TABLE I

MONOHYDROBORATION OF CYCLOPENTADIENE PRODUCTS BY GLPC ANALYSIS

Reagent	Diene, mmoles	Borane, mmoles	% diol	% monool	—Isomeric distribution of monool, %— Δ¹-Cyclopentenol	Δ²-Cyclopentenol
Diborane[a]	20	3.33	26.5	34	97	3
Thexylborane[b]	20	5	27	49.2	98.9	1.1
Disiamylborane[c]	20	10	14	64.1	99.0	1.0
Diisopinocamphenylborane	20	10	7.5	83	100	0

[a] An unknown product (6.8% based on area) was noted with a retention time similar to the cyclopentenols. [b] 2,3-Dimethyl-2-butylborane. [c] Bis(3-methyl-2-butyl)borane.

ture was maintained at 140–150°. The products, collected in a flask cooled in a Dry Ice–acetone bath, were immediately fractionated to give 9.9 g (0.118 mole, 50.5% yield) of Δ³-cyclopentenone (bp 28° at 17 mm, n^{20}D 1.4580), semicarbazone [mp 184–185° (lit.[1] bp 41° at 40 mm, n^{20}D 1.4536)], semicarbazone (mp 182°), and 3.4 g (0.041 mole, 17.2% yield) of Δ²-cyclopentenone (bp 50° at 17 mm, n^{20}D 1.4813), 2,4-dinitrophenylhydrazone (mp 168–169° (lit.[1,8] bp 50° at 15 mm, n^{20}D 1.4810)), and 2,4-dinitrophenylhydrazone (mp 169–171°).

Pyrolysis of the alcohol as above, but with 0.5 mole% palladium on carbon added, produced a 17% yield of Δ³-cyclopentenone and a 41.7% yield of Δ²-cyclopentenone.

Reduction of the Δ³-cyclopentenone with lithium aluminum hydride gave a 75% yield of Δ³-cyclopentenol: bp 63.5–64° at 33 mm; n^{20}D 1.4698.

Monohydroboration of Cyclopentadiene with Alkylboranes.—The monohydroboration of cyclopentadiene with borane and alkylboranes was carried out using the procedure previously described[11,12] for the monohydroboration of 1,3-hexadiene. A solution of (borane) alkylborane in tetrahydrofuran was added to 20 mmoles (100% excess) of cyclopentadiene at 0°. After oxidation of the organoborane, the organic layer was isolated and the products were studied by capillary glpc on FFAP (free fatty acid phase). The isomeric distribution of cyclopentenols was determined by conversion of the alcohols to their acetates and analysis by capillary glpc on diethylene glycol succinate. The results are given in Table I. Because of its slower reactivity, the reaction of diisopinocampheylborane with cyclopentadiene was altered (see below).

Δ³-Cyclopentenol (VI).—In a dry 1-l. flask, equipped with a magnetic stirrer, condenser, nitrogen inlet, and side arm, was placed 90 g (0.66 mole, 10% excess)[13] of dry α-pinene.[14] The flask, flushed with nitrogen, was immersed in an ice bath and 197 ml of a 1.52 *M* solution of borane (0.3 mole of BH_3) in tetrahydrofuran was added over a period of 15 min. The reagent was stirred for 2 hr at 0° and 39.6 g (0.6 mole, 100% excess) of freshly distilled cyclopentadiene (n^{20}D 1.4439) was added. The reaction mixture was slowly warmed to room temperature and stirred at room temperature for 17 hr. Excess hydride was decomposed by adding 10 ml of water and the organoborane was oxidized by adding 96 ml of 3 *N* sodium hydroxide, followed by dropwise addition of 96 ml of 30% hydrogen peroxide.

The aqueous layer was salted out with sodium chloride and the organic layer was removed. Cyclopentadiene and tetrahydrofuran were removed under vacuum. The mixture was then dissolved in 100 ml of ether and stirred for 30 min with 300 ml of a 1 *M* aqueous silver nitrate solution. The organic layer was removed and washed twice with aqueous silver nitrate. The aqueous layer was washed twice with ether. The aqueous layers were combined, an excess of sodium chloride was added to precipitate out silver chloride, and the alcohol was extracted with ether. After the ether layer was dried over magnesium sulfate, the ether was removed and the alcohol was distilled to give 14.4 g (0.172 mole, 57% yield) of Δ³-cyclopentenol, bp 59–60° at 27 mm, n^{20}D 1.4698, and phenylurethan, mp 140–140.5° (lit.[4] bp 67–68° at 36 mm, n^{20}D 1.4673, mp 140.4–140.8°). The alcohol was shown to be contaminated by less than 1% of dicyclopentadiene by capillary glpc analysis on FFAP. Conversion of the alcohol to the acetate and capillary glpc analysis on diethylene glycol succinate showed the absence of Δ²-cyclopentenol. The nmr and infrared spectra were identical with those of the Δ³-cyclopentenol obtained from the lithium aluminum hydride reduction of Δ³-cyclopentenone.

