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Novel Method for Preparation of 4-Oxo-2-alkenoic Acid Derivatives from 2,4-Alkadienoic Acid Derivatives by Cobalt(II) Porphyrin-catalyzed Oxygenation

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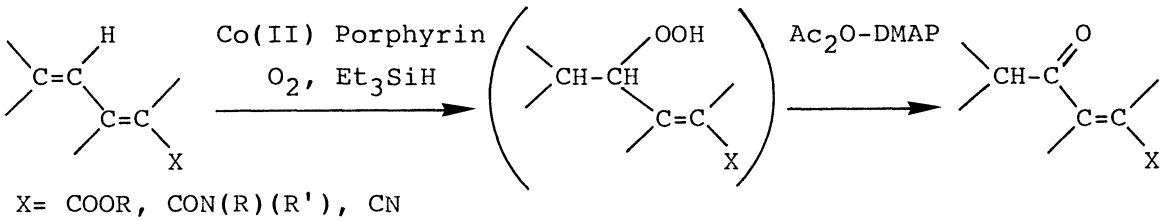
2,4-Alkadienoic acid derivatives such as ester, amide, and nitrile were converted to the corresponding 4-oxo-2-alkenoic acid derivatives in good yields by the oxygenation with oxygen and triethylsilane in the presence of a catalytic amount of [5,10,15,20-tetra(2,6-dichlorophenyl)-porphinato]cobalt(II) followed by acetylation.

The compounds having 4-oxo-2-alkenoyl moiety are common to naturally occuring macrocyclic antibiotics.[1-3] In numerous methods for the preparation of 4-oxo-2-alkenoyl compounds, allylic oxidation of 2-alkenoic esters with chromium trioxide[4] or selenium dioxide[5] is a direct and simple method. However, the substrates on these oxidations have been limited to 2-alkenoic esters. We reported recently the cobalt porphyrin-catalyzed oxidation of styrenes to the corresponding acetophenones.[6] In connection with this oxidative method, we will describe herein a regio- and chemoselective method for conversion of 2,4-alkadienoic acid derivatives such as ester, amide, and nitrile to the corresponding 4-oxo-2-alkenoic acid derivatives by means of the oxygenation with oxygen and triethylsilane in the presence of [5,10,15,20-tetra(substituted phenyl)porphinato]cobalt (II) followed by acetylation of the crude oxygenative product in order to decompose the intermediary hydroperoxide[7] (Scheme 1).

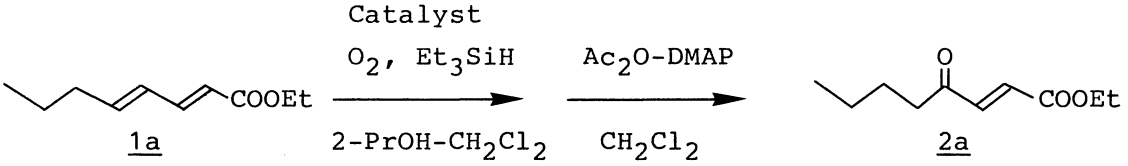


X= COOR, CON(R)(R'), CN

Scheme 1.

First, ethyl (2*E*,4*E*)-2,4-octadienoate (1a) was allowed to react with 1.1 equiv. of triethylsilane and 0.001 equiv. of cobalt(II) complex under an oxygen atmosphere, followed by acetylation with 1.5 equiv. of acetic anhydride and 0.1 equiv. of 4-(*N*,*N*-dimethylamino)pyridine (DMAP), to give ethyl (*E*)-4-oxo-2-octenoate (2a) (Table 1). As can be seen from the results on the catalyst effect of several cobalt(II) complexes, CoTDCPP is the most effective for the oxidation of 1a. The lower yield of 2a in cases of CoTPP, CoTCMPP, and CoOEP was due to the incomplete oxygenation; their reaction solutions changed from red to green during the early stage of the reaction, indicating that the oxidative degradation of porphyrin skelton occured easily. On the other hand, CoTBPc showed no catalytic activity.

Table 1. Effect of Catalyst on the Conversion of Ethyl (2*E*,4*E*)-2,4-Octadienoate (1a) to Ethyl (*E*)-4-Oxo-2-octenoate (2a)[a)]

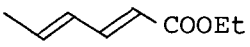
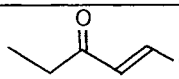
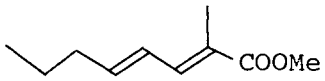
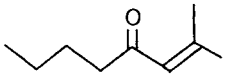
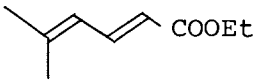
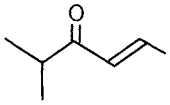
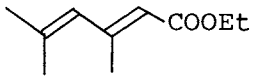
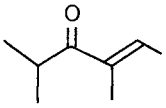
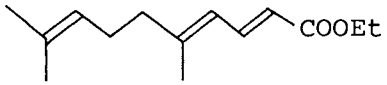
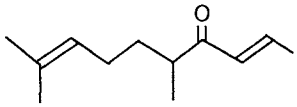
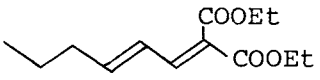
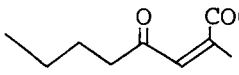
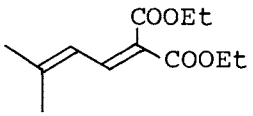
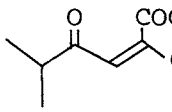
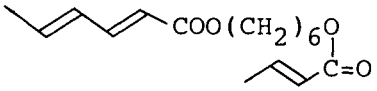
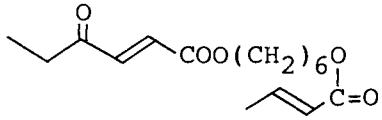
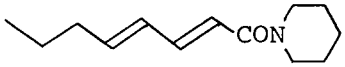
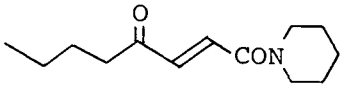
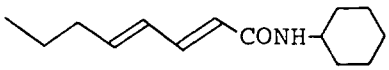
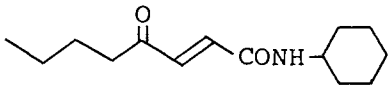
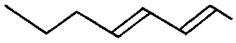
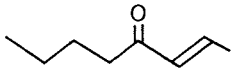


