was extracted with methanol and the extract was esterified with excess diazomethane. From 5.7 mmoles of IIa there were obtained, by gas chromatographic analysis, 1.41 mmoles of *trans*-1,2-dicarbomethoxycyclopentane, 0.70 mmoles of *cis*-1,2-dicarbomethoxycyclopentane, and 0.48 mmole of 1,5-dicarbomethoxy-1-pentene. The total yield is 45.4%. Individual yields were 24.8% of the *trans*-coupled, 12.3% of the *cis*-coupled, and 8.4% of the unsaturated dimethyl esters.

The Cyclization of N-Chloro-4-alkylpiperidines[1]

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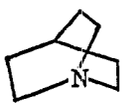
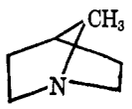
N-Chloro-4-ethylpiperidine and N-chloro-3-methyl-4-ethylpiperidine when cyclized by the Hofmann–Loeffler reaction gave a mixture of the respective quinuclidines and 1-azabicyclo[2.2.1]heptanes. N-Chloro-4-propylpiperidine in the same reaction gave 2-methylquinuclidine and N-chloro-4-methylpiperidine gave 1-azabicyclo[2.2.1]heptane. The N-chloroamines from 2-methyl- and 3-methylpiperidine gave no bicyclic amines.

The cyclization of N-halo-4-ethylpiperidines by the Hofmann–Loeffler reaction has been reported to yield quinuclidine (I) in one investigation[2] and 7-methyl-1-azabicyclo[2.2.1]heptane (II) in another study.[3]



I



II

In order to resolve these discrepancies the cyclization of N-chloro derivatives of 4-ethylpiperidine, 4-propylpiperidine, and 4-ethyl-3-methylpiperidine was reinvestigated and the products were examined by gas chromatography. In addition the study was extended to the cyclization of the N-chloro derivatives of the isomeric methylpiperidines. The amines formed were isolated as picrates and hydrochlorides. The yields of picrates and polymers isolated are given in Table I.

TABLE I

YIELDS OF PICRATES AND NONSTEAM VOLATILE MATERIALS IN CYCLIZATION OF N-CHLORO-4-ALKYLPIPERIDINES

Piperidine (g)	Temp, °C	Yield of picrates, g	Yield, %	Yield of nonsteam volatile material, g
4-Ethyl (10)	0	2.73	21.36	1.76
	20	2.41	18.66	1.93
	55	1.88	14.71	1.80
4-Methyl (20)	0–5	1.06	3.80	1.22
4-Propyl (10)	0–5	1.43	12.0	...
4-Ethyl-3-methyl (10)	0	2.78	21.58	...

The cyclizations in all cases except 2-methyl- and 3-methylpiperidines produced bicyclic nitrogen compounds. Mixtures of amines were formed in each cyclization and could be separated by gas chromatography on a column packed with base-washed Chromosorb P as a solid support and Tetronic 701 as the liquid phase using an ionization detector with a nitrogen–hydrogen mixture or argon as a carrier gas. The reaction products when present in large enough amounts were collected using a preparation size column. Separation of the products by ordinary fractional distillation was not successful.

Cyclization of N-chloro-4-ethylpiperidine at 0, 20, and 55° produced mixtures of quinuclidine (I) and 7-methyl-1-azabicyclo[2.2.1]heptane (II). Approximately equal amounts of the two compounds were formed at 0 and 55°. At the intermediate temperature of 20° the ratio of quinclidine (I) to 7-methyl-1-azabicyclo[2.2.1]heptane (II) was 60:40.

The quinuclidine (I) and 7-methyl-1-azabicyclo[2.2.1]heptane (II) were identified by comparison of their retention times and nmr spectra with samples prepared from 4-(2-hydroxyethyl)piperidine[4] and 4-(1-hydroxyethyl)piperidine, respectively. The mixture of picrates from these compounds upon repeated crystallizations from acetone–ligroin gave the pure quinuclidine derivative.

In the irradiation of N-chloro-4-ethylpiperidine at 0° a third component appeared upon analysis by gas chromatography in insufficient amounts to be characterized. The formation of this compound only at the lower temperature suggested that it was probably 3,4,5,6-tetrahydro-4-ethylpyridine.

