and collected on the same column at 100° and 60 ml/min helium flow. The lactone was recollected at 150° for final purification.

The ester mixture **15d–17d** could not be separated by glpc. That the latter mixture was indeed composed of **17d** and **15d** was shown by the infrared [5.76 μ (ester C=O)] and nmr spectra. The nmr spectrum indicated the presence of ~70% **17d** and 30% **15d**. Principal peaks of the nmr spectrum of **15d** were assigned as follows: τ 5.0 (s, C-3 proton), 7.9 (q, ester methylene), 7.9–8.3 (m, C-1, C-4, C-5 protons), 8.38 (s, C-4 methyl), 8.75 (t, ester methyl), 8.91, 9.11 (s, C-2 *gem*-dimethyls). Nmr signals of isomer **17d** were assigned as follows: τ 4.72 (m, C-5 proton), 7.9 (q, ester methylene), 7.9–8.3 (m, C-1, C-4, C-5 protons), 8.38 (s, C-4 methyl), 8.75 (t, ester methyl), 9.02, 9.03 (s, C-2 *gem*-dimethyls).

Preparation of *t*-Butyl 2,2,4-Trimethyl-3-cyclohexene-1-carboxylate (15c).—To a solution of 5.587 g (0.050 mol) of potassium *t*-butoxide in 45 ml of *t*-butyl alcohol (freshly distilled over sodium) was added 4.00 g of the acid chloride of **15a** prepared in the same manner as described for preparation of ester **15b** and this mixture was stirred at room temperature under a nitrogen atmosphere for a period of 45 min. After removal of the bulk of the *t*-butyl alcohol under reduced pressure the mixture was diluted with 25 ml of water and extracted with 150 ml of ether. The ethereal layer was washed with four 25-ml portions of water and dried over magnesium sulfate. Evaporation of solvent afforded 1.699 g of residual liquid which on short-path distillation afforded 862 mg (18%) of **15c** as a colorless liquid: bp 141° (10.5 mm); ir (neat) 5.76 μ; nmr (CCl_4) τ 5.12 (broad s, C-3), 8.0 (t, J = 6.1 Hz, C-1), 8.2–8.4 (m, C-5, C-6), 8.5 (s, fine splitting, C-4 olefinic methyl), 8.69 (s, *t*-butyl methyls), 9.02, 9.20 (s, C-2 *gem*-dimethyls).

Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 75.09; H, 10.79.

Treatment of 2,2,4-Trimethyl-3-cyclohexene-1-carboxylic Acid (15a) with Base. A. With Potassium *t*-Butoxide–Water (3:1)–THF.—To a solution of 4.011 g (0.036 mol) of potassium *t*-butoxide in 12.5 ml of tetrahydrofuran was added 200 mg of water followed by 500 mg of the acid **15a**, mp 84–85°, as described in cleavage reaction E, above. The mixture was stirred at 26–27° for 24 hr when the bulk of the THF was removed under reduced pressure. The residue was dissolved in 25 ml of water and the water layer was washed with ether. The cold aqueous layer was acidified with 23 ml of 2 N hydrochloric acid and the acid was extracted in the usual fashion to furnish 347 mg (70%) of crystalline acid. Esterification with diazomethane afforded 300 mg of ester, bp 80–105° (0.5–1.0 mm), which on analysis by glpc on two different columns (0.25 in. × 10 ft columns packed with 20% SE-30 silicon oil and with 20% Carbowax 20M TMPA on 60–80 mesh AW DMCS-300) showed a single peak of retention time identical with ester **15b**. (The isomeric ester **17b** was separated cleanly from **15b** under these conditions.) The infrared spectrum of the collected material was identical in every major respect with ester **15b** prepared above.

B. With 4 *M* 95% Methanolic Potassium Hydroxide.—A solution of 503 mg of acid **15a** in 5 ml of 4.0 M 95% methanolic potassium hydroxide solution was heated at reflux for 16 hr as in cleavage run 3 above. Removal of solvent, dilution with 20 ml of water, acidification, and ether extraction afforded 419 mg (84%) of recovered acid, mp 79–81°. Esterification with diazomethane afforded 347 mg of ester, bp 90–100° (1.0 mm). Analysis by glpc as described above for the attempted base isomerization with potassium *t*-butoxide–water indicated only ester **15b**.

