Oxygenation Studies. Part 9.[1] Mechanistic Studies on the Oxygenation of Cyclooctene at $[\{RhCl(C_8H_{14})_2\}_2]$

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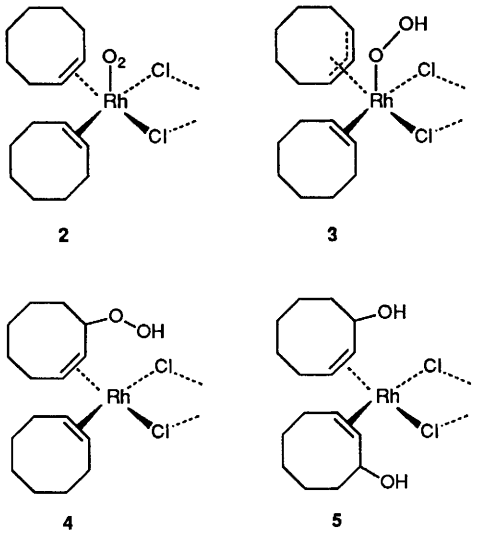
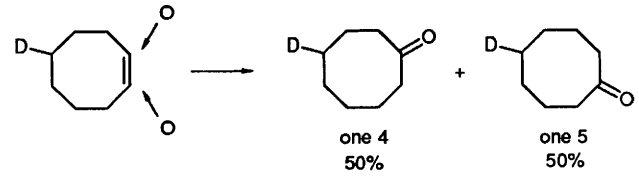
The complex $[\{RhCl(C_8H_{14})_2\}_2]$ in benzene containing *cis*-[5-$^2H_1$]-cyclooctene has been shown to undergo ligand exchange at 26 °C at a very much faster rate than oxygenative breakdown. Double-bond isomerisation competes with the latter. The principal oxygenated product is a mixture of monodeuterioisotopomers of cyclooctanone which has been shown, by ^{13}C NMR analysis, to have been formed by oxygenative attack on the vinylic carbons rather than on the allylic centres or on π-allylic intermediates. The findings are related to earlier mechanistic proposals for oxygenation of alkenes catalysed by rhodium species.

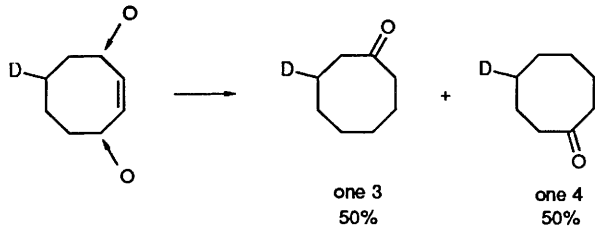
Reactions of the dimeric rhodium complex $[\{RhCl(C_8H_{14})_2\}_2]$ **1** under aerobic conditions attracted the attentions of both organometallic and organic chemists in the seventies. Oxygenated alkenes were detected but there was little cohesive evidence to provide a detailed picture of the reactions involved.

James and Ng[2] showed that complex **1** reacted readily with oxygen. Subsequently studies were reported[3] on its decomposition in CH_2ClCH_2Cl. Infrared spectroscopic changes were interpreted in terms of the formation of a co-ordinated allylic hydroperoxide which broke down to give cyclooct-2-en-1-one, the only organic product detected. The mechanism envisaged for the initial attack on the cycloalkene ligand involved the peroxorhodium intermediate **2**. It was suggested that the peroxo ligand abstracted an allylic hydrogen from the co-ordinated cycloalkene to produce the π-allylic hydroperoxidic species **3**. Subsequent intramolecular oxygenative attack by the hydroperoxidic ligand on the adjacent π-allyl ligand was thought to generate the transient allyl hydroperoxide **4**. Later work by Holland and Milner[4] on the oxygenation of the complex at 74 °C in benzene solution containing cyclooctene revealed the formation of cyclooct-2-en-1-one and cyclooctanone totalling a little over 1 mol per mol of complex. Equivalent dimethylacetamide solutions gave product yields of up to 5 mol per mol of complex indicating a weak catalytic performance. In accounting for these results Holland and Milner suggested that

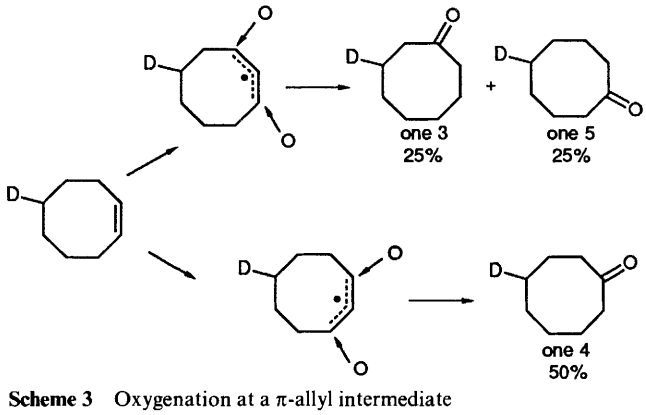




Scheme 1 Oxygenation by vinylic attack



Scheme 2 Oxygenation by allylic insertion



Scheme 3 Oxygenation at a π-allyl intermediate

the peroxorhodium species **2** entered into a concerted oxygen insertion at allylic C–H (*cf.* ref. 5) to produce complex **5** carrying two co-ordinated molecules of cyclooct-2-en-1-ol which were subsequently converted into the observed products. Both these mechanistic proposals differ from the conclusions derived from later studies on the interaction of peroxorhodium species with linear alkenes which have consistently indicated that oxygenative attack is at a vinylic centre rather than at a π-allylic system or an allylic position.[1] It therefore seemed expedient to acquire a clearer picture of the manner by which oxygen attacks the cyclooctene ligands in $[\{RhCl(C_8H_{14})_2\}_2]$.

