

partially hydrogenated in the presence of a 10% palladium on charcoal catalyst as above. Examination of the ultraviolet spectrum of the benzene solution revealed in this case too that a new peak at 378 $m\mu$ had been formed during the partial hydrogenation process. Chromatography over alumina in the same way as described for isomer I rendered [18]annulene, identity of which was proved again as above.

Tetrahydro[18]annulene (III). III (21 mg.) was dissolved in 25 ml. of benzene (thiophene free) and the solution was subjected to partial hydrogenation in the presence of 15 mg. of palladium catalyst as above. The rate of hydrogen absorption was markedly slower in this case as compared with that of tridehydro[18]annulene isomer I or II. The hydrogenation was interrupted when *ca.* 3 moles of hydrogen was absorbed and a yellow-green color due to the presence of [18]-

annulene was observed. The ultraviolet spectrum of the benzene solution was examined; it showed the presence of a new peak at 378 $m\mu$ that had been formed during the hydrogenation process. Very careful chromatography on alumina (Merck, acid washed) rendered fractions that contained some starting material III followed by fractions with little [18]annulene as evidenced by ultraviolet and t.l.c. comparisons. There could not be detected any traces of a tridehydro[18]-annulene in the chromatography fractions.

Acknowledgments. The author wishes to thank Professor Franz Sondheimer for his interest and encouragement, as well as for many helpful discussions during the course of the present work. Thanks are due also to Dr. Youval Shvo for taking the n.m.r. spectra and to Mrs. Lydia (Groppe) Fischmann for her devoted help in performing the experiments.

Molecular Asymmetry of Olefins. III. Optical Stability of *trans*-Cyclononene and *trans*-Cyclodecene¹

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Resolution of trans-cyclononene has been accomplished by the scheme employed in the resolution of trans-cyclooctene. It was found that trans-cyclononene racemized spontaneously at room temperature at such a rate that no optical activity could be observed when the olefin was recovered from the pure diastereoisomeric platinum complexes by the procedure which yielded optically active trans-cyclooctene. When the recovery was performed by a fast reaction at room temperature and the rotation of the olefin was measured below 0°, optical activity was observed and rates of racemization could be measured. trans-Cyclodecene that was recovered from pure diastereoisomeric platinum complexes under these conditions was optically inactive.

In the first publication of this series,³ the resolution of *trans*-cyclooctene via a platinum complex containing an optically active amine was reported. The same scheme of resolution has now been applied to *trans*-cyclononene and *trans*-cyclodecene. However, recovery of the olefins with aqueous potassium cyanide under the conditions employed for the recovery of optically active *trans*-cyclooctene afforded racemic olefins. Recovery of *trans*-cyclononene from the platinum complex by rapid reactions followed by immediate cooling to low temperatures afforded optically active, although optically unstable, olefin. Optically active

trans-cyclodecene could not be isolated by this procedure.

The existence of enantiomers of *trans*-cyclononene has been predicted.⁴ From inspection of models, revolution of the plane of the sp^2 -hybridized bonds appeared difficult due to ring strain and nonbonded interactions of the olefinic hydrogen atoms with the hydrogen atoms of the methylene groups across the ring. Increased hindrance to rotation of the ethylenic linkage (such as a reduction in ring size, as in *trans*-cyclooctene) would enhance the optical stability of the olefin. The nonbonded interactions apparent in Stuart-Briegleb models makes it impossible to construct a model of *trans*-cyclononene, even though the *trans*-olefinic bond can be rotated with respect to the rest of the molecule in other types of models. By the use of Barton models, the minimum distance between the nearest hydrogen atoms during the path of least interference to the rotation of the double bond unit in *trans*-cyclononene could be estimated as 1.5 Å.

trans-Cyclononene and *trans*-cyclodecene were prepared by reactions described in the Experimental section. Platinum complexes of the olefins were formed by displacement of ethylene from (+ or -)-*trans*-dichloro(ethylene)(α -methylbenzylamine)plat-

(1) Supported in part by the Army Research Office (Durham) under Grant No. DA-ARO(D)-31-124-G404.

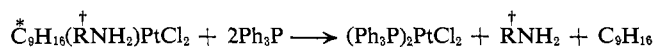
(2) National Institutes of Health Predoctoral Fellow, 1963-1965.

(3) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).

