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Manganese-catalyzed ring-opening carbonylation of cyclobutanol derivatives

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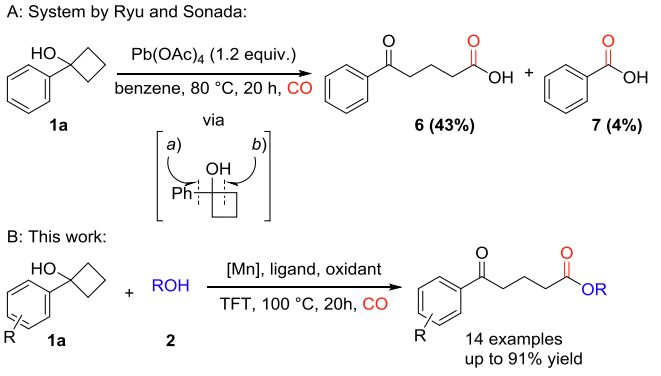
ABSTRACT

Herein, we report a manganese-catalyzed ring-opening carbonylation of cyclobutanol derivatives through cyclic C—C bond cleavage. The reaction happens via a radical-mediated pathway to selectively generate 1,5-ketoesters. A variety of substrates with substituents on the aromatic ring reacted with linear alcohols of different chain lengths. Obtained aliphatic esters are very attractive since they are usually difficult to access.

Introduction

The development of catalysts with abundant and therefore inexpensive 3d transition metal complexes is a good alternative to the extensively researched use of noble metals [1]. Such systems would be particularly attractive in combination with low-cost commercially available ligands and give improved reaction efficiency and reactivity [2]. Catalytic ring-opening reactions are highly efficient because the starting material is fully incorporated into the target molecule. Tertiary cycloalkanols caught our interest, which have proven to be privileged starting materials for oxidative ring opening reactions [3]. The using of palladium catalysts [4] and rhodium catalysts [5] have been well established in this research field. However, early publications showed that it is possible to use non-noble 3d transition metals such as Mn(III) [6], Cr(IV) [7] or V(V) [8] to induce single-electron oxidization of cyclobutanol resulting in a ring-opened free-radical intermediate. Recently, some successes have been reported with catalysts based on Mn [9] or Ag [10] to generate distally functionalized ketones. With regard to carbonylation reactions, ring opening or expansion of epoxides were reported and allow the synthesis of products with high added value (e.g. lactones [11] or succinic anhydrides [12]). The carbonylative cleavage of cyclobutanols is more challenging and much less explored. To the best of our knowledge, only one synthetic pathway was reported by Ryu and Sonada in 1994. The carbonylation could be achieved using 1.2 equivalents of Pb $(OAc)_4$ (LTA) as the one electron oxidation system and catalyst [13]. Phenylcyclobutanol **1a** could be successfully converted into the desired 4-benzoylbutyric acid **6** in 43% yield and benzoic acid **7** as the by-product in 4% yield. From this it was concluded that β-scission *a)* was a minor competitive reaction (Scheme 1). This system faces obvious drawbacks concerning the selectivity and leads to relatively low yields, besides the use of LTA in stoichiometric quantities, which is very toxic and should be avoided concerning green chemistry. In continuation of our research on first row transition-metal-catalyzed carbonylations, we succeeded in designing a new Mn-catalyzed method for 1,5-ketoesters production. The above mentioned drawbacks could be eliminated.



Scheme 1. Ring-opening carbonylation of cyclobutanol.

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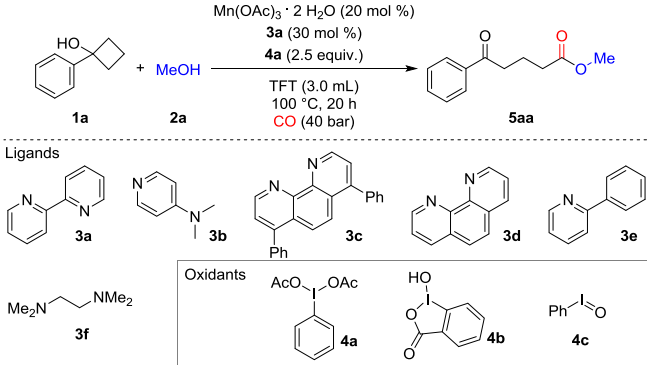
0040-4039/

