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THE STEREOCHEMISTRY OF *TRANS*-CYCLOOCTENE DERIVATIVES

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Abstract- X-Ray and NMR data are presented which suggest that *trans*-cyclooctene, 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane, *trans*-bicyclo[6.1.0]nonane and *trans*-cyclooctene oxide exist in a distorted crown conformation. The synthesis of optically active *trans*-bicyclo[6.1.0]nonane and *trans*-cyclooctene oxide is described.

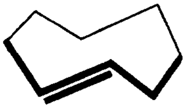
INTRODUCTION

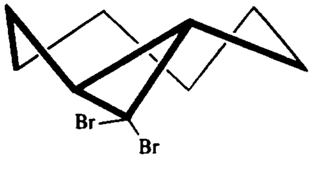
trans-CYCLOOCTENE is a highly strained dissymmetric olefin whose optical stability is dependent upon the rigidity of the hexamethylene chain that comprises the ring. The olefin was resolved by Cope in a classic experiment utilizing a platinum complex containing an optically active amine.[1] In a study of the kinetics of racemization of *trans*-cyclooctene, an activation energy of 35·6 kcal/mole was calculated from an Arrhenius plot of the rate data.[2] The effects of ring strain and of nonbonded interactions on the optical stability of *trans*-cycloalkenes is reflected by the half-lives of the antipodes of *trans*-cyclooctene (10^5 years), *trans*-cyclononene (10 sec) and *trans*-cyclodecene (10^{-4} sec) calculated at room temperature.[3]

It has been suggested that in addition to the twisted double bond, *trans*-cyclooctene contains a second chiral unit, the chiral axis associated with the C_4—C_7 butane segment of the ring. The olefin, therefore, may exist as two stable conformers, **1a** and **1b**, each of which may have a non-superimposable mirror image.

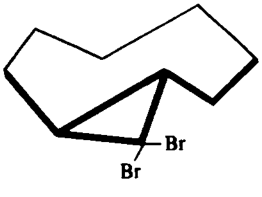
Treatment of (−)-*trans*-cyclooctene with OsO_4 and conversion to optically pure *trans*-1,2-dimethoxycyclooctane[4] (**2**) firmly established that one source of dissymmetry arises from the environment of an optically pure ethylenic linkage that is


R(−)**1a**


R(−)**1b**



1S:8S(+)**3a**



1S:8S(+)**3b**

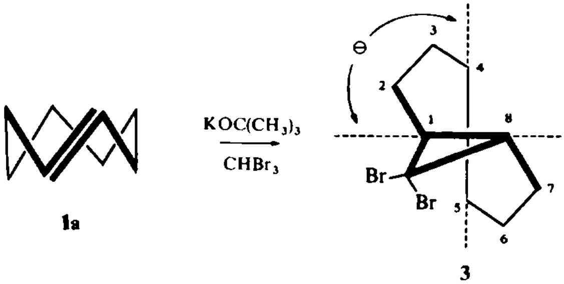
accessible to oxidation from only one side of the double bond. Independent synthesis[4] of **2** from tartaric acid established the absolute configuration of the double bond in the levorotatory alkene as (R) but did not resolve the question about the conformation of the ring in *trans*-cyclooctene.

An X-ray analysis of a copper (I) complex[5] of *trans*-cyclooctene showed the olefin to exist as conformer **1a**. Similarly, an X-ray study[6] on the platinum-olefin complex used to effect the resolution [1]of (±)-*trans*-cyclooctene also showed the conformation to be **1a** and corroborated the absolute configuration[4] of (–)-*trans*-cyclooctene. Furthermore, a least squares analysis[7a] of the non-bonded distances obtained in a gas-phase electron diffraction study of *trans*-cyclooctene implies that the molecule has a twist about the double bond and exists as conformation **1a**. Theoretical calculations[7b] are in good agreement with these experimental data suggesting that **1a** is more stable than **1b** by 2·2 kcal/mole. The relevant question however is the activation energy for interconversion of the two conformers (**1a** → **1b**). We wish to present data suggesting that *trans*-cyclooctene and its dibromocarbene adduct exist in the twisted conformations, **1a** and **3a**.

