[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Pyrolysis of γ-Hydroxyalkyl Quaternary Ammonium Hydroxides and Alkoxides. Cyclohexane Derivatives[1,2]

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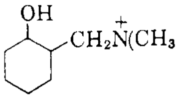
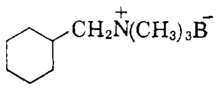
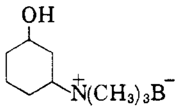
The decomposition of *trans*-2-hydroxycyclohexylmethyltrimethylammonium bases gave Hofmann elimination (2-methylenecyclohexanol) and demethylation (to *trans*-2-hydroxycyclohexylmethyldimethylamine and the corresponding methyl ether); however, pyrolysis of *cis*-2-hydroxycyclohexylmethyltrimethylammonium *t*-butoxide produced, in addition to the above compounds, 7-oxabicyclo[4.2.0]octane (13%). With *cis*-3-hydroxycyclohexyltrimethylammonium hydroxide, 1,3-cleavage to trimethylamine and hex-5-enal (which undergoes subsequent aldol and Cannizzaro condensations) was observed along with Hofmann elimination (cyclohex-2-enol) and dequaternization (*cis*-3-hydroxycyclohexyldimethylamine). When the base employed was *t*-butoxide, 1,3-cleavage occurred almost exclusively.

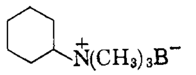
In the previous report,[4] the literature dealing with the decomposition of hydroxyalkyl quaternary ammonium bases was reviewed and data presented on the affect of a 3-hydroxy group in the decomposition of acyclic quaternary ammonium hydroxides and alkoxides. This paper is a continuation of that study and deals with the pyrolysis of the following cyclohexane derivatives.


I

cis and *trans*

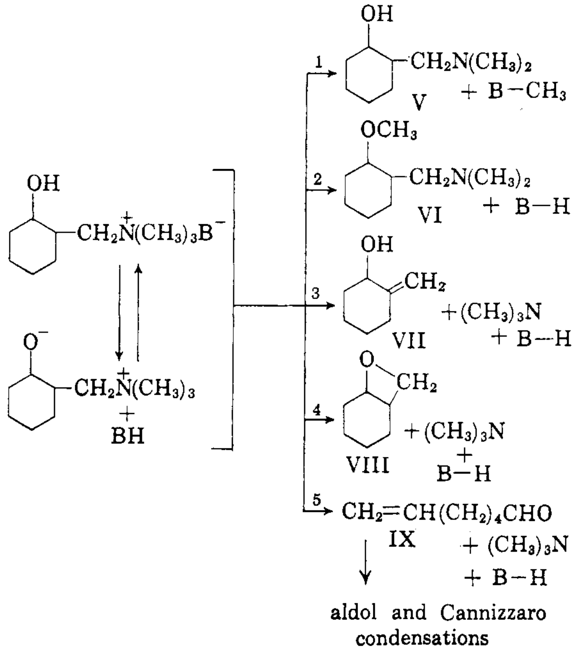

II


III


IV

$B^- = OH^-$ and t-BuO^-

The various paths available for the decomposition of γ-hydroxyalkyl quaternary ammonium bases can be illustrated with 2-hydroxycyclohexylmethyltrimethylammonium bases.



In the decomposition of *cis*-I, $B^- = t$-BuO^-, paths 1 to 5 were observed. The amines found in this reaction were trimethylamine (56%) identified by its picrate and high boiling bases (42% by titration) which after isolation and analysis by vapor phase chromatography consisted of *cis*-2-methoxycyclohexylmethyldimethylamine (VI) (6%) and *cis*-2-hydroxycyclohexylmethyldimethylamine (V) (29%). A structural assignment for *cis*-VI was made on the basis of analysis, infrared spectrum, and its methiodide. The neutral mixture which was isolated by distillation and separated by vapor phase chromatography consisted of 2-methylenecyclohexanol (VII) (12%), 2-methylenecyclohexyl methyl ether (11%), 7-oxabicyclo[4.2.0]octane (VII) (3%) and high boiling material (21%) most likely a mixture of glycol from VII and aldol condensation products of IX. In an earlier experiment a 13% yield of oxetane VII was obtained with a subsequent decrease in yield of high boiling neutral residues. Evidence for the aldol product included an infrared absorption band characteristic of an α,β-unsaturated carbonyl group. Physical constants, infrared spectra, and analysis served to characterize 2-methylenecyclohexyl methyl ether and the oxetane VIII. The structure and stereochemistry[5] of VIII was established by reduction with lithium aluminum

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[2] Presented at the 137th Meeting of the American Chemical Society at Cleveland, Ohio in April 1960.

[3] Abstracted from the Ph.D. dissertation of J.G.D., May 1960.

[4] V. J. Traynelis and J. G. Dadura, *J. Org. Chem.*, **26**, 686 (1961).

