# Amination of Cycloalkanes with Trichloramine–Aluminum Chloride[1a]

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The nature of the reaction between cycloalkanes and trichloramine–aluminum chloride was investigated. Amination of methylcyclopentane afforded 1-amino-1-methylcyclopentane; *cis*- and *trans*-decalins gave *cis*-9-aminodecalin; and hydrindan provided *cis*-8-aminohydrindan. The reaction with cyclohexane produced temperature-dependent products. At low temperatures cyclohexylamine was formed, while at higher temperatures 1-amino-1-methylcyclopentane predominated. Cycloheptane underwent rearrangement with formation of 1-amino-1-methylcyclohexane. Cyclooctane, methylcycloheptane, and 1,3- and 1,4-dimethylcyclohexane produced a mixture of rearranged products consisting primarily of 1,3- and 1,4-dimethyl-1-aminocyclohexanes. Primary and secondary amines as well as aziridines and N-alkylaziridines were generated from cyclopentane. Relative rate data were obtained for secondary *vs.* tertiary alkanes. An important step in the mechanistic pathways for the various reaction categories appears to entail interaction of a carbonium ion with a nitrogen-containing nucleophile. Synthetic utility is demonstrated for the procedure.

Prior reports from this laboratory have shown that the trichloramine–aluminum chloride combination can effect direct amination of organic compounds. Treatment of monoalkylbenzenes gave products of unusual orientation, namely, *m*-alkylanilines.[4-6] Additional studies revealed that naphthalene,[7] biphenyl,[7] and dialkylbenzenes[8] also demonstrated this unusual substitution pattern. More recent investigations have dealt with the conversion of aryldialkylmethines to *t*-benzylamines in the presence of *t*-butyl bromide.[9,10] This observation led to studies of direct amination of alkanes,[11] alkyl halides,[12,13] and hydrocarbons in the bicyclic[13] and tricyclic[14,15] category. Each type of organic substrate proved amenable to amination, thus providing a new route to amines.

Heretofore, only one simple alicyclic substrate, methylcyclohexane, was subjected to this technique, producing 1-amino-1-methylcyclohexane.[11] The purpose of the present study was to investigate the scope and mechanistic aspects of the amination of cycloalkanes, together with a consideration of synthetic utility.

## Results and Discussion

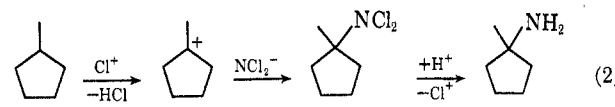
The reactions with trichloramine–aluminum chloride were generally carried out within the range of −20 to 18° with a trichloramine:aluminum chloride:alicyclic hydrocarbon:methylene chloride molar ratio of 0.1:0.2:0.5:2. The aminocycloalkanes could, in most cases, be separated from the minor reaction products by fractional distillation. Characterization of the major products was accomplished by comparison with authentic material, preparation of derivatives, and, in some cases, degradative techniques. Yields are based on an equimolar relationship between the basic, distilled product and trichloramine.

***t*-Alicyclic Hydrocarbons.**—These substrates gave the corresponding carbinamines as predominant reaction products. Their formation is consistent with the prior observation that *tertiary* centers are generally the preferred reaction sites.[11,12,14,15]

**Methylcyclopentane.**—When this hydrocarbon was aminated at 3° under standard conditions, a 61% yield of 1-amino-1-methylcyclopentane was obtained. The authentic compound was prepared by the Ritter reaction with 1-methylcyclopentanol.

Mechanistically, the result can be rationalized as shown in eq 1 and 2. Hydrogen chloride was evolved

$$Cl_3N + AlCl_3 \rightleftharpoons Cl^{\delta+}(AlCl_3NCl_2)^{\delta-} \quad (1)$$




(2)

throughout the reaction. Participation of chloronium type ion was invoked in a recent communication[16] dealing with another Lewis acid system. Alternatively, hydride abstraction might be effected by $^{+}CH_2Cl$ which may arise from the action of aluminum chloride on methylene chloride.[17] This possibility is considered unlikely since methyl chloride was formed only in trace amounts in the amination of methylcyclohexane. Other lines of supporting evidence for the proposed scheme are discussed elsewhere.[9-15]

**Decalin.**—Amination of *trans* (100%), *cis* (97%), and mixed (39% *trans*, 61% *cis*) decalins (Table I) provided the same major product, 9-aminodecalin, on the basis of physical properties and infrared spectra. Acetylation gave pure *cis*-N-9-decalylacetamide.[18] The

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stereochemistry indicated by the acetamide derivative was confirmed by comparison of the amine with authentic material obtained by Hofmann degradation of *cis*-9-decalincarboxamide. In all cases the recovered decalin consisted of the *trans* isomer only.