(4) (a) A. T. Blomquist, L. H. Liu, and J. C. Bohrer, *ibid.*, **74**, 3643 (1952). (b) V. Prelog in "Perspectives in Organic Chemistry," A. Todd, Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 129. (c) Molecular asymmetry as stated in this paper refers to the existence of nonsuperimposable enantiomers. *trans*-Cyclic olefins do possess a simple axis of symmetry, however, and would be referred to as dissymmetric in the strictest sense rather than asymmetric (denoting lack of an element of symmetry). For a complete discussion of these terms, see J. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1960, Chapter 6.

inum(II).⁸ The resulting diastereoisomers were separated by fractional crystallization. The olefin liberated from the pure crystalline diastereoisomer under the conditions used to obtain optically active *trans*-cyclooctene showed no optical activity. The recovery of the olefin was then carried out under different conditions to determine whether racemization had occurred.

Liberation at low temperature by a slow reaction might be expected to cause simultaneous although slow racemization. Reaction of (+ or -)-*trans*-dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II) and triphenylphosphine at -80° in methylene chloride according to the following equation proceeded slowly and yielded optically inactive *trans*-cyclononene when the rotation was measured at -20° .⁵



However, when the reaction of the complex with triphenylphosphine was performed at room temperature in acetic anhydride for 10 to 20 sec. and the mixture was chilled to -80° immediately, optically active samples of *trans*-cyclononene with maximum specific rotations of ca. $[\alpha]_{578}^{-20}$ 100° were obtained. Using this procedure, pentane solutions of *trans*-cyclononene were obtained and maintained at less than -60° before transfer to a precooled jacketed polarimeter tube. The change of the angle of rotation with time was measured while the temperature was kept constant. The maximum specific rotation of *trans*-cyclononene was calculated from the maximum angle read at a given wave length and the concentration of the solution determined by vapor phase chromatography using an internal standard. The specific rotation of optically pure *trans*-cyclononene could not be obtained in this way but may be estimated crudely from the rate data to be at the most 30% higher than the rotation calculated from the maximum angle read.

Decomposition of (+)-*trans*-dichloro(-*trans*-cyclononene)(α -methylbenzylamine)platinum(II) with sodium cyanide in methanol-ethylene glycol at -40° afforded *trans*-cyclononene with specific rotations similar to those obtained when the olefin was decomposed by the triphenylphosphine method. (See Table I, runs 2 and 4.)

Table I. Racemization of *trans*-Cyclononene^a

Run	Temp., °C.	$k \times 10^3$ sec. ⁻¹	Max. $[\alpha]_{578}$ observed
1	-9	0.94	
	-19	0.20	-84
2	0	4.5	
	-10	0.88	
3	-20	0.15	-79
	-10	0.47	
4 ^b	-20	0.21	-118
	+4	3.3	
	-6	0.78	
	-20	0.17	-119

^a These data were fitted on a line $y = mx + b$ ($x = -\log k$, $y = \frac{1}{T} \times 10^3, ^\circ K.$) ^b Recovery using the sodium cyanide method.

(5) The asterisk above C_9H_{16} indicates that the complexes used for the recovery were recrystallized to constant rotation and were pure diastereoisomers according to this criterion. The symbol † above RNH_2 indicates that (+ or -)- α -methylbenzylamine was used.

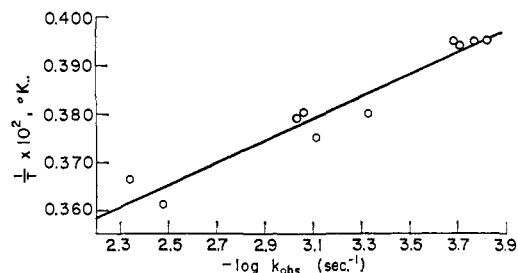


Figure 1. Logarithm of the first-order rate constant k for the racemization of *trans*-cyclononene as a function of the reciprocal of the absolute temperature.

The rates of racemization were measured at various temperatures in the range from -20 to 0° . In all cases there was agreement with the first-order rate expression

$$\frac{dx}{dt} = k(a - x)$$

or the integrated form

$$\ln \frac{\alpha_0}{\alpha_t} = kt$$

where x is the amount of material racemized at time t , a is the initial concentration, α_0 (proportional to a) is the initial angle of rotation, and α_t (proportional to $a - x$) is the angle of rotation read at time t in minutes. Table I summarizes the experiments performed.⁶

Although the kinetic study was not designed to give a precise measure of the rate constants, the logarithm of the rate constant k was found to vary linearly with the reciprocal of the absolute temperature over the range studied (-20 to 0°) (Figure 1). From the slope of this line, calculated by the standard least-squares procedure, the energy of activation for racemization was found to be 20 kcal./mole with a standard deviation of 2 kcal./mole.⁷ The enthalpy and free energy of activation for the racemization were calculated at -10° : $\Delta H^*_{263} = 19.4 \pm 2$ kcal./mole; and $\Delta G^*_{263} = 19.1 \pm 0.2$ kcal./mole. Within the accuracy of the data, the entropy of activation at -10° was zero. The half-life of optically active *trans*-cyclononene may be estimated to be about 4 min., 20 sec., and 6 sec. at 0, 20, and 30° , respectively. These observations are in qualitative agreement with the failure to observe any activity in samples of *trans*-cyclononene recovered at room temperature.

