Beilstein Journal of Organic Chemistry

CuCl-catalyzed aerobic oxidation of 2,3-allenols to 1,2-allenic ketones with 1:1 combination of phenanthroline and bipyridine as ligands

Shuxu Gao[1], Yu Liu[1] and Shengming Ma*[1,2]

Full Research Paper

Open Access

Address:
[1]Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China and [2]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Lu, Shanghai 200032, P. R. China. Fax: (+86)-21-6260-9305

Email:
Shengming Ma* - masm@sioc.ac.cn

* Corresponding author

Keywords:
allenic ketone; allenol; Cu(I) catalyst; oxidation

Beilstein J. Org. Chem. **2011,** *7,* 396–403.
doi:10.3762/bjoc.7.51

Received: 25 December 2010
Accepted: 11 March 2011
Published: 07 April 2011

This article is part of the Thematic Series "Allene chemistry".

Guest Editor: K. M. Brummond

Abstract

A protocol has been developed to prepare 1,2-allenyl ketones using molecular oxygen in air or pure oxygen as the oxidant from 2,3-allenylic alcohols with moderate to good yields under mild conditions. In this reaction CuCl (20 mol %) with 1,10-phenanthroline (10 mol %) and bipyridine (10 mol %) was used as the catalyst. It is interesting to observe that the use of the mixed ligands is important for the higher yields of this transformation: With the monoligand approach developed by Markó et al., the yields are relatively lower.

Introduction

The oxidation of alcohols is one of many fundamental reactions in organic synthesis [1,2]. Usually, stoichiometric oxidants such as MnO_2 [3], PCC [4], PDC [4], etc. were employed for this type of transformation. However, the cost and the byproducts derived from these reagents cause economic and environmental problems [5]. In the past decades, much attention has been paid to catalytic oxidation of alcohols using molecular oxygen as the oxidant with Pd [6-10], Cu [11-13], Ru [14,15] as the catalysts.

1,2-Allenic ketones have become very useful in organic synthesis [16-33]. Current methods for the oxidation of allenic alcohols to ketones include oxidation with MnO_2 [30,34,35], Swern oxidation [17,24] or Dess–Martin oxidation [16,17,24,25,28,31-33]: Catalytic aerobic oxidation has not so far been reported. Due to the synthetic potential of 1,2-allenyl ketones, it is desirable to develop an aerobic oxidation protocol for 2,3-allenols. In this paper we wish to report the CuCl-

catalyzed aerobic oxidation of 2,3-allenols by applying a mixed ligand approach using copper as the catalyst [12,13].

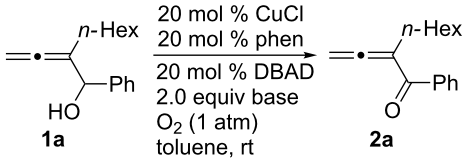
Results and Discussion

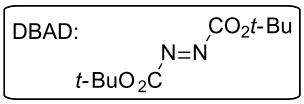
After screening the Pd- [6-10] and Ru-catalyzed [14,15] protocols without success, we began a study of the oxidation of 2-hexyl-1-phenylbuta-2,3-diene-1-ol (**1a**) with O_2 based on the pioneering study of oxidation of normal simple alcohols by Markó et al. [12]. Under the original conditions [12], the expected allenylic ketone **2a** was obtained in 59% yield when CuCl and 1,10-phenanthroline were used (Table 1, entry 1). A series of bases and solvents were then screened for the oxidation of **1a**. The results are summarized in Table 1 and Table 2. We found that (1) K_2CO_3 is the most effective base (Table 1, entry 1) and that organic bases such as NEt_3 and DBU are generally ineffective (Table 1, entries 6 and 7); (2) toluene is the best solvent (Table 2).

In order to improve the yield further, we examined the effect of ligands. When 2,2'-bipyridine, which has a weaker coordinating ability, was used [36], the yield of **2a** was lower (Table 3, entry 2). With 4,7-diphenyl-1,10-phenanthroline the yield was slightly improved to 66% (Table 3, entry 3). These experimental results obviously indicated that the CuCl-catalyzed oxidation of allenic alcohol was influenced by the coordinating ability of nitrogen ligands. Consequently, we carried out the reaction with a mixture of a stronger coordinating ligand together with a relatively weaker coordinating ligand. Indeed, it was interesting to observe that when 4,7-diphenyl-1,10-phenanthroline and 2,2'-bipyridine were mixed in the ratio of 1:1 [37,38], the isolated yield was improved to 82% (Table 3, entry 6). The yield with 1,10-phenanthroline and 2,2'-bipyridine (1:1) was 83% (Table 3, entry 10). However, 4,7-diphenyl-1,10-phenanthroline is relatively expensive (1 g, $ 94, Aldrich), so the cheaper 1,10-phenanthroline (5 g, $ 26.4, Aldrich) was used for further study. The effect of ratio of 1,10-phenanthroline vs 2,2'-bipyridine on the yield was also studied: A ratio of 1:1 proved to be the best (Table 3, entries 7–12). This may be explained by considering that the coordination of 2,2'-bipyridine is important for the formation of the catalytically active species and may be easily replaced with that of the alcohol. We also tried *N*-methylimidazole (NMI), which was used in oxidation of primary aliphatic alcohols reported by Markó et al. [13], however, both the turnover and yield were low (Table 3, entry 14). Both 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline and iPr-Pybox were ineffective in this reaction (Table 3, entries 4 and 5).