TABLE I
AMINATION OF DECALIN[a]

| Decalin | Addition time,[b] min | Yield, % Crude base[c] | Yield, % *cis*-9-Aminodecalin[d] |
|---|---|---|---|
| *trans*[e] | 53 | 55 | 41 |
| *cis*[f,g] | 60 | 49 | 31 |
| Mixed[h] | 67 | 47 | 35 |
| Mixed[i-k] | 120 | 8 | 6 |
| Mixed[i,l,m] | 100 | 42 | 17 |
| Mixed[i,n] | 75 | 68 | 50 |

[a] Temperature, 0–5°. [b] Followed by 0.5-hr stirring. [c] Distilled material. [d] The remaining base contained numerous unidentified components, all of which could be removed by distillation. [e] $NCl_3$:$AlCl_3$:decalin:$CH_2Cl_2$ = 0.1:0.2:0.35:2. [f] $NCl_3$:$AlCl_3$:decalin:$CH_2Cl_2$ = 0.1:0.2:0.4:2. [g] *cis* (97%), *trans* (3%). [h] *trans* (34%), *cis* (66%). [i] *cis* (61%), *trans* (39%). [j] Inverse addition; decalin was added to a mixture of trichloramine–aluminum chloride in methylene chloride solvent. [k] −1 to 1°. [l] Aluminum bromide was used in place of aluminum chloride; *t*-butyl bromide (0.036 mol) was added to the reaction mixture prior to the trichloramine. [m] 4–7°. [n] See Experimental Section, general procedure B.

Because of the specificity of the reaction and the synthetic advantage offered by this procedure over the circuitous literature routes, an investigation of reaction conditions was undertaken in order to optimize the yield. Earlier studies have revealed that the preferred method for amination of alkyl halides involves addition of the alkyl halide to the trichloramine–aluminum chloride mixture.[12] In an experiment in which the mode of addition was reversed the yield of crude base was drastically reduced (Table I, entry 4) perhaps resulting from destruction[19] of trichloramine by the generated hydrogen chloride. Use of the aluminum bromide–*t*-butyl bromide catalyst system[14,15] decreased the yield of desired material and increased the amount of by-product amine (Table I, entry 5). The stronger catalyst[20] might cases a deep-seated isomerization of the parent nucleus.[21] A modified work-up procedure[15] afforded the highest yields (50%). For increased efficiency, the methylene chloride solvent was removed by distillation during hydrolysis.

**Hydrindan.**—The specificity observed with decalin also pertained to hydrindan. Amination at 5–10° afforded *cis*-8-aminohydrindan in 70% yield. The authentic amine was synthesized by a Hofmann degradation procedure similar to the one used for *cis*-9-aminodecalin.

The stereospecificity observed on amination of the fused-ring substrates has precedence. Models show that *trans*-9-N,N-dichloroaminodecalin is more crowded than the *trans*-9-methyl analog. In the case of the 9-methyldecalins, it appears that the *cis* isomer is slightly favored at equilibrium.[22,23] The observed specificity may reflect the relief of axial–axial interactions in the *trans* compound. Furthermore, Bartlett and coworkers demonstrated that *cis*-decalin-9-carboxylic acid is thermodynamically favored in the isomerization of *trans*-decalin-9-carboxylic acid with fuming sulfuric acid.[24] Analogously, in 8-methylhydrindan the *cis* conformer is energetically preferred since only in the *cis* compound can the methyl group assume an equatorial position.[22] Christol and Solladie have shown that, under the conditions of the Ritter reaction, certain precursors undergo isomerization and then amination to give *cis*-8-aminohydrindan after hydrolysis of the initially formed formamide precursor.[25]

**Secondary Alicyclic Hydrocarbons.**—Many alicyclic compounds are extensively isomerized under Friedel–Crafts conditions.[21,26,27] Application of the standard reaction to substrates in this category affords alicyclic amines derived from rearranged hydrocarbons.

**Cycloheptane.**—Upon treatment at 5–10° with trichloramine–aluminum chloride, cycloheptane produced a 65% yield of 1-amino-1-methylcyclohexane. Lewis acids are known to convert cycloheptane to methylcyclohexane,[20] and in fact none of the excess starting material was found unchanged in the neutral portion of the amination mixture. The basic product was identified by comparison with authentic material.[11]

**Eight-Carbon Alicyclics.**—In the presence of aluminum chloride as catalyst, cyclooctane, methylcycloheptane, *cis*-1,3-dimethylcyclohexane, and 1,4-dimethylcyclohexane are rearranged to a mixture of dimethylcyclohexanes consisting mainly of the 1,3 and 1,4 isomers.[26,27] In our system the hydrocarbons underwent extensive isomerization, to the extent that in the recovered organic phase from the amination of cyclooctane or methylcycloheptane no unrearranged starting material was found.

