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Efficient Synthesis of γ-Lactones by Cobalt-Catalyzed Carbonylative Ring Expansion of Oxetanes under Syngas Atmosphere

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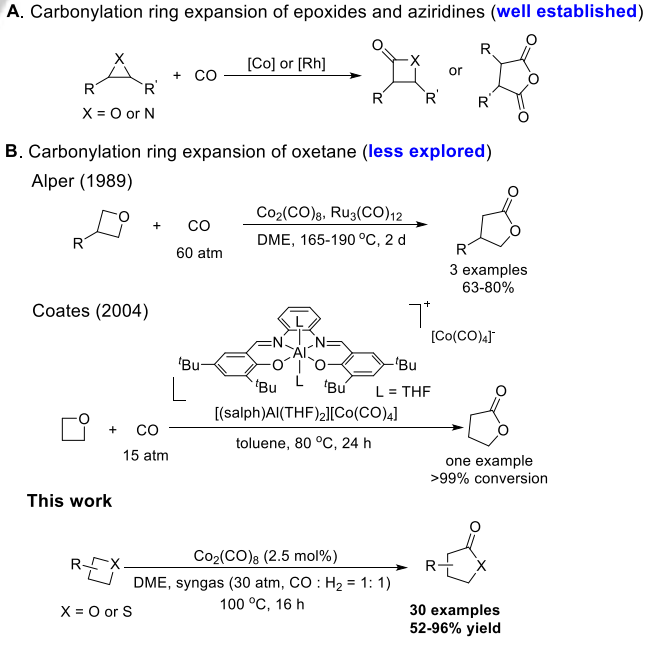
Abstract: A practical route from oxetane or thietane to γ-(thio)butyrolactone via solvated-proton-assisted cobalt-catalyzed carbonylative ring expansion under syngas atmosphere has been established. A wide variety of γ-(thio)butyrolactones can be afforded in good to excellent yield. The versatility of this method has been well demonstrated in the synthesis of intermediates for natural product Arctigenin and pharmaceuticals Baclofen and Montelukast. The observed promoting effect of glycol ether solvent has been rationally interpreted.

The γ-lactone frameworks, in particular 4-substituted γ-lactones, are versatile skeletons and building blocks for pharmaceuticals, fine chemicals, and polymeric materials.[1] These *γ*-lactones can also be important intermediates to prepare *γ*-amino acid, which are ubiquitous in pharmaceutically active molecules.[2] Comparing with those conventional accesses to *γ*-lactone, such as Baeyer-Villiger oxidation of cyclobutanones,[3] nucleophilic addition of organometallic reagent to 2,5-dihydrofuranone[4] and reduction of 2,5-dihydrofuranone,[5] transition-metal-catalyzed carbonylative ring expansion of oxetane, as a more straightforward path, has the merits of quantitative atom economy, broader functional-group tolerance, easier accessibility of substrate as well as avoiding the usage of stoichiometric additives. Oxetanes are readily available through ring closing of 1,3-diols or Paternò-Büchi reaction between olefin and carbonyl compound.[6] Therefore, we envisioned that carbonylative ring expansion of oxetane by cobalt carbonyl catalyst, as a practical waste- and noble-metal-free protocol, would be a potent alternative to the above-mentioned routes (Scheme 1).

In contrast to the well-established transition metal-catalyzed carbonylative ring expansion of epoxides[7] or aziridines[8] as well as its asymmetric catalysis variant[9] mainly based on the corporation between Lewis acid and cobalt carbonyl complexes, carbonylative ring expansion of oxetane was far less developed (Scheme 1) and more challenging due to the lower reactivity of four-membered ring than three-membered ring from ring-strain relief (inherent ring strain: 106 kJ·mol^{-1} for oxetane, 112 kJ·mol^{-1} for epoxides).[6] Until now, regarding carbonylative ring expansion of oxetane, only two cases respectively exploiting cobalt-ruthenium[10] and cobalt-aluminium binary catalyst systems were described (Scheme 1).[11] High pressure and temperature were indispensable to the cobalt-ruthenium catalyst system. For fabricating coordinative Lewis-acid catalyst, delicate salophen ligand had to be introduced into the cobalt-aluminium catalyst system and only one unsubstituted oxetane was probed. Thus, simpler and more practical catalyst system was yet to be achieved.