Some other Cu(I) catalysts, such as CuBr, CuI, and CuCN were also investigated, but no higher yield was achieved (Table 4). Further studies led to the observation that air (300 psi, 35 °C (oil bath)) could be used instead of pure oxygen

Table 1: Screening of bases for the CuCl-catalyzed oxidation of **1a**[a].

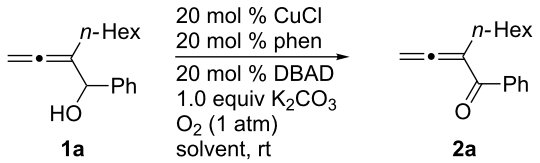




entry	base	time (h)	yield of **2a** (%)[b]
1	K_2CO_3	40	59[c,d]
2	Na_2CO_3	48	22[e]
3	Cs_2CO_3	35	27[d,f,g]
4	$KHCO_3$	45	15[h]
5	KOH[i]	48	39[j]
6	NEt_3	45	NR[k]
7	DBU	45	NR[l]

[a]The reaction was carried out using 0.3 mmol of **1a**, 20 mol % of CuCl, 20 mol % of phen, 20 mol % of DBAD, and 2.0 equiv of base in 3 mL of toluene under 1 atm of oxygen unless otherwise stated. [b]^{1}H NMR yield using CH_2Br_2 as the internal standard. [c]1.0 equiv K_2CO_3 was used. [d]Isolated yield. [e]50% of **1a** was recovered as determined by ^{1}H NMR analysis. [f]15 mol % of catalyst was used. [g]32% of **1a** was recovered by column chromatography. [h]53% of **1a** was recovered as determined by ^{1}H NMR analysis. [i]100 mg of 3 Å MS and 20 mol % of KOH was used. [j]28% of **1a** was recovered as determined by ^{1}H NMR analysis. [k]70% of **1a** was recovered as determined by ^{1}H NMR analysis. [l]72% of **1a** was recovered by column chromatography.

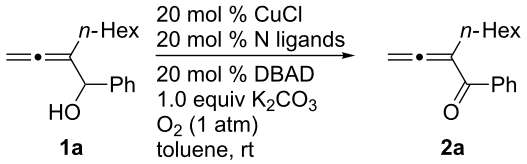
Table 2: Screening of solvents for the CuCl-catalyzed oxidation of **1a**[a].

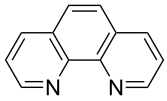
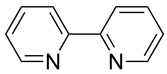
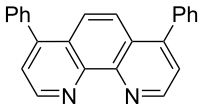
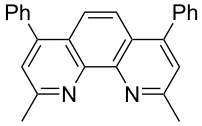
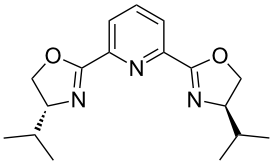
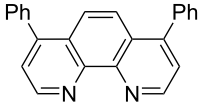


entry	solvent	time (h)	yield of **2a** (%)
1	toluene	40	59[b]
2	CH_3CN	48	NR[c]
3	DCE	47	31[d]
4	$CHCl_3$	47	20[e]
5	DMF	47	NR[f]

[a]The reaction was carried out using 0.3 mmol of **1a**, 20 mol % of CuCl, 20 mol % of phen, 20 mol % of DBAD, and 1.0 equiv of K_2CO_3 in 3 mL of solvent under 1 atm of oxygen. [b]Isolated yield. [c]64% of **1a** was recovered as determined by ^{1}H NMR analysis. [d]^{1}H NMR yield using CH_2Br_2 as the internal standard. [e]78% of **1a** was recovered as determined by ^{1}H NMR analysis. [f]76% of **1a** was recovered as determined by ^{1}H NMR analysis.

Table 3: Screening for different nitrogen ligands in the CuCl-catalyzed oxidation of **1a**[a].



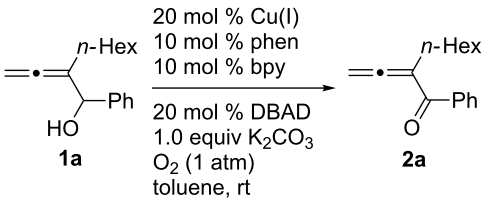
entry	ligand 1 (mol %)	ligand 2 (mol %)	time (h)	yield of **2a** (%)[b]
1	 **L-A**	—	40	61
2	 **L-B**	—	46	43[c]
3		—	14.5	66
4		—	45	NR[d]
5		—	24	NR[e]
6	 (10)	**L-B** (10)	45.5	82
7	**L-A** (17.5)	**L-B** (2.5)	40	79
8	**L-A** (15.0)	**L-B** (5.0)	40	65
9	**L-A** (12.5)	**L-B** (7.5)	40	82
10	**L-A** (10.0)	**L-B** (10.0)	42	83
11	**L-A** (7.5)	**L-B** (12.5)	42	78
12	**L-A** (5.0)	**L-B** (15.0)	40	73
13	**L-A** (2.5)	**L-B** (17.5)	40	68
14[f]	**L-A** (5.0)	**NMI** (7.0)	35	17

[a]The reaction was carried out using 0.3 mmol of **1a**, 20 mol % of CuCl, 20 mol % of nitrogen ligand, 20 mol % of DBAD, and 1.0 equiv of K_2CO_3 in 3 mL of toluene under 1 atm of oxygen. [b]^{1}H NMR yields determined by 300 MHz, ^{1}H NMR analysis using CH_2Br_2 as the internal standard. [c]52% of **1a** was recovered as determined by ^{1}H NMR analysis. [d]87% of **1a** was recovered as determined by ^{1}H NMR analysis. [e]82% of **1a** was recovered as determined by ^{1}H NMR analysis. [f]The reaction was carried out using 0.5 mmol of **1a**, 5 mol % of CuCl, 5 mol % of *t*-BuOK, 5 mol % of DBAD and the indicated ligands in 5 mL of C_6H_5F at 70 °C under 1 atm of oxygen. 52% of **1a** was recovered as determined by ^{1}H NMR analysis.