RESULTS AND DISCUSSION

There are two possible conformations for the cyclopropyl and oxirane derivatives of *trans*-cyclooctene. In order to have an X-ray study on a derivative of *trans*-cyclooctene carried out, we prepared the crystalline compound 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane (**3**).[8] The (–)-enantiomer of *trans*-cyclooctene was treated with $CHBr_3$ and $KOC(CH_3)_3$ in pentane at 0° affording optically pure **3**, $[\alpha]_D^{25}$ +44·2° (*c* 2·49, CH_2Cl_2), m.p. 51·5–53°. (Eq. 1). Consideration of the mechanism of a *cis*-addition of CBr_2 to the exposed side of the double bond allows the assignment of the absolute configuration of (+)-**3** as (1S:8S). Racemization of **3** does not occur because of the presence of the asymmetric carbon atoms C_1 and C_8. However, torsion about the C_4—C_5 element of dissymmetry would afford the other diastereoisomer **3b**. An X-ray analysis[9]* on tetragonal crystals of **3** showed this compound to exist as conformation **3a** and corroborated the above assignment of the absolute configuration of **3a** and also the absolute configuration of (–)-*trans*-cyclooctene as (R).[4,6]

Examination of molecular models suggests that the distorted crown conformation **3a** should have less transannular hydrogen-hydrogen interactions than the chair



Eq. 1

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* We are indebted to Drs. S. H. Simonsen and B. J. Bowen for the X-ray analysis.

conformer **3b**. A decrease in the bond angle* θ between the C_1—C_8 and C_4—C_5 ethane segments from 90° as depicted in **3**, relieves nonbonded interactions between the cyclopropyl hydrogens and the transannular hydrogens on C_4 and C_5. From the results of the X-ray study[9] on **3** we calculated this angle* to be 70° while the corresponding angle observed[5] with the copper (I) complex of *trans*-cyclooctene was 71°. The angle of twist of the double bond in the *trans*-cyclooctene platinum II complex[6] was estimated to be 43·5°, while the comparable dihedral angle between carbon atoms 7, 8, 1, 2 in **3a** was calculated to be 56°. Further relief of steric strain is achieved by widening the bond angles of **3a** at C_3, C_4, C_5 and C_6 to 117·2, 118·2, 116·7, and 117·2°, respectively. Similar bond angle deformation has been reported at C_4 (114°) and C_5 (117°) in *trans*-cyclooctene.[5] The *trans*-dibromide **3a**, therefore, exists in the solid state in a distorted crown conformation where a minimum of torsional and nonbonded interactions exists. The larger dihedral angle between atoms 7, 8, 1 and 2 in **3a** should render the *trans*-fused ring slightly more flexible than the complexed olefin **1a**.

Molecular models further suggest that interconversion of **1a** to **1b** by twisting the single bond in **1a** between carbon atoms five and six through the ring (*i.e.* inverting the configuration at the butane segment) may render this process more difficult than inversion of configuration of the *trans*-olefinic double bond by twisting it through the ring. Alternatively, interconversion of **1a** to **1b** or **3a** to **3b** may be achieved by rotation of carbon atoms **5** and **6** in opposite directions about the C_5—C_6 axis with no hydrogens passing through the ring. In the latter process transannular hydrogen–hydrogen interactions are reduced, but the four carbon atoms of the butane segment are eclipsed in the transition state. This process is still attractive, however, since a considerable amount of the bond angle deformation required by this mechanism already exists in the ground state of the molecule.

It is conceivable that the two conformations of *trans*-cyclooctene, **1a** and **1b**, could be of comparable energy and formed to the same degree in the Hofmann elimination reaction and still behave as a single enantiomer during the resolution[1] and racemization[2] studies. However, *trans*-cyclooctene prepared by the Hofmann elimination (120°) and by the Wittig modification[10] of this reaction (−33°) exhibited an identical NMR spectrum which did not change significantly on cooling from +36° to −56°. An interesting feature of the spectrum of **1a** is the pseudo-triplet centered at 0·8 ppm, due to the anisotropy effect of the double bond, which integrates for ~2 protons.

X-ray studies[11a] on crystalline cycloctane derivatives, NMR studies[11b,c] on alkyl cyclooctanes and fluorocyclooctanes, and molecular beam studies,[11d] all suggest that these compounds prefer to assume that boat-chair conformation when they are not fused to a three-membered ring. An NMR study on the acetonide of cyclooctane-*trans*-1,2 diol is of particular relevance to the conformation of **3a** in solution, since this compound contains a five membered ring bonded to the *trans*-cyclooctyl moiety. The temperature dependent NMR spectrum of this compound exhibited[11b] spectral changes at about −70° to −80° and the medium ring must therefore be relatively flexible. On this basis one would expect the more rigid cyclopropyl compound **3a** to exhibit spectral changes above −70°. However, the NMR spectrum of **3a** did not