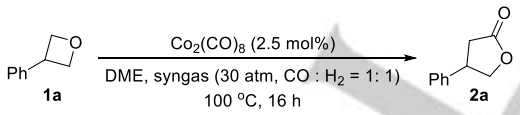
Activating the four-membered ring is the crucial precondition for the carbonylative ring expansion of oxetane. Besides the coordination with Lewis-acid catalysts, protonating oxetane by strong Brønsted acid is the other potential but long-time overlooked solution to implement the effective activation of oxetane substrate. More than being able to catalyse carbonylative reaction, $HCo(CO)_4$ also possesses the aqueous Brønsted acidity that comparable to hydrogen chloride.[12a] Herein, we elaborated a facile protocol for the carbonylative conversion of oxetane and thietane to γ-(thio)lactone by making full use of the dual function of in-situ generated $HCo(CO)_4$ catalyst. Its application in the synthesis of natural product and pharmaceutical compounds was demonstrated. Significant solvent effect on the reactivity of oxetane carbonylative ring expansion was observed and rationalized.



Scheme 1. Carbonylative ring expansion of strained small rings.

Initially, 3-phenyloxetane (**1a**) and $Co_2(CO)_8$ were employed as the model substrate and the pre-catalyst for condition optimization (Table 1). Considering that $HCo(CO)_4$ can be afforded from the hydrogenolysis of $Co_2(CO)_8$ and inspired by the previous report about the stochiometric reaction of oxetane with $HCo(CO)_4$ and carbon monoxide to give γ-hydroxy cobalt acyl complex,[12] we investigated the reaction under syngas atmosphere without any additives. Gratifyingly, β-phenyl-γ-butyrolactone (**2a**) was obtained in good yield (entry 1). In contrary, replacing syngas with carbon monoxide completely suppressed the conversion of oxetane (entry 2). Using reductive boron-, aluminum- or phenylsilyl hydrides instead of H_2 led to the undesired ring-opening reduction of oxetane and no target product was detected (entry 3). These patterns indicated the indispensability of hydrogen gas to the formation of $HCo(CO)_4$. Phosphine ligands were utilized to afford the less-acidic phosphine-substituted cobalt carbonyl hydride complexes $HCo(CO)_3L$ (L = phosphine ligand).[12a] Basic *N*-heteroaromatic compounds were utilized to facilitate $Co_2(CO)_8$ disproportion to Co(I) or Co(II) Lewis acid (e.g. $[Co(CO)_4(py)]^+$ and $[Co(py)_6]^{2+}$) and carbonylation catalyst $[Co(CO)_4]^-$ [13] or employed to promote product yield in cobalt-catalyzed carbonylation of epoxides.[14] Adding these phosphine ligands or *N*-heteroaromatic compounds had little further improvement on the yield of **2a** (entries 4-7). Fewer product was formed when $Co_2(CO)_8$ was substituted with cobalt(II) salts (Table 1, entries 8-10). Other group VIII metal carbonyl clusters were also attempted to replace $Co_2(CO)_8$, but none of them had satisfying catalytic activity under syngas atmosphere (entries 11-13). It is noteworthy that [(salph)Al(THF)$_2$][Co(CO)$_4$] catalyst developed by Coates[11a] fails to exhibit any catalytic activity for this substituted oxetane substrate in such conditions (entry 14) or conditions reported by Coates[11a] (entry 15). This pattern implies that the combination of Lewis acid and carbonylation catalyst is not suitable for the carbonylative ring expansion of oxetanes. When reducing reaction temperature to 60 °C, the yield of **2a** dropped to only 34% (entry 16).