The major product from each substrate was an inseparable mixture (glpc) of 1,3- and 1,4-dimethyl-1-aminocyclohexanes (Table II). The infrared spectra of the product mixtures were identical except for a few slight intensity differences. As an aid in identification, a Hofmann elimination was performed after conversion to the quaternary hydroxides, followed by ozonolysis of the resultant olefins. Analysis of the methylcyclo-

TABLE II
AMINATION OF $C_8$ CYCLOALKANES

| Substrate | Temp, °C | Basic product, yield, % Crude[a] | Basic product, yield, % Purified[b] |
|---|---|---|---|
| Cyclooctane | 5–10 | 70 | 50 |
| Methylcycloheptane | 0–3 | 72 | 50 |
| *cis*-1,3-Dimethylcyclohexane | 0–3 | 77 | 55 |
| 1,4-Dimethylcyclohexane | 4–6 | 72 | 50 |

[a] Total base. [b] The major product is a mixture of 1,3- and 1,4-dimethyl-1-aminocyclohexanes.

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hexanones revealed that the starting amine possessed the approximate isomeric composition of 71% 1,3 and 29% 1,4. For verification, the olefinic mixture was aromatized with palladium on carbon, producing *m*-xylene (73%) and *p*-xylene (27%). No cyclooctylamine or 1-amino-1-methylcycloheptane was detected in the base obtained from cyclooctane or methylcycloheptane, respectively.

**Cyclododecane.**—Amination of cyclododecane at 3–6° gave many products, presumably cyclohexane derivatives, which appear to arise from isomerization; no cyclododecane was recovered. Although identification of the product mixture was not carried out, it was shown that cyclododecylamine was not a component (glpc comparison with authentic material).

**Cyclohexane.**—The amination of cyclohexane was found to be quite sensitive to temperature changes and the addition of isomerization catalyst, *e.g.*, olefin (Table III). Cyclohexylamine was the predominant product

TABLE III

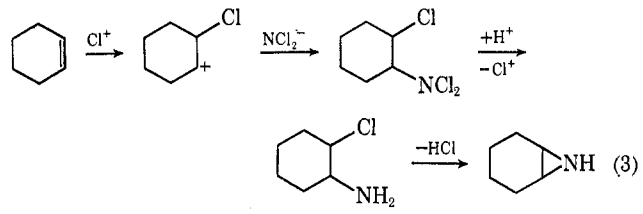
AMINATION OF CYCLOHEXANE[a]

| Cyclohexene,[b] mol | Temp, °C | Products, % of total base: Cyclohexylamine | 1-Amino-1-methylcyclopentane | 7-Azabicyclo[4.1.0]heptane | Yield,[c] % |
|---|---|---|---|---|---|
| | −10 | 80 | 6 | | 45 |
| 0.01 | −10 | 78 | 16 | | 53 |
| *d* | 10–15 | 6 | 90 | 4 | 54 |
| 0.01 | 10–15 | Trace | 98 | 1 | 46 |

[a] $NCl_3:AlCl_3:C_6H_{12}:CH_2Cl_2$ = 0.1:0.2:1:1. [b] Added before trichloramine. [c] Crude base. [d] $NCl_3:AlCl_3:C_6H_{12}:CH_2Cl_2$ = 0.1:0.2:0.5:2.

at low temperatures, even in the presence of cyclohexene. However, at higher temperatures, particularly with added promoter, 1-amino-1-methylcyclopentane is formed preferentially. Ipatieff and coworkers noted that the Lewis acid catalyzed isomerization of cyclohexane at 25°, with hydrogen bromide and cyclohexene as cocatalysts, gave only a 9% yield of methylcyclopentane.[28] It is our contention that 1-amino-1-methylcyclopentane predominates at 10–15° because amination selectively involves the tertiary center, thus siphoning off the *t*-alkane as it is formed. Since rearrangement is slow at −10°, nucleophilic attack at a secondary position of cyclohexane is favored. In some cases, 7-azabicyclo[4.1.0]heptane was formed in minor quantities. 1-Amino-1-methylcyclopentane was compared with authentic material obtained by independent synthesis. A literature method was used to prepare authentic cyclohexenimine.[29]

Mechanistically, the major products can be rationalized by the processes outlined in eq 1 and 2. An explanation for formation of the aziridine involves stepwise addition of trichloramine to cyclohexene (eq 3). The olefin was detected in the reaction mixture. The ring-closure step, believed to occur during work-up, exemplifies the Gabriel synthesis of aziridines.[30] Coleman and collaborators found that trichloramine will add



to cyclohexene in an uncatalyzed system, eventually giving rise to 2-chlorocyclohexylamine.[31]

Evidence that the N,N-dichloroamine serves as precursor to the end product (eq 2) was obtained from low-temperature amination of cyclohexane. With a modified work-up procedure, N,N-dichlorocyclohexylamine was isolated in 18% yield and identified by comparison with a sample of authentic material. Similarly, 1-N,N-dichloroaminoadamantane and N,N-dichloro-*t*-butylamine have been shown to be generated in amination of adamantane[14,15] and *t*-butyl chloride,[12] respectively.

