Anal. Calcd. for $C_{19}H_{24}$: C, 90.41; H, 9.58. Found: C, 90.38; H, 9.85.

1,1-Diphenylnonane (VII) distilled at 173–174° at 0.75 mm. to produce 37 g. (99%) of VII, $n^{25}\text{D}$ 1.5310.

Anal. Calcd. for $C_{21}H_{28}$: C, 89.93; H, 10.07. Found: C, 90.08; H, 10.15.

Attempted Alkylation with *t*-Butyl Chloride.—To a stirred solution of 0.1 mole of sodium diphenylmethide in 250 ml. of liquid ammonia and 100 ml. of ether was added 9.3 g. (0.1 mole) of freshly distilled *t*-butyl chloride in 100 ml. of ether. A Dry Ice–acetone reflux condenser was fitted to the flask. After two hours the red color of sodium diphenylmethide remained. An additional 0.1 mole of *t*-butyl chloride in 100 ml. of ether was added and ammonia was refluxed an additional two hours. Finally 0.1 mole of benzhydryl chloride in 100 ml. of ether was added, the red color being discharged. The reaction mixture was worked up as described above for hydrocarbon II. The ether solution was distilled after solid 1,1,2,2-tetraphenylethane was filtered off. Ether and *t*-butyl chloride were difficult to separate, but 12.5 g. of *t*-butyl chloride was recovered. The residue after distillation was solid 1,1,2,2-tetraphenylethane. The combined solids were recrystallized from benzene and ethanol to give 31.5 g. (94%) of the hydrocarbon, m.p. and mixed m.p. 214–215°.

Reaction of Potassium Diphenylmethide with β-Phenylethyl Chloride.—To a stirred solution of 0.1 mole of potassium amide[3] in 200 ml. of anhydrous liquid ammonia was added 16.8 g. (0.1 mole) of diphenylmethane in 100 ml. of anhydrous ether. To the resulting deep red solution was added after 10 minutes 14.05 g. (0.1 mole) of β-phenylethyl chloride in 100 ml. of anhydrous ether. The red solution turned gray after 7 minutes. The ammonia was removed on the steam-bath, and water and ether were added. The ethereal layer was dried and, after adding a few crystals of hydroquinone, the solvent was removed. The residue was distilled at 50 mm. to give 1.9 g. (18%) of styrene, b.p. 70–71°; styrene dibromide, m.p. and mixed m.p. 72–73°, reported[27] m.p. 72–73°. The residue remaining after removing styrene yielded 3.85 g. of recovered diphenylmethane, b.p. 105° at 5 mm. The residue was taken up in 30–60° petroleum ether, filtered and methanol was added. There was obtained 18 g. (70%) of 1,1,3-triphenylpropane, m.p. 47°, on cooling in a Dry Ice–acetone-bath.

Competitive Experiment of Sodium Diphenylmethide and Sodium Amide with Benzyl Chloride.—To 0.11 mole of sodium amide in 200 ml. of anhydrous liquid ammonia was added with stirring 9.24 g. (0.055 mole) of diphenylmethane in 100 ml. of dry ether. After 10 min. 6.96 g. (0.055 mole) of benzyl chloride in 50 ml. of dry ether was added rapidly. The red color of sodium diphenylmethide remained until ammonia was removed on the steam-bath. The red color faded to become purple when only ether remained. After cooling the reaction mixture, 100 ml. of water was added. The purple color was discharged and the ether layer was separated. The aqueous layer was extracted with two 50-ml. portions of ether and the combined ether layers were dried and filtered. Ether was removed from the filtrate and the residue was dissolved in 75 ml. of ethanol. A few drops of water clouded the solution which was clarified by adding a small amount of ethanol. On standing overnight in a refrigerator white crystals of stilbene separated. The solid was recrystallized from ethanol to give 2.5 g. (62%) of stilbene, m.p. 123–125°, reported[28] 125°. A mixed m.p. with an authentic sample (m.p. 124–125°) showed no depression. The mother liquor was treated with more water and cooled in a Dry Ice–acetone-bath. Crude 1,1,2-triphenylethane (I) crystallized to give 5 g. (35%) of the product, m.p. 51–56°. It was recrystallized from ethanol, m.p. 55–56°, reported m.p. 56°[7] and 54°.[9]

