

Ruthenium Catalysed Oxidations of Organic Compounds

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Ruthenium and its complexes can be used to catalyse the oxidation, both homogeneous and heterogeneous, of a wide range of organic substrates. These include olefins, alkynes, arenes, alcohols, aldehydes, ketones, ethers, sulphides, amines, and phosphines. A wide variety of oxidants can be used under mild conditions; conversions and selectivities are usually high, and the catalyst can be easily recovered. Ruthenium can also be used to catalyse the oxidative destruction of pollutants in both gas and liquid phases.

The synthetic use of ruthenium tetroxide as an oxidant for organic compounds was first reported in 1953 by Djerassi and Engle (1). The scope of ruthenium oxidations was greatly expanded by Berkowitz and Rylander in 1958 (2). All of these early workers used ruthenium tetroxide as a stoichiometric oxidant; however, ruthenium tetroxide is rather inconvenient to use in this way. It is troublesome to prepare, expensive, and its strong oxidising power tends to make it less selective than other oxidants. **Caution**—ruthenium tetroxide is an extremely powerful and volatile oxidant; it should only be handled in a well ventilated area and when wearing appropriate protective clothing.

Thus it is not surprising that work was soon initiated on using ruthenium in catalytic quantities in oxidation reactions. The first such use of ruthenium seems to have been in an obscure publication in 1956 (3). A more readily available report appeared in 1959 (4). The advantages of catalytic ruthenium oxidations over stoichiometric ruthenium tetroxide have proved to be so convincing that today virtually all ruthenium mediated oxidations are performed catalytically.

While several reviews (5–9) have been written on ruthenium mediated oxidations, the last one available in the West appeared ten years ago and dealt equally with ruthenium catalysed reactions and stoichiometric

ruthenium tetroxide reactions (9). With the emphasis shifting to ruthenium catalysed reactions, new reactions have been discovered and conditions have been found which have improved the selectivity and yields of these reactions. Thus it is appropriate to survey the subject again to summarise the state of the art.

Experimental Conditions

Many different ruthenium catalysts and oxidants have been used. Of these, the most common catalysts are $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, and the most common oxidants are HOOAc , NaIO_4 , O_2 , and NaOCl . Some catalyst/oxidant systems are very selective indeed. For example both $\text{RuCl}_2(\text{PPh}_3)_3/\text{Ph}(\text{IOAc})_2$ and $\text{RuCl}_2(\text{PPh}_3)_3/\text{N}$ -methylmorpholine-N-oxide specifically convert primary alcohols to aldehydes in high yields (10, 11) and $\text{RuCl}_2(\text{PPh}_3)_3/\text{PhCH}=\text{CHCOCH}_3$ converts vicinal diols to vicinal diketones (12).

Conditions for ruthenium catalysed oxidations are very mild; usually a few hours or less at room temperature is sufficient. A variety of solvent systems can be used, and depending on the oxidant a wide range of pH's can be tolerated. Oxidations with oxygen can be carried out at atmospheric pressure.

Many ruthenium catalysed reactions have been performed in the $\text{H}_2\text{O}-\text{CCl}_4$ solvent system. But slow or incomplete reactions are

occasionally encountered in this system, especially in the presence of carboxylic acids. Recently it has been found that adding CH_3CN to the system greatly improves yields and reaction times (13, 14). When (E)-5-decene was oxidised in $\text{H}_2\text{O}-\text{CCl}_4$ only 20 per cent conversion occurred in 2 hours; but on adding CH_3CN the reaction was complete in the same period.

Oxidation of Olefins

Cleavage of the Double Bond

When the oxidation of an olefin is catalysed by ruthenium in the oxidation state +3 or higher, the usual result is cleavage of the double bond. Ketones are produced if the carbons are fully substituted; otherwise acids, or occasionally, aldehydes are obtained, see Table I. On the other hand, osmium tetroxide when used catalytically converts olefins to aldehydes rather than to acids (21).

Non-Cleavage of the Double Bond

Only a few non-cleavage reactions are known, and these are given in Table II. The catalyst is usually a +2 ruthenium complex and the products are unpredictable.

Oxidation of Alkynes

Terminal alkynes are cleaved to give acids while internal alkynes yield diketones with no cleavage, see Table III.

