ture was refluxed for 4 hr. and allowed to stand overnight. The copious precipitate of sodium chloride was removed by filtration and washed with methanol, the filtrates were combined, and the mixture was distilled. The fraction boiling at 141–146° was mixed with 50 ml. of concentrated sulfuric acid, with cooling. The 1,4-dichlorobutane, which remained undissolved, was separated and the sulfuric acid layer was washed with petroleum ether. The sulfuric acid layer was added to a mixture of ice and water, whereupon 4-methoxy-1-chlorobutane separated from solution. The chloro ether was washed successively with water and aqueous sodium bicarbonate, dried with magnesium sulfate, and distilled. The product was collected in two fractions, b.p. 139–140° and 140–140.3° (lit.[65] b.p. 140°).

Pyrroles.—The 1-methylpyrrole used was the redistilled Ansul Chemical Co. product, b.p. 111.5° (lit.[66] b.p. 112–112.5°).

1-Ethylpyrrole was kindly synthesized by Mr. Merrill T. Hugo from the reaction of ethyl iodide in ether with pyrrolylpotassium. The product was refluxed over sodium and redistilled, b.p. 128.2–128.3° (lit.[67] b.p. 129–130°).

1-Butylpyrrole was prepared from butyl chloride and pyrrolylpotassium in refluxing pyrrole. The product boiled at 68–73° (20 mm.), lit.[38] b.p. 76–77° (24 mm.), and the redistilled compound boiled at 170°.

1-Benzylpyrrole was obtained from the reaction of benzyl chloride with pyrrolylpotassium in refluxing pyrrole. The distilled product was refluxed over sodium and redistilled, b.p. 244–245° (lit.[68] b.p. 247°).

(65) H. Normant, Compt. rend., 231, 909 (1930).
(66) A. Pictet, Ber., 37, 2792 (1904).
(67) C. U. Zanetti, ibid., 22, 2515 (1889).

2-Ethylpyrrole, b.p. 163–166° (lit.[69] b.p. 163–165°), was synthesized (54%) by the Huang-Minlon modification[70,71] of the Wolff–Kishner reduction of 2-acetylpyrrole,[72] for which we are grateful to Mr. Benjamin F. Crouse.

2,4-Dimethylpyrrole, b.p. 160.0–160.5° (lit.[73] b.p. 160–165°), was synthesized by Fischer's procedure.[73]

2,5-Dimethylpyrrole was obtained from the Aldrich Chemical Co. and redistilled, b.p. 166.0° (lit.[74] b.p. 165°).

(68) G. Ciamician and P. Silber, ibid., 20, 1368 (1887).
(69) M. E. A. deJong, Rec. trav. chim., 48, 1029 (1929).
(70) Huang-Minlon, J. Am. Chem. Soc., 68, 2487 (1946).
(71) W. Herz and C. F. Courtney, ibid., 76, 576 (1954).
(72) B. Oddo, Ber., 43, 1012 (1910).
(73) H. Fischer, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 217.
(74) C. Paal, Ber., 18, 2251 (1885).
(75) National Science Foundation Undergraduate Research Participant (NSF-G11923).

Demjanov Rearrangement of 1-Methylcyclohexanemethylamine

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1-Methylcyclohexanemethylamine has been prepared and characterized. The Demjanov rearrangement of this amine has been investigated, yielding as products 1-methylcycloheptanol (67%), 1-ethylcyclohexanol (11%), 1-methylcycloheptene (3.8%), methylenecycloheptane (1.3%), 1-ethylcyclohexene (2.8%), and ethylidenecyclohexane (0.25%). The composition of the product alcohols and cycloalkenes were determined by gas chromatography and n.m.r. spectroscopy. Isolation of 1-methylcycloheptanol using a spinning-band column has been successful, but attempts to separate others have failed. An improved synthesis of pivalic acid from t-butyl alcohol is presented.

The effect of alkyl or aryl substitution at the aminomethyl carbon atom, or at a ring carbon atom in a position other than the 1-position on the Demjanov ring expansion of cycloalkanemethylamines is well known.[1] Few investigators, however, have attempted to study the substitution effect at C-1, and the available information[2] is limited to three- and five-membered rings. This work has been undertaken to see whether substitution of the methyl group for the hydrogen atom on the 1-carbon atom in cyclohexanemethylamine would facilitate ring expansion, as compared with the unsubstituted amine.[3] 1-Methylcyclohexanemethylamine (I) is new; hence its preparation and properties also are described. It may be regarded as a cyclic neoalkylamine.

