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Heterogeneous platinum catalytic aerobic oxidation of cyclopentane-1,2-diols to cyclopentane-1,2-diones

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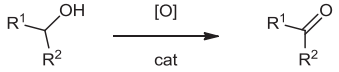
ABSTRACT

A method for the aerobic oxidation of cyclopentane-1,2-diols to the corresponding diketones over a commercial heterogeneous Pt/C catalyst is described. Unsubstituted and 3- or 4-substituted cyclopentane-1,2-diols are oxidized to 1,2-dicarbonyl compounds in good yields under the reported optimized reaction conditions (atmospheric air, 1 mol % of catalyst, 1 equiv of LiOH, aqueous solvents and 60 °C temperature). The method is applicable for producing cyclopentane-1,2-diketones in a scalable manner.

1. Introduction

Oxidative catalytic dehydrogenation is a common way of selectively converting alcohols to their carbonyl derivatives (Scheme 1). Catalytic oxidation, especially the catalytic aerobic oxidation, is preferred over the traditional stoichiometric oxidation processes, since it does not produce hazardous byproducts.[1] Starting from the 1970s, when the first reports on the metal-catalyzed aerobic oxidations appeared,[2] steady progress has occurred in this field.[3] Several catalyst systems, such as homogeneous metal complexes dissolved in water,[4,5] ionic liquids[6] or organic solvents[7] and heterogeneous systems where the catalytic metal particles are embedded on various supports, have been developed.[8] Known catalyst supports include, for example, polymers,[9–12] silica,[13] TiO_2,[14] Al_2O_3,[15] hydrotalcite,[16] hydroxyapatite,[17] metal–organic-frameworks[18] and carbonaceous materials,[19–22] which are used in organic solvents,[13,14,18,20,21] water[9–12,16,20,22,23] or super-critical CO_2.[19] Examples of metals used as the catalytically active species include, but is not limited to, platinum,[9,19,20] palladium,[12,13,15,18,19,22] ruthenium,[21,24] gold[14,23] and various bimetallic systems.[10,11,16]



Scheme 1. Oxidative catalytic dehydrogenation of alcohols.

While most of the known methods can be applied for the conversion of allylic or benzylic alcohols, only a few can be used for the oxidation of non-activated aliphatic alcohols.[8,18,21,22] Furthermore, there are even fewer aerobic oxidation methods suitable for the oxidation of *vic*-diols to their corresponding diketones[25,26] because of the easy cleavage of the carbon–carbon bond between the vicinal hydroxyl groups under oxidative conditions.[27–30] In our preliminary report, we described the first experiments on the aerobic Pt-catalyzed oxidation of cyclopentane-1,2-diols to their corresponding cyclopentane-1,2-diones (isolated as their monoenol tautomers).[31] In the present report we summarize the results of our study on the oxidation method, concerning optimization of reaction conditions and broadening the selection of reaction substrates.

2. Results and discussion

In testing different activated carbon supported platinum group metal catalysts, we found that *cis*-1,2-diols **1** (Scheme 2) can be converted to 1,2-diones **3**, and isolated in their thermodynamically

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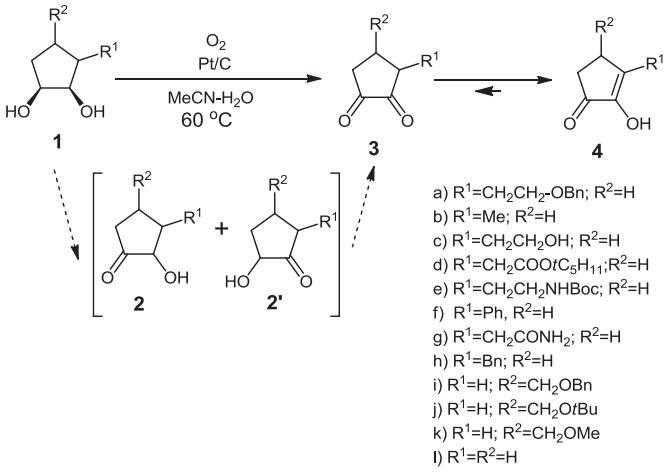


Scheme 2. Aerobic catalytic oxidation of 1,2-cyclopentanediols over Pt/C catalyst.

Table 1
Aerobic catalytic oxidation of 1,2-cyclopentanediol **1a** to **4a** over Pt/C catalyst

Entry	Alkali equiv	Time h	Product yield, %
1[31]	0	20	66
2	0.2	4	61
3	0.4	4	67
4	0.6	4	69
5	0.8	4	70
6	1	4	70
7[a]	1	4	68
8[b]	1	5.5	63
9[b,c]	1	4	59
10[b]	0.5	5.5	39

All experiments were run in 1:1 MeCN/H_2O at 60 °C with 5 mol % Pt/C catalyst loading in an open glass reactor equipped with a condenser; 1 equiv of LiOH/H_2O.
[a] Regenerated catalyst.[31]
[b] Pt/C (1 mol %) catalyst.
[c] CsOH (1 equiv).