Oxidation of Arenes

Ruthenium catalysed oxidations of arenes can proceed in three ways, see Table IV:

Alkyl side chains on the phenyl ring can be converted to $-\text{COOH}$ (IV-A, B).

The phenyl ring can be cleaved from R-Ph to form R-COOH (IV-C, D).

The phenyl ring can be degraded to form a dicarboxylic acid (IV-E, F, G).

In almost all cases where an alkyl side chain is replaced by a carboxyl group, a heterogeneous catalyst was used, for example IV-A, B. This is one of the few cases in which a heterogeneous catalyst is used in ruthenium oxidations. Oxygen is used as the oxidant since at temperatures below 400°C it can only oxidise

ruthenium as far as RuO_2 , which is insoluble. Stronger oxidants such as NaOCl or NaIO_4 will oxidise ruthenium to the +7 or +8 oxidation state and these are soluble.

The effect of the electronegativity of the substituent on the products of the oxidation of naphthalenes can be seen in reactions IV-F and IV-G. An electron-donating substituent favours cleavage of the substituted ring, while an electron-withdrawing substituent favours cleavage of the unsubstituted ring.

Oxidation of Alcohols

This is the most common synthetic use of ruthenium catalysed oxidations. Highly selective conditions are readily available; alcohols can be converted to aldehydes rather than acids and vicinal diols can be readily oxidised to either cleaved or non-cleaved products depending on conditions. In alcohols containing another oxidisable group such as a $\text{C}=\text{C}$ double bond, a $\text{C}\equiv\text{C}$ triple bond, an arene, nitrogen or sulphur, the hydroxyl group is oxidised preferentially (Table V). In substrates containing both primary and secondary alcohols the primary alcohol is oxidised preferentially, (see V-H).

Secondary Alcohols


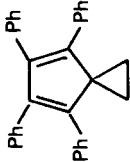
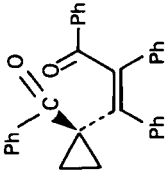
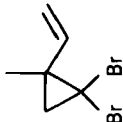
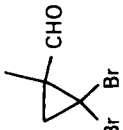
These are oxidised cleanly and in good yields to ketones, see Table VI. Cyclobutanols can be oxidised to cyclobutanones (38) (VI-F) in yields higher than with $\text{CrO}_3/\text{oxalic acid}$ (39).

Primary Alcohols

Primary alcohols are oxidised either to aldehydes (Table VII) or to acids (Table VIII). The outcome of the reaction can be highly selective depending on the conditions used. For example: $\text{RuCl}_2(\text{PPh}_3)_3$ with N-methylmorpholine-N-oxide (11), O_2 (33), $\text{PhCH}=\text{CHCOCH}_3$ (40) or $\text{Ph}(\text{IOAc})_2$ (10) always gives aldehydes. $\text{RuCl}_2(\text{PPh}_3)_3$ with excess PhIO (10), or RuCl_3 with HOOAc (42) or $\text{K}_2\text{S}_2\text{O}_8$ (32) always gives acids.

Diols

Oxidation of diols can give either cleaved or non-cleaved products, see Table IX. Stronger

Table I Oxidation of Olefins with Cleavage of the C = C Bond						
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.	
A $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	$\text{CH}_3(\text{CH}_2)_7\text{COOH} + \text{HOOC}(\text{CH}_2)_7\text{COOH}$	RuO_4	NaOCl	94	(15)	
B $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}_2$	$\text{CH}_3(\text{CH}_2)_7\text{COOH}$	RuCl_3	NaIO_4	89	(13)	
C 	$\text{HOOC}(\text{CH}_2)_{10}\text{COOH}$	RuO_2	O_2	94	(16)	
D $\text{CH}_3(\text{CH}_2)_3\overset{\text{CH}_2}{\underset{\text{ }}{\text{C}}}(\text{CH}_2)_5\text{CH}_3$	$\text{CH}_3(\text{CH}_2)_3\overset{\text{O}}{\underset{\text{ }}{\text{C}}}(\text{CH}_2)_5\text{CH}_3$	RuCl_3	NaOCl	83	(17)	
E 		RuO_2	NaIO_4	62	(18)	
F $\text{PhCH}=\text{CH}_2$	PhCOOH	RuO_2^*	O_2	92	(16)	
G $\text{PhCH}=\text{CH}_2$	PhCHO	RuO_2	NaIO_4	82	(19)	
H 		RuO_2	NaIO_4	86	(20)	

