DOI: 10.1002/cjoc.201400396

$Co_2(CO)_8$-mediated Selective Reductions of Propargyl Alcohol Derivatives to Alkenes†

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In the presence of $Co_2(CO)_8$ and additives, propargyl alcohol derivatives could be reduced to alkenes in moderate to good yield. The selectivity of this reaction could be controlled by adding different additives: with H_2O as the additive, the major configuration of product is *Z*-alkene; with CF_3COOH as the additive, the major configuration of product is *E*-alkene.

Keywords $Co_2(CO)_8$, propargyl alcohol, reduction, alkene

Introduction

$Co_2(CO)_8$ has attracted great interests from organometallic and synthetic chemists since its discovery by Mond in 1910.[1] As a well known reagent of versatile use, a key property of $Co_2(CO)_8$ is to form a moderately air stable co-alkyne complex with an alkyne substrate. Complexation of alkyne with $Co_2(CO)_8$ can be used to decrease the reactivity of the triple bond. In some cases, cobalt complex protects the alkynes from addition reactions such as reduction and hydroboration.[2] Also it can prevent sensitive endiynes from undergoing undesired Bergman cycloaromatization.[3]

Perhaps the best known cobalt-mediated cycloaddition reaction is the Pauson-Khand reaction discovered in 1971,[4] representing a formal [2+2+1] cycloaddition between an alkyne, alkene and a carbon monoxide as its simplest form. Although the traditional Pauson-Khand reactions usually required high pressure and high temperature conditions, recent advances have allowed significantly milder reaction conditions.[5] In the presence of certain additives, such as *N*-oxides or primary amines, the reaction could proceed at ambient temperature under atmospheric pressure.[6] Also the use of dicobalt hexacarbonyl alkyne unit to stabilize propargylic cations has been noted for almost forty years, and it is commonly referred as the Nicholas reaction when further reacting with a nucleophile to give an alkylated alkyne.[7] Combinational use of Nicholas and Pauson-Khand reactions has been successfully applied in natural product[8] and polycyclic structure[9] synthesis.

Reductive decomplexation of biscobalthexacarbonyl acetylenes into olefins has been rarely reported. In endo-cyclic complexes, the method for reductive decomplexation was high pressure hydrogenation using Rh-catalyst to provide olefinic ethers.[10] Except for Wilkinson catalyst, Isobe also found two new reductive decomplexation of acetylene biscobalthexacarbonyl complexes with tin hydride or silicon hydride.[11] Additional reductive reagents were necessary for these transformations. The example without any reductive additives was reported by Periasamy.[12] The similar transformation occurred only when the substituted group of alkyne contains silane. Herein we reported a conversion from propargyl alcohol derivatives to alkenes mediated by $Co_2(CO)_8$ and additives, in which the *Z*/*E* selectivity of reaction could be controlled by adding different additives.

Experimental

General procedure for the reductive of propargyl alcohol derivatives using H_2O as additive

$Co_2(CO)_8$ (1.6 mmol) was added to a solution of propargyl alcohol (1 mmol) in 4 mL CH_3CN and stirred at r.t. for 30 min. H_2O (6.0 mmol) was added to the solution and stirred at r.t. for 15 min. Then the solution was stirred at reflux temperature until no co-alkyne complex was detected by TLC. The mixture was filled through Büchner funnel, concentrated and purified by flash column chromatography to gain the product.

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Received June 16, 2014; accepted September 17, 2014; published online September 29, 2014.
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cjoc.201400396 or from the author.
† Dedicated to Professor Chengye Yuan and Professor Li-Xin Dai on the occasion of their 90th birthdays.

General procedure for the reductive of propargyl alcohol derivatives using CF_3COOH as additive

$Co_2(CO)_8$ (2.2 mmol) was added to a solution of propargyl alcohol (1.0 mmol) in 4 mL CH_3CN and stirred at r.t. for 30 min. CF_3COOH (6.0 mmol) was added to the solution and stirred at r.t. for 15 min. Then the solution was stirred at reflux temperature until no co-alkyne complex was detected by TLC. The mixture was filled through Büchner funnel, concentrated and purified by flash column chromatography to gain the product.

1-(4-(Prop-1-enyl)phenyl)ethanone (7a) *Z*-**7a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.93 (dd, J=7.2, 1.8 Hz, 3H), 2.60 (s, 3H), 5.87−5.95 (m, 1H), 6.46 (d, J=11.7, 1H), 7.38 (d, J=8.3 Hz, 2H), 7.93 (d, J=8.3 Hz, 2H); *E*-**7a**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.92 (d, J=5.1 Hz, 3H), 2.58 (s, 3H), 6.55−6.32 (m, 2H), 7.40 (d, J=8.3 Hz, 2H), 7.89 (d, J=8.3 Hz, 2H).

