Chromium(VI) or Ruthenium(II) Complex Catalysis in Oxidation of Alcohols to Aldehydes and Ketones by Means of Bis(trimethylsilyl) Peroxide

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Bis(trimethylsilyl) peroxide (BTSP) serves as an effective oxidant of alcohols in the presence of chromium-(VI) or ruthenium(II) complexes as catalysts in dichloromethane. Selective oxidation of primary alcohols in preference to secondary ones using $RuCl_2(PPh_3)_3$ as a catalyst is also described.

Dehydrogenative oxidation of alcohols to the corresponding carbonyl compounds is one of the most important reactions in organic synthesis. Many transition metal reagents have been widely employed[1] as stoichiometric oxidants or catalysts. Here we wish to report catalysis of pyridinium dichromate(VI) and dichlorotris(triphenylphosphine)ruthenium(II) for oxidation of alcohols by means of $Me_3SiOOSiMe_3$ as an oxidant.[2]

(1) Oxidation of Alcohols with $Me_3SiOOSiMe_3$ Catalyzed by Pyridinium Dichromate(VI). Hexavalent chromium reagents are commonly utilized in the oxidation of primary and/or secondary alcohols. Pyridinium chlorochromate (PCC),[3] pyridinium dichromate (PDC),[4] chromyl chloride,[5] the Collins reagent,[6] as well as the Jones reagent[7] are well-known ones used in the laboratories.[8] However, there are some significant difficulties associated with each oxidant. Particularly, the Collins reagent became popular because of the excellent yields of products, however, a large excess of the chromium complex was required due to the precipitating gummy product which occluded the oxidant and often provided troubles in carrying out the oxidation manipulation as well as workup. Moreover, toxicity of excess chromium trioxide is also a serious problem. A solution to these problems is to find out a suitable co-oxidant which can convert alcohols to the corresponding carbonyl compounds in the presence of a catalytic amount of chromium(VI) species.

The failure in the attempted oxidation of alcohols with a catalytic amount of chromium(VI) complex has been ascribed to the fact that the popular organic or inorganic oxidants can not reoxidize the resulting tri-

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valent chromium into hexavalent because of its high oxidation potential ($E^0=1.33$ V in acid solutions).[9] Thus, we have turned our attention to utilize the peroxochromium–chromium(VI) trioxide cycle in which an oxodiperoxochromium complex (1) is a key reactant for the oxidation of alcohols.

Wiede reported the generation of oxodiperoxochromium–pyridine complex (1) in 1897.[10] Treatment of chromium trioxide with hydrogen peroxide in the presence of pyridine gave the peroxo reagent as a deep blue solid. This was used only as a damp complex[11] because of the danger of explosion upon drying. It is desirable to generate the oxodiperoxochromium complex in highly diluted conditions and to utilize it in situ for the oxidation from the viewpoint of safety. We have examined suitable co-oxidants, which will oxidize chromium trioxide or its equivalent to the desired oxodiperoxychromium complex. Formation of the "peroxo complex" was checked by a visible absorption arround 580 nm.[12] Among such peroxides as t-BuOOH, t-BuOOBu-t, PhC(O)OOC(O)Ph, and aqueous hydrogen peroxide examined, only hydrogen peroxide produced desired oxodiperoxochromium species. In the case of hydrogen peroxide (30% in water), however, the transformation of primary alcohols to aldehydes accompanied overoxidation into carboxylic acid. Finally, the $Me_3SiOOSiMe_3$–pyridinium dichromate system has proved to be effective for the generation of the oxodiperoxochromium complex in dichloromethane solutions. As the peroxo complex decomposed easily, the oxidant $Me_3SiOOSiMe_3$ was added dropwise using a syringe drive to the reaction mixture. Bis(trimethylsilyl) peroxide was stable enough even upon contact with metallic surface of the syringe needle when it was diluted with dichloromethane (0.5 mol dm^{-3}). The typical results for the conversion of alcohols into carbonyl compounds are summarized in Table 1.
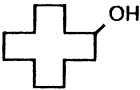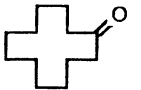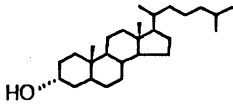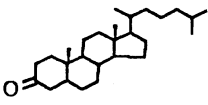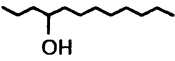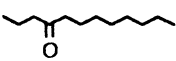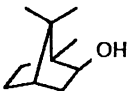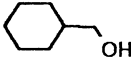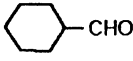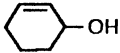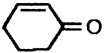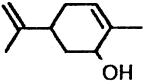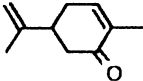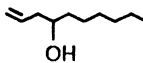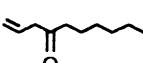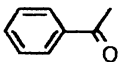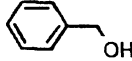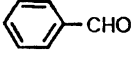
Each substrate was oxidized to the corresponding carbonyl compound in good yields. Moreover, the coexisting olefinic linkage remained intact upon treatment with the oxodiperoxochromium complex and no epoxy compounds were observed among the reaction mixture. Other hexavalent chromium reagents such as anhydrous chromium trioxide and pyri-
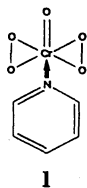
Table 1.   Oxidation of Alcohols with Pyridinium Dichromate/Me₃SiOOSiMe₃ System[a)]