In principle it is possible to distinguish clearly between these three mechanistic routes by effecting the reaction with an isotopically labelled cyclooctene. When, for example, the cyclooctene in the complex is [5-$^2H_1$]cyclooctene, the isotopomers of cyclooctanone formed by each mechanistic pathway would be as shown in Schemes 1–3 and the theoretical abundance of each monodeuterioisotopomer would be as indicated. The isotopomeric products and their abundances could be established by ^{13}C NMR spectroscopy using the approach pioneered by Staunton and co-workers[6] who, in biosynthetic studies, assessed the level of deuterium incorporation at specific centres by quantitative measurement of β-hydrogen-shifted signals. We report the findings of such an investigation in this paper.

Experimental

Carbon-13 NMR measurements were made using a Bruker AM 250 spectrometer with $CDCl_3$ as solvent and $SiMe_4$ as internal standard. Gas-liquid chromatography was carried out using a Pye Unicam GCD gas chromatograph. Infrared measurements were made on a Perkin-Elmer 398 spectrometer. For measurements of isotopic abundances samples were purified by gas chromatography, using a Pye 104 instrument, before being led directly into a Micromass 16F mass spectrometer. The isotopic abundances were calculated by the method detailed in ref. 7.

cis-Cyclooctene (Aldrich) and *cis*-[5-$^2H_1$]cyclooctene[7] were distilled from $LiAlH_4$ under N_2 before use and stored at 0 °C in the dark. Benzene (A.R.), after heating under reflux with chromic acid for 24 h and being washed successively with aqueous NaOH, aqueous $NaHSO_3$ and water, was further purified by fractional distillation and dried by refluxing over sodium wire for 1 h before being redistilled and collected over molecular sieves of type 4A (BDH). Oxygen (B.O.C.) and nitrogen (B.O.C. White Spot) were used without further purification.

Oxygenation of [{RhCl(C_8H_{14})$_2$}$_2$].—*With cyclooctene at* 74 °C. In a typical study [{RhCl(C_8H_{14})$_2$}$_2$] (2.1 g, 2.9 mmol) and cyclooctene (5.76 g, 0.052 mol), with *p*-bromoanisole as an internal GC standard, were stirred in benzene (100 cm^3) at 74 °C with oxygen bubbling gently through the solution. Almost immediately a brown precipitate began to form. The reaction was allowed to proceed for up to 8 h, during which time samples (1 μl) were taken for GLC analysis (see Fig. 1).

The precipitate, isolated at the end of the reaction by centrifugation, was washed repeatedly with benzene and dried under high vacuum. It decomposed at 220 °C (Found: C, 30.30; H, 4.05; Cl, 12.40%), ν_{max}(KBr disk)/cm^{-1} 3998w, 3365vs, 2916vs, 2845vs, 1997w, 1561s, 1534vs, 1436vs, 1399s, 1246vs, 1160m, 1119m, 1020m, 823w, 751m, 723m, 694m and 536s [lit.[3] (Found: C, 26.6; H, 3.75; Cl, 12.7; Rh, 36.20), ν_{max}/cm^{-1} 3350 and 2900 cm^{-1}]; cryoscopy in dimethyl sulphoxide indicated a relative molecular mass of *ca.* 252.

With [5-$^2H_1$]*cyclooctene at* 26 °C. Oxygen was slowly bubbled through a stirred solution of [5-$^2H_1$]cyclooctene (7.56 g, 0.068 mol, 98% isotopic purity) in benzene (100 cm^3) held at 26 °C in a thermostatted water-bath. The complex [{RhCl(C_8H_{14})$_2$}$_2$] (1.0 g, 1.39 mmol) was added and the conditions were maintained for 1 h before 1,2-bis(diphenylphosphino)ethane (2.3 g, 5.8 mol) was added. After stirring for 5 min, the reaction solution was passed through a Kieselgel 60H column (4 cm). The column was eluted with benzene (100 cm^3) followed by benzene–ethyl acetate (1:1, 200 cm^3).

Unreacted cyclooctene was recovered from the benzene eluate and examined for deuterium distribution by high-field ^{13}C NMR spectroscopy [see Discussion and Table 1(*a*)]. The cyclooctanone was isolated from the benzene–ethyl acetate eluate and purified by chromatography (light petroleum–ethyl acetate, 4:1) on a column of 'flash' silica to give the $^2H_1$-labelled ketone (0.02 g, 0.16 mmol) showing an 89.6% isotopic abundance [see Discussion and Table 1(*b*)].

