Oxo Complexes of Ruthenium(VI) and (VII) as Organic Oxidants

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Oxidation of a variety of saturated and unsaturated primary and secondary alcohols by tetraoxoruthenate(VI), $[RuO_4]^{2-}$, tetraoxoruthenate(VII), $[RuO_4]^-$, barium *trans*-trioxodihydroxoruthenium(VI), *trans*-$Ba[Ru(OH)_2O_3]$, dioxotrichlororuthenate(VI), $[RuO_2Cl_3]^-$, and dioxodichlorobipyridylruthenate(VI), $[RuO_2(bipy)Cl_2]$, has been studied; $[RuO_4]^{2-}$ may be used catalytically in conjunction with $[S_2O_8]^{2-}$ under basic aqueous conditions. For some of these systems, the oxidation of several aldehydes and amines were also examined. Both $[RuO_4]^{2-}$ and $[RuO_4]^-$ oxidise primary alcohols to carboxylic acids and secondary alcohols to ketones; the reactivity of these reagents towards unsaturated alcohols was studied in particular. The new species $[PPh_4][RuO_2Cl_3]$ and also $[RuO_2(bipy)Cl_2]$ cleanly oxidise a wide range of alcohols to aldehydes and ketones *without* attack of double bonds. $Ba[Ru(OH)_2O_3]$ functions as a heterogeneous oxidant in dichloromethane, oxidising only the most reactive alcohols to aldehydes.

While many reagents for the conversion of alcohols into ketones, aldehydes or carboxylic acids are now known, the difficulties involved in the synthesis of structurally complex compounds has demanded the continued development of new and more highly selective oxidants. Ruthenium tetraoxide (RuO_4) is a powerful if somewhat unselective oxidant;[1] recently, the use of the ruthenate ion ($[Ru^{VI}O_4]^{2-}$) as an oxidant for simple alcohols has been explored,[2-8] and that of the perruthenate ion ($[Ru^{VII}O_4]^-$) briefly considered.[8,9] In a preliminary communication,[5] we have described a catalytic system for the oxidation of alcohols in which $[RuO_4]^{2-}$ is generated *in situ* from $RuCl_3 \cdot xH_2O$ in excess of aqueous base by persulphate. Other ruthenium complexes have been used catalytically for the oxidation of alcohols in which the secondary oxidant has been *N*-methylmorpholine *N*-oxide [10] and iodosylbenzene,[11] but the nature of the oxidising species has not been shown. Here we describe the uses and limitations of the catalytic ruthenate system more fully and explore the use of perruthenate as an oxidant as well as other oxo ruthenium complexes.

Results and Discussion

The Ruthenate Ion, $[RuO_4]^{2-}$.†—In the absence of a secondary oxidant, $[RuO_4]^{2-}$ in aqueous alkali at room temperature oxidises primary alcohols to carboxylic acids and secondary alcohols to ketones;[2] the clean conversion of cyclobutanol to cyclobutanone suggests that two-electron processes are operative.[3] In general, $[RuO_4]^{2-}$ does not appear to oxidise isolated double bonds at room temperature although some olefinic cleavage was observed with ricinoleic acid;[8] at 80 °C however, $[RuO_4]^{2-}$ in aqueous alkali does cleave the double bond of acrylate, crotonate, and cinnamate, and rate data for these reactions were obtained.[4] Notwithstanding the above results it has recently been claimed on the basis of electrochemical [7] and spectroscopic evidence [6] that $[RuO_4]^{2-}$ will not oxidise alcohols other than methanol and that such apparent oxidations are due to traces of $[RuO_4]^-$.