When *trans*-cyclodecene was liberated from the corresponding optically active platinum complex using the techniques employed for *trans*-cyclononene, no optical activity was observed.

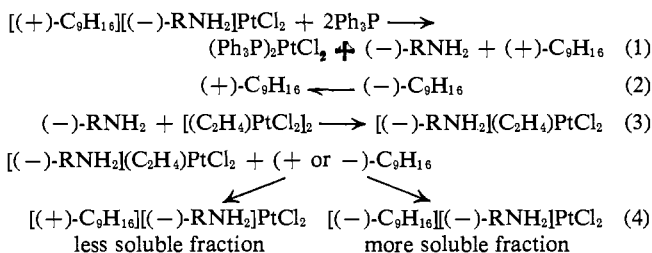
Several differences between *trans*-cyclooctene and *trans*-cyclononene complexes of the type *trans*-dichloro-(*trans*-cycloalkene)(α -methylbenzylamine)platinum(II) were found. The *trans*-cyclononene complex underwent mutarotation in solution in contrast to the optical stability of the *trans*-cyclooctene complex.

(6) It should be noted that the rate constants referred to in this paper are for the rate of racemization and not for the rate of interconversion of the two enantiomers. The rate of racemization is equal to twice the rate of interconversion. For a general discussion see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 33, 34.

(7) The first-order rate constants were obtained by analysis of the data by a nonlinear, least-squares, first-order rate equation program on the IBM 7094.

Solutions of *trans*-cyclononene complexes changed rotation very rapidly if a trace of pyridine was added whereas the *trans*-cyclooctene complex was stable in the presence of pyridine.⁸ It is probable that a slow equilibrium between the complex and the free olefin exists and that the olefin once liberated racemizes and then recombines to form the starting material or its diastereoisomer.

A series of reactions was carried out which also demonstrates the optical instability of these olefins. Decomposition of (–)-*trans*-dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II) with triphenylphosphine in methylene chloride at –60° (conditions known to cause complete racemization of the olefin) followed by recombination with di- μ -chloro-1,3-dichloro-2,4-bis(ethylene)diplatinum(II) afforded a mixture of diastereoisomers. The less soluble isomer was preferentially formed in *ca.* 80% yield (eq. 1–4).



In this experiment, reaction 3 must precede the olefin exchange with the added complex since if this were not so an equimolar ratio of the diastereoisomers would result. Preferential formation of the less soluble diastereoisomer was also observed in the fractional crystallization of the complexes, especially when the olefin exchange reaction was carried out at low temperatures.

In order to ensure that the preferential formation of the less soluble diastereoisomer was not due to incomplete racemization of the olefin, the above sequence of reactions was repeated under the same conditions but with the addition of an equimolar amount of amine of opposite rotation prior to reaction 3. In this case, the mixture of platinum complexes (a mixture of two racemic modifications) was found to be optically inactive.

The sequence of reactions (including the addition of amine of opposite rotation) was then carried out using the triphenylphosphine–acetic anhydride method described previously. These conditions had afforded optically active *trans*-cyclononene. The mixture of complexes was found to have some optical activity even though the amine was racemic. The optical activity must be due to partial retention of configuration of *trans*-cyclononene.

The reactions described in the preceding paragraph were repeated with the *trans*-cyclooctene complex, (+)-*trans*-dichloro-(*trans*-cyclooctene)(α -methylbenzylamine)platinum(II). The product had the rotation expected from an equimolar mixture of [(+)-RNH₂][(-)-C₈H₁₄]PtCl₂ and [(-)-RNH₂][(-)-C₈H₁₄]PtCl₂. (Note that this is a diastereoisomeric mixture due to the presence of *dl*-amine and not because of *dl*-olefin.) As expected an inactive mixture was obtained when the reactions were performed on the corresponding *trans*-

cyclodecene complex, showing that *trans*-cyclodecene racemized completely to give an equimolar mixture of the two racemic modifications.