(1 atm, 15–24 °C) to shorten the reaction time from 40 to 10 hours and the yield was similar (86%) (Table 5, entry 1). Thus, 20 mol % of CuCl, 10 mol % of 1,10-phenanthroline, 10 mol % of 2,2'-bipyridine and 50 mol % of K_2CO_3 in toluene with air (300 psi, 35 °C) as the oxidant were defined as the standard conditions.

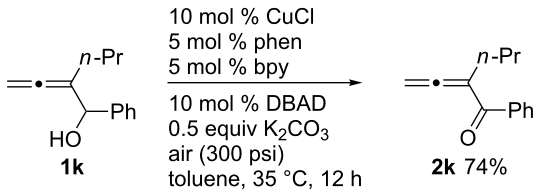
Under the standard conditions a series of 1-aryl-2,3-allenols were oxidized to the corresponding 1,2-allenic aryl ketones: A *para*-nitro group led to a 63% yield of **2e** (Table 5, entry 5); heteroaryl groups such as furanyl and thienyl were also tolerated under the reaction conditions, affording the corresponding allenic ketones **2f** and **2g** in 61% and 73% yields, respectively (Table 5, entries 6 and 7), whilst the reaction of 1-naphthyl-substituted **1h** afforded **2h** in 74% yield (Table 5, entry 8). Trisubstituted allenic alcohol **1j** was also oxidized to the corresponding allenic ketone **2j** in 91% yield (Table 5, entry 10).

Table 4: Screening of other Cu(I) sources.



entry	Cu(I)	time (h)	isolated yield of **2a**
1	CuBr	40	68%
2	CuI	40	49%
3	CuCN	41	45%

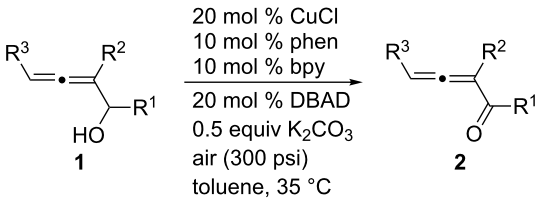
The reaction may be easily carried out on a 1 g scale: the oxidation of allenol **1k** afforded the corresponding allenic ketone **2k** in 74% yield in 12 hours with just 10 mol % of CuCl and 5 mol % each of 1,10-phenanthroline and 2,2'-bipyridine (Scheme 1).



Scheme 1: 1 gram scale reaction of allenol **1k**.

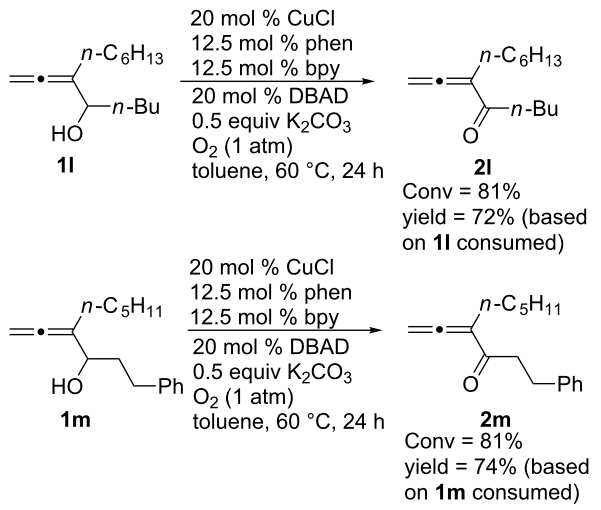
When the reaction of 1-alkyl-substituted-2,3-allenols oxidation was conducted under 1 atm of oxygen at 60 °C, 81% of conversion was observed and the corresponding allenic ketones **2l** and **2m** were obtained in 58% and 60% isolated yields (72% and 74% based on the starting material consumed), respectively (Scheme 2). As a comparison, it should be noted that when **1l** was oxidized with air (300 psi, 60 °C), the allenic ketone **2l** was formed in 43% ^{1}H NMR yield with 73% conversion of **1l** within 10 hours.