Table 1. Comparison of reaction conditions



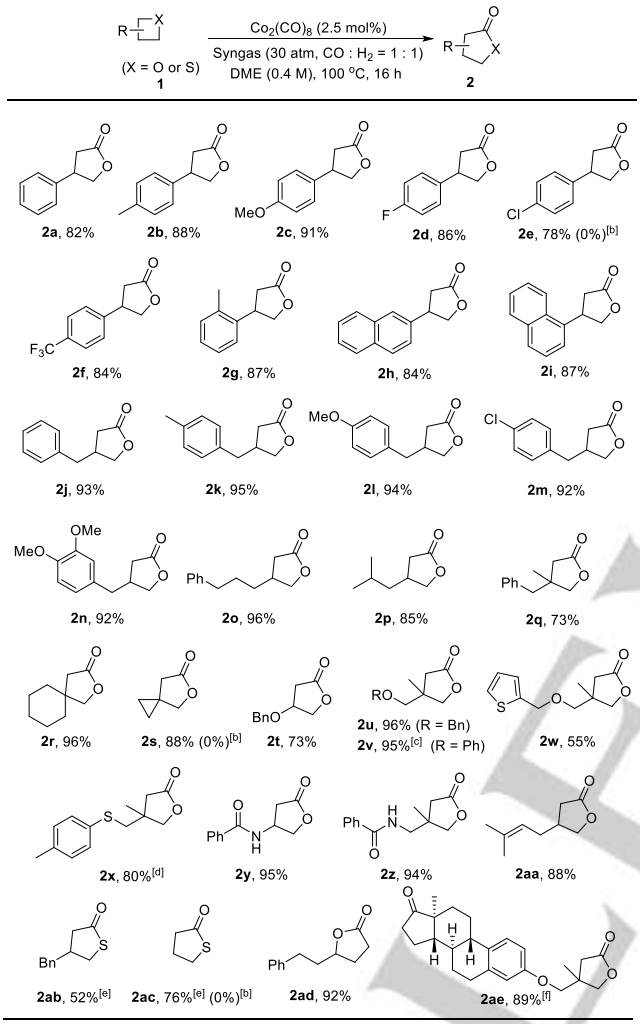
entry	Deviation from standard conditions	Yield (%)
1	None	85 (82)[a]
2	CO (30 bar) instead of syngas	0
3	$NaBH_4$, $LiAlH_4$ or $PhSiH_4$ (10 mol%) instead of H_2	0
4	Adding PPh_3 (10 mol%)	0[b]
5	Adding DPPE (5 mol%)	0[b]
6	Adding 3-hydroxypyridine (10 mol%)	12[b]
7	Adding pyrazole (10 mol%)	75[b]
8	$CoCl_2$ instead of $Co_2(CO)_8$	0
9	$Co(acac)_2$ instead of $Co_2(CO)_8$	0
10	$Co(OAc)_2$ instead of $Co_2(CO)_8$	13
11	$Ru_3(CO)_{12}$ instead of $Co_2(CO)_8$	0
12	$Fe_2(CO)_9$ instead of $Co_2(CO)_8$	0
13	$Mn_2(CO)_{10}$ instead of $Co_2(CO)_8$	0
14	[(salph)Al(THF)$_2$][Co(CO)$_4$] (2 mol%) instead of $Co_2(CO)_8$	0[c]
15	[(salph)Al(THF)$_2$][Co(CO)$_4$] (2 mol%) instead of $Co_2(CO)_8$	0[d]
16	Performed at 60 °C	34

Reaction conditions: **1a** (0.4 mmol), $Co_2(CO)_8$ (0.01 mol), DME (1 mL), 100 °C, 16 h. Conversions and yields were determined by GC. DME= dimethoxyethane; DPPE = 1,2-bis(diphenylphosphino)ethane; THF = tetrahydrofuran [a] yield of isolated **2a**. [b] 30 atm syngas (CO : H_2 = 1: 1). [c] 30 atm CO. [d] Using the conditions of ref. 11a (toluene, 15 atm CO, 80 °C, 24 h).

