The RuO$_4$ Oxidation of Cyclic Saturated Hydrocarbons. Formation of Alcohols

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The RuO$_4$ oxidations of adamantane, endo-tetraydrodicyclopentadiene (I) and norbornane gave adamantanol (82 %), 4-hydroxy-endo-tetraydrodicyclopentadiene (2, 71 %) and 2-norbornanone (92 %). The oxidation of bicyclo[2.2.2]octane and exo-tetraydrodicyclopentadiene resulted in complex mixtures. The reactions are proposed as proceeding via hydride abstraction and carbocation formation.

Ruthenium tetroxide (RuO$_4$) is a vigorous oxidizing agent which can cause violent explosions when mixed with solvents like diethyl ether or hydrocarbons. In halogenated solvents, RuO$_4$ is a valuable synthetic reagent, especially for the oxidative cleavage of unsaturated systems. The transformation of ethers to esters and secondary alcohols to ketones are additional examples of useful oxidations by this reagent. On the other hand, RuO$_4$ oxidation of saturated hydrocarbons appears to have been less studied, contrary to the prediction of the authors of the review of 1973. The high reactivity and low selectivity of RuO$_4$, resulting in complex reaction mixtures, may be the reason for this. However, the derivatisation of saturated hydrocarbons is of great importance, and it is therefore of interest to investigate reagents with a potential for such transformations.

We have now studied the RuO$_4$ oxidation of some bi and tricyclic hydrocarbons. These hydrocarbons were chosen because they present both secondary and tertiary carbon atoms with varying degrees of steric crowding. The five compounds studied, together with the oxidation products and yields, are presented in Table 1.

Results

The oxidations were carried out by the procedure of Carlsen et al., in a mixture of acetonitrile, carbon tetrachloride and water. Sodium periodate was used as an oxidant with RuO$_4$ present in catalytic amounts. Adamantane and endo-tetraydrodicyclopentadiene (I) were also oxidized without acetonitrile present. The yields with and without acetonitrile were similar, although adamantane was oxidized more slowly in the run without acetonitrile (Table 1, 1. and 2.).

For three of the oxidations, good yields were obtained: 1-adamantanol from adamantane (82 %, 1. and 2.); 4-hydroxy-endo-tetraydrodicyclopentadiene (2) from endo-tetraydrodicyclopentadiene (I, 71 %, 3. and 4.); 2-norbornanone (92 %, 6.). On the other hand, the oxidations of exo-tetraydrodicyclopentadiene (5.) and bicyclo[2.2.2]octane (7.) gave complex mixtures containing several products.

The structure of product (2) from endo-tetraydrodicyclopentadiene followed from the mass spectrum (C$_{12}$H$_{18}$O), IR spectrum (hydroxyl group), $^{13}$C NMR-DEPT spectrum (1 t. C, 3 tert and 6 sec C), and the $^1$H NMR spectrum (no CHOH); and the structure of the by-product from the oxidation (3), see below; which was also formed by oxidation of the main product (2).

From the oxidation of endo-tetraydrodicyclopentadiene, one minor product was isolated (15 %, Table 1, 3. and 4.). Its structure followed from the mass spectrum (C$_{12}$H$_{18}$O), the IR spectrum (carbonyl group(s)), $^{13}$C NMR-DEPT spectrum (1 C=O, 1 tert C, 4 sec C) and from the $^1$H Spectroscopy.
Table 1. Oxidation of hydrocarbons by RuO₄/NaO₄ at 40°C

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Acetonitrile present</th>
<th>Reaction time (h)</th>
<th>Substrate reacted (%)</th>
<th>Product</th>
<th>Yield (%) of reacted substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Adamantane</td>
<td>+</td>
<td>26</td>
<td>81</td>
<td>1-Adamantanol</td>
<td>82</td>
</tr>
<tr>
<td>2. Adamantane</td>
<td>−</td>
<td>72</td>
<td>80</td>
<td>1-Adamantanol</td>
<td>81</td>
</tr>
<tr>
<td>3. Endo-tetraydrodi-cyclopentadiene (1)</td>
<td>+</td>
<td>48</td>
<td>85</td>
<td>4-Hydroxy-endo-tetraydrodi-cyclopentadiene (2)</td>
<td>71*</td>
</tr>
<tr>
<td>4. Endo-tetraydrodi-cyclopentadiene (1)</td>
<td>−</td>
<td>48</td>
<td>83</td>
<td>− &quot;−&quot;</td>
<td>69*</td>
</tr>
<tr>
<td>5. Exo-tetraydrodi-cyclopentadiene</td>
<td>+</td>
<td>96</td>
<td>65</td>
<td>Complicated mixture</td>
<td>14 compounds, (GC)</td>
</tr>
<tr>
<td>6. Norbornane</td>
<td>+</td>
<td>96</td>
<td>60</td>
<td>2-Norbornanone</td>
<td>92</td>
</tr>
<tr>
<td>7. Bicyclo[2.2.2]octane</td>
<td>+</td>
<td>48</td>
<td>20</td>
<td>Complicated mixture</td>
<td></td>
</tr>
</tbody>
</table>

*Minor product: 2,5-methylene-1,6-cyclononadione (3, 15%).

NMR spectrum (parameters in experimental section) which were in accordance with the structure 3. From the chemical shift of H₂ (3.1 ppm) and its coupling constant with H₁ (J₁₂ = 13.0 Hz), the conformation in Scheme 1 appeared reasonable. The structures of the products from the oxidation of adamantanetate and norbornane followed from the spectroscopic and chromatographic properties as compared to those of authentic samples.