[5] Recently D. S. Tarbell and A. Rosowsky (Abstracts of Papers, 136th Meeting of the American Chemical Society, Atlantic City, N. J., September 1959, p. 67F.) have described the synthesis of VIII and reported the conversion of VIII to *cis*-2-methylcyclohexanol by lithium aluminum hydride.

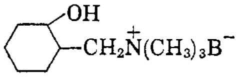
hydride to *cis*-2-methylcyclohexanol whose identity and purity was determined by comparison of infrared spectra and vapor phase chromatography behavior on two different columns with that of an authentic sample.

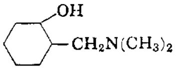
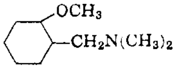
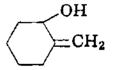
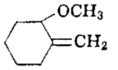
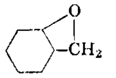
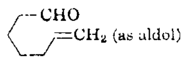
Since the four and six membered rings in VIII are fused *cis* and the formation of the oxetane ring did not involve bond making with the carbons of the cyclohexane ring, the amino alcohol used in the Hofmann decomposition must have a *cis* arrangement of hydroxy and dimethylaminomethyl groups and thus the other isomer must be *trans*. Additional support for this assignment is found upon examination of physical constants (see Experimental) and application of the von-Auwers–Skita rule.[6]

A summary of the data from the decomposition of *cis*-I, $B^- = OH^-$ and *trans*-I, $B^- = OH^-$ and $t\text{-}BuO^-$ appear in Table I. Since the *trans*-amino ether VI was a new compound, an authentic sample was prepared by a Williamson ether synthesis with the potassium salt of *trans*-V and methyl chloride. This proved to be identical with the product from decomposition. The most significant difference between the *cis* and *trans*-I systems was the absence of oxetane VIII in the *trans*-I decomposition. This could be rationalized on the basis of the strain introduced when a six and four membered ring are fused *trans*.

TABLE I

DECOMPOSITION OF 2-HYDROXYCYCLOHEXYLMETHYLTRIMETHYLAMMONIUM BASES



Compound	Yield, %			
	trans		*cis*	
$B^- =$	OH^-	$t\text{-}BuO^-$	OH^-	$t\text{-}BuO^-$
Olefin titer[a]	41	28	27	31
$(CH_3)_3N$	44	28	51	56
High-boiling Amines (titer)	55	66	48	42
	43(32)[b]	50(35)	38(24)	35(29)
	12(9)	16(11)	10(1.3)	7(6)
	(3.5)	17	23	12
	....	8.6	4	11
			1	3[c]
	1	4[d]	0	21[e]

[a] This was determined by a volumetric procedure employing bromine in potassium bromide.[7] [b] The quantities in parenthesis refer to amounts isolated from the reaction mixture. [c] In a second experiment a yield of 13% oxetane was found. [d] Estimated amount in the high boiling residue. [e] This quantity is most probably a mixture of glycol resulting from the ring opening of oxetane VII and aldol products.

Cope and co-workers[8] have reported that cyclohexylmethyltrimethylammonium hydroxide gave 68% methylenecyclohexane upon pyrolysis; and we have found that the decomposition of the corresponding *t*-butoxide II, $B^- = t\text{-}BuO^-$ produced 3.5% trimethylamine (characterized as the picrate) and 93% (by titration, 77% isolation as the methiodide) of cyclohexylmethyldimethylamine. A comparison of the amount of olefin formation in I, $B^- = t\text{-}BuO^-$ to that in II, $B^- = t\text{-}BuO^-$ indicates that the hydroxyl group has an enhancing effect on the Hofmann elimination. These observations were also made with 3-hydroxyisobutyltrimethylammonium bases.[4]

The decomposition of *cis*-3-hydroxycyclohexyltrimethylammonium hydroxide (III, $B^- = OH^-$) gave as the basic components trimethylamine (58%) characterized as the picrate and *cis*-3-hydroxycyclohexyldimethylamine (39% by titration, 19% by isolation) identified by physical constants and methiodide. The low boiling neutral fraction was separated and analyzed by vapor phase chromatography and contained cyclohex-2-enol (14%), 3-methoxycyclohex-1-ene (9%), hex-5-enal (2.4%) and hex-5-enol (3.7%); while the high boiling neutral fraction (30%) was aldol condensation products. The two aldehydes (hex-5-enal and its aldol product) were identified by their 2,4-dinitrophenylhydrazones while hex-5-enol[9] was characterized as its α-naphthylurethan. An independent synthesis of this alcohol was accomplished by treating a portion of the reaction mixture of 3-methoxycyclohex-1-ene, hex-5-enal, hex-5-enol, and cyclohex-2-enol with lithium aluminum hydride and by vapor phase chromatography showing the disappearance of the hex-5-enal peak and an enhancement of the hex-5-enol peak equal to the initial concentration of hex-5-enal. The presence of hex-5-enol could be rationalized by a Cannizzaro reaction. Cyclohex-2-enol was identified by its infrared spectrum and preparation of an α-naphthylurethan, while the structure for 3-methoxy-

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[6] W. G. Dauben and K. S. Pitzer in M. S. Newman's *Steric Effects in Organic Chemistry*, John Wiley & Sons, Inc., New York, 1956, p. 20.

