Condensation of cinnamaldehyde with β-methylglutaconate. The directions given previously[4] gave yellow crystals, m.p. 205° dec. (on a heated metal surface). Several recrystallizations from aqueous methanol gave yellow needles, m.p. 207° dec. (capillary); m.p. 228° dec. (metal surface) of 4-carboxy-3-methyl-7-phenyl-2,4,6-heptatrienoic acid (III. R = H).

Anal. Calcd. for $C_{15}H_{14}O_4$: Neut. equiv. 258.3. Found: Neut. equiv. 261.

The di(*n*-butylamine) salt was prepared as described previously[5] as white crystals, m.p. 139–141° (cap.), 148° dec. (metal). The dimethyl ester (III, R = CH_3) was prepared as above from diazomethane, m.p. 95.5–96°, from cyclohexane.

Anal. Calcd. for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.46; H, 6.31.

Decarboxylation. The dicarboxylic acid refluxed in lutidine with copper acetate[3] evolved the theoretical amount of carbon dioxide. The product was isolated and recrystallized from benzene-cyclohexane to give a 41% yield of the acid, m.p. 191–193°; mixed melting point with acid from the Reformatsky reaction, 192–194°. Same infrared absorption characteristics.

Methyl 4-carbomethoxy-3-methyl-5-phenyl-2-cis-4-cis-pentadienoate (IV. R = CH_3). The crude acid obtained from benzaldehyde and β-methylglutaconic ester prepared as described previously[6] was esterified with diazomethane in ether solution and fractionated to give the product, b.p. 125°/0.3 mm.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.10, H, 6.11.

The ultraviolet absorption measurements were made with a Beckman DK-3 recording spectrometer in the solvents (spectrograde) stated. The infrared absorption measurements were made with a Baird double beam recording spectrometer with sodium chloride optics and in chloroform (0.04 g./ml.) or as potassium bromide pellets. The NMR measurements were made with a Varian High Resolution (Model HR-4302) spectrometer with 60 megacycle oscillator with superstabilizer and field homogeneity control. The calibrations were made by the side band technique at several frequencies. Tetramethylsilane was used as an internal reference standard. Data for the acids were obtained in pyridine solutions, data for the esters in the carbon tetrachloride at about 15% concentration. Values are given in τ units.[13] Microanalyses by Micro Tech Laboratories, Skokie, Ill.

Acknowledgment. The authors gratefully acknowledge partial support of this research under Grant NSF G-11108 from the National Science Foundation. One of us (T. H. Crawford) is grateful for a National Science Foundation Cooperative Graduate Fellowship (1959–1961) and another (P. F. G. Nau) is grateful for a Fulbright Travel Grant in support of a postdoctoral appointment. The authors also acknowledge grants from the Atomic Energy Commission AT-(40-1)-229 and AT-(40-1)-2055; National Institutes of Health H-4952; from the Lilly Co.; and from the Mead Johnson and Co. which made possible purchase of the NMR spectrometer used in this study.

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[13] G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, DUKE UNIVERSITY]

Synthesis of Some 2,2-Disubstituted Dihydrodicyclopentadienes

CHICITA F. CULBERSON AND PELHAM WILDER, JR.

Received May 1, 1961

Alkylation and cyclization of the ditosylate of *endo-cis*-2,3-bis(hydroxymethyl)norbornene with sodio diethyl malonate or sodio phenylacetonitrile yields 2,2-disubstituted 1,2-dihydro-*endo*-dicyclopentadienes. Attempted reactions with several other anions failed. Sodio diethyl malonate and the ditosylate of *exo-cis*-2,3-bis(hydroxymethyl)norbornene yield diethyl 1,2-dihydro-*exo*-dicyclopentadiene-2,2-dicarboxylate. These dihydrodicyclopentadienes represent the first of established ring geometry substituted exclusively in the 2-position. Other derivatives and a synthesis of the new hydrocarbons 2,2-dimethyl-1,2-dihydro-*endo*-dicyclopentadiene and 2,2-dimethyl-1,2-dihydro-*exo*-dicyclopentadiene are described.

In 1956, Cope and Anderson[1] described a new synthetic method leading to bicyclic products, illustrated by the preparation of 3,6-epoxycycloheptane derivatives (II) upon condensation of *cis*-2,5-bis(hydroxymethyl)tetrahydrofuran ditosylate (I) with either sodio diethyl malonate or sodio ethyl cyanoacetate. Later, Cope and Fournier[2] obtained substituted epoxycyclooctane derivatives IV by treating ditosylate III with sodio diethyl malonate. We have now used this condensation-cyclization to synthesize 2,2- disubstituted dihydrodicyclopentadienes from the known ditosylates of *endo-cis-* and *exo-cis*-bicyclo[2.2.1]-5-heptene-2,3-dimethylol (V and XIV). Preparative routes leading to 2-substituted dicyclopentadienes are of especial interest at the present time since recent studies have emphasized the proximity of the 9,10-double bond and the 2-position in *endo*-dicyclopentadiene type molecules, and the effects of this geometry on reactions of related compounds.[3,4]

Diethyl malonate reacted with both *endo-cis-* and *exo-cis*-ditosylates V and XIV, yielding 59% and 83% respectively of 2,2-diethyl esters, VIII and XV. Sodio phenylacetonitrile and *endo-cis*-ditosylate V yielded 89% of an isomeric mixture of

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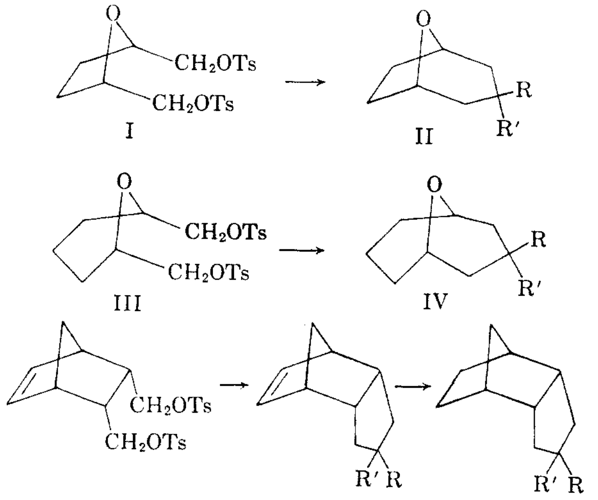
[1] A. C. Cope and B. C. Anderson, *J. Am. Chem. Soc.*, 78, 149 (1956).

