into the chromatographic column in the manner described by Ray.[36]

The mixtures of olefins, with the exceptions of the isomeric butenes and *cis*- and *trans*-2-pentene, were separated by a 183 × 0.3-cm. column of 30% by weight carbethoxydimethylformamide impregnated on Celite 545 of 100–200 mesh size with helium as the eluent. The mixture of 1-butene and *cis*- and *trans*-2-butene was analyzed by a similar column packed with 30% by weight dimethylformamide on Celite 545 and cooled to −30°, while the mixture of *cis*- and *trans*-2-pentene was separated by saturated silver nitrate in diethylene glycol, both with helium as eluent. In all cases, a thermal conductivity cell was used as a detector.

The composition of each olefin mixture was computed from the chromatogram by determining the ratios of the individual peak areas. The individual peak areas were measured by the method of Cremer and Muller,[37] employing the product of peak height and half-band width, and were multiplied by a response factor which was obtained from the ratios of the areas produced by equal gaseous volumes of the standard olefins which comprised the mixture analyzed. The corrected area ratios gave directly the relative concentrations of the components in the mixture. Each ratio reported in Table VI and VII is the average of the ratios obtained from the analyses of two or more separate mixtures of olefins produced from decompositions of the same amine oxide or quaternary base. By the above procedure, each *ratio* was determined with an average deviation of 1–3% when the concentrations of the components in the mixture did not differ widely and of 6% when the mixture consisted mainly of one olefin. On the basis of numerous calibration experiments carried out during the course of this work, it is estimated that the absolute errors of the analyses are not significantly different from these deviations.

The volatile components of the olefin mixtures that were obtained from decomposition of the amine oxides and quaternary bases that produce either styrene or 1-decene were obtained by the procedure described above, whereas the other olefins (styrene or 1-decene) were isolated as liquids by the methods which follow. The mixture of water, dialkylhydroxylamine (or tertiary amine) and styrene retained in the first tube of the decomposition apparatus (Fig. 1) was kept at 0° and stirred with a magnetic stirrer throughout the elution process. The mixture was diluted with ethanol and the concentration of styrene was determined by comparison against standards with a Beckman DU spectrophotometer. The mixture of reaction products obtained from methyl-*n*-propyl-*n*-decylamine oxide and dimethyl-*n*-propyl-*n*-decylammonium hydroxide, after removal of the propylene, was extracted with three 20-ml. portions of purified pentane. The combined pentane extracts were washed with 10 ml. and 5 ml. portions of 2.5 *N* hydrochloric acid, then with 5 ml. of water and dried over anhydrous magnesium sulfate. The pentane was removed by distillation, and the residue, after weighing, was analyzed by vapor-phase chromatography to determine the concentration of 1-decene.

CAMBRIDGE, MASSACHUSETTS

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[36] N. H. Ray, *J. Appl. Chem.*, **4**, 82 (1954).

[37] E. Cremer and R. Muller, *Z. Elektrochem.*, **55**, 217 (1951); M. Dimbat, P. E. Porter and F. H. Stross, *Anal. Chem.*, **28**, 290 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

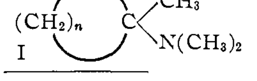
Amine Oxides. IV. Alicyclic Olefins from Amine Oxides and Quaternary Ammonium Hydroxides[1,2]

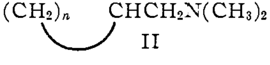
BY ARTHUR C. COPE, CARL L. BUMGARDNER[3] AND EDWARD E. SCHWEIZER

RECEIVED MARCH 11, 1957

Thermal decompositions of the N-oxides of N,N-dimethyl-1-methylcycloalkylamines containing five-, six- and seven-membered rings have been shown to give olefins containing 97.5, 2.8 and 84.8%, respectively, of the endocyclic isomers. The corresponding quaternary ammonium hydroxides follow the Hofmann rule when thermally decomposed to yield mainly the methylenecycloalkanes. These results are interpreted in terms of the steric requirements of these various ring systems. Pyrolyses of the amine oxides and quaternary hydroxides derived from N,N-dimethylcycloalkylmethylamines have been shown to produce exclusively the expected methylenecycloalkanes in all cases but one. Trimethylcyclopentylmethylammonium hydroxide gave appreciable amounts of 1-methylcyclopentene. Possible mechanisms for the formation of this product are discussed.