[7] A. Polgar and J. L. Jungnickel, *Organic Analysis*, Vol. 3, Interscience Publishers, New York, N. Y., 1956, p. 240.

[8] A. C. Cope, C. L. Bumgardner, and E. E. Schweizer, *J. Am. Chem. Soc.*, 79, 4730 (1957).

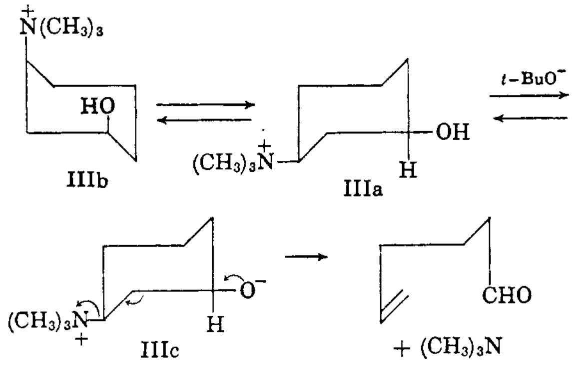
[9] This compound had been previously characterized as the 3,5-dinitrobenzoate, m.p. 42–43° by R. R. Burford, F. R. Hewgill, and P. R. Jeffries, *J. Chem. Soc.*, 2937 (1957). These workers obtained hex-5-ene-1-ol from a similar cleavage reaction involving the action of nitrous acid on 3-aminocyclohexanol.

cyclohex-1-ene was assigned on the basis of an infrared spectrum and physical constants.[10]

In the pyrolysis of III, $B^- = t\text{-BuO}^-$, the major reaction was cleavage (path 5) followed by aldol condensation (72%). The other products isolated and identified as described for the corresponding hydroxide were trimethylamine (92%), *cis*-3-hydroxycyclohexyldimethylamine (6%), 3-methoxycyclohex-1-ene (1%), cyclohex-2-enol (1%), and hex-5-enol (1%).

When one compares the results of the decomposition of III, $B^- = OH^-$ to $B^- = t\text{-BuO}^-$, the major differences are a marked decrease (23% to 2%) in Hofmann elimination (path 3) and a corresponding increase (36% to 72%) in the cleavage reaction (path 5). These observations on the elimination reaction agree well with the decomposition of cyclohexyltrimethylammonium hydroxide and *t*-butoxide. The pyrolysis of IV, $B^- = OH^-$ gave 39% trimethylamine, 21% cyclohexene, and 57% dimethylaminocyclohexane[11]; while the corresponding IV $B^- = t\text{-BuO}^-$ gave 6.6% trimethylamine, 6% cyclohexene, and 93% dimethylaminocyclohexane.[12]

The increase in the cleavage reaction with III, $B^- = t^-\text{BuO}^-$ could be rationalized by consideration of the conformation of III. The structure IIIa should be by far the predominant species in view of the diequatorial position of the two substituents and in particular the trimethylammonium group.[12] With this conformation the E_2 *trans* and coplanar Hofmann elimination is hindered. Since *t*-butoxides ions are present, the conversion of IIIa to the dipolar ion IIIc would be favorable and this species which possesses the proper stereochemistry for cleavage[13,14] leads to hex-5-enal which after aldol condensation gives the isolated product.



In summary of the results reported in this and the previous paper,[4] it appears that in the pyrolysis of γ-hydroxyalkyltrimethylammonium bases the Hofmann elimination is favored whenever the molecule can assume the proper orientation for such a reaction. When olefin formation is impossible or difficult, the contribution of the remaining paths is governed by the geometry of the molecule, steric factors, and strength of the base.

EXPERIMENTAL[15]

cis- and trans-2-Hydroxycyclohexylmethyldimethylamine. 2-Dimethylaminocyclohexanone (117 g., 0.76 mole), prepared according to the procedure of Mannich and Braun,[16] was reduced by sodium borohydride (12.0 g., 0.32 mole) in 50% aqueous ethanol and gave 99 g. (85%) of *cis*- and *trans*-2-hydroxycyclohexylmethyldimethylamine, b.p. 97–120° (17–18 mm.), n_D^{20} 1.4670–1.4683 [lit.,[16] b.p. *ca.* 108° (13 mm.)].