1-Methylcyclohexanol, prepared from cyclohexanone, was converted to 1-methylcyclohexanecarboxylic acid

by Koch and Haaf's method,[4] from which 1-methylcyclohexanecarboxamide and I were prepared. The over-all yield was 31%. The amine is a colorless liquid with a strong, fishy odor. Gas chromatographic analysis showed it to be pure and elemental analysis agreed with the formula $C_8H_{17}N$. Several derivatives such as ureas, amides, and imides were prepared. The n.m.r. spectrum[5] of the amine consisted of three resonances with areas in the ratio 2:12:3. These are assigned to the methylene hydrogens on the carbon to which the nitrogen atom is attached (τ 7.59, singlet), the ten ring protons and the amino group (several lines with one main peak at 8.56 and a broad base line), and the methyl group (9.17, singlet). The observed chemical shifts and relative intensities are in good agreement with the structure of the amine.

The reaction of I (25.4 g.) with nitrous acid in dilute orthophosphoric acid solution[6] yielded 1.8 g. of cycloalkenes and 20 g. of alcohols. Examination of the

(1) P. A. S. Smith and D. R. Baer, Org. Reactions, 11, 157 (1960).
(2) (a) G. Errera, Gazz. chim. ital., 22, II, 109 (1892), cited by ref. 1; (b) H. Rupe and I. Splittgerber, Ber., 40, 4311 (1907); (c) J. Bredt, J. prackt. Chem., [2] 95, 70 (1917), cited by ref. 1; (d) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, J. Am. Chem. Soc., 81, 4390 (1959); (e) P. A. S. Smith, D. R. Baer, and S. N. Ege, ibid., 76, 4564 (1954); (f) E. F. Cox, M. C. Caserio, M. S. Silver, and J. D. Roberts, ibid., 83, 2719 (1961).
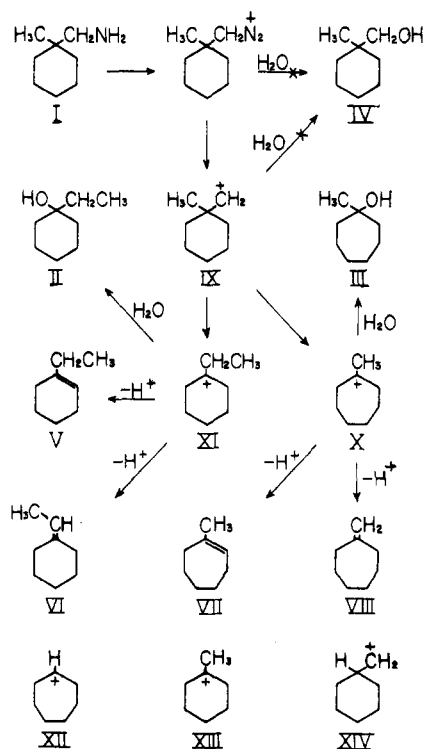(3) (a) L. Ruzicka and W. Brugger, Helv. Chim. Acta, 9, 399 (1926); (b) P. A. S. Smith and D. R. Baer, J. Am. Chem. Soc., 74, 6135 (1952).

(4) H. Koch and W. Haaf, Ann., 618, 251 (1958).
(5) The spectrum was determined at 25° without solvent by Dr. Shiro Satoh of this laboratory on a Varian Associates Model V-4311 high-resolution spectrometer with cyclohexane (τ 8.56) as an internal standard at 60 Mc. The same instrument and experimental conditions were employed throughout this work, unless noted otherwise.

H₃C CH₂NH₂ (I) → H₃C CH₂N₂⁺ —H₂O→ H₃C CH₂OH (IV)

↓ H₂O

HO CH₂CH₃ (II)   H₃C CH₂⁺ (IX)   H₃C OH (III)

CH₂CH₃ (V) ←–H⁺– CH₂CH₃⁺ (XI)   CH₃⁺ (X) ↑H₂O

H₃C CH (VI)   –H⁺   CH₃ (VII)   –H⁺   CH₂ (VIII)   –H⁺

H⁺ (XII)   CH₃⁺ (XIII)   H CH₂⁺ (XIV)