Table 5: The CuCl-catalyzed oxidation of allenic alcohols using air as the oxidant[a].



entry	substrate			time (h)	yield (%)[b]
	R^1	R^2	R^3		
1	Ph	*n*-C_6H_{13}	H (**1a**)	10	86 **(2a)**
2	*p*-EtC_6H_4	*n*-Pr	H (**1b**)	10	83 **(2b)**
3	*p*-BrC_6H_4	*n*-Pr	H (**1c**)	6	80 **(2c)**
4	*p*-ClC_6H_4	*n*-C_6H_{13}	H (**1d**)	6	78 **(2d)**
5	*p*-$O_2NC_6H_4$	*n*-C_6H_{13}	H (**1e**)	6	63 **(2e)**
6	3-furanyl	*n*-C_6H_{13}	H (**1f**)	11	61 **(2f)**
7	3-thienyl	*n*-C_5H_{11}	H (**1g**)	8.5	73 **(2g)**
8	1-naphthyl	Me	H (**1h**)	11	74 **(2h)**
9	Ph	allyl	H (**1i**)	11	75 **(2i)**
10	Ph	Bu	*n*-C_5H_{11} (**1j**)	11	91 **(2j)**

[a]The reaction was carried out using 0.3 mmol of **1**, 20 mol % of CuCl, 10 mol % of phen, 10 mol % of bpy, 20 mol % of DBAD, and 0.5 equiv of K_2CO_3 in 3 mL of toluene, air (300 psi, 35 °C (oil bath)). [b]Isolated yields.



Scheme 2: The oxidation of **1l** and **1m** under 1 atm of oxygen.

Conclusion

In conclusion, we have developed a method for the aerobic oxidation of 2,3-allenols, which uses molecular oxygen in air or pure oxygen as the oxidant. In this reaction, CuCl with a 1:1 ratio of 1,10-phenanthroline and bipyridine was used as the catalyst to provide the best results. A series of 1,2-allenic ketones were obtained in moderate to good yields under mild conditions. Compared to the traditional monoligand approach, allenols are obviously unique demanding a mixed ligands approach for better yields probably as a consequence of the coordinating ability of the allene moiety. Further study in this area is being pursued in this laboratory.

Experimental

General experimental methods for starting materials

The starting allenols **1a–e**, **1i**, **1k**, **1l**, **1m** were prepared via the reaction of propargyl bromides and corresponding aldehydes in the presence of $SnCl_2$ and NaI in DMF [39,40]; allenols **1f** [41], **1g** [42], **1h** [43], and **1j** [44] were prepared as reported. These starting allenols were purified by flash chromatography before use.

General experimental procedure for the aerobic oxidation of allenic alcohols

2-Hexyl-1-phenylbuta-2,3-dien-1-one (**2a**)

Typical procedure: 1,10-phenanthroline (5.5 mg, 0.03 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), CuCl (5.9 mg, 0.06 mmol), K_2CO_3 (20.6 mg, 0.15 mmol), and 1.5 mL of dry toluene were added successively into an oven dried reaction vessel (sealed with a stopper to isolate the contents from atmospheric moisture). The resulting mixture was stirred at rt for 0.5 h. Then the stopper was removed to add DBAD (13.7 mg, 0.06 mmol), 2-hexyl-1-phenylbuta-2,3-dien-1-ol (69.6 mg, 0.3 mmol), and 1.5 mL of dry toluene. The reaction vessel was then transferred to an autoclave, which was charged with air to a pressure of 300 psi, and stirred at 35 °C (oil bath). After 10 h, the pressure was carefully released in the hood, the mixture filtered through a short column of silica gel (100–140 mesh) and washed with diethyl ether. Evaporation of the solvent and flash chromatography on silica gel (eluent: petroleum ether/diethyl ether = 30:1) afforded **2a** (59.3 mg, 86%): liquid; ^{1}H NMR (300 MHz , $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.2 Hz, 2H), 5.04 (t, J = 2.7 Hz, 2H), 2.46–2.35 (m, 2H), 1.58–1.45 (m, 2H), 1.45–1.20 (m, 6H), 0.89 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.0, 194.9, 138.3, 131.9, 129.0, 127.8, 106.9, 79.3, 31.6, 28.9, 27.8, 22.6, 14.0 ppm; MS (m/z) 228 (M^+, 7.25), 105 (100); IR (neat) 2927, 2857, 1933, 1653, 1599, 1450, 1312, 1273 cm^{-1}; HRMS-EI (m/z) calcd for $C_{16}H_{20}O^+$ [M^+]: 228.1514; found: 228.1517.

2-Propyl-1-(4-ethylphenyl)buta-2,3-dien-1-one (**2b**)

The reaction of 1,10-phenanthroline (5.3 mg, 0.03 mmol), 2,2'-bipyridine (4.6 mg, 0.03 mmol), CuCl (5.9 mg, 0.06 mmol), K_2CO_3 (20.8 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.7 mg, 0.06 mmol), and 2-propyl-1-(4-ethylphenyl)buta-2,3-dien-1-ol (64.7 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2b** (53.0 mg, 83%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73 (d, J = 8.1 Hz, 2H), 7.22 (d, J = 8.1 Hz, 2H), 5.05 (t, J = 2.9 Hz, 2H), 2.69 (q, J = 7.6 Hz, 2H), 2.44–2.32 (m, 2H), 1.63–1.45 (m, 2H), 1.25 (t, J = 7.5 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.5, 194.4, 148.8, 135.8, 129.3, 127.3, 106.5, 79.1, 30.1, 28.8, 21.1, 15.1, 13.7 ppm; MS (m/z) 214 (M^+, 1.75), 133 (100); IR (neat) 2964, 2931, 2872, 1933, 1650, 1607, 1458, 1414, 1273, 1182, 1058 cm^{-1}; HRMS-EI (m/z) calcd for $C_{15}H_{18}O^+$ [M^+]: 214.1358; found: 214.1360.