Run	Substrate	Product	Yield/%[b)]
1			100
2			71
3			83
4			74
5			76
6			98
7			71[c)]
8			90[c)]
9			81[c)]
10			87[c)]
11			97
12			91

a) Me₃SiOOSiMe₃ (3.0 mmol) and pyridinium dichromate (0.1 mmol) were employed per one mol of alcohol. b) Isolated and purified yield. c) GLPC yields using decane, tridecane, or tetradecane as an internal standard.

dinium chlorochromate were examined as catalysts, and found to be less effective than pyridinium dichromate. For instance, oxidation of 4-t-butylcyclohexanol with CrO₃-Me₃SiOOSiMe₃ or PCC-Me₃SiOOSiMe₃ gave 4-t-butylcyclohexanone in 30% or 55% yield, respectively under the same reaction conditions as pyridinium dichromate-Me₃SiOOSiMe₃ system.   These results show that oxodiperoxochromium complex is rather unstable either under acidic conditions or in the absence of pyridine.[13)]

(2)   **Selective Oxidation of Primary Alcohols with**

Ruthenium Catalyst.   Ruthenium complex is also a popular catalyst for the oxidation of alcohols.   Many organic and inorganic co-oxidants such as amine oxide,[14)] t-BuOOH,[15)] hypervalent iodine compound,[16)] molecular oxygen,[17)] as well as inorganic NaBrO₃,[18)] and periodate[19)] were widely examined for the oxidation of alcohols.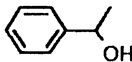   Dehydrogenative oxidation with hydrogen acceptor such as α,β-unsaturated carbonyl compounds has also been studied.[20)]   Being encouraged with the results obtained with chromium(VI)-catalyzed oxidation, we examined the combination of

Me₃SiOOSiMe₃ with a ruthenium complex, RuCl₂-(PPh₃)₃ to find that simple mixing of the substrate, the catalyst, and the oxidant in one portion gave results as summarized in Table 2.[21] Olefinic double bonds in the substrate were completely inert under the reaction conditions. This observation shows that ruthenium is not oxidized to octavalent oxidation state with Me₃SiOOSiMe₃, in sharp contrast with the ruthenium catalysis reaction using periodate as oxidant.[19]