Attempted Benzylation of Sodium Di-*p*-methoxyphenylmethide.—To a stirred suspension of 0.05 mole of sodium amide in 250 ml. of anhydrous liquid ammonia was added with stirring 11.4 g. (0.05 mole) of di-*p*-methoxyphenylmethane in 100 ml. of ether. A red color developed and after 15 minutes 6.33 g. (0.05 mole) of benzyl chloride in 50 ml. of ether was added. The red color was discharged when only a small fraction of the halide solution was added. A purple color was produced when the remaining halide was added. After 15 minutes solid ammonium chloride (4 g.) was added and ammonia was removed on the steam-bath. More ether (100 ml.) was added and then 100 ml. of water. The ether layer was separated and the aqueous layer was extracted with two 50-ml. portions of ether. The ether solvent was removed to give an oil which was taken up in ethanol. Stilbene (4.0 g., 89%) was obtained by alternately adding water and cooling in a Dry Ice–acetone-bath. The pure product melted at 124° after crystallization from methanol and chloroform. A mixed melting point with an authentic sample (m.p. 124–125°) showed no depression. Water was added to the remaining solution to precipitate unchanged di-*p*-methoxyphenylmethane (10.7 g., 94%).

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[27] I. Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1953, Vol. IV, p. 380.

[28] I. Heilbron, ref. 27, p. 374.

DURHAM, NORTH CAROLINA

[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Reactions of Amines. II. Degradation via Tertiary Amine Oxides[1]

BY HENRY E. BAUMGARTEN, FRANK A. BOWER[2] AND TED T. OKAMOTO[3]

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Degradative sequences (see chart) for amines derived from acids related to the naphthenic acids are described that include as an important step the pyrolysis of a *t*-amine N-oxide. Evidence is offered indicating that in the pyrolysis of *t*-amine N-oxides the direction of elimination may follow the Hofmann rule.

One of the most attractive procedures for the degradation of naphthenic acids in structural studies is the conversion of the acids into the amines of one less carbon atom by the Schmidt reaction.[4,5] The utility of this procedure is lessened somewhat, however, by the apparent unavailability of entirely satisfactory, unambiguous processes for the further degradation of the resultant amines. Of the reactions previously used, the Hofmann degradation[4] to the olefin is reasonably unambiguous but, as carried out by von Braun,[6] requires an undue amount of manipulation with a resultant relatively low yield of olefin (20-35%). The reaction of naphthenylamines with nitrous acid[7] to give olefins and alcohols has been shown to lead to extensive rearrangements of the Demjanov type, and the amine phosphate degradation to the olefin has been found also to proceed with considerable

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[1] Paper I, THIS JOURNAL, **76**, 4561 (1954).

[2] Standard Oil Co. (of Indiana) Fellow, 1951–1953.

[3] Standard Oil Co. (of Indiana) Fellow, 1953–1955.

[4] J. von Braun, *Ann.*, **490**, 100 (1931).

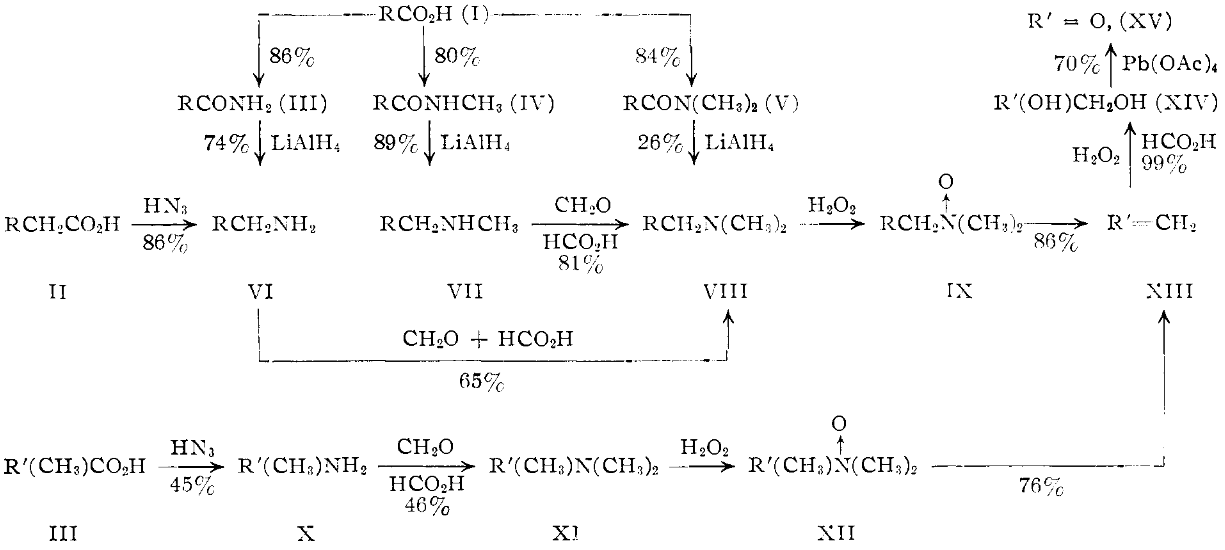
[5] H. L. Lochte and E. R. Littmann, "Petroleum Acids and Bases," Chemical Publishing Co., Inc., New York, N. Y., 1955, p. 100.