The reaction of ruthenium trichloride in aqueous base with persulphate gives $[RuO_4]^{2-}$, and using this we have devised a catalytic system for organic oxidations in which $[RuO_4]^{2-}$ is regenerated by the use of persulphate as a secondary oxidant.[5] Using this system, good yields of carboxylic acids from primary alcohols and of ketones from secondary alcohols are obtained (Table 1). Oxidations are typically conducted at room temperature using aqueous solutions of $RuCl_3 \cdot xH_2O$ in M-KOH with added $K_2S_2O_8$. This catalytic system may be applied to large-scale synthesis as demonstrated by the oxidations of 4-nitrobenzaldehyde and benzyl alcohol to the corresponding acids in 92 and 81% yields respectively on a 0.35—0.5M scale.[5] Oxidation does not occur to any appreciable extent (within the timescale of the experiment) with alkaline persulphate alone but is effected by stoicheiometric alkaline ruthenate. That the reagent functions as an overall two-electron oxidant is indicated by titration of alkaline ruthenate solution in the absence of persulphate with alcohols (ethanol and benzyl alcohol require a 2 : 1 $[RuO_4]^{2-}$/substrate ratio while acetaldehyde and benzaldehyde need a 1 : 1 ratio). As with stoicheiometric $[RuO_4]^{2-}$,[3] we find that the catalytic system oxidises cyclobutanol to cyclobutanone in high yield, again suggesting that a two-electron oxidation is operative. It is of interest to note that the rate of oxidation of a series of substituted benzyl alcohols and benzaldehydes (entries 6, 8, 9,19, 20, and 21 in Table 1) varies according to the electron withdrawing or donating capacity of the substituent, the oxidation rate decreasing in the order 4-NO_2 > 4-H > 4-OMe. Similar rate effects have been noted for oxidation of substituted benzyl alcohols and benzaldehydes by CrO_3[15] and $[FeO_4]^{2-}$.[16] It should be noted that oxidation of mandelic acid, hydrobenzoin (and benzoin) gives benzoic acid arising from additional C–C cleavage (Table 1, entries 15 and 18). However, this only occurs with these oxidatively sensitive substrates as ruthenate catalysed oxidation of methyl mandelate gives the corresponding glyoxalate with no C–C cleavage (entry 16). Table 1 also includes examples of amine dehydrogenations by this catalytic system. For example, benzylamine (entry 24) is dehydrogenated to benzonitrile in 66% yield and n-butylamine (entry 23) is converted into n-butanoic acid in 34% yield *via* hydrolysis of the intermediate nitrile. The reason for the different oxidation products in these reactions is not clear and we did not undertake a full study on such amine oxidations. However, we observe that amine dehydrogenations with catalytic ruthenate are generally not useful as multiple products frequently occur and there is severe inhibition of the catalyst.

The reagent does not react with alkenes (or alkynes) unlike some other two-electron oxidants such as CrO_3 and OsO_4. However, our original suggestion [5] that the double bond of unsaturated alcohols is not attacked needs modification. Although cinnamyl alcohol is oxidised to cinnamic acid in

† Both magnetic [12] and vibrational spectroscopic data [13,14] indicate that $[RuO_4]^{2-}$ has a tetrahedral structure in aqueous solution.

Table 1. Oxidations with catalytic $[RuO_4]^{2-}$

	Substrate	Product	Yield [a] (%)	Time (h)
1	Allyl alcohol	Acrylic acid	45	3.5
2	*E*-Crotyl alcohol	β-Methylacrylic acid	24	3
3	*E*-Cinnamyl alcohol	Cinnamic acid	99	3
4	n-Nonanol	n-Nonanoic acid	94	12
5	Borneol	Camphor	75	5
6	Benzyl alcohol	Benzoic acid	98	1.5
7	α-Tetralol	α-Tetralone	84	2
8	4-Nitrobenzyl alcohol	4-Nitrobenzoic acid	97	1
9	4-Methoxybenzyl alcohol	4-Methoxybenzoic acid	98	5
10	Cyclohex-3-enylmethanol	Cyclohexene-3-carboxylic acid	68	6
11	Chrysanthemyl alcohol	Chrysanthemic acid	66	7
12	Cyclobutanol	Cyclobutanone	70 [b]	2
13	Cyclopentanol	Cyclopentanone	87	2
14	Cyclohexanol	Cyclohexanone	64	2
15	Mandelic acid	Benzoic acid	91	4
16	Methyl mandelate	Methylphenylglyoxalate	62	2
17	Butane-1,4-diol	Succinic acid	32	5
18	Hydrobenzoin	Benzoic acid	75	2
19	Benzaldehyde	Benzoic acid	98	1
20	4-Nitrobenzaldehyde	4-Nitrobenzoic acid	98	0.7
21	4-Methoxybenzaldehyde	4-Methoxybenzoic acid	96	7.5
22	2-Hydroxybenzaldehyde	2-Hydroxybenzoic acid	71	5
23	n-Butylamine	n-Butanoic acid	34	24
24	Benzylamine	Benzonitrile	66	24

[a] Yield refers to the pure isolated product unless otherwise stated. [b] G.c. yield.

