product, 9,10-dihydroxyanthracene, would be very readily oxidized to anthraquinone.[21–23] Thus, it seems that this alternative is not an important one in the reaction sequence occurring in the drier electrolysis solutions. It may, however, account for the fact that anthraquinone was obtained in appreciable amounts from electrolysis solutions which contained greater amounts of water even when the electrolysis was performed at an anode potential of +1.0 V. Apparently when the water content of the electrolysis solution is increased, the rate of the second hydrolysis reaction may be enchanced sufficiently to compete effectively with the dimerization step. A somewhat similar situation has been described by Mann and O'Donnell.[15] Anthraquinone is the principal product of the oxidation of anthracene in water solution, either by chemical or by electrochemical means.[24]

Acknowledgment. This work was supported in part by a grant from the National Science Foundation to the Institute of Research, Lehigh University, and presented at the Middle Atlantic Regional Meeting, American Chemical Society, New York, N. Y., Feb 7, 1967.

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(21) R. L. Edsberg, D. Eichlin, and J. J. Garis, *Anal. Chem.*, **25**, 798 (1953).

(22) N. H. Furman and K. G. Stone, *J. Amer. Chem. Soc.*, **70**, 3055 (1948).

(23) J. R. A. Pollock and R. Stevens, "Dictionary of Organic Compounds," Vol. 2, 4th ed, Oxford University Press, New York, N. Y., 1965, p 1049.

(24) R. S. Tipson, "Oxidation of Polycyclic, Aromatic Hydrocarbons," National Bureau of Standards Monograph 87, U. S. Department of Commerce, Washington, D. C., 1965.

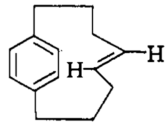
Molecular Asymmetry. VIII. *trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene[1]

Arthur C. Cope[2a] and Beverly A. Pawson[2b]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received June 30, 1967*

Abstract: *trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (**1**) has been synthesized by reduction of *trans*-bicyclo-[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione (**2**) with an excess of lithium aluminum hydride and aluminum chloride in a 1:3 ratio. Platinum complexes of the olefin **1** containing optically active α-methylbenzylamine were prepared. Fractional crystallization to constant rotation of the complex containing (*R*)-(+)-α-methylbenzylamine afforded (−)-*trans*-dichloro(*trans*-bicyclo[8.2.2.]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4a**), $[\alpha]^{25}\mathrm{D}$ −35.1°. Fractional crystallization of the enantiomeric complex containing (*S*)-(−)-α-methylbenzylamine gave complex **4b**, $[\alpha]^{25}\mathrm{D}$ +37.7°. Decomposition of partially resolved complex **4a** with aqueous sodium cyanide at room temperature afforded optically inactive olefin **1**. This observation suggests that the molecule is undergoing spontaneous racemization at this temperature.

The optical instability of *trans*-cyclononene and *trans*-cyclodecene[3] led to a consideration of suitably substituted *trans*-cyclic olefins which would possess molecular dissymmetry and which would be capable of existence as stable optically active enantiomers.[4] *trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (**1**) seemed



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a logical choice. With only eight carbon atoms bridging the *para* positions of the benzene ring, the molecule is highly strained, and rotation of the *trans*-olefinic bond with respect to the rest of the ring would be expected to be severely hindered. The olefin **1** was obtained by reduction of *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione (**2**) with an excess of lithium aluminum hydride and aluminum chloride in a 1:3 ratio.[5–7] The *trans*-enedione **2** results from oxidative cleavage of the furan ring of 15-oxatricyclo-$[8.2.2.1^{4,7}]$pentadeca-4,6,10,12,13-pentaene (**3**), the product of cross-dimerization of *p*-xylylene and 2,5-dihydro-2,5-dimethylenefuran.[8,9]

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(2) (a) Deceased, June 4, 1966; (b) National Institutes of Health Predoctoral Fellow, 1963–1966; to whom inquiries may be addressed at Hoffmann-La Roche, Inc., Nutley, N. J. 07110.

(3) A. C. Cope, K. Banholzer, H. Keller, B. A. Pawson, J. J. Whang, and H. J. S. Winkler, *J. Amer. Chem. Soc.*, **87**, 3644 (1965).

