Molecular Asymmetry. VII. *trans*-6,7,10,11-Tetrahydro-5H-benzocyclononene[1]

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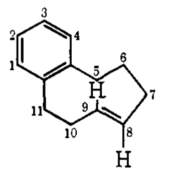
Abstract: The title compound **1** was prepared and converted into (+)-*trans*-dichloro-(*trans*-6,7,10,11-tetrahydro-5H-benzocyclononene)((*R*)-α-methylbenzylamine)platinum(II) (**8**). After fractional crystallization the platinum complex had $[\alpha]^{25}\text{D}$ +37.4°. Decomposition of the complex at −60° afforded optically inactive *trans*-olefin **1** suggesting that the *trans*-olefinic linkage in **1** is rotating very rapidly causing spontaneous racemization of olefin **1**. The nuclear magnetic resonance spectrum of **1** was unchanged in the temperature range of +107 to −87°.

As part of our continuing studies[3] of molecular dissymmetry of *trans*-cyclic olefins, *trans*-6,7,10,11-tetrahydro-5H-benzocyclononene (**1**) was prepared for resolution *via* the platinum complex containing (*R*)-(+)-α-methylbenzylamine.



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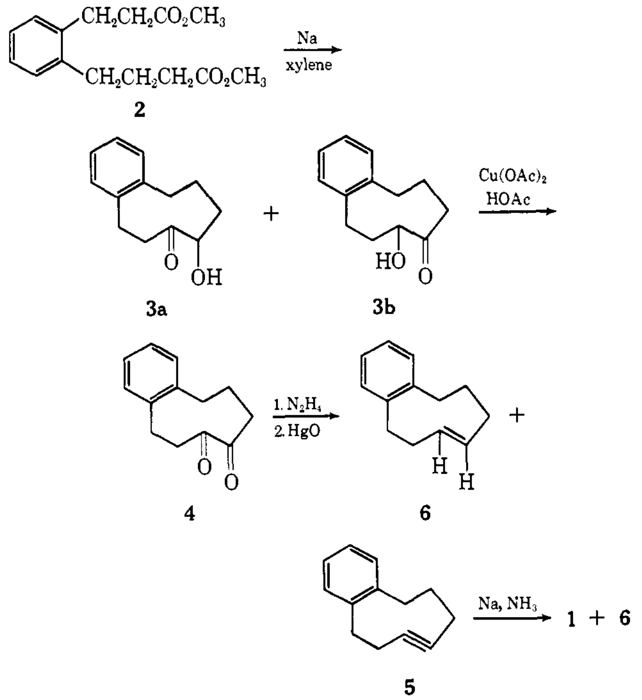
Acyloin condensation of methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**), which was prepared from the corresponding dinitrile,[4] afforded the two isomeric α-hydroxy ketones, 8-hydroxy-6,7,8,9,10,11-hexahydro-5H-benzocyclononen-7-one (**3a**) and 7-hydroxy-6,7,-8,9,10,11-hexahydro-5H-benzocyclononen-8-one (**3b**). Oxidation of this mixture with cupric acetate gave a single α-diketone, 6,7,8,9,10,11-hexahydro-5H-benzocyclononene-7,8-dione (**4**), which was converted into the corresponding bishydrazone. Oxidation of the bishydrazone with mercuric oxide gave a mixture of the acetylene, 6,7,10,11-tetrahydro-8,9-dehydro-5H-benzocyclononene (**5**), and the *cis*-olefin **6**. A mixture of the *trans*-olefin **1** and the *cis* isomer was prepared from the acetylene **5** by reduction with sodium in liquid ammonia (Scheme I). The two isomeric hydrocarbons were separated *via* silver nitrate extraction. The material which was silver nitrate soluble was the *trans* isomer **1** which exhibited infrared absorption bands at 1655 cm^{-1} for HC═CH and 975 cm^{-1} for *trans*-HC═CH.[5] In the nuclear magnetic resonance spectrum, two one-proton multiplets were present for the two vinyl protons between δ 5.88 and 5.14 and between 4.88 and 4.31. Models of **1** indicate that one of the vinyl protons lies above the benzene ring and hence is shifted approximately 1 ppm upfield.[6] The silver nitrate insoluble compound was the *cis* isomer **6**. The infrared spectrum of **6** exhibited a band at 1655 cm^{-1} for HC═CH and 695 cm^{-1} for *cis*-HC═CH.[5] The two vinyl protons appeared as a multiplet between δ 6.08 and 5.00 in the nuclear magnetic resonance spectrum.

Scheme I



Both the *trans*-olefin **1** and the *cis*-olefin **6** were oxidatively cleaved at the double bond, and the resulting dicarboxylic acid was treated with diazomethane. Vapor phase chromatographic analysis of each of the crude reaction products indicated the presence of only one component, methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**), indicating that the double bond in both olefins is in the position shown.

Catalytic reduction of the *cis*-olefin **6** afforded the saturated hydrocarbon, 6,7,8,9,10,11-hexahydro-5H-benzocyclononene (**7**), which showed no vinyl hydrogens in the nuclear magnetic resonance spectrum.

