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Cobalt(II) Porphyrin-Catalyzed Oxidation of Olefins to Ketones with Molecular Oxygen and Triethylsilane in 2-Propanol

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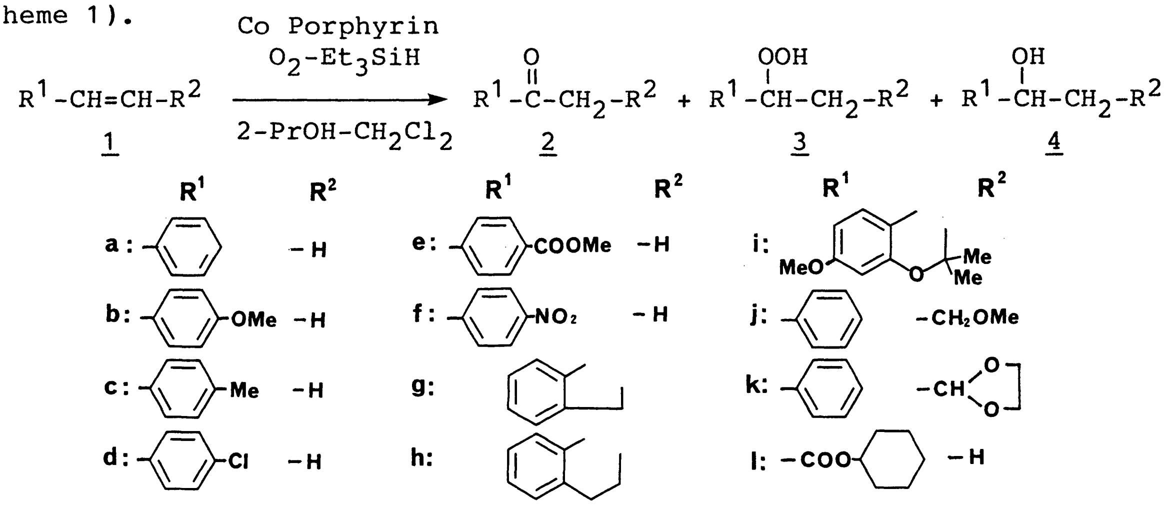
An efficient conversion of olefins to ketones was achieved by the use of molecular oxygen and triethylsilane in the presence of a catalytic amount of cobalt(II) complex of porphyrin. The oxidation was accelerated remarkably in alcohols and had chemoselectivity for conjugated olefins.

Metalloporphyrin-catalyzed oxidation of olefins is of interest from the standpoint of models for oxidases and oxygenases. Various chemical oxidants were used as oxygen sources in these oxidations.$^{1-6)}$ Recently it was reported that manganese,$^{7)}$ iron,$^{8)}$ cobalt,$^{9)}$ or rhodium porphyrin$^{10)}$ promotes the oxidative hydration of olefins with molecular oxygen and tetrahydroborate. In addition, bis(1,3-diketonato)cobalt(II) complexes were found to catalyze the hydration of olefins in the presence of oxygen and triethylsilane.$^{11)}$ However, in these reactions, primarily produced hydroperoxide or ketone was reduced to alcohol under the reaction conditions. We report herein a facile and direct oxidation of olefins to ketones with oxygen and triethylsilane by the use of cobalt(II) porphyrin as a catalyst (Scheme 1).



$$\underset{\underline{1}}{R^1\text{-CH=CH-}R^2} \xrightarrow[\text{2-PrOH-CH}_2\text{Cl}_2]{\substack{\text{Co Porphyrin} \\ O_2\text{-Et}_3\text{SiH}}} \underset{\underline{2}}{R^1\text{-}\overset{\overset{O}{\|}}{C}\text{-CH}_2\text{-}R^2} + \underset{\underline{3}}{R^1\text{-}\overset{\overset{OOH}{|}}{C}H\text{-CH}_2\text{-}R^2} + \underset{\underline{4}}{R^1\text{-}\overset{\overset{OH}{|}}{C}H\text{-CH}_2\text{-}R^2}$$

Scheme 1.

The effects of solvent and catalyst were studied by reacting 1 mmol of aromatic olefin 1a or 1b with Et_3SiH(1.1 mmol) under an oxygen atmosphere at room temperature. The results are summarized in Table 1. The oxidation of styrene (1a) proceeded rapidly in 2-propanol-CH_2Cl_2, where CH_2Cl_2 was added in order to dissolve metalloporphyrin, to give acetophenone (2a) as a major product (Entry 1). The use of methanol instead of 2-propanol as solvent resulted in major formation of hydroperoxide 3a (Entry 2). When the reaction was carried out in CH_2Cl_2 or tetrahydrofuran, 1a was not consumed completely even at a prolonged time (Entries 3 and 4). CoTDCPP was the most effective catalyst for conversion of 1b to 2b among cobalt porphyrins. The ratio of ketone 2b to hydroperoxide 3b was changed by the substituents on phenyl rings of porphyrin (Entries 5-7). These results suggest that the hydroperoxide produced at the primary step decomposed into the ketone depending upon the different catalytic activities of cobalt porphyrins. Other metalloporphyrins and cobalt complex of acetylacetonate or Schiff base were not effective (Entries 8-11).

A typical example of the oxidation is as follows. A mixture of 4-methylstyrene (1c) (1 mmol), CoTDCPP (10^{-3} mmol), and Et_3SiH(1.1 mmol) in 5 ml of 2-PrOH-CH_2Cl_2 (1:1) was stirred at room temperature under an oxygen atmosphere for 3 h, and then solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc) to afford 4-methylacetophenone (2c) (62%) and 1-(1-hydroperoxyethyl)-4-methylbenzene (3c) (26%).

