The combined organic layers, weighing 12.4 g., were dried over potassium carbonate and distilled to give 7 g. (55%) of 2-ethyl-1-butene, b.p. 65–70°, and 4.5 g. (26%) of 3,3-diethyloxetane, b.p. 135–140°. The identity of the products in each case was established by means of the properties given in Tables VI and VII and their infrared spectra.

The reactions with alcoholic base were carried out at about 20° lower temperature except for the final baking.

No products were isolated from the reaction of base with 2,2-trimethylene-3-bromo-1-propanol.

MANHATTAN, KAN.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY]

Stereochemistry of the Cycloheptane Ring. Synthesis and Deamination of *cis* and *trans*-2-Aminocycloheptanol

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Cis and *trans*-2-aminocycloheptanol have been prepared by the route: cycloheptene oxide → *trans*-2-aminocycloheptanol → *trans*-2-(*p*-nitrobenzoylamino)cycloheptanol → *cis*-2-*p*-nitrophenyl-4,5-cycloheptanoöxazoline → *cis*-2-aminocycloheptanol. Deamination of the *trans* isomer with nitrous acid gives cyclohexylmethanal, whereas the *cis* isomer affords a mixture of cyclohexylmethanal and cycloheptanone. These results are compared with those obtained from *cis*- and *trans*-2-aminocyclohexanol and are interpreted in terms of the rate of reaction versus the rate of conformational change.

Although a great deal of work has been done on the steric relationships of cyclohexane compounds,[1] comparatively little systematic work has been done on the steric effects operative in seven membered ring systems. Several isolated aspects of the stereochemistry of cycloheptanes have been discussed recently, and a few earlier workers attempted a systematic study of the stereochemistry of medium sized rings.

Ayres and Raphael[2] have recently prepared *trans*-cycloheptane 1,2-dicarboxylic acid, and found that this compound readily forms a *trans* fused cyclic anhydride, in contrast to the behavior of *trans*-cyclohexane-1,2-dicarboxylic acid. The ease of formation of a *trans* anhydride may be explained on the basis that the cycloheptane ring is considerably more flexible than that of cyclohexane. The greater flexibility of the seven-membered ring may also be invoked to explain the formation from both *cis* and *trans* cycloheptane-1,2-diol of a cyclic ketal, under the same conditions, and to rationalize the observation that both *cis* and *trans*-1,2-cycloheptanediol increase the conductivity of boric acid solutions, while neither of the cyclohexane-1,2-diols will do so.[3]

We felt that the application to cycloheptane compounds of a reaction, the steric requirements of which are well defined, would shed additional light on the preferred conformation of cycloheptane derivatives. Such a reaction appeared to be the deamination of *cis* and *trans*-2-aminocycloheptanol. The steric requirements of the reaction of amino alcohols with nitrous acid has been studied thoroughly,[4] and the reaction has been applied to, and its steric implications interpreted for *cis* and *trans*-2-aminocyclohexanol.[5]

Trans-2-aminocycloheptanol (I) was prepared by the reaction of aqueous ammonia with cycloheptene oxide.[6] Of the possible synthetic routes available for the preparation of *cis*-2-aminocycloheptanol, that which appeared best was the general method employed for the conversion of *trans*-2-aminocyclohexanol to the *cis*-isomer.[7]

Trans-2-aminocycloheptanol was converted smoothly to *trans*-2-(*p*-nitrobenzoylamino)cycloheptanol (II), by the action of *p*-nitrobenzoyl chloride and aqueous base. Treatment of this amide with thionyl chloride afforded *cis*-2-*p*-nitrophenyl-4,5-cycloheptanoöxazoline (III). Prolonged boiling of (III) with aqueous hydrochloric acid yielded *cis*-2-aminocycloheptanol (IV) which with *p*-nitrobenzoyl chloride and base gave *cis*-2-(*p*-nitrobenzoylamino)cycloheptanol (V).