[2] A. C. Cope and A. Fournier, Jr., *J. Am. Chem. Soc.*, 79, 3896 (1957).

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

[4] P. Wilder, Jr., and Chicita F. Culberson, *J. Am. Chem. Soc.*, 81, 2027 (1959); Chicita F. Culberson and P. Wilder, Jr., *J. Am. Chem. Soc.*, 82, 4939 (1960).

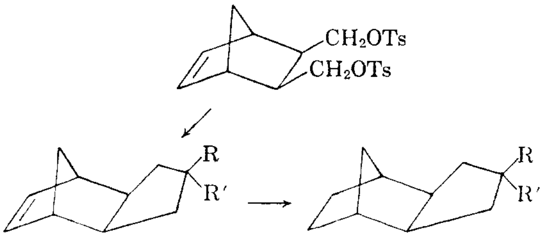


I → II

III → IV

V → VI-X → XI-XIII

VIa. R = C_6H_5, R′ = CN
b. R = CN, R′ = C_6H_5
VIIa. R = C_6H_5, R′ = COOH
b. R = COOH, R′ = C_6H_5
VIII. R = R′ = $COOC_2H_5$
IXa. R = COOH, R′ = COOK
b. R = COOK, R′ = COOH
X. R = R′ = COOH
XIa. R = C_6H_5, R′ = CN
b. R = CN, R′ = C_6H_5
XII. R = R′ = $COOC_2H_5$
XIII. R = R′ = COOH



XIV

XV. R = R′ = $COOC_2H_5$
XVI. R = R′ = COOH
XVII. R = R′ = $COOC_2H_5$
XVIII. R = R′ = COOH

the 2-phenyl-2-cyano derivative VI. Attempted condensations of *endo-cis*-ditosylate V with ethyl acetate, ethyl phenylacetate, *t*-butyl acetate, and diphenylmethane failed. It might be concluded that this condensation-cyclization reaction is sensitive to changes in the condensing anion but that the reaction may prove useful with a variety of *cis*-ditosylates.

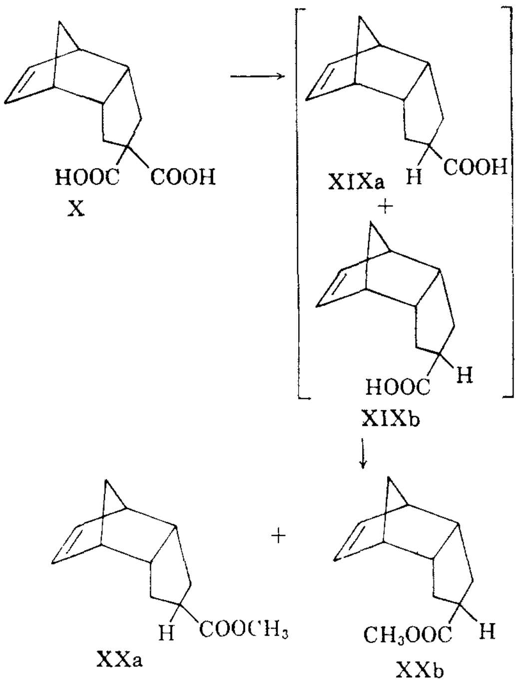
The procedure used by Cope and Anderson required rocking the reaction mixture for eighteen to twenty-one hours in a stainless steel bomb at 110–120°. Investigations of other reaction conditions showed that cyclized product could be isolated after refluxing the reactants in dry toluene for three to five days. Perhaps this inconveniently long reaction time could be shortened by using a higher boiling solvent, but possible thermal instabilities of the compounds involved in this study made it undesirable to increase the reaction temperature. It is quite possible that the bis(hydroxymethyl)-norbornene ditosylates, especially the less hindered *exo-cis* isomer, undergo the condensation-cyclization more readily than the systems previously reported because in the norbornene derivatives the tosylate groups are constrained in almost perfect geometry for cyclization. In no case was it possible to isolate di- or monoalkylated product, indicating that the ring closure step proceeds with ease; the initial alkylation reaction is perhaps the rate-limiting step. While sodium hydride was used to prepare the carbanion in the condensations previously reported, this reagent could not be used in the present study. The higher boiling cyclized products obtained from the ditosylates V and XIV were invariably contaminated with mineral oil in which the sodium hydride reagent was suspended. Purification was almost impossible and was accompanied by considerable loss of product. To avoid this difficulty the condensing anions were prepared with sodium amide, every care being taken to remove excess ammonia before the addition of ditosylate.

Reaction of *endo-cis*-ditosylate V with phenylacetonitrile appears to yield a mixture of isomers, probably VIa and VIb. These products were not separated by distillation, but upon catalytic reduction the mixture absorbed the calculated volume of hydrogen. A small sample, hydrolyzed with base, yielded an acid which could be purified to a single isomer (VIIa or VIIb) by careful recrystallization, but the arrangement of the phenyl and carboxylic acid groups was not determined. The excellent yield obtained by condensation of phenylacetonitrile suggests that other activated nitriles may also give cyclized products.