Experimental⁹

trans-Cyclononene. Dimethyl azelate¹⁰ was cyclized by the acyloin condensation as described for the synthesis of sebacoins.¹¹ The azeloin, b.p. 85–87° (2 mm.), obtained in 42% yield, was reduced by zinc in acetic acid–hydrochloric acid¹² to cyclononane, b.p. 84–85° (10 mm.), *n*_D²⁰ 1.4753. From this the oxime¹³ was prepared in 96% yield and reduced as follows. Lithium aluminum hydride (20.1 g.) was suspended in 540 ml. of ether, and 40.9 g. of cyclononane oxime in 280 ml. of ether was added slowly. After 48 hr. of heating under reflux, 20 ml. of water, 20 ml. of 15% sodium hydroxide, and 40 ml. of water were added in succession. The white precipitate was removed by filtration and washed with small portions of ether. The combined ether solutions were extracted with two 300-ml. portions of 1 *N* hydrochloric acid. The acid extracts were made alkaline and extracted with ether. The ether solution was dried over potassium carbonate, concentrated, and distilled, yielding 26.7 g. (71%) of cyclononylamine, b.p. 105–107° (25 mm.).

Cyclononylamine was converted to *N,N,N*-trimethylcyclononylammonium iodide.¹⁴ The hydroxide, obtained by treatment of the iodide with excess silver oxide, was subjected to the Hofmann degradation as previously described.¹⁵ The once-distilled product contained approximately 5% of *cis*-cyclononene as shown by vapor phase chromatography. The liquid phase (22%) was a mixture of 7.6% of silver nitrate, 8.4% of tetraethylene glycol, and 84% NMPN (4-methyl-4-nitropimelonitrile). The *cis*-cyclononene could be removed by precipitation of the silver nitrate complex of *trans*-cyclononene and recovery of the *trans*-cyclononene by decomposition with concentrated ammonium hydroxide.¹⁵ For the resolution work it was found sufficient to use the crude distillate from the Hofmann degradation, purified by collection from an NMPN column.¹⁶

(9) Melting points of complexes are uncorrected capillary melting points; boiling points are uncorrected. Analyses were performed 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 a Zeiss precision polarimeter or with a Zeiss photoelectric precision polarimeter. With the latter instrument, the rotations measured at 546.1 and 577.8 $m\mu$ were used to calculate the value at the sodium D-line (589.2 $m\mu$). Gas chromatographic analyses were carried out using 180 \times 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.

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(11) N. L. Allinger, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p. 840.

(12) A. C. Cope, J. W. Barthel, and R. D. Smith, ref. 11, p. 218.

(13) L. Ruzicka, M. Kobelt, O. Haflinger, and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949).

(14) A. C. Cope, E. Ciganek, L. J. Fleckenstein, and M. A. P. Meisinger, *J. Am. Chem. Soc.*, **82**, 4651 (1960).

(15) A. C. Cope, D. C. McLean, and N. A. Nelson, *ibid.*, **77**, 1628 (1955).

(16) This purification by collection from vapor phase chromatography was necessary since the product was found to be contaminated with about 0.5% of *trans*-cyclooctene, undoubtedly arising from dimethyl suberate in the dimethyl azelate. In earlier work, this contaminant remained throughout the sequence of reactions and, after the resolution via the platinum complex, afforded small amounts of optically active *trans*-cyclooctene in the *trans*-cyclononene.

(8) A. C. Cope and T. V. Van Auken, unpublished results.

trans-Cyclodecene. This olefin was prepared from sebacoïn in the manner described for *trans*-cyclononene.

trans-Dichloro-(*trans*-cycloalkene)(α -methylbenzylamine)platinum(II). These complexes were prepared as previously described³ by the addition of the olefin to the optically active *trans*-dichloro(ethylene)(α -methylbenzylamine)platinum(II) in methylene chloride. Removal of the solvent left a mixture of diastereoisomeric platinum complexes. Fractional crystallizations were carried out on these mixtures using methylene chloride-hexane for *trans*-cyclononene complexes and carbon tetrachloride-hexane for *trans*-cyclodecene complexes. Since the complexes underwent mutarotation, the recrystallizations were carried out at -10° or below and rotations were measured immediately after the sample had been dissolved.

The less soluble diastereoisomers containing enantiomeric amines were prepared separately from the enantiomeric ethylenamine-platinum complexes. (+)-*trans*-Dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II), recrystallized to a constant rotation, had m.p. 135–136°, $[\alpha]^{26}_D +74.6^\circ$, $[\alpha]^{29}_{546} +91.3^\circ$ (*c* 1.05, carbon tetrachloride).

Anal. Calcd. for $C_{17}H_{27}Cl_2NPt$: C, 39.91; H, 5.32; N, 2.75; Pt, 38.17. Found: C, 39.84; H, 5.22; N, 2.82; Pt, 37.92.

The complex (–)-*trans*-dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II) containing (–)-amine had m.p. 138–140°, $[\alpha]^{26}_D -73.5^\circ$ (*c* 0.8, carbon tetrachloride).

