complex (near-statistical) distribution of d_1, d_2, and higher deuterated species.

(20) Melting points are corrected and boiling points are uncorrected.

(21) A. C. Cope, C. L. Bumgardner and E. E. Schweizer, *J. Am. Chem. Soc.*, **79**, 4729 (1957).

(22) The tetradeuterioacetic acid, purchased from Merck and Co., Ltd., Montreal, was specified to be of at least 99% isotopic purity.

species with less than 2% of the d_3-species and less than 0.4% of the d_4-species. The same analysis was obtained when the amine was prepared by reduction of the quaternary iodide without prior conversion to the hydroxide.

Pyrolysis of Quaternary Hydroxides.—The quaternary hydroxides were prepared from the quaternary iodides and silver oxide in the usual way,[23] concentrating solutions at reduced pressure below 35° to prevent decomposition and exchange.

The decompositions were carried out in a small pear-shaped flask fitted with a sidearm capillary gas inlet tube for nitrogen which extended to the bottom of the flask. A short right-angle exit tube led from the flask through a two-way stopcock to a short hypodermic needle. The products were collected in a series of small U-shaped traps fitted on both ends with No-air stoppers. The exit side of each trap was connected, by means of a hypodermic needle plunged through the stopper, to a rubber tube which was joined to a vacuum manifold. The manifold led through a large surge vessel to a manostat which was connected to the usual pumping system. At the start of a pyrolysis, the first trap was joined to the hypodermic needle on the exit arm of the pyrolysis flask and the flask and all of the traps were evacuated with a continuous nitrogen bleed passing through the flask. The traps were then cooled in liquid nitrogen. At time 0, a large, magnetically-stirred oil-bath, preheated to the desired temperature, was raised into position, submerging the pyrolysis flask up to the exit tube. After the desired time interval, the exit tube stopcock was closed, the first trap was replaced by the second, and the exit tube stopcock was reopened. This process, which did not affect the pressure in the system, was repeated whenever subsequent fractions were collected. Since the No-air stoppers were leak-free, the U-tube could be removed from the system allowing storage of the products under reduced pressure.

Pyrolysis of Cyclohexylmethyl-β-d-trimethylammonium Hydroxide (I).—In preliminary pyrolyses of I in which the products were collected in a single fraction (employing a large trap to avoid losses) it was found that the decomposition resulted in 45–40% elimination, measured by the yield of either trimethylamine or methylenecyclohexane, and 55–60% displacement, measured by the yield of the tertiary amine III. This result is what is expected if the isotope effect k_H/k_D in elimination is about 4, since the rate of displacement should be the same for both I and the non-deuterated quaternary base, cyclohexylmethyltrimethylammonium hydroxide, which was found to give ca. 77% elimination and 23% displacement (reported,[21] 76% elimination and 24% displacement). In experiments in which the products were collected in several fractions, the low-boiling components in each fraction were transferred by distillation at −40° (1 mm.) to a large calibrated trap. The trap was warmed to room temperature to vaporize the distillate and the resultant mixture of gases was analyzed by gas chromatography (silicone oil, 4 m. column, 25°) and samples of trimethylamine were collected for analysis by mass spectrometry. In addition to trimethylamine, dimethyl ether, identified by its infrared spectrum (gas phase), was found in varying amounts (up to 0.09 mole per mole of I). This product must result from the displacement reaction of methoxide ion with I. This reaction is not surprising in this system since the methanol which is formed in considerable amount by the displacement reaction of hydroxide ion with I must yield some methoxide ion by rapid proton transfer to hydroxide ion.

After removal of the volatile materials from each fraction, the higher boiling products were extracted with pentane and the yields of methylenecyclohexane and III were determined by analysis of the pentane solution by gas chromatography (silicone oil, 2 m. column, 118°) employing p-xylene as an internal standard. Samples of III and in some cases methylenecyclohexane were collected for analysis by mass spectrometry.

Material balance was ca. 65% for experiments in which the products were collected in 7–9 fractions (U-tubes) as compared to 90–95% when the products were collected in a single fraction (large trap). Loss of material (not critical for the present purposes) appeared to be uniform throughout a decomposition. The extent of decomposition (defined for the nth fraction as 100 times the amount of a product col-

lected in fractions 1 to n divided by the total amount of the product collected in all fractions) through a given fraction was the same whether estimated from the amount of trimethylamine formed or the amount of methylenecyclohexane formed, but a somewhat smaller extent of decomposition was indicated from the amount of III formed. This result suggests that III, the highest boiling product, lagged a little behind the olefin and trimethylamine in traveling from the decomposition flask to a trap. (The alternative explanation, that the ratio of elimination to displacement decreased during the reaction, seems less likely.)

The results of a typical decomposition are summarized in Table I.