preferred monoenol form **4**, by an aerobic oxidation reaction over a commercially available Pt/C catalyst.[32] The presence of water in the catalyst and/or in the reaction medium is essential for the reaction to occur. Out of several commercial Pt/C catalysts tested, only those two that contained around 50% (w/w) of water were active. A similar wet Pd/C catalyst showed only low catalytic activity, which may have been due to the lower oxidizing ability of Pd compared to that of Pt.[9]

When the active catalyst was dried before use and the reaction was run in dry toluene, a complete loss of activity was observed, demonstrating the significant role of water in the reaction. It has been suggested that water may serve as a weak base, assisting the abstraction of the alcohol proton and thus helping the alcohol to absorb on the metal surface.[33]

It was found that the main consideration in selecting the solvent for the oxidation is the solubility of the substrate: a variety of solvents, such as toluene, H_2O or a mixture of MeCN and H_2O can be used. When running the reaction in toluene, small amounts of hydroxyketones **2** and **2′** were also detected among the reaction products,[31] indicating that the hydroxyl groups are oxidized in two steps via formation of the intermediate hydroxyketone.

The yield of ketoenol **4** depended on the amount of air available. The activated carbon supported catalyst initially contains some oxygen and dissolved oxygen is usually present in solvents. We have previously observed that this amount of oxygen is not sufficient for the optimal conversion of **1** to **4**.[31] At the same time, we have observed that an unrestricted access of atmospheric air may hinder the oxidation of diols, probably due to the excessive oxidation of the Pt surface, which will deactivate the catalyst.[33,34]

The beneficial effect of adding inorganic bases as additives to the oxidation system has been described by Bäckvall for the heterogeneous catalytic dehydrogenations[35] and Mueller and Sigman for the aerobic oxidations.[36] Following these suggestions, we investigated the influence of alkali on the oxidation of 1,2-diol **1a** (Scheme 2, Table 1). We found that the addition of an inorganic base significantly influences the process by increasing the reaction rate and catalyst turnover, allowing us to reduce the reaction time and the catalyst loading. In the presence of a base the process was also less sensitive to higher oxygen concentration, which made it possible to use a simple open top vertical condenser on the reaction vessel and obtain stable yields. The sensitivity drop towards oxygen concentration was similar to that discussed by Steinhoff and Stahl for the aerobic homogeneous Pd catalysis.[37] Our observations are in good accordance with earlier findings on the role of the base in the dehydrogenation process[38] where base facilitates the β-hydrogen elimination step during the reaction.[39] By adding 1 equiv of LiOH, we achieved a stable process in acetonitrile/water with unrestricted access of atmospheric air to the reaction medium.

When the substrate was oxidized in a 1:1 mixture of acetonitrile/water in the presence of different amounts of LiOH and 5 mol % Pt/C loading (Table 1, entries 1–6), it was found that the optimal amount of alkali was around 1 M equiv to the substrate. In the presence of base, no formation of hydroxyketone **2** was detected. Presence of alkali considerably enhanced the reaction rate: without alkali we obtained 66% of product **4a** in 20 h, while adding 1 equiv of LiOH provided 70% of product **4a** in 4 h (Table 1, entries 1 and 6). Prolonging the reaction time further had no beneficial effect on the conversion of the remaining **1a** but caused a gradual degradation of the product **4a**.

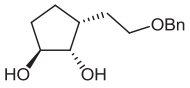
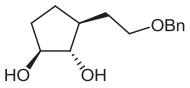
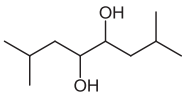
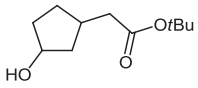
When the Pt/C catalyst was filtered from the reaction mixture and reused for the oxidation of diol **1a** under the conditions described above, only a minor decrease of the yield was observed and the product **4a** was isolated in 68% yield (Table 1, entry 7). Thus the catalyst could be reused at least once without a noticeable decrease in the catalyst activity.

Reducing the catalyst loading to 1 mol % slightly decreased the yield when compared to 5 mol % loading (Table 1, entries 6 vs 8). At the same time the TON value increased from 14 to 63, making the lower catalyst loading highly feasible. The same tendency was observed for all substrates, with the highest observed TON being approximately 72 in the case of substrate **1e** (Table 2, entries 4 and 5). The reduction of catalyst loadings below 1 mol % resulted in an excessive decrease in the yield. In all investigated cases the unreacted starting material could be easily separated and recovered when deemed necessary.

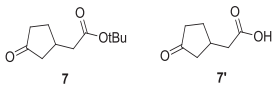
The product yield with 1 mol % of Pt/C catalyst depended similarly on the amount of LiOH, as with 5 mol % of catalyst. However, with lower catalyst loadings the yield was more sensitive to the alkali amount (Table 1, entries 3 and 10). Replacing LiOH with CsOH resulted in a small reduction in the product yield (to 59%), accompanied by a complete loss of starting material (Table 1, entry 9). We suggest that CsOH does considerably influence the reaction, but the product **4a** decomposes with CsOH under reaction conditions. The optimal reaction temperature was around 60–70 °C: below 60 °C the reaction became significantly slower and above 70 °C the product started to decompose, resulting in reduced yields.

