trans-Cycloalkenes. Part IV.[1] Some Aspects of the Chemistry of trans-Cyclo-octene

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The following aspects of trans-cyclo-octene chemistry are discussed: (i) proton n.m.r. (including ^{13}C–H satellite) data, (ii) rates of addition of 1,3-dipoles. (iii) cyclo-addition of buta-1.3-diene. (iv) rate of epoxidation with peroxy-acid. (v) stereochemistry of addition of [^{2}H$_4$]acetic acid. and (vi) reaction with benzenesulphenyl chloride. All the results are explicable in terms of the unusual structure of trans-cyclo-octene which possesses a highly torsionally twisted double bond. only one face of which is accessible to attacking reagents.

trans-CYCLO-OCTENE was first reported by Ziegler and Wilms in 1950.[2] Since then it has attracted sustained interest on account of its chirality,[3] its structure and conformation,[4] its unusual reactivity,[5] and its use as a stringent objective for stereospecific olefin syntheses.[6,7] It is now fairly readily available by a variety of routes starting from cis-cyclo-octene,† and we report here some further aspects of its chemistry.

RESULTS AND DISCUSSION

N.m.r. Data.—From a first order analysis of the ^{13}C–H satellites of the absorption due to the olefinic protons in the ^{1}H n.m.r. spectrum of trans-cyclo-octene the following coupling constants were obtained: $J_{^{13}C–H}$

151, $J_{H-1,H-2}$ 16·0, $J_{H-2,H-3}$ 10·0, and $J_{H-2,H-3'}$ 4·5 Hz [see formula (1) for numbering system].

For comparison, values of $J_{^{13}C–H}$ for a 'normal' olefin (cyclohexene) and norbornene [8] are 157 and 174 Hz respectively. The value for trans-cyclo-octene can be

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† We currently prefer the β-hydroxyphosphine oxide route,[7] since the immediate precursor is a stable crystalline material which can be conveniently stored, but easily converted into trans-cyclo-octene when required.

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used as further evidence that one of the major components to the strain in this olefin is an out-of-plane distortion of the C-8,C-1,C-2,C-3 unit by torsion about the double bond.[9] This may be interpreted in terms of an enforced rehybridisation of the olefinic carbons towards sp^3, leading to decreased s-character of the orbitals involved in the relevant C–C and C–H bonds and resulting in a value for $J_{^{13}C-H}$ lower than that for a normal olefin. In contrast, the strain in norbornene is essentially an in-plane compression of the $C–\overset{\frown}{C}=C$ angle, leading to an effective increase in the s-character of the olefinic C–H bond and consequently to a higher $J_{^{13}C-H}$.

The vicinal trans-olefinic coupling constant, $J_{H-1,H-2}$, is surprisingly normal, but closely similar values have been obtained for trans-cyclo-oct-2-enyl derivatives [10] and it appears to be insignificantly affected by olefin strain.

The diastereotopic methylene protons at C-3 (and C-8) are identified in terms of the above assignments, on the basis of the known dependance of the vicinal vinyl–allylic coupling constants on dihedral angle.[11] Again corroboration is provided by similar values obtained for the diastereoisomeric trans-cyclo-oct-2-enols.[10]

(I)   (II)
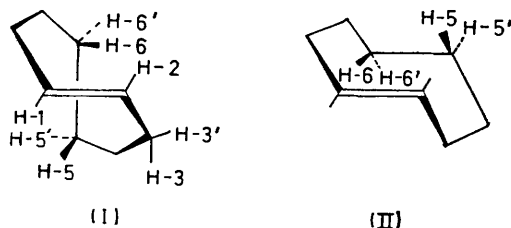
A characteristic feature in the ^{1}H n.m.r. spectrum of trans-cyclo-octene is a broad peak at τ 9·2—9·3 (2H).[12] This is at ca. 0·5 p.p.m. to higher field than the absorption due to the remaining methylene protons, itself in the normal region for alicyclic $-CH_2-$. Two conformations have been considered for trans-cyclo-octene, a ' twist ' conformation (I) and a ' chair ' conformation (II), and although molecular mechanics calculations,[4b,c] and two X-ray structure determinations on metal complexes [13] favour the twist conformation, a recent electron diffraction study has been interpreted in terms of the chair as the preferred conformation.[4a] If the equation developed by Mathieson et al.[14] for the shielding effect due to the anisotropy of the magnetic susceptibility of the double bond can be applied here,* the shielding experienced by the protons across the ring from the double bond can be calculated for the chair and twist conformations using angles and distances estimated from Dreiding models.

