Derivatisation of Saturated Hydrocarbons. The Mechanism of RuO_4 Oxidations

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The reaction mechanism of RuO_4 oxidations of saturated hydrocarbons has been investigated by several methods. (1) By oxidation of *endo*-tetrahydrodicyclopentadiene (**1H**) and 2,6-dideuterio-*endo*-tetrahydrodicyclopentadiene (**1D**) a kinetic deuterium isotope effect of 5.3 was observed, indicating transfer of a hydrogen species and not a single electron in the rate-determining step. (2) No chlorinated products were formed from the reaction in CCl_4. Radical intermediates are therefore not likely. (3) In the presence of chloride ion, 2-chloro-*endo*-tetrahydrodicyclopentadiene (**2**-Cl) was formed in addition to *endo*-tetrahydrodicyclopentadien-2-ol (**2**-OH), indicating a carbocation intermediate. (4) Further oxidation of **2**-OH to bicyclo[5.2.1]decane-2,6-dione (**8**) proceeds via a ruthenium complex with the hydroxy group as the corresponding acetate **2**-OAc was not oxidised. These points indicate that the reaction proceeds by hydride abstraction and carbocation formation and not by a cyclic one-step formation of the ruthenium ester from the saturated hydrocarbon.

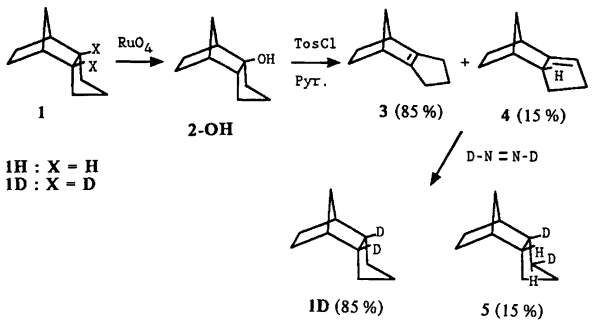
We have reported the RuO_4 oxidation of saturated hydrocarbons to form oxygenated products.[1] The oxidation of adamantane and *endo*-tetrahydrodicyclopentadiene (**1H**, *endo*-tricyclo[5.2.1.$0^{2,6}$]decane) gave good yields of the tertiary alcohols 1-adamantanol and *endo*-tricyclo-[5.2.1.$0^{2,6}$]decan-2-ol (**2**-OH) respectively. Norbornane was oxidised to 2-norbornanone in 92 % yield. We now report experiments pertinent to the mechanism of RuO_4 oxidations of saturated hydrocarbons.

Results and discussion

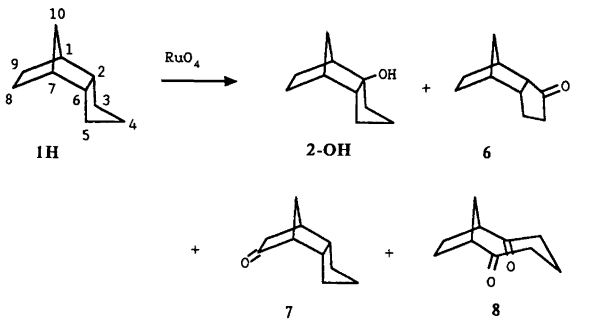
The mechanism of the RuO_4 oxidation of saturated hydrocarbons has not been studied in detail. Spitzer and Lee[2] oxidised five-, six-, seven- and eight-membered cycloalkanes and from a comparison of the relative rates with those of the solvolysis of the corresponding toluenesulfonates (reacting via carbocations) they concluded that the RuO_4 oxidation of saturated hydrocarbons proceeded with homolytic carbon–hydrogen bond cleavage. Tenaglia *et al.*[3] recently reported the RuO_4 oxidations of a number of cyclic hydrocarbons. For bicyclo[2.2.1]alkanes no rearrangements were observed and because of this, a four-membered transition state giving an alkoxyruthenium hydride as an intermediate, rather than a carbocation, was proposed.