Ring closure of N-chloro-4-ethyl-3-methylpiperidine at 0° produced 3-methylquinuclidine and 3,7-dimethyl-1-azabicyclo[2.2.1]heptane in equal amounts. The product with the smaller retention time was identified as 3,7-dimethyl-1-azabicyclo[2.2.1]heptane by its nmr spectrum. The compound, however, was obtained in amounts too small to be characterized. 3-Methylquinuclidine was identified by its nmr spectrum and by its picrate.[5]

The cyclization of N-chloro-4-propylpiperidine gave six products according to gas chromatographic analysis; only one was identified positively. The first peak which comprised 70% of the products was obtained pure by preparative gas chromatography and was identified by its nmr spectrum and picrate[6] as 2-methylquinuclidine.

The fifth component was the only product that could be separated in large enough amounts by preparative gas chromatography for spectral analysis. The infrared and nmr spectra indicated the presence of an imine (CH=N) group, and the nmr spectrum showed a methyl triplet. These data definitely rule out 7-

(1) Abstracted in part from the Ph.D. Thesis, June 1965, of T. C. Wilkinson.

(2) S. Wawzonek, M. F. Nelson, Jr., and P. J. Thelan, *J. Am. Chem. Soc.*, **73**, 2806 (1951).

(3) R. Lukes and M. Ferles, *Collection Czech. Chem. Commun.*, **20**, 1227 (1955).

(4) S. Wawzonek, M. F. Nelson, Jr., and P. J. Thelen, *J. Am. Chem. Soc.*, **74**, 2894 (1952).

(5) V. Prelog and E. Cerkovnikov, *Ann.*, **525**, 292 (1936).

(6) J. Meisenheimer, *ibid.*, **420**, 196 (1920).

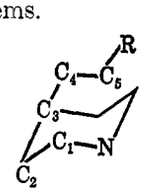
ethyl-1-azabicyclo[2.2.1]heptane as a possibility and favor 4-propyl-3,4,5,6-tetrahydropyridine as the structure for this compound. Further evidence against the former compound was the retention time; the azabicycloheptanes in general show an earlier retention time than that of the corresponding quinuclidine.

N-Chloro-4-methylpiperidine, when cyclized, produced three compounds in a total yield of 3.8%. 1-Azabicyclo[2.2.1]heptane was identified by comparison of its retention time and nmr spectrum with a sample prepared from 4-hydroxymethylpiperidine. Component B could not be obtained in sufficient amount to identify satisfactorily; the structure which best fit the nmr spectrum was 4-methylenepiperidine which may not have been removed completely by the Hinsberg separation. The possibility of 4-methyl-1-azabicyclo[2.0.2]hexane was not eliminated since the sample used was too dilute to obtain an accurate integration line for the nmr spectrum.

Component C was identified as 4-methyl-3,4,5,6-tetrahydropyridine by comparison of the vpc retention time with the compound formed in the reaction of potassium ethoxide on N-chloro-4-methylpiperidine. Further characterization of this compound was not pursued further since compounds of this type dimerize in a manner similar to that reported for 3,4,5,6-tetrahydropyridine.[7]

Irradiation of N-chloro-2-methylpiperidine and N-chloro-3-methylpiperidine produced no tertiary amines.

A simple comparison of the yields of 1-azabicycloalkanes in these reactions does not necessarily give a true picture of the ease of formation of the intermediate halides in these systems.



Irradiation can produce a halide with a halogen on either the C-4 or C-5 atom. Basification of the reaction mixture would cause dehydrohalogenation and yield a bicyclic amine or a polymeric product. It is reported that good yields are obtained in the cyclization of 4-halomethylpiperidines to 1-azabicyclo[2.2.1]-heptanes in spite of the strain involved.[8,9] The amount of nonvolatile amine left after steam distillation would be a fair estimate of the amount of polymerization that occurred. A summation of the amount of bicyclic product and the nonvolatile products would be therefore a better estimate of the amount of alkyl halide formed. Such a comparison indicates that the amount of C-4 halogenation of 4-ethylpiperidine is greater than the corresponding C-4 halogenation of 4-methylpiperidine. These results are in agreement with the free-radical mechanism of the reaction; secondary free radicals are more stable than primary.

