Aziridines. X. Cyclodecenimine and Cycloöctenimine[1]

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Reaction of *cis*-2-aminocyclodecyl hydrogen sulfate with hot, aqueous sodium hydroxide gave cyclodecanone and *trans*-2-cyclodecen-1-ylamine. Under the same reaction conditions, *trans*-2-aminocyclodecyl hydrogen sulfate gave the same two products plus 11-azabicyclo[8.1.0]undecane (cyclodecenimine). The reactions are rationalized in terms of the Dunitz conformation of cyclodecane. On treatment with methyl iodide, cycloöctenimine and cyclodecenimine both formed stable quaternary iodides, and each aziridine on attempted benzoylation gave the isomeric N-benzoyl-*cis*-2-cycloalken-1-ylamine. Pyrolysis of 9,9-dimethyl-9-azoniabicyclo[6.1.0]-nonane hydroxide gave an amino alcohol instead of the anticipated product of Hofmann elimination.

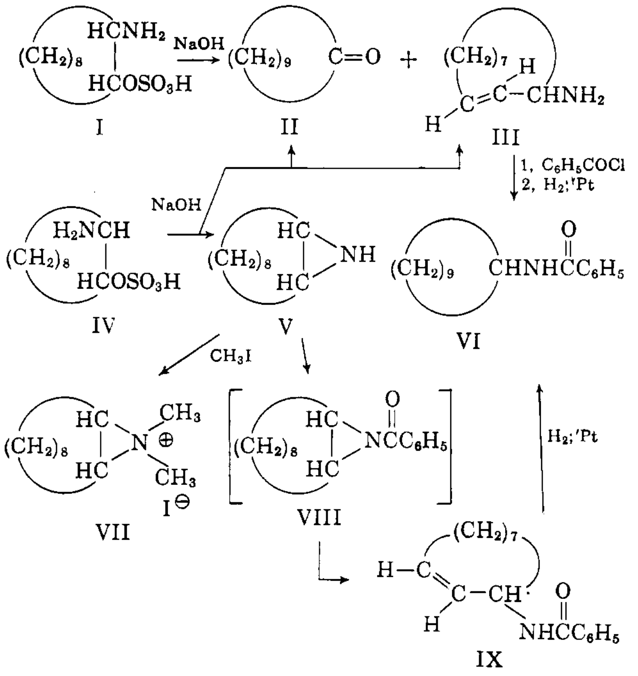
As an extension of our previous work on the cycloalkenimines,[3] one of the objectives of the present research was to study the reactions of *cis*- and *trans*-2-aminocyclodecyl hydrogen sulfates with hot, aqueous sodium hydroxide, and to determine whether the products obtained can be rationalized in terms of the Dunitz conformation of the cyclodecane ring.[4]

A possible route to the required *cis*- and *trans*-2-aminocyclodecanols appeared to be the ammonolysis of the known oxides. However, it was found that the reaction of *cis*-cyclodecene oxide with aqueous ammonia gave no amino alcohol, but only a product which appeared to be the same mixture of alcohols obtained from the reaction with lithium diethylamide.[5]

However, *cis*-2-aminocyclodecanol was conveniently prepared by hydrogenation of sebacoin oxime and converted to the *trans* isomer essentially as reported by Sicher and Svoboda.[6] On treatment with sulfuric acid at elevated temperature and reduced pressure, each amino alcohol yielded the corresponding sulfate ester in normal fashion.

Reaction of *cis*-2-aminocyclodecyl hydrogen sulfate (I) with hot, aqueous sodium hydroxide gave a mixture of cyclodecanone (II) and *trans*-2-cyclodecen-1-ylamine (III). The unsaturated amine, previously unreported, was characterized by its infrared absorption spectrum, which contained a very strong band at 10.2 μ, and by preparation of a benzoyl derivative, which on hydrogenation gave the known N-benzoylcyclodecylamine (VI).

The reaction of *trans*-2-aminocyclodecyl hydrogen sulfate (IV) with hot, aqueous sodium hydroxide gave three products, identified as cyclodecanone, the unsaturated amine III, and 11-azabicyclo[8.1.0]undecane (cyclodecenimine) (V). The imine did not discharge the purple color of potassium permanganate in aqueous methanol, and was further characterized by the preparation of N-phenylthiocarbamyl and N-acetyl derivatives.



Physical evidence for the presence of the aziridine ring in cyclodecenimine was provided by the infrared absorption spectrum, in which a strong band to the high wave length side of the C—H bending band was found at 1330 cm.$^{-1}$ (KBr). Analogous bands are found in the spectra of cyclohexenimine and cycloöctenimine at 1250 and 1230 cm.$^{-1}$, respectively (pure liquids). No such bands in this region are found in the spectra of compound III or cyclodecylamine. Furthermore, the intense bands at 760, 785, and 840 cm.$^{-1}$, characteristic of *cis*-cyclodecene, are absent from the spectrum of cyclodecenimine, thus excluding *cis*-2-cyclodecen-1-ylamine as a possible structure for the product.