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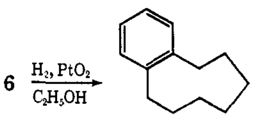
[3] (a) A. C. Cope, C. R. Ganellin, and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962); (b) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3476 (1963); (c) A. C. Cope and B. A. Pawson, *ibid.*, **87**, 3649 (1965); (d) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *ibid.*, **87**, 3644 (1965); (e) A. C. Cope and B. A. Pawson *ibid.*, in press.

[4] The dinitrile was prepared according to the scheme of E. M. Fry and L. F. Fieser, *ibid.*, **62**, 3489 (1940), with those modifications given in the Experimental Section.

[5] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1960, p 34.

[6] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," The Macmillan Co., New York, N. Y., 1959, p 18.



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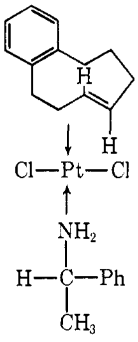
Reaction of the racemic *trans*-olefin **1** with (+)-*trans*-dichloro(ethylene)((*R*)-α-methylbenzylamine)platinum(II)[3b] effected displacement of ethylene and formation of (+)-*trans*-dichloro-(*trans*-6,7,10,11-tetrahydro-5H-benzocyclononene)((*R*)-α-methylbenzyl amine)platinum(II) (**8**). Fractional crystallization of the complex **8** from a mixture of carbon tetrachloride and cyclohexane gave as the least soluble fraction yellow crystals having $[\alpha]^{25}\text{D}$ +37.4°.[7] The residue from the mother liquor had $[\alpha]^{25}\text{D}$ −4.7°. This residue was obtained only as an oil; attempted crystallization from carbon tetrachloride and cyclohexane was unsuccessful.



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Liberation of the olefin from partially resolved complex **8** with aqueous sodium cyanide[3b] at room temperature gave olefin **1** which showed no optical activity when the rotation was measured at room temperature. Optically inactive olefin **1** was also obtained from partially resolved complex **8** when the liberation was carried out by means of small-scale rapid reactions with triphenylphosphine followed by immediate cooling to −70°.[3d]

These results suggest that the *trans*-olefinic linkage is rotating very rapidly causing spontaneous racemization of the olefin under the liberation conditions. A similar phenomenon was also observed for *trans*-cyclononene[3d] and *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene[3e] at room temperature and for *trans*-cyclodecene[3d] both at room temperature and at lower temperatures.

The rotation of *trans*-olefinic bonds has been studied *via* variable-temperature nuclear magnetic resonance spectrometry in other cases.[8,9] The nuclear magnetic resonance spectrum of the olefin **1** was measured in three solvent systems at 14 temperatures in the range of +107 to −87°. None of the changes previously observed[8,9] were present in these spectra. The only observed change in the spectrum over this range of temperatures was a slight broadening of the lines at the lowest temperatures perhaps due to the increase in viscosity of the solution. From these nuclear magnetic resonance data it can be concluded that either the rate of rotation of the olefinic linkage is very slow as in *trans*-cyclooctene[3c] or rapid as in *trans*-cyclodecene[8] and *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene.[3e,9] Failure to observe optically active olefin **1** upon decomposition of the platinum complex suggests that the latter conclusion is justified.

The reason for the large difference in optical stability between olefin **1** and *trans*-cyclononene[3d] may be due to the removal of the interaction of the transannular methylene hydrogens with the vinyl hydrogens by replacement of two methylene groups with the benzene ring. The interaction between the vinyl hydrogens and the hydrogen atoms across the ring seems to be much more important than any additional strain introduced into the nine-membered ring by the benzene ring.

Experimental Section[10]

***o*-(Carboxymethyl)hydrocinnamic Acid.** This compound was prepared from 3-hydroxy-2-naphthoic acid by reduction with sodium in amyl alcohol according to the method of Fry and Fieser.[4] The crude reaction product was partially purified by washing with chloroform. The chloroform-insoluble material was a mixture of product and the starting material, 3-hydroxy-2-naphthoic acid, which were separated by crystallization from aqueous ethanol. The product, obtained in 27% yield, had mp 140–142° (lit.[4] mp 140–143°).

Ethyl *o*-(Carbethoxymethyl)hydrocinnamate. A solution of 318 g (1.53 moles) of *o*-(carboxymethyl)hydrocinnamic acid in 2 l. of ethanol containing 50 ml of concentrated sulfuric acid was heated at reflux for 14 hr. Approximately 1700 ml of ethanol was removed by distillation. The reaction mixture was cooled, added to 2 l. of water, and extracted with one 500-ml portion of ether and four 250-ml portions of ether. The ether was washed with one 500-ml portion of water, four 250-ml portions of saturated sodium bicarbonate solution, and two 500-ml portions of water and was dried with magnesium sulfate. Removal of solvent and distillation afforded 336 g (84%) of ethyl *o*-(carbethoxymethyl)-hydrocinnamate having bp 133–140° (0.6–0.8 mm) (lit.[4] bp 160–162° (2 mm)); $\nu_{\max}^{\mathrm{CCl_4}}$ 1735 cm^{-1}; $\lambda_{\max}^{\mathrm{C_2H_5OH}}$ (ϵ) 257 sh (272), 262 (292), and 271 mμ sh (208); nmr (CCl_4): δ 7.05 (4 H, singlet), 4.04 (4 H, quartet, J = 7 cps, with additional fine splitting), 3.55 (2 H, singlet), 3.1–2.2 (4 H, A_2B_2 multiplet), and 1.18 (6 H, triplet, J = 7 cps, with additional fine splitting).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.17; H, 7.66.