Table 1 Treatment of ^{13}C NMR integration measurements

		Factor		Component signal		
Carbon		*m*	*n*	Unshifted	β-Shifted	α-Shifted
(*a*) Cyclooctene						
C^1	(i)*	—	—	1.119	0.055	—
	(ii)	1.882	—	2.106	0.104	—
C^3	(i)*	—	—	0.906	0.160	0.050
	(ii)	1.980	1.000	1.794	0.317	0.099
	(iii)	1.965	1.178	1.780	0.314	0.116
	(iv)	1.963	1.199	1.778	0.314	0.118
	(v)	1.963	1.201	1.778	0.314	0.118
C^4	(i)*	—	—	0.623	0.339	0.111
	(ii)	2.060	1.000	1.283	0.698	0.229
	(iii)	2.022	1.178	1.260	0.686	0.264
	(iv)	2.018	1.199	1.257	0.684	0.269
	(v)	2.018	1.201	1.257	0.684	0.269
C^5	(i)*	—	—	0.404(4)	0.418	0.266
	(ii)	2.031	1.000	0.821	0.849	0.540
	(iii)	1.946	1.178	0.787	0.813	0.610
	(iv)	1.936	1.199	0.783	0.809	0.617
	(v)	1.935	1.201	1.783	0.809	0.618
(*b*) Cyclooctanone						
C^2	(i)*	—	—	0.927	0.072	—
	(ii)	2.234	—	2.071	0.161	—
C^3	(i)*	—	—	0.710	0.230	0.073
	(ii)	2.203	1.000	1.564	0.507	0.161
	(iii)	2.175	1.179	1.544	0.500	0.187
	(iv)	2.171	1.207	1.541	0.499	0.191
	(v)	2.170	1.211	1.541	0.499	0.192
C^4	(i)*	—	—	0.422	0.391	0.164
	(ii)	2.285	1.000	0.964	0.893	0.375
	(iii)	2.218	1.179	0.936	0.867	0.429
	(iv)	2.208	1.207	0.932	0.863	0.437
	(v)	2.206	1.211	0.931	0.863	0.438
C^3	(i)*	—	—	0.145	0.201	0.139
	(ii)	2.301	1.000	0.334	0.463	0.320
	(iii)	2.189	1.179	0.317	0.440	0.359
	(iv)	2.172	1.207	0.315	0.437	0.364
	(v)	2.170	1.211	0.315	0.436	0.365

Refinement of ^{13}C NMR *Integration Measurements.*—In Table 1, the signal intensity [(i)*], as measured by integration, is multiplied by factor *m* [(ii)–(v)], adjustment for the response factor and the abundance of undeuteriated molecules in the samples, and by factor *n* [(iii)–(v)], adjustment for slower relaxation and nuclear Overhauser loss at the α-shifted signal, to give the fractions of each component of the carbon signal. Data in (iii), (iv) and (v) show the results of the iterative refinement of '*n*', as described in the Discussion, and its impact on both '*m*' and the size of the components within each signal.

(*a*) *Cyclooctene.* Only carbons C^3, C^4 and C^5 carry any significant fraction of deuterium label. The sum of component intensities of each carbon signal is taken as 2.210 on the basis of the full ligand equilibration giving a 90.5% abundance of monodeuterioisotopomers. For the contribution to each signal component of unlabelled cyclooctene and the three monodeuterioisotopomers see Table 2(*a*) (Discussion).

(*b*) *Cyclooctanone.* Only carbons C^3, C^4 and C^5 carry any significant fraction of the deuterium label. The sum of the component intensities of each signal from C^2, C^3 and C^4 and the sum of component intensities of the signal from C^5 are taken as

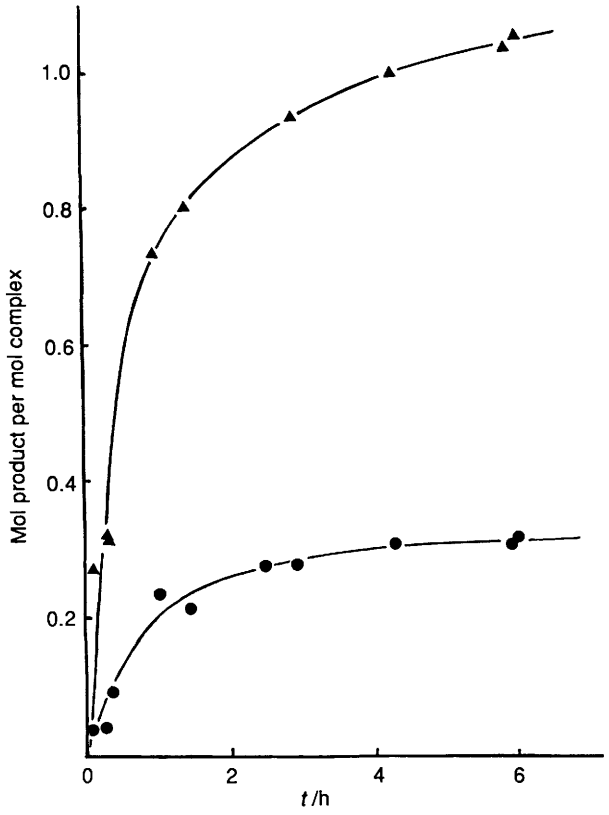


Fig. 1 Oxygenation of $[\{RhCl(C_8H_{14})_2\}_2]$ (2.9×10^{-2} mol l^{-1}) and cyclooctene (5.2×10^{-1} mol l^{-1}) in benzene at 74 °C under O_2: (▲) cyclooctanone; (●) cyclooct-2-en-1-one