Registry No.—III, 14320-37-7; VI, 14320-38-8.

(13) When stoichiometric amounts of α-pinene were used, lower yields of Δ³-cyclopentenol were obtained. Even when a 10% excess of diborane was used, α-pinene was observed in the product, making extraction with silver nitrate necessary.

(14) α-Pinene was dried by distillation from lithium aluminum hydride.

Base-Catalyzed Disproportionation of 2-Cyano-1,3-cyclohexadiene

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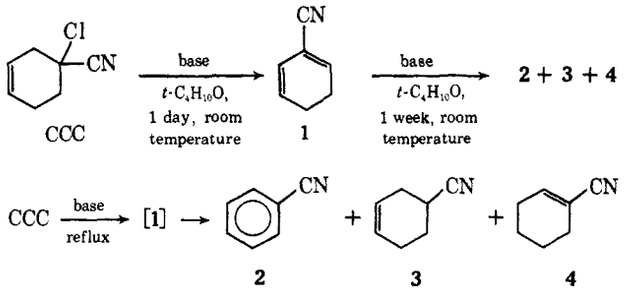
It was recently reported[1] that 1,3-cyclohexadiene treated with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) underwent quantitative disproportionation to benzene and cyclohexene (55°, 24 hr). The kinetics exhibited a second-order dependence on cyclohexadiene concentration and it was postulated that the rate-determining step was hydride transfer from cyclohexadienyl anion to cyclohexadiene. In *t*-butyl alcohol, rather than DMSO, isomerization but not disproportionation occurred. More recently it was disclosed[2] that 1- and 2-bromo-1,3-cyclohexadiene treated with potassium *t*-butoxide in DMSO mostly underwent isomerization and disproportionation (which was not actually detected) was at best a very minor reaction.

In a related study conducted in these laboratories, it has been found that 2-cyano-1,3-cyclohexadiene when treated with sodium *t*-butoxide in refluxing *t*-butyl alcohol undergoes a very facile disproportionation to benzonitrile and a mixture of 1- and 4-cyanocyclohexene. The over-all course of the reactions involved is summarized in Scheme I. At room temperature, 4-chloro-4-cyanocyclohexene (hereinafter CCC) reacted smoothly with sodium *t*-butoxide in *t*-butyl alcohol to

SCHEME I



(1) J. E. Hofmann, P. A. Argabright, and A. Schriesheim, *Tetrahedron Letters*, No. 17, 1005 (1964).

(2) A. T. Bottini and W. Schear, *J. Org. Chem.*, **30**, 3205 (1965).

yield **1** and sodium chloride as the only detectable products after 25 hr.[3,4] However, prolonged treatment (*e.g.*, 1 week) at room temperature resulted in the formation of a more complex product mixture containing **1**, **2**, **3**, and **4**.

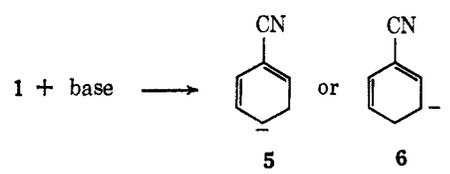
When CCC was treated with sodium *t*-butoxide in refluxing *t*-butyl alcohol, the reaction terminated after 3 hr, and then worked up, it was found that a quantitative yield of sodium chloride had been formed and the organic products consisted of **1** (41.8%), **2** (25.7%), and a mixture of **3** and **4** totaling 24.7% (these isomers were not separable by glpc on the columns available to us but were readily identifiable *via* nmr). As expected, the quantities of **2** and the mixture of **3** and **4** were essentially equal on a molar basis.

When the mixture of **1**, **2**, **3**, and **4** described above was treated for 6 hr more with sodium *t*-butoxide in refluxing *t*-butyl alcohol, all of **1** completely disappeared and **2**, **3**, and **4** were the sole detectable products, again with the quantity of **2** and the mixture of **3** and **4** equal. The quantities of **3** and **4** formed were estimated from nmr which showed that 59% of the monoene was **3** and 41% **4**. No evidence was found for the presence of 3-cyanocyclohexene in the product mixture.