(4) For studies of the enantiomers of *trans*-cyclooctene, see (a) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *ibid.*, **85**, 3276 (1963); (b) A. C. Cope and B. A. Pawson, *ibid.*, **87**, 3649 (1965).

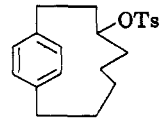
(5) (a) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, **29**, 105, 116 (1964); (b) J. H. Brewster and J. E. Privett, *J. Amer. Chem. Soc.*, **88**, 1419 (1966).

(6) J. Broome, B. R. Brown, A. Roberts, and A. M. S. White, *J. Chem. Soc.*, 1406 (1960).

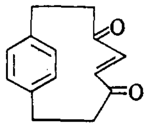
(7) B. R. Brown and A. M. S. White, *ibid.*, 3755 (1957).

(8) (a) D. J. Cram and G. R. Knox, *J. Amer. Chem. Soc.*, **83**, 2204 (1961); (b) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).

(9) The olefin **1** has been described as the product of solvolysis of bicyclo[8.2.2]tetradeca-10,12,13-trien-4-ol *p*-toluenesulfonate (a) in acetic acid.[8b]



a



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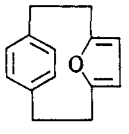

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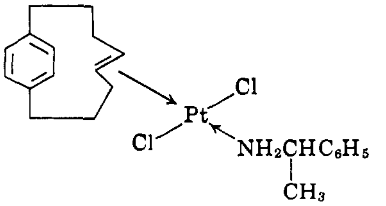
Reaction of the racemic olefin **1** with (+ or −)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II)[4a] effected displacement of the ethylene and formation of the diastereoisomeric complex (+ or −)-*trans*-dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4a** or **4b**). Fractional crystallization of the mixture of diastereoisomers containing (R)-(+)-α-methylbenzylamine from carbon tetrachloride–cyclohexane afforded as the less soluble fraction (−)-*trans*-dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4a**), having $[\alpha]^{25}{}_{578}$ −38.7°, $[\alpha]^{25}{}_{546}$ −53.6°, and $[\alpha]^{25}$D (calcd) −35.1°.[10]



4a,4b

The less soluble fraction[10] from the diastereoisomeric complex containing (S)-(−)-α-methylbenzylamine, (+)-*trans*-dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4b**) had $[\alpha]^{25}{}_{578}$ +41.3°, $[\alpha]^{25}{}_{546}$ +55.3°, and $[\alpha]^{25}$D (calcd) +37.7°.

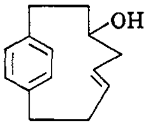
Decomposition of partially resolved complex **4a** with aqueous sodium cyanide[4a] at 0° afforded the olefin **1**, which showed no optical activity when the rotation was measured at room temperature. These results suggest that the olefin may be undergoing spontaneous racemization under the conditions used in the liberation. Similar rapid racemizations had previously been observed in the case of *trans*-cyclononene[3] and *trans*-6,7,10,11-tetrahydro-5H-benzocyclononene.[11a] A subsequent investigation[11b] of the low-temperature nuclear magnetic resonance spectrum of **1** has shown that the *trans*-olefinic bond is undergoing facile rotation with respect to the remainder of the molecule at room temperature, with a rate constant which is consistent with the failure to obtain optically active olefin **1** under the conditions used in the decomposition of the platinum complex.

The benzene–furan dimer **3** was prepared in 21% yield as described previously.[8b] Treatment of **3** with bromine in methanol at −30° followed by hydrolysis under acidic conditions afforded the *trans*-enedione **2** in 48% yield.[12,13] Reduction of the keto groups in the *trans*-enedione **2** to methylene groups without changing the stereochemistry or position of the double bond would afford the desired olefin **1**. Reduction of the *trans*-enedione **2** directly with an excess of lithium aluminum hydride and aluminum chloride in a 1:3 ratio[5-7] afforded two products in 70–85% total yield. The predominant product (52%), isolated by column chromatography on alumina by elution with pentane, was an unsaturated hydrocarbon of the expected molecular composition which was shown by spectral and chemical evidence to be the desired olefin **1**. The infrared spectrum had a strong absorption at 970 cm^{-1} assignable to *trans*-HC=CH;[14] the mass spectrum had a molecular ion at m/e 186 and other major fragmentation peaks at m/e 145, 118, 117, 104, and 91. The nuclear magnetic resonance spectrum of the olefin **1** consisted of a singlet at δ 6.77 for the four aromatic protons, a broad singlet at δ 3.72 for the olefinic protons, a broad singlet at δ 2.5 assigned to the benzylic protons, and a broad unsymmetrical band at δ 1.8–1.3 for the remaining eight allylic and saturated protons.

