Cobalt(III) Complex Catalyzed Aerobic Oxidation of Propargylic Alcohols

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Received 2 August 2007

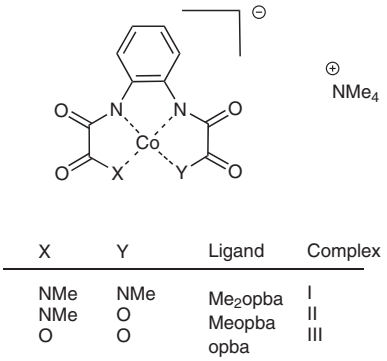
Abstract: An *o*-phenylenebis(*N*′-methyloxamidate) cobalt(III) complex works as an efficient catalyst for the oxidation of propargylic alcohols to the corresponding α,β-acetylenic carbonyl compounds, in the presence of pivalaldehyde, under an atmospheric pressure of molecular oxygen.

Key words: alcohols, alkynes, cobalt complexes, oxidation, homogeneous catalysis, oxygen

α,β-Acetylenic carbonyl compounds (ynones) are extremely interesting substrates because of their versatility for further synthetic transformations. They have been used in the synthesis of a variety of biologically active compounds, such as nucleosides,[1] anti-cancer agents,[2] sex pheromones[3] and alkaloids,[4] among others.[5] They have also been employed as building blocks in the preparation of aromatic compounds,[6] including a full range of heterocyclic derivatives.[5,7]

A wide variety of synthetic approaches to the synthesis of α,β-acetylenic carbonyl compounds have been reported.[5] Among them, acylation of alkynyl organometallic reagents,[8] cross-coupling between terminal alkynes and acyl chlorides,[9] carbonylation of terminal alkynes in the presence of aryl halides,[10] and alkynylation of aldehydes[11] followed by oxidation of the resulting propargylic alcohols,[12] are usually considered to be the methods of choice.

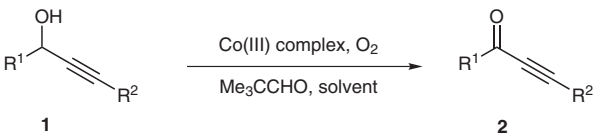
Traditionally, oxidation of alcohols have been performed with high-valent metal oxides or their mineral salts, notably of middle first-row transition metals.[13] In most instances, these inorganic oxidants are required in stoichiometric amounts and are usually toxic, hazardous or both. Moreover, purification of the reaction products is often demanding and laborious. In recent years, different catalytic methods using small amounts of metal derivatives and clean oxidants have been developed.[14] However, to the best or our knowledge, only a few examples of transition-metal-catalyzed aerobic oxidation of propargylic alcohols to the corresponding ynones have been published. Uemura and co-workers have described two catalytic systems that work effectively for this purpose with a number of propargylic alcohols. In both systems, the oxidation is carried out under an atmospheric pressure of molecular oxygen, using an oxovanadium acetylacetonate complex as catalyst in the presence of 3 Å molecular sieves in the first system,[15] and calcium phosphate–vanadate apatite in the second.[16] Some isolated examples of oxidation of propargylic alcohols with other catalytic systems (only one example of propargylic alcohol in each case) have been reported with differing results: Ishii and co-workers used $Cu(acac)_2$-NHPI (NHPI = *N*-hydroxyphthalimide),[17] Katsuki and co-workers employed (nitroso)(salen)Ru as catalysts,[18] Sain and co-workers used a cobalt phthalocyanine as catalyst[19] and Toste and co-workers employed an oxovanadium complex as catalyst in the asymmetric oxidation of an acetylenic α-hydroxy ester.[20]



X	Y	Ligand	Complex
NMe	NMe	Me_2opba	I
NMe	O	Meopba	II
O	O	opba	III

Figure 1 Structure of cobalt(III) complexes used in this study

In this context, we have previously reported the preparation of square-planar cobalt(III) complexes with the *o*-phenylenebis(*N*-methyloxamidate) ligand (Me_2opba) and its oxamate (Meopba) and bis-oxamate (opba) derivatives (Figure 1), as well as their use as catalysts in the oxidation of several kinds of organic compounds with oxygen and pivalaldehyde[21] (Mukaiyama's conditions).[22] Herein, we report a new application of this catalytic system to the oxidation of propargylic alcohols (Scheme 1).