Condensations with diethyl malonate do not give over-all yields as high as those obtained with phenylacetonitrile, but the former reaction has the distinct advantage of providing a single product. The *endo*-ring ester VIII is a viscous liquid which can be hydrolyzed to a diacid X, slightly soluble in water and soluble in ether. This hydrolysis proceeds relatively slowly in aqueous potassium hydroxide. Careful neutralization of the basic solution yields a monopotassium salt IX which is slightly soluble in both water and ether. No decarboxylation was observed during neutralization following hydrolysis. Ester VIII yielded a phenyl azide adduct very slowly. The nitroso chloride which forms readily, appeared to be a mixture of two forms but this was not further investigated. In the presence of Adams catalyst, ester VIII absorbed hydrogen rapidly and the saturated ester XII was readily hydrolyzed to dibasic acid XIII.

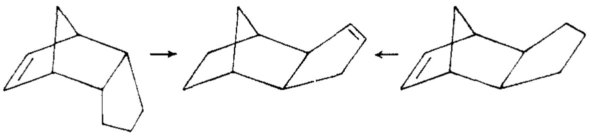
Because the *exo-cis*-ditosylate XIV is difficult to obtain in quantity, only one cyclization reaction leading to 2-substituted dihydro-*exo*-dicyclopentadienes was attempted. Condensation of ditosylate XIV with diethyl malonate proceeds smoothly yielding ester XV which can be hydrolyzed to the diacid XVI, or reduced catalytically and then hydrolyzed to the saturated diacid XVIII. No attempt was made to isolate a monopotassium salt analogous to that obtained in the *endo* case.

As a possible route to mono-substituted dihydrodicyclopentadienes, decarboxylation of 1,2-dihydro-*endo*-dicyclopentadiene-2,2-dicarboxylic acid (X) was investigated briefly.

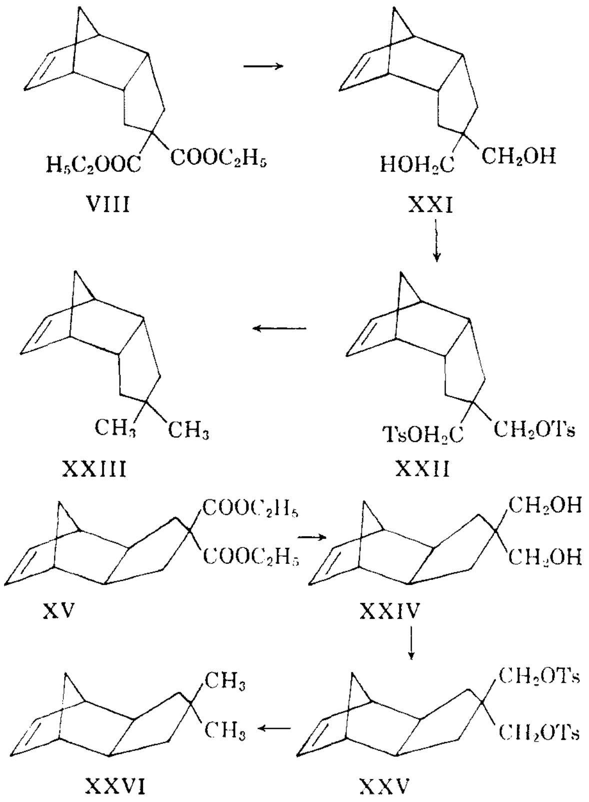


In diphenyl ether, acid X loses carbon dioxide at temperatures over 150°. A pure monobasic acid, separated from the crude waxy product by recrystallization, gave the correct elemental analysis for a dihydrodicyclopentadiene carboxylic acid, but rigorous proof of the structure of this compound was not undertaken. It seemed likely that the decarboxylation would yield the two isomers XIXa and XIXb, although the possibility of thermally rearranged products could not be excluded. To determine the number of compounds resulting from decarboxylation a sample of crude monoacid was methylated with diazomethane and analyzed by gas chromatography. Only two components were detected, the compound of longer retention time accounting for approximately 65% of the mixture. When a sample of the mixed ester was equilibrated in sodium methoxide–methanol for four hours, the same peaks were observed in the chromatograph, but the relative heights of the peaks had changed indicating almost equal amounts of the two components. Thus it appears that methanolic sodium methoxide may convert one isomer to the other but does not isomerize either isomer to yet a third ester. This evidence suggests that the products are epimeric, as indicated in structures XXa and XXb, and are *not* thermally rearranged ring isomers.

It was of particular interest at this point to prepare the 2,2-dimethyl-1,2-dihydrodicyclopentadienes XXIII and XXVI, since reaction of these hydrocarbons with phosphoric acid might give some information concerning the route by which either *endo*- or *exo*-1,2-dihydrodicyclopentadiene is converted to 9,10-dihydro-*exo*-dicyclopentadiene.[5,6]



While this unusual rearrangement has been known for some time, the mechanism is not understood. The most probable pathways involve hydride ion shifts. If the 2,2-dimethyl compounds XXIII and XXVI undergo the same type of transformation when treated with phosphoric acid, the positions of the methyl groups in the product would be of great interest. Although only small samples of these hydrocarbons were available, a preliminary study of the reaction with phosphoric acid was undertaken using gas chromatographic and infrared analyses.



Lithium aluminum hydride reduction of esters VIII and XV proceeds smoothly to the corresponding 2,2-bis(hydroxymethyl)-dihydrodicyclopentadienes XXI and XXIV. With pyridine and toluenesulfonyl chloride, each diol yields the corresponding

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(5) P. R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **78,** 5702 (1956).

(6) P. Wilder, Jr., and G. T. Youngblood, *J. Am. Chem. Soc.*, **78,** 5706 (1956).

ditosylate XXII and XXV, and these solid products are readily reduced with lithium aluminum hydride to the respective *endo*- and *exo*-dimethyldicyclopentadienes, XXIII and XXVI. Each olefin yielded a phenyl azide adduct and a nitro chloride dimer.