Earlier work comparing the selective formation of olefins from unsymmetrical amine oxides and quaternary ammonium hydroxides has shown that these thermal decompositions give results that are quite similar except in cases where steric interactions influence the direction of elimination of quaternary ammonium ions but not amine oxides.[2] Because of the steric interactions associated with alicyclic compounds, a study of the effect of ring size on the course of the two elimination reactions was undertaken. The olefins formed on thermal decomposition of amine oxides and quaternary ammonium hydroxides derived from homologous N,N-dimethyl-1-methylcycloalkylamines (I, *n* = 4, 5, 6) were examined, in order to determine the relative amounts of methylenecycloalkane (Hofmann rule elimination) and 1-methylcycloalkene (Saytzeff rule elimination). In addition, the thermal decompositions of the amine oxides and quaternary ammonium hydroxides of the N,N-dimethylcycloalkylmethylamines, II (*n* = 4, 5, 6), were investigated.


I


II

The compounds of type I were prepared by application of the Ritter reaction[4] to the olefins obtained by dehydration of the corresponding 1-methylcycloalkanols. Properties of the six tertiary amines that were employed in this study, I and II (*n* = 4, 5, 6), are summarized in Table I. The picrates, prepared as crystalline derivatives, are listed in Table II. The corresponding amine oxides were prepared by allowing the amines to react with aqueous hydrogen peroxide. The methiodides of the tertiary amines (Table III) were prepared and converted to the quaternary hydroxides.

Two thermal decompositions of each amine oxide and quaternary base were conducted. The olefins were analyzed by vapor-phase chromatography, and the relative amounts of exo- and endo-cyclic

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[1] Sponsored by the Office of Ordnance Research, U. S. Army, under Contract No. DA-19-020-ORD-3226, Project TB 2-0001(1112).

[2] Paper III, THIS JOURNAL, **79**, 4720 (1957).

[3] United States Rubber Co. Fellow, 1954–1955.

[4] J. J. Ritter and J. Kalisb, THIS JOURNAL, **70**, 4048 (1948).

TABLE I

N,N-DIMETHYL TERTIARY AMINES

Amine	Yield, %	B.p., °C.	$n^{25}D$	d^{25}_4	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
						Calcd.	Found	Calcd.	Found	Calcd.	Found
$\underline{(CH_2)_4-C}(CH_3)N(CH_3)_2$	92	152.5	1.4475	0.8508	$C_8H_{17}N$	75.52	75.51	13.47	13.50	11.01	11.31
$\underline{(CH_2)_5-C}(CH_3)N(CH_3)_2$	98	108.5	1.4590	.8695	$C_9H_{19}N$	76.53	76.82	13.56	13.38	9.91	10.07
$\underline{(CH_2)_6-C}(CH_3)N(CH_3)_2$	95	104.5 (35 mm.)	1.4686	.8834	$C_{10}H_{21}N$	77.34	77.13	13.64	13.64	9.02	9.20
$\underline{(CH_2)_4-C}HCH_2N(CH_3)_2$	67	149.5[a]	1.4385	.8158	$C_8H_{17}N$						
$\underline{(CH_2)_5-C}HCH_2N(CH_3)_2$	74	78.5–79.5 (33 mm.)[a]	1.4464	....	$C_9H_{19}N$						
$\underline{(CH_2)_6-C}HCH_2N(CH_3)_2$	84[b]	102.5 (35 mm.)	1.4581	.8621	$C_{10}H_{21}N$	77.34	77.12	13.64	13.73	9.02	9.22

[a] Previously reported by M. Mousseron, R. Jaquier and R. Zagdoun, *Bull. soc. chim. France*, 197 (1952). [b] After acidifying with hydrochloric acid and concentrating, the mixture was extracted continuously with ether for three days. The aqueous layer was made basic and the amine was isolated in the same manner as the other amines.