Scheme 1 Aerobic catalytic oxidation of propargylic alcohols to ynones

First, the oxidation of 1,3-diphenyl-2-propyn-1-ol (**1a**) was examined using the Me_2opba cobalt(III) complex (**I**) as catalyst and following the experimental protocol reported previously by us.[21] Thus, under an atmospheric

SYNTHESIS 2007, No. 21, pp 3329–3332
Advanced online publication: 21.09.2007
DOI: 10.1055/s-2007-990804; Art ID: P09607SS

Table 1 Oxidation of 1,3-Diphenyl-2-propyn-1-ol (**1a**) with Oxygen and Pivalaldehyde To Give **2a**[a]

Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	**I**	MeCN	8	93
2	**I**	$CHCl_3$	8	75
3	**I**	CH_2Cl_2	8	70
4	**I**	PhF	8	52
5	**II**	MeCN	8	90
6	**III**	MeCN	8	94

[a] Reaction conditions: see experimental section.
[b] Yields refer to isolated pure products.

pressure of molecular oxygen, in the presence of pivalaldehyde (aldehyde–propargylic alcohol, 3:1) in acetonitrile as solvent, complex **I** catalyzed the oxidation of the propargylic alcohol at room temperature, to give 1,3-diphenyl-2-propyn-1-one (**2a**) in good yield (Table 1, entry 1). When other solvents such as chloroform, dichloromethane or fluorobenzene were used, the conversion of **1a** to the corresponding ketone **2a** was lower (entries 2–4), probably due to the lower solubility of the cobalt complexes in these solvents. Finally, we also tested the oxidation of **1a** using the Meopba cobalt(III) (**II**) and the opba cobalt(III) (**III**) complexes as catalysts in order to evaluate the effects of the catalyst ligand structure on the catalytic activity. Under identical conditions, in acetonitrile at room temperature, both complexes **II** and **III** gave similar results to complex **I** (entries 5–6).

Next, the oxidation of propargylic alcohols **1** was examined using complex **I**. Typical results are listed in Table 2. Among the 1-aryl-3-phenyl-2-propyn-1-ols investigated, those having a slightly electron-donating methyl group or an electron-withdrawing chloro substituent at the *meta* or *para* positions on the aryl group (**1c**, **1d**, **1f**, **1g**) were efficiently oxidized to give the corresponding ketones in high yields (entries 3, 4, 6, 7). Oxidation of the corresponding *ortho*-substituted alcohols (**1b**, **1e**) was slower and afforded the oxidized products in somewhat lower yields (entries 2, 5). These results reflect the relative importance of steric effects compared with electronic ones. However, the oxidation of substrates bearing a strong electron-donating methoxy substituent on the aromatic ring gave comparatively lower yields because of the formation of over-oxidized by-products (entries 8–10). Propargylic alcohols having a naphthyl (**1k–l**) or thienyl (**1m–n**) substituent also gave the corresponding ynones in excellent yields under these conditions (entries 11–14). The oxidation of propargylic alcohols having an alkyl substituent at the 3-position, such as 1-aryl-5-phenyl-2-pentyn-1-ols **1o–q**, gave the corresponding ketones in very good yields (entries 15–17), regardless of the type of aromatic ring substituent.

On the other hand, propargylic alcohols having an alkyl substituent at the 1-position, such as 1-alkyl-3-phenyl-2-propyn-1-ols **1r–s** (entries 18–19) or 1,3-dialkyl-2-propyn-1-ols **1t–u** (entries 20–21), were oxidized to the corresponding ketones in good yields, although the reactions were slower and required the addition of a second load of pivalaldehyde (aldehyde–propargylic alcohols, 6:1). Finally, propargylic alcohols bearing a terminal acetylene moiety, such as **1v–x**, also gave good yields of the corresponding ketones with our catalytic system (entries 22–23).

