

acetic acid. The resulting oil was separated by decantation, and gradually crystallized on standing. Recrystallization from hexane gave 6-amy1-3-cyano-2(1)-pyridone (Vc), m.p. 99–100.5° (reported¹⁴ m.p. 95–96°).

Preparation of Triacylbenzenes VIa–b from Monocarbanions IIIa–b.—An aqueous solution of monocarbanion IIIa, obtained from 0.052 mole of dicarbanion II and 0.052 mole of benzyl chloride, was acidified with hydrochloric acid. The liberated β -ketoaldehyde was taken up in ether and 10 ml. of glacial acetic acid was added. The acidified ethereal solution was warmed and then allowed to stand to room temperature for 24 hr. The solvent was evaporated and the residue was recrystallized from methanol to give 2.4 g. (29% based on I) of 1,3,5-tris-(3-phenylpropionyl)-benzene, m.p. 114–117°. Another recrystallization from methanol raised the m.p. to 121.5–122.5°, reported¹⁸ m.p. 122°.

A solution of monocarbanion IIb, obtained from 0.12 mole of dicarbanion II and 0.13 mole of methyl iodide, was acidified with acetic acid, heated 12 hr. at 60°, and then allowed to stand at room temperature for 3 days. A precipitate formed which was removed by filtration and recrystallized from hexane to give 2.7 g. (27% based on I) of 1,3,5-tripropionylbenzene (VIb), m.p. 66–69°. Chromatography of a pentane solution of VIb on alumina raised the m.p. to 71–73°, reported¹⁹ m.p. 74–75°.

Independent Synthesis of Monocarbanion IIIa, Copper Chelate IVa, and Cyanopyridone Va.—To a stirred suspension of 2.70 g. (0.05 mole) of sodium methoxide in 200 ml. of anhydrous ether was added a mixture of 7.40 g. (0.05 mole) of 4-phenyl-2-butanone and 3.70 g. (0.05 mole) of ethyl formate.^{7,8} The reaction mixture was allowed to stand at room temperature with occasional shaking for 6 hr., during which a thick suspension of IIIa appeared. Copper chelate IVa was isolated in the same manner as above. The crude chelate was blue-green, m.p. 164–170°, indicating the presence of some of the chelate of VIII. One recrystallization from chloroform-ethanol gave 4.35 g. (42%) of chelate IVa, m.p. 173–175° and 173–176° after two more recrystallizations. Although the recrystallized chelate was blue-green, while that prepared *via* the dicarbanion was blue, a mixture melting point of the two samples was undepressed and their infrared spectra were essentially identical.

A portion of the purified chelate IVa, m.p. 173–176°, was decomposed with dilute hydrochloric acid, and the liberated β -ketoaldehyde was taken up in ether. The ethereal solution was extracted with cold dilute sodium hydroxide solution, and the alkaline extract was neutralized to pH 8. This solution was treated with cyanoacetamide to give cyanopyridone Va, m.p. 193–198° after one recrystallization from water. Further recrystallization from ethanol gave m.p. 204–205°, reported⁷ m.p. 198°. A mixture m.p. with Va (m.p. 204–205°) prepared above was undepressed.

2-Benzyl-1,3-butanedione (IX).—4-Phenyl-2-butanone was acylated with ethyl formate in ethanol solution by the method of Roch⁹ to give β -ketoaldehyde IX, m.p. 99–101°, reported m.p. 100–101°.

Preparation of Dicarbanion X.—To a stirred solution of 0.24 mole of potassium amide, prepared from 9.4 g. of potassium, in 250 ml. of liquid ammonia was added 15.8 g. (0.09 mole) of 2-benzyl-1,3-butanedione in 100 ml. of tetrahydrofuran. After

stirring for 90 min., formation of dicarbanion X was assumed to be complete.

Benzylation of Dicarbanion X.—To a suspension of 0.09 mole of dicarbanion X in a mixture of liquid ammonia and tetrahydrofuran was added 35 g. (0.278 mole) of benzyl chloride and the mixture stirred for 2 hr. The ammonia was evaporated and the tetrahydrofuran removed under reduced pressure. The residue was taken up in ice water and excess benzyl chloride and any neutral products were removed by extraction with ether. The aqueous solution was acidified with acetic acid and extracted three times with ether. The ethereal extracts were combined and dried. Distillation at reduced pressure gave initially several grams of starting β -ketoaldehyde IX, which crystallized in the column, followed by 12.1 g. (51%) of 2-benzyl-5-phenyl-1,3-butanedione (XIIa), b.p. 170–173° at 0.6 mm.