2.232 and 1.116 respectively on the basis of an 89.6% abundance of monodeuterioisotopomers. For the contribution to each signal component of the unlabelled cyclooctanone and the three monodeuterioisotopomers see Table 2(*b*) (Discussion).

Treatment of Cycloalkene Isomerisation Kinetics.—The normalised values for the concentrations of isotopomers ene 1 to ene 5 (Scheme 4) are expressed as a_1 to a_5 respectively. The four rate equations which follow from the kinetic considerations presented in the Discussion section, can be expressed in the matrix form $(d/dt)\ \boldsymbol{x} = -k\ \boldsymbol{A}\ \boldsymbol{x}$, *i.e.* as shown in (1) The

$$\frac{d}{dt}\begin{bmatrix} a_5 \\ a_4 \\ a_3 \\ a_1 \end{bmatrix} = -k \begin{bmatrix} +1 & -1 & 0 & 0 \\ -1 & +2 & -1 & 0 \\ 0 & -1 & +\frac{3}{2} & -1 \\ 0 & 0 & -\frac{1}{2} & +1 \end{bmatrix} \begin{bmatrix} a_5 \\ a_4 \\ a_3 \\ a_1 \end{bmatrix} \quad (1)$$

boundary conditions for the system are: (*i*) $a_5 + a_4 + a_3 + a_1 = 1$; (*ii*) when $t = 0$, $a_5 = 1$ and $a_4 = a_3 = a_1 = 0$; and (*iii*) when $t = \infty$, $a_5 = a_4 = a_3 = 2/7$ and $a_1 = 1/7$. The concentrations vary with time as sums of exponentials, with time constants given by the eigenvalues of the unsymmetric matrix $\boldsymbol{A}$.

Expansion of $|\boldsymbol{A} - \lambda\boldsymbol{1}| = 0$ gives one zero eigenvalue (corresponding to the long-time limit) and three eigenvalues λ_1, λ_2 and λ_3 that satisfy the cubic (2) and correspond to the

$$\lambda^3 - (11/2)\lambda^2 + (17/2)\lambda - 7/2 = 0 \quad (2)$$

time-dependent solutions of the matrix differential equation. Numerically these values are $\lambda_1 = 0.659\,335$, $\lambda_2 = 1.678\,963$ and $\lambda_3 = 3.161\,702$. Evaluation of the right-hand eigenvectors of $\boldsymbol{A}$ and imposition of the boundary conditions gives the variation of a_5, a_4, a_3 and a_1 with time as in equations (3)–(6),

$$a_5 = 0.372\,74e^{-\lambda_1 kt} + 0.219\,61e^{-\lambda_2 kt} + 0.121\,93e^{-\lambda_3 kt} + 2/7 \quad (3)$$

$$a_4 = 0.126\,98e^{-\lambda_1 kt} - 0.149\,11e^{-\lambda_2 kt} - 0.263\,58e^{-\lambda_3 kt} + 2/7 \quad (4)$$

$$a_3 = 0.202\,50e^{-\lambda_1 kt} - 0.267\,48e^{-\lambda_2 kt} + 0.184\,27e^{-\lambda_3 kt} + 2/7 \quad (5)$$

$$a_1 = 0.297\,21e^{-\lambda_1 kt} + 0.196\,98e^{-\lambda_2 kt} - 0.042\,62e^{-\lambda_3 kt} + 1/7 \quad (6)$$

where λ_1, λ_2 and λ_3 have the values given above. The variation of a_5, a_4, a_3 and a_1 with time is shown in Fig. 4.

Theoretical Relationships between the Cyclooctene Isotopomeric Ratio at the time of Quench and the Cyclooctanone Isotopomeric Ratio in the Product.—The normalised values for the concentrations of isotopomers one 2 to one 5 (Schemes 1–3) are expressed as b_2 to b_5 respectively [equations (7)–(18)]. In all cases integrations are with respect to kt between the limits $t = 0$ and $t =$ time of quench.

