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AEROBIC EPOXIDATION OF ALKENES CATALYSED BY COBALT(II) 1,1,1,5,5,5-HEXAFLUOROACETYLACETONATE OR COBALT(II) BENZOYLACETONATE

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Abstract

The aerobic epoxidation of terminal or electron deficient alkenes with an aldehyde does not proceed with cobalt(II) acetylacetonate but goes to completion with the cobalt(II) benzoylacetonate and cobalt(II) 1,1,1,5,5,5-hexafluoroacetylacetonate complexes.

Much work has been published on aerobic epoxidation of various alkenes using a range of metals, especially Co and Mo with an extensive range of ligands.¹⁻³ Many of these reports concentrate on reactive alkene substrates, which contain cyclic or electron rich double bonds (i.e. substituted alkenes). Catalytic systems that have received recent attention include the cobalt(II) AcAc 1,¹ and cobalt(II) acetate mediated aerobic epoxidations in the presence of aldehydes which act as correducing agents.⁴⁻⁶

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During our work in this area we became aware that these reactions only progress to high conversion for reactive (highly substituted or cyclic) alkenes. We now report that these epoxidations can be further extended to less reactive alkenes, such as terminal or electron deficient alkenes, by use of benzoylacetonate or 1,1,1,5,5,5-hexafluoroacetylacetonate ligands, i.e. cobalt(II) complexes, **2** and **3** respectively.



It can be seen from Table 1 that **3** effectively mediated the epoxidation of both cyclic (entry 1) and highly substituted alkenes (entry 3). Catalyst **1** had little effect in the epoxidation of vinyl alkenes (entries 7 and 10) and was only moderately successful for the vinylidene alkenes (entry 4). However, **2** and **3** both mediated epoxidations of the vinyl alkene, 1-hexene, under the same conditions (entries 8, 9, 11 and 12). Catalyst **2** was effective for the epoxidation of the vinylidene alkene, 2,4,4-trimethylpent-1-ene (entry 6) whilst epoxidation with **3** was only moderately successful (entry 5). The epoxidation of cyclohexene with **3** (entry 2) produced comparable results to the use of **1** (entry 1). Epoxidations with less reactive electron deficient alkenes, such as chalcone and 3-octen-2-one, did proceed when catalysed by **1** but gave only low to moderate yields of the epoxides (entries 13 and 16). Epoxidations of both substrates by **3** were considerably more efficient (entries 14 and 17). Whilst **2** was observed to be especially suitable for

the epoxidation of chalcone it was not successful in the epoxidation of 3-octen-2one (entries 15 and 18).

	Substrate	Aldehyde	Catalyst	Temp (°C)	Yield (%) ^a
1	Cyclohexene	2MP	1	60	96.4
2	Cyclohexene	2MP	3	60	97.1
3	2,3-Dimethylbutene	2MP	1	60	98.2
4	2,4,4-Trimethyl-1- pentene	2MP	1	60	33.0
5	2,4,4-Trimethyl-1- pentene	2MP	3	60	38.0
6	2,4,4-Trimethyl-1- pentene	2MP	2	60	67.0
7	1-Hexene	2MP	1	60	7.0
8	1-Hexene	2MP	3	60	21.0
9	1-Hexene	2MP	2	60	12.0
10	1-Hexene	Hex	1	80	10.0
11	1-Hexene	Hex	3	80	74.0
12	1-Hexene	Hex	2	80	85.0
13	Chalcone	2MP	1	60	3.5
14	Chalcone	2MP	3	60	73.6
15	Chalcone	2MP	2	60	100
16	3-Octen-2-one	2MP	1	RT	18.7
17	3-Octen-2-one	2MP	3	RT	84.1
18	3-Octen-2-one	2MP	2	RT	1.3

Table 1. Epoxidation of alkenes catalysed by Co(II) acetylacetonate derivatives

^a Determined by GC.

Next we studied the epoxidation of 4-vinyl-1-cyclohexene. Selective partial epoxidation of this material was expected to yield 4-vinyl-1-cyclohexene-1,2-epoxide 4 while total epoxidation would yield 4-vinyl-1-cyclohexene diepoxide 5. The results are shown in Table 2. Epoxidation, gave only negligible yields of 5 when the reactions were conducted at atmospheric pressure and when catalysed by either 1, 2 or 3 (entries 1-3). However, 5 could be prepared at higher pressure (10 atmospheres of compressed air) when the reaction was catalysed by 3 (entry 5) but

not with 1 (entry 4). The use of 1 under higher pressure only produced a very modest amount of 5 (entry 6). It is believed that the phenyl group in 2 and the six fluorine atoms in 3 withdraw electron density away from the diketone anion. Consequently, there is a reduction in electron density about the cobalt centre, which may aid the co-ordination of one of the reactants, making 2 and 3 more reactive catalysts than 1. At the current time it does not appear to be possible to state whether 2 or 3 is the most active catalyst. For example, 2 is a superior catalyst for the epoxidation of chalcone but 3 is more effective in epoxidizing 3-octen-2-one.