In order to gain additional mechanistic insight, competitive aminations were performed with hydrindan–cyclohexane mixtures. Relative rate data were obtained with two different molar ratios of tertiary *vs.* secondary hydrocarbon. The value (1 *t*-H *vs.* 1-*sec*-H) for a 1:1 mixture was $1.5 \times 10^3$, while that for a 1:10 composition was $3 \times 10^3$, yielding an average figure of $2.25 \times 10^3$. From the data of Hughes, a value of $4.8 \times 10^3$ for the relative rate of the unimolecular hydrolysis of *t*-butyl chloride:isopropyl chloride in 80% aqueous ethanol can be calculated.[32] A comparison of the data is valid since solvolysis at a tertiary position incorporated in a cyclohexane ring proceeds at approximately the same rate as for the acyclic analog.[33] Corroboration is provided from the relative rates of solvolysis of 1-chloro-1-methylcyclohexane:*t*-butyl chloride and isopropyl chloride:cyclohexyl chloride,[33] together with Hughes' value for solvolysis of *t*-butyl chloride:isopropyl chloride. Computation furnishes a relative rate of about $2.6 \times 10^3$ for solvolysis of 1-chloro-1-methylcyclohexane:cyclohexyl chloride. Thus, good evidence is in hand for cation formation in the rate-determining step of amination.[10]

Several experiments[2] were carried out pertaining to reversibility during amination; *cf.* the Ritter reaction.[34] There was no positive evidence, since 1-amino-1-methylcyclopentane was not formed in systems containing N,N-dichlorocyclohexylamine, aluminum chloride, and cocatalysts, such as hydrogen chloride, *t*-butyl chloride, and trichloramine.

**Cyclopentane.**—With cyclopentane as substrate, several simultaneous reactions are occurring which give rise to various types of amines (Table IV). In keeping with earlier postulates,[11,12] plausible pathways for formation of the products are described. The cyclopentylamine route can be visualized as proceeding in the same manner as for eq 2. Two of the products, dicyclopentylamine and N-cyclopentyl-6-azabicyclo-

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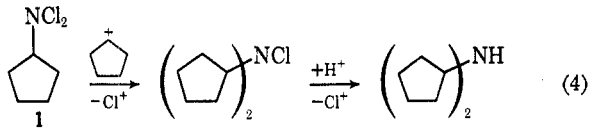
TABLE IV
AMINATION OF CYCLOPENTANE[a]

| Substrate | Temp, °C | Products, % Cyclopentylamine | 6-Azabicyclo[3.1.0]hexane | N-Cyclopentyl-6-azabicyclo[3.1.0]hexane | Dicyclopentylamine | Yield,[b] % |
|---|---|---|---|---|---|---|
| Cyclopentane | 15–18 | 6 | 66 | 24 | 4 | 54 |
| Cyclopentane | 3–7 | 25 | 19 | 47 | 10 | 43 |
| Cyclopentene | −10 to −15 | | 9 | | | 23[c] |
| *trans*-1,2-Dichlorocyclopentane | −5–0 | | 5 | | | 15[c] |

[a] See Experimental Section, general procedure C. [b] Crude base. [c] Contained many unidentified components.

[3.1.0]hexane are believed to arise as shown in eq 4 and 5. The presence of 6-azabicyclo[3.1.0]-



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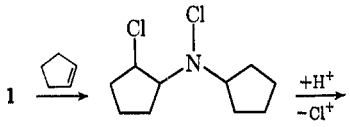


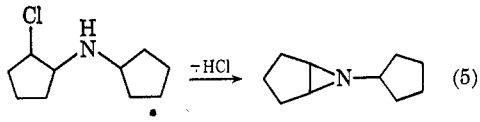

(5)

hexane can be rationalized on the basis of the steps outlined in eq 3. Cyclopentenimine is the major product at 15–18°, suggesting that addition of the nitrogenous nucleophile to 2-chlorocyclopentyl cation is involved. One would expect cyclopentene formation to increase with rise in temperature. Cyclopentenimine is also produced, in low yield, from *trans*-1,2-dichlorocyclopentane, one of the chlorinated hydrocarbons found in the neutral portion of the reaction mixtures from cyclopentane and cyclopentene. Imine formation with vicinal dichloride as a precursor has been observed previously.[12] The amination of cyclopentyl bromide gave similar results; however, the presence of cyclopentenimine was not determined.[12]

**Synthetic Utility.**—In relation to synthetic utility, the merits of certain examples from the present method become evident on comparison with literature procedures. Several uncomplicated syntheses are known which yield *trans*-9-aminodecalin;[34,35] however, no simple method is available for preparation of the *cis* isomer. Thus, treatment of decalin with trichloramine–aluminum chloride comprises the preferred route to *cis*-9-aminodecalin. Similarly, *cis*-8-aminohydrindan may be obtained in one step from hydrindan. Several alternative pathways are reported. The Ritter reaction on spiro[4.4]nonan-1-ol and $\Delta^{1,6}$-bicyclo[4.3.0]nonene give the desired material,[36] as does the Schmidt reaction with *cis*-8-hydrindancarboxylic acid.[25] The literature methods entail the use of precursors which must be synthesized. Amination of cyclopentane provides 6-azabicyclo[3.1.0]hexane or N-cyclopentyl-6-azabicyclo[3.1.0]hexane by simple fractional distillation. In comparison with this one-step procedure, a prior synthesis of 6-azabicyclo[3.1.0]hexane entailed four steps with an overall yield of 4%.[37,38] Aziridines unsubstituted on nitrogen may be obtained in several steps in high yield from iodine isocyanate and olefins.[39,40]