Table 2 Oxidation of Propargylic Alcohols **1** with Oxygen and Pivalaldehyde Catalyzed by Complex **I** in Acetonitrile

Entry	Product	R^1	R^2	Time (h)	Yield (%)[b]
1	**2a**	Ph	Ph	8	93
2	**2b**	2-MeC_6H_4	Ph	10	78
3	**2c**	3-MeC_6H_4	Ph	8	91
4	**2d**	4-MeC_6H_4	Ph	8	92
5	**2e**	2-ClC_6H_4	Ph	10	75
6	**2f**	3-ClC_6H_4	Ph	8	87
7	**2g**	4-ClC_6H_4	Ph	8	85
8	**2h**	2-$MeOC_6H_4$	Ph	10	65
9	**2i**	3-$MeOC_6H_4$	Ph	8	81
10	**2j**	4-$MeOC_6H_4$	Ph	6	60
11	**2k**	α-naphthyl	Ph	10	92
12	**2l**	β-naphthyl	Ph	8	90
13	**2m**	α-thienyl	Ph	8	92
14	**2n**	β-thienyl	Ph	10	97
15	**2o**	Ph	$PhCH_2CH_2$	8	87
16	**2p**	4-MeC_6H_4	$PhCH_2CH_2$	8	88
17	**2q**	4-FC_6H_4	$PhCH_2CH_2$	8	85
18	**2r**	*n*-Pr	Ph	24	80
19	**2s**	*c*-Hex	Ph	24	82
20	**2t**	*n*-C_9H_{19}	Me	36	75
21	**2u**	*c*-Hex	Me	36	72
22	**2v**	4-ClC_6H_4	H	10	82
23	**2x**	β-naphthyl	H	10	84

[a] Reaction conditions: see experimental section.
[b] Yields refer to isolated pure products.

In summary, we have described here an efficient oxidation of propargylic alcohols to α,β-ynones with molecular oxygen, using pivalaldehyde (Mukaiyama's conditions) and a low load (5 mol%) of a cobalt (III) complex with the *o*-phenylene-bis(*N*′-methyloxamidate) (Me_2opba) ligand as catalyst. The system works very efficiently with a

broad range of propargylic alcohols, affording good yields of the expected ynones.

All melting points are uncorrected. Column chromatography was performed on silica gel (Merck, silica gel 60, 230–400 mesh). NMR spectra were recorded on a Bruker Advance 300 DPX spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR) and referenced to TMS as internal standard. The carbon type was determined by DEPT experiments. Mass spectra (EI, 70 eV) were recorded on a Fisons Instruments VG Autospec spectrometer. All starting propargylic alcohols **1** were prepared according to literature procedures.[11,23] Data for compounds **2a**,[8] **2b**,[9c,e] **2c**,[9b] **2d**,[9c,e,10b] **2g**,[5,9c,e] **2h**,[5] **2i**,[5,10a] **2j**,[9b,e] **2k**,[10a,b] **2m**,[9c,e,10b] **2r**,[24] **2s**,[25] **2v**[16] and **2x**[15b] were consistent with those reported in the literature.

Catalytic Oxidation of Propargylic Alcohols 1; General Procedure

A solution of propargylic alcohol **1** (0.22 mmol), NMe_4·Co(III)-Me_2opba complex (5.3 mg, 0.013 mmol) and pivalaldehyde (74 μL, 0.66 mmol) in MeCN (1.5 mL) was stirred under an oxygen atmosphere (balloon) until consumption of the starting material was complete (TLC). H_2O (10 mL) was added and the mixture was extracted with Et_2O (3 × 20 mL). The organic layer was washed with sat. $NaHCO_3$ (10 mL), brine (2 × 10 mL) and dried ($MgSO_4$). The reaction product **2** was obtained after flash chromatography on silica gel (hexane–EtOAc). Yields are included in Table 2.

1-(2-Chlorophenyl)-3-phenyl-2-propyn-1-one (2e)
Oil.

MS (EI): *m*/*z* (%) = 242 (31), 241 (16), 240 (100) [M$^+$], 141 (10), 139 (35), 77 (17).

HRMS (EI): *m*/*z* calcd for $C_{15}H_9ClO$: 240.0342; found: 240.0339.

