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TRANSITION-METAL CATALYZED OXIDATION OF ALCOHOLS TO ALDEHYDES AND KETONES BY MEANS OF $Me_3SiOOSiMe_3$

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Abstract: Pyridinium dichromate-$Me_3SiOOSiMe_3$ system has been found to be effective for the oxidation of alcohols to the corresponding carbonyl compounds. Selective oxidation of primary alcohols in the presence of secondary ones with $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ is also described.

Many reagents containing the chromium(VI) as a key atom for the oxidation of alcohols have been developed and widely used in organic synthesis. However, there are some significant difficulties associated with each reagent. A very large excess (for Collins reagent[1]) or modest excess of oxidants (chromyl chloride,[2] pyridinium chlorochromate,[3] and pyridinium dichromate[4]) is required and gummy precipitate containing chromium often provides troubles in carrying out the oxidation as well as in workup. Our studies have been aimed at finding a suitable co-oxidant which can convert alcohols to the corresponding carbonyl compounds in the presence of a catalytic amount of chromium(VI) species.

A solution of $Me_3SiOOSiMe_3$[5] (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). Instantaneous reaction occurred under rapid colour change to deep purple.[6] 4-*t*-Butylcyclohexanol (0.16 g, 1.0 mmol) was added and additional $Me_3SiOOSiMe_3$ (0.45 g, 2.5 mmol) was added dropwise over 1 h at 25°C and the resulting mixture was stirred for 30 min. Workup (CH_2Cl_2, $NaHSO_3$) and successive purification by silica gel column chromatography gave 4-*t*-butylcyclohexanone (0.15 g) in 98% yield. Primary and secondary alcohols were easily oxidized to the corresponding aldehydes and ketones in fair to good yields (Table 1).

Anhydrous CrO_3 and pyridinium chlorochromate were less effective as catalysts. The yields of 4-*t*-butylcyclohexanone were 30% and 55%, respectively under the same reaction conditions as pyridinium dichromate-$Me_3SiOOSiMe_3$ system.

Table 1. Oxidation of alcohols with pyridinium dichromate-$Me_3SiOOSiMe_3$ system[a]

Alcohol	Yield(%) of Carbonyl Compound	Alcohol	Yield(%) of Carbonyl Compound
Cyclododecanol	100	Cyclohexylmethanol	71
3-β-Cholestanol	71	2-Cyclohexen-1-ol	90
4-Dodecanol	83	Carveol	81
10-Undecen-1-ol	76	1-Decen-4-ol	87
1-Dodecanol	74	Benzyl Alcohol	91
Borneol	98	1-Phenylethanol	97

[a] $Me_3SiOOSiMe_3$ (3.0 mmol) and pyridinium dichromate (0.1 mmol) were employed per one mmol of alcohol.

$RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ system has proven to be a selective oxidant of alcohols. Benzyl alcohol (0.22 g, 2.0 mmol) and $Me_3SiOOSiMe_3$ (0.71 g, 4.0 mmol) were added to a solution of $RuCl_2(PPh_3)_3$ (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 water. The organic layer was washed with aq. $NaHSO_3$ and brine, dried, and concentrated. Purification by silica gel column chromatography gave benzaldehyde (0.19 g) in 91% yield. The results are summarized in Table 2.

It is worth noting that the primary alcohols are oxidized much faster than secondary ones with this system. The relative rate of oxidation between 1-dodecanol and 4-dodecanol was 20:1 at the stage of 5% completion

Table 2. Oxidation of alcohols with $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ system[a]

Alcohol	Yield(%) of Carbonyl Compound	Alcohol	Yield(%) of Carbonyl Compound
Benzyl Alcohol	97	2-Decen-1-ol	72
Geraniol	96	Cyclohexylmethanol	83
Nerol	85	1-Dodecanol	56
Cinnamyl Alcohol	80	1-Phenylethanol	30[b]

[a] $Me_3SiOOSiMe_3$ (2.0 mmol) and $RuCl_2(PPh_3)_3$ (0.05 mmol) were employed per one mmol of alcohol. [b] Reaction mixture was stirred for 20 h. Starting material (60%) was recovered.