*3 ppm cobalt naphthenate added

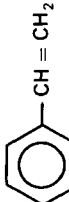
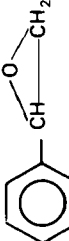

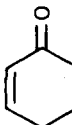
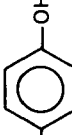

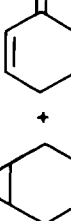
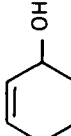
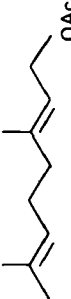
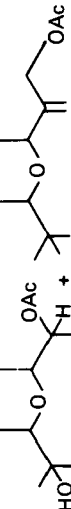
Table II Oxidation of Olefins without Cleavage of the C = C Bond					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A $\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{CH}_2$	$\text{CH}_3(\text{CH}_2)_6\text{COOH} + \text{CH}_3(\text{CH}_2)_6\text{CH}(\text{O})\text{CH}_2$	$\text{RuCl}_2(\text{PPh}_3)_3$	O_2	30, 52	(22)
B 		$\text{RuCl}_2(\text{PPh}_3)_3$	t-BuOOH	53	(23)
C 	 + 	$[\text{Ru}(\text{trpy})(\text{bipy})(\text{H}_2\text{O})]^{2+}$	electricity	—	(24)
D 	 + 	$\text{RuCl}_2(\text{PPh}_3)_3$	O_2	27 (conv.) ratio 1:5:3	(25)
E 		RuCl_3	NaIO_4	51, 12	(13)

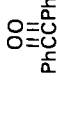
Table III Oxidation of Alkynes					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A $\text{PhC}\equiv\text{CPh}$		RuO_2	NaOCl	83	(26)
B $\text{BuC}\equiv\text{CBu}$	$\text{BuCCBu} + \text{BuCCOH}$	RuO_2	NaOCl	70, 19	(26)
C $\text{PhC}\equiv\text{CH}$	PhCOOH	RuO_2	NaOCl	66	(26)
D ${}^t\text{BuC}\equiv\text{CH}$	${}^t\text{BuCOOH}$	RuO_2	NaOCl	60	(26)
E $\text{HC}\equiv\text{CCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COOH}$	$\text{HOOCCH}(\text{NH}_2)\text{CH}_2\text{CH}_2\text{COOH}$	RuO_2	NaIO_4	50	(27)

Table IV Oxidation of Arenes						
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.	
A 		Ru/Al ₂ O ₃	O ₂	—	(28)	
B 		Ru/Al ₂ O ₃	O ₂	—	(29)	
C 		RuCl ₃	NaIO ₄	94	(13)	
D 		RuO ₂	NaOCl	80	(30)	
E 		RuO ₂	NaOCl	70	(31)	
F 		RuO ₂	NaOCl	50, 5	(31)	
G 		RuO ₂	NaOCl	7, 63	(31)	

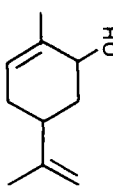
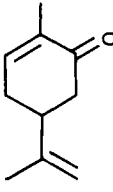
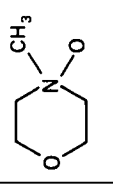

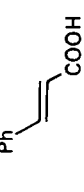
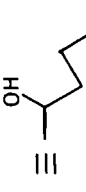
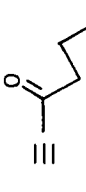
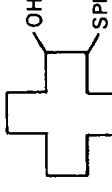
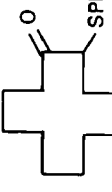
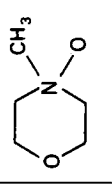
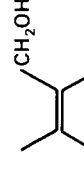
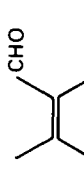
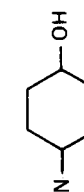
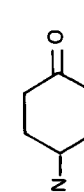
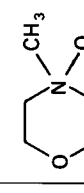

