Direct Spectroscopic Evidence for the Formation of an Asymmetric Intermediate in the Oxidation of Alkenes by Osmium Tetraoxide

(2)

6π.

(3)

Scheme 1

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¹H N.m.r. spectral investigation of the reaction of osmium tetraoxide, OsO_4 , with 1,1'-diphenylethene has shown, for the first time, direct evidence for the formation of an asymmetric intermediate which may be assigned as involving a cyclic four-membered ring species with an osmium–carbon bond.

The cis-hydroxylation of alkenes by OsO4 to give the corresponding *cis*-diols is well established.¹ The reaction has been shown to occur via the formation of an osmium(vi) ester complex,^{2,3} for example (1) and (2), (L = tertiary amine) which can be hydrolysed reductively^{2,4} or oxidatively⁵ to give high yields of cis-diol products. The mechanism of formation of the five-membered ring osmium(vI) system has recently been the subject of much speculation. For many years the reaction has been generally assumed to proceed via a concerted 6π electron cyclisation, the symmetric five-membered ring transition state (3) explaining the exclusive *cis*-addition to alkenes⁶ (Scheme 1). This mechanism, however, invokes direct nucleophilic attack of carbon on oxygen and has led to the proposal of an alternative mechanism involving the formation of an asymmetric organometallic intermediate (4), which rearranges and dimerises in a rate-determining step to give $(1)^7$ (Scheme 2). This latter mechanism is consistent with kinetic data suggesting a two-step process for the formation of osmium(vi) ester complexes⁸ and with the observation that attack by nucleophiles on OsO4 occurs exclusively at the metal centre and not at oxygen.9 In addition, Scheme 2 satisfactorily explains the dramatic increase in the rate of formation of osmium(vi) ester complexes on addition of tertiary amines, L, such as pyridine,² attack by L inducing osmium-carbon bond

(1)

determining step.⁷ However, up to this time, no direct experimental evidence has been put forward for the existence of asymmetric intermediates of the type (4); we have therefore carried out ¹H n.m.r. studies on the reaction of OsO_4 with alkenes to determine whether such intermediates may be detected spectroscopically in solution. It was essential to investigate this reaction using an alkene that would react slowly with OsO_4 , so that any intermediate formed would have a long lifetime, and would lead to an easily discernable ¹H n.m.r. spectrum. For these reasons we chose 1,1'-diphenylethene, disubstituted alkenes being well known to react with OsO_4 relatively slowly, and the presence of two geminal protons giving a potential AX spectrum.

cleavage in (4) with a corresponding rate increase at the rate-







J. CHEM. SOC., CHEM. COMMUN., 1982

735

The reaction of 1,1'-diphenylethene with OsO₄ was followed by ¹H n.m.r. spectroscopy (400 MHz) at 20 °C in CDCl₃, with particular reference to the olefinic region of the spectrum (Figure 1). On addition of OsO₄, the reaction mixture turned dark yellow, and the olefinic proton resonance, δ 5.45 (s, 2H) was seen to decay slowly as a resonance at δ 5.53 (s) corresponding to the osmium(v1) ester complex product developed. In addition to these two resonances four doublets could be clearly observed at δ 5.83, 5.72, 5.355, and 5.35 (all J 11 Hz). Irradiation at δ 5.83 led to the collapse of the doublet at δ 5.355 to a singlet, whilst irradiation at δ 5.72 led to the collapse of the doublet at δ 5.35 to a singlet. Likewise, irradiation of the two doublets centred at δ 5.35 led to the collapse of the other two doublets to singlets. In addition, the integrals of each of these doublets confirm that these resonances are due to two species in solution, each responsible for two doublets. After 2 h, the singlet at δ 5.45 due to free alkene had disappeared, and after 24 h the four doublets of the intermediate species



Figure 1. ¹H N.m.r. spectrum (400 MHz) of reaction solution of OsO_4 with 1,1-diphenylethene in $C(^2H)Cl_3$ at 20 °C: (a) asymmetric intermediate, (b) osmium(vi) ester product, (c) free alkene.

had decayed, leaving a singlet at δ 5.53 for the final darkbrown osmium(v1) product. During the course of the reaction, the phenyl region of the spectrum was too complex to be assigned with any confidence. Addition of pyridine to the above reaction solutions led to quenching of the intermediate species.

The spectral data described above are fully consistent with the formation in solution of low concentrations of two asymmetric intermediate species which we assign as involving fourmembered ring species with an osmium to carbon bond, (5) and (6). The chemical shifts for protons H_{α} and H_{β} are consistent with these structures, large downfield shifts being expected for these protons, as is observed for some substituted metallocyclobutane derivatives.¹⁰ Attempts to obtain ¹³C n.m.r. spectra of (5) and (6) have been dogged by concentration and relaxation problems associated with these species.

We have investigated the reaction of OsO_4 with a range of other disubstituted alkenes (*trans*-1,2-diphenylethene, *cis*-but-2-ene, and 2-methylprop-1-ene). Although the ¹H n.m.r. spectra obtained show features consistent with the formation of intermediates analogous to (5) and (6), low concentrations of side-products, presumably formed *via* carbon-carbon bond cleavage, or in the case of methyl substitution, by β -elimination reactions, complicate and hinder assignment of these spectra. This notwithstanding, our results with 1,1-diphenylethene are consistent with the formation of intermediate organometallic species, as previously proposed by Sharpless and co-workers,⁷ and indicate a complexity of reactivity of alkenes with OsO₄ that has generally not been fully appreciated.

We thank the S.E.R.C. for financial support, and Professor Sir Jack Lewis and Dr W. P. Griffith for helpful advice and encouragement.

Received 14th April 1982; Com. 414

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