***o*-(3-Hydroxypropyl)phenethyl Alcohol.** To a cooled, stirred suspension of 100 g (2.64 moles) of lithium aluminum hydride in 900 ml of tetrahydrofuran was added a solution of 336 g (1.27 moles) of ethyl *o*-(carbethoxymethyl)hydrocinnamate in 900 ml of tetrahydrofuran during a 3-hr period. The reaction mixture was then heated at reflux for 15 hr. Then the reaction mixture was cooled with an ice bath, and 350 ml of methanol was slowly added followed by addition of 200 ml of water. The resulting thick mixture was stirred for 4 hr and then filtered. Concentration of the tetrahydrofuran filtrate afforded 128 g (56%) of dialcohol. The filter cake was washed with chloroform and then twice with methylene chloride to give an additional 81.1 g (35%) of dialcohol. The

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[7] This material was recrystallized to constant rotation and is a pure diastereoisomer according to this criterion.

[8] G. Binsch and J. D. Roberts, *J. Am. Chem. Soc.*, 87, 5157 (1965).

[9] G. M. Whitesides, B. A. Pawson, and A. C. Cope, *ibid.*, in press.

[10] Melting points were determined on a Kofler hot stage; boiling points are uncorrected. Infrared spectra were measured on either a Perkin-Elmer Model 237B or 337 recording spectrophotometer. Ultraviolet spectra were measured on a Cary Model 14 spectrophotometer. Nuclear magnetic resonance spectra were measured on a Varian Associates A-60 instrument. A Varian Associates V-6040 variable-temperature controller was used in variable-temperature experiments. Peak positions are reported in ppm using tetramethylsilane as an internal standard. Mass spectra were determined with a C.E.C. 21-130 mass spectrometer or with a Hitachi Perkin-Elmer RMU-6D mass spectrometer. Optical rotations were measured with a Zeiss photoelectric precision polarimeter. The rotations measured at 546.1 and 577.8 mμ were used to calculate the value at the sodium D line according to the equation given in the instruction manual. Vapor phase chromatographic studies were performed on a F & M Model 720 instrument with a flow rate of 1 cc of helium/sec. Microanalyses were performed by Scandinavian Microanalytical Laboratory, Midwest Microlab, Inc., Galbraith Laboratories Inc., and by Dr. S. M. Nagy and associates.

product had bp 145–148° (0.3 mm) (lit.[4] bp 174.5–175.5° (2 mm)); $\nu_{max}^{CHCl_3}$ 3610, 3375, and 1040 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 257 sh (221), 263 (268), and 272 mμ (221); nmr ($CDCl_3$): δ 7.05 (4 H, singlet), 4.0–3.4 (6 H, multiplet), 3.0–2.5 (4 H, multiplet), and 2.0–1.6 (2 H, multiplet). Upon addition of a drop of pyridine to the sample, the δ 4.0–3.4 signal became 4.71 (2 H, broad singlet) and 4.0–3.4 (4 H, multiplet).

1-(2-Chloroethyl)-2-(3-chloropropyl)benzene. Thionyl chloride (100 g) was slowly added to 36.91 g (0.204 mole) of *o*-(3-hydroxypropyl)phenethyl alcohol dissolved in 10 ml of pyridine.[11] The resulting reddish brown solution was heated at 95° for 15 min and then, after cooling to room temperature, was placed on the rotary evaporator (50 mm) for 14 hr. The mixture was dissolved in ether, and the insoluble pyridine hydrochloride was removed by filtration. Then the ether was dried with magnesium sulfate and removed at reduced pressure to afford 41.84 g of a brown-red oil. Distillation afforded 31.49 g (71%) of 1-(2-chloroethyl)-2-(3-chloropropyl)benzene having bp 94–102° (0.13–0.20 mm) (lit.[4] bp 130–132° (2 mm)); $\nu_{max}^{CS_2}$ 760, 710, and 655 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 258 (226), 263 (267), 267 sh (220), and 272 mμ (209); nmr (CCl_4): δ 7.05 (4 H, singlet), 3.7–3.3 (4 H, multiplet), 3.2–2.6 (4 H, multiplet), and 2.2–1.8 (2 H, multiplet).

Anal. Calcd for $C_{11}H_{14}Cl_2$: C, 60.84; H, 6.50; Cl, 32.66. Found: C, 61.13; H, 6.58; Cl, 32.33.