2-Propyl-1-(4-bromophenyl)buta-2,3-dien-1-one (**2c**)

The reaction of 1,10-phenanthroline (5.4 mg, 0.03 mmol), 2,2'-bipyridine (4.6 mg, 0.03 mmol), CuCl (5.9 mg, 0.06 mmol), K_2CO_3 (20.6 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.8 mg, 0.06 mmol), and 2-propyl-1-(4-bromophenyl)buta-2,3-dien-1-ol (80.3 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2c** (64.1 mg, 80%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 5.07 (t, J = 2.9 Hz, 2H), 2.41–2.30 (m, 2H), 1.60–1.45 (m, 2H), 0.97 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.0, 193.7, 137.0, 131.1, 130.5, 126.7, 106.7, 79.7, 29.7, 21.1, 13.7 ppm; MS (m/z) 266 (M^+ (^{81}Br), 1.68), 264 (M^+ (^{79}Br), 1.76), 185 (100); IR (neat) 2961, 2929, 2870, 1931, 1653, 1585, 1458, 1391, 1270, 1071, 1010 cm^{-1}; HRMS-EI (m/z) calcd for $C_{13}H_{13}O^{81}Br^+$ [M^+]: 266.0129; found: 266.0136.

2-Hexyl-1-(4-chlorophenyl)buta-2,3-dien-1-one (**2d**)

The reaction of 1,10-phenanthroline (5.5 mg, 0.03 mmol), 2,2'-bipyridine (4.8 mg, 0.03 mmol), CuCl (6.0 mg, 0.06 mmol), K_2CO_3 (20.9 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.8 mg, 0.06 mmol), and 2-hexyl-1-(4-chlorophenyl)buta-2,3-dien-1-ol (79.6 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2d** (62.0 mg, 78%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 5.06 (t, J = 2.6 Hz, 2H), 2.43–2.32 (m, 2H), 1.55–1.42 (m, 2H), 1.43–1.18 (m, 6H), 0.88 (t, J = 6.3 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.0, 193.6, 138.2, 136.6, 130.4, 128.1, 106.9, 79.6, 31.6, 28.9, 27.7, 22.5, 14.0 ppm; MS (*m*/*z*) 264 (M^+ (^{37}Cl), 0.76), 262 (M^+ (^{35}Cl), 2.08), 139 (100); IR (neat) 2927, 2857, 1931, 1654, 1590, 1460, 1397, 1274, 1091 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{16}H_{19}O^{35}Cl^+$ [M^+]: 262.1124; found: 262.1130.

2-Hexyl-1-(4'-nitrophenyl)buta-2,3-dien-1-one (**2e**)

The reaction of 1,10-phenanthroline (5.5 mg, 0.03 mmol), 2,2'-bipyridine (4.7 mg, 0.03 mmol), CuCl (5.9 mg, 0.06 mmol), K_2CO_3 (20.8 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.9 mg, 0.06 mmol), and 2-hexyl-1-(4-nitrophenyl)buta-2,3-dien-1-ol (82.7 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2e** (51.4 mg, 63%) (eluent: petroleum ether/diethyl ether = 20:1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (d, J = 8.7 Hz, 2H), 7.84 (d, J = 8.7 Hz, 2H), 5.12 (t, J = 2.9 Hz, 2H), 2.44–2.33 (m, 2H), 1.57–1.44 (m, 2H), 1.44–1.20 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 218.0, 193.4, 149.4, 143.6, 129.7, 123.1, 107.6, 80.4, 31.5, 28.8, 27.7, 27.3, 22.5, 14.0 ppm; MS (*m*/*z*) 273 (M^+, 2.56), 150 (100); IR (neat) 2927, 2857, 1930, 1660, 1602, 1526, 1461, 1349, 1272, 1104, 1011 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{16}H_{19}NO_3^+$ [M^+]: 273.1365; found: 273.1367.

2-Hexyl-1-(3-furanyl)buta-2,3-dien-1-one (**2f**)

The reaction of 1,10-phenanthroline (5.4 mg, 0.03 mmol), 2,2'-bipyridine (4.8 mg, 0.03 mmol), CuCl (6.2 mg, 0.06 mmol), K_2CO_3 (21.3 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.6 mg, 0.06 mmol), and 2-hexyl-1-(3-furanyl)buta-2,3-dien-1-ol (66.2 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2f** (40.4 mg, 61%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.37 (s, 1H), 6.81 (d, J = 1.2 Hz, 1H), 5.21 (t, J = 2.9 Hz, 2H), 2.39–2.27 (m, 2 H), 1.52–1.38 (m, 2H), 1.38–1.18 (m, 6H), 0.87 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 215.8, 186.4, 147.4, 143.0, 126.7, 110.0, 108.1, 80.0, 31.6, 28.9, 27.8, 27.6, 22.6, 14.1 ppm; MS (*m*/*z*) 218 (M^+, 3.49), 95 (100); IR (neat) 2956, 2928, 2857, 1933, 1724, 1645, 1561, 1509, 1458, 1379, 1311, 1163, 1077, 1009 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{14}H_{18}O_2^+$ [M^+]: 218.1307; found: 218.1305.