The substrate scope of the reaction was studied by oxidizing cyclopentane-1,2-diols with different structures (Table 2). In most cases, 1,2-diones **4** formed in good yield (around 70%). In the case of hydroxyalkyl substituent **1c** with an unprotected OH group, a modest yield of compound **4c** was observed (49%, Table 2, entry 2). However, it is noteworthy that only the secondary OH groups in the cyclopentane moiety in the substrate **1c** were oxidized, leaving the primary hydroxyl group in the hydroxyethyl side chain intact.

Table 2
Aerobic oxidation of alcohols to carbonyl compounds over Pt/C catalyst

Entry	Substrate	Time h	Product yield, %
1[a]	**1b**	5	74
2[a]	**1c**	5	49
3[a]	**1d**	1.3	28
4[a]	**1e**	4	76
5[b]	**1e**	4	72
6[31]	**1f**	3.5	69
7[a,b]	**1g**	3	0
8[b]	**1h**	5	65
9[b]	**1i**	5	63
10[b]	**1j**	5	61
11[b]	**1k**	5	62
12[b]	**1l**	4	19
13[b]	**1m** 	4	38
14[b]	**1n** 	4	36
15[b]	**5** 	4	0
16[b]	**6** 	3.5	28 (+33[c])

All experiments were run in 1:1 MeCN/H_2O at 60 °C with Pt/C and 1 equiv of LiOH·H_2O in an open glass reactor equipped with a vertical condenser.
Catalyst loadings:
[a] Pt/C (5 mol %) catalyst.
[b] Pt/C (1 mol %) catalyst.
[c] Yield of corresponding carboxylic acid **7′**.


7 7′

The oxidation of *tert*-amylcarbonyloxydiol **1d** proceeded quickly during 1 h, until a yield of **4d** reached 28% after which no further conversion occurred (Table 2, entry 3). Boc-aminoalkyl substrate **1e** resulted in the best isolated yield of dione **4** (76%, Table 2, entry 4). At the same time the carbamoyl group bearing diol **1g** did not oxidize and the expected dione **4g** was not detected (Table 2, entry 7).

The oxidation tolerates different substitutions in the cyclopentane ring. Both, 3- and 4-substituted diols were successfully oxidized with good yields (Tables 1 and 2). Oxidation of 4-substituted diols **1j** and **1k** afforded the corresponding diketones **4j** and **4k**. The latter two readily formed single crystals suitable for X-ray diffraction studies (Fig. 1). The low yield in the case of unsubstituted cyclopentane-1,2-dione **4l** was probably due to the loss of the volatile product during the standard work-up and purification steps.

The spatial arrangement of the substituents in the cyclopentane ring influenced the reactivity of the substrate. We observed that *trans*-diol afforded a lower yield than the *cis*-diol (Table 1, entry 8 vs Table 2, entries 13 and 14). At the same time, no noticeable difference was observed when the alkyl substituent was either cis or trans with the α-hydroxyl group (Table 2, entries 13 and 14).

A non-cyclic *vic*-diol **5** was completely consumed after 4 h, but did not afford any of the expected dicarbonyl compound. Instead, formation of a complex mixture of different carbonyl compounds was observed (Table 2, entry 15). When the cyclic secondary alcohol **6** was subjected to oxidation, 3-oxo-cyclopentyl acetic acid *t*-Bu ester **7** in 28% yield together with the corresponding carbocyclic acid **7′** in 33% yield were obtained (Table 2, entry 16). The total yield of the dehydration reaction was 61%. This hints that the described oxidation procedure can also be applied to cyclopentanols in order to get cyclic ketones.

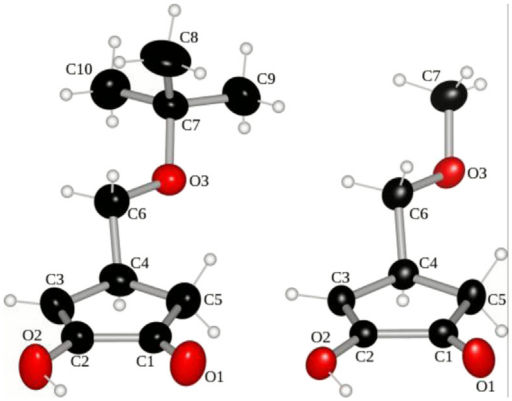


Fig. 1. Molecular moieties in the crystal structures of the racemic enols **4j** (left) and **4k** (right). Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

We also checked the possibility to scale up the reaction volume from 100-mg scale to gram scale. When larger reaction volumes were simply run in larger reaction vessels with unrestricted air access, the obtained reaction yield remained low and most of the starting material was left unreacted (Table 3, entry 1), most probably due to insufficient oxygen transfer from the surrounding atmosphere into the reaction mixture. Indeed, bubbling a constant air flow of 0.2–0.3 mL/min into the reaction mixture in the reactor was sufficient to successfully oxidize 1,2-diols to 1,2-diones with a reasonable yield (Table 3; to avoid loss of the reaction medium the air flow was saturated with reaction solvent vapours by passing through an identical solvent mixture in a separate flask prior to entering the reactor). Unreacted material was separated and recovered in all cases. Thus, although quantitative turnover was not achieved, overall loss in material was small.