trans-2-Hydroxycyclohexylmethyldimethylamine. According to the procedure of Mannich[17] the above mixture of *cis* and *trans* amino alcohols was converted in 92% yield to the corresponding benzoate ester hydrochloride, m.p. 178–180°. Repeated recrystallization from water led to pure *trans*-2-dimethylaminomethylcyclohexyl benzoate hydrochloride, m.p. 218–220° (lit., α-isomer m.p. 218–220°). Saponification[17] of 63.3 g. (0.213 mole) of the benzoate hydrochloride gave 28.9 g. (87%) of *trans*-2-hydroxycyclohexylmethyldimethylamine, b.p. 97–98° (13 mm.) n_D^{20} 1.4635 [lit.,[17] α-isomer, b.p. 96–97° (12 mm.)].

cis-2-Hydroxycyclohexylmethyldimethylamine. When the above residues of benzoate hydrochlorides melted below 180°, fractional crystallization from dry acetone gave pure *cis*-2-dimethylaminomethylcyclohexyl benzoate hydrochloride, m.p. 195–197° (lit.,[17] β-isomer, m.p. 196–197°). Saponification[17] of 67.6 g. (0.227 mole) of this ester gave 32.9 g. (92%) of *cis*-2-hydroxycyclohexylmethyldimethylamine, b.p. 110° (13 mm.), n_D^{20} 1.4731 (lit.,[17] β-isomer, b.p. 106–108° (12 mm.), m.p. 40–41°).

m-Acetamidophenol. A solution of 1.0 mole of *m*-aminophenol hydrochloride in 500 ml. of water was treated with 1.1 moles of acetic anhydride and 1.0 mole of sodium acetate at 50°. Upon cooling the reaction mixture, 59 g. of *m*-acetamidophenol, m.p. 146–148° (lit.,[18] m.p. 147–148°) was obtained. An additional 0.5 mole of acetic anhydride was added to the filtrate and the above process repeated. A second crop of *m*-acetamidophenol, 60 g., m.p. 146–148° was isolated for a total of 119 g. (79%).

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[10] The isolation from vapor phase chromatography gave only sufficient material for an infrared spectrum and n_D^{25} 1.4530. This eliminated the possibility of 1-methoxyhex-5-ene, $n_D^{12.5}$ 1.4147 (R. Dionneau, *Ann. chim. et phys.*[9], **3**, 266 (1915)). Since cyclohex-2-enol was the only other alcohol present, the assignment of 3-methoxycyclohex-1-ene is preferred over 4-methoxycyclohex-1-ene.

[11] In the report by A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953) the decomposition temperature of 145–160° at 11 mm. gave cyclohexene (62%) and dimethylaminocyclohexane (16%); however, the data above were obtained for pyrolysis at 117–130° and atmospheric pressure.

[12] D. Y. Curtin, R. D. Stolow, and W. Maya, *J. Am. Chem. Soc.*, **81**, 3330 (1959) reported identical values for the reaction of cyclohexyltrimethylammonium chloride and potassium *t*-butoxide in *t*-butyl alcohol.

[13] F. V. Brutcher, Jr., and H. J. Cenci, *Chem. & Ind. (London)*, 1625 (1957).

[14] R. B. Clayton, H. B. Henbest, and M. Smith, *J. Chem. Soc.*, 1982 (1957).

[15] All melting points and boiling points are uncorrected. The carbon, hydrogen analysis were determined by Midwest Microlabs Inc., Indianapolis, Ind. Infrared spectra were recorded on a Baird Associates infrared spectrophotometer by R. F. Love and C. Lynch. All vapor phase chromatography was carried out using the aerograph Model A-90 instrument. We wish to thank Dr. E. D. Holley and the Dow Chemical Co. for a generous sample of Dowex 2 × 7.5 (20–50 mesh) anion exchange resin used in these experiments.

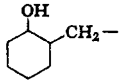
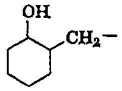
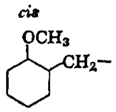
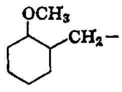
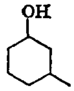
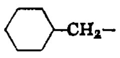
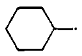
[16] C. Mannich and R. Braun, *Ber.*, **53B**, 1874 (1920).

[17] C. Mannich, *Arch. Pharm.*, **265**, 251 (1927).

[18] F. Reverdin and A. deLac, *Ber.*, **47**, 1537 (1914).

TABLE II

METHIODIDES $RN(CH_3)_3I^-$

R	Solvent	Crude Yield, %	M.P. Crude	M.P. Anal. sample	Iodine,[a] % Calcd.	Iodine,[a] % Found
 trans	A	95	143–144	144–145	42.42	42.44
 cis	A	98	198–200	198–200	42.42	42.45
 trans	A	—	126–127	136–137	40.54	40.45
 cis	B	—	230–231 dec.	230–231 dec.	40.54	40.59
 cis	A	98	192–193	192–193	44.51	44.46
	C	93	225–227	[b]	—	—
	A	90	267–268	267–268[c]	47.15	46.95

A = ethanol/ethyl acetate (1:10); B = ethyl acetate; C = ethyl ether. [a] Iodine analysis were by the Volhard procedure. [b] Lit.,[8] m.p. 226.5–227.5°. [c] Lit., m.p.[24] 277°, m.p.[25] 263°.