Table 2. Oxidations of $K[RuO_4]$

	Substrate	Product	Yield (%)	Time (h)
	(a) In M-aqueous NaOH			
1	n-Octanol	n-Octanal	67	2
2	Menthol	Menthone	87	1
3	*E*-Crotyl alcohol	*a*		
4	*E*-Cinnamyl alcohol	Benzoic acid [b]	89	3
5	Benzyl alcohol	Benzoic acid	99	1
6	4-Nitrobenzyl alcohol	4-Nitrobenzoic acid	94	1
7	4-Methoxybenzyl alcohol	4-Methoxybenzoic acid	94	1
8	Diphenylmethanol	Benzophenone	99	1
	(b) In dichloromethane with 18-crown-6			
9	n-Nonanol	n-Nonanoic acid	49	
10	Benzyl alcohol	Benzoic acid		
11	Diphenylmethanol	Benzophenone	64	

[a] Mixture obtained using a stoicheiometric amount of oxidant. [b] Yield of benzoic acid was obtained using a large excess of oxidant; stoicheiometric amount of oxidant gives incomplete reaction.

high yield, we find that other allylic and homoallylic alcohols are not cleanly oxidised. The desired reaction product is isolated in low yield with decomposition of substrate and intractable water-soluble product mixtures. It is possible that in these systems, the deactivation of the alkoxy-ruthenium intermediate may occur by complexation of the double bond to the metal. This intermediate may break down in different ways to give a mixture of products. The formation of such an intermediate was initially proposed by Sharpless [10] and later by Müller and Godoy.[11]

It has recently been claimed that the oxidation of alcohols by ruthenate solutions carried out either catalytically or stoicheiometrically is due to traces of $[RuO_4]^-$ rather than $[RuO_4]^{2-}$, and that the latter will oxidise aldehydes but not alcohols.[6] These observations were made in basic aqueous acetone solutions, rather than the pure aqueous solutions which we and others have used. We find that $K_2[RuO_4]$ (prepared by the standard oxidising flux procedure) [17] does not oxidise benzyl alcohol under basic aqueous acetone conditions, but does so in the absence of acetone. Further evidence that $[RuO_4]^-$ is not implicated in these reactions is provided by our observations, reported below, that $[RuO_4]^-$ gives double bond cleavage in cinnamyl (and crotyl) alcohols while $[RuO_4]^{2-}$, used either stoicheiometrically or catalytically gives cinnamic acid in high yield with no detectable cleavage.*

* The oxidations described by Burke and Healey were performed by generation of ruthenate in acetone–water (1 : 9) with 0.5M-KOH as opposed to generation of ruthenate in M-KOH which we typically use. This results in the formation of a green solution rather than the orange-red solution obtained under the latter conditions. It was further reported that $[RuO_4]^{2-}$, generated by oxidation of RuO_2 with $NaBiO_3$ will not oxidise benzyl alcohol. However, we have similarly prepared $[RuO_4]^{2-}$ by this method and in aqueous M-KOH but in the absence of acetone it was effective for the oxidation of benzyl alcohol.

Table 3. Oxidations with $Ba[Ru(OH)_2O_3]$

Substrate	Product	Yield (%)	Time (h)
1 Benzyl alcohol	Benzaldehyde	99 [a]	48
2 4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	85 [a]	48
3 4-Methylbenzyl alcohol	4-Methylbenzaldehyde	86	48
4 Diphenylmethanol	Benzophenone	98	48
5 Phenylene-1,2-dimethanol	Phthalide	83	48
6 Geraniol	Geranial	95	48

[a] Isolated as the 2,4-dinitrophenylhydrazone.

The Perruthenate Ion, $[RuO_4]^-$.*—Earlier studies showed that $[RuO_4]^-$, like $[MnO_4]^-$, cleaves double bonds; thus, at 21 °C, $[RuO_4]^-$ in 0.4M-aqueous alkali oxidises cinnamate and fumarate to benzoate and oxalate.[9] Recent work has shown that alkaline $[RuO_4]^-$ converts 12-hydroxystearate into 12-ketostearate; the double bond in oleate and methyl oleate is cleaved by the reagent, while ricinoleic acid, in addition to the expected cleavage products, gives heptanoic acid. With vicinal dihydroxyalkanoates, cleavage also occurs, *e.g.* of *erythro*-9,10-dihydroxystearate and its methyl ester.[8]

We find that $[RuO_4]^-$ is a strong but non-selective oxidant (Table 2); saturated primary alcohols give carboxylic acids and secondary alcohols yield ketones, while for unsaturated alcohols, there is competing double bond cleavage. Use of an excess of oxidant results in complete cleavage. Attempts to obtain a catalytic system using secondary oxidants such as ClO_3^-, IO_4^-, and $S_2O_8^{2-}$ were unsuccessful.