For the chair conformation each pair of equivalent hydrogens H-5, -6 and H-5', -6' [cf. formulae (I) and (II)] are only predicted to be shielded by ca. 0·05 p.p.m. For the twist conformation values of 0·09 p.p.m. for H-5', -6', and 0·23 p.p.m. for H-5, -6 are estimated. On the basis of this crude assessment, therefore, we find corroboration for the twist conformation as the preferred one for trans-cyclo-octene.

Angle Strain and Reactivity of trans-Cyclo-octene.—Another consequence of the torsional strain about the double bond in trans-cyclo-octene is its high reactivity in reactions leading to products in which the olefinic carbon atoms become tetrahedral. Qualitative evidence for this, in the case of addition of phenyl azide, was provided by Ziegler in his original work.[2,5k,l] We have described elsewhere [15] our determination of the second order rate constants for addition of phenyl azide, C-phenyl-N-methylnitrone, and N-methylene-1-ethylcyclo-hexylamine N-oxide to trans-cyclo-octene, which give quantitative verification. Thus, for addition of phenyl azide (in CCl_4 at 25°) k(trans-cyclo-octene) : k(cyclo-hexene) = 2·1 × 10^5, which may be compared with k(norbornene) : k(cyclohexene) = 5·7 × 10^3. If the rate constant for trans-cyclo-octene is considered in the light of the correlation proposed by Huisgen et al.[16] between rate constant for addition of phenyl azide and i.r. C=C stretching frequency for the olefin, the point for trans-cyclo-octene [ν(C=C str.) 1652 cm^{-1} (CCl_4)] falls far below the line. Thus trans-cyclo-octene is $>10^5$ times more reactive than expected if such a relationship existed. Clearly the suggested correlation does not apply to those olefins which possess out of plane torsional strain, such as trans-cyclo-octene.

The high reactivity of trans-cyclo-octene in cyclo-addition reactions is underlined by the observation that it acts as a dienophile towards butadiene in a Diels–Alder reaction to give trans-bicyclo[6.4.0]dodec-10-ene (III).† Under the same conditions the cis-isomer is unaffected. The reaction provides a convenient synthetic entrée into this bicyclic system.

One reaction which might be expected to discriminate between an in-plane angle-strained and an out-of-plane torsionally-strained olefin is epoxidation with a peroxy acid. The $H–\overset{\frown}{C}–C$ bond angle for ethylene oxide is 120° [17] so little relief of strain is expected in an epoxide-like transition state for an olefin such as norbornene, as we have found.[18] On the other hand the H–C–C–H torsion angle is 155° for ethylene oxide compared with 180° for ethylene. Thus the transition state for epoxidation of a

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* It is not considered that the ' calculated ' values for such an unusual olefin have any quantitative significance, but the qualitative difference found may be diagnostically significant.

† This reaction has also been briefly mentioned by Wheland and Bartlett.[5a]

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torsionally strained olefin should benefit from release of strain, in so far as epoxide character is developed at the transition state. In agreement we find the second order rate constant for epoxidation of trans-cyclo-octene by perbenzoic acid in tetrahydrofuran * to be 5.34×10^{-2} compared with cis-cyclo-octene 9.67×10^{-4}, and cyclohexene 5.92×10^{-4} l mol^{-1} s^{-1}. Thus the relative rates are cyclohexene, 1.0; cis-cyclo-octene, 1.6; trans-cyclo-octene, 90.† The enhanced rate with trans-cyclo-octene is particularly noteworthy in the light of a recent paper [21] commenting on the lack of a rate–strain relationship in the epoxidation of olefins.

A reaction of trans-cyclo-octene which clearly occurs as a consequence of the highly strained double bond, is the addition of acetic acid to give cyclo-octyl acetate. We investigated the addition of [^{2}H$_4$]acetic acid to trans-cyclo-octene in order to examine the stereochemistry of the reaction and also to see if any transannular process could be detected.