1-Methoxy-4-(prop-1-enyl)benzene (7b) *Z*-**7b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.89 (dd, J=1.8, 7.2 Hz, 3H), 3,81 (s, 3H), 5.71 (qd, J=7.2, 11.6 Hz, 1H), 6.38 (d, J=11.6, 1H), 6.87 (d, J=8.7 Hz, 2H), 7.24 (d, J=8.7 Hz, 2H); *E*-**7b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.87 (dd, J=1.6, 7.3 Hz, 3H), 3.77 (s, 3H), 6.09 (qd, J=7.2, 16.0 Hz, 1H), 6.33 (d, J=16.0 Hz, 1H), 6.82 (d, J=7.5 Hz, 2H), 7.24 (d, J=8.7 Hz, 2H).

2-(Prop-1-enyl)naphthalene (7c) *Z*-**7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.99 (d, J=6.8 Hz, 3H), 5.89 (dq, J=11.7, 6.8 Hz, 1H), 6.57 (d, J=11.7 Hz, 1H), 7.47−7.54 (m, 3H), 7.70−7.87 (m, 4H); *E*-**7c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.95 (d, J=6.8 Hz, 3H), 6.37 (dq, J=17.0, 6.8 Hz, 1H), 6.57 (d, J=17.0 Hz, 1H), 7.39−7.84 (m, 7H).

Prop-1-ene-1,3-diyldibenzene (7e) *Z*-**7e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.71 (d, J=7.5 Hz, 2H), 5.85−5.94 (m, 1H), 6.62 (d, J=11.1 Hz, 1H), 7.21−7.40 (m, 10H); *E*-**7e**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.58 (d, J=6.4 Hz, 2H), 6.27−6.51 (m, 1H), 6.46 (d, J=16.4 Hz, 1H), 7.21−7.40 (m, 10H).

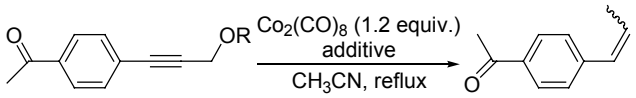
(4-(Benzyloxy)but-1-enyl)benzene (7f) *Z*-**7f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.67 (q, J=6.3 Hz, 2H), 3.57 (t, J=6.6 Hz, 2H), 4.52 (s, 2H), 5.71 (dt, J=7.2, 10.8 Hz, 1H), 6.51 (d, J=10.8 Hz, 1H), 6.98−7.52 (m, 10H); *E*-**7f**: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.53 (q, J=6.6 Hz, 2H), 3.58 (t, J=6.6 Hz, 2H), 4.54 (s, 2H), 6.24 (dt, J=6.9, 15.6 Hz, 1H), 6.51 (d, J=15.6 Hz, 1H), 7.17−7.35 (m, 10H).

(1,2,3-Trideuteroprop-1-ene-1,3-diyl)dibenzene (7e') ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.66 (s, 1H), 7.20−7.37 (m, 10H); EIMS *m*/*z* (%): 197 (M^+); HRMS (EI) calcd for $C_{15}H_1D_3^+$: 197.1284, found: 197.1279; IR (KBr) ν: 2934, 1764, 1106, 703 cm^{-1}.

Results and Discussion

Firstly, we investigated the reduction reaction of propargyl alcohol **1a** under different conditions. We found that the reaction could not proceed when using cyclohexylamine or trimethylamine *N*-oxide as additive (Table 1, entries 1, 2). Trace of alkene **7a** could be detected when using H_2O as additive (Table 1, entry 3), and alkene **7a** could be separated in 38% yield (Z : E= 26 : 74) when using CF_3COOH as additive (Table 1, entry 4). In order to improve the yield, we investigated the reactivity of hydroxyl protected substrates using H_2O or CF_3COOH as additive. For the Ac protected substrate **2a**, the reaction gave mainly *Z*-**7a** (Z : E= 86 : 14) with moderate yield (51%) when using H_2O as additive (Table 1, entry 5), and for the Bz protected substrate **3a**, the reaction gave mainly *E*-**7a** (Z : E= 21 : 79) with moderate yield (50%) when using CF_3COOH as additive (Table 1, entry 8). For other substrates, the reaction only gave *Z*/*E*-**7** with low yields and low selectivities when using H_2O or CF_3COOH as additive (Table 1, entries 6, 7, 9−14).