TABLE I

PYROLYSIS OF CYCLOHEXYLMETHYL-β-d-TRIMETHYLAMMONIUM HYDROXIDE[a]

Fraction	Total elapsed time, min.	Extent of pyrolysis, approx. %	Trimethylamine Found[b]		Cyclohexylmethyl-dimethylamine			
					Found[c]		Calculated[d]	
			d_1	d_2	d_2	d_1	d_2	d_1
1[e]	2	0 }	<0.3	..				
2[e]	5	3 }						
3[e]	7	6	0.3	0.0				
4	10	15	1.6	.2				
5	13	30	4.1	.3	2.8	<0.4	2.9	0.1
6[f]	18	60	10.0	.6	6.6	0.2	7.0	0.2
7	25	95	19.4	2.2	10.7	0.8	14.0[i]	0.9
8[g,h]	31	100	..	..	21.5	2.7	..	..

[a] Bath temperature 94–99°; pressure, 6 mm.; nitrogen atmosphere. [b] The remainder is undeuterated trimethylamine. [c] The remainder is d_1-amine. Identical values were obtained from the molecular ion region (mass number 142) and the $CH_2N(CH_3)_2$ fragment (mass number 58). [d] These values were calculated assuming that only exchange occurred, in which case the deuterium content of the methyl groups of trimethylamine and I must have been identical. Assuming that the deuterium distribution was random, that the α-methylene groups of I contained no deuterium and that the removal of a methyl group from I in the displacement reaction was random (no secondary isotope effects), the following relations can be derived: % III-d_2 = 0.67 (% Me$_3$N-d_1) + 0.50 (% Me$_3$N-d_2); % III-d_1 = 0.42 (% Me$_3$N-d_2). [e] The methylenecyclohexane obtained from fractions 1, 2 and 3 combined contained less than 0.4% of the d_1-olefin. [f] The methylenecyclohexane contained less than 0.3% of the d_1-olefin. [g] The methylenecyclohexane contained ca. 2% of the d_1-olefin. [h] The amount of trimethylamine isolated was too small to permit accurate mass spectral analysis.

This difference between calculated and found values almost certainly is due to a slightly slower transfer of III from the flask to the trap compared to trimethylamine. Since the deuterium content of the amines is increasing rapidly as the completion of the decomposition is approached (compare fractions 7 and 8), this difference will be magnified in the final fractions.

Pyrolysis of Ethyl-β-d_3-trimethylammonium Hydroxide (II).—Preliminary pyrolyses of II in which the products were collected in a single fraction (two large traps in series) and then were vaporized and analyzed as a gas mixture by gas chromatography (silicone oil, 4 m. column, 25°) established that the decomposition gave ca. 99.6% elimination (as determined from the yield of either trimethylamine or dideuterioethylene) and 0.4% displacement (ethyl-β-d_3-dimethylamine, identified by its mass spectrum). No dimethyl ether was detected.

Samples of II were pyrolyzed nearly completely, collecting the products in several fractions. The dideuterioethylene and trimethylamine in each fraction were separated readily by low temperature distillation affording pure samples of the amine which were analyzed by mass spectrometry. The recovered II was neutralized with hydriodic acid and the solution was evaporated to dryness. The quaternary iodide was recrystallized from acetone and then reduced with lithium aluminum hydride in tetrahydrofuran. The ethyl-β-d_3-dimethylamine so formed was isolated by gas chromatography (silicone oil, 4 m. column, 25°) and analyzed by mass spectrometry. The results of a typical decomposition are presented in Table II.

Pyrolysis of II with Superheated Steam.—The decomposition of II was carried out in a small pear-shaped flask which had a side arm fitted with a one-hole silicone rubber stopper

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

TABLE II

PYROLYSIS OF ETHYL-β-d_3-TRIMETHYLAMMONIUM HYDROXIDE (II)[a]

Fraction	Total elapsed time, min.	Trimethylamine	
		d_1	d_2
1	0.8	0.0	0.0
2	1.5	0.0	.0
3	2.8	2.7	.2
4	4	10.4	1.2
5	7.5[b,c]	20	2.5

[a] Bath temperature 115°, pressure, 6 mm., nitrogen atmosphere. [b] The reaction (nearly complete) was stopped at this time by immersing the reaction flask in a cold bath. The recovered quaternary hydroxide upon conversion to the iodide and reduction with lithium aluminum hydride yielded ethyldimethylamine with the deuterium analysis: 80% d_3, 19% d_4 and 1% d_5. This would correspond to ca. 27% of the d_4-species in the ethyltrimethylammonium hydroxide. [c] In a similar pyrolysis, carried to ca. 85% completion, the ethylene produced was found to be only the d_2-species (no d_3-species detected).

through which a steam inlet tube (15 gauge stainless steel tubing) could be introduced. A short exit tube led from the flask to a large trap (cooled at −80°). Superheated steam was generated by passing steam from the laboratory supply through a copper coil heated in an air-bath at 220°. With the steam inlet tube removed from the flask, the flow rate of steam was adjusted to 8 g. of water per minute[24] (ca. 16 l. of steam per minute at the operating temperature). The temperature of the steam at the exit of the steam inlet tube was 165–170° (measured with a thermocouple in the steam). At time 0, the steam inlet tube was inserted through the silicone rubber stopper and extended to the bottom of the flask (which contained 4 mmoles of II). Simultaneously the oil-bath (heated to 160°) was raised, submerging the flask nearly to the level of the flask exit tube. Extremely violent agitation of the sample of II resulted. After 2 min., the steam inlet tube was removed from the flask and the heating bath was simultaneously replaced by a cold oil-bath.