***o*-(3-Hydroxypropyl)phenethyl Alcohol Di-*p*-toluenesulfonate.** A solution of 208.5 g (1.16 moles) of *o*-(3-hydroxypropyl)phenethyl alcohol in 2 l. of pyridine was prepared and cooled to −10° with a Dry Ice–isopropyl alcohol bath. To the cooled solution 467 g (2.45 moles) of *p*-toluenesulfonyl chloride was added. The resulting solution was stirred at −10° for 3 hr and then poured into 2500 ml of water and ice. The product was removed by ether extraction; the ether was washed with water, 10% hydrochloric acid, saturated sodium bicarbonate solution, and again with water. The ether was dried with magnesium sulfate and removed at reduced pressure to give 458 g (81%) of a yellow oil, *o*-(3-hydroxypropyl)phenethyl alcohol di-*p*-toluenesulfonate having $\nu_{max}^{CHCl_3}$ 1360 and 1170 cm^{-1}; nmr ($CDCl_3$): δ 7.82–6.90 (12 H, multiplet with a sharp singlet at 6.98), 4.02 (4 H, quartet, J = 6.5 cps), 2.78 (4 H, multiplet), 2.36 (6 H, singlet), and 1.82 (2 H, multiplet). An analytical sample was prepared by removing the last traces of solvent at 25° (0.1 mm) for 24 hr.

Anal. Calcd for $C_{25}H_{28}O_6S_2$: C, 61.45; H, 5.78; S, 13.12. Found: C, 61.57; H, 5.91; S, 12.88.

***o*-(3-Cyanopropyl)hydrocinnamonitrile from 1-(2-Chloroethyl)-2-(3-chloropropyl)benzene.** A solution of 31.30 g (0.114 mole) of 1-(2-chloroethyl)-2-(3-chloropropyl)benzene and 14.8 g (0.3 mole) of sodium cyanide in 350 ml of dimethyl sulfoxide was stirred at room temperature for 5 days. The resulting brown solution was poured into 1000 ml of water and extracted with two 750-ml portions and three 500-ml portions of methylene chloride. The organic extracts were washed with three 500-ml portions of water and dried with magnesium sulfate. Removal of the solvent under reduced pressure afforded 29.41 g of a red oil. Distillation afforded 26.62 g (93%) of *o*-(3-cyanopropyl)hydrocinnamonitrile having bp 165–170° (0.25 mm) (lit.[4] bp 196–212° (2 mm)); $\nu_{max}^{CHCl_3}$ 2245 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 257 sh (288), 262 (318), 267 sh (263), and 272 mμ (221); nmr ($CDCl_3$): δ 7.20 (4 H, singlet), 3.1–2.2 (8 H, multiplet), and 2.1–1.7 (2 H, multiplet).

Anal. Calcd for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.72; H, 7.23; N, 14.35.

***o*-(3-Cyanopropyl)hydrocinnamonitrile from *o*-(3-Hydroxypropyl)phenethyl Alcohol Di-*p*-toluenesulfonate.** To a solution of 457 g (0.936 mole) of *o*-(3-hydroxypropyl)phenethyl alcohol di-*p*-toluenesulfonate in 2 l. of dimethyl sulfoxide was added 103 g (2.1 moles) of sodium cyanide. The resulting solution was stirred at room temperature for 5 days. The reaction was worked up as described above, and yielded 180 g of a dark oil, which upon distillation afforded 154.3 g (84%) of the dinitrile having bp 168–173° (0.3 mm) and infrared spectrum identical with that above.

Methyl *o*-(3-Carbomethoxypropyl)hydrocinnamate (2). A solution of 154.3 g (0.778 mole) of *o*-(3-cyanopropyl)hydrocinnamonitrile in 3 l. of methanol was prepared and cooled to 0° with an ice bath.[12] The solution was saturated with anhydrous hydrogen chloride which was added *via* a gas dispersion tube for 4 hr. The reaction mixture was heated at reflux for 2 hr and then 1500 ml of methanol was removed by distillation and the resulting solution was poured into 2 l. of water. The product was removed by extraction with five 250-ml portions of methylene chloride. The methylene chloride was washed with saturated sodium bicarbonate solution and with water, dried with magnesium sulfate, and concentrated at reduced pressure to afford 178 g of an oil.

Acidification of the sodium bicarbonate wash solution with 10% sulfuric acid afforded 16.7 g of an oil which was removed by ether extraction. The infrared spectrum of this oil exhibited two carbonyl bands at 1745 and 1715 cm^{-1}. Esterification of this material with methanol–sulfuric acid afforded 16 g of an oil having an infrared spectrum identical with that of the neutral material obtained above. Distillation of the combined materials afforded 171.8 g (84%) of methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**) having bp 147–151° (0.25 mm); $\nu_{max}^{CCl_4}$ 1740 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 258 sh (266), 263 (308), and 272 mμ (231); nmr (CCl_4): δ 7.09 (4 H, singlet), 3.59 (6 H, singlet), and 3.06–1.58 (10 H, multiplet).