In refluxing, aqueous perchloric acid, although cyclopentenimine, cyclohexenimine, and cycloheptenimine are hydrolyzed to the corresponding *trans*-2-aminocycloalkanols[3a–c] cycloöctenimine[3d] and cyclodecenimine are recovered unchanged. We have now found that cycloöctenimine is hydrolyzed in aqueous perchloric acid at 150°. In view of the resistance of *cis*-cyclodecene oxide to normal ring opening with ammonia, the behavior of cyclodecenimine is not expected. These observations suggested that whereas attempted quaternization of aziridines frequently leads to ring-opened products,[7] cycloöctenimine and cyclodecenimine might form stable quaternary salts.

This expectation was realized by the observation that treatment of cyclodecenimine with methyl iodide in benzene solution gave the quaternary iodide, 11,11-

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[2] National Science Foundation Undergraduate Research Participant, 1960.

[3] (a) P. E. Fanta, *J. Chem. Soc.*, 1441 (1957); (b) P. E. Fanta and O. E. Paris, *J. Am. Chem. Soc.*, **74**, 3007 (1952); (c) P. B. Talukdar and P. E. Fanta, *J. Org. Chem.*, **24**, 555 (1959); (d) D. V. Kashelikar and P. E. Fanta, *J. Am. Chem. Soc.*, **82**, 4927 (1960).

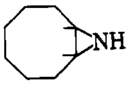
[4] See J. Sicher in "Progress in Stereochemistry," Vol. 3, Butterworths, London, 1962, p. 202, for discussion and further references.

[5] A. C. Cope, M. Brown, and H. H. Lee, *J. Am. Chem. Soc.*, **80**, 2855 (1958).

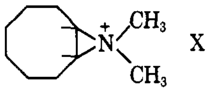
[6] J. Sicher and M. Svoboda, *Collection Czech. Chem. Commun.*, **23**, 1252 (1958).

dimethyl - 11 - azoniabicyclo[8.1.0]undecane iodide (VII). Structure VII was supported by the solubility behavior of the substance, its infrared absorption spectrum, and the fact that it did not decolorize an aqueous solution of potassium permanganate.

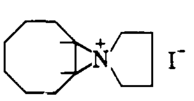
Similarly, cyclooöctenimine (X) on treatment with methyl iodide gave 9,9-dimethyl-9-azoniabicyclo[6.1.0]-nonane iodide (XIa) and on treatment with 1,4-diiodobutane gave spiro[9-azoniabicyclo[6.1.0]nonane-9,1′-pyrrolidinium] iodide (XII).



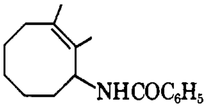
X



XIa. X = I
XIb. X = OH
XIc. X = $OC_6H_5(NO_2)_3$



XII

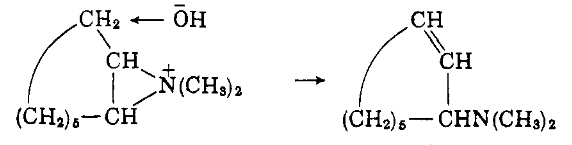


XIII

Attempted benzoylation of cyclodecenimine gave a product which had an NH band in the infrared absorption spectrum, decolorized methanolic potassium permanganate solution and was converted to N-benzoylcyclodecylamine (VI) on catalytic hydrogenation. On the basis of this evidence, the benzoylation product is assigned the structure N-benzoyl-*cis*-2-cyclodecen-1-ylamine (IX), and is undoubtedly the product of a facile isomerization of the benzoyl imine (VIII).[8]

Similarly, treatment of cyclooöctenimine with benzoyl chloride gave N-benzoyl-*cis*-2-cyclooöcten-1-ylamine (XIII).[8] Since the corresponding *p*-nitrobenzoyl derivative of X is readily isolated and requires a much higher temperature for the isomerization,[3d] the ease of this rearrangement appears to be greatly dependent on the nature of the acyl group. The structure of XIII was conclusively demonstrated by its preparation from authentic *cis*-2-cyclooöcten-1-ylamine obtained by the ammonolysis of *cis*-3-bromocyclooöctene.