Acknowledgments.—The authors are indebted to Mr. Logan Stone for his skilled technical assistance and to Mr. Peter Bakuzis for his critical review of the manuscript.

Registry No.—**15a**, 13746-43-5; **15b**, 19766-10-0; **15c**, 19766-11-1; **15d**, 19766-12-2; **16b**, 19766-13-3; **17b**, 19766-14-4; **17d**, 19766-15-5; **18b**, 1862-61-9; **19b**, 1189-09-9; **21**, 19766-16-6; **22b**, 19766-17-7.

Syntheses, Spectra, and Identification of Isomeric, Fused-Ring Paracyclophane Derivatives

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We report the stereoselective syntheses and chemical structure proof of the *exo* (**1a**) and *endo* (**1b**) isomers of 17-hydroxymethyl-4,5-tetramethylene[2.2]paracyclophane. We have also examined the spectral properties of these and related isomeric, fused-ring paracyclophanes, and have discovered an interesting nmr correlation which is indicative of *exo* or *endo* substitution in these systems.

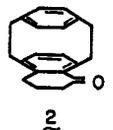
The acetolysis of 2-([2.2]paracyclophenyl)ethyl *p*-toluenesulfonate involves intermediate formation of a phenonium ion.[1] Because of the presence of two aromatic rings in paracyclophanes, several questions arise concerning the stereochemistry of this acetolysis reaction. To examine the stereochemical details of solvolysis reactions of [2.2]paracyclophane derivatives,[2] we have synthesized the *exo* (**1a**) and *endo* (**1b**) isomers of 17-hydroxymethyl-4,5-tetramethylene[2.2]paracyclophane. In this paper we discuss the details of the stereoselective syntheses. We also report an interesting nmr correlation that may be a general method for determining the *exo* or *endo* stereochemistry at the 17 position of 4,5-tetramethylene[2.2]paracyclophanes that have an oxygen atom in the substituent group.

1a, Y = CH_2OH, X = H

1b, Y = H, X = CH_2OH

Results

Synthetic.—The starting material for the syntheses of alcohols **1a** and **1b** is 4,5-tetramethylene-17-oxo-[2.2]paracyclophane (**2**).[3] We were not consistently

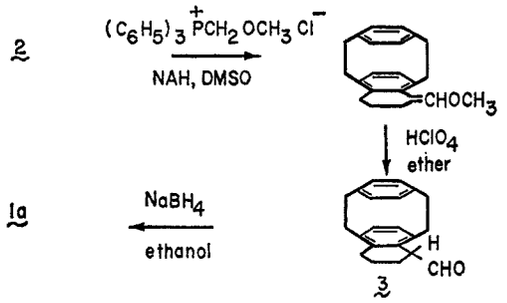


2

(1) D. J. Cram and L. A. Singer, *J. Amer. Chem. Soc.*, **85**, 1075 (1963).
(2) M. J. Nugent and T. L. Vigo, unpublished results.
(3) D. J. Cram, C. K. Dalton, and G. R. Knox, *J. Amer. Chem. Soc.*, **85**, 1088 (1963).

able to obtain satisfactory yields of 2; therefore the modified synthetic sequence described in the Experimental Section was used. The synthesis of **1a** in 60% yield from ketone 2 is shown in Scheme I. The α

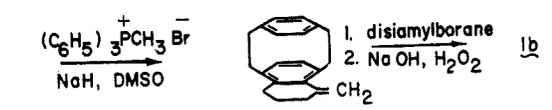
SCHEME I



carbon of **3** completely incorporates deuterium after 68 hr at room temperature in a mixture of sodium–deuterium oxide–tetrahydrofuran[4] as was evidenced by the collapse of the aldehyde proton doublet to a singlet. The starting aldehyde is recovered from sodium–water–tetrahydrofuran reaction mixture in 65% yield after the same period of time. Nearly quantitative reduction of this recovered aldehyde with sodium borohydride shows no contamination by the *endo* isomer **1b**.