Table 3
Scaled up oxidation of diols **1** to diketones **4**

Entry	Substrate	Time h	Product yield, %	Regenerated **1** %
1[a]	**1i**	5	34	62
2	**1i**	6	64	28
3	**1j**	6	51	46
4	**1e**	4	66	26
5	**1k**	6	53	40

All experiments were run in 1:1 MeCN/H_2O at 60 °C with 1 mol % Pt/C catalyst in an open glass reactor equipped with a condenser. A 0.3 mL/min flow of atmospheric air saturated with solvent mixture was maintained through the reactor during the reaction.
[a] Without additional air flow.

3. Conclusion

In summary a practical method for the catalytic aerobic oxidation for cyclopentane-1,2-diols to cyclopentane-1,2-diones was developed. The reaction was run under relatively mild conditions (60 °C in MeCN/H_2O) in the presence of 1 mol % of a heterogeneous Pt/C catalyst and 1 equiv of LiOH. The method tolerates a wide choice of solvent systems, ranging from organic solvents to aqueous mixtures to water. Under the described reaction conditions, only secondary hydroxyl groups of cyclopentane rings were selectively oxidized. A number of different functional groups on the cyclopentane ring tolerated well the oxidation conditions. The reaction method could also be scaled up for preparative use.

4. Experimental section

4.1. General remarks

All reagents purchased from common suppliers were used without further purification. All solvents were distilled according to common procedures prior to use. Silica gel 40–100 μm was used for column chromatography. All NMR spectra were measured at room temperature on a Bruker Avance III 400 MHz instrument. MS (EI) spectra were obtained on a Shimadzu GCMS-QP2010 spectrometer, FT-IR spectra were recorded on a Perkin–Elmer Spectrum BX spectrometer, HRMS (APCI-MS) measurements were performed on an Agilent Technologies 6450 UHD Accurate-Mass Q-TOF LC/MS instrument. Single crystal X-ray diffraction data were collected on a Bruker SMART X2S. The Supplementary data contains additional synthetic procedures for the preparation of oxidation substrates, NMR spectra and the crystallographic data for this paper (compounds **4j** and **4k**, deposited with the Cambridge Crystallographic Data Centre (CCDC 833165 (**4j**) and 833166 (**4k**))).

4.2. Preparation of oxidation substrates

Diols **1b** and **1l** were purchased from Aldrich. The preparation of diols **1a** and **1c**–**g** was described earlier.[31,40] Diols **1h**–**k** were prepared from their preceding cyclopentenes by the general dihydroxylation procedure described below. The preparation of the above mentioned cyclopentenes is described in the Supplementary data. The preparation of diols **1m**, **1n**, **5** and alcohol **6** is described in the Supplementary data.

*4.2.1. General procedure for the dihydroxylation of cyclopentenes used for the preparation of diols **1h**–**k**.* Corresponding cyclopentene (4 mmol) was dissolved in 13 mL of 3:1 mixture of *t*-BuOH and water. 1.1 mL of 50% w/w aqueous NMO solution (5.2 mmol) and 13.5 mg of 7.5% solid supported OsO_4 catalyst (0.004 mmol) were added. The mixture was stirred at 60 °C until no more of the corresponding cyclopentene was observed in the reaction mixture. The catalyst was filtered off, 20 mL of EtOAc was added and the mixture was washed with 10 mL of 10% $Na_2S_2O_3$. The aqueous phase was separated and extracted with EtOAc. All organics were combined and dried over $MgSO_4$, the solvent was evaporated and the product was purified by column chromatography over silica gel.