Entry	Catalyst[b)]	Yield of 2a/%[c)]
1	CoTDCPP	89
2	CoTPP	67
3	CoTCMPP	47
4	CoOEP	9
5	CoTBPc	No Reaction

a) Conditions: 1a (2.0 mmol), catalyst (0.002 mmol), Et_3SiH (2.2 mmol), 2-PrOH-CH_2Cl_2 (1/1, 10 cm^3), under O_2 atmosphere, 28°C, 5 h; acetic anhydride (3.0 mmol), DMAP (0.2 mmol), CH_2Cl_2 (10 cm^3), rt, 6 h.
b) CoTDCPP= [5,10,15,20-tetra(2,6-dichlorophenyl)porphinato]cobalt(II), CoTPP= (5,10,15,20-tetraphenylporphinato)cobalt(II), CoTCMPP= [5,10,15,20-tetra(4-carboethoxyphenyl)porphinato]cobalt(II), CoOEP= (2,3,7,8,12,13,17,18-octaethylporphinato)cobalt(II), CoTBPc= (2,9,16,23-tetra-tert-butylphthalocyaninato)cobalt(II).
c) Isolated yield.

Next, the oxidation of various 2,4-alkadienoic acid derivatives was carried out in the presence of 0.001 equiv. of CoTDCPP; the other conditions were the same as described above. The results were summarized in Table 2. Alkyl chain length, alkyl substituents at 2-, 3-, and/or 5-positions, and ethoxycarbonyl substituent at 2-position on 2,4-alkadienoic esters had little effect on the yields of the corresponding 4-oxo-

Table 2. Oxidation of Various 2,4-Alkadienoic Acid Derivatives Catalyzed by CoTDCPP[a)]

Entry	Substrate	Product	Time/h[b)]	Yield/%[c)]
1			5	82
2			5	84
3			5	70
4			5	82
5			5	76
6			2	78
7			5	81
8			2	68
9			5	78
10			2	81
11			5	89[e)]

a) Reaction was conducted under the same conditions as described in Table 1 except for CoTDCPP(0.002 mmol) using as a catalyst and reaction time. b) Reaction time for the oxygenation step. c) Isolated yield. d) The mixture of geometrical isomers was employed; *2E,4E/2Z,4E*= 3/1. e) Total yield of isomers; *E*- (67%) and *Z*-isomer (22%) as isolated.

2-alkenoates (Entries 1-7). The chemoselective oxidation of the 2,4-alkadienoyl moiety of the substrates was capable in Entries 5 and 8. The reactivity of 2,4-alkadienoyl moiety on this oxidation was much higher than that of non-conjugated alkenyl or 2-alkenoyl moiety. Furthermore, the oxidation of both 2,4-alkadienamides and 2,4-alkadienenitrile proceeded similarly to afford the corresponding 4-oxo compounds in good yields, respectively (Entries 9-11).

A typical example of the reaction is as follow. A mixture of ethyl (*2E,4E*)-2,4-octadienoate (1a) (2.0 mmol), CoTDCPP (0.002 mmol), and Et_3SiH (2.2 mmol) in 10 cm^3 of 2-PrOH-CH_2Cl_2 (1:1) was stirred at 28°C under an oxygen atmosphere for 5 h. The reaction mixture was diluted with 30 cm^3 of ether, washed with water and brine, dried over Na_2SO_4, and then the solvent was removed under reduced pressure. The crude oxygenative product was treated with acetic anhydride (3.0 mmol) and DMAP (0.2 mmol) in CH_2Cl_2 (10 cm^3) at room temperature for 6 h. The reaction mixture was diluted with 30 cm^3 of ether, washed with aqueous 10% $NaHCO_3$, and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by silica gel column chromatography using hexane and ethyl acetate (20:1) as an eluent, to yield ethyl (*E*)-4-oxo-2-octenoate (2a)(89%).

It is noted that regio- and chemoselective conversion of 2,4-alkadienoic acid derivatives to the corresponding 4-oxo-2-alkenoic acid derivatives was achieved in good yields by the CoTDCPP-catalyzed oxygenation with molecular oxygen and Et_3SiH followed by acetylation of the oxygenative product. Further extension of this oxidation is currently in progress.

References

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6) Y. Matsushita, T. Matsui, and K. Sugamoto, Chem. Lett., 1992, 1381.
7) In the reaction described in Entry 1 of Table 1, the crude oxygenative product was directly purified by silica gel chromatography to give ethyl (*E*)-4-hydroperoxy-2-octenoate (59%) along with the ketone 2a (16%).

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