On heating under reflux with [^{2}H$_4$]acetic acid, trans-cyclo-octene was converted into a mixture of deuterio-cyclo-octyl acetate and cis-cyclo-octene. The acetate was isolated, hydrolysed, and re-acetylated. Comparison of the i.r. spectrum with that of mixtures of known composition prepared from authentic specimens indicated that it contained $>95\%$ of trans-[2-^{2}H]cyclo-octyl acetate. Authentic samples of cis- and trans-[2-^{2}H]-cyclo-octyl acetate were prepared via deuterioboration of cis-cyclo-octene and opening of cis-cyclo-octene epoxide with lithium aluminium deuteride–aluminium chloride respectively.

Addition of acetic acid to trans-cyclo-octene thus appears to occur in a highly stereospecific syn-fashion. It is attractive to consider that addition involves a 6-centre concerted process (IV) ⟶ (V), the effective microscopic reverse of an ester pyrolysis, as we suggested

(III)   (IV)   (V)
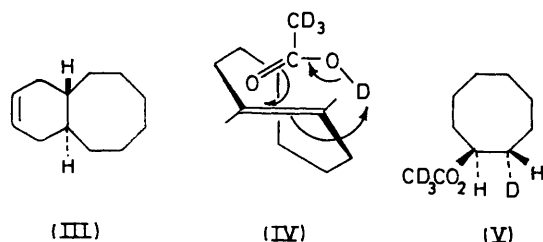
for addition of acetic acid to trans-cyclo-oct-2-enyl acetate.[1] Such concerted mechanisms have been proposed for addition to norbornenes,[22] but they have been criticised by Brown [23] on the basis that 7,7-dimethyl-norbornene, which does undergo exo-addition by acetic acid, should not be susceptible to concerted exo-attack.

* The choice of the unusual solvent (tetrahydrofuran) was dictated by the high reactivity of trans-cyclo-octene: the rate of epoxidation in the more usual solvents would be too fast to measure by conventional titrimetric techniques. However, rates of epoxidation by peroxy-acids in hydrogen-bond acceptor solvents, such as tetrahydrofuran, are an order of magnitude slower than in less basic solvents.[19]

† These values contrast with a report [20] that 'the relative reactivity of trans-cyclo-octene with m-chloroperbenzoic acid is only about eight times that of the cis-isomer.' However the latter statement was based on a competitive kinetic study only.

However, since Huisgen et al.[24] have recently shown that bona fide cycloadditions can occur exo- to 7,7-dimethyl-norbornene, the objection seems to be removed.

The other point to be noted in the addition of acetic acid, is the lack of transannular reaction despite the close proximity of H-5 and H-6 to the inside face of the double bond, and the known propensity of the cyclo-octyl action to undergo a transannular hydride shift.[25] A tentative explanation is that the postulated rehybridisation of the olefinic carbon atoms of trans-cyclo-octene towards sp^3 (see above) could lead to a situation where overlap between the transannular C–H and the (small) inside lobe of the relevant orbital cannot effectively occur.

We have also investigated addition of benzenesulphenyl chloride to trans-cyclo-octene. For normal olefins the usual reaction is the anti-addition of PhS and Cl, and epi-sulphonium ions have been shown to be intermediates.[26] In the case of trans-cyclo-octene the inside face of the double bond is so shielded that such a trans-addition could not occur. In fact the major product (65%) from addition of benzenesulphenyl chloride to trans-cyclo-octene was 3-phenylthiocyclo-octene (VI) presumably formed by intramolecular elimination in the episulphonium ion (VII). In contrast, addition to cis-cyclo-octene proceeded normally to give trans-2-phenylthiocyclo-octyl chloride (VIII).

(VI)   (VII)   (VIII)
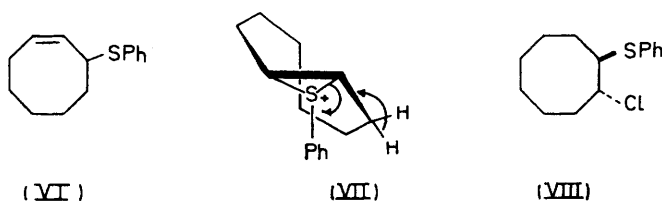
In summary, trans-cyclo-octene is unusual in that it is strained by out-of-plane torsion about the double bond. This strain is manifested in certain spectroscopic data, and also in the particularly high reactivity of the olefin in reactions involving a syn-addition to which it is particularly prone since only one face of the double bond is exposed.

