

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 $[\alpha]^{26D} +27^\circ$ (*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

Arthur C. Cope and Beverly A. Pawson²

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received February 18, 1965

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. Spenser, *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.

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(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).

Table I. Rate of Racemization of *trans*-Cyclooctene

	132.7°			156.4°			183.9°		
$[\alpha]_{578}$ at t_0	+450.7	+438.2	-444.0	-444.9	-451.0	+456.1			
$k_1 \times 10^5 \text{ sec.}^{-1}$	0.0167	0.0142	0.0164	1.29	1.23	1.26			
Half-life, hr.	114.9	135.2	117.0	14.9	15.6	15.2			
$[\alpha]_{578}$ at t_0	-479.8	+426.0	-405.7	-426.2	+423.0	+422.9	-422.1	-421.1	
$k_1 \times 10^5 \text{ sec.}^{-1}$	23.8	17.0	24.5	16.6	16.0	20.6	22.0	19.5	
Half-life, hr.	0.81	1.13	0.78	1.16	1.20	0.93	0.87	0.98	

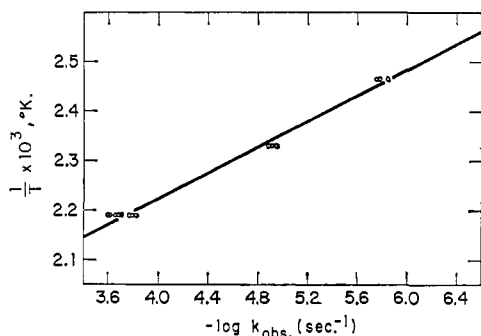


Figure 1. The logarithm of the rate constant k for the rate of racemization of *trans*-cyclooctene as a function of the reciprocal of the absolute temperature.

As described in the Experimental section, the Pyrex glass tubing used to make the sealed ampoules was cleaned with chromic acid solution and finally rinsed with ammonium hydroxide. In order to ensure that no residual acid on the glass surface was affecting the results, the rate was measured at 132.7° using glass tubes which had been cleaned with an alkaline laboratory detergent. No change was observed between the rate of racemization measured under these conditions and the rate obtained when the acid cleaning procedure was used.

Possible surface catalysis of the racemization was shown to be unimportant by increasing the surface area tenfold with glass wool. This increase in surface area resulted in only a 30% increase in the rate of racemization after 1 half-life, and it is therefore expected that under the normal reaction conditions not more than 3% of the racemization was surface catalyzed. However, the formation of polymer and *cis*-cyclooctene was increased by over 100% after 1 half-life.

The logarithm of the rate constant k was found to vary linearly with the reciprocal of the absolute temperature over the range studied (130 to 185°) (Figure 1). The slope of the line was calculated by fitting the 14 individual first-order rate constants to the line $y = mx + b$ according to the least-squares procedure.⁷

From the slope of this line, the Arrhenius activation energy was calculated to be 35.6 kcal./mole with a standard deviation of 0.9 kcal./mole. The enthalpy and free energy of activation for the racemization were calculated at 155.3° ($\Delta H^*_{428.3} = 34.7 \pm 0.9$ and $\Delta G^*_{428.3} = 34.9 \pm 0.02$ kcal./mole). Within the accuracy of the data, the entropy of activation at 155.3° was zero. The magnitude of the activation

(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.

energy is consistent with the strong nonbonded interactions hindering rotation of the ethylenic linkage as shown by molecular models. The activation energy found for *trans*-cyclononene, where there is an increase of one carbon atom in the methylene bridge which lessens the nonbonded interactions considerably, was found to be 20 kcal./mole.⁴

Experimental⁸

(+ or -)-*trans*-Cyclooctene. (\pm)-*trans*-Cyclooctene⁵ was resolved via the complexes (+ and -)-*trans*-dichloro-(*trans*-cyclooctene)(α -methylbenzylamine) platinum(II).³ (+ and -)-*trans*-Cyclooctene were obtained from the appropriate resolved complex by displacement of the olefin with 15% (by weight) aqueous sodium cyanide.³ Typical optical rotations obtained for the olefin were $[\alpha]_{578}^{25} +443.4^\circ$, $[\alpha]_{546}^{25} +512.4^\circ$, and $[\alpha]_{578}^{25} +422.1^\circ$ (c 0.84, methylene chloride); and $[\alpha]_{578}^{25} -431.9^\circ$, $[\alpha]_{546}^{25} -499.1^\circ$, and $[\alpha]_{578}^{25} -411.3^\circ$ (c 0.68, methylene chloride).¹⁰ For each rate measurement, *trans*-cyclooctene was freshly liberated from the platinum complex.

Thermal Racemization of (+ or -)-trans-Cyclooctene. Pyrex glass tubing (3 mm. diameter) was cleaned in chromic acid solution, rinsed with distilled water and finally with ammonium hydroxide, and dried. Solutions of approximately constant composition of (+ or -)-*trans*-cyclooctene, cyclooctane (an internal standard), and 2,6-di-*t*-butylphenol (polymerization inhibitor) were prepared as follows. A known weight of *trans*-cyclooctene was diluted with a 10% (by weight) solution of the phenol in cyclooctane at a ratio of 50 μ l. of cyclooctane solution per 100 mg. of *trans*-cyclooctene. This mixture was then divided and placed in the glass ampoules which were sealed under nitrogen. The ampoules were heated in a constant temperature bath (Dow Corning fluid) and the reaction rates were measured at 132.7, 156.4, and 183.9°; the temperature was constant to $\pm 0.2^\circ$. At various time intervals, a tube was removed and immediately cooled in a Dry Ice-acetone bath, and the optical rotation of a known weight of sample was measured in methylene chloride solution. A correction for a change in composition (decrease in *trans*-cyclooctene concentration) due to the formation of polymer and *cis*-cyclooctene was obtained

(8) Optical rotations were measured with a Zeiss photoelectric precision polarimeter. Chromatographic analyses were carried out on a 7 ft. \times 0.25 in. Pyrex column having as stationary phase 22% NMPN (4-methyl-4-nitropimelonitrile) on Chromosorb P. The samples were eluted with helium at 15 p.s.i. and thermal conductivity cells were used as detectors.