TABLE II

N,N-DIMETHYL TERTIARY AMINE PICRATES

Amine	Yield, %	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Nitrogen, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\underline{(CH_2)_4-C}(CH_3)N(CH_3)_2$	94	250.8–252.0 d.[a]	$C_{14}H_{20}N_4O_7$	47.19	46.93	5.66	5.80	15.72	15.73
$\underline{(CH_2)_5-C}(CH_3)N(CH_3)_2$	92	232.6–233.8 d.[a]	$C_{15}H_{22}N_4O_7$	48.64	48.52	5.99	5.90	15.13	15.25
$\underline{(CH_2)_6-C}(CH_3)N(CH_3)_2$	94	217.4–218.4[a]	$C_{16}H_{24}N_4O_7$	49.99	50.15	6.29	6.36	14.58	14.63
$\underline{(CH_2)_4-C}HCH_2N(CH_3)_2$	90	142.8–143.8[a]	$C_{14}H_{20}N_4O_7$	47.19	47.08	5.66	5.71	15.72	15.78
$\underline{(CH_2)_6-C}HCH_2N(CH_3)_2$	100	124.6–125.5[b]	$C_{16}H_{24}N_4O_7$	49.99	50.29	6.29	6.45	14.58	14.63

[a] Recrystallized from dry ethyl acetate. [b] Recrystallized from absolute ethanol.

TABLE III

TRIMETHYLAMMONIUM IODIDES

Methiodides	Yield, %	M.p., °C.	Formula	Carbon, %		Hydrogen, %		Iodine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
$\underline{(CH_2)_4-C}(CH_3)N(CH_3)_3I$	79	255.4–258.4 d.[a]	$C_9H_{20}NI$	40.16	39.88	7.49	7.21	47.15	47.35
$\underline{(CH_2)_5-C}(CH_3)N(CH_3)_3I$	92	257.6–260.4 d.[b]	$C_{10}H_{22}NI$	42.41	42.48	7.83	7.71	44.82	44.79
$\underline{(CH_2)_6-C}(CH_3)N(CH_3)_3I$	82	263.6–264.6 d.[b]	$C_{11}H_{24}NI$	44.45	44.35	8.14	7.82	42.70	42.63
$\underline{(CH_2)_4-C}HCH_2N(CH_3)_3I$	94	205.8–206.8[b]	$C_9H_{20}NI$	40.16	40.36	7.49	7.49	47.15	47.23
$\underline{(CH_2)_5-C}HCH_2N(CH_3)_3I$	99	226.5–227.5 d.[b,c]	$C_{10}H_{22}NI$						
$\underline{(CH_2)_6-C}HCH_2N(CH_3)_3I$	95	240.2–240.6[b,d]	$C_{11}H_{24}NI$	44.45	44.52	8.14	8.05	42.70	42.71

[a] Recrystallized from absolute ethanol. [b] Recrystallized from methanol-acetone mixtures. [c] Previously reported by O. Wallach, *Ann.*, **353,** 284 (1907). [d] Previously reported by O. Wallach, *Ann.*, **353,** 302 (1907).

isomers were determined. A summary of the results obtained from the amine oxides and quaternary ammonium hydroxides derived from the N,N-dimethyl-1-methylcycloalkylamines is shown in Table IV. Table V contains the results of the thermal decompositions of the compounds of type II.

TABLE IV

OLEFINS OBTAINED FROM AMINE OXIDES AND TRIMETHYLAMMONIUM HYDROXIDES OF $\overline{\underline{(CH_2)_a\quad C}}(CH_3)N(CH_3)_2$

n	Ave. yield, %		Composition of olefin mixture in weight %	
Amine oxides	Olefin	Amine	Exocyclic	Endocyclic
4	77	2	2.5	97.5
5	84	3	97.2	2.8
6	84	2	15.2	84.8
Trimethylammonium hydroxides				
4	71	1	91.0	9
5	85	0	98.6	1.4
6	84	2	78.2	21.8

Whereas the relative amounts of olefins produced from acyclic amine oxides are nearly proportional to the numbers of β-hydrogen atoms in the alkyl groups,[2] the results in Table IV show that no such generalization can be made for the isomeric products obtained from the N,N-dimethyl-1-methylcycloalkylamine oxides. Methylenecyclohexane (97.2%) was the major product from the decomposition of N,N-dimethyl-1-methylcyclohexylamine oxide. For both the five- and seven-membered ring compounds, however, the chief isomer obtained was the 1-methylcycloalkene. These data are interpreted on the basis of the steric requirements for the particular ring systems involved.