Presumably the failure of cyclohexadiene to undergo disproportionation in *t*-butyl alcohol[1] is the result of very rapid transfer of a proton from alcohol to cyclohexadienyl anion as opposed to the slower, less favorable transfer of hydride from the anion to cyclohexadiene. The same two reactions apparently compete far better in the case of **1**. That is, k_1/k_{-1} is

$$1 + \text{base} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 1^- \xrightarrow[\text{slow}]{1} 2 + 3^- + 4^- \xrightarrow[\text{alcohol}]{\text{alcohol}} 2 + 3 + 4$$

much larger in the case of cyanocyclohexadiene since either of the two "formal" anions formed from it (**5** or **6**) should be considerably more stable than an



5 **6**

unsubstituted cyclohexadienyl anion. Also, **1** would be expected to be particularly receptive to the addition of basic or nucleophilic reagents (in this case, hydride ion) by analogy with the well-known tendency for other cyano-conjugated olefins, notably acrylonitrile, to do so. On the other hand, 1^- might be a less active hydride donor than cyclohexadiene anion, owing to its stability. It is difficult to predict the relative rate of hydride transfer from the present results, although the over-all product composition indicates that this step is not unfavorable. One might postulate an alternative explanation involving a synchronous mechanism whereby proton and hydride transfer reactions occur in a concerted fashion. This would necessitate that **1** be associated into at least a dimer, perhaps similar to the complexation suggested for some Diels–Alder reactions,[5] so that 1^- as such never really exists in the reaction mixture. This neither seems necessary nor correct, especially in view of the fact that Diels–Alder adducts were not detected in higher temperature reactions in the presence of much milder bases (see discussion below).

Since disproportionation of **1** was found to occur so readily under conditions which were not successful for analogous molecules,[1,2] it was of interest to determine whether a milder base than *t*-butoxide would function as well. When an equimolar mixture of CCC and pyridine was allowed to reflux (approximately 120°) for 20 hr, it was found that dehydrochlorination was complete and that the derived products were **1** (24.5%), **2** (38.9%), and a mixture of **3** and **4** (36.6%). Therefore, **1** is sufficiently reactive to undergo disproportionation in the presence of mild as well as strong bases. The possibility that **1** undergoes thermal disproportionation[4] cannot be ruled out; however, the similarity in product composition suggests that a similar pathway was followed in these experiments as well as those conducted at lower temperatures.

As mentioned before, only two of the three possible isomeric cyanocyclohexenes were detected. The undetected 3 isomer may have been present in small (5%) amounts. It is likely that equilibration occurs under the conditions of these reactions since isomerization appears to be facile.[1,2] Finally, preliminary experiments have shown that methylated derivatives of CCC (from isoprene and α-chloroacrylonitrile) undergo most of the same reactions.

Experimental Section[6]

4-Chloro-4-cyanocyclohexene was prepared in the following manner. A 1-l. autoclave was charged with 350 g (4.0 moles) of α-chloroacrylonitrile[7] and 19 g (0.17 mole) of hydroquinone. This mixture was cooled to Dry Ice temperature and 260 g (4.80 moles) of 1,3-butadiene (also maintained at Dry Ice temperature) was added. The autoclave was sealed and then heated and vigorously stirred at 90–110° for 24 hr. Distillation (after removal of hydroquinone) afforded 341 g (60.3%, based on α-chloroacrylonitrile) of a colorless liquid, bp 73–74° at 22 mm. The infrared spectrum of this compound, 4-chloro-4-cyanocyclohexene, showed an unconjugated nitrile absorption at 2235 cm^{-1}.

Anal. Calcd for C_7H_8NCl: C, 59.38; H, 5.66; N, 9.90; Cl, 25.05. Found: C, 59.41; H, 5.70; N, 9.67; Cl, 25.28.

The viscous residue weighed 74 g. No attempt was made to maximize yields.

4-Cyanocyclohexene was purchased.[8] The olefinic protons in this compound (all nmr spectra were taken on neat liquids) appeared at τ 4.35 (TMS at τ 10.0). This resonance appeared as a first-order doublet with very small splitting (at approximately 1.3 cps) and underlying fine structure. The methine proton appeared, as a first approximation, as two overlapping quartets centered at τ 7.17. The methylene resonances appeared as a

(3) The *a priori* expectation had been that 1-cyano-1,3-cyclohexadiene would be the major dehydrochlorination product. However, the 2-cyano derivative was the only one detected (see Experimental Section). This was also the major product obtained from dehydrobromination of a mixture of 3- and 6-bromocyclohexene-1-carbonitrile.[4]

(4) We are indebted to a referee for bringing our attention to this paper: P. Scheiner, K. K. Schmiegel, G. Smith, and W. R. Vaughn, *J. Org. Chem.*, **28**, 2960 (1963).