[6] Reference 5, pp. 103, 149.

[7] B. Shive, J. Horeczy, G. Wash and H. L. Lochte, THIS JOURNAL, **64**, 385 (1942).

rearrangement.[8] This communication is the first of a series to be devoted to the study of the degradation of naphthenylamines (and other types) to olefins of the same number of carbon atoms by various procedures, both old and new. Of the procedures studied to date that described here based upon the pyrolysis of tertiary amine oxides, recently rediscovered and elegantly applied by Cope and co-workers,[9] has been most satisfactory and will be used in future papers as a standard for comparison.

For use as model compounds in these studies three acids were selected, cyclohexanecarboxylic acid (I), cyclohexaneacetic acid (II) and 1-methylcyclohexanecarboxylic acid (III). At the time this work was started both I and II were commercially available and III was synthesized readily in 81% over-all yield by condensation of butadiene with methacrylic acid,[10] followed by catalytic hydrogenation of the intermediate, 1-methyl-3-cyclohexenylcarboxylic acid.



R = cyclohexyl; R' = cyclohexylidene

The individual steps required for the degradation of I to cyclohexene in about 52% over-all yield, *via* the successive application of the Schmidt reaction,[11] the Eschweiler–Clarke reaction[12] and the Cope amine oxide pyrolysis,[9] have already been described. In the chart several alternative degradations of I as well as degradations of II and III are outlined.

The key sequence in the chart is the degradation of II. Application of the Schmidt reaction to II gave cyclohexylmethylamine (VI) in 86% yield. Methylation of VI *via* the Eschweiler–Clarke procedure (formaldehyde and formic acid) gave dimethylcyclohexylmethylamine (VIII) in 65% yield. From oxidation of the latter with hydrogen peroxide an 89% yield of crude dimethylcyclohexylmethylamine oxide (IX) was obtained. Pyrolysis of the oxide at 115–160° under reduced pressure gave an 86% yield (based on VIII) of methylenecyclohexane (XIII), free from any detectable amounts of isomerization products (based on infrared spectra).

An attractive degradation of I based on that of II was developed as outlined in the flow sheet. Conversion of I, *via* treatment of the acid chloride with ammonia or the appropriate amine, into cyclohexanecarboxamide (III), N-methylcyclohexanecarboxamide (IV) and N,N-dimethylcyclohexanecarboxamide proceeded in 86, 80 and 84% yields. Reduction of III, IV and V with lithium aluminum hydride, using the excellent technique of Micovic and Mihailovic[13] as a model, gave VI, N-methylcyclohexylamine (VII) and VIII in 74, 89 and 26% yields, respectively. From the reaction mixture from the reduction of V, crude cyclohexanemethanol was isolated in 32% yield as a by-product. Other workers have reported alcohol by-products in the lithium aluminum hydride reduction of disubstituted amides.[13–16] The crude cyclohexanemethanol was converted into its acetate, and the latter was pyrolyzed in the usual manner to give XIII in 71% over-all yield.

The further methylation of VII by the Eschweiler–Clarke technique gave VIII in 81% yield. From these results it appears that the maximum yield of VIII (57% over-all) was obtained by the sequence I → IV → VII → VIII. Indeed, this sequence gave essentially the same yields as the shorter sequence II → VI → VIII (56% over-all yield). It is interesting to note that the yield of

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(8) Reference 5, pp. 104, 177.

(9) A. C. Cope, T. T. Foster and P. H. Towle, THIS JOURNAL, **71**, 3929 (1949); A. C. Cope, R. A. Pike and C. F. Spencer, *ibid.*, **75**, 3212 (1953); A. C. Cope, D. C. McLean and N. A. Nelson, *ibid.*, **77**, 1628 (1955); A. C. Cope and C. L. Bumgardner, *ibid.*, **78**, 2812 (1956).

(10) A. A. Petrov and N. P. Sopov, *J. Gen. Chem. U.S.S.R.*, **18**, 1781 (1948); *C. A.*, **43**, 3373 (1949).

(11) M. Oesterlin, *Z. angew. Chem.*, **45**, 536 (1932).

(12) A. Skita and H. Rolfes, *Ber.*, **53**, 1242 (1920).

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

(14) R. F. Nystrom and W. B. Brown, THIS JOURNAL, **70**, 3738 (1948).

(15) A. L. Morrison, R. F. Long and M. Konigstein, *J. Chem. Soc.*, 952 (1951).

