

The RuO₄ Oxidation of Cyclic Saturated Hydrocarbons. Formation of Alcohols

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The RuO₄ oxidations of adamantane, *endo*-tetrahydrodicyclopentadiene (1) and norbornane gave adamantanol (82%), 4-hydroxy-*endo*-tetrahydrodicyclopentadiene (2, 71%) and 2-norbornanone (92%). The oxidation of bicyclo[2.2.2]octane and *exo*-tetrahydrodicyclopentadiene resulted in complex mixtures. The reactions are proposed as proceeding via hydride abstraction and carbocation formation.

Ruthenium tetroxide (RuO₄) is a vigorous oxidizing agent which can cause violent explosions when mixed with solvents like diethyl ether or hydrocarbons.¹ In halogenated solvents, RuO₄ 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.^{2–6} On the other hand, RuO₄ oxidation of saturated hydrocarbons appears to have been less studied, contrary to the prediction of the authors of the review of 1973.² The high reactivity and low selectivity of RuO₄, resulting in complex reaction mixtures, may be the reason for this.⁷ However, the derivatisation of saturated hydrocarbons is of great importance,⁸ and it is therefore of interest to investigate reagents with a potential for such transformations.

We have now studied the RuO₄ 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, car-

bon tetrachloride and water.⁹ Sodium periodate was used as an oxidant with RuO₄ present in catalytic amounts. Adamantane and *endo*-tetrahydrodicyclopentadiene (1) 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*-tetrahydrodicyclopentadiene (2) from *endo*-tetrahydrodicyclopentadiene (1, 71%, 3. and 4.); 2-norbornanone (92%, 6.). On the other hand, the oxidations of *exo*-tetrahydrodicyclopentadiene (5.) and bicyclo[2.2.2]octane (7.) gave complex mixtures containing several products.

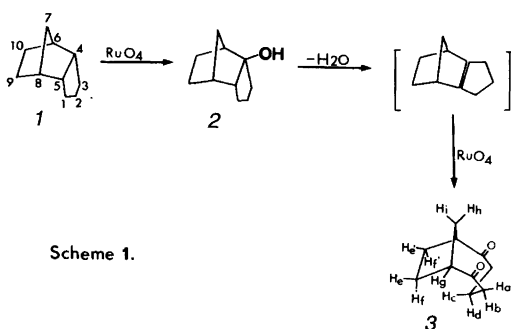
The structure of product (2) from *endo*-tetrahydrodicyclopentadiene followed from the mass spectrum (C₁₀H₁₆O), IR spectrum (hydroxyl group), ¹³C NMR-DEPT spectrum (1 *t.* C, 3 *tert* and 6 *sec* C), and the ¹H NMR spectrum (no CHOH); and the structure of the by-product from the oxidation (3), see below; which was also formed by oxidation of the main product (2).

From the oxidation of *endo*-tetrahydrodicyclopentadiene, one minor product was isolated (15%, Table 1, 3. and 4.). Its structure followed from the mass spectrum (C₁₀H₁₄O₂), the IR spectrum (carbonyl group(s)), ¹³C NMR-DEPT spectrum (1 C=O, 1 *tert* C, 4 *sec* C) and from the ¹H

Table 1. Oxidation of hydrocarbons by RuO₄/NaIO₄ at 40°C

Substrate	Acetonitrile present	Reaction time (h)	Substrate reacted (%)	Product	Yield (%) of reacted substrate
1. Adamantane	+	26	81	1-Adamantanol	82
2. Adamantane	-	72	80	1-Adamantanol	81
3. <i>Endo</i> -tetrahydrodicyclopentadiene (1)	+	48	85	4-Hydroxy- <i>endo</i> -tetrahydrodicyclopentadiene (2)	71 ^a
4. <i>Endo</i> -tetrahydrodicyclopentadiene (1)	-	48	83	- " -	69 ^a
5. <i>Exo</i> -tetrahydrodicyclopentadiene	+	96	65	Complicated mixture 14 compounds, (GC)	
6. Norbornane	+	96	60	2-Norbornanone	92
7. Bicyclo[2.2.2]octane	+	48	20	Complicated mixture	

^aMinor product: 2,5-methylene-1,6-cyclononadiene (3, 15%).



Scheme 1.