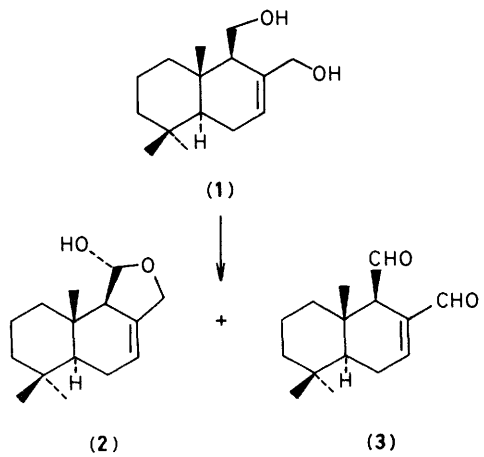
Since $K[MnO_4]$ with 18-crown-6 in benzene is a successful organic-solvent-soluble oxidant [20] we attempted to use $K[RuO_4]$ in a similar manner. A solution of $K[RuO_4]$ in benzene with 18-crown-6 is unstable, resulting in attack of solvent, but it may be used in dichloromethane. A number of oxidations were performed using this system, but solubility is limited and reaction times are longer than for the aqueous system.

The mechanism of oxidations by $[RuO_4]^-$ is presumably similar to that for $[MnO_4]^-$; we find that cyclobutanol is oxidised by the reagent to give a mixture of products containing a small amount of cyclobutanone, suggesting that one-electron processes are predominant.[3,21]

Barium Ruthenate, trans-*Ba*$[Ru(OH)_2O_3]$.†—In an effort to develop a milder oxidant and to circumvent the problems of an excess of base associated with the use of ruthenate and perruthenate, a heterogeneous reagent was employed. The highly insoluble barium ruthenate, an oxoruthenium(VI) complex, as a suspension in dichloromethane, reacts with only the most activated alcohols (*e.g.* benzylic and allylic) in contrast to $[RuO_4]^{2-}$ and $[RuO_4]^-$, giving the corresponding aldehyde (Table 3). All examples of primary and secondary alcohols which we examined with barium ruthenate were unreactive to oxidation. Upon exposure of n-octanol to barium ruthenate in refluxing dichloromethane over an extended period of time (1 week), less than 20% of n-octanal was formed. In summary, barium ruthenate functions as a very selective, mild reagent for the dehydrogenation of activated alcohols. Its reactions and activity are similar to the previously described barium manganate [24] with the exception of the oxidation of phenylene-1,2-dimethanol (entry 5) to phthalide in good yield. Barium manganate is reported to give the corresponding dialdehyde with *no* lactone formation.[24]

$[RuO_2Cl_3]^-$ *and* $[RuO_2(bipy)Cl_2]$.‡—The previously described reagents suffer from either strongly basic conditions or very mild, although selective, oxidative ability. Of importance to organic synthesis would be a more general, organic-solvent-soluble reagent which still retains high selectivity.

The ruthenium complexes, $[RuO_2(bipy)Cl_2]$ [25] and $[LPh_4][RuO_2Cl_3]$ (L = P or As) dissolve easily in dichloromethane and function as mild and effective oxidants, converting primary alcohols into aldehydes and secondary alcohols into ketones in good yield (Table 4). Unlike $[RuO_4]^{2-}$, the oxidative ability is not limited by unsaturation: thus geraniol and chrysanthemyl alcohol (entries 12 and 13) are oxidised to geranial and chrysanthemaldehyde without competing double bond cleavage by $[RuO_2Cl_3]^-$. The only exceptions we find so far is in the inability of both complexes to oxidise cholesterol and in the $[RuO_2Cl_3]^-$ mediated oxidation of lanost-8-en-3β-ol



* Single crystal and vibrational spectra of solid $K[RuO_4]$ [13,18,19] show that $K[RuO_4]$ contains a tetrahedral anion; we also find that the Raman spectrum of $[RuO_4]^-$ in aqueous alkali is very similar to that of the solid suggesting retention of tetrahedral symmetry in alkaline solution.

† Until recently, this salt was thought to be $Ba[RuO_4]\cdot H_2O$ [22] but a single-crystal *X*-ray study has shown it to contain the trigonal bipyramidal $[Ru(OH)_2O_3]^{2-}$ anion with hydroxo ligands in the *trans* axial positions.[23] The Raman and i.r. spectra of the brick-red solid are fully in accordance with this structure.

‡ The complex $[RuO_2(bipy)Cl_2]$ has been described previously.[25] The Raman and i.r. spectra of $[LPh_4][RuO_2Cl_3]$ (L = P or As) are similar to $[\{OsO_2(O_2R)L\}_2]$ and exhibit Ru = O bands near 880 cm^{-1} rather than at *ca.* 800 cm^{-1} in *trans*-$[RuO_2Cl_4]^{2-}$. The osmium complexes are dimeric in the solid state [29] but monomeric in solution; [30] it is possible that a similar situation is found for the ruthenium salts which should then more correctly be formulated as $[LPh_4]_2[Ru_2O_4Cl_6]$.