(*a*) Based on vinylic oxygenative attack

$$b_5 = \tfrac{1}{2}\textstyle\int a_5 \quad (7)$$

$$b_4 = \tfrac{1}{2}(\textstyle\int a_5 + \int a_4) \quad (8)$$

$$b_3 = \tfrac{1}{2}(\textstyle\int a_4 + \int a_3) \quad (9)$$

$$b_2 = \tfrac{1}{2}\textstyle\int a_3 + \int a_1 \quad (10)$$

(*b*) Based on oxygen insertion into an allylic C–H bond

$$b_5 = \tfrac{1}{2}\textstyle\int a_4 \quad (11)$$

$$b_4 = \tfrac{1}{2}(\textstyle\int a_5 + \int a_3) \quad (12)$$

$$b_3 = \tfrac{1}{2}(\textstyle\int a_5 + \int a_1) + \tfrac{1}{4}\int a_3 \quad (13)$$

$$b_2 = \tfrac{1}{2}(\textstyle\int a_4 + \int a_1) + \tfrac{1}{4}\int a_3 \quad (14)$$

(*c*) Based on oxidative attack on a π-allylic intermediate

$$b_5 = \tfrac{1}{4}(\textstyle\int a_5 + \int a_4) \quad (15)$$

$$b_4 = \tfrac{1}{2}\textstyle\int a_5 + \tfrac{1}{4}\int a_4 \quad (16)$$

$$b_3 = \tfrac{3}{8}(\textstyle\int a_3 + \int a_1) + \tfrac{1}{4}(\int a_5 + \int a_4) \quad (17)$$

$$b_2 = \tfrac{5}{8}(\textstyle\int a_3 + \int a_1) + \tfrac{1}{4}\int a_4 \quad (18)$$

Results

Under conditions which closely paralleled those used by Holland and Milner,[4] cyclooctanone (1.05 mol per mol complex) and cyclooct-2-en-1-one (0.3 mol per mol complex) were obtained on bubbling oxygen through a solution of $[\{RhCl(C_8H_{14})_2\}_2]$ and cyclooctene in benzene at 74 °C for 6 h (see Fig. 1). As reported,[4] the complex was rapidly converted into an insoluble brown precipitate but in our study the product ratio differed considerably from the 1:1 ratio previously reported. The added cyclooctene contributed to only a portion of the organic products since cyclooctanone (0.64 mol per mol complex) and cyclooct-2-en-1-one (0.23 mol per mol complex) were obtained when only the complex was present. Spectroscopic and elemental analyses of the amorphous solid formed in the reaction provided little by way of structural information apart from indicating an absence of co-ordinated olefin (NMR spectroscopy). At room temperature, with added olefin, lower yields of cyclooctanone and cyclooct-2-en-1-one (0.5 and 0.12 mol per mol complex respectively) were produced in a 24 h period. Trace amounts of cyclooct-3-en-1-one, cyclooct-2-en-1-ol and cyclooctene oxide were also detected.

In this study our original intention was to prepare the complex labelled with [5-$^2H_1$]cyclooctene[7] and to treat this with oxygen in the presence of [5-$^2H_1$]cyclooctene under the conditions used by Holland and Milner. However all attempts to prepare the complex with the deuterium labelling specifically confined to C^5 in the four cyclooctene ligands failed. Extensive double-bond migration occurred during the preparations. The evidence for this was provided by the deuterium distribution in both the excess of cyclooctene, recovered from the various preparative attempts, and the oxygenated products, obtained from the complexes produced. The synthetic methods examined included formation of the complex from $C_8H_{13}D$–$RhCl_3$–propan-2-ol–water[8] (which also led to considerable D/H exchange) and displacements of C_2H_4 and C_8H_{14} from $[\{RhCl(C_2H_4)_2\}_2]$[9] and complex **1** respectively with the deuteriated cyclooctene. Faced with this complication an attempt was made to secure mechanistically significant information by preparing $[\{RhCl(C_8H_{13}D)_2\}_2]$ *in situ* invoking the assumption that *ligand exchange would be much faster than ligand oxygenation.* Unlabelled complex was oxygenated at 63 °C in benzene in the presence of [5-$^2H_1$]cyclooctene. The ^{13}C NMR spectrum of the resulting cyclooctanone and the unreacted cyclooctene showed that the labelled cycloalkane had exchanged with unlabelled co-ordinated cyclooctene and had contributed to the oxygenated products under these conditions. However, randomisation of the label remained extensive. Eventually greater but incomplete control over the offending isomerisation was achieved by reducing the reaction temperature to 26 °C and quenching the reaction after 1 h with 1,2-bis(diphenylphosphino)ethane.

Measurement on the monodeuteriated ketonic product (0.12 mol per mol complex) isolated from the reaction at 26 °C gave an isotopic abundance of 89.6% which is very close to the theoretical value of 90.5% for complete equilibration between the labelled substrate and the unlabelled ligand and is also in accord with competition between fast ligand exchange and slow oxygenation. The recovered cyclooctene and cyclooctanone were examined by high-field ^{13}C NMR spectroscopy. Inspection of the crude data clearly showed detectable levels of deuterium at only the 3, 4 and 5 carbons in both the recovered cycloalkene and the cycloketone. As hoped, at each carbon, separation of the α- and β-shifted signals from the unshifted signals was sufficient for measurement to be made of their fractional contributions to the overall signal.