The olefins were distilled from 85% phosphoric acid under slightly reduced pressure, and a portion of each crude product was reduced catalytically for two hours at atmospheric pressure. Judging from gas chromatographic retention times of the unsaturated and saturated products, each mixture contained starting olefin, rearranged olefin, and two unknown compounds. The retention times of the products were the same *whether the starting olefin had the endo or the exo ring fusion.* The major component from the *exo* olefin, obtained in about 85% purity by distillation of the small sample available, gave a carbon-hydrogen analysis consistent with the empirical formula $C_{12}H_{18}$, isomeric with starting material. Infrared analysis of the starting materials and of the partially purified product from the reaction of the *exo*-olefin XXVI with phosphoric acid provided excellent evidence for a methyl shift and a change in the nature of the unsaturated linkage. While both starting olefins possess a band at 6.37 μ generally assigned to the norbornylene double bond, the product revealed only a very weak band in this region at 5.97 μ. Furthermore, absorptions attributed to vinyl hydrogens in the starting olefins are absent in this product. These results suggest a highly substituted, unstrained olefinic linkage. The *gem*-dimethyl present in the starting materials, giving rise to double peaks (7.23 μ and 7.33 μ) in the infrared spectrum, appears to have been replaced by simple C-methyl substituents characterized by a single absorption at 7.26 μ. This preliminary evidence indicates that the major single product of the distillation from phosphoric acid results from a methyl shift and double bond migration. Whether the reaction is related to the previously observed rearrangements of the dihydrodicyclopentadienes awaits further study.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and Dr. Ing. A. Schoeller Microanalytisches Laboratorium, West Germany.

endo-cis-Bicyclo[2.2.1]-5-heptene-2,3-dimethylol ditosylate (V). The ditosylate was prepared exactly as previously described[7], but the product used in these studies appeared to be a higher melting crystal modification. Once the high-melting form had been purified in our laboratory, the low-melting form was never obtained again. The ditosylate recrystallized from methanol, m.p. 104.5-105° (reported m.p. 90-91°,[8] 90-90.5°),[7] a mixed fusion melted over a range between the two pure forms.

Anal. Calcd. for $C_{23}H_{26}O_6S_2$: C, 59.71; H, 5.67. Found: C, 59.96; H, 5.59.

2-Phenyl-2-cyano-1,2-dihydro-endo-dicyclopentadiene (VI). A solution of 44.5 g. (0.38 mole) of phenylacetonitrile in 100 ml. of dry toluene was added to a stirred suspension of sodium amide (0.37 mole) in about 500 ml. of liquid ammonia. When addition was complete, the ammonia was evaporated on a steam bath while adding simultaneously 1200 ml. of dry toluene. The toluene solution was heated to reflux to help expel residual ammonia and finally 69.6 g. (0.15 mole) of solid *endo-cis*-ditosylate was introduced through a Gooch tube. The reaction was stirred under reflux for 5 days. Cooling and filtering the reaction mixture separated 67.2 g. of crude sodium toluenesulfonate. Concentration of the filtrate yielded a residue which when diluted to about 300 ml. with ether did not precipitate ditosylate starting material after 3 hr. at room temperature. The ether solution, washed with 10% hydrochloric acid, water, 10% sodium carbonate, and again with water was dried over magnesium sulfate and filtered through a funnel of alumina. Removal of the ether and distillation of the residue yielded 21.5 g. of low-boiling forerun, primarily phenylacetonitrile; 34.0 g. of product, collected rapidly with superheating, b.p. 100-155°/0.25 mm.; and a tarry pot residue of 3.0 g. which was not investigated. The high boiling product was redistilled yielding 31.3 g. (89%) of a viscous liquid probably a mixture of the two possible 2-phenyl-2-cyano *endo*-ring derivatives VIa and VIb, b.p. 136-137°/0.25 mm. An attempt to separate two isomers or to purify one isomer by distillation was unsuccessful. A sample of the mixture was redistilled for analysis, b.p. 126-128°/0.075 mm. $n_D^{26.5}$ 1.5605.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.76; H, 7.28. Found: C, 86.89; H, 7.55.

A small sample of the product (2.1 g., 0.009 mole) absorbed the calculated volume of hydrogen when reduced in 50 ml. of absolute ethanol in the presence of Adams' catalyst at ambient temperature and pressure. The product was distilled, yielding 1.90 g. (90%) of the saturated nitrile XI. An analytical sample was prepared by redistillation, b.p. 147°/0.4 mm., n_D^{27} 1.5557.

Anal. Calcd. for $C_{17}H_{19}N$: C, 86.03; H, 8.07. Found: C, 86.33; H, 8.19.

Basic hydrolysis of a small sample of the unsaturated nitrile yielded the acid VII which recrystallized from dilute ethanol, m.p. 164-165°.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.18; H, 7.13.

Diethyl 1,2-dihydro-endo-dicyclopentadiene-2,2-dicarboxylate (VIII). To sodium amide (0.37 mole) in approximately 800 ml. of liquid ammonia was added a solution of 61 g. (0.38 mole) of diethyl malonate in 150 ml. of dry toluene and then ammonia was replaced by toluene (1050 ml.). The solution was refluxed rapidly under slightly reduced pressure to remove most of the ammonia which was not readily expelled by heat alone. Then 69.6 g. (0.15 mole) of solid *endo-cis*-ditosylate V was added through a Gooch addition tube and the reaction mixture was stirred and refluxed vigorously for 4 days. During this time a voluminous precipitate of sodium toluenesulfonate accumulated. This solid was removed by filtering the cooled reaction mixture. After air drying, the precipitate collected weighed 53.5 g. Toluene was distilled from the filtrate under diminished pressure, and the viscous residue, diluted to 110 ml. with ether, precipitated 19.1 g., (27%) of unchanged ditosylate after standing overnight at room temperature. The filtrate was diluted to about 1,000 ml. with ether and washed successively with dilute hydrochloric acid, water, 10% sodium carbonate, and again with water. The solution was dried over magnesium sulfate and then passed through a funnel of absorption alumina. Evaporation of this filtrate yielded a yellowish residue which distilled under reduced pressure. Some diethyl malonate (9.63 g.), b.p. 43-46°/0.35 mm. was recovered and then the temperature rose slowly as 0.30 g. of liquid, b.p. 46-104°/0.35 mm., distilled. The distillation was then continued

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(7) Chicita F. Culberson, J. H. Seward, and P. Wilder, Jr., *J. Am. Chem. Soc.*, 82, 2541 (1960).