Application of the general procedure to tertiary alicyclic hydrocarbons which do not readily undergo acid-catalyzed isomerization seems to constitute a general method for effecting direct amination to the corresponding *t*-carbinamine. The Ritter reaction normally employes carbinol and alkene-type substrates.[41,42]

## Experimental Section[43]

**Materials.**—Most reagents were used as received after their purity had been checked by glpc analysis. Methylene chloride was distilled from calcium hydride.

**Analytical Procedures.**—Infrared spectra were obtained with a Beckman IR-8 spectrophotometer on neat samples or Nujol mulls. Mass spectra were obtained on a Varian M-66 mass spectrometer. All spectra were taken on samples purified by glpc. Gas chromatography was carried out with an Aerograph Hi-Fi 1200 (column E), and a homemade unit (columns A–D): (A) 15 ft × 0.25 in., Carbowax 6000 (20%) on Chromosorb P (30–60 mesh; 5% NaOH); (B) 6 ft × 0.25 in., SE-52 (10%) on Chromosorb P (30–60 mesh); (C) 5 ft × 0.25 in., SE-30 (3%) on Var-A-Port 30 (100–120 mesh); (D) 11 ft × 0.25 in., Bentone-34 (5%) and dioctyl phthalate (5%) on firebrick (60–80 mesh); (E) 10 ft × 0.13 in., Carbowax 20M (10%) on Chromosorb P (60–80 mesh; 5% NaOH). Melting points (uncorrected) were determined on a Thomas–Hoover capillary melting point apparatus. Galbraith Laboratories, Knoxville, Tenn., performed the elemental analyses.

**Preparation of Trichloramine Solution.**—A published procedure (method B) was used with methylene chloride as solvent.[4] Positive halogen analysis was carried out as previously described.[4] *Caution:* Use the necessary precautions when working with N-halamines.[44] Trichloramine solution may be stored at −20° for 1 month without decomposition. Disposal can be effected by slowly adding to a cold dilute solution of sodium metabisulfite and stirring until the contents are colorless.[44]

**Amination of Alicyclic Hydrocarbons. General Procedure A.**—The apparatus consisted of a 500-ml, three-necked flask equipped with a mechanical stirrer, thermometer, condenser, and a funnel for below surface addition. A slow sweep of nitrogen was maintained throughout the reaction. After a mixture of the alicyclic hydrocarbon (0.5 mol) and methylene chloride (2 mol) was cooled to 0°, aluminum chloride (0.2 mol) was added in one portion, producing a heterogeneous system. A cold solution of trichloramine (0.1 mol) in methylene chloride was added dropwise during 1 hr at the desired temperature. After 30 min, the

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contents were stirred into a mixture of ice (400 g) and 75 ml of concentrated hydrochloric acid. The organic layer was separated and treated twice with 100-ml portions of dilute hydrochloric acid. The aqueous fractions were combined, extracted with ether, and treated with cold 50% sodium hydroxide. The amine was extracted with ether and dried. Removal of solvent by rotary evaporation was followed by distillation, usually through a Bantamware Minilab apparatus at reduced pressure. In some cases further purification was accomplished by means of a 25-plate spinning-band column. *cis*-9-Aminodecalin and N-cyclopentyl-6-azabicyclo[3.1.0]hexane were isolated in purity greater than 99% by this procedure.

**Water-Insoluble Amine Hydrochlorides. General Procedure B.**—Procedure A was modified in the work-up. After completion of the trichloramine addition and subsequent stirring, 75 ml of concentrated hydrochloric acid and 100 ml of water were added, solvent was removed by distillation, and the mixture was heated to 95° during 1 hr. Procedure A was followed for the remainder of the work-up.

**Water-Soluble Amines. General Procedure C.**—The aqueous layer obtained as in procedure A was concentrated by rotary evaporation to a viscous, dark liquid. The amine was liberated by treatment with 50% sodium hydroxide solution.

**Competitive Aminations.**—Procedure A was followed at approximately −20°. Molar ratios of trichloramine:aluminum chloride:cyclohexane:hydrindan of 1:2:5:5 and 1:2:50:5 were used. Glpc analysis (column A) with cyclopentylamine as an internal standard afforded the product ratios.