Table 4. Oxidations of $[LPh_4][RuO_2Cl_3]$

	Substrate	Product	Yield (%)	Time (h)
1	n-Decanol	n-Decanal	99 [a]	0.5
2	Menthol	Menthone	48 [a]	0.5
3	Benzyl alcohol	Benzaldehyde	68 [a]	0.5
4	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	99 [a]	0.5
5	2-Chlorobenzyl alcohol	2-Chlorobenzaldehyde	99 [a]	0.5
6	2-Hydroxybenzyl alcohol	2-Hydroxybenzaldehyde	48	4
7	*E*-Cinnamyl alcohol	Cinnamaldehyde	83	0.5
8	Cyclobutanol	Cyclobutanone	99 [c]	0.5
9	Cyclopentanol	Cyclopentanone	66 [a]	0.5
10	α-Tetralol	α-Tetralone	99 [a]	0.5
11	Phenylene-1,2-dimethanol	Terephthaldehyde	98	0.5
12	Geraniol	Geranial	92	0.5
13	Chrysanthemyl alcohol	Chrysanthemaldehyde	86	0.5
14	Phenylene-1,2-dimethanol	Phthalide	28	1
		Benzene-1,2-dicarbaldehyde	56	
15	Cyclohexane-1,2-diol	2-Oxocyclohexanone	51	3
16	5α-Cholestan-3β-ol	5α-Cholestan-3-one	100	15
17	5α-Cholestane-3β,6β-diol	5α-Cholestane-3,6-dione	89	16
18	Lanost-8-en-3β-ol	Lanost-8-en-3-one	30	36
		Lanost-3,8,9-trione	60	
19	Drimanediol	Isodrimeninol	35	0.2
		Polygodial	18	
20	Cholesterol	*b*		
	Oxidations of *trans*-$[RuO_2bipylCl_2]$			
21	Octadecanol	Octadecanal	87	3
22	Menthol	5,5-Dimethylcyclohexane-1,2-dione	54 [a]	78
23	Benzyl alcohol	Benzaldehyde	68 [a]	12
24	Cinnamaldehyde		98 [a]	14
25	5α-Chloestan-3β-ol	5α-Cholestan-3-one	93	1.5
26	Cholesterol	*b*		

[a] Isolated as the 2,4-dinitrophenylhydrazone. [b] Cholesterol recovered in virtually quantitative yield. [c] G.c. yield.

in which the major product is that derived from cleavage of the electron-rich, tetra-substituted double bond (entry 18). The former result appears to be a common facet of ruthenium oxidations, and is similarly reported by Sharpless [10] and Müller and Godoy.[11] In our examples, cholesterol was recovered in virtually quantitative yield. Oxidation of 5α-cholestane-3β,6β-diol at 0 °C (entry 17), disappointingly afforded no selectivity for the *axial vs. equatorial* alcohol, but use of two equivalents of $[RuO_2Cl_3]^-$ gave the corresponding dione in 89% yield. A unique and selective oxidation [26] of drimanediol, (1) with one equivalent of $[RuO_2Cl_3]^-$ gave the natural product isodrimeninol,[27] (2), in 35% yield, resulting from preferential oxidation of the least reactive alcohol and no further oxidation of the lactol moiety (entry 19). The low yield of (2) was partially compensated for by the secondary product, the insect antifeedant polygodial (3) [28] in 18% yield. Oxidation of the simpler 1,4-diol, phenylene-1,2-dimethanol gave, in contrast, a mixture of benzene-1,2-dicarbaldehyde and phthalide (entry 14).

Summary.—In conclusion we find that the catalytic $[RuO_4]^{2-}$ system is effective for the conversion of simple primary alcohols into carboxylic acids and secondary alcohols into ketones, and may be used in large-scale synthesis. Its counterpart, $[RuO_4]^-$, is less useful, although an excess of reagent will cleanly cleave unsaturated substrates. The heterogeneous oxidant barium ruthenate proves to be entirely selective for the oxidation of benzylic and allylic alcohols, but suffers from long reaction times. Conversely, the reagents $[RuO_2Cl_3]^-$ and $[RuO_2(bipy)Cl_2]$ are soluble in organic media and cleanly oxidise simple alcohols to the corresponding carbonyl compounds under mild conditions.

Experimental

M.p.s were determined on a Kofler heating block and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 298 spectrometer and mass spectra on a V.G. Micromass 7070 instrument. ^1H N.m.r. spectra were recorded on a Varian EM-360A instrument at 60 MHz or a Perkin-Elmer R32 at 90 MHz in deuteriochloroform with tetramethylsilane as an internal standard. Petroleum refers to light petroleum b.p. 40—60 °C which was distilled before use. Dichloromethane and carbon tetrachloride were dried by reflux over P_2O_5 and redistilled. Thin-layer analytical chromatography was performed on pre-coated aluminium-backed plates (Merck silica gel 60 F_{254}) and column chromatography was performed using Merck silica gel 60. Products were identified by comparison (t.l.c., n.m.r., and/or i.r.) with authentic material.