(16) From the reduction of V using inverse addition of reagents M. Mousseron, R. Jacquier, M. Mousseron-Canet and R. Zagdoun (*Bull. soc. chim. France*, 1042 (1952)) obtained 25% of VIII, 60% recovered V and 5% of cyclohexanecarboxaldehyde.

VIII by the monomethylation of VII was appreciably higher than that by dimethylation of VI, due in large part to a smaller incidence of by-product formation in the former example.

The degradation of III to 1-methylcyclohexylamine (X) by the Schmidt reaction has been reported to proceed in only 42% yield,[17] and a rationale explaining in part this behavior has been offered. In our hands a similar yield (45%) of X was obtained. Treatment of X by the Eschweiler–Clarke procedure gave N,N-dimethyl-1-methylcyclohexylamine (XI) in 46% yield. Oxidation of the amine to the N-oxide XII and pyrolysis of XII gave a 76% yield of methylenecyclohexane (XIII). The identity of the latter was established by distillation through a precision distillation column and examination of the infrared spectra of the distillate and the column holdup and pot residue for evidence of the other most probable olefinic product, 1-methylcyclohexene. As far as we were able to determine by physical constants and infrared spectra, the pyrolysis product consisted solely of XIII.

Since general conclusions drawn from a single example are not especially compelling, the above result can only suggest that the direction of elimination in the Cope pyrolysis of tertiary amine oxides may follow the Hofmann rule much as in the controlled pyrolysis of acetates.[18] The validity of this generalization is under study. Very probably considerations[19] similar to those already suggested for acetate pyrolysis play a large part in determining the selectivity, even though the present elimination apparently takes place in the liquid phase and acetate pyrolysis in the vapor phase. Furthermore, in the pyrolysis of XII no special precautions as to technique (such as are required in acetate pyrolysis[18,19]) other than those normally observed appeared to be necessary to ensure this high degree of selectivity.

Studies of the further degradation of olefins such as XIII have not progressed to the point where an entirely satisfactory procedure can be offered; however, a procedure based on the conversion of methylenecyclobutane to cyclobutanone[20] has been very successful with XIII itself.[21] Oxidation of XIII with performic acid (formic acid and hydrogen peroxide) followed by alkaline hydrolysis of the resultant hydroxyformate gave up to 99% yields of crude 1-hydroxymethylcyclohexanol (XIV). Yields of this magnitude were made possible by the following deviation from the usual isolation procedure.[22] The alkaline reaction mixture from the hydrolysis was saturated with potassium carbonate and the glycol was extracted with ethanol.[23] Oxidation of XIV with lead tetraacetate in benzene solution gave cyclohexanone in 67% yield.[24] The oxidation of XIV with periodic acid under a variety of conditions gave only traces at best of ketone. This observation is consistent with that of Roberts and Sauer[20] relative to the oxidation of 1-hydroxymethylcyclobutanol.

Evaluations of the original degradation procedure of von Braun[4] by application of the process to the model acid II have been carried out by Lochte and co-workers[25] and in this Laboratory. Employing as nearly as possible the original techniques of von Braun (reagents over the arrows) in the sequence

$$\mathrm{II} \longrightarrow \mathrm{VI} \xrightarrow[\text{or MeI}]{\mathrm{Me_2SO_4}} \underset{\mathrm{XVI}}{\mathrm{RCH_2N(CH_3)_3X}} \xrightarrow[\text{IRA-400-OH}]{\text{KOH or}}$$

$$\underset{\mathrm{XVII}}{\mathrm{RCH_2N(CH_3)_3OH}} \xrightarrow[\text{heat}]{} \underset{\mathrm{XIII}}{\mathrm{R'{=}CH_2}} \xrightarrow{\mathrm{O_3}} \underset{\mathrm{XV}}{\mathrm{R'{=}O}}$$

Lochte and co-workers obtained an 89% yield of VI, an undetermined yield of trimethylcyclohexylmethylammonium sulfate (XVI) and of the corresponding hydroxide XVII and a 19–25% yield (over-all from VI) of XIII. Ozonolysis of XIII gave a 39% yield of XV (as the semicarbazone). In our study (reagents under the arrow) the reaction of VI with methyl iodide gave trimethylcyclohexylmethylammonium iodide in 94–98% yield. The latter was converted into the quaternary ammonium hydroxide XVII and decomposed by the excellent modification of the Hofmann procedure described recently by Weinstock and Boekelheide,[26] giving XIII in 31–38% yield together with 34–21% of recovered VIII. The maximum over-all yield of XIII from the von Braun degradation as run by Lochte was about 7% (this would be about 11% if the modified Hofmann degradation were employed), compared with a maximum over-all yield of about 32% using the tertiary amine oxide pyrolysis and subsequent oxidation as described herein. Even in comparing only the over-all change VI → XIII by the Hofmann degradation and by the Cope amine oxide pyrolysis, the results favor the latter (56 to 37%).[27]

Details of the application of the degradation described here to the naphthenic acids will be reported elsewhere. However, the results may be summarized by noting that, in applying this procedure to some twenty fractions of acids in the C_8–C_{12}

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[17] C. Schuerch, Jr., and E. H. Huntress, THIS JOURNAL, **71**, 2233 (1949).

