Ishiguro, *et al.*,[7] passed N,N-bis(2-hydroxyethyl)piperazine into an evacuated vessel containing silicon oxide–alumina at 325° during six hours. Ultimate treatment with *p*-nitrophenol gave 1,4-diazabicyclo[2.2.2]octane bis(*p*-nitrophenolate).

Prelog, *et al.*,[8] treated tetrahydropyran-4-propionic acid with sodium azide and obtained 4-(2-aminoethyl)tetrahydropyran. Treatment with hydrogen bromide at 100° for seven hours gave 3-(2-aminoethyl)-1,5-dibromopentane hydrobromide which with sodium hydroxide gave quinuclidine.

Prelog[9] approached the synthesis of quinuclidine from another direction. The methods he developed were based on the action of ammonia under pressure at 100–120° on aliphatic tribromides and on alkali treatment of dibromoalkylamines.

Rubtsov and Volskova[10] prepared 2-(1-benzoyl-4-piperidyl)ethyl bromide. This compound, upon treatment with hydrogen bromide and ultimate refluxing with sodium hydroxide, gave quinuclidine, which was isolated as the picrate.

Quinuclidine was prepared in this laboratory by the vapor phase dehydration over alumina of commericially available 4-hydroxyethylpiperidine. Purification of the product was conveniently acheived by sublimation.

Experimental

4-Hydroxyethylpiperidine,[11] 40 g., was distilled at 88°/0.1 mm. The vapors were passed through a column (18 × 0.5 in.) packed with dried alumina. The column temperature was maintained at 400–450° in a muffle furnace. The distillate was poured into a Dry Ice–acetone mixture, whereupon a solid precipitated. Filtration yielded 20 g. of a white product and starting material. The residue, after being dried in a vacuum desiccator for 5 min. at 30° and then sublimed, gave 11.2 g. of quinuclidine, m.p. 156° (sealed tube); reported m.p., 154°,[2] 156°.[12] Picrate from alcohol, m.p. 278°, reported m.p. 274°,[2] 274–275°.[11]

Anal. Calcd. for $C_{13}H_{16}N_4O_7$ (quinuclidine picrate): C, 45.88; H, 4.74; N, 16.47. Found: C, 46.27; H, 4.72; N, 16.15.

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Isolation and Identification of 1,1'-Dimethylbicyclohexyl

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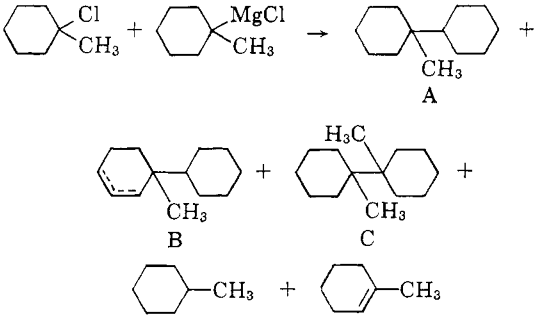
The preparation of a small amount of 1,1'-dimethylbicyclohexyl was required as a part of an Air Force program being conducted in this laboratory to develop new hydrocarbon fuels. Khromov, *et al.*[2a] reported that 1-chloro-1-methylcyclohexane reacts with its Grignard reagent when heated in the presence of cuprous chloride and copper turnings to yield the expected coupling product 1,1'-dimethylbicyclohexyl. They indicated difficulty in removing unsaturated impurities from their final product, and found it necessary to distil, chromatograph on silica gel, and finally redistil to obtain a pure product, described as having b.p. 99.5–100°/5 mm., $n^{20}{}_D$ 1.4920, d_4^{20} 0.9045, MR_D calcd. for $C_{14}H_{26}$: 62.45; found: 62.32.

Our work, following their procedure, has led to the isolation of a different hydrocarbon. Instrumental evaluation has demonstrated that our product, a solid melting at 42–43°, and not the material described by Khromov and co-workers, is, in fact, 1,1'-dimethylbicyclohexyl.