With the optimized reaction conditions in hand, the substrate diversity of this carbonylative ring expansion protocol was surveyed (Table 2). This method is applicable to various 3-substituted oxetanes and is also suitable for 2-substituted oxetane. Oxetanes possessing substituted aryl and benzyl groups at 3-position can be well tolerated (**2a-n**). Among these carbonylative expansion products, **2e** and **2n** are the key intermediates in the synthesis of pharmaceutical Baclofen[15] and natural product Arctigenin.[16] Oxetanes with mono-alkyl substituents or di-substituents at 3-position can be converted to corresponding β-substituted γ-butyrolactones in good yields (**2o-q**). This carbonylative reaction proceeded smoothly in the ring expansion of spiro-oxetane substrates to spiro-γ-butyrolactone (**2r** and **2s**). Strained cyclopropane ring remains intact in the reaction conditions. Oxetane bearing functional group, such as benzyloxy, phenoxy, thienyl, thioether and amide, gave the γ-butyrolactone products in good to excellent yields (**2t-z**). More impressively, the alkenyl group survived under the reductive syngas atmosphere and the desired γ-butyrolactone **2aa** was obtained in 88% yield. Moreover, the remarkable versatility of this carbonylative ring expansion reaction is reflected on the conversion of thietane (**2ab** and **2ac**) and 2-substituted oxetane (**2ad**). Thietane is even less strained than oxetane (inherent ring strain: 80.3 kJ/mol for thietane).[17] By highly correlated wave function based ab initio method,[18] we evaluated the free-energy changes (ΔG) of carbonylative ring expansion of oxetane and thietane with CO to generate γ-butyrolactone and γ-thiobutyrolactone. It shows that ΔG of γ-thiobutyrolactone is less exothermic than γ-butyrolactone by about 13 kcal/mol (details see Table S1 of SI). These figures imply that the carbonylative ring-expansion of thietane is more arduous. By elevating the loading of cobalt carbonyl catalyst and conducting the reaction at elevated temperature, the transformation from thietane to γ-thiobutyrolactone was also accomplished in fair to good yield (**2ab** and **2ac**). This simple approach avoids the usage of both costly platinum Lewis acid and bidentate phosphine ligand in the carbonylative ring expansion of thietane,[19] and it still remains comparable catalytic effect. For 2-phenethyloxetane (**2ad**), the carbonyl group was inserted exclusively from the less steric-hindered side. In the carbonylative ring expansion of estrone-attached 3-hydroxymethyl-3-methyloxetane, the ketone moiety of estrone fragment was unaffected in syngas atmosphere and 89% product yield was attained (**2ae**). One important

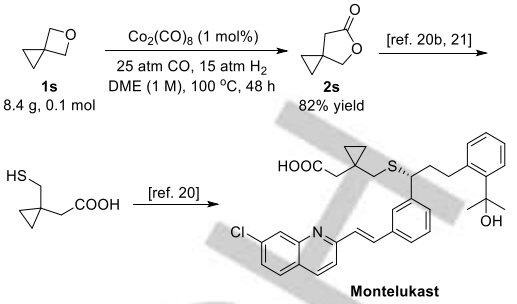
comparison should be underlined that by employing the cobalt-aluminium binary catalyst [(salph)Al(THF)$_2$][Co(CO)$_4$] and the reaction conditions reported by Coates and co-workers, neither the conversion of substrates **1e**, **1s** and **1ac** nor the corresponding carbonylative ring expansion products **2e**, **2s** and **2ac** was observed or obtained.

Table 2. Carbonylative ring expansion of various oxetanes and thietanes by in-situ generated HCo(CO)$_4$.



