and the formation of a yellow color. Subsequent to 1 hr. of stirring, the black solution was added to 3 g. (0.01 mole) of chlorotriphenylsilane dissolved in 30 ml. of THF.

The reaction mixture was then hydrolyzed with dilute acid and filtered. The filtrate was concentrated and treated with petroleum ether (b.p. 60–70°). On standing 2.2 g. of crude triphenylsilanol crystallized and was removed by filtration. The mother liquor was then chromatographed on alumina. Petroleum ether (b.p. 60–70°) eluted 0.5 g. of crude allyltriphenyl-silane.[26] A recrystallization from the same solvent gave 0.4 g. (13.3%) of product, m.m.p. 84–86°.

# Nitrous Acid Deamination of cis- and trans-2-Hydroxycyclooctylamines[1,2]

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*Contribution from Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803. Received November 9, 1964*

*Deaminations of cis- and trans-2-hydroxycyclooctylamines in aqueous acetic acid have been found to be completely different from the related reactions of cyclooctene oxides and glycols. The amino alcohols react to form cyclooctanone and cycloheptanecarboxaldehyde as major products. Transannular processes, which dominate reactions of cyclooctene oxides and glycols, account for less than 4% of the products from the amino alcohols. Alternate descriptions of reaction mechanisms are discussed, but the available data do not dictate an unequivocal choice.*

The report[3] that the oxide, glycol, halohydrin, and amino alcohol derivatives of tetramethylethylene all give equivalent proportions of glycol (substitution) and ketone (rearrangement) products has led to the claim that "the accepted mechanism for pinacolic transformation involves the prior formation of a carbonium ion intermediate."[4] When the leaving group is attached to a tertiary carbon, this path appears to be well established. However studies of pinacolic transformations with compounds in which the leaving group is attached to a secondary carbon are far less extensive, and descriptions of reaction mechanism are considerably less certain. A recent paper from this research group described a study of some medium ring cycloalkene glycols, and the suggestion was made that, at least in some cases, acid-catalyzed rearrangements of these glycols may not involve carbonium ion mechanisms.[5] The present paper is a continuation of our investigation of rearrangements of 2-substituted cycloalkanols[5] and describes nitrous acid deaminations of cis- and trans-2-hydroxycyclooctylamines. The data to be described lead us to the conclusion that either these deaminations do not involve carbonium ions or carbonium ions from different, but related, sources behave totally differently from each other.

Nitrous acid deaminations of primary amines have been extensively investigated.[6] In some systems rearrangements quite similar to those characteristic of solvolyses occur during deamination,[3,6i] while in others substantial differences in stereochemistry[6e] and/or proportions of the same products[6f,k,7a] have been reported. Both solvolytic and deamination reactions have often been described as carbonium ion processes, with differences in composition of product mixtures from different (related) reactants usually being ascribed to energetic differences in the ions formed by the two kinds of reaction.[6f,j,l,o] The cation left by exothermic loss of nitrogen from a diazonium ion has been described as a "hot" carbonium ion which may react differently from a "normal" solvolytic carbonium ion. On occasion, direct displacement on the diazonium cation has been preferred over "hot"

(1) We gratefully acknowledge support of this research by grants from the National Science Foundation (Grant Gl4461), the Petroleum Research Fund administered by the American Chemical Society (Grant 1817-A4), and the Louisiana State University Council on Research.

(2) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(3) Y. Pocker, *Chem. Ind.* (London), 332 (1959).

(4) Y. Pocker in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 1.

(5) J. G. Traynham and P. M. Greene, *J. Am. Chem. Soc.*, 86, 2657 (1964).