A similar comparison of the yields of quinuclidine and 1-azabicyclo[2.2.1]heptane indicates that C-5 halogenation of 4-ethylpiperidine occurs more readily than the C-4 halogenation of 4-methylpiperidine. Both halogenations would involve the formation of a primary free radical but the former would go through a seven-membered CHN^+ transition state, whereas the latter involves a six-membered transition state. This factor is apparently all important in these systems since the irradiation of N-chloro-4-pyropylpiperidine yields no 1-azabicycloheptane even though hydrogen abstractions at C-4 and C-5 would both yield secondary free radicals.

The preference of the 5 carbon over the 4 carbon for hydrogen abstraction in 4-alkylpiperidines is borne out by examination of Dreiding models for the 4-alkylpiperidines. These models show that the CHN^+ angle for the hydrogen transfer is 180° for the seven-membered ring transition state involving C-5 and 128° for the analogous six-membered ring involving C-4. The carbon–nitrogen interatomic distances are 1.80 and 2.53 A for the C-5 and C-4 carbon atoms, respectively, when the piperidine ring is in the boat form. The limiting factors for aminium radical abstraction of a hydrogen proposed by Cory and Hertler[10] require a linear transition state and a minimum nonbonded hydrogen interaction. These conditions would predict the formation of the C-5 radical in preference to a C-4 radical for the 4-alkylpiperidines. This ease of formation of radicals is opposite to that found for noncyclic secondary amines.[11]

The involvement of C-1 and C-2 would give smaller angles in the transition state and would be prohibited in these cyclic systems. This fact was verified by a study of the irradiation of N-chloro-2-methyl- and N-chloro-3-ethylpiperidine; no tertiary amines were formed.

The unsaturated products formed may arise by a pathway similar to that proposed for the formation of butylamine from the irradiation of N-chlorodibutylamine[12] or by a simple 1,2-dehydrohalogenation of unreacted N-chloroamine when the reaction mixture is basified; 3,4,5,6-tetrahydropyridine has been prepared in this manner by the action of base on N-chloropiperidine.[7] The possibility that other tetrahydropyridines are formed in this reaction cannot be eliminated since these compounds should be removed by the Hinsberg separation.

The discrepancy in the literature[2,3] about the products formed from the cyclization of N-halo-4-ethylpiperidines was caused probably by the use of different isolation techniques. The mixture of bicyclic amines when treated with picric acid gave a mixture of picrates which upon repeated recrystallizations from a mixture of acetone and ligroin gave the pure quinuclidine derivative as reported.[2] The purity of this derivative was verified by vpc after decomposition of the picrate with base. Concentration of the filtrates followed by fractional crystallization gave a more soluble picrate which contained 7-methyl-1-azabicyclo[2.2.1]heptane (II) as the major component (90% by vpc).

The report for the sole formation of 7-methyl-1-azabicyclo[2.2.1]heptane[3] may have been caused by the greater volatility of quinuclidine with ether than that of 7-methyl-1-azabicyclo[2.2.1]heptane (II). A 50:50 mixture of the two compounds in ether when stored in a capped bottle for 60 days lost more than

(7) C. Schopf, A. Komzak, F. Brown, and E. Jacobi, *Ann.*, **559**, 1 (1948).
(8) G. Clemo and T. P. Metcalf, *J. Chem. Soc.*, 1523 (1937).
(9) G. Clemo and V. Prelog, *ibid.*, 400 (1938).
(10) E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960)
(11) S. Wawzonek and T. P. Culbertson, *ibid.*, **82**, 441 (1960).
(12) S. Wawzonek and J. D. Nordstrom, *J. Org. Chem.*, **27**, 3726 (1962).