Trans-2-aminocycloheptanol was deaminated with sodium nitrite in acetic acid to afford as the only isolable product hexahydrobenzaldehyde (VI), identical in all respects to a sample prepared from cyclohexylmagnesium bromide and triethyl orthoformate.[8] The infrared spectrum of the crude de-

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[1] a. W. Klyne, *Progress in Stereochemistry*, Vol. I, Butterworths, London, 1954, pp. 36–90. b. W. G. Dauben and K. S. Pitzer in M. J. Newman, *Steric Effects in Organic Chemistry*, J. Wiley and Sons, New York, 1954, pp. 1–60. (c) D. H. R. Barton and R. C. Cookson, *Quart. Revs.*, **10**, 1 (1956).

[2] D. C. Ayres and R. A. Raphael, *J. Chem. Soc.*, 3151 (1958). We are indebted to Prof. Raphael for communicating his results to us prior to their publication.

[3] a. P. H. Hermans and C. J. Maan, *Rec. trav. chem.*, **57**, 643 (1938). b. J. Boeseken, *Rec. trav. chem.*, **58**, 856 (1939).

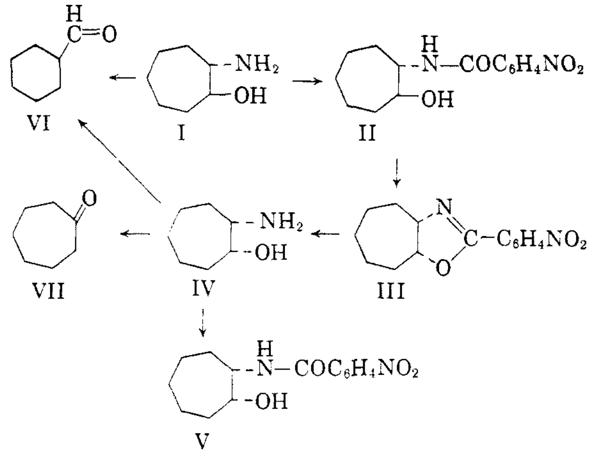
[4] P. I. Pollak and D. Y. Curtin, *J. Am. Chem. Soc.*, **72**, 961 (1950).

[5] G. E. McCasland, *J. Am. Chem. Soc.*, **73**, 2294 (1951).

[6] a. M. Mousseron and R. Granger, *Bull. soc. chim.*, 850 (1947). b. P. B. Talukdar and P. E. Fanta, *J. Org. Chem.*, **24**, 555 (1959).

[7] G. E. McCasland and D. A. Smith, *J. Am. Chem. Soc.*, **72**, 2194 (1950).

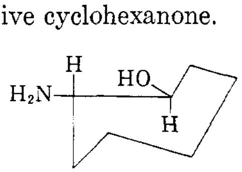
[8] C. E. Wood and M. C. Comley, *J. Soc. Chem. Ind.*, **42**, 429T (1923).



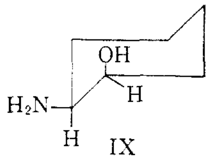
amination showed only one carbonyl band, at 5.81 μ. The 2,4-dinitrophenylhydrazone crystallized readily and was easily purified, giving additional evidence for the homogeneity of the product. Although the product from the *cis*-amino alcohol under the same conditions gave cycloheptanone-2,4-dinitrophenylhydrazone on treatment with dinitrophenylhydrazine, this derivative required several recrystallizations to reach the melting point of an authentic sample. The infrared spectrum of the crude product showed in addition to the ketone band at 5.89 μ, a shoulder at 5.81 μ. Isolation of the total aldehyde fraction by means of dimedone solution indicated that 18% of the crude product was hexahydrobenzaldehyde, while infrared measurements for two runs showed 20.4 ± 1% of aldehyde. The balance of the product was assumed to be cycloheptanone.