(6) Some selected recent references particularly pertinent to the present discussion are: (a) V. Prelog, H. J. Urech, A. A. Bothner-By, and J. Würsch, *Helv. Chim. Acta*, 38, 1095 (1955); (b) A. Streitwieser, Jr., *J. Org. Chem.*, 22, 861 (1957); (c) B. M. Benjamin, H. J. Schaeffer, and C. J. Collins, *J. Am. Chem. Soc.*, 79, 6160 (1957) [footnote 9 of this paper provides a succinct summary, with references, of some data pertaining to carbonium ions in deaminations]; (d) C. J. Collins, W. A. Bonner, and C. T. Lester, *ibid.*, 81, 466 (1959); (e) J. A. Berson and B. A. Ben-Efraim, *ibid.*, 81, 4094 (1959); (f) M. S. Silver, *ibid.*, 83, 3482, 3487 (1961); (g) J. A. Berson and D. Willner, *ibid.*, 84, 675 (1962); (h) J. Meinwald, P. G. Gassman, and J. J. Hurst, *ibid.*, 84, 3722 (1962); (i) P. Warrick, Jr., and W. H. Saunders, Jr., *ibid.*, 84, 4095 (1962); (j) E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, 85, 169 (1963); (k) D. J. Cram and M. R. V. Sahyun, *ibid.*, 85, 1257 (1963); (l) E. J. Corey and R. L. Dawson, *ibid.*, 85, 1782 (1963); (m) W. Hückel and L. Heyder, *Ber.*, 96, 220 (1963); (n) J. A. Berson and A. Remanick, *J. Am. Chem. Soc.*, 86, 1749 (1964); (o) G. J. Karabatsos, C. E. Orzech, Jr., and S. Meyerson, *ibid.*, 86, 1994 (1964); (p) T. Cohen and E. Jankowski, *ibid.*, 86, 4217 (1964).

(7) (a) D. Y. Curtin and M. C. Crew, *ibid.*, 76, 3719 (1954); (b) D. J. Cram and J. E. McCarthy, *ibid.*, 79, 2866 (1957); (c) see, for example, D. Y. Curtin and M. C. Crew, *ibid.*, 77, 354 (1955), and A. Streitwieser, Jr., *J. Org. Chem.*, 22, 866 (1957).

carbonium ions as an explanation for these differences,[6e,g,h,n] and disagreement on this matter is central to some of the current controversy pertaining to amine deamination mechanisms. Alternatively, differences in carbonium ion intermediates may stem from far less anchimeric assistance to loss of nitrogen from diazonium cation than to corresponding solvolytic processes[4,7a,b]; carbonium ions formed with and without assistance (but otherwise related) may well suffer different fates. An early view that rearrangement during deamination of amino alcohols is concerted[7c] has been firmly discounted (for migrating phenyl) in favor of open carbonium ions.[6c]

Transannular processes are characteristic of carbonium ion like reactions of medium ring compounds.[8] Solvolyses of cycloalkyl tosylates and deaminations of cycloalkylamines give similar mixtures of products, 10–40% of which arise from transannular hydride shifts.[8] A 2-hydroxy substituent in the medium ring reactant promotes transannular rearrangements in solvolysis reactions: acid-catalyzed hydrolyses of medium ring cycloalkene oxides[8] and rearrangements of cyclooctene glycols[5] give transannular products almost exclusively. Therefore transannular rearrangement during deamination of medium ring 2-hydroxycycloalkylamines is heavily favored if carbonium ion intermediates at all like those in the epoxide and glycol reactions intervene. Ours has been a product analysis approach; formation of the same intermediate should be revealed by formation of the same (or at least highly similar) product mixtures; conversely, formation of greatly different product mixtures can be taken as evidence that different intermediates are involved in the reactions of epoxides, glycols, and amino alcohols

## Results and Discussion

Nitrous acid deaminations of cis- and trans-2-hydroxycyclooctylamines in about 47% aqueous acetic acid solution lead to cyclooctanone and cycloheptanecarboxaldehyde as major products; very small amounts of unsaturated alcohols and 1,2-diols accompany these carbonyl products.[9a,b] Table I summarizes the product

**Table I.** Yields of Products from Deaminations of 2-Hydroxycyclooctylamines

| Amine | Yield, % | | | | | | Total yield, % |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | |
| cis | 26 | 10 | 2.3 | 3.5 | 2.4[a] | 41 | 85 |
| trans | 12 | 67 | 1.2 | 2.9 | 4.2[b] | ... | 87 |

[a] All cis. [b] Mixture of cis and trans.