The *endo* alcohol **1b** was synthesized *via* 2 using a Wittig reaction followed by hydroboration with disiamylborane[5] as is shown in Scheme II. Alcohol **1b** is

SCHEME II



isomeric with alcohol **1a** and has the same general structure as was determined spectroscopically. The conversion of ketone 2 into alcohol **1b** proceeds in 64% over-all yield.

Spectral.—We have examined the hydroxyl stretching frequency of the alcohols **1a** and **1b** and found at high dilution (0.003 *M*) in carbon tetrachloride that **1a** had its only hydroxyl absorption at 3640 cm^{-1}, while **1b** showed hydroxyl absorption at 3634 cm^{-1}.[6] These frequencies are in the region of free hydroxyl absorptions 3650–3590 cm^{-1},[7] and higher than the π-bonded absorption at 3601 cm^{-1} for 2-phenylethanol.[8]

We have also examined the nmr spectra of various 17-substituted 4,5-tetramethylene[2.2]paracyclophanes. An *exo* or *endo* oxygen-containing substituent at this position, causes two peaks which are more intense than any other peaks to appear between 6 and 7 ppm. As an example, this part of the nmr spectra of **1a** and **1b** are shown in Figure 1. The separation of

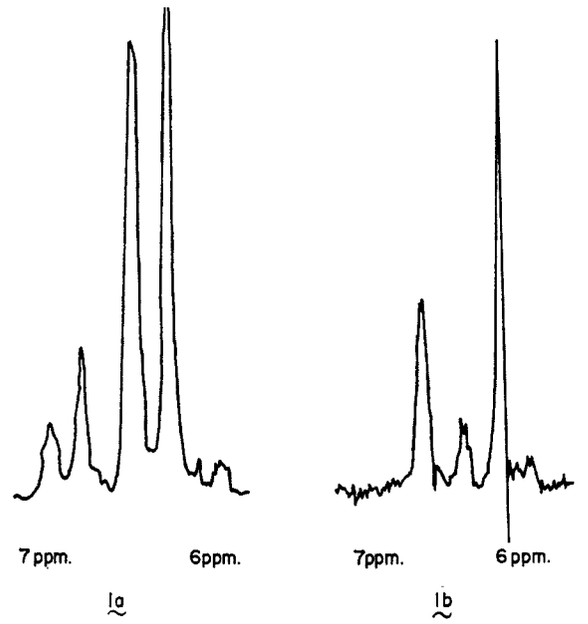


Figure 1.—Partial nmr spectra of **1a** and **1b** in deuteriochloroform.

these intense peaks is smaller for the *exo* isomer than for the *endo* isomer as is shown in Table I. In fused-

TABLE I

STEREOCHEMICAL CORRELATION OF ISOMERIC, FUSED-RING PARACYCLOPHANES WITH NMR SPECTRA

Stereochemistry	17 substituent	Integral of low field peak	Integral of high field peak	Separation, Hz
endo	OH (**5b**)[a]	1.7	1.0	13
endo	OAc[b]	1.4	1.0	17.5
endo	CH_2OH (**1b**)	0.8	1.0	22.5
endo	CH_2OTs[b]	0.9	1.0	19
exo	OH (**5a**)[a]	0.7	1.0	5
exo	CHO	1.5	1.0	4.5
exo	CH_2OH (**1a**)	1.0	1.0	10
exo	CH_2OTs[b]	1.2	1.0	10

[a] M. J. Nugent, *Chem. Commun.*, 1160 (1967). [b] M. J. Nugent and T. L. Vigo, unpublished results.

ring paracyclophane derivatives with no stereochemistry at the 17 position such as 2, the olefin precursor of **1b**, and the methylvinyl ether precursor of **1a**, only one very intense peak is observed in the region between 6 and 7 ppm, or several intense peaks are observed, no two of which can be described as the most intense in this portion of the spectrum.