Anal. Calcd. for C₁₈H₁₈O₂: C, 81.17; H, 6.81. Found: C, 81.31; H, 6.95.

Ketoaldehyde XIIa gave a violet enol test with ferric chloride and the infrared spectrum showed an enol band at 6.18 μ .

Treatment of XIIa with copper acetate solution gave a green copper chelate, m.p. 163–164° after three recrystallizations from ethanol.

Anal. Calcd. for C₃₆H₃₄O₄Cu: C, 72.77; H, 5.77; Cu, 10.69. Found: C, 72.59; H, 5.93; Cu, 10.60.

Alkaline hydrolysis of a sample of undistilled reaction product XIIa gave 1,5-diphenyl-3-pentanone (XIII), b.p. 152–154° at 0.6 mm., in 50% yield. Vapor phase chromatography showed the presence of XIII and 4-phenyl-2-butanone, which presumably arose from starting material. The semicarbazone of XIV melted at 115–117° after three recrystallizations from 80% ethanol, reported¹⁹ m.p. 120–121°.

Butylation of Dicarbanion X.—To a solution of 0.1 mole of dicarbanion X in a mixture of ammonia and tetrahydrofuran was added 40.0 g. (0.29 mole) of *n*-butyl bromide. After 6 hr., the ammonia was evaporated and ether and water were added. The aqueous layer was separated and acidified with cold dilute hydrochloric acid. The acidified mixture was extracted with ether and the combined ether extracts dried. Most of the solvent was removed to precipitate 7.0 g. (40%) of starting β -ketoaldehyde IX, which crystallized out and was removed by filtration. The remainder of the solvent was removed from the filtrate, and the residue distilled to give 2.5 g. (14%) more β -ketoaldehyde IX, b.p. 95–100° at 0.4 mm., and 6.2 g. (27%) of 2-benzyl-1,3-octanedione (XIIb), b.p. 125–140° at 0.4 mm.

Anal. Calcd. for C₁₅H₂₀O₂: C, 77.55; H, 8.68. Found: C, 77.74; H, 8.98.

Ketoaldehyde XIIb gave a violet enol test with ferric chloride solution and the infrared spectrum indicated the presence of an enol structure.

Treatment of XXIIb with cyanoacetamide in the same manner as above gave pyridoneamide XIV, m.p. 195–197° after recrystallization from acetone. The infrared spectrum showed no nitrile band near 4.5 μ but showed amide absorption at 3.02 and 3.18 μ .

Anal. Calcd. for C₁₈H₂₂N₂O₂: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.79; H, 7.32; N, 9.58.

(19) W. F. Charnick and J. B. Data, *J. Am. Pharm. Assoc.*, **45**, 65 (1956).

(18) M. Roch, *Bull. soc. chim. France*, **12**, 10 (1945).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

Molecular Asymmetry of Olefins. I. Resolution of *trans*-Cyclooctene¹⁻³

BY ARTHUR C. COPE, C. R. GANELLIN, H. W. JOHNSON, JR., T. V. VAN AUKEN,⁴ AND HANS J. S. WINKLER

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Resolution of *trans*-cyclooctene has been accomplished through platinum complexes containing optically active α -methylbenzylamine. Separate fractional crystallizations of *trans*-dichloro-(*trans*-cyclooctene)-[(+ or -)- α -methylbenzylamine]-platinum(II) were carried out to constant rotation. The complexes were destroyed with aqueous potassium cyanide, yielding optically active (-) and (+)-*trans*-cyclooctene. This novel type of asymmetry demonstrates the inability of the *trans*-olefinic linkage to rotate with respect to the rest of the molecule.

Molecular asymmetry due to restriction of rotation about a pivot bond has been well documented in bi-

(1) For preceding communications on this subject see: (a) A. C. Cope, C. F. Howell, and A. Knowles, *J. Am. Chem. Soc.*, **84**, 3190 (1962); (b) A. C. Cope, C. R. Ganelin, and H. W. Johnson, Jr., *ibid.*, **84**, 3191 (1962).

(2) This work has appeared in part in a brief communication, ref. 1b.

(3) Supported in part by the Army Research Office (Durham) under Grant No. DA-ARO-D-31-124-G240.

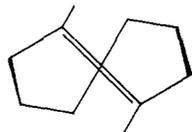
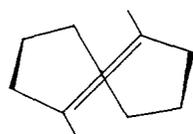
phenyl compounds suitably substituted with bulky substituents.⁵ In the cyclophane series, molecular asymmetry has been demonstrated more recently.⁶

(4) National Science Foundation Postdoctoral Fellow, 1961–1962.