(8) For a review, see V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.
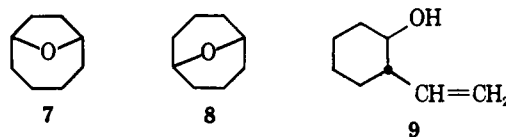
(9) (a) Detectable amounts of cycloheptanone were also present in the product mixtures. In some early runs, from which oxygen was not carefully excluded, substantial proportions of cycloheptanone were formed, but the sum of cycloheptanecarboxaldehyde and cycloheptanone proportions was essentially constant among runs. Some product mixtures, analyzed periodically over a few days, showed progressively increasing amounts of cycloheptanone and corresponding decreasing amounts of cycloheptanecarboxaldehyde. We believe that cycloheptanone is a secondary product, formed from the aldehyde, and does not figure in the mechanism of deamination itself. This surprising transformation is being studied further in our laboratory. (b) Some small, unassigned peaks in the gas chromatograms may be due to the presence of minute amounts of glycol monoacetates (products of substitution by solvent acetic acid[6p]).

data. Less than 4% of the total product mixture formed in each of these deaminations is directly attributable to a transannular hydride shift (product 4).

The product mixtures were analyzed by capillary column gas chromatography, and identification of components was achieved by combination of preparative gas chromatography, infrared spectroscopy, preparation of derivatives, and comparison with authentic samples. Although isomeric cyclooctenols and cyclooctanediols were poorly resolved by the gas chromatograph, analyses for these components of the reaction mixtures were accomplished by converting the alcohols (in the total mixtures) to their trimethylsilyl derivatives,[10] which are readily resolved.
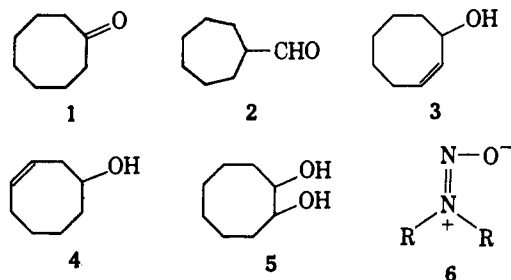


*Carbonyl Products.* Bicyclic ethers **7** and **8** and trans-2-vinylcyclohexanol (**9**) are produced as trans-



annular products in the acid-catalyzed reactions of cyclooctene oxides[11] and glycols,[5] but they were undetected among the products from deaminations of these amino alcohols. Conversely, cycloheptanecarboxaldehyde, a major product here, is completely absent in the mixtures obtained from the epoxide and glycol reactions. Our cumulative experience with mixtures containing all of these C$_8$ compounds assures us that components less than 1% of the total mixtures would have been detected in our analyses.

In summary, these amino alcohol deaminations do not resemble at all, so far as major product formation is concerned, the other rearrangements, and one must infer that the intermediates (and/or transition states) involved in the two kinds of processes must be unmistakably different. As mentioned earlier, small differences between solvolysis and deamination reactions have been attributed to "hot" carbonium ions in the deaminations,[6f,j,l,o] but seldom if ever has this description been invoked to account for differences as great as those reported here.

Some recent papers have emphasized the important influence of the leaving group on the behavior of the carbonium ion generated in various reactions.[6k,12] Certainly such influence (water vs. N$_2$ as leaving groups) may well be responsible for the different product

(10) C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Am. Chem. Soc.*, 85, 2497 (1963).

(11) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, 79, 3900 (1957); A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, 79, 3905 (1957); A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, 81, 1640 (1959).