Our results from the oxidation of saturated hydrocarbons indicate a carbocation-like intermediate because of the preferential attack on the tertiary rather than the secondary carbons. The carbocation may have been formed by a hydride abstraction or by electron transfer followed by transfer of a hydrogen atom to the ruthenium oxide.[1] It should be possible to distinguish between these two mechanisms by observation of the deuterium kinetic isotope effect (KIE). Saturated hydrocarbons have very high oxidation potentials,[4,5] presumably with corresponding high energy transition states for the formation of radical cations. If the RuO_4 oxidations of saturated hydrocarbons proceeded by electron transfer followed by transfer of a hydrogen atom, the electron transfer would most likely be the rate-determining step and we would not observe a primary KIE. This is supported by the results from the Co(III) oxidation of 9-phenyl-*N*-methylacridan where the rate-determining step was a one-electron transfer and where no primary KIE was observed.[6] This compound, with aryl substituents at the oxidised carbon, must have a lower oxidation potential than the saturated compounds studied by us. On the other hand, if the oxidation by RuO_4 proceeds by transfer of a hydrogen species in the rate-determining step, we would expect to observe a primary KIE.

In order to investigate the KIE we synthesised 2,6-dideuterio-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**1D**). We have studied the RuO_4 oxidation of **1H** and shown that the alcohol **2**-OH is the major product.[1] We also expected the synthesis of **1D** by the route shown in Scheme 1 to be a facile one. Tricyclo[5.2.1.$0^{2,6}$]dec-2(6)-ene (**3**) was formed from the alcohol **2**-OH.[7] Model experiments showed that **3** could not be hydrogenated by the use of Wilkinson's catalyst or palladium on charcoal. The reduction was therefore performed with dideuteriodiimide. The olefin **3** contained 15 % of *endo*-tricyclo[5.2.1.$0^{2,6}$]dec-2(3)-ene (**4**) which on deuteriation gave 2,3-dideuterio-*endo*-tricyclo[5.2.1.$0^{2,6}$]-decane (**5**). The presence of this causes scrambling of the



Scheme 1.



Scheme 2.

deuterium atoms in compound **1D**. From ^1H NMR spectrum, the synthetic sequence gave **1D** with 10% ^1H in positions 2 and 6. We will return to the significance of this later.

The oxidation of **1** was performed by the Sharpless procedure: a two-phase system of water/CCl_4 with MeCN added was used as reaction medium.[8] The stoichiometric oxidant ($NaIO_4$) in the aqueous phase oxidises Ru(IV) to Ru(VIII) (CCl_4 soluble). This reaction is rapid compared with the oxidation of the hydrocarbon: on addition of sodium periodate to the black suspension of RuO_2 this was transformed to a yellow solution of RuO_4 in less than a minute while the 50% oxidation of **1H** requires 4 h. We therefore assume the RuO_4 concentration in the organic phase to be constant during the experiment. Owing to the two-phase reaction medium it was not possible to obtain accurate absolute rate constants. The KIE was therefore determined in an experiment starting with an equimolecular mixture of **1H** and **1D**. The decreases in the concentrations of **1H** and **1D** were followed by GC and GC–MS. Both d[**1H**]/dt and d[**1D**]/dt showed first-order dependence (correlation coefficients 0.999 and 0.993, respectively). The observed KIE was 4.0(3). This is the KIE for the rate of reaction of **1H** and must be corrected if the KIE for the formation of the alcohol **2-OH** is to be determined. The most significant correction stems from the fact that **2-OH** is not the only product from the oxidation of **1H**. In addition, two ketones (as observed by GC–MS and GC–IR) were formed, identified as *endo*-tricyclo[5.2.1.$0^{2,6}$]decan-3-one and-8-one (**6** and **7**). The total amount of ketones corresponded to 8% of **2-OH**. If we take this into account, eqn. (1) is valid and for the deuteriated compound, eqn. (2)

$$-\mathrm{d}[\mathbf{1H}]/\mathrm{d}t = ({}^{H}k_2 + {}^{H}k_{\text{ketones}})\,[\mathbf{1H}] \quad (1)$$

$$-\mathrm{d}[\mathbf{1D}]/\mathrm{d}t = ({}^{D}k_2 + {}^{D}k_{\text{ketones}})\,[\mathbf{1D}] \quad (2)$$

holds, where k_2 is the rate constant for the formation of **2-OH** and k_{ketones} is that for the formation of the ketones. The superscripts H and D indicate **1H** and **1D** as the substrate, respectively.