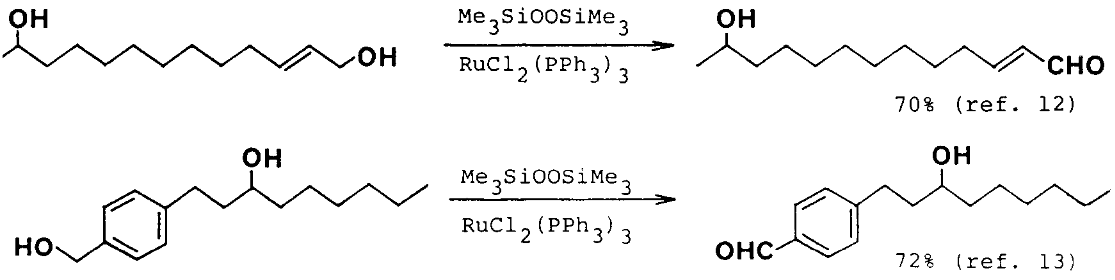
of the reaction.[7] The ratio is slightly less inferior to that (50:1) obtained with a stoichiometric amount of $RuCl_2(PPh_3)_3$.[8] Benzylic and allylic alcohols are more reactive than their saturated counterparts. For instance, geraniol reacts twice as fast as 1-dodecanol.[9,10] Thus, primary allylic alcohols were oxidized to α,β-unsaturated aldehydes[11] in high yields, while the coexisting secondary alcohols were recovered practically unchanged (Table 3).

Table 3. Selective oxidation of allylic primary alcohols in the presence of secondary ones[a]

Starting Mixtures of Alcohols	Yields (%)[b] of Aldehyde/Ketone
Geraniol/4-Dodecanol	99/3
Benzyl Alcohol/4-Dodecanol	98/8
Benzyl Alcohol/1-Phenylethanol	85/6
Geraniol/2-Dodecen-4-ol	95/6
2-Dodecen-1-ol/1-Dodecanol	63/40

[a] The hydroxy compounds (1.0 mmol each), $RuCl_2(PPh_3)_3$ (48 mg, 0.05 mmol), and $Me_3SiOOSiMe_3$ (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 20M, 5% on Celite 545, 1.5 m).

Treatment of primary, secondary diols according to this technique afforded hydroxy aldehydes arising from selective oxidation at the primary carbon.[14]



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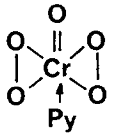

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7. The ratios were determined by monitoring the appearance of dodecanal and 4-dodecanone by glpc (PEG 20M 5% on Celite 545, 1.5m, 120°C).
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10. The reaction proceeded with high stereospecificity. Geraniol gave only geranial, while nerol afforded neral.
11. No epoxy alcohols could be detected in the oxidation with pyridinium dichromate-$Me_3SiOOSiMe_3$ and $RuCl_2(PPh_3)_3$-$Me_3SiOOSiMe_3$ systems.
12. Bp 112-114°C (0.05 Torr, bath temp); IR (neat) 3370, 2940, 2740, 1697, 975 cm^{-1}; NMR (CCl_4) δ1.11 (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/e* 211.1608. Calcd for $C_{13}H_{23}O_2$: M-1, 211.1698.
13. Bp 116-118°C (0.06 Torr, bath temp); IR (neat) 3380, 2933, 2740, 1700, 1608, 1218, 1167 cm^{-1}; NMR ($CDCl_3$) δ0.85 (t, 3H, J = 7.5 Hz), 1.05-1.85 (m, 11H), 2.43-3.0 (m, 2H), 3.75-3.95 (m, 1H), 7.05-7.5 (m, 2H), 7.7-7.95 (m, 2H), 10.0 (s, 1H); exact mass spectrum *m/e* 248.1720. Calcd for $C_{16}H_{24}O_2$: M, 248.1777.

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