(5) *Cf.* J. C. Little, *J. Am. Chem. Soc.*, **87**, 4021 (1965).

(6) Boiling points are uncorrected. Microanalysis were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Infrared spectra were obtained on a Beckman IR-10 spectrophotometer. The nmr spectra were obtained on a Varian A-60 spectrometer with TMS as an internal standard. Gas chromatography (glpc) was carried out on a Beckman GC-2 gas chromatograph, employing the following columns (6 ft × 0.25 in.) as needed: A, Carbowax 20M on Chromosorb W; B, silicone (Beckman, No. 17449); C, Polar Pack Q (Waters, Assoc., Inc., Framingham, Mass.).

(7) Commercially available from Marbon Chemical Division, Borg-Warner Corp.

(8) K & K Laboratories, Inc., Plainview, N. Y. 11803.

complex multiplet entered at approximately τ 7.85. The olefinic and methine chemical shifts and splittings were unique for all of the compounds encountered in this study and were very useful for both qualitative and quantitative analysis. The ratio of methylene–olefin–methine protons found was 6.1:2.0:1.0 (theory, 6:2:1).

1-Cyanocyclohexene was synthesized according to a literature procedure.[9] The olefinic proton appeared as a multiplet (at least seven lines) in the nmr spectrum centered at τ 3.42. The methylene protons appeared as two distinct, equal-intensity multiplets centered at τ 7.85 and 8.32.

Dehydrochlorination and Disproportionation of 4-Chloro-4-cyanocyclohexene (in *t*-Butyl Alcohol).—To a nitrogen-blanketed, stirred solution of 0.63 mole of sodium *t*-butoxide, prepared from 14.5 g (0.63 g-atom) of sodium and 1250 ml of *t*-butyl alcohol, was slowly added a solution of 89.1 g (0.63 mole) of 4-chloro-4-cyanocyclohexene in 300 ml of *t*-butyl alcohol at a rate sufficient to maintain the temperature of the reaction mixture at 20–30° (the reaction was exothermic). After addition was complete, the reaction mixture was heated under reflux for 3 hr and then allowed to cool to room temperature. The sodium chloride formed was collected by filtration, washed with ether, and then dried (36.8 g, 100%). Evaporation of the ether afforded a small amount of crystalline residue identified as benzamide *via* infrared and mixture melting point (undepressed) with an authentic sample. The filtrate from the sodium chloride isolation step was treated with water. The resulting mixture was extracted with methylene chloride. This solution was then washed with water and dried over anhydrous sodium sulfate. Fractional distillation of the residue, after evaporation of methylene chloride *in vacuo*, afforded only one fraction (27 g, 40.8%), bp 43–44° (2 mm); no attempt was made to maximize this.

The infrared absorption of this product showed two nitrile bands at 2210 and 2230 cm^{-1}, as well as typical absorptions for monosubstituted aromatic compounds. Analysis of the products *via* glpc on columns A, B, and C showed three peaks which were identified as benzonitrile (25.7%), a mixture of 1- and 4-cyanocyclohexene (24.7%) (these compounds did not separate on any of the glpc columns investigated), and 2-cyano-1,3-cyclohexadiene (41.8%). The identity of benzonitrile and the isomeric cyanocyclohexenes *via* glpc was based on comparisons of retention times with those of authentic samples and analysis of synthetic mixtures of these compounds. The identity of 2-cyano-1,3-cyclohexadiene was based on nmr and isolation of the tetracyanoethylene Diels–Alder adduct (see below). The spectrum of the reaction mixture clearly showed benzonitrile (multiplet at τ 2.41). The olefin region was complex. Rudiments of both the 1- and 4-cyanocyclohexene olefinic proton resonances were recognizable but both were broadened and contained lines not present in the pure compounds. A relatively intense multiplet not contained in either and centered at 3.95 was present. Since 2-cyano-1,3-cyclohexadiene would be expected to have three distinct olefinic resonances, this is taken as strong evidence that the strong glpc peak was attributable to this compound. As further evidence of this, the dehydrochlorination reaction was repeated exactly as described above except at room temperature throughout. Under these conditions sodium chloride is readily formed. Analysis of the reaction mixture (after 25 hr) *via* glpc showed only starting 4-chloro-4-cyanocyclohexene and the peak attributed to 1-cyano-1,3-cyclohexadiene (32.5%). No benzonitrile or cyanocyclohexene peaks were detectable. Interestingly, however, if the room-temperature reaction was allowed to proceed for prolonged periods (*e.g.*, 1 week), ample evidence (glpc) of disproportionation was detectable. Hence, the cyanocyclohexadiene disproportionation not only occurred in *t*-butyl alcohol but does so, albeit slowly, at nominal temperatures.