2-Pentyl-1-(3-thienyl)buta-2,3-dien-1-one (**2g**)

The reaction of 1,10-phenanthroline (5.5 mg, 0.03 mmol), 2,2'-bipyridine (4.8 mg, 0.03 mmol), CuCl (5.9 mg, 0.06 mmol), K_2CO_3 (20.9 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.7 mg, 0.06 mmol), and 2-pentyl-1-(3-thienyl)buta-2,3-dien-1-ol (66.4 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2g** (48.3 mg, 73%) (eluent: petroleum ether/diethyl ether = 50:1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 1.8 Hz, 1H) 7.53 (d, J = 4.8 Hz, 1H), 7.25 (dd, J_1 = 4.8 Hz, J_2 = 3.3 Hz, 1H), 5.16 (d, J = 2.7 Hz, 2H), 2.41–2.32 (m, 2H), 1.56–1.42 (m, 2H), 1.42–1.24 (m, 4H), 0.90 (t, J = 6.6 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.0, 187.1, 141.5, 132.2, 128.2, 125.1, 107.6, 79.6, 31.4, 27.9, 27.5, 22.4, 14.0 ppm; MS (*m*/*z*) 220 (M^+, 3.02), 111 (100); IR (neat) 2956, 2927, 2861, 1933, 1641, 1511, 1460, 1411, 1260, 1082 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{13}H_{16}OS^+$ [M^+]: 220.0922; found: 220.0922.

2-Methyl-1-(1-naphthyl)buta-2,3-dien-1-one (**2h**)

The reaction of 1,10-phenanthroline (5.5 mg, 0.03 mmol), 2,2'-bipyridine (4.8 mg, 0.03 mmol), CuCl (6.2 mg, 0.06 mmol), K_2CO_3 (21.4 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.5 mg, 0.06 mmol), and 2-methyl-1-naphthylbuta-2,3-dien-1-ol (63.6 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2h** (47.2 mg, 74%, an unknown substance could not be separated via column chromatography and the purity of **2h** is 95%, which was determined by ^{1}H NMR with mesitylene as the internal standard): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–8.03 (m, 1H), 7.95–7.81 (m, 2H), 7.61–7.39 (m, 4H), 4.80 (q, J = 2.8 Hz, 2H), 2.11 (t, J = 2.7 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 218.6, 197.5, 136.8, 133.5, 130.6, 130.4, 128.2, 126.9, 126.5, 126.1, 125.3, 123.9, 104.8, 78.2, 13.8 ppm; MS (*m*/*z*) 208 (M^+, 63.16), 155 (100); IR (neat) 3059, 1957, 1930, 1650, 1508, 1285, 1251, 1204, 1155, 1080, 1059 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{15}H_{12}O$ [M^+]: 208.0888; found: 208.0887.

2-Allyl-1-phenylbuta-2,3-dien-1-one (**2i**)

The reaction of 1,10-phenanthroline (5.4 mg, 0.03 mmol), 2,2'-bipyridine (4.6 mg, 0.03 mmol), CuCl (6.1 mg, 0.06 mmol), K_2CO_3 (21.5 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.7 mg, 0.06 mmol), and 2-allyl-1-phenylbuta-2,3-dien-1-ol (55.1 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2i** (41.1 mg, 75%) (eluent: petroleum ether/diethyl ether = 40:1): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 5.98–5.82 (m, 1H), 5.22–5.04 (m, 4H), 3.20–3.14 (m, 2H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.2, 194.1, 138.0, 134.9, 132.1, 129.0, 127.8, 116.4, 105.3, 79.8, 32.5 ppm; MS (*m*/*z*) 184 (M^+, 2.53), 105 (100); IR (neat) 3081, 3062, 2982, 1956, 1931, 1651, 1598, 1578, 1447, 1422, 1316, 1272 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{13}H_{12}O$ [M^+]: 184.0888; found: 184.0889.

2-Butyl-1-phenylnona-2,3-dien-1-one (**2j**)

The reaction of 1,10-phenanthroline (5.6 mg, 0.03 mmol), 2,2'-bipyridine (4.9 mg, 0.03 mmol), CuCl (6.2 mg, 0.06 mmol), K_2CO_3 (21.5 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (14.1 mg, 0.06 mmol), and 2-butyl-1-phenylnona-2,3-dien-1-ol (82.2 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2j** [43] (74.8 mg, 91%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) 7.71 (d, J = 7.8 Hz, 2H), 7.50–7.42 (m, 1H), 7.40–7.32 (m, 2H), 5.36 (t, J = 7.2 Hz, 1H), 2.48–2.30 (m, 2H), 2.16–1.96 (m, 2H), 1.55–1.11 (m, 10H), 0.93 (t, J = 6.9 Hz, 3H), 0.84 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 213.3, 195.7, 138.9, 131.5, 128.8, 127.6, 107.4, 95.0, 31.1, 30.2, 28.6, 28.4, 27.8, 22.31, 22.29, 13.89, 13.86 ppm.

2-Propyl-1-phenylbuta-2,3-dien-1-one (**2k**)

The reaction of 1,10-phenanthroline (49.1 mg, 0.27 mmol), 2,2'-bipyridine (42.6 mg, 0.27 mmol), CuCl (54.2 mg, 0.54 mmol), K_2CO_3 (373.8 mg, 2.7 mmol), dry toluene (9 mL), DBAD (124.4 mg, 0.54 mmol), and 2-propyl-1-phenylbuta-2,3-dien-1-ol (1.0141 g, 5.4 mmol)/dry toluene (9 mL) afforded **2k** (0.7512 g, 74%): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 5.05 (s, 2H), 2.39 (t, J = 7.2 Hz, 2H), 1.62–1.46 (m, 2H), 0.99 (t, J = 7.5 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 217.1, 194.9, 138.3, 131.9, 129.0, 127.8, 106.7, 79.3, 29.9, 21.1, 13.7 ppm; MS (*m*/*z*) 186 (M^+, 6.46), 105 (100); IR (neat) 2961, 2932, 2872, 1933, 1651, 1598, 1578, 1447, 1315, 1271 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{13}H_{14}O^+$ [M^+]: 186.1045; found: 186.1045.