Table 1 The influences of additives and protecting groups for the reduction of propargyl alcohol derivatives



1a, 2a, 3a, 4, 5 or 6 **7a**

Entry	Substrate	R	Additive (equiv.)	Yield[a]/%	*Z*/*E*[b]
1	**1a**	H	$CyNH_2$ (3.5)	—	—
2	**1a**	H	TMANO (6.0)	—	—
3	**1a**	H	H_2O (3.0)	trace	—
4	**1a**	H	CF_3COOH (3.0)	38	26 : 74
5	**2a**	Ac	H_2O (3.0)	51	86 : 14
6	**2a**	Ac	CF_3COOH (3.0)	47	29 : 71
7	**3a**	Bz	H_2O (3.0)	26	71 : 29
8	**3a**	Bz	CF_3COOH (3.0)	50	21 : 79
9	**4**	Ts	H_2O (3.0)	trace	—
10	**4**	Ts	CF_3COOH (3.0)	34	50 : 50
11	**5**	COOEt	H_2O (3.0)	5	50 : 50
12	**5**	COOEt	CF_3COOH (3.0)	28	50 : 50
13	**6**	CO^{t}Bu	H_2O (3.0)	49	83 : 17
14	**6**	CO^{t}Bu	CF_3COOH (3.0)	37	26 : 74

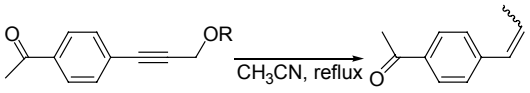
[a] Isolated yield. [b] Determined by ^{1}H NMR.

To further improve the yield, we screened the equivalents of the $Co_2(CO)_8$ and the additive. For the Ac protected substrate **2a** using H_2O as additive, the equivalents of H_2O had no remarkable effect on the selectivity (Table 2, entries 1−4), but the equivalents of $Co_2(CO)_8$ had great influence on the selectivity and yield. With increasing equivalents of $Co_2(CO)_8$, the selectivity of the reaction decreases albeit yield increases (Table 2, entries 5−7). A yield of 82% (Z : E=85 : 15) could be gained by using 1.6 equiv. of $Co_2(CO)_8$ and 6.0 equiv. of H_2O (Table 2, entry 5). For the Bz protected substrate **3a** using CF_3COOH as additive, a yield of 80% (Z : E=12 : 88) could be gained by using 2.2

CHINESE JOURNAL OF CHEMISTRY

equiv. of $Co_2(CO)_8$ and 6.0 equiv. of CF_3COOH (Table 2, entry 10).

Table 2 The influences of equivalents of $Co_2(CO)_8$ and additives



2a or 3a **7**

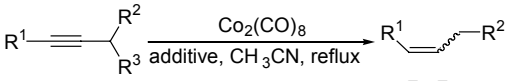
Entry	Substrate	$Co_2(CO)_8$ (equiv.)	Additive (equiv.)	Yield[a]/%	Z/E[b]
1	**2a**	1.2	H_2O (3.0)	51%	86∶14
2	**2a**	1.2	H_2O (5.0)	52%	86∶14
3	**2a**	1.2	H_2O (6.0)	54%	86∶14
4	**2a**	1.2	H_2O (8.0)	29%	86∶14
5	**2a**	1.6	H_2O (6.0)	82%	85∶15
6	**2a**	2.2	H_2O (6.0)	86%	38∶62
7	**2a**	3.0	H_2O (6.0)	85%	26∶74
8	**3a**	1.2	CF_3COOH (3.0)	50%	21∶79
9	**3a**	2.2	CF_3COOH (3.0)	52%	19:81
10	**3a**	2.2	CF_3COOH (6.0)	80%	12∶88
11	**3a**	2.2	CF_3COOH (13.0)	40%	11∶89

[a] Isolated yield. [b] Determined by ^1H NMR.

Then the scope of the selective reduction reaction was examined for a series of propargyl alcohol derivatives **2a**—**2g** and **3a**—**3e** (Table 3). For the Ac protected substrates **2a**—**2g**, the reaction was carried out using 1.6 equiv. of $Co_2(CO)_8$ and 6.0 equiv. of H_2O. For **2b** we mainly got the *E*-**7b** in moderate yield (61%, *Z*∶*E*=33∶67) (Table 3, entry 2), but we could maily gain the *Z*-**7b** in moderate yield by using 1.2 equiv. of $Co_2(CO)_8$ and 3.0 equiv. of H_2O (35%, *Z*∶*E*=78∶22) (Table 3, entry 3); for **2c**, we mainly got the *Z*-**7c** in moderate yield (58%, *Z*∶*E*=84∶16) (Table 3, entry 4); for **2d**, we mainly got the bromide-removed product (Table 3, entry 5). For the secondary alcohol acetate esters **2e** and **2f**, we mainly got the *Z*-**7e** (97%, *Z*∶*E*=86∶14) and *Z*-**7f** (53%, *Z*∶*E*=91∶9) in moderate to high yield (Table 3, entries 6, 7). The reduction of alkyl substituted propargyl alcohol acetate ester **2g** was accompanied with alkene rearrangement product (Table 3, entry 8). For the Bz protected substrates **3a**—**3e**, the reaction was carried out using 2.0 equiv. of $Co_2(CO)_8$ and 6.0 equiv. of CF_3COOH. For **3b** and **3c**, we mainly got the *E*-**7b** (36%, *Z*∶*E*=16∶84) and ***E***-**7c** (71%, *Z*∶*E*=24∶76) in moderate to high yield (Table 3, entries 10, 11); for **3d**, we maily got the bromide-removed product (Table 3, entry 12). For the secondary alcohol benzoate easter **3e**, we got the *E*-**7e** in only low yield (11%, *Z*∶*E*=39∶61) (Table 3, entry 13).