Demjanov alcohols by gas chromatographic analysis[7] showed two peaks having retention volumes 522.7 cc. (A) and 593.6 cc. (B) with areas[8] in the ratio 12:88. It was expected, based on the accepted mechanism,[1] that these Demjanov alcohols would consist of either 1-ethylcyclohexanol (II) involving migration of the methyl group, or 1-methylcycloheptanol (III) involving ring expansion, or unrearranged 1-methylcyclohexanemethanol (IV). Letters A and B represent compounds produced by the Demjanov rearrangement, whereas II, III, and IV represent compounds made by other authentic methods. It will be shown that A = II and B = III. Retention volumes of II, III, and IV were 521.7, 593.9, and 644.1 cc., respectively. Gas chromatographic analysis of a mixture of IV and the Demjanov alcohols indicated three peaks of retention volumes 520.9, 586.2, and 642.3 cc. Evidently, 1-methylcyclohexanemethanol[9] is not one of the products. A mixture of II and the Demjanov alcohols was gas chromatographed, showing only two peaks with retention volumes 520.9 and 589.0 cc., with a resulting increase in relative area of A. Fractional distillation of the Demjanov alcohols using a spinning-band column gave pure B. The gas chromatogram of a mixture of the isolated B and the synthetically prepared III revealed a single peak, showing the identity of B and III. It may be concluded from the analysis that

the reaction of 1-methylcyclohexanemethylamine with nitrous acid gave rise to 1-ethylcyclohexanol and 1-methylcycloheptanol in 9.4 and 68.7% yields, respectively.

Analysis of the Demjanov alcohols by n.m.r. spectrum, determined at 120° without solvent, confirmed this conclusion. The spectrum of the isolated B consisted of three resonances with areas in the ratio 1:12:3. These are assigned to the hydroxyl group (τ 7.71, singlet), the twelve ring protons (several lines with one main peak at 8.45 and a broad base line), and the methyl group (8.83, singlet). The observed chemical shifts and relative intensities are in good agreement with 1-methylcycloheptanol. The spectrum of B is also identical with that of III, but quite different from those of II and IV. The spectrum of II exhibited characteristic signals of τ 8.18 (the hydroxyl group, singlet), 8.56 (the ten ring protons and methylene group, multiplet with one main peak and a broad base line), and 9.14 (the methyl group, triplet with one main peak) with relative intensities of 1:12:3. The spectrum of IV showed signals at τ 6.69 (the methylene group), 6.91 (the hydroxyl group), 8.56 (the ten ring protons), and 9.13 (the methyl group) with relative intensities 2:1:10:3. Quantitative analysis by n.m.r. spectrum, by reference to the spectra of the synthetically prepared II and III, demonstrated the Demjanov alcohols to be a mixture of 1-ethylcyclohexanol and 1-methylcycloheptanol in the ratio[10] 14:86 (11 and 67% yields), a value in good agreement with that obtained by gas chromatography (12:88). No signal corresponding to the methylene group of IV was detected.

Cycloalkenes which might be derived from the amine used would be 1-ethylcyclohexene (V), ethylidenecyclohexane (VI), 1-methylcycloheptene (VII) and methylenecycloheptane (VIII). Gas chromatographic analysis[11] of the Demjanov cycloalkenes showed only two peaks having retention volumes 332.1 and 346.7 cc. with peak heights in the ratio 3.2:5.

Cycloalkenes obtained by dehydration of 1-ethylcyclohexanol and of 1-methylcycloheptanol were used as reference in gas chromatographic analysis, and each of the cycloalkenes showed a single peak. The retention volume of the former was 332.9 cc. and that of the latter was 348.3 cc. On the contrary, the n.m.r. studies revealed the former to be a mixture (7.5:1) of V and VI, and the latter to be a mixture (7:1) of VII and VIII. The spectrum of the former (V and VI), determined at 25° (in CCl₄), had signals at τ 4.56 (the olefinic proton of V, triplet), 4.80 and 4.91 (the olefinic proton of VI; the proton might be expected to show a quartet by spin–spin coupling with the three protons of the methyl group with relative intensities 1:3:3:1, but only two lines were detected), and 9.04 (the methyl group of V, triplet). The signal due to the methyl group of VI could not be identified since the signal was obscured by signals of the methylene group

(6) Under customary conditions (aqueous acetic acid solution), large amounts of acetates are formed. For example, see ref. 3a and 3b. To avoid this complication Smith and Baer used sodium dihydrogen phosphate solution with success.

(7) The analysis was effected on a Yanagimoto Model GCG-220, equipped with a 3-m. column of 30% Apiezon grease L on 80-100-mesh Celite, operating at 165°, helium outlet flow rate of 36.8 cc./min. The same experimental conditions were used throughout the analysis of the alcohols.

(8) The areas were determined with a planimeter and each component was calibrated.

(9) One may argue that 1-methylcyclohexanemethanol might have been lost during distillation, if it would be present in a trace amount. No peak corresponding to it, however, was detected even in the undistilled, whole reaction mixture.

(10) The ratio was determined based on the relative intensities of the methyl groups of 1-ethylcyclohexanol (τ 9.14, triplet) and 1-methylcycloheptanol (8.83, singlet).