(5) (a) R. Adams and H. C. Yuan, *Chem. Rev.*, **12**, 211 (1931); (b) R. L. Shriner and R. Adams in H. Gilman, Ed., "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 343–382.

This type of asymmetry arises from the inability of part of a ring, a substituted benzene nucleus in all cases, to rotate with respect to the rest of the molecule.⁷

It has been suggested that *trans*-cyclic olefins of intermediate size (8–10 membered rings) should be capable of existence in stable enantiomorphous conformations.⁸ The molecular asymmetry of *trans*-cyclic olefins depends on the inability of the *trans*-olefinic bond to rotate with respect to the remainder of the molecule; see **1a** and **1b**. Presupposing a fixation of

**1a****1b**

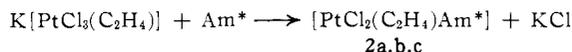
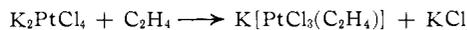
the double bond (roughly with the plane of the sp^2 -hybridized bonds perpendicular to the "plane" of the methylene groups) it may be seen from the figure and confirmed by inspection of models that the mirror images **1a** and **1b** are nonsuperimposable. Conversion of one enantiomorph of a *trans*-cycloalkene into its mirror image involves rotation by 180° of the plane containing the sp^2 -hybridized carbon bonds. The ease with which this rotation can occur depends on the ease with which the hydrogen atoms bonded to the olefinic linkage can pass through the loop of the methylene groups. It is evident that the ease of racemization will increase as the nonclassical strain (nonbonded interactions) decreases, or the larger the methylene bridge is.

The particular difficulty in attempting resolution of *trans*-cycloalkenes is due to the absence of groups suitable for the direct formation of a diastereoisomeric pair of compounds by reaction of such a group with an optically active compound. The ease with which strained *trans*-cycloalkenes isomerize to *cis*-cycloalkenes⁹ likewise discourages schemes of resolution requiring attachment and subsequent removal from the ring of such a group.

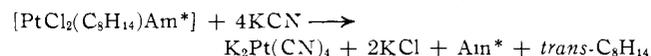
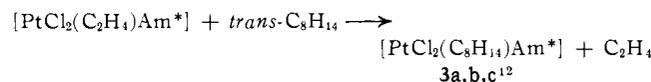
It has now been found that the strong complexing tendency of *trans*-cycloalkenes with platinum may be used in a method of resolution that should be general. Olefins are known to form coordination compounds with platinum.^{10,11} The resolution of *trans*-cyclooctene has been accomplished through the formation of a diastereoisomeric pair of platinum(II) complexes con-

taining the olefin and optically active (+ or -)- α -methylbenzylamine. The difference in solubility of the diastereoisomers makes a separation by fractional crystallization possible. The olefin is recovered by the ready decomposition of the platinum complex with aqueous potassium cyanide under conditions which do not cause *cis*-*trans* isomerization of the *trans*-cyclooctene. This resolution scheme does not intrinsically depend on the geometry of the platinum complex, square-planar dsp^2 -hybridization, but rather on the convenience of attaching both the olefin and the amine to the platinum atom and the subsequent readiness with which these can be removed.

The coordination chemistry involved in this resolution scheme is outlined below.



(a) $Am^* = (+)$ - $C_6H_5CH(CH_3)NH_2$; (b) $Am^* = (-)$ - $C_6H_5CH(CH_3)NH_2$; (c) $Am^* = (+)$ - $C_6H_5CH_2CH(CH_3)NH_2$



Zeise's salt,¹³ potassium trichloro-(ethylene)-platinate(II) was prepared from ethylene and potassium tetrachloroplatinate(II). This salt on reaction with (+)- α -methylbenzylamine in aqueous medium yielded **2a**, (+)-*trans*-dichloro-(ethylene)-(α -methylbenzylamine)-platinum(II). This compound was generally obtained as a viscous oil, but the infrared spectrum and specific rotation were identical with those of a crystalline sample. Purification of the compound by chromatography has been shown to give crystalline material.¹⁴ An olefin-exchange reaction is a well-known route to olefin-platinum complexes.¹⁵ In this case the ethylene was readily displaced by *trans*-cyclooctene to give **3a**, **3b**, or **3c**.¹⁶ The crude complex of type **3a** is a mixture of the diastereoisomers *trans*-dichloro-[($-$)-*trans*-cyclooctene]-[($+$)- α -methylbenzylamine]-platinum(II)¹⁷ (**3a'**),¹² which is dextrorotatory, and *trans*-dichloro-[($+$)-*trans*-cyclooctene]-[($+$)- α -methylbenzylamine]-platinum(II) (**3a''**), which is levorotatory with an angle of smaller absolute magnitude. The less soluble isomer **3a'** can readily be obtained by fractional crystallization to constant rotation, $[\alpha]^{25D} +67^\circ$, from carbon tetrachloride.¹⁸ However, since it proved difficult to obtain the more soluble isomer **3a''** from the mother liquors, the enantiomorph of the less soluble fraction, **3b'**, $[\alpha]^{21.5D} -68.2^\circ$, was prepared