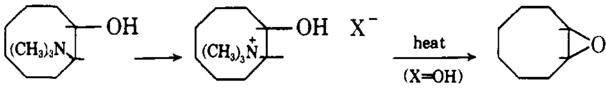
Passage of an aqueous solution of XIa through an ion exchange column gave a solution of the base XIb, which was not isolated, but was characterized by the preparation of a crystalline picrate, XIc. In view of the resistance of aziridine X to acid-catalyzed nucleophilic ring-opening, and the known fact that pyrolysis of cyclooctyltrimethylammonium hydroxide gives a mixture of *cis*- and *trans*-cyclooöctene,[9] it was anticipated that pyrolysis of the quaternary base XIb would result in the formation of a cyclooöctene derivative as a result of a Hofmann elimination concerted with the opening of the aziridinium ring as shown in equation A.



cis and/or *trans*

(A)

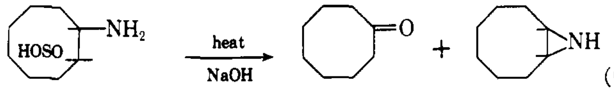
However, the product of the pyrolysis of XIb was instead the amino alcohol XIV, the structure of which was proved by conversion to the known methiodide XVa.[10] This observation is readily rationalized in terms of conformation XVI for the 9,9-dimethyl-9-azoniabicyclo[6.1.0]nonane cation,[11] which maintains both of the β-hydrogens required for Hofmann elimination according to equation A in a very unfavorable orientation. The cation XVI therefore must be much more rigid than the cyclooöctyltrimethylammonium ion, since in the latter instance both β-hydrogens can assume the antiperiplanar orientation required for the Hofmann elimination reaction, thus leading to a high yield of a mixture of *cis*- and *trans*-cyclooöctene.



XIV

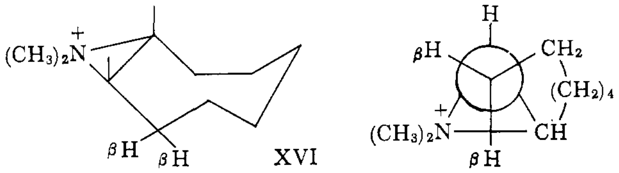
XVa. X=I
XVb. X=OH

(B)



(C)

Pyrolysis of the free base XVb gave *cis*-cyclooöctene oxide free of cyclooöctanone, equation B, in contrast to the Wenker ring-closure of *trans*-2-aminocyclooöctyl hydrogen sulfate which gave a mixture of ketone and aziridine,[3d] equation C.



XVI

Perspective formula

Newman projection

Experimental[12]

Reaction of *cis*-Cyclodecene Oxide with Ammonia.—A mixture of 8.2 g. of *cis*-cyclodecene oxide[5] and 70 ml. of concentrated aqueous ammonium hydroxide was shaken in a steel bomb at 100° for 2.5 hr. The product isolated by evaporation of solvent, ether extraction, and distillation contained no basic component, and had a boiling range of 112–130°/24 mm. and an infrared absorption spectrum which suggested that it consisted of a mixture of alcohols.[5] (Experiment by L. M. Clemens.)

***cis*-2-Aminocyclodecanol.**—Sebacoin oxime[6] (160 g.) in 1500 ml. of methanol with 7.0 g. of commercially available rhodium-on-charcoal catalyst was shaken for 1 hr. at 100° and a hydrogen pressure of 70 atm. A single crystallization of the crude product from 60° petroleum ether gave a 52% yield of *cis*-amino alcohol, m.p. 97–98° (lit.,[6] 98–99°).

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(7) For example, on treatment with methyl iodide in ether, cyclohexenimine gives *trans*-2-iodo-N,N-dimethylcyclohexylamine; T. Taguchi and M. Eto, *J. Am. Chem. Soc.*, **80**, 4075 (1958). Further references to the literature on aziridinium salts are given by N. J. Leonard and K. Jann, *ibid.*, **82**, 6418 (1960). On the basis of a few examples, it appears that those aziridines which are resistant to acid-catalyzed hydrolysis also form relatively stable quaternary salts: P. B. Talukdar and P. E. Fanta, *J. Org. Chem.*, **24**, 526 (1959); E. W. Gassenmeier and C. Schuster, U. S. Patent 2,694,704.

(8) This observation provides a further example of the pyrolytic *cis* elimination reported in earlier papers in this series; D. V. Kashelikar and P. E. Fanta, *J. Am. Chem. Soc.*, **82**, 4930 (1960).

(9) A. C. Cope, R. A. Pike, and C. F. Spencer, *ibid.*, **75**, 3212 (1953).

(10) A few examples of the formation of amino alcohols in the pyrolysis of quaternary ammonium hydroxides are given by A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 350 (1960).

(11) Independent evidence for this conformation was obtained by Dr. Louis M. Trefonas, Department of Chemistry, Louisiana State University in New Orleans, by an X-ray diffraction study of crystalline compound XIa. Details of his work are to be published elsewhere.

(12) Analysis by Micro-Tech Laboratories, Skokie, Ill.