3-Acetamidocyclohexanol. Reduction according to the procedure of Billman and Buehler[19] converted *m*-acetamidophenol (25 g., 0.166 mole) in 75 ml. of absolute ethanol with 3 g. of W-7 Raney nickel[20] and 1350 p.s.i. of hydrogen at 175° to 23.9 g. (92%) of *cis*- and *trans*-3-acetamidocyclohexanol, m.p. 90–94° (lit.,[19] m.p. 95–98°).

cis- and trans-3-Aminocyclohexanol. A solution of 40 g. (0.255 mole) of 3-acetamidocyclohexanol and 20 g. (0.5 mole) of sodium hydroxide in 400 ml. of water was refluxed gently for 6 hr. under nitrogen. The dark red solution was continuously extracted with chloroform for 60 hr. After the chloroform was removed, distillation of the residue gave 17.9 g. (61%) of *cis* and *trans*-3-aminocyclohexanol, b.p. 118–122° (13 mm.) plus 10 g. of a high boiling residue (lit.,[9] *cis*-isomer, b.p. 128° (18 mm.), m.p. 70°; *trans*-isomer, b.p. 122° (18 mm.), m.p. 94°).

cis- and trans-3-Dimethylaminocyclohexanol. Employing the procedure described by Perrine[21] the reaction of 3-aminocyclohexanol (49.2 g., 0.43 mole), 90% formic acid (92 ml., 2.2 moles) and 36% formalin (86 g., 0.93 mole) gave 28.7 g. (47%) of 3-dimethylaminocyclohexanol, b.p. 114–118° (13 mm.) (lit.,[21] b.p. 66° (0.05 mm.), n_D^{25} 1.4843). A continuous ether extraction of the aqueous layer afforded an additional 4.3 g. (7%) of product, b.p. 120–122° (17 mm.), n_D^{20} 1.4855.

cis- and trans-3-Dimethylaminocyclohexyl benzoate hydrochloride. Separation of the cis isomer. To a chilled solution of 28.7 g. (0.201 mole) of *cis* and *trans*-3-dimethylaminocyclohexanol in 25 ml. of dry chloroform was added dropwise 30 g. (0.22 mole) of benzoyl chloride. After standing overnight, the solid was filtered, washed with ether and dried. The yield of *cis*- and *trans*-3-dimethylaminocyclohexyl benzoate hydrochloride, m.p. 160–200° (lit.,[22] *cis* isomer m.p. 229–230°) was 55 g. (99%).

The mixture of benzoate ester hydrochlorides was recrystallized from absolute ethanol and gave 33.8 g. (62% recovery) of *cis* rich material, m.p. 210–222°. Recrystallization of 38 g. of this substance from absolute ethanol–ethyl acetate (1:1) gave 31 g. (81% recovery) of nearly pure *cis*-3-dimethylaminocyclohexyl benzoate hydrochloride, m.p. 225–227°. Further recrystallization failed to raise the melting point.

cis-3-Dimethylaminocyclohexanol. Saponification of 31.0 g. (0.11 mole) of *cis*-3-dimethylaminocyclohexyl benzoate hydrochloride, m.p. 225–227°, with 30 g. (0.54 mole) of potassium hydroxide in 200 ml. of water and 150 ml. of 95% ethanol (refluxed 4 hr. under nitrogen) gave after distillation 13 g. (81%) of *cis*-3-dimethylaminocyclohexanol, b.p. 130–131° (27 mm.), n_D^{20} 1.4852 (lit., *cis*-isomer, b.p.[9] 130° (20 mm.); b.p.[22] 126–127° (22 mm.), n_D^{20} 1.4846).

Cyclohexylmethyldimethylamine. This compound was prepared by the procedure of Cope and Ciganek.[23]

Preparation of methiodides. These compounds were obtained according to standard procedures. Analytical samples were prepared by recrystallization to constant melting point from absolute ethanol and/or ethyl acetate. Table II

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[19] J. H. Billman and J. A. Buehler, *J. Am. Chem. Soc.*, **75**, 1345 (1953).

[20] H. Adkins and H. R. Billica, *J. Am. Chem. Soc.*, **70**, 695 (1948).

[21] T. D. Perrine, *J. Org. Chem.*, **16**, 1303 (1951).

[22] H. Heckel and R. Adams, *J. Am. Chem. Soc.*, **47**, 1712 (1925).

[23] A. C. Cope and E. Ciganek, *Org. Syntheses*, **39**, 19 (1959).

[24] A. Skita and H. Rolfe, *Ber.*, **53**, 1250 (1920).

[25] G. Breuer and J. Schnitzer, *Monatsch.*, **68**, 301 (1936).