General experimental procedure for the oxidation of allenic alcohols with pure oxygen

3-Hexylocta-1,2-dien-4-one (**2l**)

Typical procedure: 1,10-phenanthroline (6.9 mg, 0.0375 mmol), 2,2'-bipyridine (5.8 mg, 0.0375 mmol), CuCl (5.9 mg, 0.06 mmol), and K_2CO_3 (20.9 mg, 0.15 mmol) were added sequentially to an oven dried Schlenk tube, which was purged with air and refilled with oxygen (twice). Then 1.5 mL of dry toluene was added, the resulting mixture was stirred at rt for 0.5 h which was followed by the sequential addition of DBAD (14.0 mg, 0.06 mmol), 2-hexyl-1-butylbuta-2,3-dien-1-ol (63.8 mg, 0.3 mmol) and 1.5 mL of dry toluene. After stirring at 60 °C for 24 h, the reaction mixture was filtered through silica gel (100–140 mesh) and washed with diethyl ether. Evaporation of the solvent and flash chromatography on silica gel (eluent: petroleum ether/ether = 50:1) afforded **2l** (37.1 mg, 58%) (conv. = 81%, yield = 72% (based on the alcohol consumed)): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.14 (d, J = 2.7 Hz, 2H), 2.62 (t, J = 7.4 Hz, 2H), 2.18–2.09 (m, 2H), 1.60–1.47 (m, 2H), 1.42–1.18 (m, 10H), 0.92–0.78 (m, 6H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.2, 201.3, 108.5, 79.3, 38.9, 31.6, 28.8, 27.8, 27.2, 26.2, 22.5, 22.3, 14.0, 13.8 ppm; MS (*m*/*z*) 208 (M^+, 1.00), 85 (100); IR (neat) 2958, 2929, 2862, 1934, 1679, 1461, 1174 cm^{-1}; HRMS-EI (*m*/*z*) calcd for $C_{14}H_{24}O^+$ [M^+]: 208.1827; found: 208.1828.

4-Pentyl-1-phenylhexa-4,5-dien-3-one (**2m**)

The reaction of 1,10-phenanthroline (6.9 mg, 0.0375 mmol), 2,2'-bipyridine (5.9 mg, 0.0375 mmol), CuCl (6.1 mg, 0.06 mmol), K_2CO_3 (21.4 mg, 0.15 mmol), dry toluene (1.5 mL), DBAD (13.9 mg, 0.06 mmol), and 2-pentyl-1-(phenylethyl)buta-2,3-dien-1-ol (72.7 mg, 0.3 mmol)/dry toluene (1.5 mL) afforded **2m** (43.8 mg, 60%) (conv. = 81%, yield = 74% (based on the alcohol consumed)): liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.22 (m, 2H), 7.22–7.13 (m, 3H), 5.13 (s, 2 H), 3.02–2.85 (m, 4H), 2.22–2.10 (m, 2H), 1.45–1.20 (m, 6H), 0.88 (t, J = 6.5 Hz, 3H) ppm; ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 216.3, 200.1, 141.3, 128.3, 126.0, 108.6, 79.7, 40.9, 31.4, 30.9, 27.4, 26.1, 22.4, 14.0 ppm; MS (*m*/*z*) 242 (M^+, 0.87), 105 (100); IR (neat) 2956, 2928, 2861, 1933, 1678, 1496, 1456, 1171, 1100 cm^{-1}; Anal. calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. found: C, 84.16; H, 9.50.

Supporting Information

Supporting Information File 1

^{1}H and ^{13}C NMR spectra of products prepared.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-7-51-S1.pdf]

Acknowledgements

Financial support from the National Basic Research Program of China (2009CB825300) is greatly appreciated.

References

1. Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds;* Academic Press: New York, 1981.
2. Trost, B. M.; Fleming, I.; Ley, S. V. *Comprehensive Organic Synthesis;* Pergamon: Oxford, 1991; Vol. 7.
3. Fatiadi, A. J. *Synthesis* **1976,** 65. doi:10.1055/s-1976-23961
4. Cainelli, G.; Cardillo, G. *Chromium Oxidations in Organic Chemistry;* Springer: Berlin, 1984.
5. Anastas, P.; Warner, J. *Green Cemistry: Theory and Practice;* Oxford University Press: Oxford, 1998.
6. Blackburn, T. F.; Schwartz, J. *J. Chem. Soc., Chem. Commun.* **1977,** 157. doi:10.1039/C39770000157
7. Peterson, K. P.; Larock, R. C. *J. Org. Chem.* **1998,** *63,* 3185. doi:10.1021/jo971268k
8. Nishimura, T.; Onoue, T.; Ohe, K.; Uemura, S. *J. Org. Chem.* **1999,** *64,* 6750. doi:10.1021/jo9906734
9. ten Brink, G. J.; Arends, I. W. C. E.; Sheldon, R. A. *Science* **2000,** *287,* 1636. doi:10.1126/science.287.5458.1636