According to the well known steric requirements for group migration in the nitrous acid deaminations of amino alcohols,[1,4,5] the amino group must be located antiparallel to the bond which migrates. On this basis, a study of molecular models of *trans*-2-aminocycloheptanol indicates that the amino group, and consequently the hydroxyl group, must occupy a position analogous to the equatorial position in cyclohexane compounds. We obtained in our deaminations of *trans*-2-aminocycloheptanol no detectable amount of cycloheptene oxide, which would arise if the functional groups on the cycloheptane ring had a conformation similar to the 1,2-diaxial position for cyclohexanes. Of the several possible conformations, (VIII) seems to best fulfill these requirements. These results are in accord with those obtained in the cyclohexane series, where *trans*-2-aminocyclohexanol gives cyclopentylmethanal upon treatment with nitrous acid.

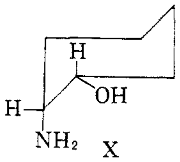
The formation of a large amount of cycloheptanone from the deamination of *cis*-2-aminocycloheptanol is in direct contrast to the products obtained from the deamination of *cis*-2-aminocyclohexanol.[6] In the cyclohexane series, deamination of the *cis* compound proceeds to give about 70% cyclopentylmethanal. If it be assumed, as is probable, that the amino group is somewhat larger than the hydroxyl group, then the conformation of *cis*-2-aminocyclohexanol which would predominate at equilibrium would be that where the amino group is equatorial and the hydroxyl group is axial (IX). Deamination of a compound of this conformation will proceed with ring contraction to give the aldehyde, whereas the slightly less favorable conformation (X), would give cyclohexanone.



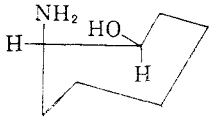
VIII



IX



X



XI

The production of cycloheptanone as the principal product in the deamination of *cis*-2-aminocycloheptanol demands that at the time of reaction the amino group be in an axial conformation, and antiparallel to a hydrogen atom (XI). As we have already seen as a result of the deamination of *cis*-2-aminocyclohexanol that the amino group tends to assume an equatorial position in six membered rings, and as a result of the deamination of *trans*-2-aminocycloheptanol, that bulky groups occupy a quasi-equatorial position in seven-membered rings, we would be led to predict that, on purely conformational grounds, the deamination of *cis*-2-aminocyclohexanol and *cis*-2-aminocycloheptanol should give nearly the same ratio of aldehyde to ketone.

It is, therefore, difficult to reconcile the large proportion of cycloheptanone formed from *cis*-2-aminocycloheptanol purely in terms of conformational arguments. These apparently incompatible results may be interpreted in terms of the relatively great flexibility of the cycloheptane ring as compared with that of cyclohexane, however.

The mechanism of the deamination of aliphatic primary amines should proceed in a manner similar to that of aromatic amines,[9] namely the amine is first converted to a *N*-nitroso derivative, which can isomerize and dehydrate to an aliphatic diazonium salt. This diazonium salt loses nitrogen forming a carbonium ion, or undergoes nucleophilic attack to yield the product of the reaction. In the case of the *cis*-aminocyclanols this reaction can be pictured in terms of the formulas (XII) to (XIX).

If it is assumed that the principal conformation of both *cis*-2-aminocyclohexanol and *cis*-2-aminocycloheptanol is that where the amino group is

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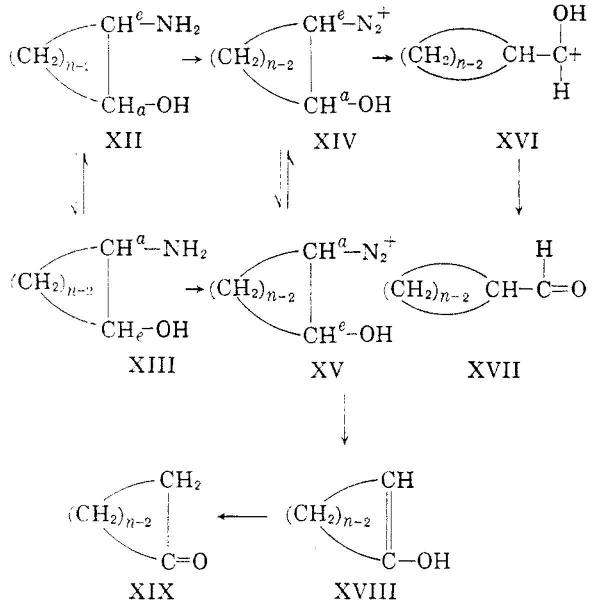
(9) (a) J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, 1956, p. 364. (b) E. R. Alexander, "Ionic Organic Reactions," Wiley, New York, 1950, p. 266.