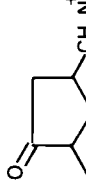

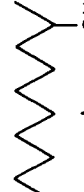
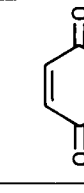
Table V Selective Oxidation of Alcohols in the Presence of Other Functional Groups					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A 		$\text{RuCl}_2(\text{PPh}_3)_3$		94	(11)
B 		RuCl_3	$\text{K}_2\text{S}_2\text{O}_8$	97	(32)
C 		$\text{RuCl}_2(\text{PPh}_3)_3$	PhIO	66	(10)
D 		$\text{RuCl}_2(\text{PPh}_3)_3$		73	(11)
E 		$\text{RuCl}_2(\text{PPh}_3)_3$	O_2	47	(33)
F 		$\text{RuCl}_2(\text{PPh}_3)_2$		65	(11)
G 		RuCl_3	NaOCl	79	(34)
H 		$\text{RuCl}_2(\text{PPh}_3)_3$		70 (conv.) 5:1	(35)


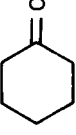

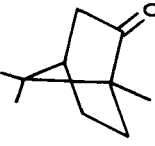
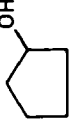
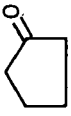
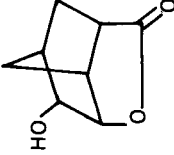
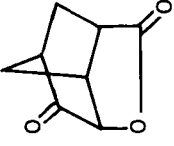

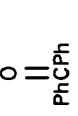
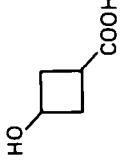
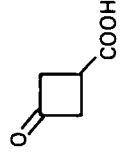
Table VI Oxidation of Secondary Alcohols						
	Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A			RuCl ₃	NaOCl	95	(36)
B			RuCl ₂ (PPh ₃) ₃	PhIO	86	(10)
C			RuCl ₃	K ₂ S ₂ O ₈	71	(32)
D			RuO ₂	NaIO ₄	80	(37)
E			RuCl ₃	K ₂ S ₂ O ₈	95	(32)
F			RuO ₂	NaIO ₄	78	(38)

Table VII
Oxidation of Primary Alcohols to Aldehydes

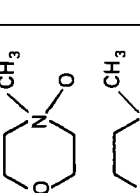
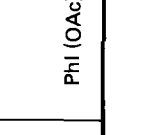
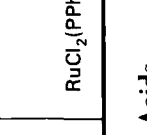
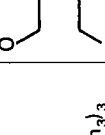
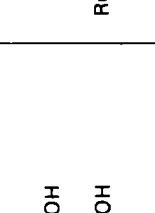
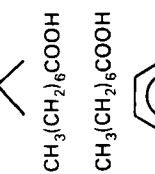
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A $\text{CH}_3(\text{CH}_2)_8\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_8\text{CHO}$	$\text{RuCl}_2(\text{PPh}_3)_3$		90	(11)
B 		$\text{RuCl}_2(\text{PPh}_3)_3$		79	(11)
C PhCH_2OH	PhCHO	$\text{RuCl}_2(\text{PPh}_3)_3$	PhCH=CHCOCH_3	90	(40)
D 		$\text{RuCl}_2(\text{PPh}_3)_3$	O_2	100	(33)
E $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	$\text{RuCl}_2(\text{PPh}_3)_3$	$\text{PhI}(\text{OAc})_2$	97	(10)

Table VIII
Oxidation of Primary Alcohols to Acids

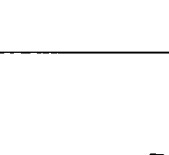
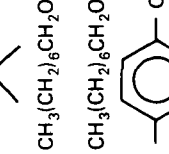
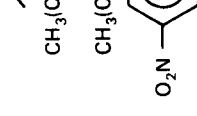
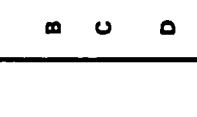


Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A 		RuO_2	NaIO_4	83	(41)
B $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	RuCl_3	HOOAc	83	(42)
C $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{COOH}$	$\text{RuCl}_2(\text{PPh}_3)_3$	PhIO (3 equ.)	88	(10)
D 		RuCl_3	$\text{K}_2\text{S}_2\text{O}_8$	97	(32)
E 		RuCl_3	$\text{K}_2\text{S}_2\text{O}_8$	86	(32)

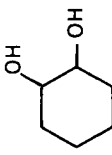
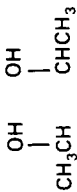
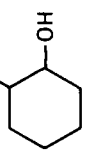
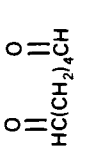
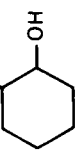
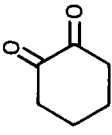
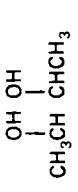