Treatment of the amino alcohol with phenyl isothiocyanate in the usual way gave the phenylthiocarbamyl derivative, m.p. 164–165°.

Anal. Calcd. for $C_{17}H_{26}N_2OS$: C, 66.62; H, 8.55; N, 9.14. Found: C, 66.78; H, 8.61; N, 9.49.

***trans*-2-Aminocyclodecanol.**—The *cis*-amino alcohol was converted to the *trans* isomer, m.p. 92–94° (lit. 94–95°) as described.[6]

***cis*- and *trans*-2-Aminocyclodecyl Hydrogen Sulfate.**—The sulfate esters were prepared by the usual procedure.[3c] An analytical sample of *cis*-2-aminocyclodecyl hydrogen sulfate (I) was obtained by recrystallization of the crude product from a large volume of water, m.p. 248–254° dec.

Anal. Calcd. for $C_{10}H_{21}NO_4S$: C, 47.59; H, 8.79; N, 5.55. Found: C, 47.68; H, 8.53; N, 5.55.

***trans*-2-Aminocyclodecyl hydrogen sulfate IV** was too insoluble to permit recrystallization from water. The crude product melted with decomposition at 270–273°.

Reaction of *cis*-2-Aminocyclodecyl Hydrogen Sulfate with Sodium Hydroxide.—A solution of 27.3 g. of crude *cis* sulfate and 46.4 g. of sodium hydroxide in 100 ml. of water was slowly steam distilled. When oily droplets no longer appeared in the distillate, it was extracted with ether, and the ether extract was washed with dilute hydrochloric acid. Evaporation of the residual ether solution gave 5.1 g. of crude cyclodecanone, which was identified by preparation of the 2,4-dinitrophenylhydrazone, m.p. 162–163° (lit.,[13] 165°; mixture m.p. with authentic sample undepressed). The hydrochloric acid extract was made basic by addition of sodium hydroxide and extracted with ether. Drying and evaporation of the ether gave 6.8 g. of crude *trans*-2-cyclodecen-1-ylamine (III). Distillation of the crude amine at reduced pressure gave a viscous, colorless oil which slowly darkened on standing. The infrared absorption spectrum was very similar to that of *trans*-cyclodecene and, in particular, contained a very intense band at 10.2 μ.

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.50; N, 9.14. Found: C, 77.73; H, 12.53; N, 8.66.

A *picrate* of the amine melted at 207–210°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.26; H, 5.80; N, 14.65. Found: C, 50.62; H, 5.69; N, 14.50.

The amine was further characterized by treatment with phenyl isothiocyanate to give a *phenylthiocarbamyl derivative*, m.p. 136–137°.

Anal. Calcd. for $C_{17}H_{24}N_2S$: C, 70.78; H, 8.39; N, 9.71. Found: C, 70.73; H, 8.45; N, 9.67.

N-Benzoyl-*trans*-2-cyclodecen-1-ylamine.—Treatment of the unsaturated amine with benzoyl chloride and pyridine by the usual procedure gave the N-benzoyl derivative. m.p. 111–112°, which had the expected bands in the infrared absorption spectrum at 3.1 μ (NH) and 10.2 μ (*trans*-cyclodecene).

Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.50; H, 9.27; N, 5.45.

Hydrogenation of this benzoyl derivative over platinum catalyst in methanol gave N-benzoylcyclodecylamine (VI) m.p. 142–144°, undepressed on admixture with authentic amide, m.p. 145–147° (lit.,[6] 142–144°).

Reaction of *trans*-2-Aminocyclodecyl Hydrogen Sulfate with Sodium Hydroxide.—A solution of 15 g. of the crude *trans* sulfate and 14.5 g. of sodium hydroxide in 100 ml. of water was slowly steam distilled. When oily droplets no longer appeared, the distillate was nearly saturated with sodium hydroxide and extracted with ether. Extraction of the ether solution with dilute hydrochloric acid followed by drying and distillation of the ethereal residue gave cyclodecanone (12% yield) which was identified by the preparation of the 2,4-dinitrophenylhydrazone.[13] The hydrochloric acid solution was made basic by addition of sodium hydroxide and extracted with ether. Drying and distillation of the ethereal extract gave a viscous liquid which partly solidified on standing. The liquid and solid components of the mixture were separated by recrystallization from hexane. By preparation of the N-phenylthiocarbamyl derivative, the liquid amine was shown to be identical to the *trans*-2-cyclodecen-1-ylamine previously obtained. The solid fraction melted at 94–95° after a second recrystallization from hexane, and was identified as 11-azabicyclo[8.1.0]undecane (cyclodecenimine) (V) (13% yield).

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.36; H, 12.49; N, 9.14. Found: C, 78.09; H, 12.45; N, 9.33.