*4.2.2. Characterization of the prepared diols **1***

*4.2.2.1. 3-Benzylcyclopentane-cis-1,2-diol **1h**.* Compound **1h** was obtained by the general dihydroxylation procedure over 3 days (711 mg, 93%) as a 1:0.6 mixture of diastereomers (white crystals, mp 46–47 °C). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.31–7.16 (m, 5H, Ph), 4.07 (dd, *J*=8.8, 5.3 Hz, 1H, H1), 3.64 (t, *J*=5.6 Hz, 1H, H2), 2.88 (dd, *J*=13.5, 6.3 Hz, 1H, Bn), 2.59 (dd, *J*=13.5, 8.5 Hz, 1H, Bn), 2.42 (broad s, 1H, O*H*1), 2.25–2.16 (m, 2H, H3, O*H*2), 2.01–1.82 (m, 2H, H4, H5), 1.68–1.57 (m, 1H, H5), 1.25–1.14 (m, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.8 (Ph), 129.0 (Ph), 128.6 (Ph), 126.2 (Ph), 78.9 (C2), 73.0 (C1), 45.5 (C3), 39.8 (Bn), 30.4 (C5), 26.5 (C4). Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.31–7.16 (m, 5H, Ph), 4.16–4.10 (m, 1H, H1), 3.83 (t, *J*=4.0 Hz, 1H, H2), 2.92 (dd, *J*=13.5, 7.9 Hz, 1H, Bn), 2.66 (dd, *J*=13.6, 7.6 Hz, 1H, Bn), 2.42 (broad s, 1H, O*H*2), 2.34 (broad s, 1H, O*H*1), 2.14–2.02 (m, 1H, H3), 2.01–1.82 (m, 1H, H5), 1.68–1.57 (m, 3H, H4, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.6 (Ph), 128.9 (Ph), 128.5 (Ph), 125.9 (Ph), 74.7 (C1), 74.3 (C2), 44.3 (C3), 36.0 (Bn), 30.9 (C5), 27.3 (C4). IR: 3409, 2924, 1604, 1495, 1453, 1341, 1100, 1038, 752, 701 cm^{-1}; MS (EI): *m*/*z*=192, 174, 156, 145, 130, 117, 91, 83. Anal. Calcd for $C_7H_{14}O_3$: C, 74.97; H, 8.39. Found: C, 74.95; H, 8.44.

*4.2.2.2. 4-(Benzyloxymethyl)cyclopentane-cis-1,2-diol **1i**.* Compound **1i** was prepared by the general dihydroxylation procedure over 2 days (868 mg, 98%) as a 1:2.8 mixture of diastereomers. The preceding cyclopentene was prepared from 3-cyclopentene carboxylic acid according to a known procedure.[41] Compound **1i** was obtained as a white crystalline material with spectral and physical properties matching literature values.[42]

*4.2.2.3. 4-(tert-Butoxymethyl)cyclopentane-cis-1,2-diol **1j**.* Compound **1j** was obtained by the general dihydroxylation procedure over 3 days (467 mg, 62%) as a colourless oil (1:2.5 mixture of diastereomers). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.08–4.04 (m, 2H, H1, H2), 3.91 (broad s, 2H, 2×OH), 3.17 (d, *J*=6.3 Hz, 2H, –C*H*$_2$O–), 2.48–2.37 (m, 1H, H4), 1.89–1.79 and 1.62–1.56 (m, 2×2H; H3, H5), 1.16 (s, 9H, *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$): δ=73.7 (C1, C2), 72.2 (–*C*(CH$_3$)$_3$), 65.8 (–COH–), 34.7 (C4), 34.4 (C3, C5), 27.4 (*t*-Bu). Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.91 (broad s, 4H, 2×OH, H1, H2), 3.31 (d, *J*=3.4 Hz, 2H, –C*H*$_2$O–), 2.31–2.23 (m, 1H, H4), 2.07–2.00 and 1.53–1.47 (m, 2×2H, H3, H5), 1.21 (s, 3.6H, *t*-Bu′). ^{13}C NMR (100 MHz, $CDCl_3$): δ=74.0 (C1, C2), 73.5 (–*C*(CH$_3$)$_3$), 64.3 (–COH–), 33.9 (C4), 33.5 (C3, C4), 27.3 (*t*-Bu). IR: 3405, 2973, 1391, 1363, 1200, 1083, 1021 cm^{-1}; MS (EI): *m*/*z*=188, 173, 155, 131, 113, 102, 97, 83, 69, 57. APCI-MS: *m*/*z* observed 192.1145, calcd for $C_7H_{14}O_3$ 192.1150.

*4.2.2.4. 4-(Methoxymethyl)cyclopentane-cis-1,2-diol **1k**.* Compound **1k** was obtained by the general dihydroxylation procedure over 2 days (325 mg, 56%) as a colourless oil (1:0.4 mixture of diastereomers). Major diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.09 (t, *J*=4.8 Hz, 2H, H1, H2), 3.33 (s, 3H, OMe), 3.23 (d, *J*=6.5 Hz, 2H, –C*H*$_2$OMe), 2.54 (tt, *J*=9.2, 6.5 Hz, 1H; H4), 1.88–1.81 (m, 2H, H3, H5), 1.64–1.57 (m, 2H, H3, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=77.3 (–CH$_2$OMe), 73.9 (C1, C2), 58.8 (OMe), 34.6 (C3, C5), 34.5 (C4). Minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ=3.92 (q, *J*=5.5 Hz, 2H, H1, H2), 3.40 (s, 3H, OMe), 3.34 (d, *J*=4.0 Hz, 2H, –C*H*$_2$OMe), 2.30–2.20 (m, 1H, H4), 2.10–2.02 (m, 2H, H4, H5), 1.51 (dt, *J*=13.9, 5.5 Hz, 2H, H4, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=76.4 (–CH$_2$OMe), 74.1 (C1, C2), 59.1 (OMe), 34.2 (C5), 34.0 (C3, C4). IR: 3396, 2930, 1442, 1388, 1338, 1115, 927 cm^{-1}; MS (EI): *m*/*z*=146, 128, 114, 101, 96, 83, 69, 55, 45. APCI-MS: *m*/*z* observed 146.0942, calcd for $C_7H_{14}O_3$ 146.0943.