In the case of N,N-dimethyl-1-methylcyclohexylamine oxide, the bulky dimethylamine oxide group would be expected to exist predominantly

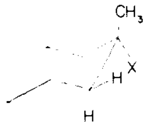
TABLE V

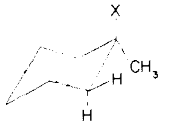
OLEFINS OBTAINED FROM AMINE OXIDES AND TRIMETHYLAMMONIUM HYDROXIDES OF (CH$_2$)$_n$ CHCH$_2$N(CH$_3$)$_2$

n Amine oxides	Ave. yield, % Olefin	 Amine	Composition of olefin mixture in weight % Exocyclic	 Endocyclic
4	61[a]	10	100	0
5	85[b]	..	100	0
6	82[c]	..	99.7	0.3
Trimethylammonium hydroxides				
4	50	28	94.4	5.6
4(a)[d]	..	..	75.2	24.8
4(b)[d]	..	..	71.1	28.9
5	69	22	100	0
6	74	9	99.8	0.2

[a] B.p. 77°, n^{25}D 1.4334. R. T. Arnold, R. W. Amidon and R. M. Dodson, THIS JOURNAL, **72**, 2871 (1950), report b.p. 74° (745 mm.), n^{20}D 1.4354. [b] B.p. 101–103.5°, n^{25}D 1.4467–1.4473. G. Egloff in "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1940, p. 160, reports b.p. 103.5°, n^{20}D 1.4502. [c] B.p. 134°, n^{25}D 1.4603, d^{25}_4 0.8309. O. Wallach, *Ann.*, **345**, 139 (1906), reports b.p. 138–140°, $n^{19.5}$D 1.4581. [d] A concentrated solution of the quaternary hydroxide was decomposed by adding dropwise to a flask at (a) 120° or at (b) 160°; the yields were not determined in these cases.

in the equatorial conformation III, rather than in the axial conformation IV.[5]

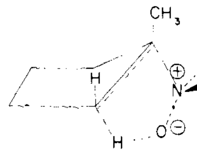




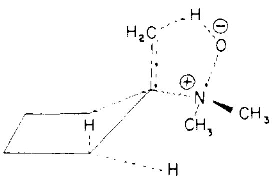
III, X = (CH$_3$)$_2$N$^\oplus$—O$^\ominus$ IV, X = (CH$_3$)$_2$N$^\oplus$—O$^\ominus$
VII, X = (CH$_3$)$_3$N$^\oplus$ VIII, X = (CH$_3$)$_3$N$^\oplus$

In order for elimination to produce 1-methylcyclohexene, attainment of the preferred planar *quasi* five-membered transition state[6,7] would alter the stable staggered conformation of the six-membered ring. Elimination of a β-hydrogen atom of the 1-methyl group does not suffer from this steric restriction, and the more energetically favorable transition state is apparently that leading to methylenecyclohexane. Similar considerations have been used to explain the production of the corresponding methylmethylenecyclohexanes from the pyrolysis of 1,2-, 1,3- and 1,4-dimethylcyclohexanyl acetates.[8]

The olefin obtained by thermal decomposition of N,N-dimethyl-1-methylcyclopentylamine oxide was composed of 97.5% 1-methylcyclopentene and 2.5% methylenecyclopentane, while the olefin formed from the corresponding seven-membered ring compound contained 84.8% of 1-methylcycloheptene and 15.2% of methylenecycloheptane. In the cyclopentyl compound, a *cis*-β-hydrogen atom attached to a carbon atom of the ring is held in a planar arrangement with the C$_1$–N bond, a situation that is favorable for an intramolecular *cis* elimination as formulated in the transition state V. The formation of methylenecyclopentane *via* the transition state VI is analogous to the formation of methylenecyclohexane which is favored over the isomeric 1-methylcyclohexene by a factor of 35 to 1. Since elimination to produce 1-methylcyclopentene is 39 times faster than elimination to yield the exocyclic isomer, transition state V is evidently the lower energy state. A possible explanation for this fact is that elimination *via* V requires orientation of only the N$^\oplus$–O$^\ominus$ bond, whereas transition state VI necessitates orientation of a H$_2$C–H bond (1-methyl group) and the amine oxide bond. That such an interpretation alone is sufficient to account for the observed results has not been established. Examination of molecular models shows no internal steric interactions that would clearly favor V over VI. Pyrolysis of N,N-dimethyl-1-methylcycloheptylamine oxide, containing the larger seven-membered ring, still favors formation of the endocyclic olefin but by a much smaller ratio (84.8:15.2).