TABLE III

CONDITIONS FOR DECOMPOSITIONS

Compound	Mmoles	Dec. Temp.	Time, Hr.	Final Temp.[a]	Total Base Titer, %[b]
		METHOD A			
cis-I B = OH⁻	64	130	1	160	99
trans-I B = OH⁻	133	123–140	3	165	99
cis-III B = OH⁻	50	120–130	2	150	98
IV B = OH⁻	150	117–130	3	140	99
		METHOD B			
Compound	Mmoles	*t*-C_4H_9OK, Mmoles	*t*-C_4H_9OH, G.	Temp.	Time, Hr.
cis-I B = I⁻	29.3	35.7	32	81–84	45
trans-I B = I⁻	112	135	116	80–83	47
cis-III B = I⁻	52.5	75.7	65	82–83	43
		METHOD C			
II B = I⁻	18.2	29.2	28	82–84	47
IV B = I⁻	25.1	33.8	32	83–85	48

[a] Temperature at conclusion of reaction. [b] The sum of evolved amines and residue in the decomposition flask.

lists the reaction medium, yields, and physical constants of the methiodides.

General procedures for decompositions. The preparation of quaternary hydroxides, the apparatus, and work-up procedures for Methods A, B, and C were used as described in the previous report.[4] Conditions for the decompositions are recorded in Table III.

Identification of products.' *cis-2-Hydroxycyclohexylmethyltrimethylammonium t-butoxide.* The yields of products appear in Table I. Trimethylamine was characterized as the picrate, m.p. 216° (lit.,[26] m.p. 216°) and the 0.62 g. (7.1 mmoles, 24%) of methyl *t*-butyl ether which collected in Flask IV was identified by n_{D}^{20} 1.3702 (lit.,[27] n_{D}^{20} 1.3690). After the excess potassium *t*-butoxide was neutralized with 2 g. of ethereal hydrogen chloride (8 mmoles of hydrogen chloride), fractional distillation removed the solvent and gave fraction I, b.p. up to 66° (52–54 mm.) collected in an acetone–Dry Ice trap plus a residue, fraction II. A second distillation removed the *t*-butyl alcohol in fraction I and the residue was analyzed and fractions isolated by vapor phase chromatography on a 5-ft. ucon "polar" column at 126° with a helium flow rate of 40 ml./min. 2-Methylenecyclohexyl methyl ether, retention time 2.8 min., n_{D}^{20} 1.4515 was characterized by an infrared spectrum and analysis.

Anal. Calcd. for $C_8H_{14}O$: C 75.98; H, 11.14. Found: C, 75.85; H, 11.31.

cis-7-Oxabicyclo[4.2.0]octane, retention time 6.7 min. was characterized by its infrared spectrum. From an earlier experiment in which the yield of the above oxetane was 13%, an analytical sample was obtained by vapor phase chromatography.

Anal. Calcd. for $C_7H_{12}O$: C, 74.90; H, 10.80. Found: C, 74.77, 74.72; H, 10.80; 11.00.

After acidification of the above residue fraction II, a low boiling neutral mixture, b.p. 34–87° (13 mm.) and a high boiling neutral fraction b.p. 90–180° (1.4 mm.) were isolated. The low boiling fraction was analyzed by vapor phase chromatography under the above conditions, except at 115°, and contained 2-methylenecyclohexyl methyl ether retention time 3.5 min., and 2-methylenecyclohexanol, retention time 17.7 min. which had an infrared spectrum identical with that of the sample characterized under *cis-I*, B = OH⁻. The basic material in the residue, fraction II, was analyzed by vapor phase chromatography on a 10 ft. silicone oil column at 175° with a flow rate of 40 ml. helium/min. The components isolated were *cis*-2-dimethylaminomethylcyclohexyl methyl ether, retention time 16.5 min., b.p. 90–92° (13 mm.) methiodide, m.p. 136–137° (see Table II) and *cis*-2-hydroxycyclohexylmethyldimethylamine, retention time 22.3 min., m.p. 38–39° (lit.,[17] m.p. 40–41°) which had an infrared spectrum identical to an authentic sample.

Identification and stereochemistry of cis-7-oxabicyclo[4.2.0]-octane. Preliminary work established that vapor phase chromatography on a 5 ft. ucon "polar" column at 115° and a flow rate of 40 ml. of helium/min. could effect the separation of 7-oxabicyclo[4.2.0]octane, retention time 7.8 min.; *cis*-2-methylcyclohexanol, retention time 12.3 min.; and 2-methylenecyclohexanol, retention time 17.8 min. After 0.50 g. of the reaction mixture containing 2-methylenecyclohexyl methyl ether, 7-oxabicyclo[4.2.0]octane and 2-methylenecyclohexanol was reduced with lithium aluminum hydride and processed in the usual manner to give 0.30 g., b.p. 37–75° (13 mm.), vapor phase chromatography under the conditions above showed a marked decrease in the oxetane peak, retention time 7.3 min. and the appearance of a new compound, retention time 11.7 min. The new compound was isolated and had an identical infrared spectrum as authentic *cis*-2-methylcyclohexanol.[28] Also this material gave only one peak, retention time 6.0 min., when chromatographed on a 10-ft. glycerol column at 137° with a flow rate of 48 ml. helium/min. The authentic material under these conditions had two peaks at 6.3 min. and 7.8 min., corresponding to the *cis-* and *trans*-2-methylcyclohexanols, respectively.