The observed isotope effect is then given by eqn. (3).

$$(k_H/k_D)_{obs} = ({}^{H}k_2 + {}^{H}k_{\text{ketones}})/({}^{D}k_2 + {}^{D}k_{\text{ketones}}) \quad (3)$$

For the formation of the ketones no C–D bond is broken and there will at most be secondary kinetic isotope effects for the formations of these compounds. We will therefore assume that eqn. (4) holds. From this, we obtain ${}^{H}k_2/{}^{D}k_2$

$${}^{H}k_{\text{ketones}} = {}^{D}k_{\text{ketones}} = 0.08\,{}^{H}k_2 \quad (4)$$

= ca. 5.3. The presence of 10% ^1H in position 2 of **1D** means that the observed isotope effect is slightly smaller than what would have been observed for 100% deuterium in the 2,6 positions of **1**. However, the conclusion of the KIE experiment is nevertheless clear, a substantial effect (ca. 5.3) exists for the oxidation of **1** to **2-OH** and the reaction therefore proceeds by cleavage of the C–H (C–D) bond in the rate-determining step and not by electron transfer. The same conclusion was reached for the RuO_4 oxidation of alcohols; oxidation of cyclobutanol gave cyclobutanone and not ring-opening products (Rocek's criterion[9]).[10] This is an indication of a two-electron oxidation (e.g. a hydride shift).

However, even if the oxidation proceeds by a transfer of a hydrogen species in the rate-determining step, several reaction mechanisms are nevertheless possible [eqns. (5)–(7); (R–H = *endo*-tetrahydrodicyclopentadiene, with –H in position 2].

$$\text{R–H} + RuO_4 \rightarrow [\text{R}]^{\cdot} + RuO_4H \xrightarrow{H_2O} \text{R–OH} \quad (5)$$

$$\text{R–H} + RuO_4 \rightarrow [\text{R}]^{+} + RuO_4H^{-} \rightarrow \text{R–O–}RuO_3H \xrightarrow{H_2O} \text{R–OH} \quad (6)$$

$$\text{R–H} + RuO_4 \rightarrow \text{R–O–}RuO_3H \xrightarrow{H_2O} \text{R–OH} \quad (7)$$

Many attempts have been made to correlate the magnitude of the KIE with the type of hydrogen species being transferred in the rate-determining step. It is, however, clear that such a correlation is not possible, even if quantum-mechanical tunnelling is ignored.[11–13] We must therefore use other criteria to gain further insight into the reaction path.

Mechanism (5) above, with free radicals, can be ruled out from the product study: no chlorinated products were formed. The reaction was run in CCl_4 and free radicals

would have reacted with the solvent to form such products. However, a radical pair collapsing to the ruthenate ester at a higher rate than the reaction with the solvent cannot be ruled out from this. Nevertheless, results reported by Yamada *et al.*[14] show that the collapse would have to be very rapid: on oxidation of alkylcyclopropanes with RuO_4, alkyl cyclopropyl ketones were the major products. If the RuO_4 oxidation of the hydrocarbons had proceeded by a radical mechanism, we would have expected ring opening to occur as the cyclopropylmethyl radical is reported to ring-open at a rate of ca. 10^8 s^{-1}.[15] If the reaction had proceeded by hydrogen atom abstraction, we would also have expected a less specific reaction of **1H** and of adamantane: for adamantane, the relative reactivity of tertiary to secondary hydrogens is 1:1 for radical formation by reaction with chlorine atoms,[16] while we observed a reactivity of ca. 100:1 for these two types of hydrogen (in both cases calculated per H-atom, four tertiary and twelve secondary in adamantane). From this body of evidence, we consider eqn. (5) to be unlikely.

Mechanism (7), with a one-step ruthenate ester formation was proposed by Tenaglia *et al.* for the RuO_4 oxidation of some saturated hydrocarbons: the oxidation of bicyclo[2.2.1] hydrocarbons did not result in rearranged products, as expected if carbocations were intermediates.[3] A three-membered ring transition state has been proposed for the peracid hydroxylation of saturated hydrocarbons in order to explain the small deuterium KIE for that reaction (2.2).[17]

In the four-membered ring transition state leading to the ruthenate ester[3] there undoubtedly exists considerable strain which will be distributed over the three carbon–carbon bonds of the tertiary carbon atom. For a molecule like adamantane one would expect this to result in a slower reaction than for *endo*-tetrahydrodicyclopentadiene (**1H**). Although no kinetic investigation was performed, there was no qualitative difference in the time needed for e.g. 65 % consumption of these two compounds (19 h for adamantane, 24 h for **1H**). Furthermore, the transition state for the one-step formation of the ruthenate ester appears to be analogous to that of a front-side nucleophilic substitution. This is a type of reaction that has not been observed. Every case of observation of retention of configuration has been explained by other mechanisms, e.g. ion-pair intermediates. Moreover, the high reactivity of tertiary as compared with secondary hydrogens is not well accommodated by a concerted cyclic transition state and we would also expect a non-linear transition state to result in a smaller KIE than the one we observed.