EXPERIMENTAL

For general points see ref. 10.

trans-Cyclo-octene was prepared by the dioxolan synthesis.[6d] For spectroscopic determinations it was purified via the silver nitrate complex [27] followed by extraction of the olefin into redistilled light petroleum (b.p. 30—40°). Removal of solvent on a rotary evaporator at 0° gave trans-cyclo-octene uncontaminated with cis-olefin (g.l.c.).

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trans-*Bicyclo*[6.4.0]*dodec*-10-*ene* (*with* E. J. THOMAS).—
trans-Cyclo-octene (3·7 g) and butadiene (3·3 g) were heated in a sealed tube at 90—100° for 20 h. After evaporation of the excess of butadiene, the residue was distilled to give trans-*bicyclo*[6.4.0]*dodec*-10-*ene* (4·6 g, 86%) as an oil, b.p. 50° at 0·2 mmHg (Found: C, 87·7; H, 12·3. $C_{12}H_{20}$ requires C, 87·7; H, 12·3%), τ 4·4—4·6 (2H, m, olefinic) and 7·8—8·8 (18H, m).

cis-[2-^{2}H]*Cyclo-octanol*.—A suspension of lithium aluminium deuteride (0·35 g) in ether (35 ml) was added with stirring to a solution of cis-cyclo-octene (2·65 g) and BF_3–Et_2O (48%; 1·7 g) in dry ether (50 ml) over 20 min. After 18 h at 20°, acetone (10 ml) was added (at 0°) followed by saturated sodium sulphate (15 ml) and solid sodium sulphate (2·5 g). The ethereal phase was evaporated, and the residue dissolved in ethanol (90%; 15 ml) containing sodium hydroxide (0·4 g). Hydrogen peroxide (20%; 5·1 ml) was added during 5 min, and the temperature rose to 70° and was maintained for a further 5 min. After cooling, the product was isolated with ether. I.r. spectroscopy and g.l.c. showed the presence of cyclo-octanol and cyclo-octanone, and purification by p.l.c. (4 × 1 m plates; elution with ether–light petroleum 3 : 7) followed by distillation gave cis-[2-^{2}H]cyclo-octanol (0·7 g), b.p. 109—110° at 17 mmHg, single peak on g.l.c. (PEG, 155°).

The acetate, prepared in the usual way by using pyridine–acetic anhydride, had b.p. 104° at 10 mmHg, $\nu_{max.}$ (CS_2) 900sh, 878, 815, 801, 790, 774, 767sh, 753, 745, and 732 cm^{-1}.

trans-[2-^{2}H]*Cyclo-octanol*.—A solution of cis-1,2-epoxy-cyclo-octane (1·0 g) in ether (15 ml) was added to lithium aluminium deuteride (1·0 g) and aluminium chloride (1·0 g) in dry ether (25 ml) at 0°. After 16 h at 20°, water (20 ml) was added followed by sulphuric acid (10%; 100 ml) and the product was isolated with ether to give trans-[2-^{2}H]-cyclo-octanol (0·59 g), b.p. 102° at 11 mmHg, single peak on g.l.c. (PEG, 155°).

The acetate, b.p. 108° at 14 mmHg, had $\nu_{max.}$ (CS_2) 901, 820,*809sh, 783, 760, 729, and 709 cm^{-1}.

Reaction of trans-*Cyclo-octene with* [$^2H_4$]*Acetic Acid*.—A mixture of trans-cyclo-octene (1·0 g) and [$^2H_4$]acetic acid (5 ml) was heated under reflux (dry N_2) for 48 h. Water (10 ml) was added, and the product isolated with ether. cis-Cyclo-octene was removed by chromatography on a short column of silica gel and elution with light petroleum, and further elution with ether followed by evaporation gave deuteriocyclo-octyl acetate (0·36 g).

The deuterio-ester was hydrolysed to the alcohol with ethanolic potassium hydroxide (5%; 10 ml) and reacetylation with acetic anhydride–pyridine in the usual way followed by distillation gave [^{2}H]cyclo-octyl acetate. Comparison of the i.r. spectrum (5% soln. in CS_2) in the 900—700 cm^{-1} region with that of standard mixtures of cis- and trans-[2-^{2}H]cyclo-octyl acetate showed that it contained >95% of the trans-isomer.