V



VI

Thermal decomposition of the trimethyl-1-methylcycloalkylammonium hydroxides produces mainly the methylenecycloalkanes in accordance with the Hofmann rule. This product distribution can be accounted for by a steric interpretation. Steric effects concerning the interactions between the bulky leaving group and β-alkyl groups[9] are dependent upon the conformation of the alicyclic ring. In the compounds studied such interactions would be expected to be important only in the case of the cyclohexane derivative when the trimethylammonium group is in the axial configuration and possibly in the comparable situation with the seven-membered ring compound.

In the case of trimethyl-1-methylcyclohexylammonium hydroxide with the trimethylammonium group in the equatorial configuration (VII), preferred planar *trans* elimination can occur only with the β-hydrogen atoms of the 1-methyl group. The higher energy associated with VIII, which could lead to 1-methylcyclohexene, is reflected in the fact that the product is almost exclusively methylenecyclohexane. The *trans*-β-hydrogen atoms in the cyclopentyl ring of trimethyl-1-methylcyclopentylammonium hydroxide are not coplanar with the leaving group, as is the case with the six-membered ring homolog, and elimination once again favors the exocyclic olefin. The product distribution is not as striking in the seven-membered ring analog which yields a mixture containing 78.2% methylenecycloheptane and 21.8% of 1-methylcycloheptene.

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(5) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 1.

(6) A. C. Cope, R. A. Pike and C. F. Spencer, THIS JOURNAL, **75**, 3212 (1953).

(7) D. J. Cram and J. J. McCarty, *ibid.*, **76**, 5740 (1954).

(8) S. Siegel and M. Dunkel, Abstracts of Papers, American Chemical Society 129th Meeting, Dallas, Texas, April 8–13, 1956, p. 28N.

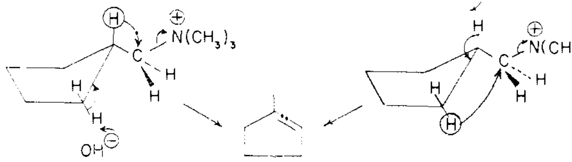
(9) H. C. Brown and I. Moritani, THIS JOURNAL, **78**, 2203 (1956), and references cited therein.

The dependence of the olefin ratios upon ring size can be attributed to specific steric interactions only in the case of the six-membered ring compounds, where the stereochemistry of the cyclohexane ring is firmly established. The present study will be extended to the higher homologs containing medium-sized rings.

Thermal decomposition of the amine oxides and quaternary ammonium hydroxides derived from the N,N-dimethylcycloalkylmethylamines lead exclusively to the expected methylenecycloalkanes in every case but one. For the compounds studied, pyrolysis of the amine oxide gives a higher yield of olefin than the corresponding quaternary base. Thermal decomposition of trimethylcyclopentylmethylammonium hydroxide produced an olefin mixture consisting of 94% methylenecyclopentane and 6% of 1-methylcyclopentene. In order to preclude the possibility that base-catalyzed or thermal rearrangements explained the formation of 1-methylcyclopentene, the following experiments were conducted.

A sample of pure methylenecyclopentane was heated with a 50% aqueous solution of tetramethylammonium hydroxide in a sealed tube at 150° for 48 hr. The olefin was recovered unchanged, as shown by vapor-phase chromatography. Dropwise addition of the quaternary hydroxide to an evacuated flask heated to 120 and 160°, conditions which are known to produce less rearrangement of olefins in systems prone to base-catalyzed rearrangement, produced an olefin containing 24 and 29%, respectively, of 1-methylcyclopentene. It is concluded that base-catalyzed or thermal rearrangement of methylenecyclopentane is unlikely under the conditions of the Hofmann exhaustive methylation. Furthermore, higher temperatures apparently favored the formation of a larger proportion of the endocyclic isomer.