Treatment of the imine with phenyl isothiocyanate gave the N-phenylthiocarbamyl derivative, m.p. 95–96°.

Anal. Calcd. for $C_{17}H_{24}N_2S$: C, 70.78; H, 8.39; N, 9.71. Found: C, 71.12; H, 8.52; N, 9.61.

Treatment of the imine with acetic anhydride and triethylamine in benzene gave 11-acetyl-11-azabicyclo[8.1.0]undecane, white flakes from hexane, m.p. 38–39°. There was no NH band in the infrared absorption spectrum.

Anal. Calcd. for $C_{12}H_{21}NO$: C, 73.79; H, 10.84; N, 7.17. Found: C, 74.15; H, 10.86; N, 7.10.

Attempted Benzoylation of Cyclodecenimine.—Reaction of the imine with benzoyl chloride and triethylamine in benzene, followed by recrystallization from ethanol, gave a crystalline solid, m.p. 155–156°. This product was evidently not the anticipated N-benzoyl derivative of the imine, since it had an intense NH band at 2.9 μ in the infrared absorption spectrum and rapidly discharged the purple color of a solution of potassium permanganate in aqueous methanol. It was therefore assigned the structure N-benzoyl-*cis*-2-cyclodecen-1-ylamine (IX).

Anal. Calcd. for $C_{17}H_{23}NO$: C, 79.33; H, 9.01; N, 5.44. Found: C, 78.75; H, 8.91; N, 5.50.

Hydrogenation of benzoyl derivative IX over platinum catalyst in ethanol gave VI, m.p. 147–149°, mixture m.p. with authentic sample, 146–148°.

11,11-Dimethyl-11-azoniabicyclo[8.1.0]undecane Iodide (VII).—A solution of 100 mg. of cyclodecenimine and 142 mg. of methyl iodide in 3.5 ml. of benzene was allowed to stand at room temperature for 1 day. The white, crystalline solid which separated from the solution was recrystallized from ethanol, m.p. 222–225°.

The compound was readily soluble in water and the aqueous solution remained clear when it was made strongly alkaline by addition of sodium hydroxide solution. This solubility behavior is anticipated for the quaternary structure VII, but not for any conceivable isomeric structure. The aqueous solution did not discharge the purple color of aqueous potassium permanganate.

In addition to the C—H bands near 3000 and 1500 cm.$^{-1}$, the infrared spectrum (KBr) showed a strong, sharp band at 1260 cm.$^{-1}$, which was the first strong band to the high wave length side of the C—H bending band.

Anal. Calcd. for $C_{12}H_{24}NI$: C, 46.60; H, 7.82; N, 4.53. Found: C, 46.86; H, 7.58; N, 4.51.

These analytical data exclude structures resulting from reaction of cyclodecenimine with one or three molecules of methyl iodide.

Anal. Calcd. for $C_{11}H_{22}NI$: C, 44.75; H, 7.52; N, 4.74.

Anal. Calcd. for $C_{13}H_{26}NI$: C, 48.30; H, 8.11; N, 4.33.

Cycloöctenimine (X).—The preparation as previously described[3d] was greatly facilitated by the commercial availability of cycloöctene[14] which was found to be 97% pure by vapor phase chromatography on silver nitrate–triethylene glycol.

Hydrolysis of Cycloöctenimine.—A solution of 1.25 g. of cyclooctenimine and 2.14 g. of 70% perchloric acid in 20 ml. of water was heated in a glass-lined steel bomb at 150° for 4 hr. The solution was made basic by addition of excess sodium hydroxide and extracted with chloroform. Drying and evaporation of the chloroform solution gave 0.84 g. of crude *trans*-2-aminocycloöctanol, which was identified by preparation of the N-benzoyl derivative, m.p. 135–137° (lit., 134–135°),[6] undepressed on admixture with authentic material.

9,9-Dimethyl-9-azoniabicyclo[6.1.0]nonane Iodide XIa.—A solution of 5 g. of cycloöctenimine and 14.2 g. of methyl iodide in 50 ml. of benzene was allowed to stand overnight at room temperature. The white, crystalline precipitate was collected and recrystallized from ethanol, yield 3.59 g. of large, colorless plates, m.p. 181°.

Anal. Calcd. for $C_{10}H_{20}NI$: C, 42.71; H, 7.17; N, 4.98. Found: C, 42.68; H, 7.27; N, 4.82.

Spiro [9-azoniabicyclo[6.1.0]nonane-9-1′-pyrrolidinium] Iodide (XII).—A solution of 1.25 g. of cycloöctenimine, 3.10 g. of 1,4-diiodobutane, and 0.4 g. of sodium hydroxide in 12 ml. of methanol was refluxed for 7 hr. Evaporation of the solution gave a sticky, orange residue which was twice recrystallized from methanol–ether, giving white crystals, m.p. 196–198°.