half of the ether solution. Analysis by vpc of the remaining solution gave peaks for 7-methyl-1-azabicyclo-[2.2.1]heptane (II) and quinuclidine (I) in a ratio of 71:29. Quinuclidine which has a longer retention time in vpc, evaporated faster with ether. A work-up of the reaction mixture by extraction with ether followed by a partial evaporation of the ether could have given mainly 7-methyl-1-azabicyclo[2.2.1]heptane as reported.[3]

Experimental Section[13]

Column Preparation for Gas Chromatography.[14]—Thirty grams of Chromosorb P was mixed with 5 ml of 0.5 *N* alcoholic potassium hydroxide and the alcohol was removed at reduced pressure. To this material Tetronic 701 (3 g) and enough acetone to make a slurry was added. The mixture after removing the acetone under reduced pressure was packed into 6- and 10-ft columns. The columns were conditioned for 8 hr at 150° with argon as a carrier gas.

4-(2-Hydroxyethyl)piperidine.—A mixture of freshly distilled commercial 4-(2-hydroxyethyl)pyridine (30 g), glacial acetic acid (250 ml), and platinum oxide catalyst (3 g) was treated with hydrogen at 50 psi until the absorption of hydrogen ceased. Removal of the catalyst and excess acetic acid gave a semisolid which was neutralized with cold 40% sodium hydroxide. Extraction with ether using a liquid extractor gave an oil which distilled at 118-124° (2 mm), lit.[4] 131–136° (10 mm): yield 26 g; nmr ($CDCl_3$), δ 1.40 multiplet (CH_2), 2.50 and 2.85 overlapping multiplets (NCH_2), 3.48 broad singlet (CH), 3.99 broad singlet (OCH_2), no vinyl protons; infrared (film), 3.0 (br, s), 3.4 (s), 6.9 (m), 7.6 (m), 8.72 (m), 9.45 μ (s).

4-(1-Hydroxyethyl)piperidine.—A mixture of 4-acetylpyridine (20 g), glacial acetic acid (200 ml), and 10% palladium on charcoal (6 g) was hydrogenated at 50 psi with external heating. Removal of the catalyst was followed by neutralization with 5 *N* sodium hydroxide solution to a pH of 13–14 and extraction with ether in a liquid-liquid extractor for 2 days. The ether solution after drying over potassium carbonate gave an extremely hygroscopic white solid (21.4 g): mp 63-64°; nmr ($CDCl_3$), δ 1.15 doublet (J = 6.5 cps) (CH_3), 2.32 singlet (OH and NH), no vinyl protons.

Anal. Calcd for $C_7H_{15}NO$: C, 65.07; H, 11.70; N, 10.84. Found: C, 64.75; H, 11.74; N, 10.54.

4-Hydroxymethylpiperidine.—Solid 4-piperidine carboxylic acid (50 g) was added in small amounts to a slurry of lithium aluminum hydride (22.9 g) in tetrahydrofuran (1500 ml) and the mixture was refluxed for 24 hr. Decomposition of the reaction mixture with 10% sulfuric acid was followed by filtration and extraction with ether. The acid layer was neutralized and extracted with ether in a liquid-liquid extractor for 7 days. Removal of the ether gave a light yellow oil which solidified upon drying under reduced pressure, yield 7.63 g. Purification by sublimation gave a white solid, mp 61–62° (sealed tube).

Anal. Calcd for $C_6H_{13}NO$: C, 62.57; H, 11.38; N, 12.16. Found: C, 62.45; H, 11.20; N, 12.12.

Quinuclidine (I) was prepared from 4-(2-hydroxyethyl)piperidine by the directions reported previously.[4] Sublimation gave a sample melting at 158–159° (sealed tube): nmr ($CDCl_3$), δ 1.52 multiplet (CH_2), 2.89 multiplet (NCH_2); infrared (CCl_4), 3.39 (s), 3.45 (s), 6.88 (m), 7.59 (m), 9.45 (s), 10.05 (w), 10.3 μ (w).

7-Methyl-1-azabicyclo[2.2.1]heptane. (II).—4-(1-Hydroxyethyl)piperidine (20.2 g) was refluxed with 100 ml of 48% hydrobromic acid for 16 hr. The resulting solution was added dropwise to a rapidly stirred solution of saturated potassium carbonate. Extraction with chloroform gave a colorless liquid: bp 146–150°, lit.[5,15] bp 135–137°; yield 4.3 g; nmr ($CDCl_3$), δ 1.07 (J = 8 cps) doublet (CH_3), no vinyl protons.