Two possible mechanisms for the formation of 1-methylcyclopentene by a concerted process are: (1) attack at a γ-hydrogen atom by hydroxyl with a 1,2-hydride shift (IX), or (2) attack at a β-hydrogen atom by the base with a 1,3-hydride shift (X).



IX X

Elimination by the second mechanism might occur at the expense of normal 1,2-elimination because the compound would probably exist in the configuration shown in X, *i.e.*, with the β-hydrogen atom and $(CH_3)_3N^{\oplus}$ nearly eclipsed. Investigation of this abnormal Hofmann reaction is in progress.

Experimental[10]

1-Methylcycloalkylamines.—Cyclopentanone, cyclohexanone and cycloheptanone were allowed to react with methylmagnesium iodide, and, after hydrolysis, the resulting carbinols were dehydrated by treatment with *p*-toluenesulfonic acid according to the procedure described by Chavanne and Vogel.[11] The olefins that were obtained had the following physical properties: 1-methylcyclopentene (57% yield), b.p. 76°, n^{25}_{D} 1.4295; 1-methylcyclohexene (60% yield), b.p. 108–109.5°, n^{25}_{D} 1.4474–1.4480; 1-methylcycloheptene (44% yield), b.p. 134–135.5°, n^{25}_{D} 1.4563–1.4568.[12] Each of these olefins was converted to the *t*-alkylamines by a modification of the method of Ritter and Kalish.[4] The steam distillate obtained after saponification of the *t*-alkylformamide was neutralized with dilute hydrochloric acid and extracted with three 100-ml. portions of ether. The organic base was liberated by the addition of sodium hydroxide and extracted with three 100-ml. portions of ether. The combined ether solutions were dried over magnesium sulfate and concentrated. Distillation of the residue gave the primary amine. Amines that were prepared by this method are: 1-methylcyclopentylamine, b.p. 114°, n^{25}_{D} 1.4406 (lit.[13] b.p. 104°); 1-methylcyclohexylamine, b.p. 142.4°, n^{25}_{D} 1.4527 (lit.[14] b.p. 143° at 744 mm., n^{20}_{D} 1.4536); 1-methylcycloheptylamine, b.p. 82.5° (35 mm.), n^{25}_{D} 1.4644, d^{25}_{4} 0.8787.

Anal. Calcd. for $C_8H_{17}N$: C, 75.52; H, 13.47; N, 11.01. Found: C, 75.80; H, 13.46; N, 11.11.

1-Methylcycloheptylamine picrate, prepared by adding a solution of the amine in ethanol to a saturated solution of picric acid in ethanol, was recrystallized from benzene and melted at 171.6–173°.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.39; H, 5.56; N, 15.63.

Cyclohexylmethylamine.—Hydrogenation of benzylamine by the method of Hiers and Adams[15] produced cyclohexylmethylamine, b.p. 73–74° (27 mm.), n^{25}_{D} 1.4605.

1-Cycloheptene-1-carbonitrile.—Cycloheptanone cyanohydrin, prepared from the bisulfite addition compound (from 150 g. of cycloheptanone) and potassium cyanide,[16] was dehydrated by treatment with thionyl chloride in the presence of pyridine.[17] The product was distilled over Raney nickel yielding 141 g. (44%) of 1-cycloheptene-1-carbonitrile, b.p. 103–108° (22 mm.), n^{25}_{D} 1.4855–1.4857. An analytical sample had b.p. 108° (22 mm.), n^{25}_{D} 1.4856, d^{25}_{4} 0.9482.

Anal. Calcd. for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.32, H, 9.29; N, 11.67.