Anal. Calcd. for $C_{12}H_{22}NI$: C, 46.91; H, 7.22; N, 4.56. Found: C, 46.78; H, 7.28; N, 4.37.

9,9-Dimethyl-9-azoniabicyclo[6.1.0]nonane Hydroxide (XIb) and Picrate (XIc).—A solution of 2.0 g. of Ia in 100 ml. of water was passed through a column containing 40 g. of Amberlite IRA-400 ion exchange resin, giving an aqueous solution of XIb free of

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[13] V. Prelog and K. Schenker, *Helv. Chim. Acta*, **35**, 2044 (1952).

[14] Cities Service Research and Development Co., Sixty Wall Tower, New York 5, N. Y.

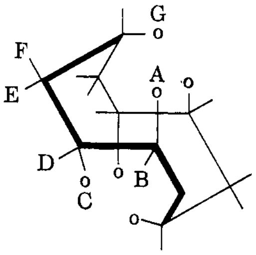


Fig. 1.—Dunitz conformation of cyclodecane. o = axial positions; AD, BC are *cis* and antiperiplanar; CF, EG are *trans* and antiperiplanar.

iodide ion. Addition of saturated aqueous picric acid to a portion of the solution gave a yellow, crystalline precipitate of XIc, m.p. 136.6°.

Anal. Calcd. for $C_{16}H_{22}N_4O_7$: C, 50.25; H, 5.80; N, 14.65. Found: C, 50.34; H, 5.83; N, 14.92.

Pyrolysis of XIb.—Water was removed from the aqueous solution of XIb by distillation at atmospheric pressure and the residue was distilled at 125–150°/3 mm. A solution of the crude distillate in petroleum ether (b.p. 60°) was chromatographed on alumina and eluted successively with petroleum ether, benzene, ether, and methanol. Nothing was obtained on evaporation of the petroleum ether eluate, but evaporation of the benzene and ether eluates gave *trans*-2-dimethylaminocyclooctanol (XIV) in the form of a colorless oil which could not be induced to crystallize. The infrared spectrum showed a strong OH band at 3500 cm.$^{-1}$. Addition of XIV to an alcoholic solution of picric acid gave the picrate, m.p. 108–109°.

Anal. Calcd. for $C_{16}H_{24}N_4O_8$: C, 47.99; H, 6.04; N, 14.00. Found: C, 47.93; H, 6.03; N, 14.00.

A drop of XIV was warmed with an excess of methyl iodide, then cooled to give a white precipitate of *trans*-2-hydroxycyclooctyl trimethylammonium iodide (XVa), m.p. 213–215° (lit.,[15] m.p. 214–215°), undepressed on admixture with authentic sample. Authentic XVa was prepared by refluxing a methanol solution of *trans*-2-aminocyclooctanol and methyl iodide, with further periodic additions of methyl iodide and sodium methoxide.

Pyrolysis of XVb.—A dilute, aqueous solution of 1 g. of XVa was passed through a column containing Amberlite IRA-400 ion exchange resin and eluted with a further portion of water. The aqueous eluate was distilled to dryness at atmospheric pressure. A white solid separated from the final portion of distillate, which was extracted with ether. Drying and evaporation of the ether gave a 61% yield of cyclooctene oxide, m.p. after sublimation 52–54° (lit.,[16] 56–57°). The presence of cyclooctanone in the crude cyclooctene oxide was not detectable with 2,4-dinitrophenylhydrazine reagent or by examination of the infrared absorption spectrum.

2-Cycloöcten-1-ylamine.—A mixture of 24.24 g. of *cis*-3-bromocyclooctene[17] and 164 ml. of 30% aqueous ammonium hydroxide was heated in a rocking steel bomb at 95–100° for 40 min. After the mixture had been heated at atmospheric pressure to expel ammonia, it was acidified with hydrochloric acid and extracted with ether to remove the neutral by-products. The aqueous residue was made strongly basic by the addition of sodium hydroxide and fractionally distilled, giving a colorless liquid, b.p. 55°/2.6 mm. which was shown by vapor phase chromatography to contain about 90% of a single component. As anticipated, this material was not analytically pure.

Anal. Calcd. for $C_8H_{15}N$: C, 76.74; H, 12.08; N, 11.18. Found: C, 75.33; H, 11.85; N, 10.99.

Treatment of the amine with phenyl isothiocyanate in petroleum ether gave the phenylthiocarbamyl derivative, white crystals from ethanol, m.p. 124–125°.

Anal. Calcd. for $C_{15}H_{20}N_2S$: C, 69.18; H, 7.74; N, 10.76. Found: C, 69.28; H, 7.97; N, 10.61.