In addition to Khromov's method, we have also used the coupling procedure employing methylmagnesium bromide and cobaltous salts described by Kharasch and his co-workers.[2b] Low-boiling products resulting from disproportionation and free radical fragmentation account for about 90–95% of the yield by either synthetic method. These products, principally methylcyclohexane and methylcyclohexene, were not separated from the solvent. After removal of these low-boiling compounds, both synthetic methods produced three principal coupling products in approximately equal amounts, as demonstrated by vapor phase chromatography (v.p.c.). In order of increasing retention time these components will be designated A, B, and C. Careful fractionation enabled us to isolate the highest boiling component of this triad, C, as a solid in reasonable purity. Recrystallization from ethanol yielded the hydrocarbon in at least 99 area % purity by v.p.c. Compound C has been shown to be 1,1'-dimethylbicyclohexyl, and A and B are probably 1-methyl-1-cyclohexylcyclohexane and 1-methyl-1-cyclohexylcyclohexene-2 or -3, respectively.



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[1] To whom correspondence should be addressed.

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Khromov's procedure has also been repeated on a larger scale using 10.6 moles each of 1-chloro-1-methylcyclohexane and its Grignard reagent.

Spectrosopic Evidence for the 1,1′-Dimethylbicyclohexyl Structure for C.—The infrared spectrum of compound C is entirely compatible with the proposed structure. The usual strong hydrocarbon absorptions at 2900- and 1450-cm.$^{-1}$ regions were present, with partially resolved peaks at 1468 and 1445 cm.$^{-1}$ in the assigned areas for asymmetric methyl bending and cyclohexyl methylene scissoring vibrations,[3] respectively. The strong, sharp symmetric methyl bending absorption appeared at 1370 cm.$^{-1}$. Examination of spectra of many hydrocarbons containing monosubstituted cyclohexyl groups[4-6] showed useful 850, 900 cm.$^{-1}$ paired peaks generally to be present, as those in the parent cyclohexane spectrum. With 1,1-disubstitution of the ring, seen in the spectra of 1,1-dimethyl-,[7] 1,1-diethyl-,[6] 1-methyl-1-ethyl-,[5] 1-chloro-1-methyl-,[6] and 1-ethyl-1-bromoethylcyclohexane,[6] the 850-cm.$^{-1}$ peak consistently appears, while the 900-cm.$^{-1}$ region varies in complexity with shifting and splitting of peaks. The spectrum of C exhibited the 850-cm.$^{-1}$ absorption and a simpler pattern around 900–1000 cm.$^{-1}$ than that found for less symmetric mono- or 1,1-disubstituted cyclohexanes.

Initial evidence for the presence of two methyl groups per molecule was provided by infrared differential spectrophotometry. The intensity of the absorptions at about 1460 and 1370 cm.$^{-1}$ were compared to those in similarly run spectra of appropriate cyclic hydrocarbons with none and one methyl group per molecule. The spectrum of C had intensities relative to this selected series indicative of two methyl groups per molecule.

The near infrared spectrum gave substantiating structural information. A strong cyclohexyl methylene peak (the second overtone of the C—H stretching fundamental) at 1.21 μ and the methyl peak (the second overtone) at 1.19 μ were recorded. No peak for the second overtone of the non-aromatic methine ($\equiv$C—H) group was observed, although reference compounds (methylcyclohexane and bicyclohexyl) showed a clearly resolved peak at the reported 1.225 μ.[8] This finding would substantitate the 1,1′-dimethyl substitution that results in two quaternary carbon atoms.

The final confirmatory spectroscopic evidence was supplied by nuclear magnetic resonance analysis.[9] As theory would predict for 1,1′-dimethylbicyclohexyl, only two proton peaks were found in the spectrum. A strong, sharp peak at τ = 9.15 was assigned to methyl protons and a peak at τ = 8.63 to cyclohexyl methylene protons. These absorptions were in the expected approximate area ratio of 1:3.3. The lack of multiplet structure (spin coupling) for the τ = 9.15 peak indicates that the equivalent methyl groups are attached to atoms that have no hydrogen directly bonded to them; *i.e.*, to quaternary carbon atoms. Chamberlain[10] noted that saturated alicyclic rings produce sharp peaks if they are unsubstituted or *gem*-disubstituted, while other low degrees of substitution produce unresolved broad peaks at 30 or 40 Mc. The 60-Mc. spectrum of 1,1′-dimethylbicyclohexyl agrees with the observations for the *gem*-disubstituted alicylic form.