Results and discussion

For our preliminary studies we have chosen 1-phenyl-cyclobutanol **1a** as the model substrate to establish this procedure [9,14]. We conducted comprehensive optimization of the reaction conditions that are outlined in Table 1. Of all the manganese-based catalysts tested, manganese acetate has proven to be the most effective one (entries 1–5). To provide a more efficient catalytic system, we examined various commercially available ligands (entries 6–12, **3a**–**3f**). The *N*,*N*-bidentate ligands (**3c**, **3d** and **3f**) tested all gave worse results. The uses of simple pyridine as the ligand could not futher improve the yield (entries 10–12). In order to demonstrate the importance of the ligand to be bidentate, 2-phenylpyridine **3e** was used, which differs from **3a** only by a missing nitrogen, but the yield was 11% lower. With a monodentate ligand having a strong electron-donating group in unobstructed *para*-position such as DMAP **3b**, it was possible to get the same results as with BiPy (entry 6). The effect of different oxidants was explored subsequently. In line with the recently reported results for oxidative ring-opening reactions [9a], the hypervalent iodine oxidants (entry 13, **4b**) stand out due to their high reactivity. It is noteworthy that $Ce(SO_4)_2$ provided similar results compared to iodosylbenzene **4c** (entries 13–15). PIFA ((bis(trifluoroacetoxy)iodo)benzene) was tested as oxidant in our system as well, but only 15% of the desired product could be obtained. With the suitable ligand and oxidant at hand, we started a thorough screening of solvents. Trifluorotoluene (TFT), which was used from the beginning, emerged as the best solvent. However, the same yield could be achieved with *m*-xylene (51%, entry 16). Interesting regarding green chemistry would be if a mixture of isomers would give comparable results, since xylenes are petrochemically produced on large scale by catalytic reforming. Other tested solvents all gave decreased yields (entries 16–20). Interestingly, the use of less polar "non-fluorinated" toluene resulted in a significantly lower yield (31%, entry 17). In a comparative reaction with methanol as reactant and solvent, only a minor amount of desired product was generated (8%, entry 20). Finally, the CO pressure was increased from 40 to 60 bar and the yield improved dramatically (80%, entry 21). In order to establish direct comparability with the aforementioned system of Ryu and Sonada, LTA was tested under the final conditions and lead to a low yield here (33%, entry 22).

Table 1
Optimization of Reaction Conditions.



Entry[a]	Deviation from standard conditions	Yield (%)[b]
1	None	51
2	$Mn(CO)_5Br$ as catalyst	41
3	$MnCl_2$ as catalyst	38
4	$Mn(acac)_2$ as catalyst	26
5	$MnBr_2$ as catalyst	19
6	DMAP **3b** as ligand	51
7	Batophen **3c** as ligand	50
8	1,10-Phenantroline **3d** as ligand	41
9	2-Phenylpyridine **3e**	41
10	Pyridine as ligand	36
11	No ligand	34
12	TMEDA **3f** as ligand	27
13	BI-OH **4b** as oxidant	34
14	$Ce(SO_4)_2$ as oxidant	28
15	**4c** as oxidant	27
16	*m*-Xylene as solvent	51
17	Toluene	31
18	Dimethylcarbonate	26
19	Dioxane	25
20	MeOH	8
21	CO (60 bar)	80 (79[c])
22	CO (60 bar), $Pb(OAc)_4$ **4e** as oxidant	33

[a] Unless otherwise noted, all the reactions were conducted on a 0.2 mmol scale in the presence of the alcohol **2** (5.0 mmol) using an autoclave

[b] GC yields were determined by GC-FID analysis using *n*-hexadecane as internal standard

[c] The isolated yield of isolated product **5aa** was obtained from a reaction on a 0.3 mmol scale.

With the optimal conditions in hand, our method was applied on several substrates in combination with different alcohols (Table 2) [15]. The reaction was studied with linear alcohols of different chain lengths (**2a**–**2e**) and several substrates with substituents on the aromatic ring of different electronic properties (**1a**–**1g**) including di-substituted ones (**1e**, **1g**). In general, good yields of the corresponding products with different aliphatic alcohols (**5aa**–**5ae**) can be achieved. Among them, ester product **5ac** could be obtained in an excellent yield of 91% (entry 3). To our delight, it was also possible to use long chained alcohols like *n*-octanol **2e** to generate the elusive aliphatic ester **5ae** in a synthetically useful yield (73%, entry 5). However, only trace amount of the desired product could be detected when i-proponal or *tert*-butanol was tested. Our carbonylation system exhibited functional group tolerance with fluoro and methoxy groups on the aromatic ring. Encouraged by the good results with *n*-butanol, *n*-butanol and methanol were tested with the substrates, respectively. Remarkably, the trend of increased reactivity in combination with *n*-butanol and the associated increased yields also continued for the various substituted cyclobutanols. In case of the alkyl-substituted substrate **1c** together with methanol **2a**, the corresponding product **5ca** was obtained in moderate yield (55%, entry 7) and in presence of *n*-butanol corresponding product **5cc** could be obtained in a good yield (74%, entry 8). This phenomenon could also be observed for single and double substituted products, with a dramatic improvement in yields for *para*-methoxy substituted esters **5da** (40%, entry 9) and **5dc** (89%, entry 10). The same was true for the *meta*-fluoro substituted esters **5fa** (30%, entry 13) and **5fc** (86%, entry 14). In both cases the respective yield has more than doubled when *n*-butanol was used instead of methanol. Di-substituted products with a methoxy group in *para*- and *meta*-position **5ea** (31%, entry 11) and **5ec** (46%, entry 12) also showed an improvement, but less significant. In the case of difluorosubstituted substrate, the desired product could only be isolated in traces, even with *n*-butanol **5gc** (<12%, entry 15). Additionally, alkyl substituted and non-substituted cyclobutanol were tested under standard conditions as well, but no desired products could be detected.