(12) (a) M. Cocivera and S. Winstein, *ibid.*, 85, 1702 (1963); (b) P. S. Skell and W. L. Hall, *ibid.*, 85, 2851 (1963).
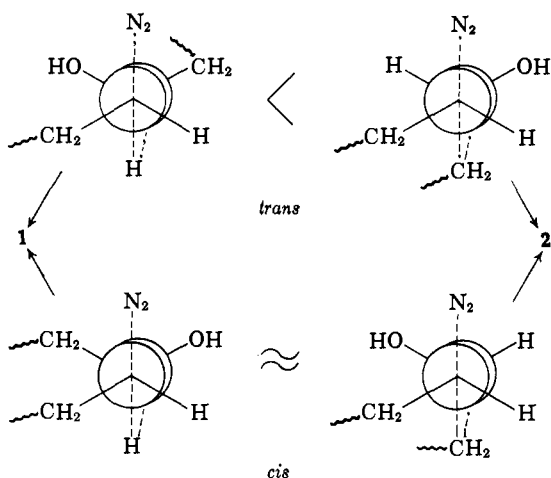
Figure 1.

mixtures formed from different 2-substituted cyclo-octanols. However, little or no variation in product proportions with change in leaving group was observed with highly aqueous solvents.[6k] It seems highly unlikely, in the face of the careful studies reported, that the almost totally different product mixtures obtained from the cyclooctene glycol and amino alcohol reactions, both largely aqueous, can arise mainly from influence on a carbonium ion center by the leaving group.
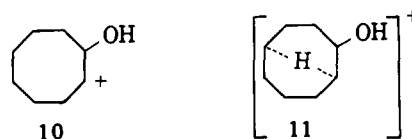
Two reasonable, alternate descriptions of mechanisms of product formation accounting for difference among these reactants utilize both bridged and unbridged carbonium ions: (I) (a) Cyclooctene oxide and glycol react mainly through a 2-hydroxycyclooctyl cation which gives products almost exclusively after transannular hydride shift, but (b) amino alcohol (or more precisely, 2-hydroxycyclooctanediazonium cation) reacts by concurrent migration of hydrogen or alkyl during departure of nitrogen, without substantial carbonium ion development. (II) (a) Cyclooctene oxide and glycol react by formation of a transannular hydrogen-bridged carbonium ion[11] which gives mostly or exclusively transannular products, but (b) deamination of amino alcohol leads to an unbridged 2-hydroxycyclooctyl cation in which 1,2-shifts rather than transannular shifts lead to products.

Although concurrent 1,2-migration (path Ib) has been rejected for phenyl migration in aryl-substituted amino alcohols,[6c] it might be important for the cyclooctane derivatives studied here.[13] The transition states (Figure 1) expected to be favored for the amino alcohols do account satisfactorily both for the relative extents of hydrogen and alkyl migration (products 1 and 2, respectively) and for the greater selectivity with the *trans*-amino alcohol than with the *cis* isomer (more difference in energy between alternate *trans* conformations).[14a]

(13) A free carbonium ion has been dismissed as "the sole or even predominant intermediate" in favor of an ion pair intermediate (diazonium cation) for the substitution portion of deaminations of *trans,-trans*-2-decalylamine.[6p]
(14) (a) For a discussion of the Curtin–Hammett principle see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 151, 152, 237–239. (b) Deamination studies with *cis*-2-hydroxycyclohexylamine and *cis*-2-hydroxycycloheptylamine have led to the conclusion that an intermediate, presumably diazo hydroxide, survives sufficiently long for confor-

Alternatively, amino alcohol deamination may follow path IIb. Two speculations about the 2-hydroxy-cyclooctyl cation[10] favor this proposal: loss of nitrogen from diazonium cation would be expected to require little if any assistance from migrating hydrogen or alkyl,[4,7a,b] and the virtual absence of 1,2-shifts in the carbonium ion (a required condition if the carbonium ion is intermediate in epoxide and glycol rearrangements) would be surprising. Direct formation of a transannular hydrogen-bridged carbonium ion (for example, 11) in the epoxide and glycol rearrangements will account for the stereochemistry of the 1,4-diol products[11] as well as for the lack of 1,2-shifts. Al-



though individual tastes may favor description I or description II, few data are now available to dictate the choice. The data do exclude major involvement of 10 in *both* deaminations of 2-hydroxycyclooctylamine and rearrangements of cyclooctene oxide and glycol. Further work which we hope will indicate a clearer choice of description of mechanisms is in progress.