^{1}H NMR ($CDCl_3$): δ = 8.08 (d, *J* = 7.2 Hz, 1 H), 7.65 (dd, *J* = 8.7, 1.8 Hz, 2 H), 7.49–7.38 (m, 6 H).

^{13}C NMR ($CDCl_3$): δ = 176.8 (s), 135.8 (s), 133.5 (s), 133.4 (d), 133.1 (d), 132.5 (d), 131.5 (d), 130.9 (d), 128.6 (d), 126.8 (d), 120.0 (s), 93.9 (s), 88.3 (s).

1-(3-Chlorophenyl)-3-phenyl-2-propyn-1-one (2f)
Mp 212–215 °C.

MS (EI): *m*/*z* (%) = 242 (15), 241 (7), 240 (41) [M$^+$], 212 (46), 176 (15), 129 (100).

HRMS (EI): *m*/*z* calcd for $C_{15}H_9ClO$: 240.0342; found: 240.0335.

^{1}H NMR ($CDCl_3$): δ = 8.17 (t, *J* = 1.8 Hz, 1 H), 8.11 (dt, *J* = 7.8, 1.2 Hz, 1 H), 7.71–7.68 (m, 2 H), 7.62–7.58 (m, 1 H), 7.51–7.41 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 176.5 (s), 138.4 (s), 135.0 (s), 134.0 (d), 133.2 (d), 131.1 (d), 130.0 (d), 129.4 (d), 128.7 (d), 127.7 (d), 119.8 (s), 93.9 (s), 86.5 (s).

1-(2-Naphthyl)-3-phenyl-2-propyn-1-one (2l)
Mp 94–95 °C.

MS (EI): *m*/*z* (%) = 256 (71) [M$^+$], 228 (100), 129 (74), 101 (16), 75 (17).

HRMS (EI): *m*/*z* calcd for $C_{19}H_{12}O$: 256.0888; found: 256.0870.

^{1}H NMR ($CDCl_3$): δ = 8.70 (s, 1 H), 8.12 (dd, *J* = 8.7, 1.8 Hz, 1 H), 7.94 (d, *J* = 7.8 Hz, 1 H), 7.82 (t, *J* = 8.4 Hz, 2 H), 7.65 (dd, *J* = 8.1, 1.8 Hz, 2 H), 7.56–7.46 (m, 2 H), 7.42–7.32 (m, 3 H).

^{13}C NMR ($CDCl_3$): δ = 177.9 (s), 136.1 (s), 134.4 (s), 133.0 (d), 132.6 (d), 132.4 (s), 130.8 (d), 129.9 (d), 129.0 (d), 128.7 (d), 128.5 (d), 127.9 (d), 126.9 (d), 123.9 (d), 120.2 (s), 93.0 (s), 87.0 (s).

3-Phenyl-1-(3-thienyl)-2-propyn-1-one (2n)
Oil.

MS (EI): *m*/*z* (%) = 212 (100) [M$^+$], 184 (86), 129 (56).

HRMS (EI): *m*/*z* calcd for $C_{13}H_8OS$: 212.0296; found: 212.0265.

^{1}H NMR ($CDCl_3$): δ = 8.36 (d, *J* = 1.8 Hz, 1 H), 7.68–7.64 (m, 2 H), 7.48–7.34 (m, 5 H).

^{13}C NMR ($CDCl_3$): δ = 171.4 (s), 142.9 (s), 135.5 (d), 133.0 (d), 130.7 (d), 128.7 (d), 126.80 (d), 126.77 (d), 120.0 (s), 91.3 (s), 87.3 (s).

1,5-Diphenyl-2-pentyn-1-one (2o)
Oil.

MS (EI): *m*/*z* (%) = 234 (53) [M$^+$], 206 (16), 129 (100).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{14}O$: 234.1045; found: 234.1017.

^{1}H NMR ($CDCl_3$): δ = 7.48 (d, *J* = 6.9 Hz, 2 H), 7.38–7.14 (m, 8 H), 2.95 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 186.9 (s), 140.2 (s), 133.0 (d), 130.7 (d), 128.59 (d), 128.52 (d), 128.3 (d), 126.3 (d), 119.8 (s), 91.2 (s), 87.7 (s), 46.9 (t), 29.9 (t).