	Catalyst	Pressure/Atms [#]	Yield (%) of 4	Yield (%) of 5
1	2	1	23	1-2
2	3	1	24	1-2
3	1	1	26	1-2
4	2	10	10	0
5	3	10	80	20
6	1	10	40	5

Table 2. The epoxidation of 4-vinyl-1-cyclohexene

Experimental

All reactions were analysed by GC-MS (Perkin Elmer Turbo Mass, EI^+ at 70 eV). Proton NMR spectra were recorded at 200 MHz on a Varian Gemini NMR spectrometer (58.28 MHz for ¹³C) using a dual ¹³C/¹H probe.

The following compounds were commercially available (Aldrich): cyclohexene oxide, 1,2-epoxyhexane, 4-vinyl-1-cyclohexene diepoxide and chalcone α , β -epoxide (Lancaster). 2,3-Dimethyl-2,3-epoxybutane was synthesised using a literature procedure.⁷ The same procedure was applied in the synthesis of 1,2-epoxy-2,4,4-trimethylpentane⁸ and 3,4-epoxyoctan-2-one.⁹

1,2-Epoxy-2,4,4-trimethylpentane⁸

Bp. 139-140° (lit.⁸ 140-141°); δ_H (ppm) 1.00 (9H, s, RC(CH₃)₃), 1.28 (1H, d, J 14

Hz, H₂COC(CH₃)CHHR), 1.39 (3H, s, H₂COC(CH₃)R), 1.73 (1H, dd, *J* 14 and 1 Hz, H₂COC(CH₃)CHHR), 2.60 (2H, m, H₂COC(CH₃)R); δ_{C} (ppm) 23.3, 30.6, 30.8, 50.9, 54.6, 55.7.

3,4-Epoxyoctan-2-one⁹

Purified by flash chromatography (hexanes:dichloromethane 1:1 (v/v), R_f 0.44); $\delta_{\rm H}$ (ppm) 0.92 (3H, t, *J* 7 Hz, RCH₂CH₃), 1.32-1.64 (6H, m, R(CH₂)₃CH₃), 2.10 (3H, s, RCOCH₃), 3.10 (1H, dt, *J* 1 and 6 Hz, RCHOCHR'), 5.32 (1H, d, *J* 1 Hz, RCHOCHR'); $\delta_{\rm C}$ (ppm) 13.8, 20.8, 22.2, 27.2, 29.2, 57.3, 76.5, 170.6 (C=O); $v_{\rm max}$ (cm⁻¹) 1766 (C=O).

Reactions at atmospheric pressure

The reactions at atmospheric pressure were carried out in a flask, equipped with an efficient condenser and a gas inlet probe, immersed in a thermostatically controlled oil bath. In a typical example, 3-octen-2-one (2.24g, 17.8 mmol) was added to dichloroethane (DCE) (50 mL) along with 2 (0.10g, 0.4 mmol). 2-Methyl propanal (3.8g, 53.4 mmol) was then added. Upon addition of the aldehyde, the solution rapidly turned dark green, indicating the presence of Co(III) complex. Oxygen was then continually bubbled through the solution, at room temperature for 20 hours. Each substrate was reacted in the same manner except that the reactions containing hexaldehyde, a higher boiling point aldehyde, were (Table 1, entries 10-12) carried out at higher temperatures as denoted in Table 1.

Reactions under pressure

4-Vinyl-1-cyclohexene (0.47g, 4.4 mmol) was added to DCE (15 mL) and catalyst (1.6 mmol), either 1, 2 or 3, was then added. 2-Methylpropanal (1.5 mL, 16.56 mmol) was then added. The mixture was then placed in an autoclave, sealed and compressed added up to a pressure of 10 atmospheres. The reactions were then run for 24 hours at room temperature after which time the vessel was opened and sampled for analysis by GC-MS.

Analysis

Initially, GC-MS data of the pure authentic epoxides was obtained. The data was then used to corroborate the GC-MS data derived from sampling of the various reactions. The analytical data derived from the various pure compounds was as follows: 1,2-epoxyhexane m/z 100 (M⁺, <1%), 71, 67, 41, 39, 29, 27; 4-vinyl-1-cyclohexene diepoxide m/z 140 (M⁺, 3%), 122, 109, 95, 91, 81, 79, 77, 67; 3,4-epoxyoctan-2-one m/z 142 (M⁺, <1%), 85, 69, 57, 55, 43; chalcone α,β -epoxide m/z 224 (M⁺, <1%), 105, 77, 51; 2,3-dimethyl-2,3-epoxybutane m/z 100 (M⁺, <1%), 86, 71, 59, 58; cyclohexene oxide m/z 98 (M⁺, 4%), 97, 83, 80, 79, 77, 70, 69, 57, 55; 1,2-epoxy-2,4,4-trimethylpentane m/z 128 (M⁺, <1%), 95, 72, 69, 67, 57, 55, 43, 41, 39, 29, 27.

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