Treatment of ^{13}C NMR Measurements.—The contributions per carbon from the cyclooctene species and the cyclooctanone species to the individual components of each of the ^{13}C NMR signals are shown in Table 2. In this table a_3, a_4 and a_5 indicate the fraction of cyclooctene isotopomers carrying deuterium at C^3, C^4 and C^5 (ene 3, ene 4 and ene 5; Scheme 4) respectively and b_3, b_4 and b_5 indicate the fraction of cyclooctanone isotopomers carrying deuterium at C^3, C^4 and C^5 (one 3, one 4 and one 5; Schemes 1–3) respectively. The contribution per carbon of unlabelled molecules to each signal is given by a_u and b_u. Table 2(*a*) shows that the α- and β-shifted signals in the cyclooctene spectrum provide two independent values for a_3, two for a_4, and one for a_5. By using the average independent values for a_3 and a_4, two interdependent values for a_5 can also be calculated from the β-shifted C^4 and C^5 signals. Similarly, Table 2(*b*) shows that for cyclooctanone two independent values for b_3, three independent values for b_4 and one independent value for b_5 can be obtained. An interdependent value for b_5 can be calculated from the β-shifted C^4 signal using the average of the independent values for b_3.

To relate the observed signals to the terms in Table 2, the recorded total integration across each carbon was multiplied by factor *m* (see the Experimental section) which takes the response factor of the instrument and the abundance of the unlabelled molecules into account. This treatment cannot make allowance for the inherently lower intensities of the α-shifted signals.[10]

Table 2 Contributions to the individual components of the ^{13}C NMR signals

Carbon	Unshifted	β-Shifted	α-Shifted
(*a*) From cyclooctene species			
C^1	$2a_u + 2a_5 + 2a_4 + a_3$	a_3	—
C^3	$2a_u + 2a_5 + a_4 + a_3$	a_4	a_3
C^4	$2a_u + a_5 + a_4 + a_3$	$a_5 + a_3$	a_4
C^5	$2a_u + a_4 + 2a_3$	$a_4 + a_5$	a_5
	$a_u = 0.105$	$a_5 + a_4 + a_3 = 1.000$	
(*b*) From cyclooctanone species			
C^2	$2b_u + 2b_5 + 2b_4 + b_3$	b_3	—
C^3	$2b_u + 2b_5 + b_4 + b_3$	b_4	b_3
C^4	$2b_u + b_4 + b_3$	$2b_5 + b_3$	b_4
C^5	$b_u + b_3$	b_4	b_5
	$b_u = 0.116$	$b_5 + b_4 + b_3 = 1.000$	

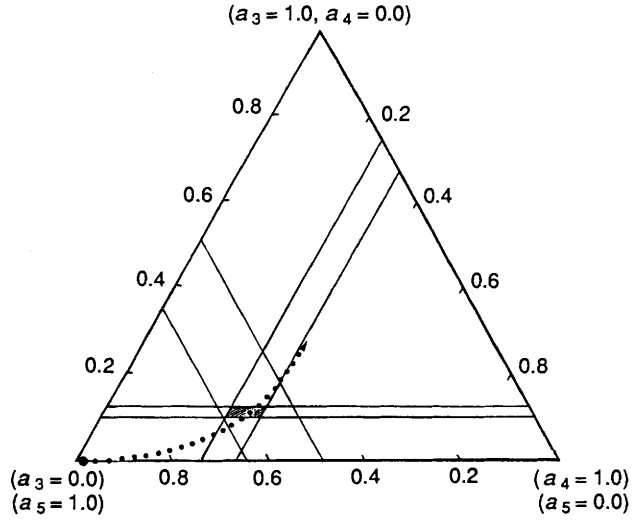


Fig. 2 Isotopomeric composition of the recovered cyclooctene after treating [5-$^2H_1$]cyclooctene with complex **1** in benzene at 26 °C under aerobic conditions. The predicted development of the isotoperisation is shown as ●●●●●●▸

However, on the assumption that this loss is similar at each α-shifted signal, a correction for this weaker signal (factor *n* in the Experimental section) was made using an iterative procedure based on the average factor *m* and the relationships $a_5 + a_4 + a_3$ and $b_5 + b_4 + b_3 = 1.0$. When these values from the cyclooctene spectrum [Table 1(*a*)] were equated to the terms in Table 2(*a*) and further allowance was made for experimental error (5%), the ranges of values obtained for a_3, a_4 and a_5 were 0.099–0.124, 0.256–0.330 and 0.492–0.650 respectively. However, these ranges are inter-related and a less diffuse measure of the deuterium distribution is obtained by plotting these experimentally derived values as a triangular graph (Fig. 2) in which the limits of the experimental values are restricted to the shaded area.

A similar treatment of the adjusted data from the spectrum of the cyclooctanone sample [Table 1(*b*)] gave values for the monodeuterioisotopomer fractions b_3, b_4 and b_5 of 0.153–0.202, 0.415–0.524 and 0.327–0.383 respectively. Graphical interrelation of these ranges restricted them to the shaded area shown in Fig. 3.