To differentiate between the mechanisms given in eqns. (6) and (7), we ran the oxidation in the presence of added nucleophiles. Many nucleophiles will be oxidised by RuO_4 and particularly by $NaIO_4$. We have tried chloride and acetate ions. To avoid oxidation of the nucleophiles by periodate, we prepared a stoichiometric solution of RuO_4 in CCl_4. This was added to a solution of the nucleophile in water together with tetrabutylammonium salts for transport of the ions into the CCl_4 solution. At this stage, **1H** was added to the mixture. Chloride ion would not be oxidised by RuO_4 ($Cl^{\cdot}/Cl^-$, ca. 2.5 V;[18,19] RuO_4/RuO_4^-, 1.00 V[20]). The oxidation in the presence of chloride resulted in a yield of **2**-OH of 56 % and of 2-chloro-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**2**-Cl) of 5 %. The alcohol **2**-OH did not react with chloride ion under these conditions. The reaction in presence of acetate gave only the alcohol **2**-OH and no acetate.

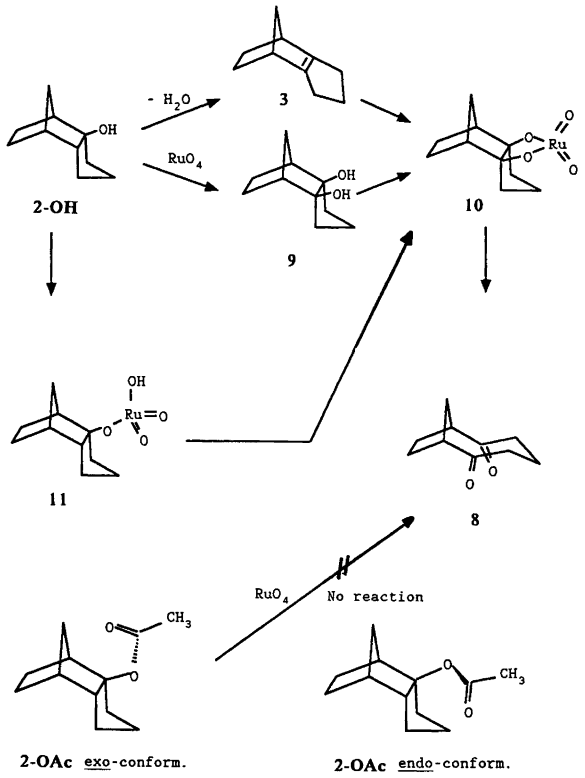
The formation of **2**-Cl indicates that an intermediate is formed which can react with a nucleophile, most probably a carbocation formed by hydride abstraction from **1H**. The concentration of water in the organic phase was 180 mM, that of chloride ion 4 mM. The relative reactivities of nucleophiles in S_N1 reactions are not well known[21] and the low chloride-to-alcohol ratio may either mean that the carbocation reacts at a diffusion-controlled rate with the nucleophile or that the carbocation is in a tight ion pair with the ruthenium species and reacts with this at a high rate. The reason for the lack of formation of 2-acetoxy-*endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**2**-OAc) from the oxidation in the presence of acetate ion was due to the fact that acetate ion was not transported into the organic phase (as evidenced by the IR spectrum of the organic phase and lack of formation of acetic acid on acidification). The reason for this is not known.

Another explanation for the formation of **2**-Cl would be that the ruthenate ester was first formed [eqn. (7)] and that this ester reacted with chloride ion in an S_N2-like reaction to give **2**-Cl. However, such a reaction would be impossible on the bridgehead of **1H** or adamantane.