Cycloheptylmethylamine.—1-Cycloheptene-1-carbonitrile (115 g.) in 400 ml. of methanol was hydrogenated over 8 g. of 10% palladium-on-Norit catalyst.[18] The saturated nitrile was not isolated, and the reaction mixture was passed through a filter to remove the catalyst. The filtrate was placed in a steel reaction vessel and saturated with ammonia. Raney nickel (2 teaspoons) was added, and the mixture was hydrogenated at an initial pressure of 1600 p.s.i. at 120° for 4 hr. The catalyst was removed by filtration and 600 ml. of 20% hydrochloric acid solution was added. After removing the solvent under reduced pressure, the solid hydrochloride was taken up in water, and the amine was liberated by addition of 750 g. of 50% sodium hydroxide solution. The amine was extracted with three 100-ml. portions of ether, and the ethereal solutions were dried over magnesium sulfate and concentrated. Distillation of the residue gave 96 g. (81%) of cycloheptylmethylamine, b.p. 97.5° (35 mm.), n^{25}_{D} 1.4725, d^{25}_{4} 0.8893 (lit.[19] b.p. 193–195°, $n^{21.5}_{\mathrm{D}}$ 1.4719).

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[10] Melting points are corrected and boiling points are uncorrected. We are indebted to Dr. S. M. Nagy and his associates for analyses.

[11] G. Chavanne and L. Vogel, *Bull. soc. chim. Belg.*, **37**, 141 (1928).

[12] Each of these olefins contained from 2–5% of the exocyclic isomer, as shown by vapor-phase chromatography. Further purification was not attempted since conversion to the *t*-alkylamine presumably would proceed through the same intermediate starting from either isomer.

[13] F. Markownikow and M. Konowalow, *Ber.*, **28**, 1234 (1895).

[14] S. Nametkin, *J. Russ. Phys. Chem. Soc.*, **42**, 691; *Chem. Zentr.*, **81**, II, 1377 (1910).

[15] G. S. Hiers and R. Adams, *Ber.*, **59**, 162 (1926).

[16] A. H. Cooke and R. P. Linstead, *J. Chem. Soc.*, 956 (1934); 200 ml. of ether was added with the aqueous solution of potassium cyanide.

[17] The procedure employed was essentially that described by W. S. Rapson and R. Robinson, *ibid.*, 1533 (1935).

[18] A. C. Cope, C. M. Hofmann, C. Wyckoff and E. Hardenbergh, THIS JOURNAL, **63**, 3452 (1941).

[19] O. Wallach, *Ann.*, **353**, 302 (1907).

Cycloheptylmethylamine picrate, recrystallized from ethyl acetate, had m.p. 206.2–207.5°.

Anal. Calcd. for $C_{14}H_{20}N_4O_7$: C, 47.19; H, 5.66; N, 15.72. Found: C, 47.17; H, 5.50; N, 15.64.

N,N-Dimethylcycloalkylamines.—The primary amines described above were converted to the corresponding N,N-dimethylamines by treatment with formaldehyde and formic acid.[20] The properties of the tertiary amines are summarized in Table I.

N,N-Dimethylcyclopentylmethylamine.—Alkylation of diethyl malonate with 1,4-dichlorobutane in the presence of sodium iodide by a procedure otherwise similar to one described by Lucas and Pressman[21] gave 82% of diethyl cyclopentane-1,1-dicarboxylate, b.p. 66.5° (0.2 mm.); $n^{25}\text{D}$ 1.4384–1.4392 (lit.[22] b.p. 83° at 3 mm., $n^{20}\text{D}$ 1.4435). Hydrolysis and decarboxylation of the dicarboxylic ester[23] produced cyclopentanecarboxylic acid (85%), b.p. 121.5–122° (20 mm.), $n^{25}\text{D}$ 1.4512 (lit.[24] b.p. 215–216°, $n^{20}\text{D}$ 1.4520). The acid was converted to N,N-dimethylcyclopentanecarboxamide (78%), b.p. 64° (0.5 mm.), $n^{25}\text{D}$ 1.4759, d^{25}_4 0.9944 (lit.[24] b.p. 115–118° at 20 mm.), by the method previously described.[24] Reduction of the amide in ether solution with lithium aluminum hydride[25] gave a 67% yield of N,N-dimethylcyclopentylmethylamine, which had the properties listed in Table I.

N,N-Dimethylcycloalkylamine picrates were prepared as described above and recrystallized to constant melting point from ethyl acetate or absolute ethanol (Table II).