Thus, spectral data strongly support the proposed 1,1′-dimethylbicyclohexyl as the isolated solid product.

Evidence for the 1-Methyl-1-cyclohexylcyclohexane Structure for A.—Component A was collected by v.p.c. as a liquid in 95 area % purity and examined by infrared. Heavy hydrocarbon absorptions at about 2900 and about 1450 cm.$^{-1}$ and a sharp methyl peak at 1374 cm.$^{-1}$ were recorded. Absorptions were about 850 and 900 cm.$^{-1}$ as in monosubstituted cyclohexyls and additional peaks about 930 and 960 cm.$^{-1}$ were present. The n^{20}D 1.4820, compares favorably with the literature value of 1.4824 for 1-methyl-1-cyclohexylcyclohexane, obtained by hydrogenation of 1-methyl-1-phenylcyclohexane.[1] This saturated hydrocarbon is therefore presented as the structure of component A, based upon relative v.p.c. retention time, spectral data, and refractive index information only.

Evidence for the 1-Methyl-1-cyclohexylcyclohexene Structure for B.—Component B was collected by v.p.c. in 83 area % purity, contaminated with 17 area % of component A, and its infrared spectrum obtained. Absorptions at about 2900, 1450 cm.$^{-1}$ and a sharp methyl peak at 1374 cm.$^{-1}$ were recorded. The other region of interest contained peaks about 850, 920, and 970 cm.$^{-1}$ similar to those in the spectra of 1,1-disubstituted rings. In addition, a weak-medium band at 1661 cm.$^{-1}$ was present which is close to the intensity and frequency of the 1656-cm.$^{-1}$ band found in a cyclohexene spectrum run concurrently. Other values have been reported for this band: 1646,[11] 1648,[12] 1650,[13] and 1656 cm.$^{-1}$.[14]

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[3] R. N. Jones and C. Sandorfy, "Technique of Organic Chemistry, Vol. IX: Chemical Applications of Spectroscopy," W. West, ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 361.

[4] K. T. Serijan, I. A. Goodman, and W. J. Yankauskas, "Infrared Spectra of Fifty-nine Dicyclic Hydrocarbons," NACA Technical Note 2557, 1951.

[5] American Petroleum Institute Research Project 44, Infrared Spectral Data, Serial 539, 1946; Serial 1949, 1958.

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This absorption is characteristic of the *cis* ethylenic linkage RCH=CHR′ in a six-membered ring. Substitution at this linkage increases the frequency to 1681 cm.$^{-1}$ [14] (1674)[11,15] as noted in 1-methylcyclohexene spectra (RR′C=CHR″). On the basis of relative VPC retention time and spectral evidence only, an unsaturated isomer of component A is suggested as the structure of the second by-product, component B; *i.e.*, 1-methyl-1-cyclohexylcyclohexene-2 or -3.

Since components A and B were only obtained in minute quantities by v.p.c. collection, it was not possible to obtain direct chemical evidence, such as carbon–hydrogen analyses.

Experimental

Infrared spectra were obtained with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer with sodium chloride optics. Frequencies were checked with a polystyrene film reference and estimated to be accurate and reproducible to 0.01 μ. Components A and B were collected in a micro cavity cell (0.05 mm.) and their spectra obtained using a beam condenser attachment. Component C was examined in carbon tetrachloride solution and in a potassium bromide pellet.

Near infrared spectra were run on a Cary Model 14 recording spectrophotometer in liquid sample cells of 1- and 10-mm. path lengths.