Table 1. Effects of Solvent and Catalyst on the Oxidation of Olefins[a)]

Entry	Olefin	Catalyst[b)] (10^{-3} equiv.)	Solvent	Time / h	Yield/%[e)] 2	3	4
1	1a	CoTDCPP(1)	2-PrOH-CH_2Cl_2[c)]	3	76	13	0
2	1a	CoTDCPP(1)	MeOH-CH_2Cl_2[d)]	3	27	63	0
3	1a	CoTDCPP(1)	CH_2Cl_2	24	8	0	10
4	1a	CoTDCPP(1)	THF	24	7	0	9
5	1b	CoTDCPP(1)	2-PrOH-CH_2Cl_2	2	71	13	3
6	1b	CoTPP(1)	2-PrOH-CH_2Cl_2	2	29	48	3
7	1b	CoTCMPP(1)	2-PrOH-CH_2Cl_2	2	41	52	5
8	1b	FeTDCPP(1)	2-PrOH-CH_2Cl_2	24	0	0	0
9	1b	MnTDCPP(1)	2-PrOH-CH_2Cl_2	24	0	0	0
10	1b	Co(acac)(15)	2-PrOH-CH_2Cl_2	5	4	0	6
11	1b	Co(salen)(15)	2-PrOH-CH_2Cl_2	5	3	1	0

a)Conditions;olefin(1 mmol),Et_3SiH(1.1 mmol),solvent(5 ml),O_2(1 atm),rt.
b)See Ref.12. c)2-PrOH:CH_2Cl_2=1:1. d)MeOH:CH_2Cl_2=1:1. e)Isolated yield.

The results of the oxidation of various olefins with combination of CoTDCPP, O_2, and Et_3SiH are listed in Table 2. In the cases of olefins 1c-1i, the corresponding ketones were obtained in good or excellent yields accompanied with small amounts of the hydroperoxides and the alcohols (Entries 1-7). Substituents on the aromatic ring had no influence on the oxidation of the olefin. Non-conjugated olefins such as 1-decene and allylbenzene were not oxidized. On the other hand, the reaction of 1j, 1k, or 1l gave the mixture of ketone, hydroperoxide, and alcohol. However, the hydroperoxide could be converted to the corresponding ketone quantitatively by the acetylation with acetic anhydride and 4-(N,N-dimethylamino)pyridine (DMAP) in CH_2Cl_2 (Scheme 2). Based on this result, we examined the successive treatment of the crude oxidative products with acetic anhydride and DMAP for the preparation of the ketone (Table 3). The desired ketones were obtained in high yields compared with the results shown in Table 2.

A typical example of successive acetylation of the oxidative product is as follow. To 10 ml of CH_2Cl_2 solution of the crude oxidative product obtained from 1c by the above procedure was added acetic anhydride (1.5 mmol) and DMAP(0.1 mmol) at room temperature, and then the mixture was stirred for 6 h. The reaction mixture was diluted with 30 ml of ether, washed with aqueous 10% $NaHCO_3$, and dried over Na_2SO_4. Solvent was removed under reduced pressure, and the residue was purified by the same method as described above, to yield 4-methylacetophenone (2c) (82%).

Table 2. CoTDCPP-catalyzed Oxidation of Conjugated Olefins$^{a)}$

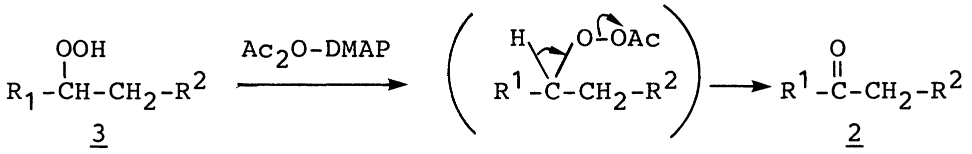
Entry	Olefin	Time/h	Yield/%$^{b)}$		
			2	3	4
1	1c	3	62	26	0
2	1d	3	73	10	8
3	1e	3	74	4	9
4	1f	3	89	0	8
5	1g	3	87	0	5
6	1h	3	84	0	13
7	1i	3	94	0	0
8	1j	3	43	33	22
9	1k	6	22	24	25
10	1l	6	29	25	13

a)Conditions; olefin(1 mmol), Et_3SiH(1.1 mmol), CoTDCPP(0.001 mmol), O_2(1 atm), 2-PrOH-CH_2Cl_2(1:1), rt. b)Isolated yield.

Table 3. Preparation of Ketones by Successive Acetylation of the Oxidative Product of Olefins$^{a)}$

Entry	Olefin	Product 2 Yield/%$^{b)}$
1	1c	82
2	1j	83
3	1k	62
4	1l	87

a)Conditions; Ac_2O(1.5 mmol), DMAP(0.1 mmol), CH_2Cl_2(10 ml), rt. b)Isolated yield.



Scheme 2.

Thus the cobalt(II) porphyrin-catalyzed oxidation of olefins with molecular oxygen and Et_3SiH proceeded rapidly in 2-propanol to afford ketones in a high yield. The present reaction provides a selective and direct method for preparation of ketones from conjugated olefins. Further studies of this oxidation are now in progress.

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12) Abbreviations used; TDCPP= 5,10,15,20-tetra(2,6-dichlorophenyl)-porphinato, TPP= 5,10,15,20-tetraphenylporphinato, TCMPP= 5,10,15,20-tetra(4-carbomethoxyphenyl)porphinato, Co= cobalt(II), Fe= iron(III) chloride, Mn= manganese(III) chloride, Co(acac)= bis(acetylacetonato)-cobalt(II), Co(salen)= N,N'-ethylenebis(salicylideniminato)cobalt(II).

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