The Structure of Intermediates Formed in the Reaction of Osmium Tetroxide with 1,1-Diphenylethylene

Charles P. Casey*

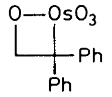
Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, U.S.A.

It is proposed that the two intermediates which have recently been reported to have been observed in the reaction of OsO_4 with 1,1-diphenylethylene are isomers of dimeric osmium(VI) ester compounds and not oxametallacyclobutanes.

Two mechanisms for the reaction of OsO_4 with alkenes[1] have been proposed: a concerted reaction leading directly to a 5-membered ring Os^{VI} ester and Sharpless's[2] two-step mechanism involving initial formation of an undetected oxametallacyclobutane which then rearranges to the observed 5-membered ring product. Sharpless's mechanism is appealing since it involves an initial nucleophilic attack of the alkene at the metal centre rather than at oxygen. There has been no direct evidence for an oxametallacyclobutane intermediate and we believe that Shröder and Constable's recent claimed detection of such an intermediate[3] was misinterpreted.

Schröder and Constable studied the reaction of OsO_4 with 1,1-diphenylethylene by ^1H n.m.r. spectroscopy and observed two intermediates in the reaction which they asserted were isomeric oxametallacyclobutanes, (**1**) and (**2**). However, we believe that their n.m.r. data are inconsistent with their proposed structures and are more consistent with a mixture of dimeric osmium(VI) ester complexes (**3**), (**4**), (**5**), and (**6**).

Schröder and Constable assigned a peak at δ 5.53 as a singlet due to an unspecified osmium(VI) ester dimer; however, in our view, inspection of their reported n.m.r. spectrum clearly shows that the peak at δ 5.53 is the centre of an AB spectrum (J 11 Hz, $\Delta\nu$ *ca.* 1 Hz) since the outer lines of the AB are apparent. More importantly, they also observed two sets of less intense coupled doublets (J 11 Hz each) at δ 5.83 and 5.355 and at δ 5.72 and 5.35 which they assigned to the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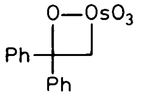
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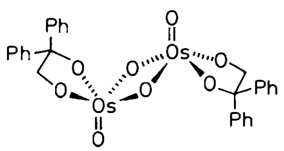
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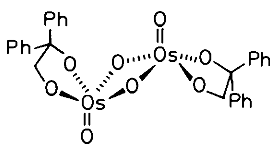
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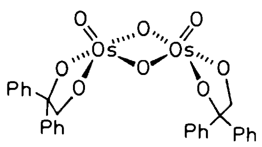
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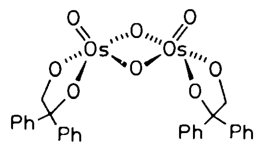
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osmium metallacycles (**1**) and (**2**). However this assignment appears to be clearly in error since the expected rapid pseudorotation of the OsO_3 group would render the protons of the methylene groups of (**1**) and (**2**) equivalent. In addition, it would be highly unlikely that the chemical shifts of the methylene unit adjacent to oxygen in (**1**) and adjacent to osmium in (**2**) would be nearly the same. Moreover it would not be expected that nearly equal amounts of the two intermediates would be observed if the metallacycles were formed by electrophilic attack of osmium on the alkene as suggested.

The product of reaction of OsO_4 with tetramethylethylene was shown to be an osmium(VI) ester dimer with *anti*-oxo groups.[4] Marzilli *et al.*[5] have shown that isomers with both *syn*- and *anti*-oxo groups are observable by ^1H n.m.r. spectroscopy and that each isomer has non-equivalent methyl groups. In the light of these n.m.r. results, the three products of the reaction of OsO_4 with 1,1-diphenylethylene may reasonably be assigned to three of the four possible dimeric osmium(VI) esters (**3**), (**4**), (**5**), and (**6**). The major product is most likely the *anti*-oxo isomer (**3**) having a centre of inversion. The two minor products are most likely the *anti*-oxo isomer (**4**) which has a C_2 symmetry axis passing through the two bridging oxygen atoms and the *syn*-oxo isomer (**5**) which has a C_2 axis of symmetry. The *syn*-oxo isomer (**6**) which has a plane of symmetry is most likely not observed since it would be destabilized by phenyl–phenyl interactions. The close similarity of chemical shifts of the major and minor products are readily explained since all are osmium(VI) ester dimers.

We propose that (**3**), (**4**), and (**5**) are formed simultaneously with a kinetically controlled product ratio and that (**4**) and (**5**) subsequently undergo a slow rearrangement to the observed final product (**3**). It seems to us that this proposal is in better accord with the observation that the minor products rearrange slowly to the major product than Schröder and Constable's proposal that the minor products are sequential intermediates in the formation of the major product. For a sequential reaction, small amounts of an intermediate compared to the final product are seen at early reaction times only if the intermediate rearranges to the final product more rapidly than it is formed. The slow rearrangement of the intermediate observed here is inconsistent with the proposal of a sequential reaction scheme.

In the light of the present reinterpretation of Schröder and Constable's data, oxametallacyclobutanes remain attractive intermediates in OsO_4 oxidations but we believe we have shown that they have not yet been directly observed.

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