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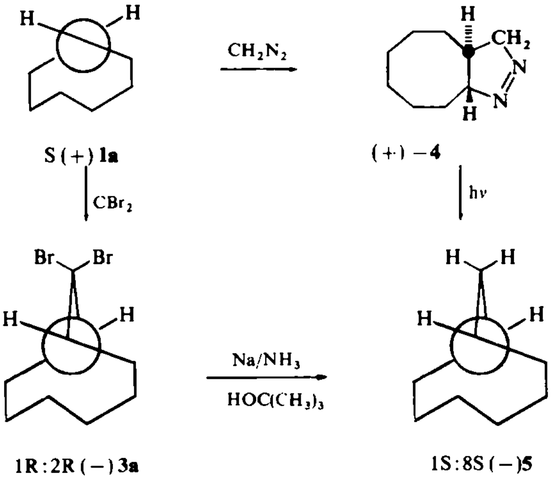
* This is the dihedral angle between C_1 at the midpoint of the C_1—C_8 bond with C_4 at the midpoint of the C_4—C_5 bond.

change significantly from −100° to +30° in CH_2Cl_2 solvent. Furthermore, the NMR spectrum of **3a** in 1,2,4-trichlorobenzene did not exhibit a significant change between +30° and +150°, suggesting that the energy barrier to interconversion of **3a** and **3b** is not attainable in this temperature range either. The spectrum exhibited a broad multiplet (0·8–2·4 ppm) containing two major envelopes whose centers are separated by approximately 1 ppm. By contrast, the NMR spectrum of the meso-isomer of **3**, derived from *cis*-cyclooctene, showed essentially a single envelope centered at 1·6 ppm characteristic of the hydrogens of a flexible medium ring. If the activation energy of the interconversion of the crown and chair conformers of **1** and **3** were on the order of 10–22 kcal/mole, we would expect to see evidence of line broadening and coalescence phenomena in the NMR spectra of these compounds in the temperature range of −100° to +150°. Either the NMR spectrum of **3a** is insensitive to temperature changes, or the activation energy of interconversion of **3a** to **3b** is greater than 22 kcal/mole. It should also be emphasized that to date no experimental evidence has been reported for the chair conformers **1b** and **3b**.

The usual reactivity of the highly strained *trans*-double bond in **1a** was recently demonstrated[12] by the reaction of optically active *trans*-cyclooctene with CH_2N_2 which gave the pyrazoline **4**. Photolysis of (−)-**4** afforded optically active *trans*-bicyclo[6.1.0]nonane (**5**) of unknown optical purity, $[\alpha]_D^{25}$ + 25·3°, contaminated with 4% of the meso *cis*-fused isomer. We have carried out an independent synthesis of **5** that unequivocally establishes its absolute configuration (Scheme 1). Reaction of **3a**, $[\alpha]_D^{25}$ − 43·8°, with two equivalents of tri-n-butyltin hydride over a three day period, afforded **5**, that was homogeneous to GC on several columns and had $[\alpha]_D^{25}$ −27·1°. Reduction of the same compound with sodium in liquid ammonia using ethyl ether as a cosolvent and t-butyl alcohol as a proton donor afforded **5** that had $[\alpha]_D^{25}$ −31·3°*[13] which is essentially optically pure.

SCHEME 1



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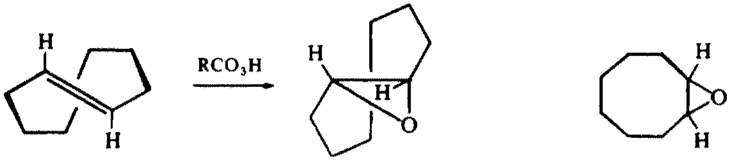
* Professor W. R. Moore has informed us prior to publication that reduction of (+) **3a** by the same method also afforded **5**, $[\alpha]_D$ +31°.

The established[9] absolute configuration of **3a** allows the assignment of the absolute configuration of (−) **5** as (1S:8S). The photolysis of **4** is relevant to the conformation of **5** since the more highly strained *trans*-cyclopropane was the major product. Considerable relief of strain could have been realized by carbon–carbon bond rotation of the *trans*-pyrazoline on photolysis affording the less strained *cis*-fused *meso* isomer. In consideration of the above discussion C_1—C_8 bond rotation would most likely be slow even if a diradical intermediate were involved. Alternatively, loss of nitrogen could occur concomitantly with ring closure to **5**.

