Ruthenium-catalysed Oxidative Cleavage Reaction of Carbon–Carbon Double Bonds Using Molecular Oxygen

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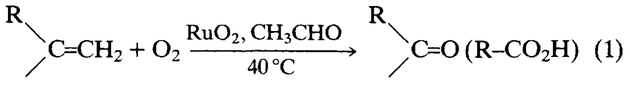
A RuO_2–CH_3CHO system selectively catalyses oxidative cleavage of carbon–carbon double bonds of terminal and α,β-unsaturated carbonyl compounds using molecular oxygen to give the corresponding carbonyl compounds.

There are many synthetic methods using the oxidative cleavage of alkenes to produce carbonyl compounds.[1] But, metal-catalysed cleavage reactions using molecular oxygen have not yet been extensively developed.[2] We report here a catalytic cleavage reaction of alkenes using a RuO_2–CH_3CHO–O_2 system. The present Ru catalyst system shows a high activity for terminal alkenes and α,β-unsaturated carbonyl compounds to give selectively corresponding carbonyl compounds (eqn. 1).

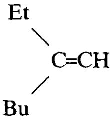
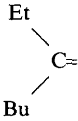
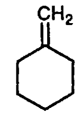
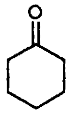
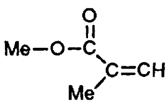
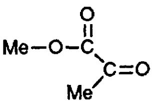
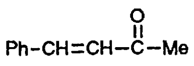
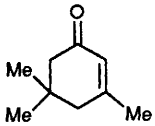
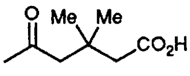


$$\mathrm{R(\,)C{=}CH_2 + O_2 \xrightarrow[40\,^{\circ}C]{RuO_2,\ CH_3CHO} R(\,)C{=}O\ (R\text{-}CO_2H)} \quad (1)$$

A typical reaction procedure for the title alkene oxidation is as follows. Oxygen was bubbled into a mixture of RuO_2 (0.04 mmol), acetaldehyde (136 mmol), pyromellitic acid (0.01 mmol) and acetone (50 ml) at 40 °C for 30 min. An acetone solution (10 ml) of isophorone (6 mmol) was added and the resulting mixture was stirred under an oxygen atmosphere at 40 °C for 2.5 h. After quenching the mixture (Na_2SO_3), oxidation products were analysed by GLPC. 3,3-Dimethyl-5-oxo-hexanoic acid was isolated by distillation (0.75 g, 140–145 °C/10 mmHg).

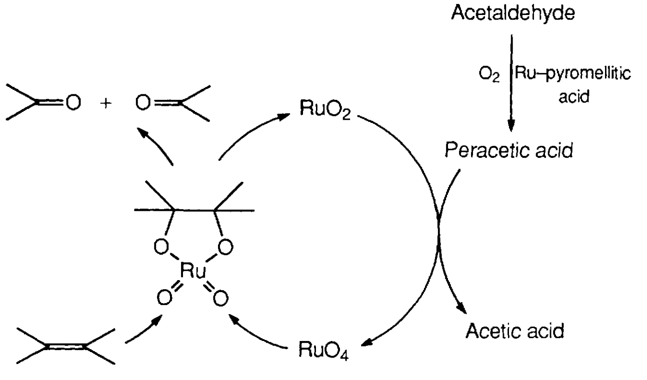
Representative examples for this cleavage reaction using Ru catalysts are shown in Table 1. Double bonds of terminal alkenes, *e.g.* octene and dodecene (Runs 1 and 5) were cleaved to give corresponding carboxylic acids in high yields. In a separate experiment, aldehydes of initial cleavage products were smoothly oxidized to the corresponding carboxylic acids under the present reaction conditions. This Ru–CH_3CHO–O_2 system has a dual function of the cleavage

Table 1 Oxidative cleavage of alkenes using ruthenium–aldehyde–O_2 systems[a]