Preparation of the Tetracyanoethylene Adduct of 2-Cyano-1,3-cyclohexadiene.—A 5.4-g portion of the reaction mixture obtained from treatment of 4-chloro-4-cyanocyclohexene with sodium *t*-butoxide in *t*-butyl alcohol (bp 43–44° (2 mm)) was mixed with 3.8 g (0.03 mole) of tetracyanoethylene and 0.1 g of hydroquinone. This combination was heated in a sealed tube at 105–110° for 3 hr. The dark reaction mixture was allowed to cool to room temperature slowly (over a period of 2 hr) and the solid precipitate which formed was collected *via* filtration. The precipitate was washed with cold toluene and cold carbon tetrachloride and then dried *in vacuo* (2.7 g, pale yellow crystals). Recrystallization from benzene gave a white crystalline solid, mp 214–215° (sealed tube). Bicyclo[2.2.2]oct-5-ene-2,2,3,3,5-pentacarbonitrile was reported[4] to melt at 214–215°.

Anal. Calcd for $C_{13}H_7N_5$: C, 66.94; H, 3.03; N, 30.03. Found: C, 66.52; H, 2.95; N, 30.48.

Only one peak was obtained on glpc analysis (Carbowax 20M (20%) on Chromosorb W at 160° (retention time, 19.8 min). The nmr spectrum in hexadeuteriodimethyl sulfoxide showed only one olefinic hydrogen (multiplet, at least three lines, at 3.08). The presence of 1-cyano-1,3-cyclohexadiene was not established; however, small amounts would not have been detected by the above procedure.

Disproportionation of 2-Cyano-1,3-cyclohexadiene.—A portion of the reaction product isolated above (containing 2-cyano-1,3-cyclohexadiene, benzonitrile, and the isomeric cyanocyclohexenes) was treated an additional 6 hr with sodium *t*-butoxide (equimolar, based on the cyclohexadiene derivative) in refluxing *t*-butyl alcohol. At the end of this period, the only products detectable by glpc were benzonitrile and 1- and 4-cyanocyclohexene (41 and 59%, respectively, as determined from nmr). All peaks attributable to the cyclohexadiene completely disappeared in the nmr spectrum as well and only olefinic proton resonances attributable to the two isomeric monoenes described above were found (these were superimposable in every detail with those of the known reference compounds).

Dehydrochlorination and Disproportionation in Pyridine.—A solution of 4-chloro-4-cyanocyclohexene (7.08 g, 0.05 mole) in 3.96 g (0.05 mole) of pyridine (dried over barium oxide) was protected from atmospheric moisture and allowed to reflux for 20 hr. The crude reaction mixture was directly analyzed *via* glpc. All of the original chloro compound had disappeared and the products derived from it were benzonitrile (38.9%), 2-cyano-1,3-cyclohexadiene (24.5%), and a mixture of 1- and 4-cyanocyclohexene (36.6%).

Registry No.—**1**, 14210-94-7; **2**, 100-47-0; **3**, 100-45-8; **4**, 1855-63-6; CCC, 14210-93-6; bicyclo[2.2.2]oct-5-ene-2,2,3,3,5-pentacarbonitrile, 7149-13-5.

Acknowledgment.—We are indebted to Professor William Huntsman, Department of Chemistry, Ohio University, for obtaining all of the nmr spectra discussed in this paper.

(9) S. M. McElvain and R. E. Starr, Jr., *J. Am. Chem. Soc.*, **77**, 4571 (1955).

Mass Spectrometry and the Stereochemistry of the Pentacyclic Oxindole Alkaloids

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Following the elucidation of the stereochemistry of the pentacyclic oxindole alkaloids by a combination of spectral, chemical, and kinetic methods,[1] it was decided to carry out a comparative study of the mass spectra of these compounds in the hope that some correlations could be established between stereochemistry and intensity of fragment ions.

The mass spectral fragmentation patterns for some of the pentacyclic oxindoles have previously been reported and the mechanism of formation of the principal ions has been supported by deuterium labeling. It has been shown that the three most intense ions in the mass spectra of the pentacyclic oxindoles arise from the cleavages seen in Scheme I.[2]

(1) M. Shamma, R. J. Shine, I. Kompis, T. Sticzay, F. Morsingh, J. Poisson, and J. L. Pousset, *J. Am. Chem. Soc.*, **89**, 1739 (1967).

(2) B. Gilbert, J. A. Brissolese, N. Finch, W. I. Taylor, H. Budzikiewicz, J. M. Wilson, and C. Djerassi, *ibid.*, **85**, 1523 (1963).