[18] (a) W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955); (b) W. J. Bailey, J. J. Hewitt and C. King, *ibid.*, **77**, 357 (1955); (c) W. J. Bailey and L. Nicholas, *J. Org. Chem.*, **21**, 854 (1956).

[19] S. Siegel and M. Dunkel, Abstracts of Papers, Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956, p. 28N.

[20] J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

[21] Extension of this procedure, unmodified, to the olefins derived from naturally occurring naphthenic acids has not given as satisfactory results as of this writing.

[22] A. C. Cope, H. E. Johnson and J. S. Stephenson, THIS JOURNAL, **78**, 5599 (1956).

[23] This procedure was suggested to us several years ago by Dr. G. H. Richter. A similar procedure (without the ethanol extraction) was reported recently by C. C. Price and G. Berti, *ibid.*, **76**, 1211 (1954).

[24] Although the cyclohexanone obtained appeared to be substantially free of by-products arising from attack of lead tetraacetate on the ketone, the possibility of such attack should be recognized in using this procedure and may account for some of the results observed with ketones derived from the naphthenic acids (*cf.* O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923); G. W. K. Cavill and D. H. Solomon, *J. Chem. Soc.*, 4426 (1955)).

[25] Reference 5, p. 174.

[26] J. Weinstock and V. Boekelheide, THIS JOURNAL, **75**, 2546 (1953).

[27] Recyclization of the recovered VIII would be expected to raise the over-all yield of XIII in the modified Hofmann reaction, but in small runs this recyclization is often impractical.

range, in the majority of the experiments yields of olefin equal to or greater than that reported here for the degradation of II were obtained.

In the Experimental section the results of some orienting experiments are described in which β-phenylethylamine was converted *via* the tertiary amine N-oxide into styrene in 56% over-all yield.

Experimental[28]

1-Methylcyclohexanecarboxylic Acid (III).—1-Methyl-3-cyclohexenecarboxylic acid, m.p. 77–78°, was prepared in 85% yield as described by Petrov and Sopov,[10] substituting an equivalent quantity of hydroquinone for pyrogallol and effecting a first isolation of the crude acid by steam distillation. In one run at the boiling point of toluene[29] none of the desired product was obtained. Hydrogenation of 61 g. of the unsaturated acid was carried out in usual manner in 150 ml. of ethanol at 45 p.s.i. over platinum oxide and required 2 hr. for completion. Distillation of the product gave 59 g. (96%) of 1-methylcyclohexanecarboxylic acid, b.p. 133–135° (17 mm.) (lit.[30] b.p. 137–138° (24 mm.)).

Amides of Cyclohexanecarboxylic Acid (III, IV and V).—Cyclohexanecarboxylic acid (90 g., 0.7 mole) was refluxed with 166 g. (1.4 moles) of thionyl chloride for 2 hr. Distillation of the reaction mixture gave 102 g. (99%) of cyclohexanecarbonyl chloride, b.p. 77° (21 mm.) (lit.[31] b.p. 76° (17 mm.)).

Dropwise addition of 130 g. (0.8 mole) of cyclohexanecarbonyl chloride to 400 ml. of chilled, concentrated ammonium hydroxide, filtration, washing with water and drying gave 98 g. (86%) of crude cyclohexanecarboxamide, m.p. 184–186° (lit.[32] m.p. 184°), which was used without further purification.

From the similar treatment of 80 g. (0.55 mole) of cyclohexanecarbonyl chloride and 200 g. of ice-cold 33% aqueous methylamine, 63.5 g. (80%) of crude N-methylcyclohexanecarboxamide, m.p. 109–111° (lit.[14] m.p. 110–111°), was obtained and was used without further purification.

Cyclohexanecarbonyl chloride (120 g., 0.83 mole) was added dropwise with stirring to 143 ml. of cooled 33% aqueous dimethylamine. After stirring the solution for 1 hr., the organic layer was separated and the aqueous layer was extracted with ether. The combined organic layer and ether extracts were dried over magnesium sulfate, filtered and distilled, giving 107.5 g. (84%) of N,N-dimethylcyclohexanecarboxamide, b.p. 158° (44 mm.) (lit.[14] b.p. 135–140° (20 mm.)).