We therefore consider eqn. (6) to be the best model for the reaction but with the carbocation in a tight ion-pair with the ruthenium species. Owing to the rapid reaction between these two, with the formation of the ruthenate ester, there is no time for isomerisation of the bicyclo[2.2.1]alkanes as expected by Tenaglia *et al.*[3] The isomerisation of cations of the type $\mathbf{1}^+$, even in highly polar solvents such as SO_2 is far from instantaneous. The isomerisation of $\mathbf{1}^+$ to 1-adamantyl cation in SO_2 at −10 °C required several hours to reach completion. The carbocation $\mathbf{1}^+$ was formed by the reaction of **2**-OH with SbF_5 or by deamination of *endo*-tricyclo[5.2.1.$0^{2,6}$]decan-2-amine.[22]

In conclusion on this point, the available evidence on the RuO_4 oxidation of saturated hydrocarbons is best explained by a model where a hydride ion is transferred to the ruthenium species in the rate-determining step, followed by a rapid formation of a ruthenate ester. This is then hydrolysed to the product.

Upon oxidation of **1H** the product **2**-OH was further oxidised to bicyclo[5.2.1]decane-2,6-dione (**8**). By analogy with the OsO_4 oxidation of olefins, a cyclic ruthenium ester might be the last intermediate in the formation of the diketone **8** (Scheme 3). This could have been formed either from the olefin **3** or from *endo*-tricyclo[5.2.1.$0^{2,6}$]decane-2,6-diol (**9**). We have oxidised these compounds with RuO_4 and both reacted rapidly (compared with the oxidation of



Scheme 3.

1H) to give the diketone **8** as the major product (more than 80 % by GC). However, the olefin **3** was not formed from **2**-OH in the reaction mixture *without* RuO_4. The most likely intermediate of these two is therefore the glycol **9**.

It is also possible, however, that the cyclic ester **10** was formed directly from an initially formed ruthenium complex e.g. (**11**). To check this point we tried to block or mask the hydroxy group in such a way that **11** could not have been formed, but nevertheless so that the reactivity at the neighbouring tertiary carbon (C^6) would remain approximately constant. We tried the following groups in the 2-position of **1**H without success: Cl, formate (both were hydrolysed at a higher rate than the oxidation of **2**-OH to **8**) and methoxy (oxidised to formate). However, the acetate **2**-OAc was not hydrolysed and an experiment showed that this compound was not oxidised by RuO_4. The reason for this could be steric hindrance by the acetate group, however, MMPMI calculations[23] indicate the *exo* conformation (Scheme 3) to be favoured over the *endo* by ca. 1.3 kcal mol^{-1}, and also the rotational barrier to be ca. 7 kcal mol^{-1}. For the dominant *exo* conformation there cannot be any more hindrance at C^6 than there is in the alcohol. As no oxidation of C^6 took place in the acetate with the hydroxy function blocked towards complexation with RuO_4, it appears reasonable to assume that the oxidation of the alcohol **2**-OH to the diketone **8** proceeds by the formation of a ruthenium complex, e.g. **11** followed by the oxidation of C^6 (Scheme 3).

This conclusion also has consequences for the mechanism of the oxidation at C^6: for a complex such as **11** it is difficult to envisage a four-membered cyclic transition state for the oxidation of C^6 (for geometrical reasons, both bond lengths and bond angles). We therefore believe it is necessary to postulate a two-step reaction: a hydride abstraction followed by the formation of the cyclic ester **10**. This then breaks down to the diketone **8**.

If the oxidation at C^6 in the case of the alcohol **2**-OH goes by a stepwise mechanism [eqn. (6)], it is also reasonable to assume that the oxidation of saturated hydrocarbons such as **1**H and adamantane also go via eqn. (6), especially as this is in accordance with the evidence and arguments presented above for that reaction.

Conclusion. The evidence presented here for the RuO_4 oxidation of saturated hydrocarbons shows that it is best explained by a hydride abstraction followed by ruthenate ester formation and not by a one-step ester formation,[3] by a radical mechanism or by a one electron transfer in the rate-determining step.