(12) In this discussion the least soluble fraction of the diastereoisomeric pairs **3a**, **3b**, and **3c** will be designated **3a'**, **3b'**, and **3c'** and the more soluble fraction **3a''**, **3b''**, and **3c''**.

(13) W. C. Zeise, *Pogg. Ann.*, **9**, 632 (1827).

(14) A. C. Cope and H. J. S. Winkler, unpublished studies.

(15) (a) J. R. Joy and M. Orchin, *J. Am. Chem. Soc.*, **81**, 305, 310 (1959); (b) J. S. Andersen, *J. Chem. Soc.*, 971 (1933); (c) A. H. Gelman, *Compt. rend. Acad. Sci., URSS*, **22**, 347 (1941).

(16) Only one previously reported example of an olefin exchange reaction in an amine-olefin-platinum complex was found.^{15c}

(17) The first "trans" in this name refers to the configuration of the square-planar platinum complex, the configuration of the chloro ligands being *trans*. A complex containing two chlorine atoms in the *cis*-position in the ligand square of the platinum(II) would have a dipole moment of approximately 10 D. The dipole moment of the olefin complex (+)-dichloro-(*trans*-cyclooctene)-(α -methylbenzylamine)-platinum(II), **3a'**, was found to be 1.63 ± 0.06 D, proving the *trans* configuration of the platinum complex. We wish to express our appreciation to Professors Norman L. Allinger and Norman A. LeBel of Wayne State University for determining the dipole moments.

(18) See ref. 6, p. 83, for a discussion of this and other criteria of optical purity.

(6) For a general discussion of molecular asymmetry see: E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 156–179.

(7) A. T. Blomquist, R. E. Stahl, Y. C. Meinwald, and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961), and references quoted therein.

(8) (a) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *J. Am. Chem. Soc.*, **74**, 3643 (1952); (b) V. Prelog in Sir A. Todd, Ed., "Perspectives in Organic Chemistry," Interscience Publ., Inc., New York, N. Y., 1956, p. 129.

(9) A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).

(10) For reviews of such complexes see: (a) R. N. Keller, *Chem. Rev.*, **28**, 229 (1941); (b) J. Chatt, *Ann. Rept. Progr. Chem.* (Chem. Soc. London), **43**, 120 (1946); (c) J. Chatt in P. H. Plesch, Ed., "Cationic Polymerization," W. Heffer and Sons, Cambridge, Eng., 1953, p. 40; (d) B. E. Douglas in J. C. Bailar, Jr., Ed., "The Chemistry of Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 487–508.

(11) For discussions of olefin-platinum complexes see: A. A. Babushkin, L. A. Gribov, and A. D. Gelman, *Russ. J. Inorg. Chem.*, **4**, 695 (1959); D. M. Adams and J. Chatt, *Chem. Ind.* (London), 149 (1960).

by a similar procedure using $(-)\alpha$ -methylbenzylamine.

The enantiomorphs of *trans*-cyclooctene were liberated separately by decomposition of the less soluble platinum complexes **3a'** and **3b'** with aqueous potassium cyanide and subsequent removal of the amine by extraction from the organic layer with acid. The enantiomorphs of *trans*-cyclooctene, $[\alpha]^{25D} - 458^\circ$ (from **3a'**) and $[\alpha]^{25D} + 440^\circ$ (from **3b'**), were obtained by distillation at room temperature under reduced pressure. Each optical isomer of *trans*-cyclooctene was identified by comparison (infrared spectrum and gas-chromatographic retention time under conditions which separate *cis*- and *trans*-cyclooctene), by elemental analysis, and by hydrogenation to optically inactive cyclooctane. Loss of optical activity on reduction shows that the rotation was due to the molecular asymmetry resulting from the rigidity of the molecule containing the *trans* double bond. This thermal stability indicates that rotation of the ethylenic unit, which would have caused racemization, did not occur. A sample of $(-)$ -*trans*-cyclooctene did not show any loss in specific rotation after being heated at 61° for 7 days.