A plausible mechanism is proposed based on experimental observations and literatures (Scheme 2). First the hypervalent iodine reagent oxidizes the catalyst and together with cyclobutanol **a** to give the Mn(V) species **b**. Subsequent single-electron transfer (SET) releases the cyclobutyloxy radical **c**, which undergoes a 'radical clock'-type ring opening tautomerization, leading to alkyl radical **d** [14a]. Under the given pressure, it is likely that together with CO the acyl radical **e** will be formed. It can coordinate to the manganese center to generate **f**. Then X ligand exchange leads to a Mn(V) complex **g** which is able to give the final ester product **h**

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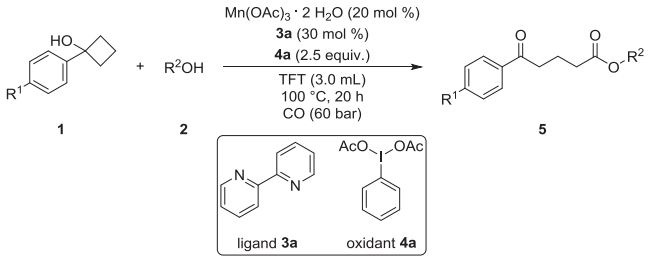
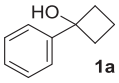
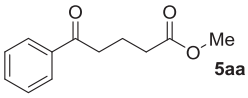
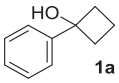
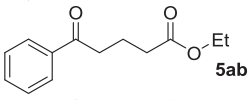
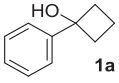
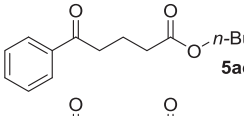
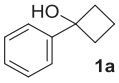
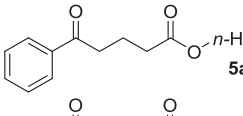
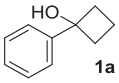
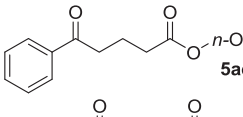
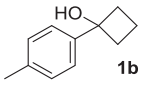
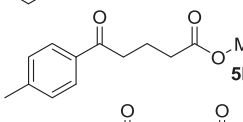
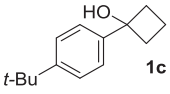
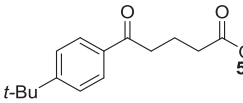
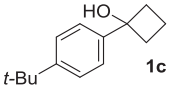
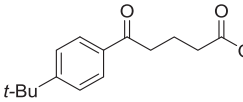
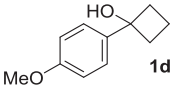
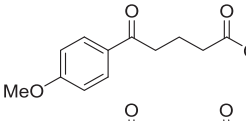
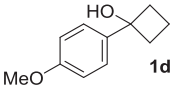
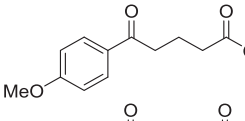
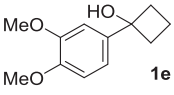
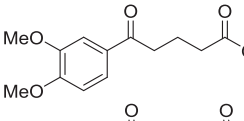
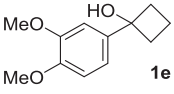
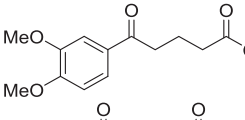
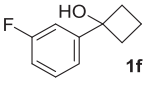
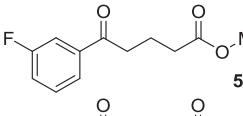
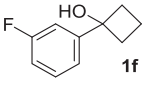
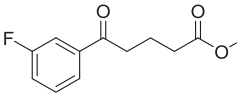
Table 2
Manganese-Catalyzed Ring-Opening Carbonylation of Cyclobutanol Derivatives: Substrate Scope.