Anal. Calcd. for $C_{17}H_{27}Cl_2NPt$: C, 39.91; H, 5.32; N, 2.75; Pt, 38.17. Found: C, 39.99; H, 5.40; N, 2.87; Pt, 37.93.

The less soluble (–)-*trans*-dichloro-(*trans*-cyclodecene)(α -methylbenzylamine)platinum(II) containing (–)-amine had m.p. 128–129°, $[\alpha]^{28}_D -62.5^\circ$ (*c* 2.0, methylene chloride).

Anal. Calcd. for $C_{18}H_{29}Cl_2NPt$: C, 41.13; H, 5.56; N, 2.66; Pt, 37.11. Found: C, 41.02; H, 5.42; N, 2.83; Pt, 36.84. The (+)-enantiomer had m.p. 128–129°, $[\alpha]^{26}_D +64.3^\circ$, $[\alpha]^{26}_{578} +68.7^\circ$, $[\alpha]^{26}_{546} +84.0^\circ$ (*c* 2.09, methylene chloride).

Recovery of trans-Cyclononene by the Triphenylphosphine Method. A three-necked, 50-ml. reaction flask was equipped with a drying tube and inlet for nitrogen or for applying vacuum. The third neck of the flask contained a cross-shaped tube which was modified so that the approximately horizontal arms were bent upward. Syringes through which the reactants were added were introduced into these arms. The vertical section of the tube, through which a small wire stirrer was placed, extended approximately halfway into the flask and ended in a U-shaped exit. The reactants were introduced through the horizontal branches and were allowed to flow into the U-shaped mixing compartment. The mixture collected in the U-shaped exit and was transferred to the bottom of the flask by applying vacuum at the nitrogen inlet for a short period. The flask was cooled in a Dry Ice-acetone bath and the contents was stirred with a magnetic stirrer. In this manner, the reaction time could be controlled adequately and spontaneous racemization could be quenched after the olefin had been liberated.

A 0.714-g. sample of (+)-*trans*-dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II), $[\alpha]^{29}_{578}$

+89.6°, $[\alpha]^{29}_{546} +91.3^\circ$ (*c* 1.045, carbon tetrachloride), was dissolved in 28.6 ml. of acetic anhydride, and 0.810 g. of triphenylphosphine was dissolved in 14.3 ml. of acetic anhydride. The flask was flushed with nitrogen, cooled in a Dry Ice-acetone bath (-75°), and 4 ml. of pentane was introduced. The reactants were added by means of graduated syringes in 0.4- and 0.2-ml. portions, respectively, and allowed to mix and react at room temperature for 10 sec. before transfer into the cooled flask. The total time needed for addition was 20 min. The reaction mixture was agitated for another 5 min. and then transferred to a precooled double Schlenk tube.¹⁷ Filtration at low temperature through the sintered glass disk separating the two compartments of the tube yielded, after recrystallization from chloroform-ether, 0.926 g. (84%) of dichlorobis(triphenylphosphine)platinum(II). The pentane layer of the filtrate was removed, kept at -70° , and combined with two 5-ml. portions of pentane which had been used in succession for washing the precipitate and extracting the acetic anhydride layer. The combined pentane layers were then extracted at -60° with two 4-ml. portions of a 1:1 mixture of methanol and ethylene glycol into which gaseous hydrogen chloride had been bubbled until the mixture was 4 *N*.

A known weight of *cis,cis*-1,5-cyclooctadiene (an internal standard) was diluted to 1.00 ml. with this solution. The concentration of *trans*-cyclononene was determined by gas chromatographic analysis (NMPN, 65°) by use of a predetermined response factor. The yield of *trans*-cyclononene thus determined was 66%. The pentane solution was used for the determination of rates of racemization.

Recovery of trans-Cyclooctene by the Triphenylphosphine Method. In order to check on the above procedure, *trans*-dichloro-(*trans*-cyclooctene)(α -methylbenzylamine)platinum(II), $[\alpha]^{26}_{578} +74.5^\circ$, was decomposed with triphenylphosphine in acetic anhydride. The specific rotations $[\alpha]^{28}_{578} -400^\circ$ and $[\alpha]^{28}_{365} -1500^\circ$ (*c* 1.5, pentane), calculated on the basis of gas chromatographic analysis using *cis,cis*-1,5-cyclooctadiene as internal standard, agreed well with the rotation found for the pure *trans*-cyclooctene obtained after distillation, $[\alpha]^{28}_{578} -438^\circ$ and $[\alpha]^{28}_{365} -1635^\circ$ (*c* 2.5, pentane).

