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Letter

Aerobic oxidative cleavage of pinanediols by cobalt(II) acetylacetonate in the presence of 2-methylpropanal

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Abstract

The catalytic system made up of cobalt(II) acetylacetonate, 2-methylpropanal and dioxygen (or air) facilitated the oxidative cleavage of (1*S*,2*S*,3*R*,5*S*)-(+)-pinanediol **1a** and (1*R*,2*R*,3*S*,5*R*)-(−)-pinanediol **1b** to enantiomerically pure *cis*-pinonic acids **4a–b**. © 2000 Elsevier Science B.V. All rights reserved.

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Oxidative cleavage of *vic*-diols and carbon–carbon double bond of olefins to carbonyl and carboxylic acids is one of the most frequently used transformations in the field of synthetic organic chemistry. In the past, periodic acid or lead tetraacetate were usually employed as oxidants [1,2]. More recently, Venturello explored the oxidative cleavage of *vic*-diols with dilute hydrogen peroxide (H_2O_2) in the presence of tungstate in conjunction with phosphate (or arsenate) ions under acidic conditions [3]. On the same topic, Ogawa et al. reported that this oxidative cleavage could be successfully achieved by tris (cetylpyridinium) 12-tungstophosphate (CWP)-H_2O_2 system under homogenous conditions [4], whereas ruthenium pyrochlore oxides ($Pb_{2.62}Ru_{1.38}O_{6.5}$) and $MoO_2(acac)_2$, in the presence or in the absence of *t*-BuOOH, were used by Felthouse [5] and Kaneda's groups [6] to carry out the oxidative cleavage of a great number of *vic*-diols.

Electrochemical [7], photochemical [8], and, in particular, thermal [9–11], induced methodologies with one-electron oxidizing agents were also explored. Aerobic oxidative cleavage of *vic*-diols in the presence of Co(II)-laurate [12] or iron-porphyrin catalysts [13] has also been described.

Following our study on the catalytic activity of β-diketonato complexes [14–19] in aerobic oxidation reactions carried out in the presence of excess sacrificial aldehyde, we have submitted

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to oxidative conditions (+)-and (−)-pinanediols **1a** {(1*S*,2*S*,3*R*,5*S*)-(+)-2,6,6-trimethyl-bicyclo{3.1.1]heptane-2,3-diol} and **1b**{(1*R*,2*R*,-3*S*,5*R*)-(−)-2,6,6-trimethyl-bicyclo {3.1.1]heptane-2,3-diol} obtaining, as overoxidated products, enantiomerically pure (+)-and (−)-*cis*-pinonic acids **4a** {*cis*-[(1*R*,3*S*)-(3-acetyl-2,2-dimethyl-cyclobutyl)]-acetic acid} and **4b** {*cis*-[(1*S*,3*R*)-(3-acetyl-2,2-dimethyl-cyclobutyl)]-acetic acid}, respectively. The time course of **1a** reaction (Fig. 1) shows that the first step is the oxidation of the secondary hydroxyl group, leading to (1*S*,2*S*,5*S*)-2-hydroxy-3-pinanone {(1*S*,2*S*,5*S*)-2-hydroxy-2,6,6-trimethyl-bicyclo-[3.1.1]heptan-3-one} **2a**. Oxidative cleavage of the C−C bond leads to (1*R*,3*S*)-*cis*-pinanaldehyde {*cis*-[(1*R*,3*S*)-(3-acetyl-2,2-dimethyl-cyclobutyl]-acetaldehyde} **3a** and eventually to (1*R*,3*S*)-(+)-*cis*-pinonic acid **4a** (Scheme 1). Similar results were obtained with (1R,2*R*,-3*S*,5*R*)-(−)-pinanediol **1b** that was converted into (1*R*,2*R*,5*R*)-2-hydroxy-3-pinanone **2b**, (1*S*,3*R*)-*cis*-pinanaldehydethe **3b** and (1*S*,3*R*)-*cis*-(−)-pinonic acid **4b**, enantiomer of **4a**.

Table 1 collects the results obtained with in reactions carried out under 1 atm of pure dioxygen or of dry air. It is apparent that in both cases the reaction reaches completion within 6 to 9 hours and leads to satisfactory yields of only one enantiomer of *cis*-pinonic acid.