Authentic N-Benzoyl-*cis*-2-cycloöcten-1-ylamine (XIII).—A suspension of *cis*-cycloöcten-1-ylamine in 5% aqueous sodium hydroxide was treated with an excess of benzoyl chloride in chloroform with shaking and cooling. The product was isolated by extraction with chloroform followed by recrystallization from hexane-benzene, fine, soft needles m.p. 156–157°.

Anal. Calcd. for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.33; H, 8.10; N, 6.06.

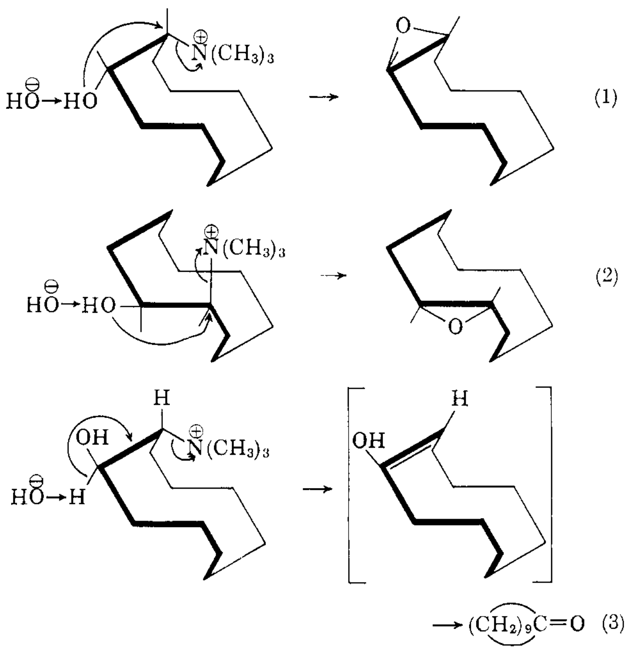
Reaction of Cycloöctenimine with Benzoyl Chloride.—A suspension of 0.5 g. of cycloöctenimine in cold 5% aqueous sodium hydroxide was cooled and shaken during the addition of 0.84 g. of benzoyl chloride in 5 ml. of chloroform. After 3 hr. of stirring, the chloroform solution was separated, dried, and distilled *in vacuo*. The residue was recrystallized from hexane, giving white needles, m.p. 150–151°. A mixture of this product with authentic XIII melted at 152–153°, and the infrared spectra of the two samples (KBr) were identical in every detail.

Discussion

For the interpretation of the stereochemical course of the reactions of cyclodecane derivatives the use of the Dunitz conformation[4] has been advocated, Fig. 1. An important feature of this conformation is that it has six axial (really intraannular) positions, three above and three below the ring. All other substituents are relatively uncrowded, corresponding approximately to the equatorial bonds in the chair form of cyclohexane. Judging from scale models, substituents somewhat larger than hydrogen can be accommodated in the axial positions with relatively small distortion of the conformation.

In the Dunitz conformation, antiperiplanar conformation of adjacent *cis* or *trans* substituents requires one of the substituents to be in an axial position. Consequently, in a reaction such as the pyrolysis of a β-hydroxytrimethylammonium hydroxide to give an epoxide, which requires antiperiplanar orientation of OH and $+N(CH_3)_3$, one of the two substituents must be in an axial position. It seems likely that in such a case, the departing group will be in the axial position, since the relief of steric strain resulting from loss of the group will provide a driving force for the reaction.

Thus, the reported formation of *cis*-cyclodecene oxide from the pyrolysis of *trans*-2-hydroxycyclodecyltrimethylammonium hydroxide may be represented by the conformations of equation 1. Pyrolysis of the corresponding *cis* isomer gives a mixture of *trans* oxide and cyclodecanone, as represented in equations 2 and 3.[4]



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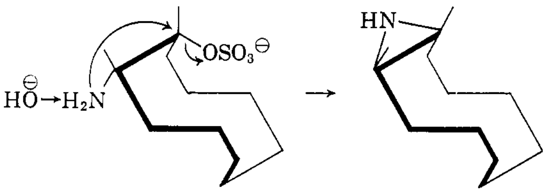
(15) L. E. Craig, U. S. Patent 2,693, 471 (1954).

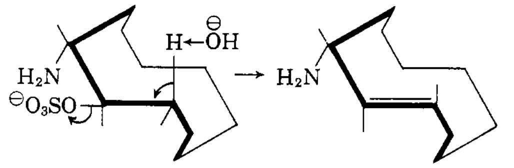
(16) A. C. Cope, S. W. Fenton, and C. F. Spencer, *J. Am. Chem. Soc.*, **74**, 5884 (1952).

(17) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950).