Discussion

The *exo* stereochemistry of **1a** follows from its aldehyde precursor being the more stable, less hindered *exo* isomer.[9,10] We have demonstrated that the aldehyde obtained from the methylvinyl ether derivative of 2 is recovered in 65% yield under conditions where enolization is complete as was evidenced by complete deuterium exchange in deuterium oxide. Since side products are formed in this reaction, as was demonstrated by tlc, this result does not mean that the reaction mixture at

(4) This procedure is similar to that described by M. Rosenblum and F. W. Abbate, *J. Amer. Chem. Soc.*, **88**, 4178 (1966).

(5) G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 1 (1963), and references cited therein.

(6) These measurements were made on a Beckman IR-7 in silica cells of 10-mm path length (Pyrocell Manufacturing Co. No. S-22-350) which transmit 90% of the light in this region. We are indebted to the chemistry faculty at Louisiana State University of New Orleans for the use of this instrument.

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley & Sons, Inc., New York, N. Y., 1964, p 96.

(8) D. S. Trifan, J. C. Weinmann, and L. P. Kuhn, *J. Amer. Chem. Soc.*, **79**, 6566 (1957).

(9) That the *endo*-17-substituted isomer is more sterically hindered has been demonstrated in the case of the *exo*- and *endo*-17-hydroxy-4,5-tetramethylene[2.2]paracyclophanes, **5a** and **5b**, respectively.[10]

(10) Reference *a*, Table I.

equilibrium consists of 65% *exo* aldehyde and 35% *endo* aldehyde. All of our attempts to prepare the *endo* aldehyde or carboxylic acid have been unsuccessful.

The assignment of *endo* stereochemistry to alcohol **1b** is based primarily on the synthetic method. Disiamylborane usually adds to cyclic olefins from the least hindered side.[5] Thus, since the alcohols **1a** and **1b** are isomeric, one is led to the assignment of *endo* stereochemistry to alcohol **1b**.

The ir absorptions of the hydroxyl groups of dilute samples of **1a** and **1b** occur for both isomers in the 3634–3640-cm^{-1} region. In the next lower homologs, *exo*-(**5a**) and *endo*-17-hydroxy-4,5-tetramethyleneparacyclophane (**5b**), hydroxyl absorption occurs at 3617–3618 cm^{-1}.[10] In neither case is there any evidence that the electron cloud above the planes of the aromatic rings in paracyclophane has more affinity for π bonding to hydroxyl hydrogens than the π cloud between the aromatic rings in these fused-ring paracyclophane derivatives.

The data in Table I show that the separation between the most intense peaks in the 6–7-ppm region of the nmr spectra of fused-ring paracyclophane derivatives varies with stereochemistry at the 17 position in a predictable way. We have examined the separation of these intense peaks for the *endo*-substituted derivatives and found that the separation varies from 13 to 22.5 Hz, while for *exo*-substituted derivatives the separation varies from 5 to 10 Hz. The applicability of this correlation in the same way to alcohols **5a** and **5b** as well as to alcohols **1a** and **1b** lends credence to the stereochemical assignments.

Experimental Section

δ-[2.2]Paracyclophanylbutyric Acid Methyl Ester.—β-[2.2]-Paracyclophanoylpropionic acid[3] (18.8 g, 61 mmol) and 9.4 ml (0.18 mol) of 100% hydrazine hydrate were dissolved in 450 ml of diethylene glycol which contained 18.7 g of potassium hydroxide. The conditions of this reaction were essentially those used for reduction of 4,5-tetramethylene-?-(γ-carboxylpropyl)-[2.2]-paracyclophane.[3] The reaction mixture was poured into 3 l. of water, and the aqueous phase was washed three times with ether. The aqueous phase was acidified with concentrated sulfuric acid and the resulting dark gum was dissolved in chloroform. The chloroform solution was washed with water until the washings were neutral, separated, dried over sodium sulfate, and evaporated to dryness. The dark gum thus obtained was dissolved in a mixture of 260 ml of methanol and 3.5 ml of concentrated sulfuric acid and was refluxed for 1 hr. The reaction mixture was then poured into 1 l. of water and extracted four times with ether. The combined ethereal extracts were washed with water, dried over sodium sulfate, and evaporated. The resulting brown oil was chromatographed on silica gel; the ester was eluted with 1:9 ether–petroleum ether (bp 35–80°) (5.5 g, 30% yield); two recrystallizations from ether produced an analytical sample, mp 89.5–91.5°.