*Products 5 and 6.* Even though the amount of 1,2-diol formed during deamination is small, its formation with complete retention of configuration from *cis*-amino alcohol strongly implicates the diazo hydroxide 12 as an intermediate.[14b] A similar accounting for the formation of alcohol of retained configuration from certain bicyclooctylamines has been given.[15] An S$_N$i type reaction of 12 would lead to glycol formation with retention.
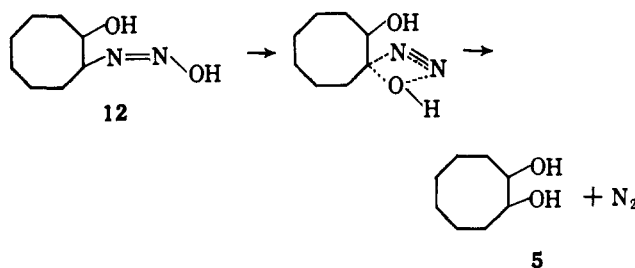


Formation of 6, tentatively formulated as 6a or 6b,[16,17] as a major product from *cis*-amino alcohol may also signal involvement of 12 as an intermediate. An intermolecular reaction between two cycloalkane derivatives, at least one of which is 12, could easily lead to another intermediate with the N-nitroso grouping. The lack of stereospecificity in formation of glycol and the absence of 6 in the deamination mixture

mational re-equilibration: M. Cherest, H. Felkin, J. Sicher, F. Sipoš, and M. Tichý, *J. Chem. Soc.*, in press. We gratefully acknowledge private communication from Professor J. Sicher about these studies. See also J. W. Huffman and J. E. Engle, *J. Org. Chem.*, 24, 1844 (1959).
(15) (a) S. J. Cristol, 18th National Organic Chemistry Symposium, Columbus, Ohio, June 1964. (b) See also E. H. White and J. E. Stuber, *J. Am. Chem. Soc.*, 85, 2169 (1963), and ref. 6p.
(16) The *meso*-ionic formulation of N-nitrosamines is strongly indicated by n.m.r. data: (a) C. E. Looney, W. D. Phillips, and E. L. Reilly, *ibid.*, 79, 6136 (1957); (b) G. J. Karabatsos and R. A. Taller, *ibid.*, 86, 4373 (1964).
(17) (a) We gratefully acknowledge the suggestion of 6b by a referee. (b) If 6b or other rearranged structure proves to be correct for 6, reevaluation of the relative extents of alkyl and hydrogen migration during deamination of the *cis* amino alcohol will obviously be required.

6a    6b
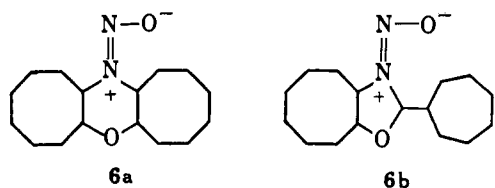
from *trans*-amino alcohol both hint that, for some unappreciated reason, diazo hydroxide intermediate is not so important with the *trans* compound as with the *cis* one.

Different speculations about the path whereby **6** is formed could be described. Some of these specify intermolecular displacement reactions of diazonium cations or oxadiazole intermediates; they are essentially unhelpful in accounting for the extensive formation of **6** from *cis*-amino alcohol and none from *trans*-amino alcohol. No information presently at hand permits a satisfying explanation for the formation of **6**, but it is clearly not a product to be expected from an intermediate carbonium ion similar to that obtained in acid-catalyzed reactions of cyclooctene oxides[11] or glycols.[5]

*Cyclooctenols.* The isomeric cyclooctenols **3** and **4**, formed as very minor products, may arise by proton loss from intermediate 2-hydroxycyclooctyl cations (path Ia) or hydrogen-bridged ions (path IIa). However, **3** may be formed by concerted elimination of proton and nitrogen from a diazonium cation, and only **4** can be associated unmistakably with transannular processes. Whether Ib or IIb (or some other account) properly describes the major reaction path, some (<4%) reaction by Ia or IIa, respectively, could occur.