Fractional crystallization (from *n*-hexane and ethanol separately) of the more soluble fractions of **3a** yielded **3a''**, $[\alpha]^{25D} - 25.2^\circ$. Decomposition of this yielded $(-)$ -*trans*-cyclooctene enantiomeric with that obtained from the diastereoisomeric platinum complex **3a'**. The $(-)$ -*trans*-cyclooctene, $[\alpha]^{25D} + 382^\circ$, $[\alpha]^{26}_{5461} 462^\circ$, was identified as described above.

It was established experimentally¹⁴ that α -methylbenzylamine could be recovered in optical purity from the decomposition of the type platinum complex utilized in this resolution scheme.

It was a fortuitous circumstance that the less soluble olefin-platinum complexes **3a'** and **3b'** had specific rotations of the same sign as the amines which they contained but of larger absolute magnitude, and likewise that the olefins rotated in directions opposite to the complexes from which they were recovered (*i.e.*, levorotatory *trans*-cyclooctene was recovered from dextrorotatory **3a'** containing $(+)$ -amine). The more soluble olefin-platinum complexes **3a''** and **3b''** had rotations of opposite signs to the amines which they contained and yielded olefins having rotations of the opposite signs as the complexes from which they were recovered.

Previous attempts at resolution according to this scheme, using 1-phenyl-2-aminopropane (Dexedrine) via the platinum complexes **3c**, had only given partial resolution with much difficulty (see ref. 1a). Thus fractional crystallization of **3c** gave diastereoisomeric complexes having $[\alpha]^{25D} + 24^\circ$ (**3c'**) and $[\alpha]^{25D} + 4^\circ$ (**3c''**), respectively, and the *trans*-cyclooctene liberated from these complexes had $[\alpha]^{25D} - 21.5^\circ$ and $[\alpha]^{25D} + 18^\circ$, respectively.

Experimental¹⁹

(+)-trans-Dichloro-(ethylene)-(α -methylbenzylamine)-platinum(II) (2a).—Potassium trichloro-(ethylene)-platinate(II) (Zeise's salt) was prepared by treatment of an acidified solution of potassium tetrachloroplatinate(II) with ethylene according to the procedure used by Chatt and Searle²⁰ in the preparation of di-

chloro-1,3-dichloro-2,4-bis-(ethylene)-diplatinum(II). Removal of solvent under reduced pressure gave a crude mixture of potassium trichloro-(ethylene)-platinate(II) and potassium chloride. To a cooled solution of 58.6 g. of this mixture in 400 ml. of 3% potassium chloride solution and 10 ml. of 10% hydrochloric acid was added a cooled solution of 20.3 g. of $(+)$ - α -methylbenzylamine,²¹ $[\alpha]^{25D} + 40.6^\circ$ (neat) (using α^{24}_4 0.9528, which was determined on *dl*- α -methylbenzylamine), in 200 ml. of water, acidified with 10% hydrochloric acid. With cooling and stirring, 3% potassium hydroxide solution was added slowly until pH 5 was reached. Filtration of the precipitate gave 41.8 g. of *trans*-dichloro-(ethylene)-(α -methylbenzylamine)-platinum(II) (**2a**), m.p. $67.5-71.5^\circ$, $[\alpha]^{25D} + 13^\circ$ (*c* 1.4, methylene chloride).

Anal. Calcd. for $C_{10}H_{15}NCl_2Pt$: C, 28.91; H, 3.64; N, 3.38; Pt, 47.00. Found: C, 28.79; H, 3.71; N, 3.41; Pt, 46.79.

(+)-trans-Dichloro-(trans-cyclooctene)-(α -methylbenzylamine)-platinum(II) (3a).—To 41.9 g. (0.101 mole) of complex **2a** in 300 ml. of methylene chloride was added 12.4 g. (0.113 mole) of *trans*-cyclooctene.²² Evolution of gas began at once. The reaction vessel was sealed with a mercury bubbler to allow the escape of ethylene without extensive loss of solvent, and the reaction mixture was stirred overnight. Removal of the solvent at 10–20 mm. gave 57.6 g. of a crude, deep orange mixture of diastereoisomers from which the solvent could be removed only by extensive pumping at 1 mm. or lower pressures. An analytical sample, after 3 days of pumping at ambient temperature, had m.p. $99.8-103.5^\circ$.

Anal. Calcd. for $C_{16}H_{26}NCl_2Pt$: C, 38.62; H, 5.06; N, 2.81; Cl, 14.24; Pt, 39.27. Found: C, 38.75; H, 5.03; N, 2.92; Cl, 14.00; Pt, 39.74.