10. Muzart, J. *Tetrahedron* **2003,** *59,* 5789. doi:10.1016/S0040-4020(03)00866-4 For a review.
11. Semmelhack, M. F.; Schmid, C. R.; Cortés, D. A.; Chou, C. S. *J. Am. Chem. Soc.* **1984,** *106,* 3374. doi:10.1021/ja00323a064
12. Markó, I. E.; Giles, P. R.; Tsukazaki, M.; Brown, S. M.; Urch, C. J. *Science* **1996,** *274,* 2044. doi:10.1126/science.274.5295.2044
13. Markó, I. E.; Gautier, A.; Dumeunier, R.; Doda, K.; Philippart, F.; Brown, S. M.; Urch, C. J. *Angew. Chem., Int. Ed.* **2004,** *43,* 1588. doi:10.1002/anie.200353458
14. Sheldon, R. A.; Arends, I. W. C. E.; ten Brink, G. J.; Dijksman, A. *Acc. Chem. Res.* **2002,** *35,* 774. doi:10.1021/ar010075n
15. Zhan, B.; Thompson, A. *Tetrahedron* **2004,** *60,* 2917. doi:10.1016/j.tet.2004.01.043
16. Marshall, J. A.; Robinson, E. D. *J. Org. Chem.* **1990,** *55,* 3450. doi:10.1021/jo00298a012
17. Mashall, J. A.; Wang, X. *J. Org. Chem.* **1991,** *56,* 960. doi:10.1021/jo00003a013
18. Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **1995,** *34,* 1581. doi:10.1002/anie.199515811
19. Hashmi, A. S. K.; Schwarz, L.; Choi, J. H.; Frost, T. M. *Angew. Chem., Int. Ed.* **2000,** *39,* 2285. doi:10.1002/1521-3773(20000703)39:13<2285::AID-ANIE2285>3.0.CO;2-F
20. Ma, S.; Zhang, J. *Chem. Commun.* **2000,** 117. doi:10.1039/a908627g
21. Ma, S.; Yin, S.; Li, L.; Tao, F. *Org. Lett.* **2002,** *4,* 505. doi:10.1021/ol0170859
22. Ma, S.; Yu, Z. *Angew. Chem., Int. Ed.* **2002,** *41,* 1775. doi:10.1002/1521-3773(20020517)41:10<1775::AID-ANIE1775>3.0.CO;2-8
23. Ma, S.; Zhang, J.; Lu, L. *Chem.–Eur. J.* **2003,** *9,* 2447. doi:10.1002/chem.200305341
24. Ma, S.; Yu, S.; Yin, S. *J. Org. Chem.* **2003,** *68,* 8996. doi:10.1021/jo034633i
25. Ma, S.; Yu, Z. *Chem.–Eur. J.* **2004,** *10,* 2078. doi:10.1002/chem.200305341
26. Ma, S.; Yu, S. *Org. Lett.* **2005,** *7,* 5063. doi:10.1021/ol052073z
27. Ma, S.; Gu, Z.; Yu, Z. *J. Org. Chem.* **2005,** *70,* 6291. doi:10.1021/jo0507441
28. Sromek, A. W.; Rubina, M.; Gevorgyan, V. *J. Am. Chem. Soc.* **2005,** *127,* 10500. doi:10.1021/ja053290y
29. Dudnik, A. S.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2007,** *46,* 5195. doi:10.1002/anie.200701128
30. Marx, V. M.; Burnell, D. J. *Org. Lett.* **2009,** *11,* 1229. doi:10.1021/ol900029d
31. Alcaide, B.; Almendros, P.; Martínez del Campo, T. *Eur. J. Org. Chem.* **2007,** 2844. doi:10.1002/ejoc.200700128
32. Sampath, M.; Loh, T.-P. *Chem. Commun.* **2009,** 1568. doi:10.1039/b819959k
33. Zhao, J.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2009,** *48,* 7232. doi:10.1002/anie.200902471
34. Russell, S. W.; Weedon, B. C. L. *J. Chem. Soc. D* **1969,** *85.* doi:10.1039/C29690000085
35. Landor, P. D.; Landor, S. R.; Mukasa, S. *J. Chem. Soc. D* **1971,** 1638. doi:10.1039/C29710001638
36. Rannulu, N. S.; Rodgers, M. T. *J. Phys. Chem. A* **2007,** *111,* 3465. doi:10.1021/jp066903h
37. Reetz, M. T.; Li, X. *Angew. Chem., Int. Ed.* **2005,** *44,* 2962. doi:10.1002/anie.200462613
38. Reetz, M. T. *Angew. Chem., Int. Ed.* **2008,** *47,* 2556. doi:10.1002/anie.200704327
39. Li, J.; Zhou, C.; Fu, C.; Ma, S. *Tetrahedron* **2009,** *65,* 3695. doi:10.1016/j.tet.2009.02.061
40. Mukaiyama, T.; Harada, T. *Chem. Lett.* **1981,** *10,* 621. doi:10.1246/cl.1981.621
41. Alcaide, B.; Almendros, P.; Aragoncillo, C.; Redondo, M. C. *Eur. J. Org. Chem.* **2005,** 98. doi:10.1002/ejoc.200400527
42. Yang, Y.; Shen, Z.; Loh, T.-P. *Org. Lett.* **2009,** *11,* 1209. doi:10.1021/ol8027362
43. Isaac, M. B.; Chan, T. H. *J. Chem. Soc., Chem. Commun.* **1995,** 1003. doi:10.1039/C39950001003
44. Ma, S.; Yu, S.; Yin, S. *J. Org. Chem.* **2003,** *68,* 8996. doi:10.1021/jo034633i

License and Terms