Recovery of trans-Cyclononene in Methylene Chloride. When the decomposition with triphenylphosphine was performed in methylene chloride at -70° for 3 hr., the *trans*-cyclononene was found to be optically inactive at -25° .

Recovery of trans-Cyclononene by the Sodium Cyanide Method. A mixture of 5 ml. of methanol and 5 ml. of ethylene glycol was cooled to -40° and 0.316 g. of finely powdered sodium cyanide was added. To this suspension, kept at -40° and agitated by means of a magnetic stirrer, 0.409 g. of (+)-*trans*-dichloro-(*trans*-cyclononene)(α -methylbenzylamine)platinum(II), $[\alpha]^{26}_D +74.6^\circ$ (*c* 1.05, carbon tetrachloride), was added. After 3 min., 5 ml. of pentane was added. A colorless solution was obtained within 5 min. after mixing and the temperature was lowered to -80° .

(17) E. Müller, Ed. (Houben-Weyl), "Methoden der Organischen Chemie," Vol. I, Part 2, Thieme Verlag, Stuttgart, 1959, p. 340.

The work-up was performed as described above and the concentration of *trans*-cyclononene determined. The yield of *trans*-cyclononene was 70%. The pentane solutions of *trans*-cyclononene were used for the determination of the rates of racemization.

Recovery of *trans*-Cyclodecene. When the *trans*-cyclodecene complex was decomposed by the triphenylphosphine-acetic anhydride method, the rotations observed at low temperature were within experimental error of zero and did not change with time.

Racemization of *trans*-Cyclononene. A jacketed polarimeter tube was modified so that nitrogen could be passed through the jacket and then to the end plates of the polarimeter tube. Nitrogen was passed through a flow meter and then through a copper coil cooled in liquid nitrogen before entering the jacketed tube which was held firmly in place in the Zeiss photoelectric precision polarimeter. After the instrument had been flushed with nitrogen for 0.5 to 1 hr., the tube containing pentane was cooled. The temperature was read on an alcohol thermometer which could be immersed in and retracted from the liquid in the tube. When the desired temperature was attained, the blank rotation of the tube plus solvent was read, the solvent was removed by means of a pipette, and the solution introduced. Rotations were read as a function of time while the temperature was maintained constant within 1°. The results of these studies are summarized in Table I. The specific rotation of *trans*-cyclononene was calculated from the maximum rotation observed and the concentration as determined by vapor phase chromatography.

The solutions on which the kinetic measurements had been performed were concentrated by removal of the solvent through a 40-cm. spinning-band column and the residual olefins were distilled through a short-path distillation apparatus at less than 1 mm. Collection of the distillate at -70° allowed 80-90% recovery and complete removal of the solvent. The olefins recovered were identified by comparison of their retention times and infrared spectra with those of authentic samples.

Mutarotation of *trans*-Cyclononene and *trans*-Cyclodecene Complexes. Solutions of resolved complexes of the general type *trans*-dichloro-(*trans*-cycloalkene)-(α-methylbenzylamine)platinum(II) were kept at constant temperature and the angle of rotation was measured as a function of time. It was found that the rate varied with the solvent and concentration. The rate constants for the cyclononene complex, 3.4×10^{-5} sec.⁻¹, and the cyclodecene complex, 4.5×10^{-5} sec.⁻¹, measured at 28° in methylene chloride solution (concentration range of 1.5-1.76 g./100 ml.) were comparable.

Optical Stability of *trans*-Cyclooctene. A 0.497-g. (1.0 mmole) sample of (+)-*trans*-dichloro-(*trans*-cyclooctene)(α-methylbenzylamine)platinum(II), $[\alpha]^{28}_{578} + 83.5^\circ$, $[\alpha]^{28}_{546} 99.5^\circ$ (*c* 4.96, acetic anhydride) was dissolved in acetic anhydride and decomposed at -70° with triphenylphosphine as described above. (-)-α-Methylbenzylamine¹⁸ (0.121 g., 1.0 mmole) was added to the cooled filtrate after removal of di-

chlorobis(triphenylphosphine)platinum(II) (recovered in 72% yield). To the filtrate, containing a 2:1 mixture of *dl*-α-methylbenzylamine and (-)-*trans*-cyclooctene, 0.300 g. (0.5 mmole) of di-μ-chloro-1,3-dichloro-2,4-bis(ethylene)diplatinum(II) was added. The clear yellow solution had $[\alpha]^{28}_{578} + 53^\circ$, $[\alpha]^{28}_{546} + 70^\circ$ (*c* 2.00, acetic anhydride); calculated $[\alpha]^{28}_{578} + 59^\circ$, $[\alpha]^{28}_{546} + 68^\circ$.