(11) Column, 3 m.; stationary phase 30% Apiezon grease L on 80-100-mesh Celite; temperature 150°; helium outlet flow rate, 32.4 cc./min. When the analysis was effected at various temperatures using silicone DC 550, polyethylene glycol 1500, or dioctyl phthalate as stationary phase, only two peaks were also detected. The same experimental conditions were used throughout the analysis of cycloalkenes.

of V and the ring protons of V and VI. The spectrum of the latter (VII and VIII) had signals at τ 4.42 (the olefinic proton of VII, triplet), 5.29 (the terminal methylene group of VIII, quintet), and 8.32 (the methyl group of VII).

The n.m.r. spectrum of the Demjanov cycloalkenes revealed these to consist of four compounds. The spectrum had signals at τ 4.43 (the olefinic proton of VII, triplet), 4.55 (the olefinic proton of V; the signal apparently was obscured[12] by the signal of the olefinic proton of VII), 4.81 and 4.92 (the olefinic proton of VI; the proton might be expected to show a quartet, but only two lines were detected), 5.30 (the terminal methylene group of VIII, quintet), 8.31 (the methyl group of VII), and 9.03 (the methyl group of V, triplet). These assignments were confirmed by the spin-decoupling technique, and are in accord with the above-mentioned assignments for the n.m.r. spectra of the synthetically prepared cycloalkenes. Quantitative analysis of the Demjanov cycloalkenes, based on the relative intensities of the methyl group of V, and the olefinic protons of V, VI, VII, and VIII, demonstrated the cycloalkenes to consist of V, VI, VII, and VIII in the ratio 34:3:47:16, respectively. The yields of V, VI, VII, and VIII based on the amine used were 2.8, 0.25, 3.8 and 1.3%, respectively. The ratio of six- to seven-membered cycloalkenes was approximately 3:5.1.

Ruzicka and Brugger[3a] reported that the Demjanov reaction with cyclohexanemethylamine, a cyclic iso-alkylamine, gave rise to cycloheptanol and cyclo-heptene in 56 and 21% yields, respectively. Smith and Baer,[3b] however, found that Ruzicka and Brugger's cycloheptanol was a mixture of its isomeric alcohols containing also the acetic ester of one or more. For this reason Ruzicka and Brugger's result can not be compared with ours. Smith and Baer's reinvestigation showed that the products included cycloheptanol (rearrangement by migration of ring carbon atom), 1-methylcyclohexanol (rearrangement by hydride migration), unrearranged cyclohexanemethanol, and a cycloalkene mixture in 29, 2, 15, and 27% yields, respectively. They, however, did not mention the composition of the hydrocarbon mixture.

The experimental facts demonstrate that substitution of the methyl group for the hydrogen atom at C-1 in cyclohexanemethylamine enhanced ring expansion by a factor of approximately 2.3 (based on the yields of 1-methylcycloheptanol and cycloheptanol). The behavior of the 1-methyl substitution favoring ring expansion is in accord with that observed in three- and five-membered rings.[2] This might be interpreted in terms of the stability of carbonium ion formed: I would give rise to a presumably more stable tertiary carbonium ion (X) when ring expansion occurs, whereas that from cyclohexanemethylamine would be secondary (XII). A steric factor also might be involved: ring expansion leading to X relieves bulkiness on C-1. Rearrangement to stable tertiary carbonium ion XI via methyl migration also relieves the bulkiness, whereas rearrangement to carbonium ion XIII via hydride migration does not. In terms of this view formations

of X and XI are competitive as are formations of XII and XIII. Hence, the situation is complicated.

Cannell and Taft[13] reported that in the study of the reaction of isobutylamine and nitrous acid the entropy of activation favors methyl migration over hydride migration by about 5 cal./deg. (based on the migration of one methyl). If the similar trend holds in alicyclic systems, the observed methyl migration over hydride migration might be well explained.

Unexpectedly, unrearranged 1-methylcyclohexane-methanol was not detected under the experimental conditions, while unrearranged cyclohexanemethanol was obtained in 15% yield from cyclohexanemethyl-amine. The lack of unrearranged product could be explained from at least two viewpoints: (1) the 1-methyl compound is a neopentyl-type substance and thus direct displacement on the amine-bearing carbon would be less favorable; (2) the idea of competing reactions suggests that rearrangements would be more favorable in the methyl substituted compound and so the direct substitution reaction would suffer.