In effort to understand the reaction mechanism, we carried out some other experiments. We found that the reduction reaction could not procceed for simple alkyne 1-(4-((trimethylsilyl)ethynyl)phenyl)ethanone instead of propargyl alcohol derivatives when using H_2O as additive. For the **2e**, we only got product **7e'** in 94% yield containing three deutium atoms when using D_2O as the additive, which could prove that the water is the hydrogen source (Scheme 1). The research of the reaction mechanism is still in process.

Table 3 Selective hydrogenation and reduction of propargyl alcohol derivatives

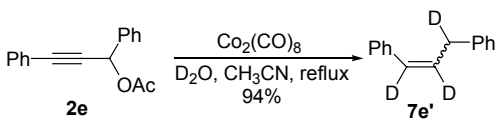


2a-2g or 3a-3e **7a-7g**

Entry	Substrate	Product	Yield[a]/%	Z/E[b]
1[c]	**2a**: R^1=4-Ac-phenyl, R^2=H, R^3=Ac	**7a**	82	85∶15
2[c]	**2b**: R^1=4-MeO-phenyl, R^2=H, R^3=Ac	**7b**	61	33∶67
3[d]	**2b**: R^1=4-MeO-phenyl, R^2=H, R^3=Ac	**7b**	35	78∶22
4[c]	**2c**: R^1=2-naphthyl, R^2=H, R^3=Ac	**7c**	58	84∶16
5[c]	**2d**: R^1=2-Br-phenyl l, R^2=H, R^3=Ac	**7d**	—	—
6[c]	**2e**: R^1=phenyl, R^2=phenyl, R^3=Ac	**7e**	97	86∶14
7[c]	**2f**: R^1=phenyl, R^2=$BnOCH_2$, R^3=Ac	**7f**	53	91∶9
8[c]	**2g**: R^1=phenethyl, R^2=phenyl, R^3=Ac	**7g**	—	—
9[e]	**3a**: R^1=4-Ac-phenyl, R^2=H, R^3=Bz	**7a**	80	12∶88
10[e]	**3b**: R^1=4-MeO-phenyl, R^2=H, R^3=Bz	**7b**	36	16∶84
11[e]	**3c**: R^1=2-naphthyl, R^2=H, R^3=Bz	**7c**	71	24∶76
12[e]	**3d**: R^1=2-Br-phenyl l, R^2=H, R^3=Bz	**7d**	—	—
13[e]	**3e**: R^1=phenyl, R^2=phenyl, R^3=Bz	**7e**	11	39∶61

[a] Isolated yield. [b] Determined by ^1H NMR. [c] The reaction was carried out using 1.6 equiv. of $Co_2(CO)_8$ and 6.0 equiv. of H_2O. [d] The reaction was carried out using 1.2 equiv. of $Co_2(CO)_8$ and 3.0 equiv. of H_2O. [e] The reaction was carried out using 2.2 equiv. of $Co_2(CO)_8$ and 6.0 equiv. of CF_3COOH.

Scheme 1 Reduction of the propargyl alcohol derivatives using D_2O as additive



2e **7e'**

Conclusions

In conclusion, the conversion of propargyl alcohol derivatives to alkenes mediated by $Co_2(CO)_8$ and different additive with good yield and *Z*/*E* ratio was demonstrated. When using H_2O as additive, *Z*-alkene was the main-

product, and when using CF_3COOH as additive, *E*-alkene was the main-product.

Acknowledgement

This work was supported by the National Basic Research Program of China (973-2010CB833200 and 973-2010CB833300), the National Natural Science Foundation of China (21102167), the Science and Technology Commission of Shanghai Municipality (12DZ1930902), Shanghai Green Chemical Engineering Technology Research Center and the Knowledge Innovation Program of the Chinese Academy of Sciences.

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(Pan, B.; Fan, Y.)