Preparation of Catalytic Ruthenate Persulphate Solutions.—An orange solution containing $[RuO_4]^{2-}$ was made by dissolving commercial ruthenium trichloride (*ca.* 5 mg, 0.02 mol) in M-aqueous potassium hydroxide (100 ml) containing potassium persulphate (3—6 mmol).

Oxidations with this solution were typically performed as follows. The substrate (1—2 mmol) was added with stirring. The end point of reaction is indicated by the reappearance of an orange solution due to regenerated $[RuO_4]^{2-}$ (after 1—6 h, depending upon scale and substrate). The product(s) were obtained either by initial extraction of the solution with ether (2 × 50 ml) if ketones, or acidification of the solution to pH 2 with sulphuric acid followed by ether extraction (2 × 50 ml) if carboxylic acids were produced. The organic extracts were combined and reduced in volume before passage through a silica gel or Celite pad to remove any residual ruthenium. The

solvent was removed under reduced pressure to give the pure ketone or carboxylic acid which was recrystallised if necessary.

In the case of unsaturated alcohols, the reaction progress was followed by t.l.c. of acidified aliquots of the reaction mixture. When an optimal product yield by t.l.c. was obtained, the reaction was subjected to work up as before.

$[RuO_4]^{2-}$ *Catalysed Oxidation of Chrysanthemyl Alcohol.*—To a solution of chrysanthemyl alcohol (617 mg, 4.0 mmol) in M-potassium hydroxide (50 ml), potassium persulphate (2.7 g, 10 mmol) followed by $RuCl_3 \cdot xH_2O$ (48 mg, 0.2 mmol) was added with vigorous stirring. The progress of reaction was followed by t.l.c. of acidified aliquots of the reaction mixture which had been extracted with small portions of ether. After 7 h, an optimal yield of product was observed. The reaction was acidified to pH 9 with conc. H_2SO_4 and extracted with ether (50 ml). Evaporation of the ether extract after passage through a Celite pad gave a small amount of starting material and chrysanthemaldehyde. Further acidification of the reaction to pH 2, extraction with ether (2 × 50 ml), and passage through a Celite pad, gave chrysanthemic acid as a 3 : 1 mixture of *trans* : *cis* (444 mg, 66%); $\nu_{max.}$ 3 400—2 500, 1 715, 1 470, 1 400, 1 310, 1 260, and 1 140 cm^{-1}; δ 60 MHz 9.9 (1 H, br s), 4.8 (1 H, br, d, *J* 7 Hz), 1.7 (6 H, s, CH_3), 1.3 (3 H, s), and 1.1 (3 H, s) *inter alia*. The presence of the *cis* isomer was indicated by a broad doublet at δ 5.2 (*J* 7 Hz).

Preparation of Tetraoxoruthenate(VII), $K[RuO_4]$.—A melt of an excess of potassium hydroxide (3 g), potassium nitrate (1 g), and commercial ruthenium trichloride (1 g, 41 mmol) in a nickel crucible was heated to dull red heat until gas evolution had ceased. The mixture was then dissolved in the minimum quantity of water (*ca.* 20 ml) and the solution filtered; the deep red ruthenate filtrate was treated with chlorine at 0 °C until the red colour was replaced by green-yellow and dark crystals had begun to form (too much chlorine leads to over oxidation and production of the volatile RuO_4). The dark green crystals were filtered off and washed with ice-cold water to give potassium perruthenate (0.67 g, 78%); $\nu_{max.}$ 840 cm^{-1} (Found: K, 19.4%. Calc. for $KRuO_4$: K, 19.2%). Systematic rechlorination of the filtrate raises the yield of potassium perruthenate to 85—90%.

$K[RuO_4]$ *Oxidation of n-Octanol.*—To a stirred solution of n-octanol (65 mg, 0.5 mmol) in 0.1M-sodium hydroxide (12 ml), solid potassium perruthenate (152 mg, 0.7 mmol) was added in small amounts. Upon completion, the reaction was acidified to pH 2 with sulphuric acid, extracted with diethyl ether (2 × 50 ml), and the combined organic extracts reduced in volume. Passage through a silica gel pad and removal of solvent gave n-octanoic acid (55 mg, 68%).

$K[RuO_4]$ *Oxidation of Benzhydrol in Dichloromethane.*—Potassium perruthenate (82 mg, 0.4 mmol) was dissolved in dichloromethane (5 ml) with 18-crown-6 (105 mg, 0.4 mmol) and filtered. Diphenylmethanol (101 mg, 0.5 mmol) dissolved in dichloromethane (2 ml) was added and the mixture stirred at 30 °C until no yellow colour remained. Solvent was removed and the residue treated with aqueous 1% potassium hydroxide (10 ml) and extracted with diethyl ether (2 × 10 ml). The combined ether extracts were filtered through Celite to give, after removal of solvent, benzophenone (64 mg, 64%; m.p., 45 °C).