equatorial (XII), then the equatorial diazonium salt (XIV) will be that initially formed in the largest amount. This diazonium salt may then follow one of two reaction paths; either it may undergo decomposition with group migration to give ultimately the aldehyde (XVII), or it may be considered to be in equilibrium with the axially substituted diazonium salt (XV). (XV) also has open to it two paths, namely, decomposition with loss of hydrogen to yield the cyclanone (XIX), or equilibration with (XIV). A similar course of reasoning may be applied to the conversion of the axial-amino conformation of the amino alcohol (XIII), which may be assumed to be in equilibrium with (XII).



In order to explain the course of the deaminations of the *cis*-amino-alcohols, it is necessary to assume that the rate of the reaction to lose hydrogen[10] (XV → XVIII) is fast with respect to the movement of a ring bond, (XIV → XVI). It may also be postulated, because of the flexibility of the cycloheptane ring, that the rate of equilibration of the two conformations of the diazonium salt from *cis*-2-aminocycloheptanol (XIV → XV, n = 7) is much faster than the rate of equilibration between the two forms of the diazonium salt from *cis*-2-aminocyclohexanol (XIV → XV, n = 6), and that as a result the ratio of rate constants k (XIV → XV)/k (XIV → XVI) for n = 7 is larger than for n = 6. Assuming that k (XV → XIV)/k (XV → XVIII) is relatively small because of the rotational barrier in cyclohexane, one would expect a greater proportion of cyclanone to be formed from *cis*-2-aminocycloheptanol than from *cis*-2-aminocyclohexanol.[11]

Thus the ratio of aldehyde to ketone from *cis*-2-aminocycloheptanol is determined by the ratio of the rate of group migration to proton loss k(XIV → XVI)/k (XV → XVIII), while in the deamination of *cis*-2-aminocyclohexanol the product ratio is determined by the position of the equilibrium for the conformational change (XII → XIII).

Effects of this type may be considered to be of no consequence in the deamination of the *trans*-2-aminocyclanols, because the rate of conversion of the diequatorial conformer to the diaxial will be negligible and the equilibrium will be greatly in favor of the diequatorial conformation, consequently the product of the reaction will be virtually exclusively aldehyde.

EXPERIMENTAL[12]

Trans-2-(p-nitrobenzoylamino)cycloheptanol. To a solution of 3.9 g. of *trans*-2-aminocycloheptanol, m.p. 74–75°,[6] in 75 ml. of water was added 5.58 g. of freshly recrystallized *p*-nitrobenzoyl chloride in 70 ml. of benzene. To the resulting heterogeneous mixture was added 24 ml. of 5% sodium hydroxide, the reaction mixture was shaken 10 min. at room temperature, cooled, and the product collected by filtration. Recrystallization from ethanol afforded 6.60 g. (77%) of cream colored crystals m.p. 190–191°; the melting point was not increased by additional recrystallizations.

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.53; N, 10.06. Found: C, 60.19; H, 6.73; N, 10.08.

2-p-Nitrophenyl-4,5-cis-cycloheptanoöxazoline. To 6.60 g. of *trans*-2-(*p*-nitrobenzoylamino)-cycloheptanol was added 11.3 g. of thionyl chloride. The flask was protected from atmospheric moisture with a calcium chloride tube and allowed to stand at room temperature for twelve hours. A large excess of dry ether was added, the precipitated solid collected, and recrystallized from aqueous alcohol to give 3.0 g. (58%) of white crystals, m.p. 118–119°. Several recrystallizations from aqueous ethanol gave material, m.p. 120–121°.