(8) K. Alder and W. Roth, *Ber.*, 87, 161 (1954).

rapidly and stopped as soon as the residue in the pot began to darken. The yield of crude product collected was 20.31 g., b.p. 104-135°/0.35 mm. The pot residue (9.38 g.) was taken up in ether and 4.72 g. of ditosylate precipitated. The ether solution, washed with dilute hydrochloric acid, water, 10% sodium bicarbonate, and again with water, was dried over magnesium sulfate and passed through a funnel of absorption alumina. From this solution 1.9 g. of ditosylate precipitated when some of the ether was evaporated. The total ditosylate recovered was 25.7 g. (0.056 mole, 37%). The ester VIII product was redistilled, b.p. 108–110°/0.30 mm. yielding 19.5 g. (0.0882 mole, 59% over-all yield, 93% yield based on ditosylate consumed). A small sample was redistilled before analysis, b.p. 102.5°/0.03 mm., n_D^{25} 1.4766.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.23; H, 7.77.

A solution of 1.39 g. (0.005 mole) of ester VIII, 0.63 g. of isoamyl nitrite in 0.5 ml. of glacial acetic acid, and 1.0 ml. of 95% ethanol was cooled in an ice bath, and 0.5 ml. of concd. hydrochloric acid in 0.5 ml. of 95% ethanol was added slowly while the reaction mixture was stirred vigorously. The product which precipitated on standing was collected by filtration and recrystallized from ethanol-water. Two crystal forms were observed and were separated from each other manually and each was recrystallized from absolute ethanol; m.p. 173.5–175° dec. (needles), m.p. 158–160° dec. (plates), mixed m.p. 160–165° dec.

Anal. Calcd. for $(C_{16}H_{22}ClNO_5)_2$: C, 55.89; H, 6.45. Found: C, 55.98; H, 6.37 (needles). C, 55.77; H, 6.36 (plates).

Seven tenths of a gram (0.0025 mole) of the ester VIII treated with excess phenyl azide in ether yielded an adduct after 3 days at room temperature. The product recrystallized from absolute ethanol, m.p. 140-141°.

Anal. Calcd. for $C_{22}H_{27}N_3O_4$: C, 66.48; H, 6.85. Found: C, 66.58; H, 6.54.

1,2-Dihydro-endo-dicyclopentadiene-2,2-dicarboxylic acid (X). A mixture of 9.26 g. (0.033 mole) of ester VIII, 4.1 g. (0.076 mole) of potassium hydroxide and 50 ml. of water was heated to reflux and stirred for 2 days. The resulting solution was cooled and poured into a 2-l. separatory funnel, washing the flask with a little water, and adding the washings to the reaction solution. Upon addition of 400 ml. of ether and acidification with cold 6*N* hydrochloric acid, the diacid X which precipitated dissolved in the ether layer. Ether washings of the aqueous solution were added to the original ether layer, which was then washed with small portions of cold water and dried over magnesium sulfate. Removal of ether and recrystallization of the residue from ethyl acetate yielded 6.63 g. (90%) of diacid X. An analytical sample was prepared by further recrystallizations from ethyl acetate, m.p. 217–218° dec.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.93; H, 6.36.

In one run, 2.78 g. (0.01 mole) of the ester X in a solution of 1.2 g. of potassium hydroxide in 15 ml. of water was stirred on a steam bath for 3 days. The basic solution was extracted with ether and then cooled and acidified by dropwise addition of cold 6*N* hydrochloric acid. As the precipitate formed, it was removed by filtration. The combined precipitates were slurried with cold water and filtered yielding 1.4 g. (47%) of the monopotassium salt IX of the diacid. A pure sample was prepared by recrystallization from water. The salt did not melt below 275°.

Anal. Calcd. for $C_{12}H_{13}O_4K \cdot 2H_2O$: C, 48.63; H, 5.78. Found: C, 48.78; H, 5.80.

Diethyl tetrahydro-endo-dicyclopentadiene-2,2-dicarboxylate (XII). A solution of 2.78 g. (0.01 mole) of the ester VIII in 50 ml. of absolute ethanol absorbed 95% of the calculated volume of hydrogen when reduced over Adams' catalyst. The product was distilled yielding 2.46 g. (88%), b.p. 113–115° (0.30 mm.), and an analytical sample was prepared by one further distillation, b.p. 111°/0.30 mm., n_D^{26} 1.4737.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.24; H, 8.86.

Tetrahydro-endo-dicyclopentadiene-2,2-dicarboxylic acid (XIII). The saturated ester XII was hydrolyzed by refluxing a solution containing 1.55 g. (0.055 mole) of ester and 1 g. of potassium hydroxide in 10 ml. of water for 2 days. Then the solution was diluted with 10 ml. of water, extracted with ether, and cooled in an ice bath. Neutralization with 4 ml. of 10% hydrochloric acid gave a precipitate which was taken up in ether. The ether extract was dried over magnesium sulfate. Evaporation of the ether followed by one recrystallization of the residue from ethyl acetate yielded 1.0 g. (81%) of diacid XIII, m.p. 222–223° dec. The product was further purified for analysis by repeated recrystallization, m.p. 222.5–223° dec.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.09; H, 7.24.