### Experimental

*Preparation of Materials.* *cis*-Cyclooctene oxide[11] was prepared by treatment of commercially available *cis*-cyclooctene with hydrogen peroxide in benzonitrile solution[18a] (77% yield) or with *m*-chloroperoxybenzoic acid[18b] in a mixture of chloroform and ethyl acetate at room temperature (93% yield); b.p. 95° (35 mm.).

*trans-2-Hydroxycyclooctylamine.* A 4:1 mixture of methanol–water (400 ml.) was saturated with ammonia at 0°, cyclooctene oxide (26 g.) was added, and the mixture was heated in a Parr medium pressure apparatus at 130° (320 p.s.i.) for 3 days. The solvent and excess ammonia were removed on a steam bath, and the residual brown oil was vacuum distilled to yield a colorless oil which quickly solidified, b.p. 80–90° (0.5 mm.). Vacuum sublimation furnished 14 g. (46%) of *trans*-2-hydroxycyclooctylamine[19a]; white crystals, m.p. 72.5–73°.

*cis-2-Hydroxycyclooctylamine.* *trans*-2-Hydroxycyclooctylamine was isomerized to the *cis* isomer by the thionyl chloride induced cyclization of the N-benzoyl derivative (m.p. 135–136°)[19a] to *trans*-2-phenyl-4,5-hexamethylene-$\Delta^2$-oxazoline and subsequent ring opening and hydrolysis by refluxing the oxazoline in ethanol–

hydrochloric acid (1:1) for 2 days.[19] When the hydrolysis mixture was concentrated, made strongly alkaline, and extracted continuously with ether, *cis*-2-hydroxycyclooctylamine[19a] was obtained and recrystallized from ethyl acetate, m.p. 57–59°.

*Deamination Reactions.* Typical experiments utilized 67 mmoles of *trans*-amino alcohol in 300 ml. of solvent and 10 mmoles of the less accessible *cis*-amino alcohol in 50 ml. of solvent. To an ice-chilled solution of amino alcohol in 50% aqueous acetic acid, under a nitrogen atmosphere, a concentrated aqueous solution of sodium nitrite (2 moles of $NaNO_2$ per mole of amino alcohol, 15 ml. of water per 0.10 mole of $NaNO_2$) was added slowly. The chilled mixture was stirred for 40–48 hr. Sulfamic acid (10% aqueous solution) was added to decompose excess nitrite, and after dilution with water, the mixture was extracted with four portions of ether. (From the *cis*-amino alcohol mixture, a solid separated and was removed by filtration before ether extraction. This faintly yellow solid amounted to 42% of the total deamination product and was subsequently identified as **6**. None of this product was obtained from the *trans*-amino alcohol.)

The combined ether extract was washed with 10% sodium carbonate solution and dried over magnesium sulfate. Evaporation of solvent left a viscous, yellow liquid which was examined by gas chromatography and infrared spectroscopy.[20] Identification of g.c. peaks was facilitated by comparison with authentic samples and by preparative g.c. separations followed by infrared spectroscopic analysis and derivative preparation. Both extract concentrates contained the same components, in different proportions. The isomeric cyclooctenols were not resolved on the analytical g.c. column, but were easily differentiated by conversion to their trimethylsilyl ether derivatives by treatment of a portion of the entire concentrate with trimethylsilyl chloride and hexamethyldisilazane in pyridine solution.[10] Samples of authentic, isomeric cyclooctenols[5,21] with coincident g.c. peaks gave easily separated trimethylsilyl ethers with longer retention times. 1,2-Cyclooctanediol was detected and estimated by titration with periodic acid[22]; stereoisomers were differentiated by conversion to their trimethylsilyl ethers,[10] which had shorter retention times in the gas chromatograph than the glycols themselves. The carbonyl compounds were characterized by conversion to 2,4-dinitrophenylhydrazones: cyclooctanone 2,4-DNPH, m.p. 170.5–172°,[5,11a] and cycloheptanecarboxaldehyde 2,4-DNPH, m.p. 132–134°.[23] Percentage compositions of product mixtures were computed by comparison of g.c. responses with those of standard samples and mixtures. The products and yields obtained are summarized in Table I. The products