NMR spectrum (parameters in experimental section) which were in accordance with the structure 3. From the chemical shift of H_a (3.1 ppm) and its coupling constant with H_c (³J_{ac} = 13.0 Hz), the conformation in Scheme 1 appeared reasonable. The structures of the products from the oxidation of adamantane 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-adamantanol and 2-norbornanone, the present procedure appears to be simpler than those applied earlier: for 1-adaman-

tol, the hydrolysis of 1-bromoadamantane (from bromination of adamantane)¹⁰ and for 2-norbornanone, the oxidation of 2-norbornanol (from hydrolysis of 2-chloronorbornane).¹¹ 4-Hydroxy-*endo*-tetrahydrodicyclopentadiene (2) has been reported, but without physical data.^{12,17} The minor product from the oxidation of (1), 2,5-methylene-1,6-cyclononadiene (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 adamantane, only reaction of the tertiary carbon atoms was observed. The same was the case for *endo*-tetrahydrodicyclopentadiene (1), 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*-tetrahydrodicyclopentadiene. In competition experiments, adamantane reacted 21 times as fast as norbornane and *endo*-tetrahydrodicyclopentadiene 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.¹³ In solvolysis reactions (with the formation of carbocation), tertiary 1-bromoadamantane reacts 10⁸ times faster than 2-bromoadamantane.¹⁴

If the RuO₄ oxidation of adamantane formed carbon radicals in the rate determining step, 1-adamantanol and adamantanone 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 trifluoroacetic acid to 1-adamantyl trifluoroacetate in high yields.¹⁸ 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.^{18,19} 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.²⁰ 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.⁵ 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 (10⁻¹ and 10⁻³ respectively).¹³ On the other hand, in carbocation forming reactions, the reactivities are 10⁻⁴ and 10⁻⁹

respectively of that of the corresponding adamantane derivative.¹⁵ 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.¹⁶ Adamantane, norbornane and bicyclo[2.2.2]octane were supplied by Fluka AG. The oxidations were performed by the procedure of Carlsen *et al.*⁹ 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 *p*-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 were 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.

¹³C DEPT (Jeol FX-100, CDCl₃, ppm from TMS): 90.19 (qt), 56.23 (*tert*), 48.58 (*tert*), 41.1 (*tert*), 40.83 (*sec*), 36.0 (*sec*), 28.5 (*sec*), 25.82 (*sec*), 23.67 (*sec*), 21.43 (*sec*).

¹H NMR (Bruker 400 MHz, CDCl₃, ppm from TMS): 2.2 (s, OH), 2.1 (d, 1H), 1.9 (m, 5H), 1.7 (m, 1H), 1.4 (m, 8H).

MS (AEI 902) 152.1203 (C₁₀H₁₆O).

IR (KBr) of the minor product (3, m.p. 64–65°) from the oxidation: 3000–2900, 2980, 1700, 1445, 1310, 1170, 890.

MS: 166.0998 (C₁₀H₁₄O₂).

¹³C NMR (CDCl₃): 213.98 (C=O), 51.34 (*tert* C), 39.10 (*sec* C), 30.94 (*sec* C), 24.73 (*sec* C), 23.57 (*sec* C).

¹H NMR: By a series of double resonance experiments the following parameters were obtained (CDCl₃, ppm from TMS, J in Hz, letters refer to compound 3 in Scheme 1): δ_a 3.1, δ_b 2.3, δ_c 1.65, δ_d 2.05, δ_e 1.65, δ_f 2.25, δ_g 2.7, δ_h 3.1, δ_i 1.95, J_{ab} -11.8, J_{ac} 13.0, J_{ad} 4.0, J_{bc} 3.8, J_{bd} 5.4, J_{cd} -13.3, J_{cf} -7.8, J_{cf} 1.8, J_{eg} 5.4, J_{fg} 0, J_{ge} -2.5, J_{gi} 7.8, J_{gh} 0, J_{hi} -14.0.

The competition experiments between norbornane and adamantane or *endo*-tetrahydrodicyclopentadiene were performed as for the other oxidation reactions,⁹ except that the substrate consisted of 50 mol % norbornane and 50 mol % adamantane or *endo*-tetrahydrodicyclopentadiene. The [RuO₄]/[substrates] ratio was 4 · 10⁻². After 47 h at 25 °C, the two reaction mixtures contained (GC, internal standard method, % of starting material): adamantane, 58 %; 1-adamantanol, 42 %; norbornane, 98 %; 2-norbornanone, 2 %; *endo*-tetrahydrodicyclopentadiene, 60 %; 4-hydroxy-*endo*-tetrahydrodicyclopentadiene, 40 %; norbornane, 98 %; 2-norbornanone, 2 %.

In a control experiment *endo*-tetrahydrodicyclopentadiene was stirred with the oxidation mixture, without RuO₄, for 72 h at 25 °C. The reaction mixture contained 92 % of 1 and 8 % of 2.

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