Table IX Oxidation of Diols					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A PhC(CH ₃)HCH(OH)CH ₂ OH	PhC(CH ₃)HCOOH	RuCl ₃	NaIO ₄	92	(13)
B 	HOOC(CH ₂) ₄ COOH	RuCl ₃	NaOCl	90	(36)
C 	CH ₃ CHO	RuCl ₃	H ₂ O ₂	88	(43)
D 		RuCl ₃	H ₂ O ₂	—	(43)
E 		RuCl ₂ (PPh ₃) ₃	PhCH=CHCOCH ₃	85	(12)
F 		RuCl ₂ (PPh ₃) ₃	PhCH=CHCOCH ₃	70	(12)

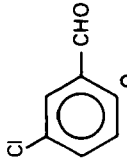
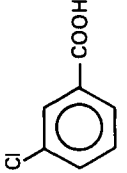
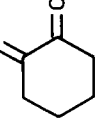
Table X Oxidation of Aldehydes and Ketones					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A CH ₃ (CH ₂) ₄ CHO	CH ₃ (CH ₂) ₄ COOH	RuCl ₂ (PPh ₃) ₃	PhIO	88	(10)
B PhCHO	PhCOOH	RuCl ₂ (PPh ₃) ₃	PhIO	96	(10)
C 		RuCl ₃	K ₂ S ₂ O ₈	99	(32)
D 	HOOC(CH ₂) ₂ COOH + HOOC(CH ₂) ₃ COOH + HOOC(CH ₂) ₄ COOH	RuCl ₃	NaOCl	3.56, 28	(36)

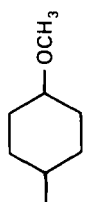
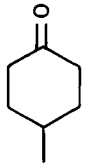
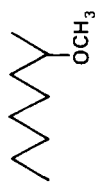
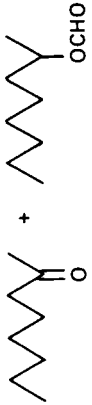
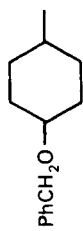
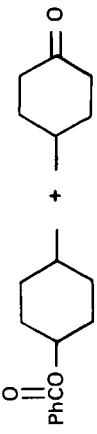

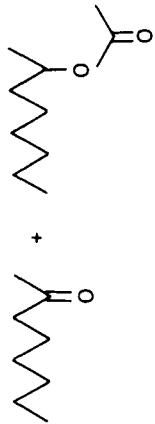

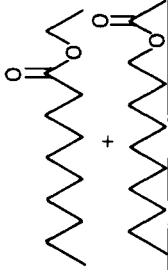
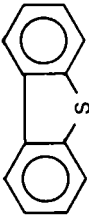
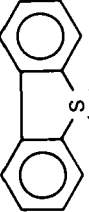
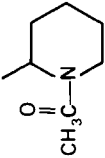
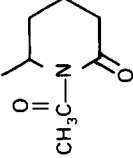
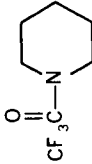
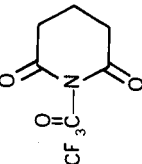
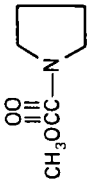
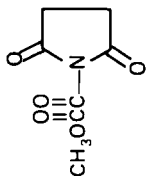
Table XI Oxidation of Acyclic Ethers					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A $\text{CH}_3(\text{CH}_2)_9\text{OCH}_3$	$\text{CH}_3(\text{CH}_2)_8\text{COCH}_3$	RuCl_3	NaIO_4	83-96	(13), (14)
B $\text{CH}_3(\text{CH}_2)_5\text{OCH}_3$	$\text{CH}_3(\text{CH}_2)_4\text{COCH}_3$	RuCl_3	NaIO_4	95	(14)
C 		RuCl_3	NaIO_4	99	(14)
D 		RuCl_3	NaIO_4	82.9	(14)
E $\text{PhCH}_2\text{OCH}_3$	PhCOCH_3	RuCl_3	NaIO_4	89	(13)
F 		RuCl_3	NaIO_4	61.8	(14)
G 		RuCl_3	NaIO_4	36.57	(14)
H 		RuCl_3	NaIO_4	52 20	(14)