The interpretation of the nmr spectrum was confirmed by the spectrum of the olefin **1** with deuterium incorporated into the allylic positions. This compound, having 90% d_4 incorporation, was obtained by reduction of the enedione **2** with lithium aluminum deuteride–aluminum chloride and work-up with deuterium oxide. The deuterium-decoupled nmr spectrum (in δ values) of this olefin displayed a singlet for the aromatic protons at 6.87, a sharp singlet for the olefinic protons at 3.84, a triplet at 2.57 for the benzylic protons, and a four-proton triplet at 1.65 for the saturated protons.

Oxidation of the olefin **1** with sodium metaperiodate–potassium permanganate[15,16] in *t*-butyl alcohol afforded a crystalline acid in quantitative yield. The dimethyl ester of this dicarboxylic acid had identical vapor phase chromatographic retention time and infrared and mass spectra with that of an authentic sample of the dimethyl ester of p-benzenedibutyric acid.[17]

Further elution of the alumina chromatography column (which had given the olefin **1** upon elution with pentane) with ether afforded 22% of an unsaturated alcohol of mol w 202 (mass spectrometer). Based on chemical and spectral evidence this material was assigned the structure of the homoallylic alcohol, *trans*-bicyclo[8.2.2]tetradeca-6,10,12,13-tetraen-4-ol (**5**). Oxidation with chromic acid in acetone at 0° (Jones' reagent) afforded in 80% yield the β,γ-unsaturated ketone, *trans*-bicyclo[8.2.2]tetradeca-6,10,12,13-tetraen-4-one (**6**), which had infrared absorption at 1695 and 965 cm^{-1} and a maximum in the ultraviolet spectrum at 226 mμ with an absorption intensity of 5900. Upon column chromatography on Woelm alumina this material was isomerized to the α,β-un-



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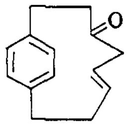

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[10] The complexes **4a** and **4b** were recrystallized to constant rotation.

[11] (a) A. C. Cope and M. W. Fordice, *J. Amer. Chem. Soc.*, **89**, 6187 (1967); (b) G. M. Whitesides, B. A. Pawson, and A. C. Cope, *ibid.*, **90**, 639 (1968).

[12] J. Levisalles, *Bull. Soc. Chim. France*, 997 (1957).

[13] The *cis*-enedione has been obtained when the hydrolysis was carried out under neutral conditions.[8b]

[14] K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 24.

[15] R. U. Lemieux and E. von Rudloff, *Can. J. Chem.*, **33**, 1701 (1955).

[16] E. von Rudloff, *ibid.*, **34**, 1413 (1956).

[17] The authentic sample of p-benzenedibutyric acid was kindly provided by Professor D. J. Cram. The material was prepared by the procedure described in D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Amer. Chem. Soc.*, **76**, 6132 (1954).

saturated ketone,[8b] which had infrared absorption at 1680, 1610, 990, and 960 cm^{-1} and an ultraviolet maximum at 222 mμ with an absorption intensity of 14,350. The mass spectra of these ketones showed them to be isomeric, but their fragmentation patterns were different.

The nuclear magnetic resonance spectrum of the unsaturated alcohol **5** exhibited an unsymmetrical doublet with additional fine splitting at δ 7.0 and 6.85 for the four aromatic protons. The olefinic protons exhibited a complex pattern of twelve lines with additional fine structure between δ 4.98 and 3.85. The remaining twelve protons showed a complex absorption between δ 3.3 and 1.0. The hydroxyl proton appeared as a sharp singlet at δ 2.4. This signal disappeared upon exchange with deuterium oxide.