1-Azabicyclo[2.2.1]heptane.—4-Hydroxymethylpiperidine was converted to 1-azabicyclo[2.2.1]heptane by the procedure used for the 7-methyl derivative. The picrate when recrystallized from an ether–alcohol mixture melted at 285° (lit.[6] 285°): nmr ($CDCl_3$), δ 1.42 and 2.66, no NH peak.

Cyclization of N-Chloro-4-alkylpiperidines.—N-Chloro-4-alkylpiperidines were prepared and irradiated in sulfuric acid according to previous directions.[2] The steam distillate after the Hinsberg separation was divided into two equal parts. One part was converted into picrates and the other part was evaporated and gave the hydrochlorides of the amines. Decomposition of the picrates was carried out with 15% hydrochloric acid in the presence of nitrobenzene. The resulting amine hydrochlorides were decomposed in water under ether with solid potassium hydroxide and the ether solutions were examined by gas chromatography.

A. N-Chloro-4-ethylpiperidine.—Irradiations were performed at 0, 20, and 55° for 6 hr. The yields of picrates based on 90% conversion to the N-haloamine are given in Table I.

The resulting crude picrates from the mixture of tertiary amines had melting points of 268–271, 270–274, and 265–270° for irradiation reactions at 0, 20, and 55°, respectively. Repeated recrystallization from an acetone–ligroin (bp 60–100°) mixture gave a picrate with a melting point of 275–276°. Gas chromatographic analysis of the amine liberated indicated that it was pure quinuclidine. Concentration of the filtrates from the recrystallization followed by fractional crystallization gave a more soluble picrate. Analysis of the amine liberated by vpc gave a ratio of 7-methyl-1-azabicyclo[2.2.1]heptane:quinuclidine of 9:1.

Analysis of the amines liberated from the hydrochlorides for the 0° irradiated solution was carried out on a 6-ft column with a diameter of 0.25 in. at 100° using argon at 20 psi as a carrier gas with the strontium 90 detector. The detector cell temperature was 120–165° and the flash heater temperature was 123–170°. The results were three peaks with retention times of 1.2, 3, and 4 min, respectively, corresponding to component A, 7-methyl-1-azabicyclo[2.2.1]heptane (II), and quinuclidine (I) in the ratio of 10.2:46.2:43.6. Using a preparative column gave sufficient amounts of 7-methyl-1-azabicyclo[2.2.1]heptane (II) and quinuclidine (I) for identification with known samples by infrared and nmr analyses. Component A could not be collected in large enough amounts to be identified.

Irradiation at 20 and 55° gave only 7-methyl-1-azabicyclo-[2.2.1]heptane (II) and quinuclidine (I) in the ratio of 39.6:60.4 at 20° and 48:52 at 55°. No component A was formed at the higher temperatures.

B. N-Chloro-4-methylpiperidine.—Irradiation at 0–5° for 8 hr gave a mixture of amines which was analyzed on a 10-ft column, $^3/_8$ in. in diameter, using hydrogen (17 cc/min) and nitrogen (8–9 psi) as a carrier gas and a hydrogen flame detector. Other conditions for the analysis were the same as given earlier. The results were three peaks with retention times of 3.5, 16.5, and 22.5 min, respectively, corresponding to component B, C, and 1-azabicyclo[2.2.1]heptane in the ratio of 20.8:38.7:40.5. Using a preparative column sufficient amounts of these compounds were collected for nmr and infrared spectral studies.

Component B: nmr ($CDCl_3$), δ 1.72 broad singlet, poorly resolved triplet centered at 2.20, 2.90 multiplet, 4.83 doublet (J = 8.0 cps); infrared spectrum (CCl_4), 3.31 (s), 6.25 (w), 6.83 (m), 7.24 (m), 11.26 μ (s).