Cyclohexylmethylamine (VI). (a) **From Cyclohexaneacetic Acid.**—Concentrated sulfuric acid (175 g., 1.80 moles) was added to a solution of 28.4 g. (0.20 mole) of cyclohexaneacetic acid in 200 ml. of chloroform. While maintaining the temperature between 52–55°, 14.3 g. (0.22 mole) of sodium azide was added in small portions over a ½ hr. period to the stirred solution (hood). Heating was continued overnight to complete the evolution of nitrogen. The reaction mixture was chilled to freeze the sulfuric acid–amine sulfate layer, and the chloroform was removed by decantation. The sulfuric acid solution, diluted with 400 ml. of ice-water, was added cautiously to 1 l. of 5 *N* sodium hydroxide solution in a flask arranged for steam distillation. The mixture was steam distilled and the distillate layers separated. The aqueous layer was extracted with ether. The combined organic layers were dried over potassium carbonate, filtered and distilled, giving 19.6 g. (86%) of cyclohexylmethylamine, b.p. 98–100° (98 mm.) (lit.[33] b.p. 56–58° (12 mm.)). In three runs, two of which were on twice the scale described, the yields were 83–86%.

(b) **From Cyclohexanecarboxamide.**—Cyclohexanecarboxamide (205 g., 1.63 moles) was powdered and suspended in 2 l. of dry ether. Lithium aluminum hydride (215 g., 5.67 moles) was added at such a rate as to maintain gentle reflux. The reaction mixture was allowed to stand overnight and then treated with water as described by Micovic and Mihailovic[13] to decompose the excess reducing agent. The inorganic solids were removed by filtration and the ethereal solution was dried and distilled giving 136 g. (74%) of cyclohexylmethylamine, b.p. 74° (35 mm.). An unidentified by-product (15 g., b.p. 180–190° (35 mm.)) was also obtained.

N-Methylcyclohexylmethylamine (VII).—N-Methylcyclohexanecarboxamide (63.5 g., 0.45 mole) was reduced with 34 g. (0.8 mole) of lithium aluminum hydride in the manner described above, giving 51 g. (89%) of N-methylcyclohexylmethylamine, b.p. 160–162° (lit.[34] b.p. 161–162° (748 mm.)).

N,N-Dimethylcyclohexylmethylamine (VIII). (a) **From Cyclohexylmethylamine.**—Technical grade 90% formic acid (89.5 g., 1.9 moles) was added with cooling to 39 g. (0.34 mole) of cyclohexylmethylamine. Formalin (10 g. of 40% solution) was added, and the mixture was warmed under reflux on the steam-bath until the evolution of carbon dioxide subsided. Additional small portions of formaldehyde were added until the total was 29.5 g. (0.7 mole). The mixture was heated for 10–15 hr. after which time the evolution of carbon dioxide had ceased. Concentrated hydrochloric acid (42.5 ml., 0.5 mole) was added and the excess formic acid and water were removed under reduced pressure. The viscous residue was made alkaline with 120 ml. of 10% sodium hydroxide solution, and the mixture was steam distilled. The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were dried over potassium carbonate and distilled, giving 31.2 g. (65%) of N,N-dimethylcyclohexylmethylamine, b.p. 102–103° (100 mm.), micro b.p. 173° (lit.[14] b.p. 75–76° (15 mm.)). Yields in other experiments ranged from 62–64%.

(b) **From N-Methylcyclohexylmethylamine.**—Following the procedure described in (a) above, from 51 g. (0.40 mole) of N-methylcyclohexylmethylamine 46 g. (81%) of N,N-dimethylcyclohexylmethylamine was obtained.

(c) **From N,N-Dimethylcyclohexanecarboxamide.**—N,N-Dimethylcyclohexanecarboxamide (41 g., 0.27 mole) was reduced with 15.2 g. of lithium aluminum hydride in the manner described for the reduction of cyclohexanecarboxamide. Distillation of the product gave 10 g. (26%) of N,N-dimethylcyclohexylmethylamine, b.p. 102–105° (100 mm.), micro b.p. 172–173°, and a second fraction, 11.8 g., which boiled at 117° (83–89 mm.), micro b.p. 184°. The latter fraction was apparently a crude mixture consisting largely of cyclohexanemethanol (b.p. 182°). This fraction was converted into the acetate, b.p. 101–103° (30 mm.), and pyrolyzed in the usual manner, giving a 71% over-all yield of methylenecyclohexane, b.p. 101–103°.