It is worth noting that the allylic alcohols are oxidized with retained configuration of the olefinic bond. Geraniol and nerol were oxidized to the corresponding (E)- and (Z)-α-enals, respectively. The ruthenium complex, when used stoichiometrically, has proved to be an efficient reagent for the selective oxidation of primary alcohols in the presence of secondary ones.[22] For instance, treatment of 1,10-undecanediol with RuCl₂(PPh₃)₃ in benzene gave 10-hydroxyundecanal in 89% yield. The oxidation presumably involves formation of a ruthenium alkoxide which undergoes β-elimination to produce the carbonyl compound and hydridochlorotris(triphenylphosphine)ruthenium. The oxidation of alcohols was completed with half mol of RuCl₂(PPh₃)₃, so that this hydridochloro complex is supposedly capable to oxidize another mol of

the alcohol to the carbonyl compound. In fact, treatment of a mixture of 1-dodecanol and 4-dodecanol (1.0 mmol each) with HRuCl(PPh₃)₃ (1.0 mmol)[23] in benzene provided dodecanal in 75% yield along with a trace of 4-dodecanone (<2%). Possibly, the formation of a ruthenium alkoxide is a rate-determining step and bulkiness of triphenylphosphine ligand plays an important role for this selectivity.

$$RCH_2OH + RuCl_2(PPh_3)_3 \longrightarrow$$
$$RCH_2O\text{-}RuCl(PPh_3)_3 + HCl$$
$$RCH_2O\text{-}RuCl(PPh_3)_3 \longrightarrow RCHO + HRuCl(PPh_3)_3$$
$$RCH_2OH + HRuCl(PPh_3)_3 \longrightarrow$$
$$RCH_2O\text{-}RuH(PPh_3)_3 + HCl$$
$$RCH_2O\text{-}RuH(PPh_3)_3 \longrightarrow RCHO + H_2Ru(PPh_3)_3$$
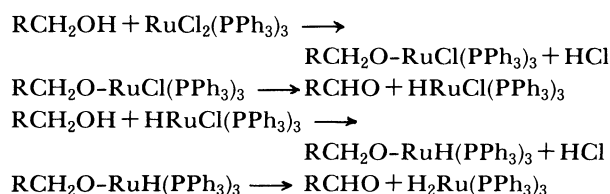
Some attempted selective oxidations of primary alcohols with a catalytic amount of RuCl₂(PPh₃)₃ resulted in failure. Such usual co-oxidants as t-BuOOH, N-methylmorpholine N-oxide were effective not only for reoxidation of reduced ruthenium complex to higher oxidation state, but also for oxidation of triphenylphosphine to phosphine oxide which was no more a ligand of ruthenium metal. With N-methylmorphorine N-oxide-RuCl₂(PPh₃)₃ system, 1-dodecanol reacted at only three times the rate of

Table 2.   Oxidation of Alcohols with RuCl₂(PPh₃)₃/Me₃SiOOSiMe₃ System[a]

Run	Substrate	Product	Yield/%[b]
1			97
2			85
3			96
4			80
5			72
6			83[c]
7			56
8			30[d]

a) Me₃SiOOSiMe₃ (2.0 mmol) and RuCl₂(PPh₃)₃ (0.05 mmol) were employed per one mmol of alcohol. b) Isolated and purified yield. c) GLPC yield using decane as an internal standard.
b) Reaction mixture was stirred for 20 h. Starting material (60%) was recovered.

4-dodecanol. Meanwhile, in our new system, Me$_3$-SiOOSiMe$_3$ was not too much strong to oxidize tri-phenylphosphine into triphenylphosphine oxide, so that the expected catalytic oxidation proceeded selectively. As expected, primary alcohols were oxidized faster than secondary ones with RuCl$_2$(PPh$_3$)$_3$-Me$_3$SiOOSiMe$_3$ system.[24] The relative rate of oxidation between 1-dodecanol and 4-dodecanol was 20 : 1 at the stage of 5% completion of the reaction.[25,26] Benzylic and allylic alcohols were more reactive than its saturated counterparts, and the ratio of reaction rate was more than 2/1. As a result, primary benzylic or allylic alcohols were oxidized more than 40 times as fast as saturated secondary alcohols. Table 3 shows the

results of selective oxidation of benzylic and allylic primary alcohols to α-enals. Coexisting secondary alcohols were recovered unchanged nearly quantitatively.

The following Scheme 1 shows that the new system was applicable for the primary-secondary diols. Only hydroxy aldehyde was obtained in good yield.