Entry	Cyclobutanol	Alcohol	Product	Yield [%][b]
1	 **1a**	HO–Me **2a**	 **5aa**	79
2	 **1a**	HO–Et **2b**	 **5ab**	61
3	 **1a**	HO–*n*-Bu **2c**	 **5ac**	91
4	 **1a**	HO–*n*-Hex **2d**	 **5ad**	70
5	 **1a**	HO–*n*-Oct **2e**	 **5ae**	73
6	 **1b**	HO–Me **2a**	 **5ba**	47
7	 **1c**	HO–Me **2a**	 **5ca**	55
8	 **1c**	HO–*n*-Bu **2c**	 **5cc**	74
9	 **1d**	HO–Me **2a**	 **5da**	40
10	 **1d**	HO–*n*-Bu **2c**	 **5dc**	89
11	 **1e**	HO–Me **2a**	 **5ea**	31
12	 **1e**	HO–*n*-Bu **2c**	 **5ec**	46
13	 **1f**	HO–Me **2a**	 **5fa**	30
14	 **1f**	HO–*n*-Bu **2c**	 **5fc**	86

(*continued on next page*)

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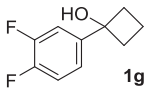
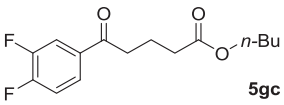
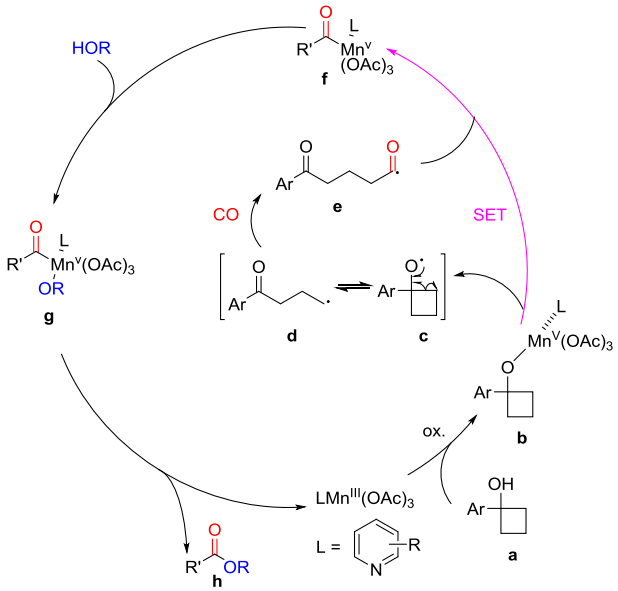
Table 2 (*continued*)

Entry	Cyclobutanol	Alcohol	Product	Yield [%][b]
15	 **1g**	HO−*n*-Bu **2c**	 **5gc**	<12

[a] Unless otherwise noted, all the reactions were conducted on a 0.3 mmol scale in the presence of the alcohol **2** (5.0 mmol) using an autoclave.
[b] Isolated yields.



Scheme 2. Proposed mechanism for the ring-opening carbonylation of cyclobutanol.

after reductive elimination. Evidence for the formation of benzoic acid via β-scission as a competitive reaction could not be provided [13]. We assume that our catalytic system selectively generates cyclobutyloxy radical **c** during the step of single-electron transfer. However, we also can not excluded a Mn(III)/Mn(II) catalytic cycle.

In conclusion, we described a method for the ring-opening carbonylation of cyclobutanols. Several elusive aliphatic 1,5-ketoesters could be generated with our system, using simple bipyridine as ligand and manganese acetate as catalyst both from chemical feedstock.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2019.02.028.

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[15] General procedure: A 4 mL screw-cap vial equipped with a septum, a small cannula, and a stirring bar was charged with starting material **1** (300 μmol), BiPy (30 mol%, 14.1 mg), $Mn(OAc)_3{\cdot}2H_2O$ (20 mol%, 16.1 mg), TFT (3 mL), PIDA **4a** (750 μmol, 242 mg), and alcohol **2** (5 mmol). The vial was sealed, connected to atmosphere with a cannula, purged with argon three times, placed on an alloy plate, and transferred into a 300 mL stovetop autoclave (4560 series from Parr instrument company®). The autoclave was flushed two times with argon and two times with CO. It was then placed into an aluminum block on a magnetic stirrer. The reaction mixture was stirred (600 rpm) for 20 h at 100 °C and under pressure of 60 bar CO. Then it was cooled to room temperature and the pressure was released carefully. As an internal standard, n-hexadecane (30 μL, 100 μmol) was added to the reaction mixture. An aliquot (1 mL) of the mixture was purified with a pipette flash column using EtOAc (3 mL) as the eluent. Samples prepared in this way were subjected to GC analysis. Isolated products were obtained by column chromatography on silica gel.