Epoxidation of racemic *trans*-cyclooctene[14] with 40% peracetic acid has been reported to be a stereospecific reaction affording only *trans*-cyclooctene oxide. The observation[8] of a small amount of the *cis*(*meso*)-dibromocarbene adduct being formed upon electrophilic addition of CBr_2 to *trans*-cyclooctene prompted us to re-examine the epoxidation reaction. Indeed, reaction of **1a** with peroxycamphoric acid in $CHCl_3$, peracetic acid in AcOH, and *m*-chloroperbenzoic acid in CH_2Cl_2, afforded 3·0, 3·3, and 4·4%, respectively, of the *cis*/(*meso*)-epoxide **7**, in addition to the expected *trans*-epoxide (Eq. 2). The origin of the *cis* epoxide is of particular interest since epoxidation reactions with alkenes are generally completely stereospecific *cis*-addition reactions. Control experiments established that the corresponding carboxylic acids derived from the peracids did isomerize the *trans* olefin to *cis*-cyclooctene but at a rate that appeared to be somewhat slower than the formation of the *cis*-epoxide. The *cis* olefin formed does not accumulate in the reaction mixture since the relative reactivity of *trans*-cyclooctene with *m*-chloroperbenzoic acid is only about eight times that of the *cis*-isomer. The relative reactivity of *cis* and *trans*-cyclooctene toward CBr_2 is about 1:3.[15a] In both reactions the product is still highly strained. However, the diimide reduction of *trans*-cyclooctene is 10^6 times faster than the *cis*-isomer when relief of strain occurs and cyclooctane is the product of both reactions.[15b, 16]*



S(+) **1a** 1R:8R (−) **6** **7** (2)

Olefins have been observed to afford optically active epoxides when dissymmetric peroxy-acids are used as oxidants, albeit in low optical yield (≤4·4%). Treatment of two equivalents of the dissymmetric olefin *trans*-cyclooctene with (+)-peroxycamphoric acid, also resulted in a low optical yield of *ca.* 0·2–0·3%. The (−)-enantiomer reacted preferentially with the peracid affording (1S:8S)-*trans*-cyclooctene oxide.

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* The epoxidation of norbornene with perlauric acid is only slightly faster than cyclohexene. This observed lack of rate difference of these olefins was used as evidence against[16a] a 1,3-dipolar mechanism[16b] of epoxidation of olefins with peracids.

This result is based upon both recovered epoxide, $[\alpha]_D^{25}$ +0·13°, and olefin $[\alpha]_D^{25}$ +1·05°. The (1R:8R)-*trans* epoxide prepared in 94% optical purity from *trans*-cyclooctene, $[\alpha]_D^{25}$ +412°, with *m*-chloroperbenzoic acid, had $[\alpha]_D^{25}$ −54·7°. The low optical yields obtained with planar and dissymmetric olefins obviously reflects the distance of the chiral center of the peracid from the developing asymmetric center in the epoxide. By contrast, with a hydroboration reaction up to 20% optically pure (−)-*trans*-cyclooctene may be obtained by kinetic resolution of racemic olefin using (−)-*sym*-tetraisopinocampheyldiborane in triglyme at −10°.[17] Both reactions involve a *cis*-addition to the double bond.

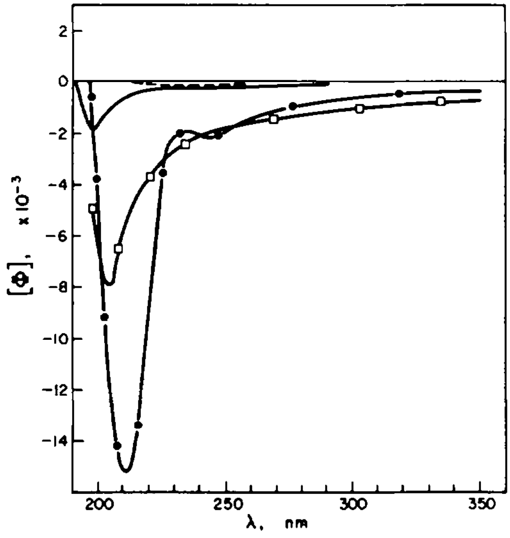
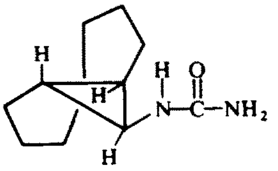


FIG 1. (−)6 - - - - - : (−)5 ·——— : (−)8 −□−□−□ : (−)3 −·−·−·

The non-bonded interactions in **5** and **6** should not differ significantly from those in **3a**, and it seems likely that the transannular hydrogen–hydrogen interactions should also render the distorted crown conformation more stable in these compounds. Since the solid phase and gas phase results both support a favored crown conformation for **3a** and **1a**, it is not unreasonable to assume that this same situation prevails in solution at room temperature.