Reaction of Benzenesulphenyl Chloride with trans-*Cyclo-octene*.—trans-Cyclo-octene (2 g) in 1,2-dibromoethane (30 ml) was treated at 0° with benzenesulphenyl chloride (2 g). Immediate decolourisation occurred. After 8 h at 0°, distillation gave a pale yellow oil (2·4 g), b.p. 130—135° at 0·7 mmHg, shown to contain one major component and three minor components by t.l.c. and g.l.c. The major component (65%, as shown by quantitative g.l.c. using 2,4-dinitro-benzene as an internal standard), was isolated by p.l.c.

(elution with ether–light petroleum 3 : 7) and had b.p. 162° at 0·9 mmHg, and was identified as 3-phenylthiocyclo-octene by comparison with an authentic sample (i.r., g.l.c., n.m.r.).

3-Phenylthiocyclo-octene.—Thiophenol (3·3 g) was added to a solution of sodium (0·7 g) in dry ethanol (20 ml). A solution of 3-bromocyclo-octene (5·7 g) [28] was then added to the stirred solution during 15 min at 25°. Rapid precipitation of sodium bromide occurred. After 14 h at 25° the suspension was filtered, the filtrate evaporated, and the residue distilled to give 3-*phenylthiocyclo-octene* (3·25 g, 50%) as a pale yellow oil, b.p. 158° at 0·8 mmHg, single peak on g.l.c. (PEGA, 149°), τ (CCl_4) 2·65—2·9 (5H, m, Ph), 4·2—4·6 (2H, m, 1-H and 2-H), 5·8—6·1 (1H, m, 3-H), and 7·8—8·8 (10H, m, methylenes) (Found: C, 76·85; H, 8·2. $C_{14}H_{18}S$ requires C, 77·0; H, 8·3%).

Addition of Benzenesulphenyl Chloride to cis-*Cyclo-octene*. —cis-Cyclo-octene (8 ml) was added to a solution of benzene-sulphenyl chloride (4 g) in dibromoethane (60 ml) and the mixture was heated on a steam-bath for 2 h. Distillation gave trans-1-*chloro*-2-*phenylthiocyclo-octane* (5·06 g, 72%) as a pale yellow oil, b.p. 158° at 0·5 mmHg, single peak on g.l.c. (PEGA, 147°), τ (CCl_4) 2·5—3·0 (5H, m, Ph), 5·7—5·95 (1H, m, 1-H), 6·3—6·6 (1H, m, 2-H), and 7·5—9·0 (12H, m, methylenes) (Found: C, 65·15; H, 6·95; Cl, 13·75; S, 12·65. $C_{14}H_{19}ClS$ requires C, 66·0; H, 7·45; Cl, 13·95; S, 12·55%).

Owing to the poor analysis the compound was further characterised by oxidation to the sulphone by using hydrogen peroxide in acetic acid to give trans-1-*chloro*-2-*phenyl-sulphonylcyclo-octane*, m.p. 83—84° (from EtOH) (Found: C, 58·9; H, 6·8; Cl, 12·75; S, 11·45. $C_{14}H_{19}ClO_2S$ requires C, 58·7; H, 6·65; Cl, 12·4; S, 11·2%). The trans-stereo-chemistry for the latter is consistent with its ready elimination reaction with potassium hydroxide in aqueous dioxan to give 1-*phenylsulphonylcyclo-octene*, b.p. 165° at 0·05 mmHg, τ (CCl_4) 2·0—2·6 (5H, m, Ph), 2·95 (1H, t, H-2), and 7·6—8·6 (12H, methylenes) (Found: C, 66·95; H, 7·4; S, 12·35. $C_{14}H_{18}O_2S$ requires C, 67·2; H, 7·2; S, 12·8%).

Rates of Epoxidation.—A solution of perbenzoic acid in benzene was prepared in the usual way.[29] Benzene was removed on a rotatory evaporator at 20° and the yellowish solid obtained was dissolved in the appropriate amount of tetrahydrofuran (THF).

Equal volumes of solutions of the olefin and perbenzoic acid in THF were mixed and kept at 20° in a thermostatted bath. At regular intervals, aliquot portions (1 ml) were removed and quenched by shaking with potassium iodide (1·5 g) in water (10 ml), carbon tetrachloride (5 ml), and glacial acetic acid (5 ml). The iodine liberated was titrated with standard thiosulphate solution.

Rate constants were obtained by standard second-order kinetic plots and are quoted in the Discussion section (average of two runs in each case).

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