Assessment of the Impact of Competing Double-bond Isomerisation.—Although the rate of catalytic isomerisation of the [5-$^2H_1$]cyclooctene relative to that of catalytic oxidation was much lower at 26 than at 63 °C it remained high enough to

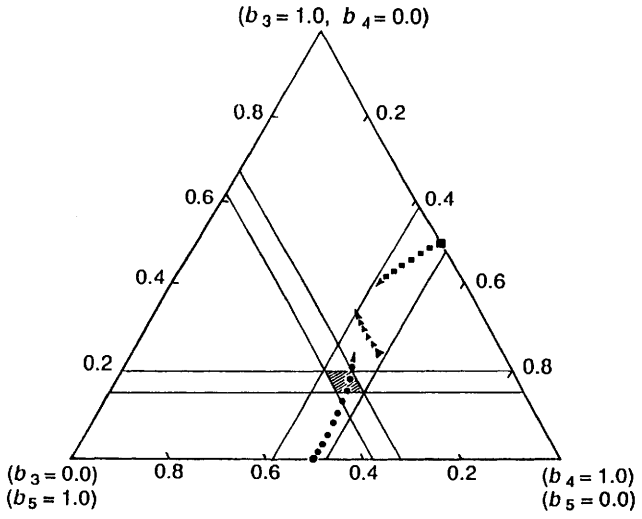
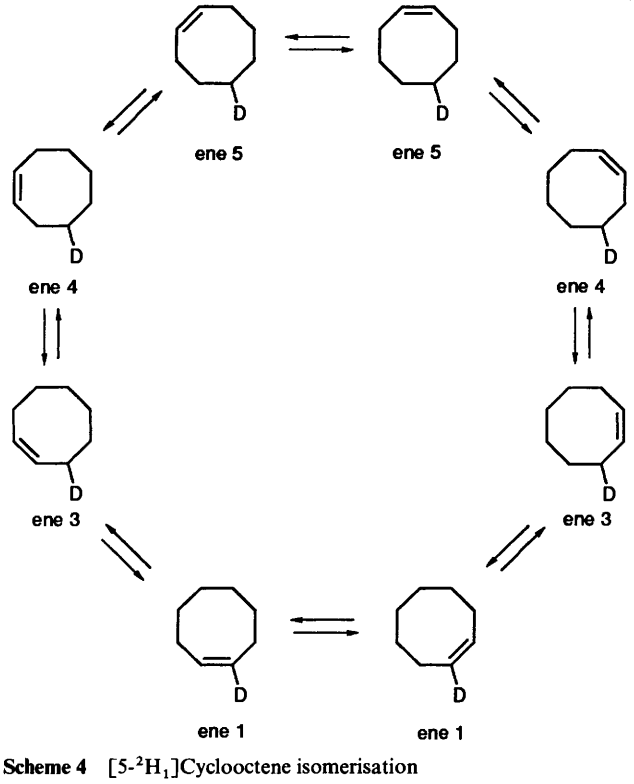


Fig. 3 Isotopomeric composition of cyclooctanone from [5-$^2H_1$]cyclooctene and complex **1** in benzene at 26 °C under aerobic conditions. The predicted development of isotopomerisation on vinylic attack, on allylic insertion, and on oxygenation of a π-allyl intermediate is shown as ●●●●●●▸, ◆◆◆◆◆◆▶ and ▶▸▸▸▸▸▸ respectively. Larger symbols denote the initial conditions



Scheme 4 [5-$^2H_1$]Cyclooctene isomerisation

prevent a direct interpretation of the data derived from the ^{13}C NMR studies. This isomerisation is depicted in detail in Scheme 4. If long-range and secondary isotopic effects are ignored, the rate constants for each transformation can, with one exception, be taken as equal. In the case of the transformation ene 3→ene 1 the rate constant is taken as half that of the others for only one hydrogen is available for migration, unlike the two in all other cases. Migration of the deuterium atom in ene 3 regenerates ene 3 and so there is no primary isotopic effect to consider. On this theoretical basis the relationships (19)–(22) apply at a *constant concentration* of the

$$(\text{d ene } 5/\text{d}t) = k(a_1 - a_5) \quad (19)$$

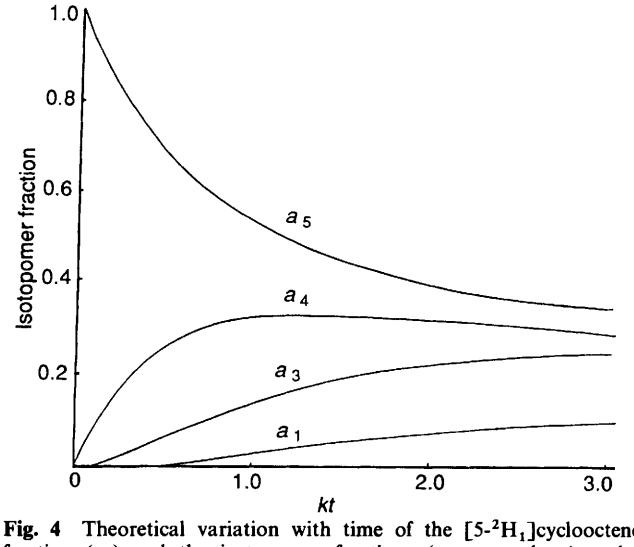


Fig. 4 Theoretical variation with time of the [5-$^2H_1$]cyclooctene fraction (a_5) and the isotopomer fractions (a_4, a_3 and a_1) under conditions of catalytic isomerisation