Experimental

The NMR spectra were recorded on a Bruker 500 MHz or a Jeol 100 MHz spectrometer. The IR and GC–IR spectra were recorded on a Nicolet 20SXC FTIR (GC Carlo Erba 5160, 25 m CP-Sil 5 CB). MS spectra were recorded on an AEI MS 902 instrument operating at 70 eV, EI, 150 °C. The GC–MS were obtained on a Hewlett Packard 5985A, equipped with a 25 m BP-1 fused silica capillary column. The reactions were monitored by GC analyses (Carlo Erba 4160, 25 m fused silica, CP-Wax 52 CB; Carlo Erba 6000, 30 m fused silica, DB-1). The sources for the starting materials have been reported.[1]

Ruthenium tetraoxide oxidation of **1**H. In a typical experiment $RuO_2 \cdot 2H_2O$ was added to a well stirred mixture of **1**H (15.3 g, 112 mmol), water (210 ml), CCl_4 (175 ml), acetonitrile (110 ml) and sodium periodate (84.3 g, 0.39 mol) at 20 °C. After 24 h, 65 % of **1**H had reacted. After two days, the reaction was stopped by addition of CH_2Cl_2 (340 ml) and 2-propanol (50 ml). The mixture was left overnight, then filtered, and the solid material extracted with CH_2Cl_2 (2×60 ml). The aqueous phase extracted with CH_2Cl_2 (2×60 ml), and the combined organic phases were washed with water (2×60 ml), saturated $NaHCO_3$ solution (75 ml) and water (75 ml), before being dried over $MgSO_4$ and evaporated. The product crystallised from methanol–water 1:1 to give **2**-OH (12.7 g, 74 % yield, m.p. 133–134 °C). GC analysis of the product before work-up showed three more products to be present: *endo*-tricyclo[5.2.1.$0^{2,6}$]decan-3-one (**6**, 3 % of the area corresponding to **2**-OH), *endo*-tricyclo[5.2.1.$0^{2,6}$]decan-8-one (**7**, 3 %, authentic compound from Aldrich) and bicyclo[5.2.1]decane-2,6-dione (**8**, 7 %). The retention times on a polar and a non-polar GC column and GC–MS and GC–IR data for these three compounds were identical with

those of the authentic compounds (reported below), but not identical with the isomeric compounds.

endo-*Tricyclo[5.2.1.0^{2,6}]decan-3-one* (**6**). *endo*-Tricyclo-[5.2.1.0^{2,6}]deca-4,8-dien-3-one (from the corresponding alcohol[24] by potassium chlorochromate oxidation[25]) (0.47 g, 32.3 mmol) in ethyl acetate (50 ml) was hydrogenated over Pd/C (5 %, 35 mg) at 4 atm and 20 °C for 86 h to give **6**, 88 % pure by GC. ^{1}H NMR (100 MHz, $CDCl_3$): δ 1.00–1.75 (7 H, m), 1.75–2.90 (7 H, m). ^{13}C (25 MHz, $CDCl_3$): δ 20.66, 22.65, 25.28, 40.61, 41.31, 42.13 (2 C), 42.83, 53.66, 214.19. MS [GC–MS, BP-1, *m/z* (% rel. int.)]: 150 (15), 95 (6), 94 (8), 93 (16), 91 (13), 84 (7), 83 (100), 81 (6), 80 (26), 79 (30), 77 (14), 67 (13), 66 (10). IR (GC–IR): 2963, 2890, 1747, 1467, 1417, 1265, 1164 cm^{-1}.

The same product was obtained by $LiAlH_4$ reduction of 3,4-epoxy-*endo*-tricyclo[5.2.1.0^{2,6}]decane followed by $KCrO_3Cl$ oxidation of the alcohol formed. This was the only ketone formed by this procedure.

endo-*Tricyclo[5.2.1.0^{2,6}]decan-10-one*. *endo*-Tricyclo-[5.2.1.0^{2,6}]decan-10-ol (from catalytic hydrogenation of *endo*-tricyclo[5.2.1.0^{2,6}]deca-3,8-dien-10-ol, Aldrich Special Chemicals) was oxidised with $KCrO_3Cl$ to give this compound. MS [GC–MS, BP-1, *m/z* (% rel. int.)] 150 (84), 121 (26), 107 (23), 94 (62), 93 (72), 91 (23), 81 (46), 80 (93), 79 (100), 77 (27). IR (GC–IR): 2962, 2879, 1786, 1462, 1116 cm^{-1}.

endo-*Tricyclo[5.2.1.0^{2,6}]decan-4-one*. This was formed in a mixture with the 3-isomer by hydroboration of *endo*-tricyclo[5.2.1.0^{2,6}]dec-3-ene followed by chromic acid oxidation.[26] Coinjection with the reaction mixture from the RuO_4 oxidation of **1H** showed the 4-keto-isomer not to have been formed in that reaction.

