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Cobalt-Catalyzed Partial Oxidation of Olefins and Ethers Using Molecular Oxygen

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Abstract: $Co(acac)_3$ catalyzes the aerobic oxidation of vinyl aromatic compounds ArCH=CH₂ with formation of ArCO₂H and ArCHO, and also the aerobic oxidation of cyclic ethers with formation of the corresponding lactones.

One of the major current challenges in synthetic organic chemistry is the partial, i. e., selective oxidation of organic compounds using molecular oxygen in the presence of transition metal catalysts.¹ We present here some preliminary results concerning the areobic oxidation of olefins and ethers using commercially available cobalt(III)-acetylacetonate [Co(acac)₃]. Upon reacting a solution of norbornene 1 in THF saturated with O₂ at 70°C (24 h) in the presence of Co(acac)₃ (2 mol-%), quantitative conversion to the exo-epoxide 2 was observed. Under these conditions partial oxidation of THF is also observed (see below). The use of ethyl acetate as solvent results in 63% conversion to 2. Oxidation products of the solvent were not obtained. Several other transition metal complexes also catalyze the reaction in THF [TiO(acac)₂: 63%; Cr(acac)₃: 93%; Ce(acac)₃: 64%], while others such as VO(acac)₂ turned out to be ineffective. Co(acac)₂ also catalyzes this reaction, but a little less efficiently.² Recently, Co(OAc)₂ was shown to be a catalyst in the aerobic oxidation of 1 in the presence of special ligands with formation of 24 % of epoxide $2.^3$



Whereas the highly reactive norbornene 1 was smoothly epoxidized, "normal" olefins such as 1-octene did not react under the same reaction conditions. In contrast, vinyl-substituted aromatics $ArCH=CH_2$ (3) underwent oxidative C-C-cleavage of the olefinic moiety with formation of the corresponding acids 4 and aldehydes 5 (Table 1).⁴ The latter are intermediates on the way to the acids 4.

Ar	O ₂ Co(acac) ₃ (2 mol-%) THF / 70°C	Ar-CO₂H	+	ArCHO
3		4		5

Table 1. Co(acac)₃ Catalyzed Aerobic Cleavage of Olefins 3.

Ar	Reaction	4:5	Yield 4 + 5
	time (h)		(%)
(a)	24	86 : 14	99
Cl	24	86 : 14	99
H ₃ CO-(c)	36	83 : 17	92
(d)	24	68 : 32	65

Upon using ethyl acetate as the solvent in place of THF under otherwise identical conditions, oxidative cleavage also set in, but the oxidation process remained primarily at the stage of the aldehyde, e. g. $3a \rightarrow 5a$ (57% yield). Thus, this catalytic process is an interesting alternative to classical ozonolysis.⁵



Although the mechanism of the above aerobic oxidations still needs to be studied, initial mechanistic indications were obtained in the case of THF as the solvent. It is likely that in this medium THF forms a hydroperoxide which functions as the oxidant.⁶ Indeed, in the absence of olefins, THF and other ethers are transformed into lactones,⁴ e. g., 7, 10 and 13. Diethyl ether is inert under the conditions. The results are comparable to or slightly better than aerobic CoCl₂- or $[Pd(PtBu_2H)(\mu-PtBu_2)]_2$ -catalyzed oxidations of cyclic ethers reported recently by Alper.⁶





In summary, commercially available $Co(acac)_3$ catalyzes the aerobic oxidation of norbornene with smooth formation of the corresponding exo-epoxide, whereas normal olefins such as 1-octene remain inert. Vinyl-substituted aromatic compounds $ArCH=CH_2$ undergo oxidative cleavage of the C-C double bond under the same conditions with formation of $ArCO_2H$ and/or ArCHO, depending upon the solvent used. In ethyl acetate $Co(acac)_3$ catalyzes the aerobic oxidation of cyclic ethers to form lactones. These processes compete well with previous catalytic O_2 -oxidations. They are environmentally more attractive than oxidations based on stoichiometric amounts of H_2O_2 , NaIO₄, Pb(OAc)₄, RuO₄, NaClO₂ or KMnO₄, even if transition metals are added as catalysts.⁷ However, a general method for aerobic epoxidation of olefins without the use of stoichiometric amounts of a reductant such as an aldehyde remains a goal for the future.

References and Notes

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- 4. Typical procedure: A glass flask (e. g., Schlenk-type) is charged with Co(acac)₃ (14.4 mg; 0.04 mmol). It is evacuated and then filled with dry oxygen. A solvent such as ethyl acetate (2 ml) and a substrate such as 1, 3, 6, 9 or 12 (2 mmol) are added. The flask is closed with a glass-stopper, and the mixture is stirred at 70°C for 24 h (sometimes 36 h). Upon cooling to room temperature, the mixture is filtered through silica gel and the filtrate is analyzed by gas chromatography.
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