Diethyl 1,2-dihydro-exo-dicyclopentadiene-2,2-dicarboxylate (XV). A solution of 30.5 g. (0.19 mole) of redistilled diethyl malonate in 100 ml. of dry toluene was added to a suspension of sodium amide (0.19 mole) in about 50 ml. of ammonia.

After replacing the ammonia with 700 ml. of toluene, 34.5 g. (0.0075 mole) of solid *exo-cis*-ditosylate XIV was introduced through a Gooch addition tube and the reaction was refluxed with stirring for 4 days. Filtration of the cooled reaction mixture removed 30.15 g. of a crude solid consisting primarily of sodium toluenesulfonate. The mother liquor was evaporated under diminished pressure to remove most of the toluene and then the residue, diluted to about 100 ml. with ether, precipitated 1.0 g. of crude unchanged ditosylate after about 1 hr. The filtered solution was diluted to about 400 ml. with ether, washed thoroughly with water and dried over magnesium sulfate. Removal of ether and distillation of the residue yielded 9.90 g. of low-boiling forerun, primarily diethyl malonate, and 17.82 g. of crude ester XV. The small amount of residue probably containing some unchanged ditosylate was discarded. The product was redistilled yielding 17.25 g. (0.062 mole, 82.5% over-all yield, 85% on the basis of consumed), b.p. 103°/0.25 mm., 100°/0.17 mm. An analytical sample was purified by distillation, b.p. 102–103°/0.16 mm., $n_D^{25.3}$ 1.4794.

Anal. Calcd. for $C_{16}H_{22}O_4$: C, 69.04; H, 7.97. Found: C, 69.08; H, 8.17.

1,2-Dihydro-exo-dicyclopentadiene-2,2-dicarboxylic acid (XVI). The ester XV (9.26 g., 0.033 mole) was stirred and heated in a solution of 50 ml. of water and 4.1 g. of potassium hydroxide for 2 days. The reaction mixture was worked up as described for the *endo* case yielding 5.77 g. (81%) of diacid XVI. An analytical sample was recrystallized from ethyl acetate, m.p. 215–216° dec.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.80; H, 6.39.

Diethyl tetrahydro-exo-dicyclopentadiene-2,2-dicarboxylate (XVII). A solution of 2.78 g. (0.01 mole) of the ester XV in 50 ml. of absolute ethanol was reduced in the presence of Adams' catalyst at ambient temperature and pressure. The volume of hydrogen absorbed was in agreement with the calculated up-take. The solution was filtered, ethanol was evaporated, and the product was distilled yielding the saturated ester XVII; b.p. 104.5–105°/0.18 mm., n_D^{25} 1.4750.

Anal. Calcd. for $C_{16}H_{24}O_4$: C, 68.54; H, 8.63. Found: C, 68.49; H, 8.37.

Tetrahydro-exo-dicyclopentadiene-2,2-dicarboxylic acid (XVIII). The saturated ester XVII (2.46 g., 0.0088 mole) was hydrolyzed by refluxing in a solution of 20 ml. of water and 2.0 g. of potassium hydroxide for 2 days. The product isolated as described for the unsaturated compound weighed 1.47 g. (75%). An analytical sample was further purified by recrystallization from ethyl acetate, m.p. 227–227.5° dec.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.48; H, 7.30.

Decarboxylation of 1,2-dihydro-endo-dicyclopentadiene-2,2-dicarboxylic acid (X). A mixture of 2.0 g. (0.0090 mole) of the acid X and 70 ml. of diphenyl ether was stirred and heated in a 100-ml. round-bottom flask fitted with a condenser and a thermometer dipping below the surface of the liquid. Gas evolution began at 155° and at 175° the insoluble starting acid disappeared. After being maintained at a reaction temperature of 175° for 30 min., the solution was cooled to room temperature, diluted with excess ethyl ether, and extracted with 0.1*N* sodium hydroxide. Acidification of the combined basic extracts yielded an oil which was taken up in ether. The ether solution was washed with cold water and dried over magnesium sulfate. Removal of ether yielded a residue which solidified slowly and could be recrystallized from ligroin (b.p. 60–90°), m.p. 98–99°, with sublimation.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.12; H, 7.92. Found: C, 74.19; H, 8.05.

In another run, 10 g. (0.045 mole) of the acid X in 200 ml. of diphenyl ether was heated to 160° over a period of 30 min. When evolution of carbon dioxide had subsided, the temperature was increased to 175° in 15 min. The crude product isolated essentially by the procedure described above was methylated directly using diazomethane in ether. After excess diazomethane was destroyed with a few drops of glacial acetic acid, the ether solution was dried over magnesium sulfate. Removal of ether and distillation of the residue yielded 5.90 g. (68%) of a colorless liquid, b.p. 115–117° (9.0 mm.). An analytical sample was taken from a center cut of a second distillation, b.p. 98–99° (3.5 mm.) during the entire distillation and 98° (3.5 mm.) for the analytical sample, n_D^{25} 1.4962.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.96; H, 8.39. Found: C, 74.76; H, 8.16.

Action of methoxide upon the ester mixture XX. The methylated crude decarboxylation product (3.0 g., 0.016 mole) was dissolved in 25 ml. of methanol and added to a solution of sodium methoxide prepared from 1.8 g. (0.078 g.-atom) of sodium and 25 ml. of absolute methanol. After being refluxed for 4 hr., the reaction mixture was cooled, diluted with excess water, and the oil which separated was extracted with ether. The ether solution, washed with water and dried over magnesium sulfate, was concentrated and chromatographed through a 1 m. × 6 mm. column of 20% polypropylene glycol crosslinked with pentaerythritol on Chromosorb W at 122° with a helium flow of about 95 cc./min. The retention times of the two esters were very close, 12.2 min. and 12.7 min., and at a higher temperature (154°) there was no resolution of the peaks. The product from the decarboxylation contained about 35% of the material having lower retention time and 65% of the second product. After reaction with sodium methoxide, no new peaks were detected, but the proportions of the peaks had changed to about 51% at 12.7 min. and 49% at 12.2 min.