The mixture of diastereoisomeric complexes was separated by fractional crystallization from carbon tetrachloride. Samples were dissolved at room temperature with stirring and then placed in a refrigerator (-15°) overnight. The dextrorotatory isomer **3a'** of complex **3a** separated as fine, pale yellow needles. After four crystallizations, complex **3a'** had $[\alpha]^{25D} + 67.1^\circ$ (*c* 1.2, methylene chloride); after seven recrystallizations, $[\alpha]^{25D} + 67.0^\circ$ (*c* 2.2, methylene chloride),²³ m.p. $133.3-135.0^\circ$, and $[\alpha]^{25D} + 68.7^\circ$ (*c* 1.7, methylene chloride).²³ Another sample was recrystallized ten times with no increase in rotation. For dipole moment measurement of **3a'** see ref. 17.

Anal. Calcd. for $C_{16}H_{26}NCl_2Pt$: C, 38.62; H, 5.06; N, 2.81; Cl, 14.24; Pt, 39.27. Found: C, 38.37; H, 4.98; N, 2.70; Cl, 14.56; Pt, 38.91.

The oils obtained from the more soluble fractions yielded **3a''** when crystallized first from *n*-hexane until no further change in rotation was observed; m.p. $88-90^\circ$, $[\alpha]^{25D} - 19.5^\circ$ (*c* 1.5, methylene chloride, *l* 1) and then from ethanol until constant rotation $[\alpha]^{25D} - 25.2^\circ$ (*c* 1.0, methylene chloride, *l* 1), m.p. $97-98^\circ$.

Anal. Calcd. for $C_{16}H_{26}NCl_2Pt$: C, 38.62; H, 5.06; Pt, 39.27. Found: C, 38.88; H, 5.07; Pt, 39.23.

(-)-trans-Dichloro-(trans-cyclooctene)-(α -methylbenzylamine)-platinum(II) (3b).—Treatment of an equimolar mixture of potassium trichloro-(ethylene)-platinate(II) and potassium chloride with 5.83 g. of $(-)$ - α -methylbenzylamine,²¹ $[\alpha]^{25D} - 40.0^\circ$ (neat), failed to give crystalline material, so the solution was extracted with methylene chloride, and the methylene chloride extracts were washed with water. Removal of solvent under reduced pressure gave 14.2 g. of a viscous oil having $[\alpha]^{25D} - 16.7^\circ$ (*c* 0.9, methylene chloride), and an infrared spectrum identical with that of complex **2a**. Treatment of this oil with 4.78 g. of *trans*-cyclooctene in the manner described for the preparation of complex **3a** gave 15.8 g. of a mixture of diastereoisomeric complexes (**3b**). After four recrystallizations from carbon tetrachloride, $(-)$ -*trans*-dichloro-(*trans*-cyclooctene)-(α -methylbenzylamine)platinum(II) (**3b'**) had $[\alpha]^{25D} - 68.2^\circ$ (*c* 3.5, methylene chloride). Further recrystallization did not increase the specific rotation. The infrared spectrum of the resolved complex **3b'** was identical with that of the resolved complex **3a'**.

(-)-trans-Cyclooctene.—A chilled solution of 2.09 g. (4.20 mmoles) of $(+)$ -*trans*-dichloro-(*trans*-cyclooctene)-(α -methylbenzylamine)platinum(II) (**3a'**) in 20 ml. of methylene chloride was shaken with 20 ml. of cold 15% aqueous sodium cyanide solution. When the yellow color had disappeared completely, the layers were separated. The aqueous layer was extracted

(20) J. Chatt and M. L. Searle, *Inorg. Syn.*, **5**, 210 (1957).

(21) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 506.

(22) A. C. Cope, R. A. Pike, and C. F. Spencer, *J. Am. Chem. Soc.*, **75**, 3212 (1953).

(23) The large variation in specific rotation observed for the same sample is the result of the small volumes (usually 2 ml.) and volatile solvent which it was necessary to use. Ten measurements of the rotation of fully resolved material gave $[\alpha]^{25D} + 67.5 \pm 1.0^\circ$, assuming no concentration and temperature effects in the ranges used.