Anal. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84. Found: C, 81.63; H, 7.87.

4,5-Tetramethylene-17-oxo[2.2]paracyclophane (**2**).—Equal weights of δ-[2.2]paracyclophanylbutyric acid methyl ester and sodium hydroxide were refluxed for 5 min in 1:1 ethanol–water. Acidification of the cooled (0°) solution with concentrated hydrochloric acid produced δ-[2.2]paracyclophanylbutyric acid in 96% yield, mp 121–124° (lit.[3] mp 123–124°). The dry acid (4.60 g, 15.6 mmol) was dissolved in 42.4 ml of trifluoroacetic anhydride and stirred at room temperature for 2 hr. The reaction mixture was then poured into an ice slush containing excess sodium bicarbonate. Water was added and the mixture was extracted four times with ether. The ethereal extracts were washed with water until neutral, separated, and dried over sodium sulfate. Evaporation of the ether produced an orange oil which was chromatographed on grade III neutral alumina to yield 2.90 g (67%) of the desired crude ketone, mp 108–113° (lit.[3] mp 107–108°). Recrystallization from ether produced material melting from 111 to 113°.

***exo*-17-Formyl-4,5-tetramethylene[2.2]paracyclophane** (**3**).—The Wittig reagent from (methoxymethyl)triphenylphosphonium chloride (3.43 g, 10.0 mmol) was prepared using the method of Corey, *et al.*[11] Ketone **2** (1.38 g, 5.0 mmol) in 15 ml of warm dimethyl sulfoxide was added at room temperature and the reaction mixture was heated at 65° for 21 hr with stirring. The reaction was quenched by careful addition of water, then extracted with five portions of ether. The combined ethereal extracts were washed seven times with water, dried over sodium sulfate, and evaporated to yield a yellow semisolid. This mixture was dissolved in a small amount of benzene and chromatographed on silica gel. The crude vinyl ether (0.90 g, 62%) was eluted with 1:9 ether–petroleum ether. The melting point of this material was 83–86°. Recrystallization from petroleum ether gave product melting at 90–93°. The methylvinyl ether (1.12 g, 3.8 mmol) was dissolved in 30 ml of ether and the solution was heated on a steam bath. Approximately 10 ml of ether saturated with 72% perchloric acid was added in portions over a 30-min period. The reaction mixture was then cooled and washed with water until neutral. Evaporation of the ether produced the *exo* aldehyde **3** (1.02 g, 97%), mp 130–131°. An analytical sample, mp 132–134°, was obtained after three recrystallizations from ether–petroleum ether.

Anal. Calcd for $C_{21}H_{22}O$: C, 86.85; H, 7.64. Found: C, 86.69; H, 7.60.

***exo*-17-Hydroxymethyl-4,5-tetramethylene[2.2]paracyclophane** (**1a**).—Sodium borohydride (0.21 g, 5.6 mmol) was added to a solution of pure aldehyde **3** (0.78 g, 2.8 mmol) in 14 ml of 95% ethanol. After 2.5 hr, water was added and the reaction mixture was extracted three times with ether. The ethereal extracts were washed with water and dried over sodium sulfate. Evaporation of the solvent produced a pale yellow oil when mixed with ether–petroleum ether to give a quantitative yield of product of mp 118–121°. An analytical sample, mp 122–123.5°, was obtained by recrystallization from ether–petroleum ether.

Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 86.01; H, 8.23.

17-Methylene-4,5-tetramethylene[2.2]paracyclophane was prepared by the Wittig reaction of triphenylmethylphosphonium bromide (4.28 g, 12 mmol) with ketone **2** (2.2 g, 8 mmol) at room temperature; the experimental conditions were essentially the same as those in the Wittig reaction described above. The olefin product was isolated in 86% yield (1.75 g, mp 94–98°). Recrystallization from 1:1 methanol–ether gave an analytical sample, mp 99–101°.

