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Oxidative Cleavage of *vic*-Diols to Aldehydes with Dioxygen Catalyzed by $Ru(PPh_3)_3Cl_2$ on Active Carbon

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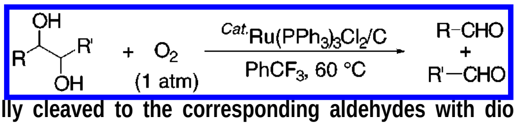
ABSTRACT



A variety of *vic*-diols were first successfully cleaved to the corresponding aldehydes with dioxygen catalyzed by $Ru(PPh_3)_3Cl_2$ on active carbon in fair to good yields. For example, treatment of 1,2-octandiol and 1,2-cyclooctanediol with dioxygen in the presence of $Ru(PPh_3)_3Cl_2/C$ in $PhCF_3$ at 60 °C for 15 h produced heptanal and 1,8-octanedial in 77% and 76% yields, respectively.

Oxidative cleavage of *vic*-diols is an important and frequently used transformation in organic synthesis. Typically, two oxidants, lead tetraacetate[1] and periodic acid,[2] are used for this purpose. On occasion, other reagents such as ceric ammonium nitrate,[3] sodium bismuthate,[4] and CrO_3[5] cause the cleavage of vicinal diols. However, these reagents have the obvious drawbacks of being toxic and producing a large amount of waste. There has been reported the catalytic cleavage of *vic*-diols to carboxylic acids with several oxidants such as *t*-BuOOH,[6] H_2O_2,[7] and O_2.[8] To our knowledge, however, few papers have been published on the catalytic cleavage of *vic*-diols to aldehydes with O_2,[9] probably because of the difficulty to suppress the formation of overoxidation products such as carboxylic acids. Our approach is to establish the oxidative cleavage of *vic*-diols to aldehydes with O_2 via transformation of *vic*-diols to aldehydes.

In an initial screening, we tested the oxidation of 1,2-octanediol (**1**) under dioxygen atmosphere (1 atm) by using several ruthenium complexes which catalyze the aerobic oxidation of primary alcohols to aldehydes (Table 1).[10]

Although tetrapropylammonium perruthenate (TPAP)[11] and $Ru(PPh_3)_3Cl_2$[12] are reported to catalyze the aerobic oxidation of primary alcohols to aldehydes, diol **1** was cleaved by these catalysts to heptanal (**2**) in low conversion and selectivity (entries 1 and 2). The formation of acetal **3** by $Ru(PPh_3)_3Cl_2$ would be based on the acetalization of the resulting heptanal **2** with **1** by an acid like hydrochloric acid, probably generated by the decomposition of a part of the $Ru(PPh_3)_3Cl_2$ during the reaction. However, $Ru_3(CO)_{12}$, $RuCl_3$, and RuO_2 were inactive in the present transformation (entries 3−5).

Previously, we have learned that the catalytic activity of a mixed addenda molybdovanadophosphate (NPMoV) whose average composition is approximately indicated as $(NH_4)_5H_6PMo_4V_8O_{40}$ in the aerobic oxidation of benzyl alcohols was considerably enhanced by supporting on the active carbon.[13]

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[10] **General Procedure.** To a solution of Ru complex (2 mol %) in α,α,α-trifluorotoluene (5 mL) in a flask was added diol (1 mmol), and a balloon filled with O_2 (1 atm) was attached to the flask. The mixture was vigorously stirred at 60 °C for 15 h. After removal of catalyst by filtration, the solvent was evaporated under reduced pressure. Products were isolated by flash chromatography on silica gel (*n*-hexane/AcOEt = 2:1).
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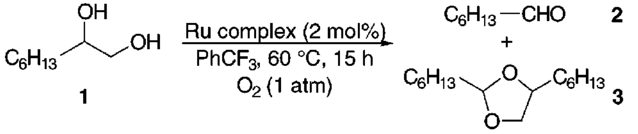
Table 1. Ruthenium-Catalyzed Aerobic Oxidation of 1,2-Octanediol[a]



entry	Ru complex	Conversion (%)	Selectivity (%) 2	Selectivity (%) 3
1	TPAP	20	49	n.d.
2	$Ru(PPh_3)_3Cl_2$	23	n.d.	48
3	$Ru_3(CO)_{12}$	no reaction		
4	$RuCl_3·nH_2O$	3.9	n.d.	42
5	$RuO_2·H_2O$	no reaction		
6[b, c]	$^{4wt.\%}Ru(PPh_3)_3Cl_2/C_W$	92(80)	77(75)	9.5(11)
7[b]	$^{4wt.\%}Ru(PPh_3)_3Cl_2/C_{KB}$	87	52	9.0
8[b]	$^{4wt.\%}Ru(PPh_3)_3Cl_2/C_{KG}$	47	77	3.9
9[b]	$^{4wt.\%}TPAP/C_W$	43	74	n.d.

[a] **1** (1 mmol) was allowed to react under 1 atm of O_2 in the presence of Ru complex (2 mol%) in $PhCF_3$ (5 mL) at 60 °C for 15 h.

[b] Activated carbons ; C_W : Wako Pure Chemical, C_{KB} : Kurare BP-25, C_{KG} : Kurare coal GLC. [c] 10 mmol of **1** was used.