The nuclear magnetic resonance spectrum of the β,γ-unsaturated ketone **6** exhibited an AB pattern centered at δ 6.95 for the four aromatic protons. The olefinic protons displayed a symmetrical ten-line pattern between δ 5.0 and 4.0. The remaining ten protons showed a complex absorption between δ 3.0 and 1.75. The presence of a methylene group on either side of the double bond is suggested by the symmetrical nature of the absorption pattern for the olefinic protons.

Experimental Section[18]

***trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (1) and *trans*-Bicyclo[8.2.2]tetradeca-6,10,12,13-tetraen-4-ol (5).** In a 200-ml three-necked, round-bottomed flask fitted with a mechanical stirrer, reflux condenser, and drying tube, 1.9 g (50 mmol) of lithium aluminum hydride was stirred with 20 ml of anhydrous ether. The mixture was cooled in an ice bath and a cooled (0°) solution of 19.8 g (150 mmol) of anhydrous aluminum chloride in approximately 30 ml of ether was added. The solid enedione **2**[8,19] (1.07 g, 5 mmol) was added all at once. The mixture was heated to the reflux temperature for 2 hr. The reaction mixture was then cooled with an ice bath, and the excess hydride was decomposed by cautious addition of ethyl acetate. Sufficient water was then added, and stirring was continued until the reaction mixture consisted of two liquid phases. The ether layer was separated, and the aqueous phase was extracted three times with ether. The combined ether extracts were washed with water and dried with anhydrous magnesium sulfate. After removal of the ether, the residue was purified by column chromatography on 50 g of Woelm alumina (activity II).

Elution with olefin-free pentane afforded 0.483 g (52%) of *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene (**1**) in the first two 100-ml fractions. The olefin, which was homogeneous on vapor phase chromatography (8 ft × 0.25 in. 5% silicone rubber column, 130°), had $\nu_{\max}^{CS_2}$ 3070, 3030, 3005, 2960, 2910, 2875, 2850, 2810, 975, 950, 920, and 800 cm^{-1}; $\nu_{\max}^{CCl_4}$ 3070, 3030, 3010, 2960, 2920, 2880, 2850, 2825, 1610, 975, 950, and 920 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ mμ (ϵ) 224 (6820), 266 sh (320), 272 (420), and 278 (390); *m/e* 186 (M$^+$), 145, 118, 117, 104 (base peak), and 91; nmr spectrum (CCl$_4$) δ 6.77 (4 H, singlet), 3.72 (2 H, broad singlet), 2.5 (4 H, broad singlet), and 1.8–1.3 (8 H, broad unsymmetrical band).

Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.44; H, 9.65.

Elution with ether afforded 217 mg (22%) of the unsaturated alcohol **5**. After two recrystallizations from cyclohexane, this material had mp 111.5–114.5°; $\nu_{\max}^{CHCl_3}$ 3590, 3410, 1020, and 965 cm^{-1}; $\lambda_{\max}^{EtOH}$ mμ (ϵ) 231 (6200), 272 sh (300), 277 (380), and 289 (330); *m/e* 202 (M$^+$), 184, 147, 118, 104 (base peak), and 91; nmr spectrum (CDCl$_3$) δ 7.0 and 6.85 (4 H, unsymmetrical doublet with additional fine splitting), 4.98–3.85 (2 H, 12 lines with additional fine structure), and 3.3–1.0 (12 H, complex multiplet). The hydroxyl proton appeared as a sharp singlet at δ 2.4. This signal disappeared upon addition of deuterium oxide.

Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.09; H, 9.06.