We also wish to report the results of an ORD study on the optically active compounds of known absolute configuration discussed above. We have previously reported[18a] the vapor phase CD spectrum of (+)-*trans*-cyclooctene which exhibited a positive COTTON effect with a very high molecular ellipticity. The compounds (−) **3a**, (−) **5**, (−) **6**, and (1R:8R)-N-(9-*trans*-bicyclo[6.1.0]nonyl) urea (**8**), $[\alpha]_D^{25}$ −117·2°,[18b] are all derived from (+)-*trans*-cyclooctene and therefore have the same relative configuration of the *trans*-cyclooctyl moiety.



1R:8R(−)8

The ORD behaviour of these chiral cyclopropanes and the oxirane **6** all exhibit a negative COTTON effect (and $[M]_D$) Fig 1. Hopefully these data will prove useful in establishing the absolute configuration of other *trans*-dialkyl substituted cyclopropanes and epoxides.

EXPERIMENTAL

trans-*Cyclooctene*. N,N-Dimethylcyclooctyl amine was prepared by the reaction of DMF and formic acid with cyclooctanone.[19a] N,N,N,-Trimethylcyclooctyl ammonium iodide was prepared from the above amine and MeI in MeOH. *trans*-Cyclooctene was prepared by the Hofmann elimination of N,N,N-trimethylcyclooctylammonium hydroxide at 100°-125 .[19b]

trans-Cyclooctene was also prepared for spectral comparison by the treatment of N,N,N-trimethylcyclooctylammonium iodide[10] with KNH_2 in liquid NH_3 at −33°. The mixture of *cis*- and *trans*-olefins was separated by $AgNO_3$aq extraction (ice water). An effort was made to keep the *trans*-isomer at 0° during purification by short path distillation. The NMR and IR spectra (25°) of *trans*-cyclooctene prepared by this method and by the Hofmann elimination at 120° were found to be identical.

Optically active *trans*-cyclooctene was obtained by resolution utilizing a platinum complex containing α-methylbenzyl amine.[8]

trans-*Bicyclo*[6.1.0]*nonane* **5**. 9,9-Dibromo-*trans*-bicyclo[6.1.0]nonane $[\alpha]_D^{25}$ −43·8° (*c* 2·16, CH_2Cl_2) was prepared as described previously[8] from the optically pure (+) enantiomer of *trans*-cyclooctene by the action of dibromocarbene. To 0·56 g of the dibromide **3a** was added 1·2 g of tri-n-butyl-tin hydride[20] dropwise over a 1 hr period. The mixture stirred at 25° for 3·5 days and the resulting hydrocarbon was collected at reduced pressure in a cold trap. Purification by GC (2′, 10% FFAP, 60°) gave 0·050 g (20%) of *trans*-bicyclo-[6.1.0]nonane, $[\alpha]_D^{25}$ −27·1° (*c* 2·47, CCl_4); reported[12] +25·3° (*c* 1·10, CCl_4). The collected product was shown to be homogeneous to GC and had principal IR bands[21] (neat) at 3050, 2985 and 1020 cm^{-1}. Reduction[22] to the monobromide was essentially complete within 3 hr while at least three days was required for complete reduction to the hydrocarbon.

Racemic **3a**, 2·82 g (0·01 mole) was allowed to react with 5·82 g of tri-n-butyltin hydride for four days. Distillation into a cold trap gave 0·90 g (72%) of racemic **5**. A sample of the *cis*-isomer was prepared from 9,9-dibromo-*cis*-bicyclo[6.1.0]nonane by the same method for spectral comparison. The *trans* isomer has IR absorptions at 820 (w) and 914 (m) cm^{-1} that are absent in the *cis* isomer.