(19) Melting points of complexes **2a**, **3a**, and **3b** were taken on a Kofler hot-stage. All others are corrected capillary melting points. Analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark; by Mr. J. Nemeth, Urbana, Ill.; and by Dr. S. M. Nagy of this department. Infrared spectra were recorded on a Perkin-Elmer model 21 spectrophotometer by Mrs. Nancy Alvord. Optical rotations were measured with Rudolph or Zeiss polarimeters. Concentrations are given in g./100 ml., lengths of polarimeter tubes in dm. Gas chromatographic analyses were carried out using 180×0.8 -cm. Pyrex tubes packed with 48-100 mesh firebrick (Johns-Manville) which was coated with the appropriate stationary phase. The samples were eluted with helium at 15 p.s.i. and thermal conductivity cells were used as detectors.

with three 30-ml. portions of pentane. The organic layers were combined, washed with 10% hydrochloric acid, aqueous saturated bicarbonate solution, and water. The solution was dried over magnesium sulfate and concentrated without heating at 400 mm. in a 46-cm. spinning-band column. Distillation of the residue without heating at 0.3 mm. into a trap cooled with Dry Ice gave 357 mg. (77%) of (-)-*trans*-cyclooctene, $[\alpha]_D^{25} -458^\circ$ (neat); $[\alpha]_D^{25} -426^\circ$, -423° (*c* 0.41, 0.49, methylene chloride). The compound had an infrared spectrum and gas chromatographic retention times [NMPN (30 and 75°) and TCEP (63°) columns¹⁹] identical with those of authentic *dl-trans*-cyclooctene.

Anal. Calcd. for C₈H₁₄: C, 86.97; H, 12.91. Found: C, 86.98; H, 12.97.

(+)-*trans*-Cyclooctene.—From 1.94 g. (3.90 mmoles) of (-)-*trans*-dichloro-(*trans*-cyclooctene)-(α-methylbenzylamine)-platinum(II) (3b') there was obtained 288 mg. (67%) of (+)-*trans*-cyclooctene using the procedure described for (-)-*trans*-cyclooctene. The (+)-*trans*-cyclooctene had $[\alpha]_D^{25} +440^\circ$ (neat), $[\alpha]_D^{25} +414^\circ$ (*c* 0.55, methylene chloride), and an identical infrared spectrum and gas chromatographic retention time [TCEP column (68°)] with authentic *dl-trans*-cyclooctene. An analytical sample was obtained by gas chromatography (NMPN, 75°).

Anal. Calcd. for C₈H₁₄: C, 87.19; H, 12.81. Found: C, 86.88; H, 12.80.

A sample of this enantiomer was also obtained from the more soluble fraction 3a'' by decomposition with aqueous potassium cyanide as previously described; this sample of (+)-*trans*-cyclooctene had $[\alpha]_D^{25} +382^\circ$ (*c* 2.01 in methylene chloride, *l* 1), $[\alpha]_D^{25} +462^\circ$ (*c* 1.52 in methylene chloride, *l* 2) and an identical retention time (NMPN column, 65°) with authentic *dl-trans*-cyclooctene. The sample contained no *cis*-cyclooctene.

Anal. Calcd. for C₈H₁₄: C, 87.19; H, 12.81. Found: C, 86.97; H, 12.91.

Hydrogenation of (-)-*trans*-Cyclooctene.—(-)-*trans*-Cyclooctene (83.0 mg.) in 8 ml. of glacial acetic acid was hydrogenated at atmospheric pressure using 92 mg. of platinum oxide catalyst. Uptake of hydrogen was quantitative. After the catalyst was removed by filtration, the reaction mixture was diluted with water and extracted with pentane. The pentane extracts were then washed with saturated aqueous bicarbonate solution and with water and dried over magnesium sulfate. The pentane solution, after concentration to 0.3 ml. using a 46-cm. spinning-band column at 400 mm., showed no rotation (*l* 1 dm.). Examination of the acetic acid solution (*l* 2 dm.) and of the bicarbonate and water washes combined (*l* 2 dm.) also showed no rotation. Cyclooctane, obtained from the pentane solution by gas chromatography, had an infrared spectrum and gas chromatographic retention times [NMPN (26 or 75°) and TCEP (68°) columns] identical with an authentic sample of cyclooctane.

A solution of (-)-*trans*-cyclooctene in glacial acetic acid showed no change in rotation after 25 hr.

Hydrogenation of (+)-*trans*-Cyclooctene.—(+)-*trans*-Cyclooctene (130 mg.) in 9.5 ml. of glacial acetic acid was hydrogenated at atmospheric pressure using 71.3 mg. of platinum oxide catalyst. The product was isolated in the manner described for the hydrogenation of (-)-*trans*-cyclooctene. Neither the concentrated pentane solution (3 ml., *l* 1 dm.), the acetic acid solution (*l* 2 dm.), nor the combined bicarbonate and water washes (*l* 2 dm.) showed optical activity. Cyclooctane, obtained by gas chromatography, had an identical infrared spectrum and identical gas chromatographic retention time [TCEP column (68°)] with authentic cyclooctane.