Run	Alkene	Cleavage product (Yield, %)[b]
1	$C_6H_{13}CH{=}CH_2$	$C_6H_{13}CO_2H$(75)[c]
2[d]	$C_6H_{13}CH{=}CH_2$	$C_6H_{13}CO_2H$(72)
3[e]	$C_6H_{13}CH{=}CH_2$	$C_6H_{13}CO_2H$(70)
4	$C_5H_{11}CH{=}CH{-}CH_3$	$C_5H_{11}CO_2H$(38)[f]
5	$C_{10}H_{21}CH{=}CH_2$	$C_{10}H_{21}CO_2H$(90)
6	 $\mathrm{(Et)(Bu)C{=}CH_2}$	 $\mathrm{(Et)(Bu)C{=}O}$ (88)
7		 (77)
8		 (85)
9	 $\mathrm{Ph{-}CH{=}CH{-}C({=}O){-}Me}$	Ph—CO_2H (76) PhCHO (7)
10		 (91)

[a] Alkene 6 mmol, RuO_2 0.04 mmol, acetaldehyde 136 mmol, pyromellitic acid 0.01 mmol, acetone 60 ml, O_2 bubbling, 40 °C, 3 h. [b] Yields are based on alkenes used. [c] 1,2-Epoxyoctane was detected in an 8% yield. [d] $RuCl_3{\cdot}nH_2O$ was used in place of RuO_2. [e] Propionaldehyde was used. [f] 2,3-Epoxyoctane (21%) and octane-2,3-dione (30%) were also formed.

reaction and of the oxidation of aldehydes. *exo*-Alkenes of methylenecyclohexane and of 2-ethylhex-1-ene gave selectively cyclohexanone and heptan-3-one, respectively. For internal- and methyl-substituted alkenes, extensive epoxidation occurred. Oxidation of oct-2-ene increased the proportion of epoxide to 21% yield, compared with that of oct-1-ene. 1-Methylcyclohexene afforded 1,2-epoxy-1-methylcyclohexane and 6-oxo-heptanoic acid in 46 and 35% yields, respectively, while cyclohexene was cleaved to give a 70% yield of adipic acid with 11% yield of epoxycyclohexane. The epoxides gave cleavage products of the carboxylic acids under the above reaction conditions only in small amounts. From the above results, it seems that electron density on alkenic double bonds might play an important role in determining the reaction course between the cleavage and epoxidation. Oxidation of α,β-unsaturated carbonyl compounds as an electron-deficient alkene was further carried out using the Ru catalyst system. As expected, methylacrylate, benzalacetone, and isophorone were oxidized to the corresponding cleavage products of carbon–carbon double bonds in high yields; 3,3-dimethyl-5-oxo-hexanoic acid is derived from decarboxylation of the corresponding α-ketocarboxylic acid under the reaction conditions.



Scheme 1

$RuCl_3{\cdot}nH_2O$ also had a high catalytic activity (Run 2). RuO_2 itself did not give the cleavage products when argon was used instead of O_2. Aliphatic aldehydes, *e.g.* acetaldehyde and propionaldehyde, were effectively precursors for an oxidant for this cleavage reaction (Runs 1 and 3). Addition of pyromellitic acid accelerated an autoxidation step for aldehydes to give peracids, which oxidized RuO_2 to RuO_4. The lower valent ruthenium compounds favour oxidation of alcohols.[3] The ruthenium compound of RuO_4 might act as a catalyst for this cleavage reaction of alkenic double bonds (Scheme 1).[4]

There are some reports of the epoxidation of alkenes[5] and of the oxidation of alcohols[6] using molecular oxygen as an oxidant in the presence of Ru catalysts. In Ru-catalysed alkene cleavage reactions, this ruthenium–CH_3CHO catalyst system is the first example using molecular oxygen and provides a convenient synthetic method for carbon–carbon double bond cleavage of terminal alkenes and α,β-unsaturated carbonyl compounds to give carboxylic acids. There are few studies concerning the oxidative cleavage of α,β-unsaturated carbonyl compounds using metal reagents.[7]

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