***trans*-Bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-4,4,7,7-*d*$_4$.** A 214-mg sample of the enedione **2** was treated as described above with 380 mg of lithium aluminum deuteride and 3.7 g of aluminum chloride in anhydrous ether. After refluxing, the reaction mixture was cooled and the excess deuteride decomposed with deuterium oxide. The mixture was worked up as described above and purified by chromatography on alumina (activity II) and elution with olefin-free pentane. Chromatography fraction 1 (100 ml) afforded 101 mg of the deuterated olefin **1**; $\nu_{\max}^{CS_2}$ 3070, 3030, 3000, 2905, 2845, and 960 cm^{-1}; nmr spectrum (with deuterium decoupling) (CDCl$_3$) δ 6.87 (4 H, singlet), 3.84 (2 H, sharp singlet), 2.57 (4 H, triplet, J = 6.5 cps), and 1.65 (4 H, triplet, J = 6.5 cps). The deuterium content was calculated from the mass spectrum[20] to be 1.5% d_0, 0.6% d_1, 1.4% d_2, 6.3% d_3, and 90.0% d_4.

***p*-Benzenedibutyric Acid Dimethyl Ester.** The olefin **1** (55 mg) was oxidized with 0.936 g of sodium metaperiodate and 15.8 mg of potassium permanganate in the presence of 50 mg of potassium carbonate in 200 ml of 30% aqueous *t*-butyl alcohol according to the procedure of Lemieux and von Rudloff.[15,16] Removal of the ether afforded a quantitative yield of a crystalline solid which had mp 167–171°. (An authentic sample of *p*-benzenedibutyric acid[17] had mp 174–177°.)

The dicarboxylic acid was converted without further purification to the dimethyl ester with diazomethane. The dicarboxylic acid ester obtained from the oxidation of the olefin **1** (which was homogeneous on vapor phase chromatography) and that prepared from an authentic sample of the dicarboxylic acid[17] had identical retention times on vapor phase chromatography (8 ft × 0.25 in. 5% silicone rubber column, 165°) and identical infrared and mass spectra.

***trans*-Bicyclo[8.2.2]tetradeca-6,10,12,13-tetraen-4-one (6).** The unsaturated alcohol **5** (303 mg, 1.5 mmol) was oxidized with Jones' reagent[21,22] in acetone at 0° for 10 sec. The product (238 mg, 80%), which was shown by vapor phase chromatography [2 ft × 0.25 in. 20% XF-1150 (silicone fluid, nitrile) column, 170°] to consist of greater than 95% of one component, was purified by sublimation at 25° (0.1 mm). The colorless crystals had mp 39.0–40.5°; $\nu_{\max}^{CHCl_3}$ 1695, 1435, and 965 cm^{-1}; $\lambda_{\max}^{EtOH}$ mμ (ϵ) 226 (5900), 267 sh (315), 275 (380), and 282 (340); *m/e* 200 (M$^+$) and 104 (base peak); nmr spectrum (CDCl$_3$) δ 6.95 (4 H, AB pattern), 5.0–4.0 (2 H, symmetrical ten-line pattern), and 3.0–1.75 (10 H, complex multiplet).

Anal. Calcd for $C_{14}H_{10}O$: C, 83.96; H. 8.05. Found: C, 83.69; H, 7.95.

Chromatography of the β,γ-unsaturated ketone described above on Woelm alumina (activity I) gave the α,β-unsaturated ketone, mp 55–57° (lit.[8b] mp 56–57°); $\lambda_{\max}^{EtOH}$ mμ (ϵ) 222 (14,350), 244 (6070), and 277 sh (1740); *m/e* 200 (M$^+$ and base peak), 131, 117, 104, and 91.

(−)-*trans*-Dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (4a). The olefin **1** (0.830 g, 4.4 mmol) in pentane solution was added to a stirred methylene chloride solution of 1.82 g (4.4 mmol) of (+)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II).[4a,23] The mixture was stirred at room temperature for 2 hr, and the solvent was removed at reduced pressure with a rotary evaporator. The resulting yellow oil was dissolved in a minimum amount of benzene and cyclohexane was added until the cloud point was reached. Upon cooling to −20°, yellow crystals formed. Three such prep-

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(18) Melting points were taken on a Kofler hot stage; boiling points are uncorrected. Infrared spectra were recorded on Perkin-Elmer Models 237B and 337 grating spectrophotometers; ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. Nmr spectra were measured on a Varian Associates A-60 instrument, and deuterium-decoupling experiments were carried out using an NMR Specialties Model HD-60A heteronuclear decoupler. Mass spectra were measured on a Hitachi Perkin-Elmer Model RMU-6D mass spectrometer. Optical rotations were measured with a Zeiss photoelectric precision polarimeter. Rotations measured at 546.1 and 577.8 mμ were used to calculate the value at the sodium D line (589.2 mμ). Analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., and Dr. S. M. Nagy and associates. Vapor phase chromatographic analyses were performed on a F & M Model 720 gas chromatograph with helium at a flow rate of 1 cc/sec as carrier gas.