Experimental

Infrared spectra of neat liquid film samples were determined on a Hitachi grating infrared spectrometer 215, or JASCO IR-810, mass spectra and exact masses on a Hitachi M-80. NMR spectra were recorded on a Varian EM-390, or Varian XL-200 spectrometer using TMS as an internal

70%

72%
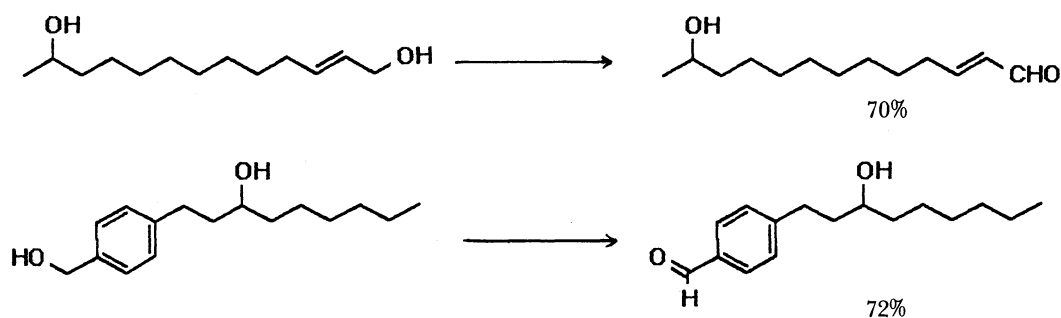
Scheme 1.

Diol (1.0 mmol), RuCl$_2$(PPh$_3$)$_3$ (0.1 mmol), and Me$_3$SiOOSiMe$_3$ (2.0 mmol) were combined in dichloromethane (10 ml) and the reaction mixture was stirred for 2 h at 25 °C.

Table 3. Selective Oxidation of Allyic Primary Alcohols in the Presence of Secondary Ones[a]

a) The hydroxy compounds (1.0 mmol each), RuCl$_2$(PPh$_3$)$_3$ (48 mg, 0.05 mmol), and Me$_3$SiOOMe$_3$ (0.45 g, 2.5 mmol) were combined in dichloromethane (15 ml) and the mixture was stirred for 3 h at 25 °C. b) Yields were calculated on the basis of GLPC (PEG 20 M, 20% on Celite 545, 1.5 m) using dodecane or tetradecane as an internal standard. Figures in parentheses vere recovery of starting secondary alcohols.

standard unless otherwise noted. Multiplicity is designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Preparative TLC plates were prepared with Merck Kiesel gel PF$_{254}$. Column chromatography was carried out with silica gel (Wakogel C-200) at atmospheric pressure.

Preparation of Bis(trimethylsilyl) Peroxide. The peroxide was prepared from hydrogen peroxide according to the reported procedure.[27] Bp 42—44 °C/30 Torr (1 Torr=133.322 Pa): IR (neat) 2960 (s), 1250 (s), 920 (w), 840 (s), 730 (s) cm⁻¹.

General Procedure for the Oxidation of Primary and Secondary Alcohols with Pyridinium Dichromate/Bis-(trimethylsilyl) Peroxide. A solution of Me₃SiOOSiMe₃ (79 mg, 0.5 mmol) in dichloromethane (2.0 ml) was added to a solution of pyridinium dichromate (37 mg, 0.1 mmol) in the same solvent (5.0 ml). The color changed immediately from dark orange to deep blue, which indicated the formation of oxoperoxochromium complex. Substrate alcohol (1.0 mmol) in dichloromethane (1.0 ml) was added to the solution and the rest of Me₃SiOOSiMe₃ (0.45 g, 2.5 mmol) in dichloromethane (5.0 ml) was added dropwise over 1 h by syringe pump at 25°C. The resulting brown reaction mixture was stirred more than 30 min after the completion of the addition of peroxide. The mixture was poured into ice-cooled saturated aqueous sodium hydrogensulfite and extracted with ether (3×20 ml). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated. Purification of crude product by silica-gel column chromatography gave a corresponding carbonyl compound in excellent yield (Table 1).