Anal. Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.09; H, 7.56.

8-Hydroxy-6,7,8,9,10,11-hexahydro-5H-benzocyclononen-7-one (3a) and 7-Hydroxy-6,7,8,9,10,11-hexahydro-5H-benzocyclononen-8-one (3b). A 3-l., three-necked, round-bottomed flask was equipped with a Hershberg stirrer fitted with an ASCO Teflon gland[13] and a modification of the high-dilution apparatus of Ziegler[14] consisting of a six-bulb condenser, a 1-l. adjustable-flow funnel, and a U tube for return of the xylene condensate, together with the ester solution, to the reaction flask. A positive pressure (1 cm of mercury) of nitrogen was maintained in the entire system.

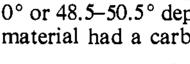
The procedure followed was that described previously.[15] Into the flask was placed 800 ml of xylene which was heated to reflux. A small amount of the xylene was allowed to distil from the apparatus to remove any remaining traces of water, and then 12.6 g (0.55 g-atom) of sodium was added and dispersed. A solution of 32.69 g (0.124 mole) of methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**) in 500 ml of xylene was added over a 32-hr period. Heating and stirring were continued for 1 hr after the addition was complete. The reaction mixture was then cooled and hydrolyzed by addition of a solution of 35 ml of glacial acetic acid in 35 ml of xylene followed by the addition of 110 ml of water.

Insoluble polymeric material was removed by filtration. The water and xylene layers were separated, and the water was washed with xylene. The combined xylene layers were dried with magnesium sulfate and then concentrated to approximately 50 ml. Crystals (5.05 g, 20%) formed and were separated by decantation of the xylene. The material was purified by sublimation at 130° (0.1 mm). After one sublimation the material had mp 118.5–126.5°; after two, 119.5–126.5°; and after three, 119.5–126.5°; $\nu_{max}^{CS_2}$ 3475 and 1700 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 257 sh (417), 262 (411), 267 sh (374), and 271 mμ sh (343); nmr ($CDCl_3$): δ 7.17 (4 H, singlet), 4.16 (1 H, broad singlet), 3.79 (1 H, broad singlet), and 3.30–1.35 (10 H, multiplet). The signal at δ 3.79 disappeared upon the addition of a drop of pyridine to the sample.

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.40; H, 7.88.

The xylene solution which remained after removal of the crystalline material was distilled affording 3.51 g of material having bp 90–100° (0.1–0.3 mm). Vpc analysis (2-ft × 0.25-in. 20% SE-30, 200°) showed 24% of **3a** and **3b**.

Column chromatography of 732 mg of this distilled material on a column of 80 g of Woelm activity I alumina (elution with ether) afforded five crystalline fractions totalling 69 mg, mp 49.0–50.5° (lit.[4] for **9**, mp 47.5–49.0° or 48.5–50.5° depending upon the method of purification). The material had a carbonyl band at 1705 cm^{-1} in the infrared spectrum. The mass spectrum showed the expected molecular weight of 174. No other compounds could be isolated from the chromatographic column.



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6,7,8,9,10,11-Hexahydro-5H-benzocyclononene-7,8-dione (4). A solution of 4.72 g (0.0231 mole) of the mixture of acyloins **3a** and

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[11] K. Ahman, F. M. Bumpus, and F. M. Strong, *J. Am. Chem. Soc.*, 70, 3391 (1948).

[12] W. Davey and D. J. Tivey, *J. Chem. Soc.*, 1230 (1958).

[13] A. F. Smith Co., Rochester, N. Y.

[14] K. Ziegler, H. Eberle, and H. Ohlinger, *Ann. Chem.*, **504**, 94 (1933).

[15] N. L. Allinger in "Organic Synthesis," Coll. Vol. IV, N. Rabjohn, Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 840.

3b (containing some polymer) and 9.5 g (0.0475 mole) of cupric acetate monohydrate in 150 ml of 50% acetic acid was heated at reflux for 2 hr.[16,17] The reaction mixture was filtered through Celite to remove cupric oxide and then poured into saturated sodium chloride solution. The Celite was washed with ether, and this ether was used to extract the sodium chloride solution. The combined ether layers were washed four times with saturated sodium chloride solution, four times with saturated sodium bicarbonate solution, and once more with saturated sodium chloride solution. The ether was dried with magnesium sulfate and concentrated to give 4.21 g of a yellow oil. Distillation afforded 2.23 g (48%) of 6,7,8,9,10,11-hexahydro-5H-benzocyclononene-7,8-dione (**4**) having bp 93° (0.1 mm); $\nu_{max}^{CS_2}$ 1705 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 256 sh (353), 263 (361), 266 sh (315), and 272 mμ (293); nmr (CCl$_4$): δ 7.08 (4 H, singlet), 3.1–2.5 (6 H, multiplet), and 2.5–1.7 (4 H, multiplet); mass spectrum *m/e* 202 (molecular ion), 184, 174, 146, 117 (base peak), 104, 91, and 55.

Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.00; H, 7.03.

6,7,10,11-Tetrahydro-8,9-dehydro-5H-benzocyclononene (5) and *cis*-6,7,10,11-Tetrahydro-5H-benzocyclononene (6). To a cooled solution of 1.052 g (5.2 mmoles) of 6,7,8,9,10,11-hexahydro-5H-benzocyclononene-7,8-dione (**4**) in 50 ml of ethanol was added 1.5 ml of 95% hydrazine. Within a few seconds a white precipitate formed which redissolved during 3 hr of stirring at room temperature. The ethanol was removed at reduced pressure on a rotary evaporator, and the residue was then maintained at 50° (0.2 mm) for 11 hr resulting in 1.49 g of a yellow glass which did not exhibit a carbonyl band in the infrared spectrum.

A suspension of 5.88 g (27 mmoles) of mercuric oxide, 3.20 g (22 mmoles) of sodium sulfate, and 0.22 g (2.5 mmoles) of powdered potassium hydroxide in 150 ml of benzene was heated to reflux, and a solution of the above yellow glass in 25 ml of benzene was added during a 35-min period. The resultant solution was heated at reflux for 2 hr, then filtered through Celite and the benzene was removed at reduced pressure. The residue was purified by chromatography on 53 g of Woelm activity I alumina. Elution with pentane afforded 125 mg (14%) of the *cis*-olefin **6** having $\nu_{max}^{CS_2}$ 3050, 3000, 2950, 2930, 2905, 2855, 1655, 775, 750, 740, 730, and 695 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 213 sh (1380), 253 (236), 257 (270), 262 sh (289), 264 (317), 268 sh (252), and 272 mμ (302); nmr (CCl$_4$): δ 6.99 (4 H, singlet), 6.08–5.00 (2 H, multiplet), 2.98–1.96 (6 H, multiplet), and 1.82–1.50 (4 H, multiplet); mass spectrum *m/e* 172 (molecular ion), 157, 144, 129, 115, 105 (base peak), and 91.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.85; H, 9.23.

Elution with ether–pentane (5:95) afforded 353 mg (41%) of the cyclic acetylene **5** having $\nu_{max}^{CS_2}$ 3045, 3000, 2905, 2820, 2200, and 750 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 211 sh (12,000), 258 (353), 263 sh (298), 265 (446), 268 sh (341), and 273 mμ (415); nmr (CCl$_4$): δ 7.08–6.84 (4 H, multiplet), 3.03–2.52 (4 H, broad singlet), and 2.41–1.84 (6 H, broad singlet); mass spectrum *m/e* 170 (molecular ion), 155, 142 (base peak), 141, 129, 128, 115, 105, and 91.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.96; H, 8.22.

***trans*-6,7,10,11-Tetrahydro-5H-benzocyclononene (1).** Into a 300-ml, three-necked, round-bottomed flask equipped with a Dry Ice condenser and a Dry Ice–isopropyl alcohol bath was distilled 150 ml of liquid ammonia. Sodium (400 mg, 17 g-atoms) was placed in the liquid ammonia and the resultant blue solution was stirred until all of the sodium had dissolved. Then a solution of 487 mg (2.82 mmoles) of 6,7,10,11-tetrahydro-8,9-dehydro-5H-benzocyclononene (**5**) in a few milliliters of pentane was added, and the resulting solution was stirred at the reflux temperature of liquid ammonia for 2 hr.[18] Excess sodium was decomposed by the addition of solid ammonium nitrate followed by the addition of 3% ammonium hydroxide solution. After the ammonia had evaporated, the resulting solution was extracted with pentane, and the pentane was washed with 3% hydrochloric acid, saturated sodium bicarbonate solution, and water. The pentane solution was dried with sodium sulfate and was concentrated at reduced pressure to afford 558 mg of an oil. Vpc analysis (8-ft × 0.25-in. 5% SE-30, 140°) showed the presence of only olefins and no starting acetylene. Vpc analysis (10-ft × 0.25-in. 15% XF-1150, 160°) indicated the presence of two components in approximately a 1:1 ratio,

The crude reaction mixture was redissolved in pentane and extracted with 15 20-ml portions of 30% aqueous silver nitrate solution.[19] The silver nitrate extracts were decomposed with 150 ml of concentrated aqueous ammonia to afford 189 mg (39%) of *trans*-6,7,10,11-tetrahydro-5H-benzocyclononene (**4**) having $\nu_{max}^{CS_2}$ 3050, 3005, 2975, 2925, 2850, 1655, 975, 940, 895, 800, 755, 735, and 695 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 216 sh (68,600), 258 (307), 263 sh (301), 266 (317), 269 sh (259), and 274 mμ (281); nmr (CCl$_4$): δ 6.96 (4 H, singlet), 5.88–5.14 (1 H, multiplet), 4.88–4.31 (1 H, multiplet), and 3.14–1.26 (10 H, multiplet); mass spectrum *m/e* 172 (molecular ion), 157, 144, 129, 115, 105 (base peak), and 91.