Optically active **5** was also prepared by reduction of **3a**, (−) 43·8°, (0·14 g, 0·5 mmol) which was added together with 0·10 g of tert-butyl alcohol to 5 ml. of diethyl ether in 15 ml of $NH_{3(l)}$ containing 0·074 g of Na. The reaction refluxed at −33° for 2 hr. A portion of the product was collected by GC and had $[\alpha]_D^{25}$ −31·3° (*c* 0·88, CCl_4).

trans-*Cyclooctene oxide* **6**. Optically active *trans*-cyclooctene was obtained by treatment of (−)-*trans*-dichloro-(*trans*-cyclooctene)-(α-methyl-benzylamine)-platinum (II), $[\alpha]_D^{25}$ −68·1° (*c* 1·68 CH_2Cl_2), with aqueous cyanide ion. To a stirred solution of 0·39 g (3·5 mmol) of the olefin, $[\alpha]_D^{25}$ +412° (*c* 1·218 CH_2Cl_2), in 5 ml of CH_2Cl_2 at 25° was added 0·71 g of *m*-chloroperbenzoic acid in 20 ml of CH_2Cl_2. After 30 min the mixture was treated with Na_2SO_3aq and the *m*-chlorobenzoic acid was extracted with 5% $NaHCO_3$aq. Removal of solvent gave 0·43 g of clear oil. The product was collected by GC (2′ 20% SE-30, 90°) in several passes affording 0·323 g (72%) of *trans*-cyclooctene oxide, $[\alpha]_D^{25}$ −54·7° (*c* 5·21 CH_2Cl_2), that contained 1% of the *cis*-isomer.

When the oxidation was carried out on a large scale with racemic olefin[19b] the yield was 92%. The NMR spectrum of the *cis*-epoxide had an envelope centered at 1·5 ppm (8H) for the ring protons, a multiplet at 2·1 ppm (4H) and a multiplet at 2·7 ppm (2H) for the protons on the oxygen bearing carbon atoms. The NMR spectrum of the *trans*-epoxide was very complex with five highly structured envelopes that ranged from 0·7 to 2·7 ppm.

When racemic *trans*-cyclooctene oxide was prepared according to the procedure of Cope[14] with 40% peracetic acid (to which NaOAc had been added to neutralize the H_2SO_4) the product mixture contained 3·3% of the *cis*-epoxide as determined by GC analysis.

When the racemic epoxide was prepared from *trans*-cyclooctene, 0·22 g (2 mmol) and 0·43 g (2 mmol) of (+)-peroxycamphoric acid in $CHCl_3$ with a total reaction time of one hr, 3·0% *cis*-epoxide was present in the mixture.

A solution of 0·25 g (2·2 mmol) of **1a** in 10 ml of CH_2Cl_2 was treated with 0·44 g (2·2 mmol) of *m*-chloroperbenzoic acid for 30 min and the *cis*/*trans* ratio of epoxides was 4·4/95·6.

Asymmetric synthesis of **6**. To a stirring solution of 0·50 g (4·5 mmol) of *trans*-cyclooctene in 10 ml of $CHCl_3$ was added 0·55 g (2·3 mmol) of (+)-peroxycamphoric acid (93% pure)[23] over 35 min. The mixture stirred for an additional 30 min at 25°. The $CHCl_3$ solution was washed with $NaHCO_3$ aq and H_2O. The organic layer was dried ($MgSO_4$) and solvent removed at an aspirator. The *cis* and *trans* epoxides were separated after some difficulty by using a 10', 10% FFAP on chromosorb W column at 125°. The *cis*/*trans* ratio was 5/95 and the collected *trans*-epoxide had $[\alpha]_D^{25}$ +0·13° (*c* 5·526 $CHCl_3$). The *cis*/*trans* ratio of the recovered olefin, was 14/86 as determined by gas chromatographic analysis on a 10' 30% NMPN column at 96°. A collected sample of the *trans*-olefin had $[\alpha]_D^{25}$ +1·05°, $[\alpha]_{365}^{25}$ +3·3° (*c* 6·146 $CHCl_3$).

Control experiments on the isomerization of **1a**. To a stirring solution of 0·11 g (1 mmol) of *trans*-cyclooctene in 5 ml ether at 25° was added 0·218 g (1·1 mmol) of dl-camphoric acid dissolved in 15 ml of ether. After 30 min the acid was extracted with $NaHCO_3$ and the olefins analyzed by GC. The *cis*/*trans* ratio was 0·6/99·4 after correction for a small amount of *cis* olefin initially present in the mixture. A similar experiment with 1 equivalent of AcOH in pentane showed 0·8% *cis* olefin to be present after 30 min. With *o*-chlorobenzoic acid in CH_2Cl_2 the *trans*-olefin was 5·6% isomerized after one hr. In the synthesis of *trans*-cyclooctene oxide with the corresponding peracids the olefin was consumed in less than 30 min.

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