The 1-methyl substitution decreased[14] the formation of cycloalkenes from 27 to 8.2%. XIV would lead to formation of cycloalkene even without hydride migration, whereas IX would yield cycloalkenes only after methyl migration or ring expansion. Since Smith and Baer did not mention the composition of their cyclo-alkenes, we can not discuss this matter further.

Gas chromatographic analysis of the undistilled, whole reaction mixture showed a small amount of a presumably high-boiling substance. This may be a nitrogen-containing compound[1] which often appears in Demjanov reactions, but no attempt was made to identify it.

As mentioned above, 1-methylcyclohexanecarboxylic acid was obtained from 1-methylcyclohexanol by re-action with formic and sulfuric acids. This method of substituting a carboxyl for the hydroxyl of a tertiary alcohol is useful synthetically. Koch and Haaf[4] prepared pivalic acid in this way. They reported a 74% yield but did not discuss the purity of their acid. We have modified their method with a resulting in-crease in yield from 74 to 86% by doubling the moles of formic acid taken, by cooling to 3–5° instead of 10–15°, and by shortening the reaction time from 120 to 80 min. Gas chromatographic analysis of the pivalic acid showed a single peak which was identical with that of an authentic sample, demonstrating absence of isomers. Its n.m.r. spectrum, determined at 75° without solvent, showed singlets at τ 8.80 (the methyl groups of t-butyl) and at −2.41 (the carboxyl group) with relative areas of 9:1, and no other signals (hence, absence of methylene and methine groups). Its neutralization equivalent was 101.5 (theory 102.1). The anilide and p-toluidide were prepared as pure derivatives. The absence of isomeric C_5 acids in the product speaks for the stability of the t-butyl carbo-nium ion formed from t-butyl alcohol. One gram of

(12) The presence of V was confirmed by the signal due to its methyl group.

(13) (a) L. G. Cannell and R. W. Taft, Jr. [J. Am. Chem. Soc., 78, 5812 (1956)] found that substitution of methyl for hydrogen on the β-carbon atom in ethylamine greatly facilitates rearrangement. (b) S. Winstein and E. Grunwald [ibid., 70, 828 (1948)] obtained similar results for anchimeric assistance in solvolysis reactions.

(14) Evidence that the cycloalkenes formed have not been lost in large quantities during distillation was given by quantitative analysis by gas chromatographic analysis of the undistilled, whole reaction mixture.

higher acids was formed for each 14 g. of pivalic acid but this material has not been identified yet.

Experimental[15]

1-Methylcyclohexanol was prepared by the usual Grignard procedure from commercial cyclohexanone (98.1 g., 1 mole, dried and distilled before use) and methylmagnesium iodide in 73% yield (83.2 g.), b.p. 68° (20 mm.), lit.[16] b.p. 72° (22 mm.).

1-Methylcyclohexanecarboxylic acid was prepared by the method of Koch and Haaf[4] from 1-methylcyclohexanol (80 g., 0.7 mole), 99% formic acid (107 ml., 2.8 moles), and 95% sulfuric acid (472 ml., 8.4 moles) at 5–7° in 91.5% yield (90 g.), b.p. 133° (20 mm.), lit.[4] b.p. 132° (20 mm.). Its neutralization equivalent was 141.1 (theory 142.2).

1-Methylcyclohexanecarboxamide was prepared by treating 1-methylcyclohexanecarboxylic acid (85.3 g., 0.6 mole) with thionyl chloride and treating the crude acid chloride with aqueous ammonia. The carboxamide was formed in 80% yield (67.7 g.), b.p. 108–109° (1 mm.), m.p. 66–67° (lit.[17] m.p. 65°).

1-Methylcyclohexanemethylamine.—1-Methylcyclohexanecarboxamide (56.5 g., 0.4 mole) was refluxed with lithium aluminum hydride (26.6 g., 0.7 mole) in dry ether (600 ml.) for 15 hr. Processing in the usual manner gave the crude amine in 70% yield (35.6 g.). Redistillation of the amine using a spinning-band column gave pure amine in 51% yield (26 g.), b.p. 51° (7 mm.). Purity was demonstrated by gas chromatographic analysis.

Anal. Calcd. for C₈H₁₇N: C, 75.52; H, 13.46; N, 11.01. Found: C, 75.49; H, 13.23; N, 10.86.

N-(1-Methylcyclohexanemethyl)-N'-phenylurea.—A mixture (1:1) of I and phenyl isocyanate was heated at 80° for 5 min. Two recrystallizations of the product from 60% aqueous ethanol gave fine white needles of m.p. 153.5–154.5°.

Anal. Calcd. for C₁₅H₂₂N₂O: C, 73.13; H, 9.00; N, 11.37. Found: C, 73.20; H, 8.96; N, 11.68.