N,N-Dimethylcyclohexylmethylamine Oxide (IX).—To 31 g. (0.22 mole) of N,N-dimethylcyclohexylmethylamine 125 g. (1.09 moles) of 30% hydrogen peroxide was added with shaking while maintaining the temperature between 35–40°. The completion of the reaction was gaged by the complete solution of the amine, requiring 48–72 hr. of shaking depending on the amount of tertiary amine being oxidized. The excess hydrogen peroxide was decomposed with a small amount of platinum oxide shaken in the solution overnight. The solution was filtered and the water was evaporated at 35–40° under reduced pressure, giving 28.3 g. (83%) of semi-solid N,N-dimethylcyclohexylmethylamine oxide. The yields in several other experiments ranged from 73–89%. The amine oxide was pyrolyzed without further purification.

Pyrolysis of N,N-Dimethylcyclohexylmethylamine Oxide.—The pyrolysis was conducted in a 100-ml., round-bottomed flask equipped with a side arm for introduction of nitrogen. The flask was connected in turn to a 6-in. Vigreux column, a Claisen head, two receivers connected in series and a vacuum pump. The receivers were immersed in a Dry Ice–acetone-bath.

The flask was charged with 5–20 g. of N,N-dimethylcyclohexylmethylamine oxide, evacuated to 10 mm. pressure and immersed in an oil-bath. The Vigreux column was heated to 120–130° and the oil-bath temperature was raised from 30–130° during 30 minutes. The amine oxide liquefied before pyrolysis, which took place at about 115–125°. The temperature was elevated to 160° for a few minutes to complete the pyrolysis. The contents of the receiver were separated and the hydrocarbon layer was washed with 2 *N* hydrochloric acid and water, dried over magnesium sulfate

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[28] Melting points are uncorrected. Analyses by Micro-Tech Laboratories, Skokie, Ill.

[29] A. C. Cope and E. C. Herrick, *Org. Syntheses*, **30**, 93 (1950).

[30] J. Gutt, *Ber.*, **40**, 2069 (1970).

[31] G. Darzens and H. Rost, *Compt. rend.*, **153**, 773 (1911).

[32] J. S. Lumsden, *J. Chem. Soc.*, **87**, 90 (1905).

[33] L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, **9**, 402 (1926).

[34] F. F. Blicke and F. B. Zienty, This Journal, **61**, 93 (1939).

and distilled, giving yields ranging from 71–86% of methylenecyclohexane, b.p. 102–103° (lit.[35] b.p. 102–103.5°).

1-Methylcyclohexylamine (X).—1-Methylcyclohexanecarboxylic acid (52 g., 0.37 mole) was converted to the amine by the Schmidt reaction as described above for the preparation of cyclohexylmethylamine. Distillation of the product gave 18.6 g. (45%) of 1-methylcyclohexylamine, b.p. 143–145° (lit.[17] b.p. 142–142.5° (750 mm.)).

N,N-Dimethyl-1-methylcyclohexylamine (XI).—1-Methylcyclohexylamine (14 g., 0.12 mole) was methylated using the procedure described for the preparation of N,N-dimethylcyclohexylmethylamine. Distillation of the product gave 8.1 g. (46%) of N,N-dimethyl-1-methylcyclohexylamine, b.p. 88.5–90° (31 mm.).

Anal. Calcd. for $C_9H_{19}N$: C, 76.52; H, 13.56; N, 9.92. Found: C, 76.81; H, 13.76; N, 9.70.

N,N-Dimethyl-1-methylcyclohexylamine Oxide (XII).—N,N-Dimethyl-1-methylcyclohexylamine (8.0 g., 0.06 mole) was oxidized as described above for the preparation of N,N-dimethylcyclohexylmethylamine oxide. The crude oxide was pyrolyzed without further purification; however, a small sample of the oxide was converted into the picrate, m.p. 163–164°, for analysis.

Anal. Calcd. for $C_{15}H_{22}N_4O_8$: C, 46.7; H, 5.75; N, 14.3. Found: C, 46.94; H, 5.63; N, 14.05.

Pyrolysis of N,N-Dimethyl-1-methylcyclohexylamine Oxide.—Utilizing the technique employed for the pyrolysis of N,N-dimethylcyclohexylmethylamine oxide, the oxide of N,N-dimethyl-1-methylcyclohexylamine was pyrolyzed and the olefinic product was distilled through a concentric-tube column rated at 45 theoretical plates or better, giving 4.1 g. (76%, based on tertiary amine) of methylenecyclohexane, b.p. 100.0–101.5° (730 mm.), $n^{25}\mathrm{D}$ 1.4481 (lit.[18b] b.p. 100–101° (730 mm.), $n^{25}\mathrm{D}$ 1.4484). The infrared spectrum of the product was identical with that of methylenecyclohexane prepared by the pyrolysis of cyclohexylmethyl acetate and of N,N-dimethylcyclohexylmethylamine oxide. In the event that the other isomer, 1-methylcyclohexene (lit.[36] b.p. 110° (760 mm.), $n^{20}\mathrm{D}$ 1.4503; our values for authentic material distilled through an 85-plate concentric-tube column, b.p. 106–107° (730 mm.), $n^{20}\mathrm{D}$ 1.4498, $n^{25}\mathrm{D}$ 1.4475), might be present in small amount, the column hold-up and pot residue was collected, flash distilled from a small distilling flask and submitted to infrared analysis. The spectrum and refractive index of this material were identical with those from the main body of the distillate.