Thermal Stability of (-)-*trans*-Cyclooctene.—Samples of (-)-*trans*-cyclooctene in sealed tubes were heated at the temperature of refluxing chloroform. After 7 days there was no significant change in rotation.

***trans*-Dichloro-(ethylene)-(1-phenyl-2-aminopropane)-platinum(II) (2c).**—The procedure used for the preparation of *trans*-dichloro-(ethylene)-(p-toluidine)-platinum(II) was used.²⁴ A solution of 3.30 g. of Dexedrine in 45 ml. of water containing just enough hydrochloric acid to dissolve the amine was added dropwise with stirring to a solution containing 7.42 g. of di-μ-chloro-1,3-dichloro-2,4-bis-(ethylene)-diplatinum(II) and 1.50 g. of sodium chloride in 45 ml. of water. An ice bath was used to keep the temperature below 5°, and the addition required 1.5 hr. The pH of the solution was raised to 6 by the dropwise addition of 3% sodium hydroxide solution with cooling and stirring. A small amount of tar formed which was removed by careful decantation. The product was separated by filtration and dried over phosphorus pentoxide for 3 days at 0.05 mm. Crystallization from cyclohexane gave 9.1 g. (86%) of yellow needles, m.p. 120–121°, $[\alpha]_D^{25} +20.5^\circ$ (*c* 2, methylene chloride).

Anal. Calcd. for C₁₁H₁₇NPtCl₂: C, 30.76; H, 3.99; N, 3.27; Pt, 45.74. Found: C, 30.54; H, 4.00; N, 3.31; Pt, 45.74.

***trans*-Dichloro-(*trans*-cyclooctene)-(1-phenyl-2-aminopropane)-platinum(II) (3c).**—A solution of 5 g. of *trans*-dichloro-(ethylene)-(1-phenyl-2-aminopropane)-platinum(II) in 15 ml. of methylene chloride was treated with a solution of 1.35 g. of *trans*-cyclooctene in 15 ml. of methylene chloride. Effervescence occurred during the addition. After the addition was complete the solution was refluxed for 2 min. The solvent was removed under reduced pressure to yield 6 g. of a viscous oil still containing a small amount of methylene chloride. The viscous oil was fractionally crystallized from hexane. The amount of solvent was adjusted to give approximately 50% of the solute in the precipitate and the remainder in the solvent. It was necessary to reflux the solvent to dissolve the gum, and by cooling to -20° a solid that appeared to be crystalline separated. On warming to room temperature, the yellow solid melted to a very viscous oil. Using low temperatures, apparently satisfactory separation occurred. After ten steps of fractional crystallization the more soluble fraction 3c'' showed $[\alpha]_D^{25} +4^\circ$ (*c* 2.5 in methylene chloride); the less soluble fraction 3c' showed $[\alpha]_D^{25} +24^\circ$ (*c* 2.5, methylene chloride). The yield of 3c'' was 0.75 g. and of 3c' 0.70 g.

Anal. Calcd. for C₁₇H₂₇NPtCl₂: C, 39.91; H, 5.32; N, 2.75; Pt, 38.17. Found for 3c'': C, 39.90; H, 5.26; N, 2.82; Pt, 38.04. Found for 3c': C, 40.28; H, 5.41; N, 3.03; Pt, 37.95.

Partially Resolved *trans*-Cyclooctene.—The complex 3c'' was dissolved in 20 ml. of methylene chloride and then shaken with 10 ml. of 20% potassium cyanide solution. The color of the methylene chloride layer changed from yellow to colorless. The methylene chloride layer was washed with three 5-ml. portions of water, three 5-ml. portions of 5% hydrochloric acid, water, 5% sodium bicarbonate, and water. After drying the organic phase over sodium sulfate, the solvent was removed on a steam bath, and the residue was distilled in a short path still, yielding 120 mg. (75%) of *trans*-cyclooctene, $[\alpha]_D^{25} +18^\circ$ (*c* 2.5, pentane). The complex 3c' was treated similarly and gave 108 mg. of *trans*-cyclooctene (70%) from the complex, $[\alpha]_D^{25} -21.5^\circ$ (*c* 2.5, pentane). The observed rotations were of the order of 0.50°.

(24) J. Chatt, *J. Chem. Soc.*, 3340 (1949).