(19) This compound was prepared from the benzene–furan dimer[8] **3** according to the procedure described in ref 12.

(20) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co. Inc., New York, N. Y., 1962, p 223 ff.

(21) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(22) C. Djerassi, R. R. Engle, and A. Bowers, *J. Org. Chem.*, **21**, 1547 (1956).

(23) The (*R*)-(+)-α-methylbenzylamine used in the preparation of this complex had $[\alpha]^{25}$D +39.93° (neat, $d^{25}{}_4$ 0.9528).

arations were combined (7.1 g, 12.4 mmol) and after three recrystallizations from benzene–cyclohexane had mp 135–139°; $[\alpha]^{25}{}_{578}$ +13.4°, $[\alpha]^{25}{}_{546}$ +15.3°, and $[\alpha]^{25}{}_{\mathrm{D}}$ (calcd) +12.7° (*c* 2.54, methylene chloride).

Fractional crystallization of this material from carbon tetrachloride–cyclohexane afforded as the less soluble fraction (−)-*trans*-dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4a**) as yellow crystals having mp 140.5–141.5°; $[\alpha]^{25}{}_{578}$ −38.7°, $[\alpha]^{25}{}_{546}$ −53.6°, and $[\alpha]^{25}{}_{\mathrm{D}}$ (calcd) −35.1° (*c* 1.11, methylene chloride) after seven recrystallizations.[10]

Anal. Calcd for $C_{22}H_{29}Cl_2NPt$: C, 46.07; H, 5.10; Cl, 12.38; N, 2.44; Pt, 34.00. Found: C, 46.56; H, 5.33; Cl, 12.30; N, 2.53; Pt, 34.26.

(+)-*trans*-Dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (4b). The olefin **1** (0.90 g, 4.8 mmol) in pentane solution was added to a stirred methylene chloride solution of 1.99 g (4.8 mmol) of (−)-*trans*-dichloro(ethylene)(α-methylbenzylamine)platinum(II).[4a,24] The mixture was treated as described above for the complex with (*R*)-(+)-α-methylbenzylamine. Three such preparations were combined (7.0 g, 12.1 mmol) and after three recrystallizations from benzene–cyclohexane had $[\alpha]^{25}{}_{578}$ −13.1°, $[\alpha]^{25}{}_{546}$ −15.3°, and $[\alpha]^{25}{}_{\mathrm{D}}$ (calcd) −12.3° (*c* 1.53, methylene chloride).

Fractional crystallization of this material from carbon tetrachloride–cyclohexane afforded as the less soluble fraction (+)-*trans*-dichloro(*trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene)(α-methylbenzylamine)platinum(II) (**4b**) as yellow crystals having mp 141.5–143.0°; $[\alpha]^{25}{}_{578}$ +41.3°, $[\alpha]^{25}{}_{546}$ +55.3°, and $[\alpha]^{26}{}_{\mathrm{D}}$ (calcd) +37.7° (*c* 1.04, methylene chloride) after eight recrystallizations.[10]

Anal. Calcd for $C_{22}H_{29}Cl_2NPt$: C, 46.07; H, 5.10; Cl, 12.38; N, 2.44; Pt, 34.00. Found: C, 46.69; H, 5.24; Cl, 12.97; N, 2.42; Pt, 32.69.