Hence, TPAP and $Ru(PPh_3)_3Cl_2$ which were effective to some extent for the cleavage of **1** to **2** were loaded on several active carbons. Among the supported catalysts examined, the best catalyst was $Ru(PPh_3)_3Cl_2$, loaded on the active carbon available from Wako Pure Chemical, $Ru(PPh_3)_3Cl_2/C_W$,[14] giving 77% selectivity of **2** in 92% conversion of **1** (entry 6). Use of $TPAP/C_W$ catalyst resulted in **2** in relatively high selectivity, although the conversion was moderate (43%) (entry 9). Thus, the oxidation of **1** using the $Ru(PPh_3)_3Cl_2/C_W$ catalyst under various conditions was examined. Aldehyde **2** was obtained in higher selectivity and conversion in hydrophobic solvents (benzene, 55% selectivity in 73% conversion; toluene, 59% selectivity in 80% conversion; dichloroethane, 59% selectivity in 80% conversion) than those in hydrophilic solvents (THF, 39% selectivity in 56% conversion; acetonitrile: 14% selectivity in 19% conversion). When the amount of catalyst (1 mol %) was halved, the conversion of **1** was reduced to 64%, but the selectivity to **2** was almost the same as that using 2 mol % of catalyst. The reaction proceeded smoothly even at 50 °C to give **2** in satisfactory conversion of **1** (74%) and selectivity of **2** (72%).

On the basis of these results, a variety of *vic*-diols were allowed to react under 1 atm of O_2 using $Ru(PPh_3)_3Cl_2/C_W$ in $PhCF_3$ at 60 °C (Table 2).

1,2-Hexanediol and 1-phenyl-1,2-ethanediol were cleaved to pentanal and benzaldehyde in 65% and 92% selectivities at 97% and 92% conversions, respectively. In the same manner as terminal diols, internal *vic*-diols such as 4,5-octanediol were also cleaved to the corresponding aldehydes. From 4,5-octanediol, butanal and its acetal with 4,5-octanediol were obtained in 126% and 31% yields, respectively.

It is interesting to note that both *cis*- and *trans*-1,2-cyclooctanediols were successfully cleaved to 1,8-octanedial in high selectivities, although *trans*-1,2-cyclooctanediol was somewhat less reactive than the *cis* one. However, the oxidation of 1,2-cyclohexanediol under the same reaction conditions gave 1-formylcyclopentene. This shows that 1,2-cyclohexanediol is cleaved to 1,6-hexanedial which, however, undergoes easily the self-aldol condensation under these conditions to form 1-formylcyclopentene. 1,2-Cyclohexanediol is reported to be cleaved to dicarboxylic acid with O_2 by a heterogeneous Ru catalyst.[7b]

In the aerobic oxidation of alcohols by a ruthenium complex, it is well-known that the oxidation proceeds via the formation of an alkoxy ruthenium complex[15] and that the resulting ruthenium hydride is oxidized with O_2 to generate the original ruthenium complex and H_2O.[9]

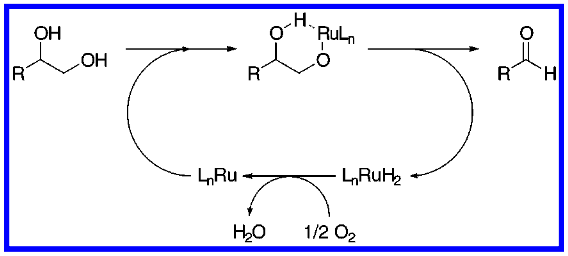
Therefore, the present reaction seems to proceed through a similar six-membered transition state as shown in Scheme

Table 2. Oxidative Cleavage of Various *vic*-Diols with O_2 by $Ru(PPh_3)_3Cl_2/C$[a]

entry	Diols	Conv. (%)	Selectivity (%)
1	1,2-hexanediol	97	pentanal (65), 2,4-dibuthyldioxolane (14)
2	1,2-octanediol	92	heptanal (77), 2,4-dihexyldioxolane (9.4)
3	2,3-octanediol	100	hexanal (61), 2,4-dipentyl-5-methyldioxolane (15)
4	4,5-octanediol	72	butanal (126), 2,4,5-tripropyldioxolane (31)
5	1-phenyl 1,2-ethanediol	92	benzaldehyde (92)
6[b,c]	*trans*-1,2-cyclohexanediol	90	1-cyclopentenealdehyde (62), adipic acid (31)
7[b,d]	*cis*-1,2-cyclooctanediol	100	1,8-octanedial (76), suberic acid (25)
8[b]	*trans*-1,2-cyclooctanediol	91	1,8-octanedial (68), suberic acid (26)
9[b]	1,2-cyclododecanediol	98	1,12-dodecanedial (45), dodecanedioic acid (50)
10[e]	1,2-benzenedimethanol	96	*o*-phthalaldehyde (2.2), phthalide (74)

[a] Diol (1 mmol) was reacted under 1 atm of O_2 in the presence of 4 wt.% $Ru(PPh_3)_3Cl_2/C_W$ (480 mg) in $PhCF_3$ at 60 °C for 15 h. [b] Catalyst (240 mg) was used with K_2CO_3 (5 mol%). [c] 95 °C. [d] 5 h. [e] 50 °C.

Scheme 1



1. However, when *trans*-2-methoxy-1-cyclooctanol was allowed to react under these conditions, the oxidation occurred with difficulty to form 2-methoxy-1-cyclooctanone in low yield. This fact shows that a six-membered transition state involving the ruthenium species is important to induce cleavage of *vic*-diols to aldehydes.

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Supporting Information Available: Experimental details and compound characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) **Preparation of Ru(PPh$_3$)$_3$Cl$_2$/C.** To a solution of Ru(PPh$_3$)$_3$Cl$_2$ (0.4 g) in benzene (300 mL) was added active carbon (9.6 g). The mixture was stirred at room temperature for 2 h. After removal of the solvent, Ru(PPh$_3$)$_3$Cl$_2$/C catalyst was dried at room temperature in vacuo overnight.

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