Optical Stability of *trans*-Cyclononene. The experiment was repeated with 0.400 g. of (+)-*trans*-dichloro-(*trans*-cyclononene)(α-methylbenzylamine)platinum(II), $[\alpha]^{26}_{578} + 105^\circ$, $[\alpha]^{26}_{546} + 119^\circ$ (*c* 2.5, acetic anhydride). The rotation of the complex prepared from the 2:1 mixture of *dl*-α-methylbenzylamine and *trans*-cyclononene recovered at low temperature was $[\alpha]^{26}_{578} + 60^\circ$, $[\alpha]^{26}_{546} + 83^\circ$ (calculated $[\alpha]^{26}_{578} + 80^\circ$ and $[\alpha]^{26}_{546} + 95^\circ$) showing partial racemization.

A 0.97-g. sample of (-)-*trans*-dichloro-(*trans*-cyclononene)(α-methylbenzylamine)platinum(II), $[\alpha]^{28}_{\text{D}} - 77^\circ$ (*c* 2.0, methylene chloride), was dissolved in 25 ml. of methylene chloride, cooled to -60°, and decomposed with 1.00 g. of triphenylphosphine in 15 ml. of methylene chloride. The reaction was allowed to proceed for 2.5 hr. at -70° before filtration into the second branch of a double Schlenk tube¹⁷ containing 0.56 g. of di-μ-chloro-1,3-dichloro-2,4-bis(ethylene)diplatinum(II). An 87% yield of dichlorobis(triphenylphosphine)platinum(II) was obtained. The reaction was permitted to proceed for 1 hr. at -60°. The solvent was removed, leaving 1.005 g. of a yellow solid which on recrystallization gave 0.857 g. of (-)-*trans*-dichloro-(*trans*-cyclononene)(α-methylbenzylamine)platinum(II), m.p. 135-137°, $[\alpha]^{26}_{\text{D}} - 65^\circ$ (*c* 2.0, methylene chloride).

When a sample of (-)-*trans*-dichloro-(*trans*-cyclononene)(α-methylbenzylamine)platinum(II), $[\alpha]^{26}_{\text{D}} - 77^\circ$ (*c* 2.2, methylene chloride), was treated at -75° in methylene chloride for 2 hr. with 2 molar equiv. of triphenylphosphine, an inactive mixture consisting of two racemic modifications was isolated after addition of 1 molar equiv. of (+)-α-methylbenzylamine and then 0.5 molar equiv. of di-μ-chloro-1,3-chloro-2,4-bis(ethylene)diplatinum(II). The two racemic modifications were separated into a less soluble and a more soluble fraction, both of which were inactive. On decomposition both yielded inactive *trans*-cyclononene and *dl*-α-methylbenzylamine.

Optical Stability of *trans*-Cyclodecene. The decomposition of 1.0 g. of (+)-*trans*-dichloro-(*trans*-cyclodecene)(α-methylbenzylamine)platinum(II), $[\alpha]^{28}_{578} + 73^\circ$ (*c* 3.0, acetic anhydride), was accomplished with triphenylphosphine in acetic anhydride. The reaction time was 5 sec. at room temperature before cooling to -80°. Removal of the dichlorobis(triphenylphosphine)platinum(II) (recovered in 74% yield) and addition of 0.232 g. of (-)-α-methylbenzylamine were performed at -70° before 0.56 g. of di-μ-chloro-1,3-dichloro-2,4-bis(ethylene)diplatinum(II) was introduced. The filtrate obtained after complete reaction had $\alpha_{\text{obsd}} < 0.40^\circ$ ($[\alpha] < 1.0^\circ$), showing that approximately an equimolar mixture of the two racemic modifications was present.

Preferential Formation of One Diastereoisomeric *trans*-Dichloro-(*trans*-cyclononene)(α-methylbenzylamine)platinum(II). A. At Room Temperature. When this com-

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

plex was prepared by addition of *trans*-cyclononene to the (+)-*trans*-dichloro(ethylene)(α -methylbenzylamine)platinum(II) complex at room temperature, the entire complex had $[\alpha]^{26D} + 15.5^\circ$.

Repetition of this experiment by adding a solution of the *trans*-dichloro(ethylene)(α -methylbenzylamine)platinum(II) to a solution of *trans*-cyclononene gave a crude mixture of diastereoisomers having $[\alpha]^{28D} + 27^\circ$ (*c* 6.0, methylene chloride). On standing this rotation changed to $[\alpha]^{26D} + 15.8^\circ$, showing a slight predominance of the less soluble diastereoisomer in the equilibrium mixture.