**Isolation of N,N-Dichlorocyclohexylamine.**—Cyclohexane (54 ml, 0.5 mol) and methylene chloride (128 ml) were placed in the standard vessel and cooled to −20°. After aluminum chloride (0.2 mol) was added in one portion, 122 ml of trichloramine solution (0.08 mol) was added dropwise between −20 and −15°. The mixture was stirred for 5 min and then quenched in ice with vigorous stirring. The organic portion was washed once with distilled water and dried. Removal of unchanged trichloramine and solvent afforded a yellow liquid which gave three fractions on distillation. The second one, bp 66° (4 mm), was shown to be N,N-dichlorocyclohexylamine (18%) by comparison of the infrared spectrum with that of authentic material.

**Product Identification.**—The amines were identified by comparison with authentic materials (glpc retention times and infrared spectra), either obtained commercially or by synthesis.

**1-Amino-1-methylcyclopentane.**—Data for this compound and its derivatives are given from the present work, Ritter product,[45] literature, respectively: yield (%) 61, 40, 30;[46] bp [°C (mm)] 35–38 (20–25), 33–38 (23), 138 (760);[46] hydrochloride mp (°C dec) 268, 268, 269–270;[47] benzamide mp (°C) 122, 122, 122–123.[46]

***cis*-9-Aminodecalin.**—Data for this compound and its derivatives are presented from present work, authentic, literature,[18] respectively: bp [°C (mm)] 74 (1.5), 70 (2), 82 (7); hydrochloride mp (°C, subl) *ca.* 315–320, ..., ...; formate mp (°C dec) 162–163, ..., 165; acetamide mp (°C) 126–126.5, 127, 127; $n^{24.5}$D 1.4949, ..., ....

*Anal.* Calcd for *cis*-9-aminodecalin hydrochloride ($C_{10}H_{20}NCl$): C, 63.31; H, 10.63; Cl, 18.69; N, 7.38. Found: C, 63.47; H, 10.68; Cl, 18.53; N, 7.35.

***cis*-8-Aminohydrindane.**—Data for this compound and its derivatives are given from present work, authentic, literature, respectively: yield (%) 70, ..., 34;[25] bp [°C (mm)] 80–82 (18), 79–80 (18), 83–84 (20);[25] mp (°C) 41–42, 42, 11;[36] acetamide mp (°C) 88–89, 88–89, 88.[35]

***cis*-9-Aminodecalin. a. 9-Decalincarboxylic Acid.**—The desired material was obtained by an available method.[48] The infrared spectrum indicated that the acid (66% yield) was largely *trans* (10.29 μ) with some *cis* isomer (11.26 μ).[24]

**b.** ***cis*-9-Decalincarboxylic Acid.**—The 9-decalincarboxylic acid isomers (15 g) were mixed with 34 g of 88% formic acid, and the resulting paste was added in small portions with stirring during 30 min at 5° to a mixture of fuming sulfuric acid (135 g, 30%) and sulfuric acid (281 g, 98%).[24] After 5 g of 88% formic acid was added dropwise, the reaction mixture was stirred for 1 hr. The mixture was quenched in ice with vigorous stirring and the organic product was taken up in ether and purified as in part a. The recovered acid, 14.9 g, displayed an infrared spectrum with strong absorption at 11.26 μ and a smaller band at 10.29 μ indicating isomerization from predominantly *trans* to mainly *cis*.

**c.** ***cis*-9-Decalincarbonyl Chloride.**—The crude *cis* acid was treated with thionyl chloride to produce the crude acid chloride (99% yield) contaminated with some *trans*-9-decalincarbonyl chloride.[49]

**d.** ***cis*-9-Decalincarboxamide.**—The amide was prepared from the acid chloride by reaction with ammonia gas. The crude yield was greater than theoretical because *trans*-9-decalincarbonyl chloride does not react under these conditions.[50] The infrared spectrum confirmed the presence of the impurity. Recrystallization from hexane–benzene gave 5.6 g of white needles, mp 126.5–127° (lit.[50] mp 129.7–130.5°). A second crop (6.3 g) was isolated from the mother liquor giving an 80% overall yield of *cis*-amide from the acid chloride.

**e.** ***cis*-9-Aminodecalin.**—A solution of 5.15 g (0.028 mol) of *cis*-amide in 40 ml of methanol was mixed with a solution prepared from 1.5 g (0.067 mol) of sodium and 48 ml of methanol.[51] Bromine (4.55 g, 0.028 mol) was added dropwise with magnetic stirring. The yellow solution was heated over steam for 20 min, and then made acidic with glacial acetic acid. After the methanol was removed by distillation, the urethan was thoroughly mixed with 23.4 g of calcium oxide and 15 ml of water. The mixture was heated to about 95° to distil the amine, then 15 ml of water was added and distillation was repeated. The distillates were combined, made acidic with concentrated hydrochloric acid, and extracted with ether. The amine was liberated by treatment with 50% sodium hydroxide solution, extracted with ether, and dried. Evaporation of the ether gave 3.4 g (79%) of pure *cis*-9-aminodecalin according to glpc analysis (column A).