*4.2.2.5. (1S,2S,3R)-3-(2-(Benzyloxy)ethyl)cyclopentane-trans-1,2-diol **1m**.* Compound **1m** was obtained as white crystals (186 mg, 20%), mp 34–35 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.33–7.25 (m, 5H, Ph), 4.50 (s, 2H, Bn), 4.05 (tt, *J*=4.3, 2.3 Hz, 1H, H1), 3.89 (dd, *J*=5.3, 2.3 Hz, 1H, H2), 3.61–3.56 (m, 1H, CH$_2$C*H*$_2$OBn), 3.49–3.42 (m, 1H, CH$_2$C*H*$_2$OBn), 2.18–2.03 (m, 2H, H3, H5), 1.88–1.77 (m, 2H, H4, C*H*$_2$CH$_2$OBn), 1.69–1.61 (m, 1H, C*H*$_2$CH$_2$OBn), 1.48–1.33 (m, 2H, H4, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.9 (Ph), 128.5 (Ph), 127.8 (Ph), 127.8 (Ph), 79.7 (C2), 79.0 (C1), 73.4 (Bn), 70.1 (–*C*H$_2$CH$_2$OBn), 41.0 (C3), 31.7 (C5), 29.4 (–*C*H$_2$*C*H$_2$OBn), 28.3 (C4); (assignment of diastereomers based on γ-*syn* effect between C2–OH and –CH$_2$CH$_2$OBn groups when comparing ^{13}C chemical shifts of compounds **1m** and **1n**). IR: 3375, 2937, 1454, 1364, 1095, 956, 738, 698 cm^{-1}; MS (EI): *m*/*z*=236, 218, 200, 174, 156, 145, 127, 107, 91. APCI-MS: *m*/*z* observed 236.1412, calcd for $C_{14}H_{20}O_3$ 236.1412.

*4.2.2.6. (1S,2S,3S)-3-(2-(Benzyloxy)ethyl)cyclopentane-trans-1,2-diol **1n**.* Compound **1n** was obtained as a colourless oil (77 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36–7.25 (m, 5H, Ph), 4.50 (s, 2H, Bn), 3.95 (q, *J*=7.3 Hz, 1H, H1), 3.60–3.55 and 3.53–3.49 (m, 2H, –CH$_2$C*H*$_2$OBn), 3.48–3.43 (m, 1H, H2), 1.98–1.89 (m, 1H, H5), 1.87–1.68 (m, 3H, H3, H4, –C*H*$_2$CH$_2$OBn), 1.64–1.57 (m, 1H,

–CH_2CH_2OBn), 1.55–1.46 (m, 1H, H5), 1.40–1.32 (m, 1H, H4). ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.7 (Ph), 128.5 (Ph), 127.8 (Ph), 127.8 (Ph), 84.3 (C2), 78.1 (C1), 73.1 (Bn), 70.0 (–CH_2CH_2OBn), 42.6 (C3), 34.4 (C5), 29.0 (–CH_2CH_2OBn), 26.4 (C4); (assignment of diastereomers based on γ-*syn* effect between C2–OH and –CH_2CH_2OBn groups when comparing ^{13}C chemical shifts of compounds **1m** and **1n**). IR: 3368, 2869, 1454, 1363, 1099, 738, 699 cm^{-1}; MS (EI): *m*/*z*=236, 218, 200, 174, 156, 145, 127, 107, 91. APCI-MS: *m*/*z* observed 236.1415, calcd for $C_{14}H_{20}O_3$ 236.1412.

4.2.2.7. 2,7-Dimethyloctane-4,5-diol ***5***. Compound **5** was prepared from isovaleric aldehyde by pinacol coupling,[43] the compound was obtained as white needles (379 mg, 63%), mp 72–74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ=3.44 (ddd, *J*=7.7, 3.1, 1.7 Hz, 2H, H4, H5), 2.52 (broad s, 2H, 2×O*H*), 1.86–1.81 (m, 2H, H2, H7), 1.41 (ddd, *J*=14.0, 9.4, 4.6 Hz, 2H, H3, H6), 1.22 (ddd, *J*=12.5, 9.5, 3.0 Hz, 2H, H3, H6), 0.93 (dd, *J*=10.2, 6.6 Hz, 12H, 4×Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ=73.0 (C4, C5), 42.7 (C3, C6), 24.5 (C2, C7), 23.8 and 21.7 (4×Me). IR: 3347, 2957, 1469, 1367, 1058, 844, 719 cm^{-1}; MS spectra coincides with public database values.[44]

4.2.2.8. tert-Butyl-(3-hydroxycyclopentyl)acetate ***6***. Compound **6** was prepared from the corresponding carboxylic acid over two steps (110 mg, 18%). ^{1}H NMR (400 MHz, $CDCl_3$): δ=4.27–4.22 (m, 1H, *C*–OH), 2.28–2.26 (m, 2H, *C*H_2COO^{t}Bu), 2.23–2.07 (m, 2H, H1, H2), 1.80–1.66 (m, 2H, H4, H5), 1.64–1.56 (m, 1H, H4), 1.46–1.38 (m, 1H, H5), 1.37 (s, 9H, *t*-Bu), 1.23–1.14 (m, 1H, H2). ^{13}C NMR (100 MHz, $CDCl_3$): δ=171.6 (*C*OO), 79.2 (*C*$(CH_3)_3$), 72.6 (C3), 40.9 (*C*H_2COO^{t}Bu), 40.7 (C2), 34.5 (C4), 33.8 (C1), 28.9 (C5), 27.1 (*t*-Bu). MS (EI): *m*/*z*=200, 144, 127, 109, 81.