Anal. Calcd. for $C_{14}H_{16}N_2O_3$: C, 64.57; H, 6.19; N, 10.76. Found: C, 65.09; H, 6.08; N, 11.11.

Cis-2-aminocycloheptanol.[13] A solution of 6.0 g. of the cycloheptanoöxazoline was dissolved in 50 ml. of 4*N* hydrochloric acid, heated under reflux for 24 hr., refrigerated for twelve hours, and the precipitated *p*-nitrobenzoic acid collected. The clear filtrate was made alkaline with 20% sodium hydroxide and continuously extracted with ether for twenty-four hours. Evaporation of the ether gave 2.4 g. (80%) of white powder, which was purified by sublimation at 10 mm. and 70° to give white crystals, m.p. 81–82°.

Anal. Calcd. for $C_7H_{15}N_2$: C, 65.07; H, 11.70; N, 10.83. Found: C, 64.64; H, 12.03; N, 10.91.

The *p*-nitroamide was prepared in the manner described for the *trans* amino alcohol, and formed cream-colored needles from aqueous ethanol, m.p. 129–130°.

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(10) We have some evidence that the enol of cycloheptanone is an intermediate in the formation of the ketone, specifically, in one deamination the infrared spectrum of the crude reaction mixture showed a distinct band at 5.68 μ which can be attributed to cycloheptanone enol acetate. In the absence of this data there is little to choose between the conversion of (XV) to (XVIII), and the direct conversion of (XV) to (XIX) by hydride transfer.

(11) D. Y. Curtin and M. C. Crew, *J. Am. Chem. Soc.*, **77**, 354 (1955), have postulated a similar effect to explain an abnormally large amount of *p*-anisyl migration in the deamination of *erythro*-1-*p*-anisyl-1-phenyl-2-aminopropanol.

(12) Analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Infrared spectra were carried out in chloroform solution or as liquid films on a Perkin Elmer Model 137 Spectrophotometer. Melting points were determined on a Fisher-Johns block, and are uncorrected.

(13) J. Sicher and M. Svoboda, *Coll. Czech. Chem. Comm.* **23**, 1252 (1958), have recently reported the synthesis of this compound and find it to have m.p. 79–81°. Their *p*-nitrobenzamide has m.p. 128–129.5°.

Anal. Calcd. for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.11; H, 6.36; N, 10.25.

Deaminations. a. A solution of 0.129 g. of *trans*-2-aminocycloheptanol in 1.0 ml. of glacial acetic acid and 2.0 ml. of water was cooled in salt-ice bath. To this cooled solution was added a chilled solution of 1.4 g. of sodium nitrite in 3.0 ml. of water, and the solution allowed to stand in the cold for 30 min. The reaction was made basic with 20% sodium hydroxide solution, and extracted with ether. The ethereal extracts were dried and the solvent removed on the steam bath through a short column, affording 0.106 g. (96%) of yellow oil. This oil was treated with 2,4-dinitrophenylhydrazine reagent to give a yellow powder, m.p. 165–169°. Recrystallization from ethanol–ethyl acetate gave yellow-orange crystals, m.p. 170–172°. A mixed melting point with the dinitrophenylhydrazone of hexahydrobenzaldehyde[14] showed no depression.

b. A solution of 0.135 g. of *cis*-2-aminocycloheptanol in 3.0 ml. of water was cooled in an ice bath. To this solution was added a cold solution of 1.0 g. of sodium nitrite in 3.0 ml. of water and 1.0 ml. of glacial acetic acid. The reaction mixture was allowed to stand in the cold 30 min., made basic with dilute sodium hydroxide, and extracted with two portions of ether. The solvent was removed on the steam bath to give 0.073 g. (62%) of oil which was converted to the 2,4-dinitrophenylhydrazone, obtained as a yellow powder, m.p. 142–145°. Recrystallization from ethanol gave yellow crystals m.p. 147–148°, undepressed on mixing with an authentic sample of cycloheptanone-2,4-dinitrophenylhydrazone.[15] Treatment of 0.073 g. of the crude product with dimedone solution gave 0.039 g. of the dimedone derivative of cyclohexylmethanal. A blank run on pure cyclohexylmethanal indicated 50% recovery of the aldehyde. Consequently the deamination mixture contained 18% of cyclohexylmethanal.