The nuclear magnetic resonance spectrum was determined by Varian Associates, Palo Alto, California, on a Varian Model A-60 spectrometer at 60 Mc., with a reported accuracy of ±1 c.p.s. The sample was run in deuteriochloroform solution, with tetramethylsilane as the internal standard.

Vapor phase chromatograms were determined on a Perkin-Elmer Model 154-B Vapor Fractometer, equipped with a 6-ft. column of 16% *m*-bis(*m*-phenoxyphenoxy) benzene on 35–80 mesh Chromosorb W, operating at 164°, outlet flow 100 cc. helium/min., inlet 15 p.s.i.g. Collection of components A and B was made from a 6-ft. column of 20% Apiezon L on 35–80 mesh Chromosorb W, operating at 168°, outlet flow 50 cc. helium/min., inlet 30 p.s.i.g.

1,1′-Dimethylbicyclohexyl.—The Grignard reagent was prepared from 1-chloro-1-methylcyclohexane[16] (245 g., 1.848 moles), magnesium turnings (49.4 g., 2.03 g.-atoms) and 840 ml. of dry ether. Cuprous chloride (11.1 g., 0.112 mole) and copper turnings (12.0 g., 0.189 g.-atom) were added, followed by the dropwise addition of 1-chloro-1-methylcyclohexane (245 g., 1.848 moles) dissolved in 490 ml. of dry ether. The mixture was refluxed for 48 hr. The bulk of the ether was distilled out of the system, being simultaneously replaced with dry toluene. The mixture was refluxed for an additional 8 hr. Hydrolysis was effected by the addition of 490 ml. of saturated aqueous ammonium chloride. The hydrolysate was filtered, and the filter cake was thoroughly washed with ether. The washings were combined with the filtrate, and solvent as well as residual low-boiling disproportionation products were removed by distillation at atmospheric pressure. The residual oil was then carefully distilled from sodium. A series of four distillation cuts were collected, at a high reflux ratio, from 80–96.5°/1 mm., n^{20}_{D} of liquid cuts 1.4926–1.4965. Distillate collected from 95.5–96.5°/1 mm. solidified in the receiver. The yield of 1,1′-dimethylbicyclohexyl (based on v.p.c.) was 8.6 g., or 2%.

When the reaction was repeated on a 10.6-mole scale, the isolated yield of hydrocarbon of at least 99 area % purity (v.p.c.) was 50 g. (2%), m.p. 42–43°.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.5; H, 13.5; mol. wt. 194. Found: C, 86.6; H, 13.5; mol. wt. (Rast Method), 191.

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Reaction of 1,2-Dihaloethanes with Sodium Cyanide

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A well known general method for the preparation of alkyl cyanides is the reaction of sodium or potassium cyanide with an alkyl halide in alcohol solution. Polymethylene dicyanides also may be prepared by this method.[1]

The reaction of 1,3-dibrompropane with cyanide ion gives trimethylene cyanide in 86% yield.[1] Reaction of 1-bromo-3-chloropropane with cyanide ion gives 4-chlorobutyronitrile in 70% yield.[1] Thus it is apparent that trimethylene dihalides react with cyanide ion by the stepwise nucleophilic substitution of cyanide ion on the carbon containing halogen. Ethylene dibromide has been treated with cyanide ion to produce succinonitrile in 80% yield.[2] Although the product corresponding to that produced from the higher polymethylene dihalides is obtained, it has been found that reaction of the ethylene dihalides proceeds by a different path.

Ethylene dichloride reacted very slowly with sodium cyanide in methanol at 50°. The approximate second-order rate constant was 3.0 × 10^{-4} l. mole^{-1} hr.$^{-1}$. Reaction of 3-chloropropionitrile, however, was extremely rapid at room temperature, having a rate constant greater than 68 l. mole^{-1} hr.$^{-1}$. The products from this latter reaction were acrylonitrile, hydrogen cyanide, and chloride ion. The following, then, represents a more reasonable path by which succinonitrile may be formed from this reaction

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[1] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, p. 590.

[2] R. B. Wagner and H. D. Zook, *ibid.*, p. 614.