N-(1-Methylcyclohexanemethyl)phthalimide.—A mixture of I and phthalic anhydride (1:1) in xylene was boiled until all the anhydride had dissolved, and then an additional 15 min. Processing in the usual manner gave white crystals of m.p. 66–67.5°.

Anal. Calcd. for C₁₆H₁₉NO₂: C, 74.68; H, 7.44; N, 5.46. Found: C, 74.72; H, 7.33; N, 5.37.

N-(1-Methylcyclohexanemethyl)-N'-phenylthiourea.—A mixture (1:1) of I and phenyl isothiocyanate, after spontaneous reaction had subsided, was heated for 5 min. over a low flame. Three recrystallizations of the product from 70% aqueous ethanol gave white crystals of m.p. 105–107°.

Anal. Calcd. for C₁₅H₂₂N₂S: N, 10.67. Found (Kjeldahl method): N, 10.29.

N-(1-Methylcyclohexanemethyl)-N'-α-naphthylthiourea.—The reaction of I and α-naphthylisothiocyanate gave white crystals which, after three recrystallizations from 95% ethanol, melted at 142.5–143.5°.

Anal. Calcd. for C₁₉H₂₄N₂S: N, 8.97. Found: N, 8.71.

3-Nitro-N-(1-methylcyclohexanemethyl)phthalimide.—The derivative was prepared from I and 3-nitrophthalic anhydride. It melted at 124.5–125.5°.

Anal. Calcd. for C₁₆H₁₈N₂O₄: N, 9.27. Found: N, 8.98.

p-Nitro-N-(1-methylcyclohexanemethyl)benzamide was prepared from I and p-nitrobenzoyl chloride in the usual manner, m.p. 117–118.5°.

Anal. Calcd. for C₁₅H₂₀N₂O₃: N, 10.14. Found: N, 9.98.

1-Methylcyclohexanemethanol.—1-Methylcyclohexanecarboxylic acid (28.4 g., 0.2 mole) was reduced in the usual way with lithium aluminum hydride in dry ether in 90% yield (23 g.), b.p. 88° (17 mm.), lit.[4] b.p. 85° (14 mm.).

1-Ethylcyclohexanol was prepared in the usual way from commercial cyclohexanone (49 g., 0.5 mole, dried and distilled before use) and ethylmagnesium bromide in 78% yield (50 g.), b.p. 76.5° (20 mm.), lit.[18] b.p. 77° (20 mm.).

Dehydration of 1-Ethylcyclohexanol.—1-Ethylcyclohexanol (3.85 g., 0.03 mole) was dehydrated following the method of Tray-

nelis.[19] The product was distilled three times, b.p. 135–136°. Gas chromatographic analysis[11] showed a single peak, whereas n.m.r. spectrum revealed the product to be a mixture of 1-ethyl-cyclohexene and ethylidenecyclohexane in the ratio 7.5:1.

Dehydration of 1-methylcycloheptanol (3.85 g., 0.03 mole) was effected similarly; yield 0.8 g., b.p. 137–138°. Gas chromatographic analysis[11] showed a single peak, whereas n.m.r. spectrum revealed the product to consist of 1-methylcycloheptene and methylenecycloheptane in the ratio 7:1.

Demjanov Rearrangement.—In a 500-ml. four-necked flask fitted with a mechanical stirrer, dropping funnel, thermometer, and reflux condenser were placed 10.4 ml. (0.0152 mole) of 85% orthophosphoric acid and 120 ml. of water. The flask was surrounded by ice–water. 1-Methylcyclohexanemethylamine (25.4 g., 0.2 mole) was added with stirring. A white salt precipitated. A solution of 13.8 g. (0.2 mole) of sodium nitrite in 30 ml. of water was added to the cold mixture, which was kept for 1 hr. at room temperature. During this time the precipitate dissolved, nitrogen was slowly evolved, and an oil separated. An additional solution of 2.76 g. (0.04 mole) of sodium nitrite in 5 ml. of water and then 1 ml. of 85% orthophosphoric acid were added to the mixture. The mixture was then heated to 95° and was maintained at this temperature for 1 hr. When the solution was cooled, the reflux condenser was rinsed with ether and the oil was extracted with four 200-ml. portions of ether. The combined ether extracts were washed with 20 ml. of 5% hydrochloric acid and four 50-ml. portions of water and dried over anhydrous magnesium sulfate. After removal of ether by distillation through a 40-cm. Vigreux column, the residue was fractionally distilled into two fractions: a low-boiling fraction, b.p. 55–65° (80 mm.), yield 1.8 g., which decolorized bromine in carbon tetrachloride solution; and a high-boiling fraction, b.p. 73–78° (20 mm.), yield 20 g., which gave a positive color test[20] with ceric nitrate reagent. Each fraction was redistilled and subjected to gas chromatography, n.m.r. spectroscopy, and analysis for the elements.