Anal. Calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.43; H, 9.55.

Methyl *o*-(3-Carbomethoxypropyl)hydrocinnamate (2) from *trans*-6,7,10,11-Tetrahydro-5H-benzocyclononene (1). To a solution of 21.2 mg (0.134 mmole) of potassium permanganate, 1.259 g (5.58 mmoles) of sodium metaperiodate, and 67 mg (0.49 mmole) of potassium carbonate in 190 ml of water was added a solution of 67 mg (0.398 mmole) of *trans*-6,7,10,11-tetrahydro-5H-benzocyclononene (**1**) in 80 ml of *t*-butyl alcohol and the resulting solution was stirred at room temperature for 24 hr.[20] The reaction mixture was acidified to pH 1 with 10% aqueous sulfuric acid solution and then extracted with four 75-ml portions of ether which were washed with three 25-ml portions of water and dried with magnesium sulfate. Removal of the ether at reduced pressure afforded 51 mg (54%) of a colorless oil which was treated with diazomethane in ether to afford methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**) which was homogeneous to vpc (2-ft × 0.25-in. 20% SE-30, 180°) and had identical retention time, infrared spectrum, and mass spectrum with those of an authentic sample.

Methyl *o*-(3-Carbomethoxypropyl)hydrocinnamate (2) from *cis*-6,7,10,11-Tetrahydro-5H-benzocyclononene (6). In the same manner as described above, 0.413 g (2.4 mmoles) of *cis*-6,7,10,11-tetrahydro-5H-benzocyclononene (**6**) in 600 ml of *t*-butyl alcohol was oxidized with a solution of 0.49 g (3.1 mmoles) of potassium permanganate, 4.0 g (18.7 mmoles) of sodium metaperiodate, and 1.0 g (7.2 mmoles) of potassium carbonate in 1000 ml of water. After work-up, the ether solution afforded 0.49 g of a partially solid material which was esterified with diazomethane in ether to give 338 mg of methyl *o*-(3-carbomethoxypropyl)hydrocinnamate (**2**) which was identified as above.

6,7,8,9,10,11-Hexahydro-5H-benzocyclononene (7). To a solution of 119 mg (0.69 mmole) of *cis*-6,7,10,11-tetrahydro-5H-benzocyclononene (**6**) in 15 ml of ethanol was added 30 mg of platinum oxide, and the resultant mixture was shaken with hydrogen gas at 25° (757 mm). After 15 min, the uptake of hydrogen was 110% of theory. The solution was filtered through Celite and concentrated to give 120 mg (100%) of an oil which was nearly homogeneous on vpc (10-ft × 0.25-in. 15% XF-1150, 160°). There were two minor contaminants. The major component had $\nu_{max}^{CS_2}$ 3050, 3005, 2960, 2910, 2855, 2830, 800, and 745 cm^{-1}; $\lambda_{max}^{C_2H_5OH}$ (ϵ) 212 sh (31,600), 258 sh (276), 262 sh (315), 264 (354), 268 sh (272), and 272 mμ (319); nmr (CCl$_4$): δ 7.00 (4 H, singlet), 2.74 (4 H, triplet, J = 7 cps), and 1.9–1.2 (10 H, multiplet); mass spectrum *m/e* 174 (molecular ion and base peak), 118, 117, 105, 104, and 91.

Anal. Calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.78; H, 10.22.

(+)-*trans*-Dichloro-(*trans*-6,7,10,11-tetrahydro-5H-benzocyclononene)((*R*)-α-methylbenzylamine)platinum(II) (8). A mixture of 157 mg (0.911 mmole) of *trans*-6,7,10,11-tetrahydro-5H-benzocyclononene (**1**) and 378 mg (0.911 mmole) of (+)-*trans*-dichloro(ethylene)((*R*)-α-methylbenzylamine)platinum(II)[3b,21] in methylene chloride was prepared and stirred at room temperature overnight. Removal of the solvent at reduced pressure afforded 512 mg (100%) of a partially crystalline yellow oil having $[\alpha]^{25}{}_{578}$ +17.2°, $[\alpha]^{25}{}_{546}$ +19.8°, and $[\alpha]^{25}{}_{D}$ +16.4° (calcd) (c 2.56, methylene chloride). Fractional crystallization of this material from carbon tetrachloride–

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(21) The (+)-α-methylbenzylamine used in the preparation of this complex had $[\alpha]^{25}{}_{D}$ +39.9° (neat, $d^{25}{}_{4}$ 0.9528). The optical purity of the amine was 99.3%.

cyclohexane gave 96 mg of a solid having mp 118.0–121.5°; $[\alpha]^{25}_{578}$ +39.2°, $[\alpha]^{25}_{546}$ +45.3°, and $[\alpha]^{25}_{D}$ +37.4° (calcd) (*c* 1.07, methylene chloride). The remainder of the material was in the mother liquor. The residue had $[\alpha]^{25}_{578}$ −5.0°, $[\alpha]^{25}_{546}$ −5.9°, and $[\alpha]^{25}_{D}$ −4.7° (calcd) (*c* 2.8, methylene chloride).

