The Rhodium Catalysed Co-oxygenation of *cis*-Cyclo-octene

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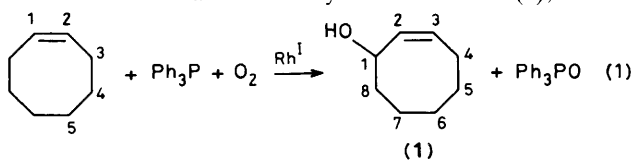
Deuterium labelling studies show that, contrary to earlier proposals, conversion at a rhodium centre of *cis*-cyclo-octene into the allylic alcohol, cyclo-oct-2-en-1-ol (**1**) involved oxygenative attack at a vinylic centre and double bond migration; a finding considered to have mechanistic implications for related co-oxygenations at group 8 metal centres.

Co-oxygenation, the introduction of oxygen into two co-ordinated ligands, has been the subject of many studies in recent years but a cohesive mechanistic picture in this area of transition metal chemistry is lacking. In early work on the activity of rhodium dioxygen species James and Ochiai[1] and Holland and Milner[2] reported the formation of cyclo-octenes carrying oxygen functions at the allylic positions when solutions of $[Rh(cyclo\text{-}octene)_2Cl]_2$ were treated with molecular oxygen at moderate temperatures. The Canadian workers interpreted their results in terms of the generation of a π-allyl complex which was subsequently oxygenatively attacked by co-ordinated hydroperoxide. The English group favoured a 'dissociative oxygen insertion'[3] into the allylic C–H bond of the substrate to form cyclo-oct-2-en-1-ol (**1**), which is



(**1**)

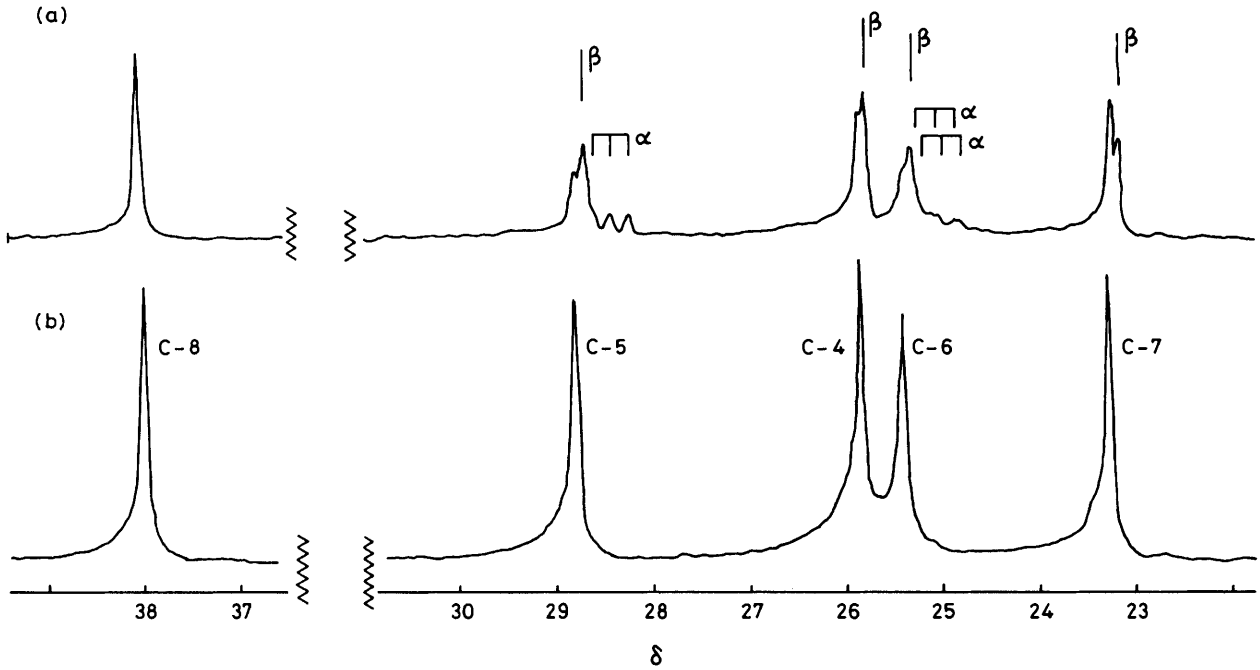


Figure 1. Part of the ^{13}C n.m.r. spectrum (at 100.484 MHz) of (a) cyclo-oct-2-en-1-ol synthesised by catalytic oxygenation of [5-^{2}H]-cyclo-octene, and (b) undeuteriated cyclo-oct-2-en-1-ol.

converted into cyclo-octanone and cyclo-oct-2-en-1-one under their conditions. As later studies have pointed exclusively to attack by rhodium oxygen species on the vinylic carbon of co-ordinated alkenes followed by vinylic proton migration to generate a ketonic product,[4,5] this apparent allylic attack to give the allylic alcohol is of considerable mechanistic interest.†

We have re-examined the oxygenation of cyclo-octene and find that, under conditions similar to those which oxygenate cyclo-octa-1,5-diene,[5] the substrate is converted into cyclo-oct-2-en-1-ol in a slow but catalytic reaction‡ which competes with the oxygenation of Ph_3P to Ph_3PO. We consider the co-oxygenation (1) to be involved. No oxygenation occurs in the absence of the rhodium catalyst. Hydroquinone has no detectable influence on the reaction.

When the reaction was carried out with [5-^{2}H]-cyclo-octene (isotopic abundance 80%) the β-shifts[7] in the ^{13}C n.m.r. spectrum of the product showed the deuterium labelling distributed between C-5 and C-6 (Figure 1).