4.3. General procedure for the catalytic aerobic oxidation of diols

Diol (0.424 mmol), Pt/C catalyst (1 or 5 mol % metal loading compared to diol),[32] LiOH·H_2O (1.0 equiv, 0.424 mmol) and solvent (2 mL, MeCN/H_2O 1:1) were added to a 10 mL glass reactor, equipped with a condenser and stirred at 60 °C for the appropriate time. The reaction progress was monitored by TLC. When the product formation had stopped, the catalyst was filtered off and rinsed with EtOAc (3×3 mL), resulting in a biphasic solution. The aqueous phase was acidified to pH 5 with 1 M HCl and the layers were separated. The aqueous layer was extracted twice with EtOAc (20 mL). All organics were combined and dried over $MgSO_4$ and were concentrated in a vacuum. The crude product was purified by column chromatography (EtOAc/petroleum ether or MeOH/CH_2Cl_2) to give the product diketone as its ketoenol tautomer **4**.

4.4. General procedure for larger scale catalytic aerobic oxidation of diols

Diol (9 mmol) was dissolved in 45 mL of solvent (MeCN/H_2O 1:1) and the Pt/C catalyst catalyst[32] was added (1 mol % metal loading based on diol), followed by 1 equiv of LiOH·H_2O (9 mmol). A 0.3 mL/min flow of solvent-saturated air was bubbled through the reaction mixture and the reaction was stirred at 60 °C for 6 h. The catalyst was filtered from the reaction mixture, rinsed three times with 10 mL of EtOAc and the biphasic solution was adjusted to pH 5 with 1.0 M HCl. The phases were separated and the aqueous phase was extracted twice with 20 mL of EtOAc. All organics were combined and dried over $MgSO_4$, the solvent was evaporated and the product and the regenerated starting material were purified by column chromatography (MeOH/CH_2Cl_2).

4.5. Characterization of oxidation products

4.5.1. 2-Hydroxy-3-(2-benzyloxyethyl)-2-cyclopenten-1-one ***4a***. The compound (68 mg, 70%) spectral properties coincided with a literature example.[40]

4.5.2. 2-Hydroxy-3-methyl-2-cyclopenten-1-one ***4b***. The compound (35 mg, 74%) was identical to a commercial sample.

4.5.3. 2-Hydroxy-3-(2-hydroxyethyl)-2-cyclopenten-1-one ***4c***. The compound (29 mg, 49%) spectral properties coincided with a literature example.[45]

4.5.4. 2-Hydroxy-3-oxo-1-cyclopentene-1-acetic acid-1,1-dimethylpropyl ester ***4d***. The compound (27 mg, 28%) spectral properties coincided with a literature example.[45]

4.5.5. N-[2-(2,3-Dioxocyclopentyl)ethyl]-carbamic acid-1,1-dimethylethyl ester ***4e***. The compound (78 mg, 76%) spectral properties coincided with a literature example.[31]

4.5.6. 2-Hydroxy-3-phenyl-2-cyclopenten-1-one ***4f***. The compound (51 mg, 69%) spectral properties coincided with an authentic sample.[46]

4.5.7. 2-Hydroxy-3-(benzyl)-2-cyclopenten-1-one ***4h***. The compound (52 mg, 65%) spectral properties coincided with an authentic example.[47]

4.5.8. 4-[(Benzyloxy)methyl]-2-hydroxycyclopent-2-en-1-one ***4i***. The compound was obtained, following the general procedures described above, as a colourless oil (58 mg, 63%): ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.38–7.26 (m, 5H, Ph), 6.53 (d, *J*=3.0 Hz, 1H, H3), 5.73 (broad s, 1H, –O*H*), 4.53 (s, 2H, Bn), 3.50–3.40 (m, 2H, –CH_2O–), 3.12–3.06 (m, 1H, H4), 2.59 (dd, *J*=19.4, 6.0 Hz, 1H, H5), 2.22 (dd, *J*=19.4, 1.6 Hz, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=203.3 (C1), 153.4 (C2), 138.0 (Ph), 130.5 (C3), 128.6 (Ph), 127.9 (Ph), 127.8 (Ph), 73.4 (Bn), 73.2 (–CH_2O–), 36.5 (C5), 35.4 (C4). IR: 3343, 2860, 1686, 1654, 1455, 1395, 1198, 1100, 740, 700 cm^{-1}; MS (EI): *m*/*z*=218, 200, 188, 172, 160, 145, 134, 121, 107, 91. APCI-MS: *m*/*z* observed 218.0937, calcd for $C_{13}H_{14}O_3$ 218.0943.