1-(4-Methylphenyl)-5-phenyl-2-pentyn-1-one (2p)
Oil.

MS (EI): *m*/*z* (%) = 248 (31) [M$^+$], 233 (17), 119 (28), 91 (100).

HRMS (EI): *m*/*z* calcd for $C_{18}H_{16}O$: 248.1201; found: 248.1209.

^{1}H NMR ($CDCl_3$): δ = 7.80 (d, *J* = 7.8 Hz, 2 H), 7.26–7.11 (m, 7 H), 2.89 (t, *J* = 7.0 Hz, 2 H), 2.71 (t, *J* = 7.0 Hz, 2 H), 2.33 (s, 3 H).

^{13}C NMR ($CDCl_3$): δ = 177.8 (s), 144.9 (s), 139.6 (s), 134.4 (s), 129.66 (d), 129.10 (d), 128.55 (d), 128.44 (d), 126.6 (d), 94.8 (s), 80.2 (s), 33.9 (t), 21.7 (q), 21.2 (t).

1-(4-Fluorophenyl)-5-phenyl-2-pentyn-1-one (2q)
Oil.

MS (EI): *m*/*z* (%) = 252 (19) [M$^+$], 233 (3), 123 (13), 91 (100).

HRMS (EI): *m*/*z* calcd for $C_{17}H_{13}FO$: 252.0950; found: 252.0939.

^{1}H NMR ($CDCl_3$): δ = 7.89 (d, *J* = 8.8 Hz, 1 H), 7.89 (d, *J* = 8.8 Hz, 1 H), 7.26–7.18 (m, 5 H), 6.99 (t, *J* = 8.7 Hz, 2 H), 2.90 (t, *J* = 7.1 Hz, 2 H), 2.74 (t, *J* = 7.1 Hz, 2 H).

^{13}C NMR ($CDCl_3$): δ = 176.4 (s), 166.3 (d, J_{C-F} = 254.9 Hz), 139.5 (s), 133.2 (d, J_{C-F} = 2.9 Hz), 132.2 (d, J_{C-F} = 9.8 Hz), 128.60 (d), 128.47 (d), 126.7 (d), 115.6 (d, J_{C-F} = 21.5 Hz), 95.7 (s), 79.9 (s), 33.8 (t), 21.2 (t).

1-(*n*-Nonyl)-2-butyn-1-one (2t)
Oil.

MS (EI): *m*/*z* (%) = 195 (1), 194 (0.8) [M$^+$], 82 (100), 67 (71).

HRMS (EI): *m*/*z* calcd for $C_{13}H_{22}O$: 194.1671; found: 194.1664.

^{1}H NMR ($CDCl_3$): δ = 2.50 (t, *J* = 7.5 Hz, 2 H), 2.00 (s, 3 H), 1.63 (m, 2 H), 1.28 (m, 12 H), 0.86 (t, 3 H).

^{13}C NMR ($CDCl_3$): δ = 188.5 (s), 89.8 (s), 80.2 (s), 45.4 (t), 31.8 (t), 29.3 (t), 29.28 (t), 29.20 (d), 28.9 (t), 24.0 (t), 22.6 (t), 14.1 (q), 4.0 (q).

1-Cyclohexyl-2-butyn-1-one (2u)
Oil.

MS (EI): *m*/*z* (%) = 150 (3) [M$^+$], 111 (15), 83 (66), 67 (34), 57 (100).

HRMS (EI): *m*/*z* calcd for $C_{10}H_{14}O$: 150.1045; found: 150.1045.

^{1}H NMR ($CDCl_3$): δ = 2.36 (tt, *J* = 11.0, 3.5 Hz, 1 H), 2.02 (s, 3 H), 1.95 (m, 2 H), 1.80–1.61 (m, 4 H), 1.42–1.24 (m, 4 H).

^{13}C NMR ($CDCl_3$): δ = 191.7 (s), 90.5 (s), 79.5 (s), 52.2 (d), 28.2 (t), 25.8 (t), 25.4 (t), 4.1 (q).

Acknowledgment

Financial support from Generalitat Valenciana (Grupos 03/168) and from Universitat de València (Grant UV-AE-20060244) is acknowledged.

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