The analogous reactions of the 2-aminocyclodecyl hydrogen sulfates with sodium hydroxide are similar, but more complicated due to the greater number of products obtained. Thus, the reactions of *trans*-2-aminocyclodecyl hydrogen sulfate with sodium hydroxide to give imine, unsaturated amine and ketone are represented by equations 4, 5, and 6. In agreement with this representation, the yield of cyclodecenimine is low compared to the yields obtained for the corresponding 5-,[3a] 6-,[3b] 7-,[3c] and 8-[3d] membered cycloalkenimines, since the transition state leading to imine formation, equation 4, is the only one of the elimination reactions which requires a bulky group in the axial position.



(4)



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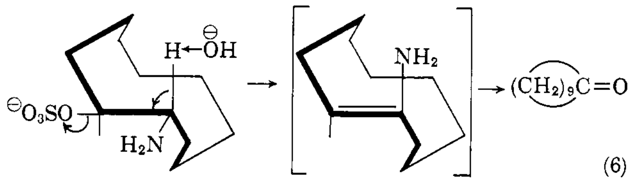
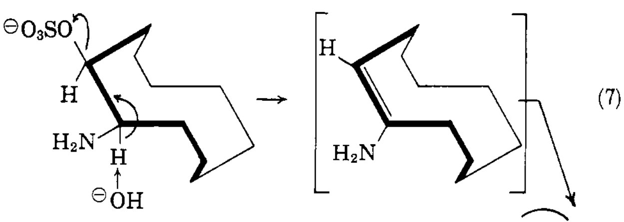


(6)

The reactions of *cis*-2-aminocyclodecyl hydrogen sulfate with sodium hydroxide may be rationalized by equation 7 for the formation of cyclodecanone, and equation 8 for the formation of unsaturated amine. An alternative formulation, equation 9, for the formation of the unsaturated amine must be rejected, since it leads to a diasterioisomeric and not identical form of the amine obtained in equation 5.

The observation that although *cis*-cyclodecene is more stable than the *trans* isomer,[4] *cis*-cyclodecen-1-ylamine is not obtained in these reactions (*i.e.*, equation 10 does not occur), has a precedent in the well known fact that the Hofmann elimination of cyclodecyltrimethylammonium hydroxide gives nearly pure *trans*-cyclodecene, equation 11 and not the *cis* isomer, equation 12.[4] Both of these observations are in agreement with the finding that all equatorial positions indicated in Fig. 1 are not equivalent, since the ammonium groups of *trans*-1,6-diaminocyclodecane dihydrochloride are found in positions corresponding to D and not F in Fig. 1.[18]



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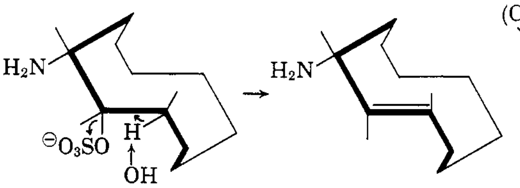

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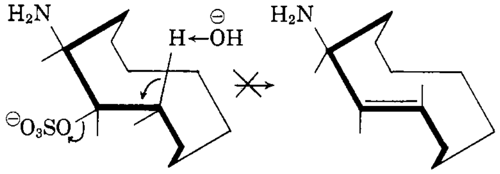

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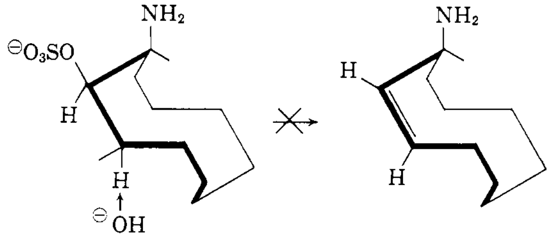

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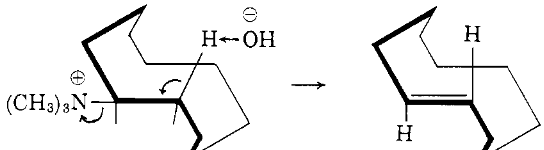

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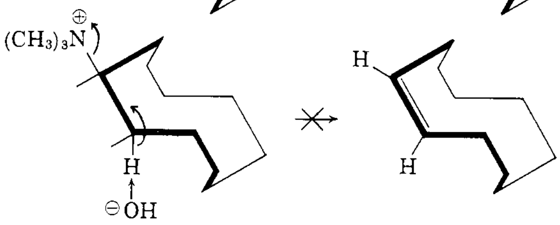

(12)

In conclusion, the Dunitz conformation of cyclodecane appears to have real utility for the rationalization of the stereochemistry of a variety of elimination reactions of cyclodecane derivatives which are known to require antiperiplanar conformation of substituents on adjacent carbon atoms.

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[18] E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, **43**, 760 (1960).