2,2-Bis(hydroxymethyl)-1,2-dihydro-endo-dicyclopentadiene (XXI). A solution of 10 g. (0.037 mole) of ester VIII in 100 ml. of anhydrous ether was added slowly to a stirred solution of lithium aluminum hydride (2.7 g., 0.071 mole) in 500 ml. of anhydrous ether. The reaction mixture was stirred under reflux for 15 hr., cooled and treated successively with 100 ml. of water saturated ether, sufficient water to coagulate the oxides of lithium and aluminum, and enough 10% hydrochloric acid to dissolve the precipitated oxides. The aqueous solution was extracted with ether several times and the extract, washed with water and dried over magnesium sulfate, was evaporated under diminished pressure. A white solid residue was recrystallized from ligroin (b.p. 90–120°) yielding 6.43 g. (92%) of the diol XXI. A sample was further purified for analysis by recrystallization from ligroin (b.p. 90–120°), m.p. 159–160°.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.14; H, 9.30.

2,2-Bis(hydroxymethyl)-1,2-dihydro-endo-dicyclopentadiene ditosylate (XXII). A solution of 3.88 g. (0.020 mole) of the diol XXI in 40 ml. of dry pyridine (freshly distilled from barium oxide) was added dropwise to a stirred solution of 8 g. (0.042 mole) of toluenesulfonyl chloride in 40 ml. of dry pyridine at 0°. When the addition was complete, the reaction mixture was allowed to stand for 2 days in a refrigerator. Then the mixture, cooled in an ice bath, was stirred while 150 ml. of ice cold water was added dropwise. The ditosylate which precipitated was recrystallized from methanol yielding 8.38 g. (78%), m.p. 115–116°.

Anal. Calcd. for $C_{26}H_{30}O_6S_2$: C, 62.13; H, 6.02. Found: C, 62.27; H, 5.88.

2,2-Dimethyl-1,2-dihydro-endo-dicyclopentadiene XXIII. Solid *endo*-ditosylate (8.88 g., 0.0176 mole) was added to 5.0 g. (0.143 mole) of lithium aluminum hydride in 600 ml. of anhydrous ether. The reaction mixture was stirred under reflux for 2 days. Excess lithium aluminum hydride was destroyed by slow addition of water-saturated ether (100 ml.) followed by water, and the precipitated oxides were dissolved in 0.1*N* hydrochloric acid. The ether extract, washed with water and dried over magnesium sulfate, was evaporated at atmospheric pressure and distillation of the crude residue yielded 2.31 g. (81%) of olefin XXIII, b.p. 91–93° (30 mm.). The product was redistilled before analysis; b.p. 92–93° (30 mm.), n_D^{25} 1.4812. The infrared spectrum showed peaks at 3.26 μ, 6.37 μ and 14.28 μ associated with C-9=C-10 unsaturation and at 7.23 μ and 7.33 μ due to the *gem*-dimethyl substituent at C-2.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 89.05; H, 11.14.

A phenyl azide adduct was prepared and recrystallized three times from absolute ethanol. The product crystallized nicely in the form of slender prisms, but did not give a sharp melting point. Instead, upon heating, the adduct appeared to dissociate or decompose without darkening, m.p. 163.5–166°.

Anal. Calcd. for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24. Found: C, 77.11; H, 8.05.

A nitroso chloride dimer was prepared and recrystallized from toluene, m.p. 167–168°.

Anal. Calcd. for $(C_{12}H_{18}ClNO)_2$: C, 63.29; H, 7.97. Found: C, 63.52; H, 7.86.

2,2-Bis(hydroxymethyl)-1,2-dihydro-exo-dicyclopentadiene (XXIV). Ten grams (0.036 mole) of ester XV in 100 ml. of anhydrous ether was added dropwise to 2.7 g. (0.071 mole) of lithium aluminum hydride in 500 ml. of anhydrous ether. The reaction mixture was refluxed and stirred for 2 days and the product was isolated by the usual procedure using 10% hydrochloric acid to dissolve the lithium and aluminum oxides. The yield of diol XXIV was 6.42 g. (92%), m.p. 151–153°. An analytical sample was prepared by recrystallization from ligroin (b.p. 90–120°)–toluene m.p. 154–154.5°, mixed melting point with the *endo* isomer XXI, 145–148°.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.24; H, 8.94.

2,2-Bis(hydroxymethyl)-1,2-dihydro-exo-dicyclopentadiene ditosylate (XXV). *exo*-Ditosylate XXV was prepared by the same procedure described for the *endo* isomer. From 3.88 g (0.020 mole) of the diol XXIV and 8.0 g. (0.042 mole) of toluenesulfonyl chloride in pyridine was obtained 7.50 g. (75%) of the ditosylate recrystallized once from methanol, m.p. 177–178°.

Anal. Calcd. for $C_{26}H_{30}O_6S_2$: C, 62.13; H, 6.02. Found: C, 62.22; H, 5.81.