Table XII Oxidation of Cyclic Ethers					
Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A 	 + HOOC(CH ₂) ₂ COOH	RuO ₂	NaIO ₄	40, 5	(47)
B 	HOOC(CH ₂) ₃ COOH	RuO ₂	NaIO ₄	79	(47)
C 	 +	RuO ₂	NaIO ₄	56, 14	(47)
D 	 HOOC	RuO ₂	NaIO ₄	72	(47)
E 		RuO ₂	NaIO ₄	82	(47)

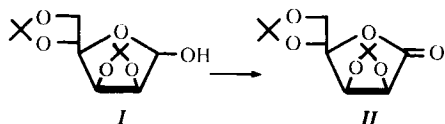
Table XIII
Oxidation of Sulphides and Amines

Substrate	Product	Catalyst	Oxidant	Yield per cent	Ref.
A Bu ₂ S	Bu ₂ SO + Bu ₂ SO ₂	RuCl ₃	O ₂	18, 76	(48)
B Bu ₂ S	Bu ₂ SO + Bu ₂ SO ₂	RuCl ₂ (AsPPh ₃) ₃	O ₂	93, 7	(48)
C 		Ru/Al ₂ O ₃	O ₂	97	(49)
D PhCH ₂ NH ₂	PhCN + PhCONH	RuCl ₃	O ₂	86 (total)	(50)
E PhCH ₂ NH ₂	PhCN	RuCl ₃	K ₂ S ₂ O ₈	66	(32)
F 		RuO ₂	NaIO ₄	60	(51)
G CH ₃ SO ₂ -N	CH ₃ SO ₂ -N	RuO ₂	NaIO ₄	90	(52)
H 		RuO ₂	NaIO ₄	33	(52)
I 		RuO ₂	NaIO ₄	71	(52)

oxidants cleave the diol, generally giving acids (IX-A, B), although under carefully controlled conditions aldehydes can be obtained as the major product (IX-C, D). The use of $\text{RuCl}_2(\text{PPh}_3)_3$ and $\text{PhCH}=\text{CHCOCH}_3$ selectively produces non-cleaved diketones from diols (IX-E, F).

Carbohydrates

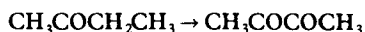
Ruthenium catalyses the oxidation of hydroxyl groups in carbohydrates, secondary hydroxyl groups being converted into carbonyls and primary groups to acids. For example L-sorbose is converted to a mixture of erythrose and glycolic acid (44) and sugar, I, is converted to its keto sugar, II, in 100 per cent yield (45).



The yields are usually better when ruthenium is used than when CrO_3 is used (9).

Oxidation of Aldehydes and Ketones

Aldehydes are readily oxidised to carboxylic acids, see Table X. There has been little published work on the oxidation of ketones. In one paper dealing with kinetics the authors reported that ketones were converted to diketones (46), for example:



However in this case a ten fold excess of substrate was used. Diketones are cleaved to give a mixture of acids (X-D).

Oxidation of Ethers

Acylic Ethers

Primary methyl ethers, RCH_2OCH_3 , are oxidised to methyl esters, RCOOCH_3 , in excellent yields, (XI-A, B). Secondary methyl ethers, $\text{RR}'\text{CHOCH}_3$, on the other hand undergo cleavage to give ketones, RCOR' (XI-C, D). Benzyl ethers, PhCH_2OR , undergo oxidation of the benzyl group to give esters,

PhCOOR , in fair to good yields (XI-E, F). Oxidation of unsymmetric ethers, ROR' where one of the substituents is not aromatic, gives unpredictable results with either R or R' being oxidised in roughly equal proportions.

Cyclic Ethers

Only carbons next to the ether linkage are oxidised. If both carbons are secondary, the products are mainly lactones with some carboxylic acids depending on the sensitivity of the lactone to hydrolysis (XII-A, B). If one carbon is secondary and the other tertiary the secondary carbon is oxidised preferentially giving a lactone (XII-C, D). Some hydrolysis to keto acids can occur. If both carbons are tertiary, cleavage to diketones occurs (XII-E).

Ethers are a class of compounds for which the yields and selectivities differ significantly when they are oxidised catalytically or stoichiometrically with ruthenium tetroxide. For example, tetrahydrofuran oxidised stoichiometrically with ruthenium tetroxide gives only γ -butyrolactone in 65 to 100 per cent yield (2, 47) but when oxidised catalytically with RuO_2 and NaIO_4 (47) the products are γ -butyrolactone, 40 per cent, and succinic acid, 5 per cent.