Anal. Calcd for $C_{21}H_{22}$: C, 91.92; H, 8.08. Found: C, 92.16; H, 7.86.

***endo*-17-Hydroxymethyl-4,5-tetramethylene[2.2]paracyclophane** (**1b**) was prepared by hydroboration of 17-methylene-4,5-tetramethylene[2.2]paracyclophane with disiamylborane, followed by alkaline oxidation with hydrogen peroxide.[5] The disiamylborane was generated by reaction of 3.3 ml (30 mmol) of 2-methyl-2-butene with 0.45 g (12 mmol) of sodium borohydride in 12 ml of diglyme and 2.08 ml (2.24 g, 16 mmol) of boron trifluoride etherate. The disiamylborane thus produced was allowed to react with 1.4 g (5 mmol) of olefin in 12 ml of diglyme at room temperature for 23 hr. The work-up was carried out according to the published procedure,[5] and the resulting oil was chromatographed on silica gel. A solution of 1:3 ether–hexane eluted the desired alcohol (1.1 g) in 75% yield. Recrystallization from ether gave an analytically pure sample, mp 121.5–123.5°. A mixture of this pure alcohol **1b** with its epimer **1a** gave a 20° depression of melting point.

Anal. Calcd for $C_{21}H_{24}O$: C, 86.25; H, 8.27. Found: C, 85.95; H, 8.18.

Isomerization Experiments with *exo*-17-Formyl-4,5-tetramethylene[2.2]paracyclophane (**3**).—To a solution of tetrahydrofuran which had been redistilled from lithium aluminum hydride and 1 ml of redistilled deuterium oxide was added 3 mg of sodium. After the reaction subsided, 87 mg of aldehyde **3** in 4 ml of redistilled tetrahydrofuran was added and the reaction was allowed to proceed at room temperature for 68 hr. After this period, solvent was removed by vacuum distillation at room temperature; the nmr spectrum of the crude reaction mixture in deuterio-

(11) R. Greenwald, M. Chaykovsky, and E. J. Corey, *J. Org. Chem.*, **28**, 2063 (1963).

chloroform showed a broadened singlet at 9.50 ppm for the aldehyde proton. When this reaction was carried out under identical conditions using water in place of deuterium oxide, the crude reaction mixture showed a doublet for the aldehyde proton with J = 1.5 Hz. Under these conditions the starting aldehyde was recovered after column chromatography in 65% yield.

Registry No.—**1a**, 19916-80-4; **1a** (*p*-toluenesulfonate), 19955-02-3; **1b**, 19916-81-5; **1b** (*p*-toluenesulfonate), 19916-82-6; **3**, 19916-83-7; **5b** (acetate), 19933-74-5; 17-methylene-4,5-tetramethylene[2.2]paracyclophane, 19933-75-6; δ-[2.2]paracyclophanylbutyric acid methyl ester, 19933-76-7.

Acknowledgment.—The authors are indebted to Mr. Paul Kronlage who helped to prepare some of the starting materials. This research was supported by a National Science Foundation Grant to Tulane University. The Varian A-60 instrument used in this work was purchased with National Science Foundation funds. [2.2]Paracyclophane was generously supplied by Union Carbide Corp.

Selective Reductions. XIII. The Reaction of Δ^2-Cyclopentenones with Representative Complex Hydrides. Aluminum Hydride as a Selective Reagent for the Reduction of the Carbonyl Group in Δ^2-Cyclopentenones

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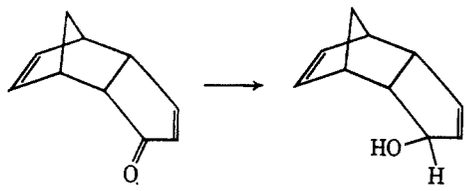
Received December 17, 1968

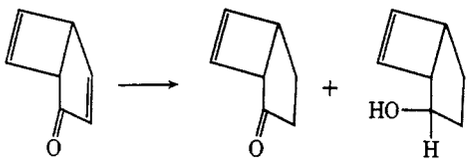
The reduction of 2-cyclopenten-1-one and 5,6-dihydro-*endo*-dicyclopentadien-1-one with metal hydrides takes place with considerable concomitant saturation of the double bond. However, the inverse addition of 0.667 mole equiv of aluminum hydride to 2-cyclopenten-1-one, 3-substituted 2-cyclopenten-1-ones, 5,6-dihydro-*endo*-dicyclopentadien-1-one, and 3-substituted 5,6-dihydro-*endo*-dicyclopentadien-1-ones, produces the unsaturated carbinols in satisfactory purity and yield and thus provides an effective route for the selective reduction of the carbonyl group in Δ^2-cyclopentenones.