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ATLANTA, GA.

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[14] M. Mousseron, R. Jacquier, M. Mousseron-Canet, and R. Zagdoun, *Bull. soc. chim.*, 1042 (1952).

[15] R. L. Shriner and R. C. Fuson, *Identification of Organic Compounds*, 3rd Ed., New York, 1948, p. 262.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, BRIGHAM YOUNG UNIVERSITY]

Rhenium and Its Compounds as Hydrogenation Catalysts.
III. Rhenium Heptoxide[1,2,3]

H. SMITH BROADBENT, GRAHAM C. CAMPBELL,[4] WILLIAM J. BARTLEY,[4] AND JOHN H. JOHNSON

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The hydrogenation catalytic activity of some rhenium "blacks" obtained by the reduction of commercially available rhenium heptoxide has been examined. The catalysts were prepared by hydrogenation of the heptoxide in a solvent prior to the addition of the reducible substrate (*ex situ*), or in the presence of the substrate subsequently and/or simultaneously being reduced (*in situ*). These rhenium "blacks" have been shown to be easily the most effective catalysts yet reported for the hydrogenation of the carboxylic acids to alcohols. They promote this conversion with a wide variety of acids at 150–250° (usually 160°)/*ca.* 200 atm. in a few hours, giving excellent yields of alcohols accompanied occasionally by ester by-product. Unreduced acid rarely survives. They are also unusually effective in the hydrogenation of amides. On the other hand, these catalysts show only moderate but definite activity toward many of the common organic functions reducible through the agency of platinum or nickel catalysts.

Relatively little work on the catalytic properties of rhenium metal in hydrogenation has been reported[5] and none on its oxides. Schmidt[6] reports that rhenium displays average activity as a hydrogenation catalyst being less active than platinum, palladium, or nickel. A colloidal rhenium sol was reported to be effective in reducing the ethylenic bonds of maleic and cinnamic acids with very high ratios of rhenium to substrates[7] Rhenium supported on unglazed porcelain by reducing the ammonium perrhenate-soaked carrier in a hydrogen stream at 500–600° was ineffective toward maleic acid and cyclohexene at 20° at 1 atm., but at 350° cyclohexene was reduced and benzene slowly decomposed stepwise to methane.[8] Nitric oxide was re-

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[1] Part I of this series: H. S. Broadbent, L. H. Slaugh, and N. L. Jarvis. "Rhenium Sulfides as Liquid-Phase Hydrogenation Catalysts. A Comparison with Molybdenum Sulfide and Cobalt Polysulfide," *J. Am. Chem. Soc.*, **76**, 1519 (1954).

[2] This research was supported by Contract No. AF 18 (600)-1164 with the United States Air Force through the Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] Presented in part at the 131st meeting of the American Chemical Society in Miami, Florida, April 11, 1957.

[4] This paper is based largely upon theses submitted by Mr. Campbell (1955) and by Mr. Bartley (1958) in partial fulfillment of the requirements for the degree of Master of Science, Brigham Young University.

[5] For a complete review to 1940 see "Gmelin's Handbuch der anorganischen Chemie," 8th Ed., Verlag Chemie, Berlin, 1941, No. 70, pp. 37–40. Since that time very little has been reported.

[6] Schmidt, *Z. physik. Chem.*, **165**, 212, 224 (1933).

[7] C. Zenghelis and K. Stathi, *Compt. rend.*, **209**, 797 (1939); *Chem. Abstr.*, **34**, 669 (1940).

[8] S. B. Anisimov, V. M. Kraseninnakova, and M. S. Platanov, *Ber.*, **68**, 762 (1935).