Preparation of Barium trans-*Trioxodihydroxoruthenate*(IV), $Ba[RuO_3(OH)_2]$.—To a solution of ruthenate prepared as before for potassium perruthenate, a saturated solution of barium nitrate was added. The red precipitate was filtered off, washed with water, and dried *in vacuo* to give barium ruthenate (80%), $\nu_{max.}$ 3 570, 920, 818, 804m, and 522 cm^{-1}.

$Ba[RuO_3(OH)_2]$ *Oxidation of Geraniol.*—To a stirred solution of geraniol (52 mg, 0.34 mmol) in dichloromethane (2 ml), solid barium ruthenate (108 mg, 0.35 mmol) was added. The reaction was monitored by t.l.c. and after 10 h, excess of reagent was added until complete consumption of starting material was indicated. The reaction was diluted with ether (6 ml) and filtered through a Celite pad. Removal of solvent under reduced pressure gave geranial (citral) (49 mg 95%), δ (60 MHz) 9.9 (1 H d *J* 6 Hz), 5.9 (1 H, br, d), 5.1 (1 H, m), 1.7 (3 H, s), and 1.6 (3 H, s) *inter alia*.

Preparation of Tetraphenylphosphonium and Tetraphenylarsonium Dioxotrichlororuthenate(VI), $[LPh_4][RuO_2Cl_3]$ (L = P or As).—Ruthenium dioxide (1.0 g, 6 mmol) in water (20 ml) was stirred with an excess of sodium periodate until most of the ruthenium had dissolved; the resulting solution of RuO_4 was extracted into carbon tetrachloride (80 ml). When shaken with 2.5M-aqueous potassium hydroxide (50 ml) reduction to ruthenate was effected. After separation of the ruthenate solution and cooling to 0 °C, a saturated solution of tetraphenylphosphonium chloride (2.8 g, 7.5 mmol) was added followed by 6M-HCl until no further green material was precipitated. The mixture was filtered and the precipitate dried *in vacuo* to give tetraphenylphosphonium dioxotrichlororuthenate(VI) as a green powder (1.9 g, 55%) which could be recrystallised by precipitation from a dichloromethane solution with hexane; $\nu_{max.}$ 1 460, 1 440, 1 375, 1 110, 995, 890, 880, 725, and 685 cm^{-1} (Found: C, 49.85; H, 3.5; Cl, 18.35. $C_{24}H_{20}Cl_3PRuO_2$ requires C, 49.80; H, 3.49; Cl, 18.37%). Similarly, the tetraphenylarsonium salt gave (2.2 g, 58%). The majority of oxidations were performed with $[PPh_4][RuO_2Cl_3]$.

Preparation of Dioxodichloro(2,2′-*bipyridine*)*ruthenium*(VI) $[RuO_2(bipy)Cl_2]$.—Ruthenium dioxide (0.5 g, 3 mmol) was stirred in acetone (2 ml) under an inert atmosphere at 0 °C and a solution of $NaIO_4$ (1.89 g, 8.9 mmol) in the *minimum* amount of water was added to the suspension. The resulting solution of RuO_4 was allowed to warm to room temperature and acetone (6 ml) was added to precipitate any inorganic salts. The solution was transferred under an inert atmosphere to a mixture of 2,2′-bipyridine (0.3 g, 1.92 mmol) in acetone (1 ml) and 2M-HCl (1.92 ml) to which K_2CO_3 (0.15 g, 0.98 mmol) had been added. The complex precipitated immediately and was filtered onto a sinter, washed with acetone–water (1 : 1, 3 ml), and dried *in vacuo* overnight. $[RuO_2(bipy)Cl_2]$ (0.37 g, 55%) was obtained as a mustard coloured powder which was light sensitive but could be adequately stored at −10 °C in the dark; $\nu_{max.}$ 810, 770, and 325 cm^{-1} (Found: C, 33.6; H, 2.4; Cl, 19.6; N, 7.9. $C_{10}H_8Cl_2N_2Ru$ requires C, 33.3; H, 2.2; Cl, 19.7; N, 7.8%.)

General Procedure for Oxidations with $[LPh_4][RuO_2Cl_3]$ *and* $[RuO_2(bipy)Cl_2]$.—Typically, the oxidant (1.1 equiv.) was added to a stirred solution of the substrate (0.05—1.5 mmol) in dichloromethane. Reaction was usually complete within a few minutes. If incomplete reaction had occurred by t.l.c. analysis after several hours, additional oxidant was added. To the reaction mixture, ether or petroleum was added to precipitate inorganic compounds, and the solution was passed through a Celite pad. The product(s) were obtained by direct removal of solvent or by chromatography where required.