1-Hydroxymethylcyclohexanol (XIV).—Methylenecyclohexane (4.8 g., 0.05 mole) was added slowly with continuous shaking to a solution consisting of 60 g. (1.1 moles) of 90% formic acid and 10 g. (0.08 mole) of 30% hydrogen peroxide. The rate of addition was such as to maintain the temperature at 40–45°. After addition of the olefin was complete, the mixture was shaken overnight. The excess reactants were removed under reduced pressure. The residual ester was hydrolyzed with 50 ml. of 10% sodium hydroxide solution warmed to 50°. The solution was saturated with potassium carbonate and the organic layer separated. The aqueous layer was extracted with absolute ethanol. The combined organic layers were dried over potassium carbonate, and the ethanol was removed carefully under reduced pressure. The yield of the crude glycol was essentially quantitative (about 97–99% in most runs). Recrystallization of the crude product from benzene gave 4.8 g. (72%) of 1-hydroxymethylcyclohexanol, m.p. 73–75° (lit.[37] m.p. 74–75°).

Oxidation of 1-Hydroxymethylcyclohexanol.—A solution of 1-hydroxymethylcyclohexanol (4.8 g., 0.04 mole) in 100 ml. of dry benzene was refluxed in a Soxhlet extractor in which the siphon tube had been replaced by a direct return tube to the distillation pot. The thimble of the extractor contained 14 g. of 90% lead tetraacetate. The benzene was refluxed for 1 hr. after the lead tetraacetate dissolved. After standing overnight the solution was filtered from the lead diacetate and the filtrate was washed with 0.5 *N* potassium carbonate and water. After drying over magnesium sulfate, the benzene solution was fractionally distilled giving 2.5 g. (70%) of cyclohexanone, b.p. 50–51° (20 mm.). In other experiments, oxidation of the crude glycol gave yields of 53–67%.

Trimethylcyclohexylmethylammonium Iodide (XVI).—To an ice-cooled solution of N,N-dimethylcyclohexylmethylamine (28 g., 0.20 mole) in 100 ml. of ether was added in four portions 18.6 ml. (0.3 mole) of methyl iodide, and the mixture was allowed to stand overnight. Evaporation of the ether left 55.4 g. (98%) of trimethylcyclohexylmethylammonium iodide, m.p. 220° (lit.[38] m.p. 225°), which was used without further purification. In other experiments the yields varied from 94–98%.

Anal. Calcd. for $C_{10}H_{22}NI$: I, 44.82. Found: I, 45.05.

Decomposition of Trimethylcyclohexylmethylammonium Iodide.—A solution of 12.3 g. (0.044 mole) of trimethylcyclohexylmethylammonium iodide in 50 ml. of water was passed through a 2 × 22-cm. column packed with ion-exchange resin, Amberlite IRA-400(OH). The methiodide was washed down the column with water until the final volume of solution was 300 ml. The solution was concentrated under reduced pressure to 50 ml. The solution was refluxed for 1 hr. in an apparatus similar to that described by Fieser,[39] and the distillate collected from the side arm was washed with 5% hydrochloric acid and with water. The hydrocarbon layer was separated, dried over magnesium sulfate and distilled, giving 1.60 g. (38%) of methylenecyclohexane. From the acid wash, 1.3 g. (21%) of dimethylcyclohexylmethylamine was recovered. In other experiments the yields of methylenecyclohexane varied from 31–34% and the yields of recovered tertiary amine from 21–34%.

Degradation of β-Phenylethylamine.—β-Phenylethylamine was methylated as described above for the methylation of cyclohexylmethylamine, giving dimethyl-β-phenylethylamine, b.p. 200–208° (lit.[40] b.p. 198–202°), in 70% yield. Oxidation of the tertiary amine and pyrolysis of the resultant N-oxide were carried out as described above for the degradation of N,N-dimethylcyclohexylmethylamine except that a few crystals of hydroquinone were added to the receiver to inhibit polymerization of the styrene. Distillation of the crude product gave an 82% yield of styrene, b.p. 46° (17 mm.), identified by oxidation in 94% yield, by the procedure described above for the oxidation of methylenecyclohexane, to phenylethylene glycol, m.p. 66–68° (lit.[41] m.p. 67–68°).

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