Anal. Calcd. for C₈H₁₄ (cycloalkenes): C, 87.19; H, 12.81. Found: C, 86.68; H, 12.98.

Anal. Calcd. for C₈H₁₆O (alcohols): C, 74.94; H, 12.58. Found: C, 74.33; H, 12.34.

The alcohol fraction (14 g.) was distilled carefully through a spinning-band column, giving 6 g. of pure 1-methylcycloheptanol. The attempt to separate other compounds was unsuccessful.

Pivalic Acid.—In a 1-l. four-necked flask, fitted with a mechanical stirrer, thermometer, gas outlet, and dropping funnel, was placed 337 ml. (6 moles) of 95% sulfuric acid. A mixture of 37 g. (0.5 mole) of t-butyl alcohol and 77 ml. (2 moles) of 99% formic acid was added dropwise into the flask with vigorous stirring at such a rate that the reaction temperature with ice-bath cooling was maintained at 3–5°. This took about 1 hr., after which further stirring was continued for 20 min. at the same temperature. The mixture was poured onto 2 kg. of cracked ice at once and then was extracted with four 200-ml. portions of ether. The combined ether extracts were washed with three 50-ml. portions of water and dried over magnesium sulfate. Ether was removed and the residue was distilled under reduced pressure. The fraction distilling at 70–72° (15 mm.) was collected, m.p. 34–35°, yield 44 g. (86%), leaving an unidentified 3.1 g. of higher acids. The product was further purified by distillation: b.p. 72° (15 mm.), 163.5° (760 mm.), m.p. 34–35°, yield 42 g. (82%) (lit.[20] b.p. 164°, m.p. 35°).

Anilide.—The anilide of pivalic acid prepared in our laboratory and of an authentic acid were prepared and shown to be identical. The mixture melting point determination showed no depression (m.p. 128–129°), m.p. 128.5–129° (lit.[20] m.p. 129°).

p-Toluidide.—The p-toluidide of our pivalic acid was prepared. It melted at 120–120.5° (lit.[20] m.p. 120°). A mixture melting point with an authentic sample was 120–120.5°.

(15) All melting points and boiling points are uncorrected. Analyses were by Dr. Sakakihara, unless noted otherwise.

(16) M. Barbier and M. F. Hügel, *Bull. soc. chim. France*, 951 (1961).

(17) K. E. Hamlin and M. Freifelder, *J. Am. Chem. Soc.*, **75**, 369 (1953).

(18) H. B. Williams and W. R. Edwards, Jr., *ibid.*, **69**, 336 (1947).

(19) V. J. Traynelis, W. L. Hergenrother, H. T. Hanson, and J. A. Valicenti [*J. Org. Chem.*, **29**, 123 (1964)] reported that their compound consisted of 94% 1-ethylcyclohexene and 6% ethylidenecyclohexane.

(20) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960.

valuable discussions and continuing interest and to Professor Charles D. Hurd of Northwestern University for his helpful suggestions and advice. The author is also indebted to Dr. Shiro Satoh for n.m.r. studies. Thanks are given to Mr. Tadashi Ikegami for his assistance in the experimental work.

β,β-Dinitroalkylamines and -nitramines, and Related Compounds[1]

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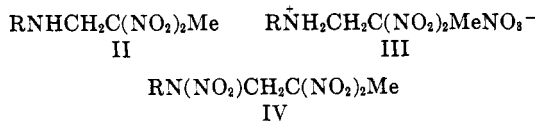*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico*

The condensation of 2,2-dinitroalkanols with ammonia, aliphatic amines, and aromatic amines has been investigated, the conditions for the preparation of the 2,2-dinitroalkylamines have been determined, and the formed amines have been nitrated. The properties of the compounds are described and it is shown that the condensation reaction can be reversed by certain weak Lewis bases. The nitration products are more stable toward such bases.