Component C: nmr ($CDCl_3$), δ 0.97 doublet (J = 5 cps) (CH_3), 1.60 multiplet (CH_2), 2.56 (J = 13 cps), 2.75 (J = 10 cps) overlapping doublets (CHN), 3.27 rounded area, 7.42 singlet (=CH); infrared spectrum (CCl_4), 3.49 (s), 6.55 (w), 6.85 (s), 7.60 (s), 8.7 (m), 9.95 (m), 10.25 μ (s).

The retention time for this compound agreed with that obtained for the product formed by the action of alkali on N-chloro-4-methylpiperidine and points to the presence of 3,4,5,6-tetrahydro-4-methylpyridine.

The 1-azabicyclo[2.2.1]heptane had the same retention time, infrared, and nmr spectra as a sample synthesized from 4-hydroxymethylpiperidine.

C. N-Chloro-4-propylpiperidine.—Irradiation at 0–5° for 16 hr gave a mixture of amines which showed upon vpc, using conditions similar to those described for the 4-methyl compound, two major peaks and four minor peaks in a ratio of 69.7:0.9:3.8:0.1:22.5:3.1. The first peak with a retention time of 48

(13) Melting points are corrected and boiling points are not. Gas chromatographic analyses were carried out with a Barber–Coleman Model 10. Infrared spectra were recorded on a Perkin-Elmer I.R. 21 or Infracord spectrophotometer. The nmr spectra were determined with a Model A-60 Varian spectrophotometer in deuteriochloroform with tetramethylsilane as an internal standard.

(14) Private communication from Wyandotte Chemical Co.

(15) V. Prelog, E. Cerkovnikov, and S. Heimbach, *Collection Czech. Chem. Commun.*, **10**, 399 (1938).

min corresponded to 2-methylquinuclidine: nmr ($CDCl_3$), δ 1.15 doublet (J = 7 cps) (CH_3), 1.55 multiplet (CH_2), 2.90 multiplet (NCH_2); infrared spectrum (CCl_4), 3.45 (s), 6.9 (s), 7.3 (s), 7.5 (s), 7.7 (w), 8.35 (m), 9.1 (m), 9.3 (s), 9.5 (s). The picrate melted at 283–285° (lit.[6] 286°).

The fifth peak had a retention time of 99 min: nmr ($CDCl_3$), δ 7.0 multiplet (N=CH), 1.17 triplet (J = 5 cps), 2.17 multiplet; infrared (CCl_4), 3.35 (s), 6.3 (m), 6.6 (m), 6.82 μ (s). These data point to the presence of 3,4,5,6-tetrahydro-4-propylpiperidine.

D. N-Chloro-4-ethyl-3-methylpiperidine.—Irradiation at 0–5° for 8 hr gave a mixture of amines which gave only two peaks with a ratio of 48:52 under conditions of vpc used for the last two compounds. The first compound had a retention time of 41.5 min and from its nmr spectrum corresponded to 3,7-dimethyl-1-azabicyclo[2.2.1]heptane: nmr ($CDCl_3$), δ 0.90 doublet (J = 7.5 cps) (CH_3), 1.02 doublet (J = 7.0 cps) (CH_3), 1.8 multiplet (CH_2), multiplet centered at 2.7 (NCH_2); infrared spectrum (film), 3.35 (s), 3.42 (m), 6.89 (w), 7.21 (w), 10.05 (w), 10.85 (w), 12.35 μ (m). The amount isolated was too small to characterize further.

The second compound, 3-methylquinuclidine, had a retention time of 52.5 min and formed a picrate, mp 227–229° (lit.[6] 227°): nmr ($CDCl_3$), δ 0.95 doublet (J = 7.0 cps) (CH_3), 1.16 multiplet (CH_2), 2.70 multiplet (NCH_2); infrared (film), 3.35 (s), 3.45 (m), 6.89 (w), 7.59 (w), 9.40 (w), 9.55 (w), 10.20 (w), 12.60 (w).

E. N-Chloro-2-methyl- and N-Chloro-3-methylpiperidines.—Irradiation of these compounds at 0° for 24 hr gave no bicyclic amines.