(9) The value at the sodium D-line (589 m μ) was calculated from the observed rotations at 546 and 578 m μ .

(10) One to two per cent of *cis*-cyclooctene was present in the *trans*-cyclooctene liberated from the platinum complexes. The specific rotations were corrected for this impurity.

by measuring the relative areas of the *trans*-cyclooctene and cyclooctane peaks in the vapor phase chromatograms of the heated sample and an unheated sample of the same composition and calculating their ratio. Three vapor phase chromatograms were ob-

tained for each sample. With this correction, values for the specific rotation of each sample were calculated, and the decrease in this value with time was followed. In all cases the reactions were followed to 80–90% completion.

Tetracyanoethylene Oxide. I. Preparation and Reaction with Nucleophiles¹

W. J. Linn, O. W. Webster, and R. E. Benson

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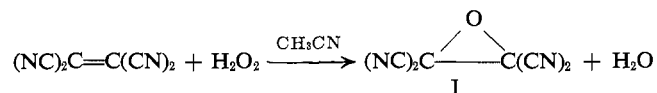
*Tetracyanoethylene oxide (TCNEO) is readily synthesized from tetracyanoethylene and hydrogen peroxide. Ethylenes substituted with two cyano groups and at least one other electronegative group may be epoxidized with hydrogen peroxide without conversion of nitrile to amide. Two different types of nucleophilic attack on TCNEO are described. Iodide and bromide ion attack at the nitrile group with the formation of cyanogen halide and tricyanovinyl alcoholate ion. Pyridine derivatives and dialkyl sulfides cleave the ring to give stable dicyanomethylides and carbonyl cyanide. A convenient high-yield synthesis of the latter has been developed using di-*n*-butyl sulfide.*

Reports of the epoxidation of α,β -unsaturated nitriles to the corresponding epoxynitrile are limited to examples in which an alkyl hydroperoxide² or hypochlorite ion³ is the oxidizing agent. Alkaline hydrogen peroxide, the more common reagent, invariably gives the epoxyamide as the major product.⁴ Payne and co-workers have provided evidence that under controlled pH conditions the intermediate is a peroxyimidic acid which makes amide formation inevitable.⁴ Even with isopropylidenemalononitrile, an olefin which should be very susceptible to nucleophilic attack by the hydroperoxide anion, the product is primarily the epoxyamide.²

Preparation and Properties of Tetracyanoethylene Oxide

In contrast to these results, tetracyanoethylene is smoothly and rapidly converted to tetracyanoethylene oxide (TCNEO, I) with aqueous hydrogen peroxide in the absence of any added base.⁵ The reaction is best carried out by the dropwise addition of 30% aqueous hydrogen peroxide to a cooled solution of tetracyanoethylene (TCNE) in acetonitrile. When the reaction is

complete, the TCNEO is recovered in 65–70% yield by dilution of the reaction mixture with water. Such a procedure would result in the loss of any water-soluble amides, but these, if any, are minor products of the



reaction. A peroxyimidic acid from the acetonitrile is probably not the active epoxidizing agent, for the reaction may also be carried out in other water-miscible solvents for TCNE such as tetrahydrofuran, acetone, or ethanol. The reaction undoubtedly involves direct nucleophilic attack of the hydroperoxide anion or hydrogen peroxide to give a highly stable anionic intermediate.⁶

Tetracyanoethylene anion radical (TCNE⁻)⁷ is also oxidized to TCNEO with acidic hydrogen peroxide in aqueous solution. It is known that acidification of TCNE⁻ solutions gives an equimolar mixture of TCNE and tetracyanoethane (H₂TCNE), and this reaction may be partially involved as the initial step in the conversion to TCNEO. However, the yield of the epoxide in some instances was greater than 50%, indicating a more complicated mechanism. Although H₂TCNE was found in some preparations, it was not present in all of them. Furthermore, TCNE and aqueous, acidic hydrogen peroxide does not directly give TCNEO; a medium to dissolve the reactants appears necessary.

TCNEO is an easily crystallized, colorless solid, m.p. 177–178°. It is stable in air but slowly decomposes in the presence of water.

The structure of TCNEO is supported by elemental analysis and ultraviolet and infrared spectral data.

Electrophilic attack on the ring of TCNEO is not observed as a result of the presence of the strongly electron-withdrawing nitrile groups. As a consequence

(1) This work was presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963, Abstracts A, p. 247.

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(4) G. B. Payne and P. H. Williams, *ibid.*, **26**, 651 (1961).

(5) These results have been communicated in preliminary form: W. J. Linn, O. W. Webster, and R. E. Benson, *J. Am. Chem. Soc.*, **85**, 2032 (1963).

(6) TCNEO has also been isolated from ozonizations conducted in the presence of tetracyanoethylene: R. Criegee and P. Günther, *Chem. Ber.*, **96**, 1564 (1963). Subsequent to our first communication on the synthesis and reactions of TCNEO, a paper appeared which also reported the preparation of the epoxide from TCNE and either H₂O₂ or *t*-butyl hydroperoxide: A. Rieche and P. Dietrich, *ibid.*, **96**, 3044 (1963).

(7) O. W. Webster, W. Mahler, and R. E. Benson, *J. Am. Chem. Soc.*, **84**, 3678 (1962).