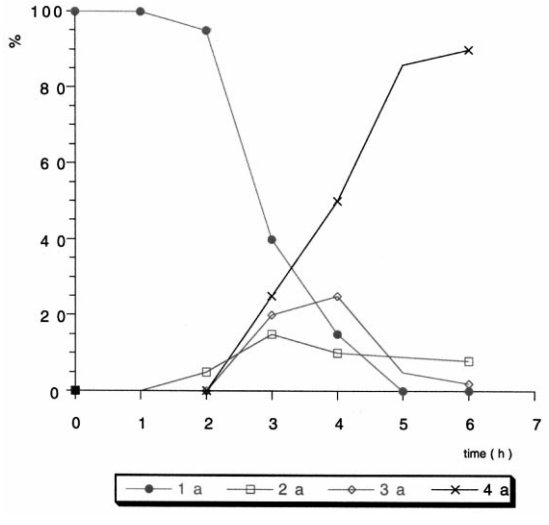
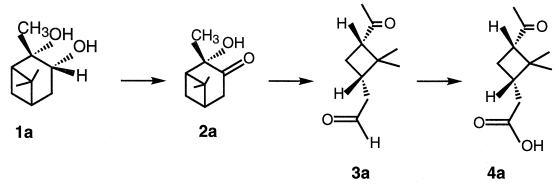


Fig. 1. Time course of **1a** oxidation (2.0 mmol) in the presence of $Co(acac)_2$(0.08 mmol), 2-methylpropanal (6.0 mmol total) in 1,2-dichloroethane (15 ml).



Scheme 1.

1. Synthesis of *cis*-pinonic acids

A Schlenk tube wrapped with aluminium foil was charged with the substrate (2.0 mmol), $Co(acac)_2$ (0.08 mmol), 2-methylpropanal (2.0 mmol) in 1,2-dichloroethane (DCE, 15 ml) and stirred under dioxygen or air at room temperature. The reactions were monitored via GCMS and GLC analysis. After 2 and 4 h two subsequent additions of 2.0 mmol aldehyde were performed. When GLC analyses showed the consumption of the substrate (6–9 h) the reaction was stopped and the products purified by silica gel column chromatography (Merck, Silica Gel 230–400 mesh) using petroleum ether 40–60°C: diethyl ether 3:2 as eluant). Obtained: 296 ÷ 316 mg of *cis*-pinonic acids. Physical and spectroscopic features of (+)-*cis*-pinonic acid are as follows:

m.p. = 65–66°C; $[\alpha]_D = +84.2°$ ($c = 0.94$ in $CHCl_3$);

Table 1
Catalytic oxidation of pinanediols: 2.0 mmol substrate, 0.08 mmol $Co(acac)_2$, 6.0 mmol 2-methylpropanal, 15 ml 1,2-dichloroethane, 1 atm O_2 or dry air

Entry	Substrate	Oxidant	Time (h)	Products yield (%)
1	**1a**	O_2	6	**2a** (8); **3a** (2); **4a** (88)
2	**1b**	O_2	6	**2b** (7); **3b** (3); **4b** (87)
3	**1a**	air	9	**2a** (5); **3a** (2); **4a** (91)
4	**1b**	air	9	**2b** (3); **3b** (2); **4b** (93)

MS (70 eV): m/e (relative intensity): 250 (M^+, 26), 235 (68), 209 (94), 185 (58), 127 (17), 123 (100), 73 (8), 67 (8), 59 (16), 53 (10), 43 (17).

^{1}H NMR ($CDCl_3$ ppm); $\delta = 0.84$ (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 2.02 (s, 3 H, CH_3), 2.85 (dd, 1H, J = 7.6, 10.1 Hz), 2.23–2.36 (m, 3 H), 1.88–2.03 (m, 2 H);

$^{13}C\{^1H\}$ NMR ($CDCl_3$, ppm): 17.77, 17.79, 22.95, 30.15, 34.80, 37.67, 43.25, 54.17, 178.45, 207.60;

IR (KBr): 3300–2800 (OH), 1702, 1718 (C═O), 1460, 1418, 1366, 1331, 1282, 1252, 1230, 1185, 1021, 955, 805, 623, 582 cm^{-1}.

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