$$(\text{d ene } 4/\text{d}t) = k(a_5 + a_3 - 2a_4) \quad (20)$$

$$(\text{d ene } 3/\text{d}t) = k(a_1 + a_4 - 1.5a_3) \quad (21)$$

$$(\text{d ene } 1/\text{d}t) = k(0.5a_3 - a_1) \quad (22)$$

apply at a *constant concentration* of the catalytic species when the total concentration of the deuteriated cyclooctene is taken as unity and the concentrations of each monodeuterioisotopomer are expressed as a_5, a_4, a_3 and a_1.

Treatment of these rate terms as outlined in the Experimental section gives the fractions of each isotopomer as a function of time. These are portrayed in Fig. 4. The above treatment is valuable in predicting the *isotopomeric ratios* of the cyclooctene species throughout the isomerisation. The relationship between the isotopomeric ratios and kt is less useful since k is not known and, in practice, the rapid decay of the rhodium species in the reaction ensures that the real time axis is not linear. Nevertheless, the observed ratio of isotopomers in the recovered cyclooctene, which reflects the extent of cyclooctene isomerisation in the solution at the time the reaction was quenched, should relate to a position on the kt axis of Fig. 4. Since the levels of ene 1 in the isotopomeric mixture are below the detection limit this position cannot be much further than 0.5 kt from the origin.

With some satisfaction we find that when the theoretical values for a_5, a_4 and a_3* are normalised and plotted [Fig. 2 (arrow)] the predicted ratios pass within the limits of the experimental values. On this basis the degree of isomerisation in the cyclooctene substrate at the time at which the reaction was quenched is close to that predicted for 0.77 kt on Fig. 4.

The theoretical kinetic treatment of the cyclooctene isomerisation can be extended to predict the isotopomeric ratios in the cyclooctanone derived from the cycloalkene by each of the mechanisms depicted in Schemes 1–3. Since the ketone formation can be regarded as irreversible, the effective isotopomeric ratio of cyclooctene responsible for the isotopic ratio in the ketone is given in theory by the normalised integrations of a_5, a_4, a_3 and a_1 between $kt = 0$ and $kt =$ reaction quench. The relationships of $\int a_5$, $\int a_4$, $\int a_3$ and $\int a_1$ to the relative concentrations of the ketonic isotopomers b_5, b_4, b_3 and b_2 for each mechanism are set out in the Experimental section.

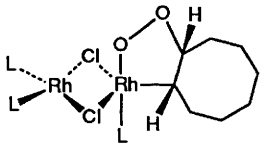
* In practice a_1 is too small to measure in the ^{13}C NMR spectrum. In Fig. 2, distortion of the theoretical values for a_5, a_4 and a_3 by omitting the theoretical value of a_1 from the normalisation is minimal over the critical range of the plot.

Normalised values for the isotopomeric products at each point in the isomerisation process can be calculated for the three mechanisms. These calculations are summarised by the three arrows in Fig. 3 using normalised figures for b_5, b_4 and b_3 only, to allow direct comparison with the experimental findings.

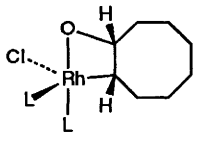
Discussion

Fig. 3 clearly shows that the isotopomeric ratios found in the cyclooctanone are consistent with oxygenative attack on the partly isomerised [5-$^2H_1$]cyclooctene at the vinylic position. The ratios are inconsistent with either of the alternative mechanisms considered, irrespective of the degree of isomerisation in the substrate. It is of some relevance to the complex mechanistic situation involved in this reaction that the degree of isomerisation associated with the observed isotopomeric ratios for the cyclooctanone is close to $kt = 1.27$ which is considerably higher than the 0.77 associated with the recovered cyclooctene. This difference is not so surprising when one considers that the level of isomerisation in the ketonic product must reflect that of the cyclooctene within the solvent cage of the rhodium complex. This level is expected to be significantly higher than the average level in the reaction media if the rate of isomerisation is high.

These studies say little more about the overall mechanistic picture. However, they do indicate that features of the oxidative attack are common to the findings in our earlier studies on catalytic oxygenation by rhodium species. These catalytic situations have all featured a strongly co-ordinated second substrate (phosphine or alkene) capable of taking up one of the two oxygen atoms in the initial rhodium oxygen complex. In the case of the peroxorhodium species **2** this role is likely to be played by the second rhodium centre which, on the basis of our earlier proposals,[11] would take up the rhodium bonded oxygen in the metallocyclic intermediate **6** to give the four-membered metallocycle **7** capable of the β-hydride shift and reductive elimination necessary to produce cyclooctanone.



6 (L = cyclooctene or solvent)



7 (L = cyclooctene, oxorhodium residue or solvent)

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