Alumina: Catalyst and Support. XXIX.[1] Dehydration of the Four Isomers of 1-Decalol over Aluminas

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Dehydrations of the four isomers of 1-decalol were carried out over various catalysts in a micropulse reactor and in a conventional flow-type reactor. The results obtained from these two techniques were in good agreement. On alumina, which was prepared from aluminum isopropoxide, the *trans* elimination was the preferred mode of reaction for all isomers. This preference ranged from 24:1 for *cis,trans*-1-decalol, to 3:1 for *trans,trans*-1-decalol. These dehydrations were pictured mechanistically as occurring preferentially between two alumina surfaces, in submicroscopical crevices, or pores in the catalyst particles. A basic site of the catalyst abstracts a proton from one side of the molecular plane; an acidic site removes a hydroxyl group from the other side. This explanation is in support of the concept of alumina acting as a "pseudo-solvent." Catalysts prepared by impregnation of pure alumina with sodium carbonate solution, or by precipitation from sodium or potassium aluminate, were less active for dehydration than pure alumina. In the presence of these catalysts the dehydration of the decalols was accompanied by the formation of 1-decalones and by the epimerization of the alcohols.

The ability of alumina to catalyze the dehydration of alcohols has been recognized since the 18th century and numerous studies have been carried out to determine the nature of the catalytic activity of this material.[3] Recent investigations from this laboratory have led, however, to the realization that alumina contains Lewis and possibly Brønsted acidic sites of variable number and strength and that the nature of the acidity depends upon the alkali content of the catalyst and its mode of preparation.[4]

While the effect of molecular structure on reactivity has been a powerful tool in the elucidation of the mechanism of homogeneous elimination reactions, this technique has been applied to a lesser degree in the study of heterogeneous reactions. Indeed, with a few exceptions, the stereochemistry of the alumina-catalyzed dehydration reaction has been largely ignored.

Pines and Pillai[5] have reported that the dehydration of menthol over this catalyst produced 2-menthene while the dehydration of neomenthol yielded 2- and 3-menthene in a 1:3 ratio. Both reaction products were found to contain small amounts of 1-menthene, which occurred as a primary dehydration product. The preferred formation of 2-menthene from menthol was interpreted as a clear indication of *trans* elimination proceeding through the axial conformation of the alcohol. These results correspond closely to those obtained from the E2 elimination of hydrogen chloride from menthyl and neomenthyl chloride.[6,7]

One of the processes suggested by Pines and Pillai for the stereospecific elimination was that the hydroxyl group of the alcohol was attacked by an intrinsic acidic site on the catalyst; a basic site was then left to abstract a proton from the opposite side of the molecular plane. In this way a normal *trans*-diaxial elimination could be effected. Such a mechanism would require two alumina surfaces and thus the dehydration might occur in a crevice, pore, or fault in the alumina particle.

The formation of 1,4-epoxycyclohexene from *trans*-1,4-cyclohexanediol,[8] tricyclene from 2-*exo*-bornanol,[9] and nortricyclene from 2-*exo*-norbornanol[9] have been described as occurring by a similar process in which alumina behaves as a "pseudo-solvent."

Lippens[10] studied the texture of the catalytically active aluminas by means of diffraction and adsorption techniques. It was concluded that the structure of η-alumina formed from bayerite consisted of lamallae with an average thickness of about 15 A with a separa-

(1) (a) For paper XXVIII, see C. T. Goetschel and H. Pines, *J. Org. Chem.*, **30**, 3548 (1965). (b) Paper 8 in the series on dehydration of alcohols. For previous papers, see ref 8; *Chem. Ind.* (London), 984 (1963); *J. Am. Chem. Soc.*, **84**, 3934 (1962); **83**, 3274 (1961); ref 5; ref. 18; *J. Am. Chem. Soc.*, **82**, 2401 (1960).

(2) Taken from a Ph.D. dissertation submitted to the Graduate School, June 1965. Monsanto Co. Fellow, 1963–1964. This research was supported in part by the Atomic Energy Commission, Contract AT(11-1)-1096.

(3) M. E. Winfield in "Catalysis," Vol. VII, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, pp 93–182.

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