Mannich condensations of 1,1-dinitroparaffins with formaldehyde and amines can be carried out by heating the components in a polar medium or by condensing 2,2-dinitro alcohols with ammonia or amines to give various substituted 2,2-dinitroalkylamines.[2]

In the present investigation the condensation reaction with 2,2-dinitropropanol (I) has been carried out with a series of primary and secondary amines. The

$$MeC(NO_2)_2CH_2OH$$
$$I$$
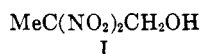
conditions for the reaction are highly specific for each case, by-products appear as contaminants, and the purification of the products is often rendered difficult by the formation of mixed crystals between product and starting material. In the case of aliphatic primary amines, the condensation product II can be isolated as a crystalline nitrate III or as the corresponding nitramine IV if it is not possible to purify II. The ease of dehydration of the nitrates III differs depending on the

$$RNHCH_2C(NO_2)_2Me \quad \overset{+}{RN}H_2CH_2C(NO_2)_2MeNO_3^-$$
$$II \qquad\qquad\qquad III$$

$$RN(NO_2)CH_2C(NO_2)_2Me$$
$$IV$$

nature of R. For R = small alkyl 100% nitric acid does not bring about the conversion to IV without an additional dehydrating agent such as acetic anhydride.[3] Amines II with R containing functional groups are usually nitrated with 100% nitric acid directly to nitramines IV and the corresponding nitrates III are then obtained only by using a stoichiometric amount of nitric acid in an inert solvent.
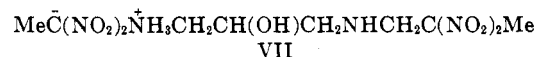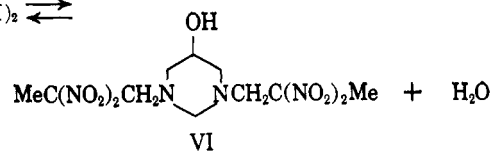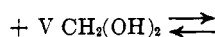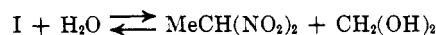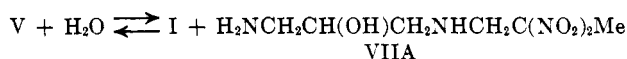
The condensation reaction with 2,2-dinitropropanol works equally well with unsaturated amines (*e.g.*, allylamine), diamines, amino alcohols, and hydrazine derivatives.

When a primary amine is used in the reaction with 2,2-dinitropropanol, a single 2,2-dinitropropyl group is usually introduced, an exception being the alkaline

condensation with glycine.[4,5] Other electron-withdrawing substituents inactivate amino groups; thus, amides, urethans, and ureas do not react with I under the conditions investigated. While I fails to condense with guanidine under the usual conditions, it can be made to react with aminoguanidine bicarbonate. The product, however, is not the expected amine but the aminoguanidine salt of 1,1-dinitroethane. It is evident that in this case I has undergone a reversal of the Henry reaction under the influence of the amine to give 1,1-dinitroethane and formaldehyde. The final product in all these reactions is probably determined to some extent by the relative solubilities of the products and the basicities of the amines. Another example of an abnormal reaction is the condensation of I with 1,3-diamino-2-propanol. The formed 2,2,10,10-tetranitro-4,8-diaza-6-undecanol (V) disproportionates in the aqueous reac-

$$MeC(NO_2)_2CH_2NHCH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me$$
$$V$$
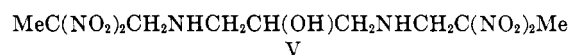
tion mixture and the resultant oil gives a formaldehyde condensation product VI on cooling or seeding and the 1,1-dinitroethane salt VII on crystallization from methanol. The following equilibria are postulated for

$$V + H_2O \rightleftharpoons I + H_2NCH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me$$
$$VIIA$$

$$I + H_2O \rightleftharpoons MeCH(NO_2)_2 + CH_2(OH)_2$$

$$+ V\ CH_2(OH)_2 \rightleftharpoons$$

$$VI$$

$$VIIA + MeCH(NO_2)_2 \rightleftharpoons$$

$$Me\bar{C}(NO_2)_2\overset{+}{N}H_3CH_2CH(OH)CH_2NHCH_2C(NO_2)_2Me$$
$$VII$$

V in aqueous solution. If the condensation of I with 1,3-diamino-2-propanol is carried out in the presence of 1 mole of aqueous formaldehyde, VI is obtained in excellent yield as the only product. The structure of VI is based on analyses, infrared absorption spectra, and reactions.

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission and presented before the Division of Organic Chemistry at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) P. Noble, Jr., F. G. Borgardt, and W. L. Reed, *Chem. Rev.*, **64**, 19 (1964).

(3) A summary of the extensive work by Wright and others on this subject is given by A. H. Lamberton, *Quart. Rev.* (London), **5**, 75 (1951).

(4) H. Feuer, G. B. Bachmann, and W. May, *J. Am. Chem. Soc.*, **76**, 5124 (1954).

(5) M. B. Frankel and K. Klager, *ibid.*, **79**, 2953 (1957).