4.5.9. 4-(tert-Butoxymethyl)-2-hydroxycyclopent-2-en-1-one ***4j***. The compound was obtained, following the general procedures described above, as colourless crystals (48 mg, 61%), mp 64–66 °C: ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.57 (d, *J*=3.0 Hz, 1H, H3), 6.04 (broad s, 1H, –O*H*), 3.38–3.28 (m, 2H, –CH_2O–), 3.00–2.95 (m, 1H, H4), 2.58 (dd, *J*=19.4, 6.0 Hz, 1H, H5), 2.18 (dd, *J*=19.4, 1.6 Hz, 1H, H5), 1.18 (s, 9H, *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$): δ=203.8 (C1), 153.3 (C2), 131.5 (C3), 73.2 (–*C*$(CH_3)_3$), 65.2 (–CH_2O–), 36.7 (C5), 35.8 (C4), 27.6 (*t*-Bu). IR: 3334, 1707, 1644, 1395, 1375, 1193, 1077, 1058, 842 cm^{-1}; MS (EI): *m*/*z*=184, 169, 153, 128, 111, 98, 87, 80, 57. APCI-MS: *m*/*z* observed 184.1103, calcd for $C_{10}H_{16}O_3$ 184.1099.

4.5.10. 4-(Methoxymethyl)-2-hydroxycyclopent-2-en-1-one ***4k***. The compound was obtained, following the general procedures described above, as colourless crystals (37 mg, 62%), mp 46–48 °C: ^{1}H NMR (400 MHz, $CDCl_3$): δ=6.53 (d, *J*=3.0 Hz, 1H, H3), 6.46–6.21 (broad s, 1H, –O*H*), 3.41–3.33 (m, 2H, –CH_2OMe), 3.37 (s, 3H, OMe), 3.08–3.05 (m, 1H, H4), 2.59 (dd, *J*=19.4, 6.0 Hz, 1H, H5), 2.21 (dd, *J*=19.3, 1.6 Hz, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=203.5 (*C*O), 153.6 (*C*OH), 130.7 (C3), 75.8 (–CH_2OMe), 59.2 (OMe), 36.5 (C5), 35.2 (C4). IR: 3222, 2910, 1705, 1654, 1394, 1200,

1099, 957, 860 cm^{-1}; MS (EI): m/z=142, 112, 97, 83, 69, 45. APCI-MS: m/z observed 142.0629, calcd for $C_7H_{14}O_3$ 142.0630.

4.5.11. 2-Hydroxy-2-cyclopenten-1-one, ***4l****.* The compound (8 mg, 19%) spectral properties coincided with an authentic sample.[48]

4.5.12. 3-oxo-Cyclopentaneacetic acid-tert-butyl ester ***7****.* The compound was obtained, following the general procedures described above, as a yellow oil (22 mg, 28%). Compound **7** had been isolated earlier.[49] ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.57–2.45 (m, 1H, H1), 2.43–2.36 (m, 1H, H2), 2.35–2.27 (m, 2H, $-CH_2COO-$), 2.27–2.19 (m, 1H, H4), 2.19–2.07 (m, 2H, H4, H5), 1.82 (ddd, J=18.2, 10.1, 1.4 Hz, 1H, H2), 1.56–1.45 (m, 1H, H5), 1.38 (s, 9H, *t*-Bu). ^{13}C NMR (100 MHz, $CDCl_3$): δ=218.7 (C3), 171.5 ($-COO-$), 80.8 ($-C(CH_3)_3$), 44.7 (C2), 41.2 ($-CH_2COO-$), 38.4 (C4), 33.8 (C1), 29.3 (C5), 28.2 (*t*-Bu); IR: 2976, 1729, 1458, 1368, 1154, 842 cm^{-1}; MS (EI): m/z=183, 142, 125, 97, 83, 57.

4.5.13. 3-oxo-Cyclopentaneacetic acid ***7′****.* The compound was obtained, following the general procedures described above, as a yellow oil (20 mg, 33%). Compound **7′** has been isolated by others earlier.[50] ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.68–2.57 (m, 1H, H1), 2.56–2.44 (m, 3H, H2, $-CH_2-COOH$), 2.36–2.15 (m, 3H, H4, H5), 1.91 (ddd, J=18.3, 10.2, 1.4 Hz, 1H, H2), 1.67–1.54 (m, 1H, H5). ^{13}C NMR (100 MHz, $CDCl_3$): δ=218.7 (C3), 177.2 (COOH), 44.7 (C2), 39.6 ($-CH_2-COOH$), 38.5 (C4), 33.4 (C1), 29.3 (C5). IR: 3352, 3209, 2963, 1733, 1660, 1403, 1161, 757 cm^{-1}; MS (EI): m/z=142, 113, 97, 85, 83, 60, 55, 41.

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Supplementary data

Additional detailed synthesis procedures, NMR spectra and crystallographic data are available in the included Supplementary data. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.03.104.

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