Anal. Calcd for $C_{21}H_{27}Cl_2NPt$: C, 45.07; H, 4.86; Cl, 12.67; N, 2.50; Pt, 34.89. Found:[22] C, 45.13; H, 5.12; Cl, 12.79; N, 2.81; Pt, 34.54.

Liberation of the Olefin 1 from Partially Resolved Complex 8 with Sodium Cyanide. A solution of 88 mg (0.155 mmole) of partially resolved complex **8** having $[\alpha]^{25}_{578}$ +2.0°, $[\alpha]^{25}_{546}$ +2.3°, and $[\alpha]^{25}_{D}$ +1.9° (calcd) (*c* 1.76, methylene chloride) was shaken with a cold (0°) solution of 15% aqueous sodium cyanide.[3b] The product was worked up as described previously.[3b] The resulting olefin (29 mg, 104%) showed no optical activity in cyclohexane solution. Vpc analysis (10-ft × 0.25-in. 15% XF-1150, 160°) indicated the presence of a slight contamination of *cis*-olefin; the major component was identified as the *trans*-olefin **1** by vpc retention time, infrared spectrum, and mass spectrum.

Liberation of the Olefin 1 from Partially Resolved Complex with Triphenylphosphine. The apparatus used was that described previously.[3d] Partially resolved complex **8** (141 mg, 0.254 mmole) having $[\alpha]^{25}_{578}$ −1.2°, $[\alpha]^{25}_{546}$ −1.4°, and $[\alpha]^{25}_{D}$ −1.1° (calcd) (*c* 7.1, methylene chloride), was dissolved in 12.5 ml of acetic anhydride, and 152 mg (0.58 mmole) of triphenylphosphine was dissolved in 12.5 ml of acetic anhydride. The two solutions were added in equal quantities as described previously.[3d] The reaction mixture was filtered through Celite into a precooled flask and the pentane layer was washed as indicated.[3d] The rotation of the pentane layer was measured at −25.5°. There was no optical activity. Removal of the pentane at reduced pressure afforded 27 mg (65%) of the *trans*-olefin **1** which was identified by vpc retention time, infrared spectrum, and mass spectrum. Vpc analysis (10-ft × 0.25-in. 15% XF-1150, 160°) showed the presence of approximately 3% of *cis*-olefin.

Variable-Temperature Nuclear Magnetic Resonance Spectra of *trans*-Olefin 1. The nuclear magnetic resonance spectrum of *trans*-olefin **1** in carbon disulfide was measured at +47, +37, −13, −25, −37, and −58°. The nuclear magnetic resonance spectrum of olefin **1** in carbon tetrachloride was measured at +107, +71, +56, and +34°. The nuclear magnetic resonance spectrum of olefin **1** in a 1:1 mixture of deuteriochloroform and acetaldehyde was measured at +14, −57, −66, and −87°. There was no change in these spectra except at the lowest temperatures where the lines become somewhat broadened. The samples were very viscous at the lowest temperatures.

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[22] The sample used for elemental analysis had $[\alpha]^{25}_{D}$ +37.4°.

Optical Properties of Hexahelicene[1]

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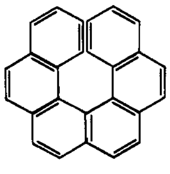
Abstract: The optical rotatory dispersion and circular dichroism spectra of (+)-hexahelicene were determined. Improvements in the synthesis are described.

Hexahelicene[3] (I) represents a classical example of an inherently dissymmetric chromophore, hence the optical properties of the resolved hexahelicene molecule can provide the basis for comparison of different theoretical treatments. To date, these analyses have restricted themselves to consideration of the sign and magnitude of the long-wavelength rotation.[4–6] However, the complexity of the problem is such that these workers have not been able to agree on the chirality of (+)-hexahelicene. Since the preliminary optical rotatory dispersion measurement[7] we have further extended these measurements to shorter wavelengths and the determination of the circular dichroism. We wish to report these results and hope they will be of value for further theoretical analysis.



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The ORD spectra have been determined in chloroform in order to allow comparison with earlier data and in methanol in order to extend the measurements to 210 mμ (Figure 1, Table II). The present chloroform curve is in good agreement with that obtained previously.[7] In the region above 250 mμ, except for small solvent shifts, the bands in both solvents are essentially identical; however, the strong negative Cotton effect associated with the 245-mμ band is clearly displayed in methanol solution. The CD and electronic absorption spectra in methanol are shown in Figure 2. The various bands in the CD can be correlated with absorption bands between 360 and 210 mμ. Interestingly of the CD bands, only the ones at 325 and 244 mμ follow approximately the CD–ORD relationship[8] derived for single transition

$$a = 0.0122 \times [\theta]$$

where *a* is the molecular amplitude of the ORD curve and $[\theta]$ is the molecular ellipticity of the CD curve (see Table I).

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