cis-2-Hydroxycyclohexylmethyltrimethylammonium hydroxide. The yields of products are recorded in Table I. *cis*-2-Hydroxycyclohexylmethyldimethylamine was isolated and identified as the methiodide, m.p. 197–198° (Table II, m.p. 198–200°); while the corresponding methyl ether *cis*-VI, b.p. *ca.* 100° (13 mm.) behaved the same as the previous sample on vapor phase chromatography and gave a methiodide, m.p. 230–231° dec. The neutral materials were separated, analyzed, and identified by vapor phase chromatography on a 5 ft. ucon "polar" column at 178° and a flow rate of 40 ml. of helium/min. In addition 2-methylenecyclohexanol, b.p. 77–79° (17 mm.) gave an α-naphthylurethan, m.p. 125–126° (lit.,[29] b.p. 81–85° (27 mm.), α-naphthylurethan, m.p. 126.4–127.5°).

trans-2-Hydroxycyclohexylmethyltrimethylammonium bases. Table I lists the yields of products. Trimethylamine was converted to a picrate, m.p. 215–216° (lit.,[26] m.p. 216°); while the neutral compounds 2-methylenecyclohexanol, b.p. 80–85° (13 mm.), n_{D}^{20} 1.4838 (lit.,[30] b.p. 82–84° (13 mm.), n_{D}^{20}

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(26) M. Delephine, *Ann. Chim. et phys.*, [7] **8**, 452 (1896).

(27) W. T. Olson, *et al.*, *J. Am. Chem. Soc.*, 69, 2453 (1947).

(28) We wish to thank Dr. E. L. Eliel for making an authentic sample of *cis*-2-methylcyclohexanol available to us.

(29) A. S. Dreiding and J. A. Hartman, *J. Am. Chem. Soc.*, **75**, 939 (1953).

(30) M. Mousseron, F. Winternits, and J. Jullerien, *Bull. soc. chim., France*, 80 (1947).

1.4843), and 2-methylenecyclohexyl methyl ether were analyzed by vapor phase chromatography on a 5 ft. ucon "polar" column at 155° and a flow rate of 40 ml. of helium/min. In the *t*-butoxide run a high boiling residue, b.p. 155–170° (1.8 mm.) was obtained and gave a small amount of a brick red 2,4-dinitrophenyl-hydrazone, m.p. 190–193° in quantity insufficient for analysis. The high boiling bases in the pyrolysis of the hydroxide were distilled and analyzed by refractive index and by vapor phase chromatography on a 10-ft. mineral oil column at 175° and a flow rate of 38 ml. of helium/min. *trans* - 2 - Hydroxycyclohexylmethyldimethylamine, retention time 39 min. and the corresponding *trans* methyl ether, retention time 29.8 min. were identified by comparison of physical constants and infrared spectra to those of authentic samples.

Cyclohexylmethyltrimethylammonium t-butoxide. Cyclohexylmethyldimethylamine was isolated and identified as the methiodide, m.p. 223–225° (see Table II) and the condensate in the cold trap was mainly methyl *t*-butyl ether but did decolorize bromine in methylene chloride.

cis-3-Hydroxycyclohexyltrimethylammonium bases. In the decomposition of the hydroxide trimethylamine (58%) was characterized as the picrate and the base in Flask I was *cis*-3-hydroxycyclohexyldimethylamine (11.5% by titration, 3% isolated) which gave a methiodide, m.p. 193–195°. From the reaction vessel crude *cis*-3-hydroxycyclohexyldimethylamine, b.p. 114–116° (13 mm.), n_D^{20} 1.4870 was analyzed by vapor phase chromatography on a 5-ft. ucon "polar" column at 178° and a flow rate of 30–40 ml. helium/min. and contained cyclohex-2-enol, retention time 5.2 min. (2 mmoles, 4%) along with the above amino alcohol, retention time 11.7 min. (8.2 mmoles, 16%), methiodide, m.p. 193–196°. The neutral mixture from Flask I was analyzed by vapor phase chromatography under the above conditions but at 120° and samples collected for identification and characterization. Hex-5-enol (2.4%), retention time 2.7 min. gave a yellow 2,4-dinitrophenylhydrazone, m.p. 94–95° (lit.,[13] m.p. 96°); the structure of 3-methoxycyclohexene (9%), retention time 3.2 min., n_D^{25} 1.4530 was based on its infrared spectrum. The third peak, retention time 9.6 min. gave an α-naphthylurethan, m.p. 65.5–66.5° which excludes cyclohex-3-enol (lit.,[31] cyclohex-3-enol α-naphthylurethan, m.p. 127°) and was assigned the structure of hex-5 enol (4%).