Oxidation of 5α-*Cholestan*-3β-*ol with* $[PPh_4][RuO_2Cl_3]$.—5α-Cholestan-3β-ol (32 mg, 0.08 mmol) was dissolved in

dichloromethane (3 ml) and the oxidant (53 mg, 0.09 mmol) was added in small portions. The initially emerald-green solution was stirred until t.l.c. indicated reaction to be complete (15 h); petroleum was then added to precipitate inorganic material. The mixture was passed through a Celite pad and removal of solvent followed by chromatography gave 5α-cholestan-3-one (32 mg, 100%), m.p., 128 °C.

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References

1 D. G. Lee and M. van den Engh, 'Oxidation in Organic Chemistry,' ed. W. Trahanovsky, 1973, Academic Press, London, vol. 5B.
2 D. G. Lee, D. T. Hall, and J. H. Cleland, *Can. J. Chem.*, 1972, **50**, 3741.
3 D. G. Lee, U. A. Spitzer, J. H. Cleland, and M. E. Olson, *Can. J. Chem.*, 1976, **54**, 2124.
4 D. G. Lee, S. Helliwell, and V. S. Chang, *J. Org. Chem.*, 1976, **41**, 3646.
5 M. Schröder and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1979, 58.
6 L. D. Burke and J. F. Healy, *J. Chem. Soc., Dalton Trans.*, 1982, 1091.
7 L. D. Burke and J. F. Healy, *J. Electroanal. Chem. Interfacial Electrochem.*, 1981, **124**, 327.
8 Y. Nakano and T. A. Foglia, *J. Am. Oil Chem. Soc.*, 1982, **59**, 163.
9 D. G. Lee, V. S. Chang, and S. Helliwell, *J. Org. Chem.*, 1976, **41**, 3644.
10 K. B. Sharpless, K. Akashi, and K. Oshima, *Tetrahedron Lett.*, 1976, 2503.
11 P. Müller and J. Godoy, *Tetrahedron Lett.*, 1981, 2361.
12 K. A. K. Lott and M. C. R. Symons, *J. Chem. Soc.*, 1960, 973.
13 W. P. Griffith, *J. Chem. Soc. A*, 1968, 683.
14 F. Gonzalez-Vilchez and W. P. Griffith, *J. Chem. Soc. A*, 1972, 1416.
15 J. Roček, 'Chemistry of the Carbonyl Group,' ed. S. Patai, 1966, p. 462, J. Wiley and Sons, New York.
16 R. J. Audette, J. W. Quail, and P. J. Smith, *J. Chem. Soc., Chem. Commun.*, 1972, 38.
17 F. Krauss, *Z. Anorg. Allg. Chem.*, 1928, **132**, 306.
18 M. O. Silverman and H. A. Levy, *J. Am. Chem. Soc.*, 1954, **76**, 3317.
19 W. P. Griffith, *J. Chem. Soc. A*, 1966, 1467.
20 See for example L. Fieser and M. Fieser, 'Reagents for Organic Syntheses,' 1967, **1**, 942, and subsequent volumes.
21 J. Roček and D. E. Aylward, *J. Am. Chem. Soc.*, 1975, **97**, 5452.
22 E. E. Mercer and D. T. Farrar, *Can. J. Chem.*, 1969, **47**, 581.
23 G. Newogrocki, F. Abrahams, J. Trehoux, and D. Thomas, *Acta Crystallogr., Sect. B*, 1976, **32**, 2413.
24 H. Firouzabadi and E. Ghaderi, *Tetrahedron Lett.*, 1978, 839.
25 W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315.
26 D. M. Hollinshead, S. C. Howell, S. V. Ley, M. Mahon, and N. M. Ratcliffe, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1579.
27 (*a*) Y. Asakawa and T. Takemoto, *Experientia*, 1979, **35**, 1420; (*b*) Y. Asakawa, S. Huneck, M. Toyota, T. Takemoto, and C. Swire, *J. Hattori Bot. Lab.*, 1979, **46**, 163.
28 C. S. Barnes and J. W. Loder, *Aust. J. Chem.*, 1962, **15**, 322.
29 B. A. Cartwright, W. P. Griffith, M. Schröder, and A. C. Skapski, *J. Chem., Soc. Chem. Commun.*, 1978, 853.
30 M. Schröder, A. J. Nielson, and W. P. Griffith, *J. Chem. Soc., Dalton Trans.*, 1979, 1607.

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