The observed spectrum is in very good agreement with that predicted for attack at the vinylic hydrogen followed by double bond migration. In particular it indicates an absence of labelling at C-7, which would occur if the oxygenated species attacked either a π-allyl complex or inserted into an allylic C–H bond (see Table 1). The deuterium label was not expected to influence the stereospecificity of the attack. Thus both *cis* and *trans* hydroxy–deuterium relationships in the C-5 and C-6 deuteriocyclo-octenols were expected. The further splitting of the α-shifted signal from C-6 confirms that this is the case for attack at C-2 of the [5-^{2}H]-cyclo-octene. Corresponding splitting at C-5 is less apparent but conformational preferences may reduce the influence of the hydroxy group on the magnetic environment at this centre.

Table 1. Fractional signals predicted for the ^{13}C n.m.r. spectrum of ^{2}H-substituted cyclo-oct-2-en-1-ols obtained by differing mechanistic routes from [5-^{2}H]-cyclo-octene (80% isotopic abundance).

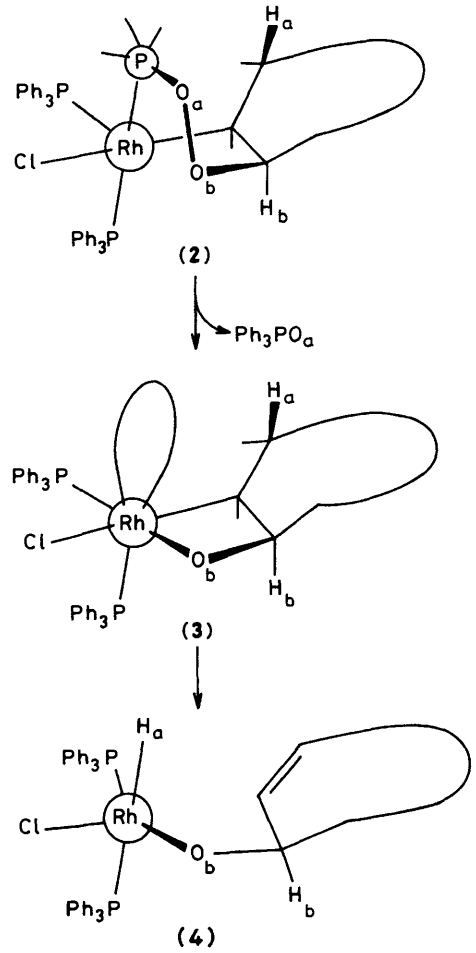
		C-4	C-5	C-6	C-7	C-8
Vinylic oxygenation mechanism	Normal	0.6	0.2	0.2	0.6	1.0
	α-shift	—	0.4	0.4	—	—
	β-shift	0.4	0.4	0.4	0.4	—
π-Allylic oxygenation mechanism	Normal	0.8	0.4	0.2	0.4	0.8
	α-shift	—	0.2	0.4	0.2	—
	β-shift	0.2	0.4	0.4	0.4	0.2
Allylic insertion mechanism	Normal	1.0	0.6	0.2	0.2	0.6
	α-shift	—	—	0.4	0.4	—
	β-shift	—	0.4	0.4	0.4	0.4

Studies of alkene isomerisation and of deuterium exchange in related oxygenations involving rhodium point to the involvement of metal hydride intermediates under aprotic[8] and protic[9] conditions. The formation of an allylic alcohol from cyclo-octene, rather than the ketone, therefore suggests that a β-hydride shift to the metal of a hydrogen which was originally allylic takes place in preference to a β-hydride shift of the hydrogen attached to the vinylic centre which was oxygenated. A candidate for the key intermediate is the six-membered metallocycle (**2**) which contains a pentavalent phosphorus and a peroxidic moiety. This could be readily formed by intramolecular expansion of a five membered peroxymetallocycle of the type frequently considered to be involved in the conversion of terminal alkenes into ketones at rhodium.[4] Models show that the metallocyclic ring in (**2**) is likely to adopt a boat conformation in which oxygen, O_b, interacts with one co-ordination site at the rhodium centre. Expulsion of Ph_3PO

† We are concerned here with oxygenation of alkenes in dilute solutions at near ambient temperatures which are not influenced by radical chain inhibitors. Allylic attack is much in evidence[6] when neat substrates are oxygenated at elevated temperatures in the presence of rhodium complexes. In such cases the C–O bond appears to be formed in the Haber–Wiess radical chain sequence, although the full mechanistic picture is not completely clear.

‡ Typically 2 moles of (**1**) per mole of catalyst per day were obtained when a solution of cyclo-octene (0.48 mol l^{-1}), Ph_3P (0.24 mol l^{-1}), hydroquinone (2.5×10^{-3} mol l^{-1}), and $RhCl(Ph_3P)_3O_2$ (2×10^{-3} mol l^{-1}) in dry benzene was stirred in air, in the dark, at 24 °C.

from this ring system generates the four membered metallocycle (**3**) (*cf* ref. 10) carrying an unfilled orbital positioned to interact with H_a (originally allylic) rather than H_b (originally vinylic). The β-hydride shift of H_a would give (**4**) from which the cyclo-octenol (**1**) could be obtained by reductive elimination.



If these suggestions are substantially correct, it follows that the overall process has rigid stereochemical requirements. In accord with this conclusion, we find that cyclo-octanone is the only alicyclic product formed when *cis*-cyclo-octene is replaced in this reaction by the *trans*-isomer.

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