B. At -70° . A solution of 0.950 g. of *trans*-cyclononene in 40 ml. of methylene chloride was divided into two portions. One portion was added

dropwise over a period of 1 hr. to a solution of *trans*-dichloro(ethylene)(α -methylbenzylamine)platinum(II) cooled to -70° . The other portion was used for the inverse addition. The product from normal addition, which was crystalline on evaporation of the solvent, had $[\alpha]^{28D} + 77.4^\circ$ (*c* 3.6, entire sample in methylene chloride) which changed rotation in solution to 19.5° . The product from the inverse addition was an oil, $[\alpha]^{29D} + 38^\circ$ (*c* 3.8, entire sample in methylene chloride) which changed rotation in solution to $+20^\circ$. Evaporation of the solution to dryness and drying under reduced pressure for 16 hr. caused crystallization and spontaneous increase in rotation to $[\alpha]^{27D} + 75.5^\circ$ (*c* 2.3, entire sample in methylene chloride).

Molecular Asymmetry of Olefins. IV. Kinetics of Racemization of (+ or -)-*trans*-Cyclooctene¹

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Thermal racemization of optically active (+ or -)-trans-cyclooctene was studied at 132.7, 156.4, and 183.9°. The reaction was found to be first order in olefin. Half-life values were 122, 15, and 1 hr., respectively, for the three temperatures. The racemization reaction had an activation energy of 35.6 kcal./mole. The enthalpy, free energy, and entropy of activation have been calculated at 155.3°.

The resolution of *trans*-cyclooctene via the complex (+ or -)-*trans*-dichloro-(*trans*-cyclooctene)(α -methylbenzylamine)platinum(II) has been described in an earlier publication in this series.³ In this work the olefin was found to have considerable stability. The optically active enantiomer could be liberated from the complex at room temperature with aqueous sodium cyanide without undergoing appreciable isomerization or polymerization. In addition, there was no change in its optical rotation at room temperature. This stability was of interest in view of the strained *trans* double bond.

In order for a *trans*-cyclic olefin to racemize, the *trans*-olefinic bond must rotate with respect to the remainder of the molecule. This rotation will be facilitated by a decrease in the nonclassical strain (nonbonded interactions), or an increase in the number of carbon atoms in the methylene bridge. The extent to which these nonbonded interactions are important as a barrier to rotation in *trans*-cyclooctene was of interest. Inspection of Dreiding models led to the expectation that their effect would be relatively large in

trans-cyclooctene and considerably diminished in *trans*-cyclononene. *trans*-Cyclononene has been found to racemize almost spontaneously at room temperature and to have a half-life time of approximately 4 min. at 0° .⁴ *trans*-Cyclodecene could not be obtained optically active when the olefin was liberated from the optically active platinum complex, (+)-*trans*-dichloro-(*trans*-cyclodecene)(α -methylbenzylamine)platinum(II), at low temperatures.⁴

The resolution of *trans*-cyclooctene⁵ via the platinum complex, *trans*-dichloro(*trans*-cyclooctene)(α -methylbenzylamine)platinum(II), was accomplished as previously described.³ The rates of racemization were measured at 132.7, 156.4, and 183.9° as described in the Experimental section, and the results are summarized in Table I.⁶ In all cases, first-order kinetics were observed through 80–90% reaction.

Isomerization to *cis*-cyclooctene and formation of polymer occurred as competing side reactions even though 2,6-di-*t*-butylphenol was employed as a polymerization inhibitor. These competing reactions together consumed only 20 to 30% of the *trans*-cyclooctene after 3 half-lives. It was possible to correct for the loss of *trans*-cyclooctene due to these side reactions through vapor phase chromatographic analysis using cyclooctane as an internal standard, and thus to calculate the specific rotation and follow its decrease with time. The method employed to obtain this correction is explained in the Experimental section.

(4) A. C. Cope, K. Banholzer, H. Keller, J. J. Whang, B. A. Pawson, and H. J. S. Winkler, *ibid.*, **87**, 3644 (1965).

(5) A. C. Cope, R. A. Pike, and C. F. Spener, *ibid.*, **75**, 3212 (1953).

(6) It should be noted that the rate constants referred to in this paper are for the rate of racemization and not for the rate of interconversion of the two enantiomers. The rate of racemization is equal to twice the rate of interconversion. For a general discussion see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 33,34.

(1) Supported in part by research grants NSF-GP-1587 of the National Science Foundation and No. DA-ARO(D) 31-124-6404 of the Army Research Office (Durham).

(2) National Institutes of Health Predoctoral Fellow, 1963–1965.

(3) A. C. Cope, C. R. Ganellin, H. W. Johnson, Jr., T. V. Van Auken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).