2,2-Dimethyl-1,2-dihydro-exo-dicyclopentadiene (XXVI). Six grams (0.16 mole) of lithium aluminum hydride was dissolved in about 600 ml. of anhydrous ether and 10.5 g. (0.021 mole) of the solid *exo*-ditosylate was added through a Gooch tube with constant stirring. The ditosylate was scarcely soluble in the volume of ether used for the reaction, but slowly disappeared during 3 days of stirring of the reaction mixture under reflux. The cooled reaction mixture was then treated in the usual way with water-saturated ether and then water until the oxides of lithium and aluminum formed a curdy filterable precipitate. The solution was filtered and the precipitate washed several times with ether. The combined ether solutions, dried over magnesium sulfate and evaporated at atmospheric pressure, yielded a crude residue which gave 2.69 g. (79%) of the hydrocarbon XXVI on distillation, b.p. 91–92° (30 mm.). An analytical sample was prepared, b.p. 91–92° (30 mm.), n_D^{26} 1.4788. The infrared spectrum showed absorption at 3.28 μ, 6.37 μ and 13.91 μ associated with C-9–C-10 unsaturation and at 7.23 μ and 7.33 μ due to the *gem*-dimethyl substituent at C-2.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.93; H, 11.12.

A phenyl azide adduct formed which did not give a sharp melting point, although it crystallized as distinctive colorless crystals from ethanol, m.p. 166–169°, mixed melting point with the *endo* isomer XIII, m.p. 137–159°.

Anal. Calcd. for $C_{18}H_{23}N_3$: C, 76.83; H, 8.24. Found: C, 77.11; H, 8.05.

A nitroso chloride dimer was prepared by the usual method and recrystallized from toluene, m.p. 163–165°, mixed melting point with the *endo* isomer, m.p. 155–159°.

Anal. Calcd. for $(C_{12}H_{18}ClNO)_2$: C, 63.29; H, 7.97. Found: C, 63.56; H, 7.60.

Reaction of the 2,2-dimethyl-1,2-dihydrodicyclopentadienes XXIII *and* XXVI *with phosphoric acid.* A small quantity of each isomer was distilled from 85% phosphoric acid at slightly reduced pressure. At first a small amount of hydrocarbon, probably starting material, appeared to distill with steam. The entire product was collected in each case and taken up in ether. The ether solutions were dried over magnesium sulfate and the ether was evaporated. In one run 1.7 g. of the *exo* isomer was distilled slowly from 2 ml. of phosphoric acid. The crude product after workup was distilled yielding a colorless liquid, b.p. 104–106° (30 mm.). During the reaction with phosphoric acid, the mixture being heated turned a greenish color and upon further heating this color was dispelled leaving a pale tan which darkened toward the end of the distillation. A very small sample (4–10 drops) of each starting material, the isomeric dimethyl compounds XXIII and XXVI, and of each phosphoric acid distillation product was reduced separately in 100 ml. of absolute ethanol using Adams' catalyst and hydrogen at ambient temperature and pressure. Two hours was allowed for each reduction and no attempt was made to measure hydrogen up-take. Each solution was filtered and concentrated. Using gas chromatography, samples of saturated and unsaturated starting materials and saturated and unsaturated reaction products, at 102° and a helium flow of about 70 cc./min. through a 1 m. × 6 mm. column of 20% Union Carbide Polypropylene Glycol-1025 on Chromosorb W (30-60 mesh). The retention times and approximate estimates of the relative proportions of the peaks observed for each sample are given below.

RETENTION TIMES

	Unsaturated			Saturated		
2,2-Dimethyl-*endo*-	9.4 min.			10.1 min. trace	12.1 min.	
Distilled from H_3PO_4	9.6 75%	12.0 6%	17.0 19%	10.2 5%	12.3 70%	17.3 25%
2,2-Dimethyl-*exo*	9.0			10.5	12.0 trace	
Distilled from H_3PO_4	9.2 30%	12.0 11%	17.2 59%	10.3 17%	12.2 15%	17.3 67%

The product from the 2,2-dimethyl-*exo* hydrocarbon which had been once distilled was estimated to be about 85% pure. A second distillation resulted in scarcely measurable purification and no change in boiling range. The product, dissolved in acetone, decolorized 3% aqueous permanganate. A sample of the mixed product, n_D^{25} 1.4975, was analyzed for carbon and hydrogen.

Anal. Calcd. for $C_{12}H_{18}$: C, 88.82; H, 11.18. Found: C, 88.61; H, 11.22.

Infrared analysis of this sample showed that all of the peaks associated with C-9-C-10 unsaturation in the starting material had disappeared. No absorption characteristic of hydrogen attached to an unsaturated carbon was observed, but a weak band at 5.97 μ suggests that the product contains a highly substituted unstrained double bond. The *gem*-dimethyl absorptions observed in the spectrum of the starting material are replaced by a C-methyl peak at 7.26 μ.

Acknowledgment. Support of this research by a grant from the Petroleum Research Fund administered by the American Chemical Society and, in part by a Research Grant (CY-4298) of the National Institutes of Health, U. S. Public Health Service, is gratefully acknowledged. The authors are indebted to Dr. Roger J. Philippe for assistance in the interpretation of several infrared traces.

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[CONTRIBUTION FROM THE UNIVERSITY OF GLASGOW]

Some Studies on Seven-Membered Ring Compounds

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Received April 10, 1961

Acid-catalyzed rearrangement of the epoxides (IVa and IVb) of methyleneanthrone and benzalanthrone produces no ring expansion, but the products are identified as 10-hydroxymethyleneanthrone (VIa) and 10-formyl-10-phenylanthrone (IXa) respectively. Similar treatment of the epoxide (V) of 2-benzal-1-tetralone leads to 2-phenyl-4,5-benzocycloheptene-1,3-dione (X). A new explanation is offered for the alkali solubility of the 4,5-dihydroxy-2,3,6,7-dibenzocycloheptadienones XIII.

Pursuing our interest in tropones[2] and their hydroxy derivatives[3] we have been examining the ring expansion process which allowed Cook[4] to prepare the first known γ-hydroxytropone (I) by the action of moist silver oxide on benzalanthrone dibromide (II). Since this reaction must involve a carbonium ion intermediate, it was of interest to explore the acid-catalyzed opening of certain epox-

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