Ruthenium tetraoxide oxidation of adamantane. Adamantane (3.03 g, 22.2 mmol), water (45 ml), CCl_4 (36 ml), acetonitrile (24 ml), sodium periodate (19.4 g, 90.7 mmol) and $RuO_2 \cdot 2H_2O$ (150 mg) were stirred vigorously for 19 h at 20 °C. The product consisted of adamantane (36 %), 1-adamantanol (62 %) and adamantanone (1.6 %).

Tricyclo[5.2.1.0^{2,6}]dec-2(6)-ene (**3**). This was made from the alcohol **2**-OH by reaction with *p*-TosCl in pyridine.[7] After mixing of the reagents, the reaction was kept at 5 °C for three days. This gave a mixture of **3** and *endo*-tricyclo[5.2.1.0^{2,6}]dec-2(3)-ene (**4**) (87:13). The reported reaction was run at 25 °C and had a ratio **3**:**4** of 75:25. Kugelrohr distillation (50–60 °C/10 Torr) gave the product used in the deuteriation experiments, consisting of 85 % **3**, 14 % **4** and 1 % unidentified products (area %, GC). The spectral data were in accordance with the structure and with those reported. The ^{1}H NMR spectrum indicated 15 % olefinic protons to be present, in accordance with the GC analysis.

2,6-Dideuterio-endo-*tricyclo[5.2.1.0^{2,6}]decane* (**1D**). The olefin **3** could not be hydrogenated at 4 atm H_2 over 5 % Pd/C or tris(triphenylphosphine)rhodium(I) chloride (Wilkinson's catalyst). To a solution of **3** (0.5 g, 3.7 mmol, containing 15 % **4**) in *O*-deuteriomethanol (20 ml) under nitrogen was added dipotassium azodicarboxylate (3.65 g, 18.8 mmol).[27] Tetradeuterioacetic acid (2.32 g, 99 % deuterium, Merck) in *O*-deuteriomethanol (5 ml) was added to the stirred solution over 2.5 h by a syringe pump. After 1.75 h of stirring after the addition, ether (80 ml) was added, the mixture filtered and the filtrate washed with water (3×30 ml) and saturated $NaHCO_3$ solution (30 ml). The combined aqueous phases were extracted three times with ether and the ether phase was dried (Na_2SO_4) and evaporated. The product (0.41 g, 83 % yield) consisted of 99 % of a mixture of **1D** and **5** (GC). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.23–1.32 (2 H, m), 1.35–1.47 (4.6 H, m), 1.47–1.55 (3 H, m), 1.55–1.67 (2 H, m), 2.08 (2 H, s), 2.31–2.37 (0.2 H, m). ^{13}C NMR {^{1}H} (125 MHz, $CDCl_3$): δ 23.02, 26.85, 28.74, 41.43, 43.23, 44.90 (t, $J_{C,D}$ = 20.3 Hz). MS [GC–MS, BP-1, *m/z* (rel. int.)]: 139 (6), 138 (51), 137 (5), 136 (0.6), 123 (38), 109 (18), 97 (100), 96 (64), 95 (56), 94 (25), 81 (41), 80 (42), 79 (24), 68 (78). IR (CCl_4): 2950 (s), 2876 (s), 2862 (s), 2204 (w), 2174 (m), 2159 (m), 1484 (m), 1466 (m), 1456 (m), 1298 (m) cm^{-1}.

Deuterium KIE in the oxidation of endo-*tetrahydrodicyclopentadiene* (**1H**). A mixture of **1H** (103.2 mg, 0.76 mmol) and **1D** (102.5 mg, 0.74 mmol), water (2.8 ml), CCl_4 (2.2 ml), acetonitrile (1.4 ml), $RuO_2 \cdot 2H_2O$ (10.4 mg) and sodium periodate (1.15 g, 5.4 mmol) was stirred vigorously at room temperature. Samples from the reaction mixture were analysed by GC and GC–MS. **1H** and **1D** were not separated on GC. Therefore, the total ratio **1**:**2**-OH was determined from the GC (internal standard method) and the **1D**:**1H** ratio from the MS. **1H** had only a negligible $M+2$ peak and **1D** a 0.6 % $M-2$ peak. The **1D**/**1H** ratio was thus determined from the M^+ peaks. Any isotope effects for the formation of the molecular ions will cancel out for the first-order reaction. The result is given in Table 1.