(18) (a) G. B. Payne, *Tetrahedron*, **18**, 763 (1962). (b) Commercial sample obtained from FMC Corp. was used as supplied.

(19) (a) J. Sicher and M. Svoboda, *Collection Czech. Chem. Commun.*, **23**, 1252 (1958); (b) W. S. Johnson and E. N. Schubert, *J. Am. Chem. Soc.*, **72**, 2187 (1950).

(20) Gas chromatographic analyses were carried out with a Barber Colman Model 20 instrument equipped with a hydrogen flame detector and a 100-ft. capillary column coated with GE-96 silicone (100–150°). An Aerograph Autoprep Model A-700 gas chromatograph equipped with a ³/₈ in. × 10 ft. PDEAS column or a ³/₈ in. × 20 ft. silicone column (140°) was used for preparative separations. Infrared spectra were obtained with a Beckman IR-5 spectrophotometer.

(21) A sample of 2-cyclooctenol was gratefully received from Columbian Carbon Co., Lake Charles, La.

(22) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p. 39.

(23) (a) A. C. Cope, N. A. Nelson, and D. S. Smith, *J. Am. Chem. Soc.*, **76**, 1100 (1954); (b) A. C. Cope, H.-H. Lee, and H. E. Petree, *ibid.*, **80**, 2849 (1958).

identified and reported in Table I account for 95% of the total product mixture obtained from the *trans*-amino alcohol and for 90% of that from the *cis* isomer.[9a,b]

Compound **6**, the major product from deamination of *cis*-2-hydroxycyclooctylamine, m.p. 85–86.5°, exhibits ultraviolet absorption (maxima at 360 and 237 m$\mu$) characteristic of an N-nitrosamine[24]; its infrared spectrum shows no absorptions attributable to O–H or N–H bonds and is consistent with the meager information available for N-nitrosamines.[25] The n.m.r. spectrum[26] is complex and not particularly helpful;

(24) S. F. Mason, *Quart. Rev.* (London), **15**, 317 (1961).
(25) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 306–307.
(26) We express our appreciation to Dr. William L. Senn, Jr.,

poorly resolved multiplets appear at approximately $-1.5$, $-3.7$, $-4.2$, and $-5.2$ p.p.m. (peak areas approximately 24–29:1:1:1, respectively), the last one similar in position to the peak for one of the tertiary hydrogens in diisopropyl-N-nitrosamine ($-4.97$ p.p.m.).[27] On the basis of these data, this product is tentatively formulated as **6a** or **6b**.

*Anal.*[28] Calcd. for $C_{16}H_{28}N_2O_2$: C, 68.5; H, 10.1; N, 10.0. Found: C, 68.6; H, 10.3; N, 10.1.

Humble Oil and Refining Co., Baton Rouge, La., and Dr. Fred J. Impastato, Ethyl Corp., Baton Rouge, La., for providing us with n.m.r. and mass spectral data on **6** before instrumentation was operating in our own laboratories (n.m.r. data obtained with CCl₄ solutions, tetramethylsilane internal standard, Varian A-60 instrument).
(27) Unpublished work from this laboratory. See also G. J. Karabatsos and R. A. Taller, *J. Am. Chem. Soc.*, **86**, 4373 (1964).
(28) Microanalyses by Mr. R. Seab of these laboratories.