The aqueous solution obtained upon warming the contents of the trap to room temperature was acidified with hydrochloric acid and evaporated to dryness under reduced pressure. The residue was made basic with a few drops of concentrated aqueous sodium hydroxide and a pure sample of trimethylamine was collected by distillation at 0° (1 mm.). Analysis by mass spectrometry showed at least 99.7% undeuterated trimethylamine and less than 0.3% of the monodeuterio species.

The recovered II was converted to the quaternary iodide. The recovery was 35%, indicating that the pyrolysis was 65% complete. The quaternary iodide was reduced with lithium aluminum hydride and the ethyl-β-d_2-dimethyl-amine was isolated by gas chromatography. Analysis by mass spectrometry showed 99.5% d_2- and 0.5% d_4-species.

(24) This corresponded to ca. 340 moles of water (H$_2$O) added as steam per mole of water (DOH) produced by the decomposition of II.

Reaction of Cyclohexylmethyl-β-d-trimethylammonium Bromide with Phenyllithium.—A suspension of 3.3 g. of the quaternary bromide (prepared from I which was known to contain 0.99 ± 0.03 atom of deuterium per molecule) in 27 ml. of 0.52 M phenyllithium in ether was shaken for 48 hr. The solids were removed by filtration and washed with ether. The ether solution was washed with 10 ml. of 3 N hydrochloric acid and then with water. Distillation of the dried solution gave two fractions higher boiling than ether which contained a total of 0.55 g. (41%) of methylene-cyclohexane as shown by analysis by gas chromatography (silicone oil, 88°). The methylenecyclohexane, isolated by gas chromatography, was found to contain 0.00 atom of deuterium per molecule (combustion analysis).

The combined aqueous acidic extracts were evaporated to dryness and the residue was treated with picric acid in ethanol. The trimethylamine picrate obtained, 1.1 g. (25%), m.p. 233.5–224.0° (no depression upon admixture with an authentic sample), contained 1.01 ± 0.03 atoms of deuterium per molecule (combustion analysis).

Reaction of Octyl-β-d_2-trimethylammonium Bromide with Phenyllithium.—Employing the series of reactions described by Hauser,[25] ethyl heptanoate was converted to 1-octanol-β-d_2, b.p. 111–113° (20 mm.), n^{25}D 1.4528–1.4263, 1.78 atoms deuterium per molecule (combustion analysis). The octanol was treated with p-toluenesulfonyl chloride in pyridine to give the tosylate which was treated with dimethylamine in benzene, yielding octyl-β-d_2-dimethylamine, b.p. 101° (20 mm.), n^{25}D 1.4212. Reaction of the amine with methyl iodide gave the quaternary iodide, m.p. 140.2–141.4° (lit.[26] m.p. 139–141°), which was treated with silver oxide and then with hydrobromic acid, giving octyl-β-d_2-trimethylammonium bromide, m.p. 214.4–217.2° (lit.[27] m.p. 215°), containing 1.58 ± 0.03 atoms of deuterium per molecule (combustion analysis). Reaction of the bromide with phenyllithium following procedures described above gave 1-octene-2-d, isolated by gas chromatography, containing 0.85 ± 0.03 atom of deuterium per molecule and trimethylamine picrate containing 0.76 ± 0.03 atom of deuterium per molecule (combustion analyses).

Deuterium Analyses.—Mass spectra were determined with a Consolidated Electrodynamics Corporation model 21-103C mass spectrometer equipped with a heated inlet system operated at 140°, using ionization potentials of 70 or 11 volts. We are indebted to Prof. K. Biemann and his associates for measuring these spectra. Deuterium distribution was calculated in the usual way employing the molecular ion region and making the necessary corrections based on reference spectra (a fragment peak could also be used for analyses of III; see Table I). Spectra of the following compounds were employed as reference spectra where appropriate: trimethylamine, cyclohexylmethyl-dimethylamine, cyclohexylmethyl-β-d-dimethylamine (III), ethyldimethylamine, ethyl-β-d_3-dimethylamine, ethylene and methylenecyclohexane.

Combustion analyses were conducted by Mr. Josef Nemeth, Urbana, Ill.

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