General Procedure for the Oxidation of Primary Alcohols to Aldehyde with RuCl₂(PPh₃)₃/Me₃SiOOSiMe₃ System. Oxidation of benzyl alcohol to benzaldehyde is representative. Benzyl alcohol (0.22 g, 2.0 mmol) and Me₃SiOOSiMe₃ (0.71 g, 4.0 mmol) were added to a solution of RuCl₂(PPh₃)₃ (96 mg, 0.1 mmol) in dichloromethane (15 ml) and the whole was stirred for 2 h at 25 °C. The resulting mixture was diluted with dichloromethane (20 ml) and poured into ice-cooled water. The organic layer was separated and water layer was extracted with dichloromethane and the combined organic layers were washed with saturated aqueous sodium hydrogensulfite and brine successively. Concentration followed by purification on preparative thin-layer chromatography gave benzaldehyde (0.19 g) in 91% yield (Table 2).

General Procedure for the Selective Oxidation of Allylic Primary Alcohols in the Presence of Secondary Ones. Selective oxidation of geraniol to (E)-citral in the presence of 4-dodecanol is representative. A solution of Me₃SiOOSiMe₃ (0.45 g, 2.5 mmol) in dichloromethane (5 ml) was added to a solution of geraniol (0.15 g, 1.0 mmol), 4-dodecanol (0.18 g, 1.0 mmol), and RuCl₂(PPh₃)₃ (0.05 g, 0.05 mmol) in dichloromethane (10 ml). The whole mixture was stirred for 3 h at 25 °C, and the resulting mixture was poured into ice water. The organic layer was separated and dried over Na₂SO₄. The yield of aldehyde and recovered secondary alcohol were checked by GLPC using tridecane as an internal standard (Table 3).

12-Hydroxy-2-tridecenal: To a solution of RuCl₂(PPh₃)₃ (96 mg, 0.1 mmol) in dichloromethane was added a mixture of Me₃SiOOSiMe₃ (0.37 g, 2.0 mmol) and 2-tridecene-1,12-diol (0.21 g, 1.0 mmol) in dichloromethane at 25 °C. The oxidation completed within 1.5 h and the reaction mixture was poured into ice water. Workup followed by purification gave 12-hydroxy-2-tridecenal in 70% yield: Bp 112—114 °C

(0.05 Torr, bath temp); IR (neat) 3370, 2940, 2740, 1697, 975 cm⁻¹; ¹H NMR (CCl₄) δ=1.11 (d, 3H, J=6.0 Hz), 1.1—1.8 (m, 14H), 2.2—2.6, (m, 3H), 3.5—3.9 (m, 1H), 6.01 (dd, 1H, J=15.0 and 7.5 Hz), 6.68 (dt, 1H, J=15.0 and 7.0 Hz), 9.39 (d, 1H, J=7.5 Hz); exact mass spectrum m/z 211.1608. Calcd for C₁₃H₂₃O₂: M−1, 211.1698.

4-(3-Hydroxynonyl)benzaldehyde: Bp 116—118 °C (0.06 Torr, bath temp); IR (neat) 3380, 2933, 2740, 1700, 1608, 1218, 1167, cm⁻¹; ¹H NMR (CDCl₃) δ=0.85 (t, 3H, J=7.5 Hz), 1.05—1.85 (m, 11H), 2.43—3.0 (m, 2H), 3.75—3.95 (m, 1H), 7.05—7.50 (m, 2H), 7.7—7.95 (m, 2H), 10.0 (s. 1H); exact mass spectrum m/z 248.1720. Calcd for C₁₆H₂₄O₂: M, 248.1777.

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24) Oxidation of secondary alcohols were very slow even in the case of benzylic alcohol, and sometimes the reaction stops in less than 50% conversion.

25) The ratios were determined by monitoring the appearance of dodecanal and 4-dodecanone by GLPC (PEG 20M 5% on Celite 545, 1.5 m, 120 °C).

26) From the synthetical point of view, the ratio of >95:5 is necessary for "selective" reaction. In order to achieve this ratio, the relative rate should be more than 50/1, which was obtained in the case of oxidation using stoichiometrical amount of ruthenium complex as oxidant.[22]

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