The results in Table 1 fit a first-order plot (LSTSQ, Serena Software, Bloomington, Indiana, USA) to give $(^{H}k)_{obs} = 3.16(6)\times10^{-2}$ h^{-1} and $(^{D}k)_{obs} = 0.79(5)\times10^{-2}$ h^{-1}.

Table 1. Concentrations of **1H** and **1D** in a competition RuO_4 oxidation experiment. For details, see the text.

React. period/h	[1H]/mM	[1D]/mM
0	278.6	233.8
3.17	249.7	234.1
8.83	218.6	215.5
21.17	147.9	194.5
28.17	113.8	190.0
45.5	66.2	164.5

Ruthenium tetraoxide oxidations in the presence of nucleophiles. A mixture of $RuO_2 \cdot 2H_2O$ (1.03 g, 6.1 mmol), $NaIO_4$ (6.14 g, 28.7 mmol) and water (50 ml) was stirred for 3 h and extracted with CCl_4 (2×5 ml). The CCl_4 solution was added to a solution of NaCl (3.73 g, 63.8 mmol), tetrabutylammonium chloride (0.84 g, 3.04 mmol) and acetonitrile (5 ml) in water (10 ml). To this was added *endo*-tricyclo[5.2.1.$0^{2,6}$]decane (**1H**, 0.84 g, 6.17 mmol) and the mixture was stirred vigorously for 50 min at 20 °C. Analysis by GC showed 84 % **1H**, 9 % **2**-OH, 0.8 % **2**-Cl, 0.7 % **6**, and 0.7 % **7**. In an analogous experiment with NaOAc instead of NaCl, no **2**-OAc was formed. The organic phase from this experiment was evaporated. The IR spectrum of the residue had a weak band at 1575 cm^{-1} but no band at 1450 cm^{-1}. Tetrabutylammonium acetate showed strong bands at both these frequencies. Acidification of the evaporated organic phase (2M HCl) gave no odour of HOAc. The concentration of chloride in the organic phase was found by running the reaction without **1H** and analysing the organic phase for chloride (by ion chromatography, SINTEF, Trondheim Norway). Water was determined by Fischer titration (SINTEF).

endo-*Tricyclo[5.2.1.$0^{2,6}$]decane-2,6-diol* (**9**). The olefin **3** (0.53 g, 3.95 mmol) in ether (11 ml) and pyridine (0.67 g, 8.47 mmol) was cooled to 0 °C and OsO_4 (1.00 g, 3.93 mmol) was added over 5 min. After 3.5 h, the osmate ester was filtered off, washed with ether and dried on the filter. The ester (1.20 g) was hydrolysed in water (20 ml) with KOH (2.00 g, 35.6 mmol) and mannitol (2.00 g, 11.0 mmol). After 20 h, the glycol **9** was extracted continuously with CH_2Cl_2, and the organic phase was dried ($MgSO_4$) and evaporated to give the glycol **9** (0.43 g, 70 % by GC). The crude product crystallised and the crystals were 90 % pure by GC and were used for further reactions and for characterisation. ^1H NMR (100 MHz, $CDCl_3$): δ 1.10–1.90 (10 H, m), 1.90–2.30 (4 H, m), 2.48 (2 H, s, OH, disappeared on D_2O treatment). MS (EI) 168 (67), 150 (35), 140 (61), 122 (39), 121 (43), 112 (67), 109 (30), 108 (20), 107 (30), 106 (40), 101 (39), 100 (30), 99 (52), 97 (80), 94 (43), 93 (35), 79 (65), 71 (85), 69 (35), 67 (100), 55 (72). IR (KBr): 3640–3020, 2940, 2870, 1450, 1310, 1110, 1045, 1025 cm^{-1}, all strong.

Ruthenium tetraoxide oxidations of derivatives of endo-*tricyclo[5.2.1.$0^{2,6}$]decan-2-ol.* This was tried under conditions analogous to those used for **1H** and adamantane (but without the added nucleophiles and phase-transfer reagent) for **2**-Cl (from **2**-OH and $SOCl_2$) which hydrolysed to **2**-OH before oxidation; for **2**-OMe (from **2**-OH and Amberlyst 15/MeOH) which was oxidised to the corresponding formate followed by hydrolysis to **2**-OH. However, the acetate **2**-OAc (from **2**-OH, acetic anhydride and pyridine, **2**-OAc gave back **2**-OH on $LiAlH_4$ reduction) did not react under these conditions, even after 75 h at 20 °C.

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