**Hydrindan.**—In a 1-l. stainless steel autoclave was placed 500 g of indene and about 170 g of Raney nickel in 100 ml of absolute ethanol. After agitation for 48 hr at 210° in the presence of hydrogen (136 atm), the catalyst was removed by filtration and the solvent by distillation. Rectification of the residue gave (1) 230.4 g, bp 163–165°, of hydrindan (67.3%), indan (30.3%), and unknown (2.4%); (2) 85 g, bp 165–170°, of hydrindan (31%) and indan (69%); (3) 65 g, bp 170–175°, of hydrindan (8%) and indan (92%). Glpc collection (column D) of the products was used in identification. The hydrindan parent ion was observed at 124 amu (10 eV). Indan was characterized by infrared comparison with a published spectrum.[52] Purification was effected by sulfonation. A mixture of 219 g of fraction 1 and 440 ml of 98% sulfuric acid was heated at 65° with a water bath. After 25 min the layers were separated, and the organic portion was washed twice with dilute sodium hydroxide solution and twice with distilled water. After drying, distillation gave 115 g of product (hydrindan 96%, and unknown, 4%), hydrindan, bp 167°, $n^{25}$D 1.4705 (lit.[35] *cis*, bp 167.8°, $n^{20}$D 1.4720; *trans*, bp 161°, $n^{20}$D 1.4636).

***cis*-8-Aminohydrindan. a. 5-Hydrindanol.**—A stainless steel autoclave was charged with 5-indanol (100 g) and Raney nickel (50 g) in 200 ml of absolute ethanol. The agitated contents were subjected to 123 atm of hydrogen pressure for 72 hr at 170°. Distillation gave 5-hydrindanol (70%), bp 112° (11 mm) [lit.[53] bp 119–120° (22 mm)].

**b.** ***cis*-8-Hydrindancarboxylic Acid.**—A known pathway was followed.[53] Hydrindanol (65 g) and 97% formic acid (84.4 g) were added dropwise over a 4-hr period at 9–14° to sulfuric acid (553 g). The crude acid (64%) was isolated after an additional 1.5 hr of stirring at 18°.

**c.** ***cis*-8-Hydrindancarbonyl Chloride.**—The acid chloride (73%) was obtained by interaction of the acid with thionyl chloride.

**d.** ***cis*-8-Hydrindancarboxamide.**—The amide was derived from the acid chloride by treatment in ether solution with anhydrous ammonia gas. The product was recrystallized from hexane, mp 109–110° (lit.[53] mp 110–111°).

**e.** ***cis*-8-Aminohydrindan.**—The procedure for *cis*-9-aminodecalin was used giving the desired amine in 46% yield.

(45) From 1-methylcyclopentanol.

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(49) W. G. Dauben, R. C. Tweit, and R. L. MacLean, *ibid.*, **77**, 48 (1955).

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(51) E. S. Wallis and J. F. Lane, *Org. React.*, **3**, 267 (1946).

(52) "Sadtler Standard Spectra," Vol. 15, The Sadtler Research Laboratories, Philadelphia, Pa., Spectrum No. 15219.

(53) H. Koch and W. Haaf, *Chem. Ber.*, **94**, 1252 (1961).

*Anal.* Calcd for $C_9H_{17}N$: C, 77.75; H, 12.22; N, 10.06. Found: C, 77.45; H, 12.38; N, 10.16.

The acetamide derivative (acetic anhydride reagent), mp 88–89°, was crystallized three times from acetone–water (lit.[35] mp 88°, stereochemistry not determined, apparently *cis*).

**Identification of Dimethylcyclohexylamines.**—Characterization was carried out on the major product from amination of cyclooctane.

**a. N,N-Dimethyldimethylcyclohexylamines.**—The literature procedure[54] involving 90% formic acid and 37% formaldehyde gave the desired material, bp 54–57° (1.5 mm), in 85% yield (essentially pure by glpc analysis, column A).

**b. N,N,N-Trimethyldimethylcyclohexyl Ammonium Iodides.**—Treatment of the product from procedure a with methyl iodide afforded the quaternary ammonium iodides in 71% yield,[55] mp 203.5–204°.

**c. N,N,N-Trimethyldimethylcyclohexyl Ammonium Hydroxides.**[55]—Silver oxide (23.2 g, 0.1 mol) was added to a mixture of 75 ml of distilled water and 14.85 g (0.05 mol) of the quaternary ammonium iodides at 2°. After being stirred for 3 hr at 2–5°, the liquid mixture was freed of excess silver salts by filtration and concentrated by rotary evaporation at 4 mm (water bath at 35°).

**d. Pyrolysis of N,N,N-Trimethyldimethylcyclohexyl Ammonium Hydroxides.**[55]—The dark red product from procedure c was transferred to a 50 ml flask attached to an Ace Glass Mini-Lab distillation apparatus equipped with two traps, first, Dry Ice–acetone, and next, liquid nitrogen. The base was decomposed under nitrogen by slowly heating with an oil bath while maintaining a pressure of 20–25 mm. Reaction appeared to occur at 73°, and by 90° all the contents of the pot had distilled.