Discussion

From Table 1, it is apparent that the oxidation of saturated hydrocarbons is of preparative value in certain cases. For both 1-adamantanetol, the hydrolysis of 1-bromoadamantane (from bromination of adamante)¹⁰ and for 2-norbornanone, the oxidation of 2-norbornanol (from hydrolysis of 2-chloronorbornane).¹¹ 4-Hydroxy-endo-tetraydrodi-cyclopentadiene (2) has been reported, but without physical data.¹²¹⁷ The minor product from the oxidation of (I), 2,5-methylene-1,6-cyclononadione (3) was also formed in an oxidation of the alcohol (2), presumably by RuO₄ oxidation of the olefin formed (Scheme 1).

From Table 1, it is evident that the rate of oxidation was influenced by the substituents of the carbon atom attacked. For adamantanetate, only reaction of the tertiary carbon atoms was observed. The same was the case for endo-tetraydrodi-cyclopentadiene (I), and only at the 4-carbon. For norbornane, the reactivity was reversed, the secondary carbons reacted faster than the tertiary ones. However, in this case also, the reactivity of the secondary carbons was lower than that of the tertiary carbons in adamantane and endo-tetraydrodi-cyclopentadiene. In competition experiments, adamantane reacted 21 times as fast as norbornane and endo-tetraydrodi-cyclopentadiene reacted 20 times as fast.

These points may be rationalized by a model in which either a carbon radical or a carbocation is formed as intermediate. The data appear to be better accommodated by the carbocation model. Thus, in hydrogen abstraction reactions (with the formation of carbon radicals), the tertiary and
secondary hydrogens of adamantane have approximately the same reactivity (the 1:3 ratio of the two types taken into account). The same is the case for bicyclo[2.2.2]octane. In solvolysis reactions (with the formation of carbocation), tertiary 1-bromoadamantane reacts 10^9 times faster than 2-bromoadamantane.

If the RuO₄ oxidation of adamantane formed carbon radicals in the rate determining step, 1-adamantanol and adamantanolone would be expected to be formed in comparable yields. If, on the other hand, carbocations were intermediates, 1-adamantanol would be the predominant product, as observed (Table 1). Furthermore, with a carbon radical intermediate, chlorinated products from reactions with carbon tetrachloride would be expected. No such compounds were detected. We therefore propose that the results from the oxidation of adamantane are best explained by a model invoking carbocations as intermediates.

The carbocations could have been formed by either a hydride ion abstraction from the substrate or by a hydrogen atom abstraction from an initially formed radical cation. Adamantane has been oxidised by Pb(IV) and Co(III) ions in trifluoroacetonic acid to 1-adamantyl trifluoroacetate in high yields. A comparison of these results with those from an anodic oxidation (presumably proceeding via radical cations) results in the conclusion that radical cations are less likely intermediates in the metal ion oxidations. In a study of Cu(III) oxidation of adamantane in acetic acid (giving a 6:1 mixture of 1- and 2-adamantyl acetate), it was not possible to reach a detailed conclusion as to the intermediates. Our own data do not permit us to distinguish between the two methods of carbocation formation.

However, as our oxidation of adamantane gave only one product in high yield (Table 1), it is reasonable to assume that radical cations, if formed, react rapidly to carbocation.

The RuO₄ oxidations of secondary alcohols and of ethers have been proposed to proceed by hydride ion abstraction. The results from the oxidation of bicyclo[2.2.2]octane and norbornane are in accordance with this proposal. In radical forming reactions, the reactivity of the bridgehead positions of these compounds are comparable to those of adamantane (10⁻² and 10⁻³ respectively). On the other hand, in carbocation forming reactions, the reactivities are 10⁻⁴ and 10⁻⁹ respectively of that of the corresponding adamantane derivative. The slow reactions observed for these compounds and the complex reaction mixtures obtained are therefore best explained by the carbocation intermediate model.

The results from the oxidation of endo-tetrahydrodicyclopentadiene (I) points towards the same conclusion. The reaction was in the 4-position, where there is a possibility of a relatively planar carbocation, rather than in the 6-position where planarity would be more difficultly achieved. The oxidations of exo- and endo-tetrahydrodicyclopentadiene gave different results. The first one reacted sluggishly and gave at least fourteen products, the second one reacted comparatively rapidly and gave only one major product. This difference is explained by the steric crowding of the 4-hydrogens of the exo isomer (by the endo C-9 and C-10 and by the eclipsed positions with regard to the C-3 hydrogen) as compared to the endo isomer.

Conclusions
The present study of RuO₄ oxidation of saturated bi and tricyclic hydrocarbons indicates that the reaction will be of preparative value in some cases and suggests that the reaction proceeds from carbocation intermediates.

Experimental
The endo- and exo-tetrahydrodicyclopentadienes were made by hydrogenation (Pd-catalyzed) of endo-dicyclopentadiene (Fluka AG) and exo-dicyclopentadiene. Adamantane, norbornane and bicyclo[2.2.2]octane were supplied by Fluka AG. The oxidations were performed by the procedure of Carlsen et al. The same procedure was used in the runs without acetonitrile, but without this solvent. The reactions were monitored by GC analyses (Carlo Erba 4160, 20 m fused silica, SE-30) with ρ-nitrotoluene as internal standard. The yields in Table 1 are from the GC analyses, except for the runs of endo-tetrahydrodicyclopentadiene where yields of isolated products are presented. The reaction mixtures where also analysed by GC/MS (Hewlett-Packard 5985).

The main product (2) from the oxidation of endo-tetrahydrodicyclopentadiene had m.p. 135 °C, IR (KBr): 3600–3100 (broad), 2960, 2880, 1450, 1325, 1040, 990, 980.
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References


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