Trimethylcycloalkylammonium Iodides.—An ether or methanol solution of the tertiary amine was allowed to stand overnight with an excess of methyl iodide. When methanol was used, the solution was concentrated and the methiodides were precipitated by the addition of ether. The quaternary ammonium iodides were collected on a filter, washed with ether and recrystallized from absolute ethanol or methanol–acetone mixtures. The yields and properties are given in Table III.

Amine Oxides.—The tertiary amines were oxidized with 30% aqueous hydrogen peroxide with or without the use of methanol as a solvent, and the excess hydrogen peroxide was decomposed by the addition of platinum black.[26] In most cases, 0.06 mole of the tertiary amine was employed, and the amine oxide solution was used directly for the pyrolysis after removal of the platinum black by filtration.

Trimethylammonium hydroxides were prepared from the methiodides by methods previously described.[2]

Pyrolysis of Amine Oxides and Trimethylammonium Hydroxides.—An aqueous solution of the amine oxide or quaternary base, prepared as described above, was concentrated under reduced pressure to a sirupy residue at a temperature of 45° or lower. The sirup was heated in a nitrogen atmosphere at about 25 mm. in a round-bottomed flask connected through a short Vigreux column to two traps in series, the first cooled with Dry Ice–acetone and the second with liquid nitrogen. The flask was heated to 160°, at a rate of approximately 1° per minute, at which point decomposition and distillation of the products into the receivers was complete.

The contents of the two traps were combined. Water was added, and the mixture of olefin and tertiary amine (or dimethylhydroxylamine) was removed by means of a pipet. The mixture was cooled in a Dry Ice–acetone-bath in order to freeze the water present, and the product dried in this manner was transferred to a pear-shaped flask and distilled through a semi-micro column. Both an olefin fraction and an amine fraction were obtained, and the yields of each are listed in Tables IV and V.

The olefins were analyzed by vapor-phase chromatography using a 183 × 0.8-cm. column packed with 40% (by weight) of a saturated solution of silver nitrate in diethylene glycol on Celite 545 (100–200 mesh) with helium as the eluent. A thermal conductivity cell was used as a detector. The weight per cent. composition of each olefin mixture was obtained by determining the ratio of the individual peak areas which were calculated from the product of the peak height and the half-band width. The relative amounts of the components (methylenecycloalkane and methylcycloalkene) are given in Tables IV and V.

Standard Olefins.—In order to identify the peaks from the vapor-phase chromatograms, standard samples of each olefin were required. Thermal decompositions of the amine oxides of type II gave pure samples of the methylenecycloalkanes (Table V). Dehydration of 1-methylcyclopentanol as described above and distillation of the olefin gave a fraction, b.p. 76°, $n^{25}\text{D}$ 1.4295 (lit.[27] b.p. 75°, $n^{25}\text{D}$ 1.4300), which was shown to be over 99% pure 1 methylcyclopentene by vapor phase chromatography. The olefin mixture from the thermal decomposition of N,N-dimethyl-1-methylcycloheptylamine oxide was separated by vapor-phase chromatography, and a pure sample of 1-methylcycloheptene was obtained which had b.p. 135°, $n^{25}\text{D}$ 1.4567 (lit.[28] b.p. 137.5–138.5°, $n^{19.5}\text{D}$ 1.4581). Pure 1-methylcyclohexene was obtained from the American Petroleum Institute. Structures of the olefins were confirmed by determination of their infrared spectra.

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[20] By a procedure similar to one described by R. N. Icke and B. B. Wisegarver in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 723.

[21] H. J. Lucas and D. Pressman, "Principles and Practice in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 450.

[22] V. P. Golm'ov, *Zhur. Obshchei Khim.*, **22**, 1944 (1952); *C. A.*, **47**, 9267 (1953).

[23] By a procedure based on one described by E. B. Vliet, C. S. Marvel and C. S. Hsueh in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 416.

[24] M. Mousseron, J. Joullian and Y. Jolchine, *Bull. soc. chim. France*, 757 (1952).

[25] V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

[26] The method used was essentially the same as the one described in ref. 6.

[27] H. Adkins and A. K. Roebuck, THIS JOURNAL, **70**, 4041 (1948).

[28] O. Wallach, *Ann.*, **345**, 139 (1906).