Anal. Calcd. for $C_{17}H_{19}NO_2$: C, 57.85; H, 7.11. Found: C, 75.91, 75.74; H, 7.44, 7.37.

Cyclohex-2-enol was identified by its infrared spectrum and α-naphthylurethan, m.p. 155–156.5° (lit.,[32] m.p. 156°). Proof that the first peak was hex-5-enal and the third peak was hex-5-ene-1-ol was obtained by reducing a sample of the above mixture with lithium aluminum hydride; and after isolation of the mixture, vapor phase chromatography under conditions identical to the analysis of the mixture before reduction showed the disappearance of the first peak (hex-5-enal) and an enrichment of the third peak (hex-5-ene-1-ol) equivalent to the initial amount of the first peak. The neutral component (38%) in the reaction flask gave a brick red 2,4-dinitrophenylhydrazone of 2-(but-3-enyl)-octa-2,7-dienal, m.p. 115–116° (lit.,[13,14] m.p. 116–117°; m.p. 115–116°).

With *t*-butoxide as base trimethylamine (92%) was characterized as the picrate, m.p. 217° and crude *cis*-3-hydroxycyclohexyldimethylamine (4%), b.p. 110–120° (18–20 mm.), methiodide, m.p. 181–185° was analyzed by vapor phase chromatography on a 10-ft. silicone oil column at 175° and a flow rate of 40 ml. of helium/min. which showed 2% of a contaminant which may be the corresponding methyl ether. The volatile neutral components were analyzed and identified by vapor phase chromatography: 3-methoxycyclohexene (1.2%), hex-5-enol (1.3%) and cyclohex-2-enol (1%); while the high boiling residue (70% as the aldol product of hex-5-enal) distilled at 118–205° (1.5–2.0 mm.).

Cyclohexyltrimethylammonium bases. In both the hydroxide and *t*-butoxide reactions trimethylamine (39% and 93%, respectively) was identified by its picrate, m.p. 215° and cyclohexene (21% and 6.4%, respectively), b.p. 82°, n_D^{20} 1.4450 (lit.,[33] b.p. 83°, n_D^{20} 1.4467) was analyzed by vapor phase chromatography on a 5-ft. ucon "polar" column at 62° on a flow rate 38–40 ml. of helium/min.; the infrared spectrum of this product was identical with an authentic sample. From the hydroxide decomposition crude cyclohexyldimethylamine (57%) upon distillation gave pure amine, b.p. 154–155°, n_D^{20} 1.4543 (authentic material, b.p. 155–156°, n_D^{20} 1.4550), methiodide, m.p. 266°; while the *t*-butoxide run gave 93% amine by titration and 81% isolated as the methiodide, m.p. 267°.

trans-2-Dimethylaminomethylcyclohexyl methyl ether. According to the procedure used to prepare 2,2-dimethyl-3-dimethylamino-1-methoxypropane,[4] potassium (3.5 g., 0.09 g.-atom), *trans*-2-hydroxycyclohexylmethyldimethylamine (8.95 g., 0.057 mole) and methyl chloride in toluene gave 3.25 g. of crude ether, b.p. 92–96° (13 mm.), n_D^{20} 1.4550–1.4555. Redistillation produced 1.0 g. of product, b.p. 90–93° (14 mm.), n_D^{20} 1.4557 which was subjected to vapor phase chromatography on a 10-ft. silicone oil column at 195° and a flow rate of 20 ml. of helium/min. and contained *trans*-2-dimethylaminomethylcyclohexyl methyl ether (85%) retention time 18.2 min. and *trans*-2-hydroxycyclohexyldimethylamine (15%), retention time 22 min. A sample of ether collected from vapor phase chromatography was distilled and gave pure *trans*-2-dimethylaminomethylcyclohexyl methyl ether, b.p. 93° (17 mm.) n_D^{21} 1.4528.

Anal. Calcd. for $C_{10}H_{21}NO$: C, 70.17; H, 12.36. Found: C, 70.08, 70.26; H, 12.39, 12.20.

The remainder was converted to *trans*-2-methoxycyclohexylmethyltrimethylammonium iodide, m.p. 136–137° (analysis reported in Table II).

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(31) H. Lindermann and H. Baumann, *Ann.*, **477**, 78 (1929).

(32) R. Willstatter and E. Sonnenfeld, *Ber.*, **46**, 2957 (1913).

(33) W. I. Waterman and H. A. Van Western, *Rec. trav. chim.*, **48**, 637 (1929).