Liberation of the Olefin 1 from Partially Resolved Complex 4a. Partially resolved complex **4a** (81 mg, 0.14 mmol) having $[\alpha]^{25}{}_{578}$ −19.7°, $[\alpha]^{25}{}_{546}$ −29.6°, $[\alpha]^{25}{}_{\mathrm{D}}$ (calcd) −17.6° (*c* 1.01, methylene chloride), in a few milliliters of methylene chloride at 0° was shaken with a cold (0°) solution of 15% (by wt) aqueous sodium cyanide.[4a] After separation of the methylene chloride layer, the aqueous phase was washed with three 20-ml portions of olefin-free pentane. The combined pentane–methylene chloride extracts were washed with 10 ml of cold 10% hydrochloric acid, with water, with three 20-ml portions of saturated sodium bicarbonate, and finally with three 10-ml portions of water. The solution was dried with anhydrous magnesium sulfate and the solvent was removed at reduced pressure on the rotary evaporator. The resulting olefin (23 mg, 88%) in cyclohexane solution showed no optical activity. The vapor phase chromatographic retention time and infrared and mass spectra established the identity of this material as olefin **1**.

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(24) The (*S*)-(−)-α-methylbenzylamine used in the preparation of this complex had $[\alpha]^{25}{}_{\mathrm{D}}$ −38.87° (neat, $d^{25}{}_{4}$ 0.9528).

Hindered Rotation in Substituted Paracyclophanes[1]

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Abstract: The rates and activation parameters describing the interconversion of enantiomers of 15-oxatricyclo-[8.2.2.1^{4,7}]pentadeca-4,6,10,12,13-pentaene-11,13-d_2 (**3**) (E_a = 11.1 ± 0.3 kcal/mol, $A = 10^{12.5\pm0.3}$ sec^{-1}), bicyclo-[8.2.2]tetradeca-10,12,13-triene-4,7-dione-3,3,5,5,6,6,8,8,11,13-d_{10} (**4**) (E_a = 9.3 ± 0.7 kcal/mol, $A = 10^{11.7\pm0.7}$ sec^{-1}), *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-4,7-dione-3,3,8,8,11,13-d_6 (**5**) (E_a = 11.2 ± 0.5 kcal/mol, $A = 10^{12.1\pm0.5}$ sec^{-1}), and *trans*-bicyclo[8.2.2]tetradeca-5,10,12,13-tetraene-3,3,5,6,8,8,11,13-d_8 (**7**) (E_a = 13.4 ± 0.7 kcal/mol, $A = 10^{12.7\pm0.5}$ sec^{-1}) have been measured using nmr spectroscopy. These data provide an instructive example of the influence of structural variation on the rates of medium-ring conformational isomerization and a practical check on the precision of kinetic analysis of spin-coupled nmr spectra.

The conformational analysis of medium-ring cycloalkanes has contributed extensive and useful information to the study of the influence of nonbonded interactions and bond-angle deformations on the properties of organic molecules.[3] Of the available spectroscopic techniques, nuclear magnetic resonance has proved to be the best suited for the direct examination of the conformations of this class of compounds in solution. The nmr spectra of these materials are usually very complicated, and in many instances it has been more convenient to investigate the simpler spectra of appropriately substituted medium-ring compounds than the more complex spectra of their unsubstituted parents. In consequence, a number of recent investigations have relied in part on nmr measurements of the rates of interconversion between conformers of substituted cyclic hydrocarbons to provide detailed information concerning not only the structures of these materials themselves, but also by inference information concerning the structures of their unsubstituted analogs.[4,5] The interpretation of these studies has been complicated by difficulties in isolating the effects of the substituents on the rates, and by uncertainty concerning the extent to which the substituents are capable of influencing the geometry of the con-

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(3) For recent examples and references see (a) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **86**, 4854 (1964); (b) K. B. Wiberg, *ibid.*, **87**, 1070 (1965); (c) M. Saunders, *Tetrahedron*, **23**, 2105 (1967); (d) M. Bixon, H. Dekker, J. D. Dunitz, H. Eser, S. Lifson, C. Mosselman, J. Sicher, and M. Svoboda, *Chem. Commun.*, 360 (1967), and references therein; (e) A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), **20**, 119 (1966); (f) J. Sicher, *Progr. Stereochem.*, **3**, 202 (1962); (g) M. Hanack, "Conformation Theory," Academic Press Inc., New York, N. Y., 1965, p 164 ff; (h) J. Dale, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1000 (1966).

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