Oxidation of Sulphides and Amines

Sulphides are usually oxidised to a mixture of sulfoxides and sulphones (XIII-A, B), but in at least one case a sulphone was obtained exclusively (XIII-C).

Linear primary amines are oxidised to nitriles with some hydrolysis to the amide (XIII-D, E). Cyclic amines are oxidised to either lactams (XIII-F, G) or imides (XIII-H, I). The yields range from poor to good. As with ethers, only the carbon adjacent to the heteroatom is oxidised and secondary carbons are oxidised preferentially to tertiary carbons.

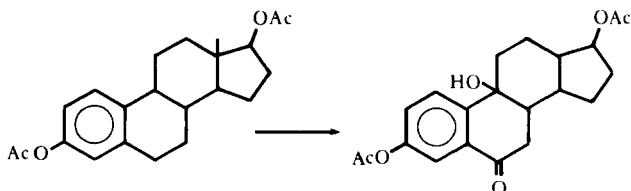
Oxidation of Steroids

Steroids generally undergo the same reactions that have already been discussed—oxidative cleavage of $\text{C}=\text{C}$ double bonds to

acids (4, 53), degradation of aromatic rings (54), and oxidation of secondary alcohols to ketones (10, 11).

It is interesting that cholesterol, which has both a secondary hydroxyl group and a C=C double bond, does not undergo any reaction (10, 11).

An atypical reaction which some steroids undergo is simultaneous oxidation of a tertiary CH group to a tertiary alcohol, and a secondary CH₂ to a ketone (54):



Pollution Control via Ruthenium Catalysed Oxidations

Wet scrubbing with KMnO₄ is used commercially to control air pollution. However with some pollutants, notably thiophenes, the reactions are too slow to be useful. It has been demonstrated (55) that oxidation of thiophenes with Ru/NaOCl is more than 100 times faster than with KMnO₄. This means that residence times are within the range that wet scrubbing of airborne thiophenes and other sulphur containing pollutants is practicable.

Ruthenium catalysed oxidations have been

suggested (56) for removing sulphur containing impurities from various petroleum fractions. Thus sulphur (500 ppm) in an n-paraffin fraction was reduced to less than 50 ppm in 4 hours by treatment with Ru/NaOCl at 20°C.

Ruthenium has also been suggested (57, 58) for the removal of ammonia from waste water by treating the waste at elevated temperatures with oxygen and a supported ruthenium catalyst. Chlorophenols and highly toxic polychlorodibenzodioxins were shown to be effectively destroyed by ruthenium catalysed oxidations (59).

Finally ruthenium has been demonstrated to remove pollutants in the gas phase. Thus 5500 ppm vinyl chloride in air was reduced to 2 ppm by passing the gas over a 0.5 per cent ruthenium on alumina catalyst at a temperature of 376°C (60).

Conclusion

Ruthenium and its complexes are extremely versatile oxidation catalysts. They will catalyse the oxidation of virtually any oxidisable organic functional group and, by choosing the appropriate conditions, the oxidations can be made to proceed in high yield and selectivity even in the presence of other oxidisable groups. Thus they offer a useful alternative to the more classical oxidation reagents.

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Platinum Group Metals in Organic Synthesis

Modern Synthetic Methods, Volume 3, 1983—Transition Metals in Organic Synthesis

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To provide chemists with an easy access to important and rapidly developing areas of synthetic organic chemistry triennial seminars on modern synthetic methods are held at Interlaken, sponsored and organised by The Association of Swiss Chemists. The May 1983 conference was devoted to the transition metals, and the above named volume of contributions is being co-produced by Salle and Sauerländer, with distribution rights in Austria, Germany and Switzerland (sfr./DM 48), and by John Wiley & Sons for the rest of the world.

The platinum group metals are featured in two of the five sections, these being "Principles of Transition Metals Chemistry" by Professor J. K. Stille and "Group VIII Metals in Organic Synthesis" by Professor L. S. Hegedus, both of Colorado State University. The contributions are well supported by references and this most useful book will undoubtedly fulfil its main purpose of serving as a guide for chemists interested in the application of transition metal chemistry to organic synthesis, in addition to aiding participants at the May conference.