# Solvolyses of *trans*-2-Halocyclooctanols[1]

## James G. Traynham and John Schneller[2]

*Contribution from Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana 70803. Received December 28, 1964*

*Product distribution data have been obtained for solvolyses of trans-2-chloro- and -bromocyclooctanols in mixed aqueous solvents and in carboxylic acid solvents. The product mixtures contain substantial amounts of both transannular and nontransannular products. The proportions of the various products are remarkably insensitive to the identity of the halogen, the presence or absence of silver salts or sodium acetate (buffer), temperature, and solvent change. Solvolyses of cis-cyclooctene oxide have been re-examined under these conditions to permit direct comparison of related reactions. The data lead to the conclusion that these halohydrin solvolyses proceed by two competing mechanisms: (1) ionization to an unbridged 2-hydroxycyclooctyl cation, and (2) formation of hydrogen- (or alkyl-) bridged species. The small shift in proportions of products with change of solvent supports the conclusion. Solvolyses of epoxide, glycol, amino alcohol, and halohydrin (all derived from cyclooctene) are compared; the amino alcohol and halohydrin reactions are distinguished from the others by the relative abundance of carbonyl products in the mixtures.*

Studies of solvolysis reactions have provided a wealth of information pertinent to considerations of reaction mechanism during the past 40 years. Very recent papers have emphasized the influence of the leaving group on product formation in elimination reactions.[3] We have reported some studies of rearrange-

ments of 2-substituted cycloalkanols,[4,5] and have attributed to medium ring systems a welcome sensitivity to reaction mechanism which is revealed by product distribution data. Acid-catalyzed rearrangements of cyclooctene oxides[6] and glycols[4] are highly similar to each other but completely different from rearrangements brought about by nitrous acid deamination of the corresponding amino alcohols.[5] We have now investigated solvolyses of *trans*-2-chloro- and -bromocyclooctanols (**1** and **2**), both with and without silver ions present, in mixed aqueous solvents and carboxylic acid solvents. Acid-catalyzed hydrolyses of *cis*-cyclooctene oxide under these same conditions have been examined for comparison. Product distribution data for the halohydrin solvolyses, falling in between those for epoxide[6,7] and glycol[4] reactions and those for amino alcohol deaminations,[5] point strongly to an influence of leaving group not only on product formation but on gross reaction mechanism as well.

The halohydrins were prepared by reaction of *cis*-cyclooctene oxide with anhydrous hydrogen halide in carbon tetrachloride solution.[8] Although the reactions of medium ring epoxides with aqueous acid proceed with extensive transannular rearrangement,[6,9] the 1,2-product is obtained in nonpolar solvent.[8] Our confidence in the simplicity of this reaction is supported by the reformation of *cis*-cyclooctene oxide in high yields from the halohydrins and base.

(3) (a) D. J. Cram and M. R. V. Sahyun, *J. Am. Chem. Soc.*, **85**, 1257 (1963); (b) M. Cocivera and S. Winstein, *ibid.*, **85**, 1702 (1963); (c) P. S. Skell and W. L. Hall, *ibid.*, **85**, 2851 (1963).

(4) J. G. Traynham and P. M. Greene, *ibid.*, **86**, 2657 (1964).
(5) J. G. Traynham and M. T. Yang, *ibid.*, **87**, 2394 (1965).
(6) (a) A. C. Cope, A. H. Keough, P. E. Peterson, H. E. Simmons, Jr., and G. W. Wood, *ibid.*, **79**, 3900 (1957); (b) A. C. Cope, A. Fournier, Jr., and H. E. Simmons, Jr., *ibid.*, **79**, 3905 (1957); (c) A. C. Cope, J. M. Grisar, and P. E. Peterson, *ibid.*, **81**, 1640 (1959).
(7) This research.
(8) A. C. Cope and H. E. Johnson, *J. Am. Chem. Soc.*, **79**, 3889 (1957).
(9) For a review, see V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, Inc., a Division of John Wiley and Sons, Inc., New York, N. Y., 1963, Chapter 9.