The material in the traps and receiver was combined. The organic layer was separated from the aqueous phase, and then washed with distilled water. The aqueous portions were combined, extracted with ether, and the ether extract added to the organic fraction which was dried. The olefin (52% from the amine) was subjected to glpc analysis (columns B and C) which revealed only one major peak. The infrared spectrum showed strong absorption at 1651 $cm^{-1}$, characteristic of a double bond exocyclic to a cyclohexane ring.[56]

**e. Dehydrogenation of Product d.**—A 100-ml stainless steel autoclave was charged with 15 g of benzene, 0.5 g of the olefin, and 0.25 g of 10% palladium on charcoal and shaken for 16.5 hr at 175°. Glpc analysis (column D) revealed the indicated mixture, starting material (16.5%), *p*-xylene (22.4%), and *m*-xylene (61.3%). The xylenes were identified by comparison with authentic material. In a control experiment in which *p*-xylene was subjected to identical conditions, no *m*-xylene was formed; *p*-xylene was the only compound present other than solvent.

**f. Ozonolysis of Product d.**[57]—The olefin (2 g) in 3.4 ml of dry pyridine and 30 ml of methylene chloride was ozonized at −72° for 45 min (Welsbach Model T-23). After standing for 6 hr the solution was washed with hydrochloric acid and then with distilled water. Glpc analysis of the dried product revealed two components, 3-methylcyclohexanone (71%) and 4-methylcyclohexanone (29%). The ketones were identified by comparison with authentic materials (retention times in glpc analysis, column A).

**7-Azabicyclo[4.1.0]heptane. a. (±)-*trans*-2-Chlorocyclohexanol.**—A literature method was used.[58] Treatment of cyclohexene with excess hypochlorous acid gave, after distillation, a colorless liquid (63%), bp 85–88° (20 mm), $n^{25.5}D$ 1.4864 (lit.[58] bp 88–90° (20 mm)).

**b. (±)-*trans*-2-Aminocyclohexanol.**—The procedure outlined by Wilson and Read was followed,[59] with the exception that the amino alcohol was isolated by sublimation (at 60°), white needles, mp 66.5–67.6° (lit.[59] mp 65°).

**c. 7-Azabicyclo[4.1.0]heptane.**—The method of Paris and Fanta[29] gave a colorless liquid, bp 150° (lit.[29] bp 149–150°). The infrared spectra of this product and the amination product were in agreement with the published spectrum.[29]

**N,N-Dichlorocyclohexylamine.**—A published procedure was used.[12] Distillation of the crude product afforded N,N-dichlorocyclohexylamine (67%), bp 65° (3.7 mm), $n^{26}D$ 1.5064 [lit.[60] bp 89–90° (17 mm)]. Infrared analysis showed NCl absorption at 690 $cm^{-1}$,[61] but no NH stretching or deformation. The product contained 99.9% of the theoretical amount of positive chlorine according to iodometric titration.

**6-Azabicyclo[3.1.0]hexane. a. (±)-*trans*-2-Chlorocyclopentanol.**—The method of Coleman and Johnstone was followed.[58] Cyclopentene with excess hypochlorous acid gave a colorless liquid (49%), bp 89° (25 mm), $n^{25}D$ 1.4805 [lit.[37] bp 75–85° (15 mm), $n^{23}D$ 1.4795].

**b. 1,2-Epoxycyclopentane.**—Application of a literature procedure[62] to product a gave a 67% yield of colorless liquid, bp 100–102°, $n^{24.5}D$ 1.4340 (lit.[37] bp 99–102°, $n^{23}D$ 1.4330).

**c. (±)-*trans*-2-Aminocyclopentanol Hydrochloride.**—1,2-Epoxycyclopentane (7.5 g) was shaken in a stainless steel autoclave with 100 ml of concentrated ammonium hydroxide for 2 hr at 70–80°. The amino alcohol was liberated by the addition of sodium hydroxide pellets and extracted with ether. After removal of ether, the amino alcohol was dissolved in dilute hydrochloric acid and vacuum distilled to dryness, giving tan crystals (50%), mp 180° (lit.[37] mp 193–194°).

**d. 6-Azabicyclo[3.1.0]hexane.**—The method of Fanta was followed.[38] The hydrochloride afforded the imine (52%) (glpc analysis, column E), bp 123°, $n^{23.5}D$ 1.4698 (lit.[38] bp 122–123°, $n^{22}D$ 1.4700).

**Registry No.**—Trichloramine, 10025-85-1; aluminum chloride, 7446-70-0; decalin (*cis*), 493-01-6; cyclohexane, 110-82-7; cyclopentane, 287-92-3; *cis*-9-aminodecalin (HCl), 24302-24-7; *cis*-9-aminodecalin (acetamide), 24302-25-8; decalin (*trans*), 493-02-7.

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