The reduction of α,β-unsaturated ketones to the corresponding unsaturated carbinols with metal hydrides has often been reported to occur with varying amounts of concomitant saturation of the double bond, thereby affording saturated ketone and alcohol.[2,3] This mode of behavior is especially enhanced in Δ^2-cyclopentenones. Thus, while Woodward and Katz[4] reported that the reduction of *endo*-dicyclopentadien-1-one (I) with



I II

lithium aluminum hydride afforded the unsaturated alcohol II, Allara[5] and Dilling[6] have been unable to reproduce these results, obtaining substantial amounts of saturated products even at considerably reduced temperatures. Allara[5] has also reported that the reduction of 5,6-dihydro-*endo*-dicyclopentadien-1-one (VII) with lithium aluminum hydride and sodium borohydride produced substantial reduction of the double bond. Cookson[7] has reported that the reduction of *exo*-dicyclopentadien-1-one with lithium aluminum hydride yielded only the saturated alcohol. Story and Fahrenholtz[8] have demonstrated that *cis*-bicyclo[3.2.0]hepta-3,6-dien-2-one (III), when reduced with



III IV V

lithium tri-*t*-butoxyaluminohydride, gave, as the major product, *cis*-bicyclo[3.2.0]-6-hepten-2-one (IV) along with a small amount of the saturated alcohol V.[9-12] Paquette[13] has reported that the reduction of *cis*-bicyclo[3.2.0]hept-3-en-2-one with lithium aluminum hydride, even at −78°, afforded a complex mixture of products accompanying the desired unsaturated alcohol.

In view of these difficulties, and because a number of Δ^2-cyclopentenols were required for other work, a systematic study of the effect of metal hydrides on 2-cyclopenten-1-one (VI) and 5,6-dihydro-*endo*-dicyclopentadien-1-one (VII) was undertaken.

(1) Research assistant on grants (G 19878 and GP 6492 X) provided by the National Science Foundation.

(2) (a) N. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, pp 180–183; (b) V. M. Micovic and M. L. Mihailovic, "Lithium Aluminum Hydride in Organic Chemistry," Naukna Knjiga, Belgrade, Yugoslavia, 1955.

(3) P. L. Southwick, N. Latif, B. M. Fitzgerald, and N. M. Zaczek, *J. Org. Chem.*, **31**, 1 (1966), and references cited therein.

(4) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(5) D. L. Allara, Ph.D. Thesis, University of California, Los Angeles, 1964.

(6) W. L. Dilling, Britton Laboratory, Dow Chemical Co., private communication.

(7) R. S. Cookson, N. S. Isaacs, and M. Szelke, *Tetrahedron*, **20**, 717 (1964).

(8) P. R. Story and S. R. Fahrenholtz, *J. Amer. Chem. Soc.*, **87**, 1623 (1965).

(9) Lithium tri-*t*-butoxyaluminohydride, in contrast to lithium aluminum hydride and lithium trimethoxyaluminohydride, has previously been reported[10-12] to reduce cinnamaldehyde without attacking the double bond.

(10) F. A. Hochstein and W. G. Brown, *J. Amer. Chem. Soc.*, **70**, 3483 (1948).

(11) H. C. Brown and P. M. Weissman, *ibid.*, **87**, 5614 (1965).

(12) H. C. Brown and P. M. Weissman, *Israel J. Chem.*, **1**, 430 (1963).

(13) L. A. Paquette and O. Cox, *J. Amer. Chem. Soc.*, **89**, 5633 (1967).