Unless otherwise noted, reaction conditions were as follows: **1** (0.4 mmol), Co$_2$(CO)$_8$ (0.01 mmol), DME (1 mL), syngas (30 atm, CO : H$_2$ = 1 : 1), 100 °C, 16 h. The isolated yields of product **2**. [b] [(salph)Al(THF)$_2$][Co(CO)$_4$] (0.01 mmol), CO (30 atm), toluene (1 mL), 80 °C, 16 h. [c] Co$_2$(CO)$_8$ (0.02 mmol). [d] Co$_2$(CO)$_8$ (0.04 mmol). [e] Co$_2$(CO)$_8$ (0.02 mmol), diglyme instead of DME, 140 °C. [f] Co$_2$(CO)$_8$ (0.08 mmol), 120 °C

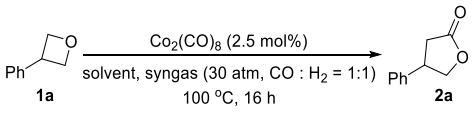
To further manifest the practicality of this protocol, carbonylative synthesis of **2s** was carried out on the multigram scale in the presence of 1 mol% Co$_2$(CO)$_8$ (Scheme 2). The resulting γ-lactone was produced in 82% yield. This γ-lactone can be further converted to (1-(mercaptomethyl)cyclopropyl) acetic acid, one of the building blocks for synthesizing asthma treatment medicine Montelukast.[20,21] In comparison to the registered patents,[20b,22] our developed carbonylative method provides a more straightforward and atom-economic route to the building block for the synthesis of Montelukast.



Scheme 2. Large-scale preparation of the key building block for Montelukast.

During the course of investigating substrate scope, we noticed that diglyme, the DME-analogue solvent with higher boiling point, was also suitable solvent for the carbonylative ring expansion. This phenomenon drew out interest to probe the role of solvent in this reaction. Once HCo(CO)$_4$ is in-situ formed through the hydrogenolysis of Co$_2$(CO)$_8$ under syngas atmosphere,[12] its dissociation to active carbonylation catalyst [Co(CO)$_4$]$^-$ and solvated proton as well as the subsequent ion complexing between oxetane substrate and solvated proton are key to the carbonylative conversion of oxetane. Following this deduction, the correlation between solvent and reactivity was assessed by using **1a** as the model oxetane substrate (Table 3). Within expectation, DME-analogue solvent diglyme can also be the effective solvent to achieve the full conversion of substrate and good chemoselectivity (entry 2). Opposite to the results of these two solvents, no conversion of **1a** was detected in other common monoether solvents (entries 3-6) or non-polar hydrocarbon solvents (entries 7 and 8). In methanol, undesired MeOH-involved ring-opening methoxylation and MeOH-initiated oligomerization products instead of carbonylative ring-expansion product was generated (entry 9). This series of results indicates that the carbonylative ring-expansion reactivity of oxetane is evidently dependent on solvent. Since DME and diglyme retain higher hydrogen-bond basicity (i.e. Abraham basicity)[23] than other ether solvents, we rationally conjecture that glycol-ether-solvated proton, as the Brønsted acid species to activate oxetane substrate, is crucial to gain the good reactivity. As a sort of cyclic glycol ether, crown ether was reported to own the capacity of binding proton.[24] To verify our conjecture, one equivalent 12-crown-4 or 18-crown-6 was added into 1,4-dioxane, one of the poor ether-type solvents for this ring-expansion reaction. Indeed, adding crown ether into 1,4-dioxane solvent boosts the carbonylative conversion of oxetane to γ-lactone (entry 10 and 11).

Table 3. Investigation of solvent effect.



entry	solvent (hydrogen-bond basicity)[a]	conversion (%)	yield (%)
1	DME (0.68)	>99	85 (82)
2	diglyme (1.17)	>99	82
3	THF (0.48)	0	0

4	2-methyl-THF (0.53)	0	0
5	dioxane (0.64)	0	0
6	MTBE (0.55)	0	0
7	hexane (0)	0	0
8	toluene (0.14)	0	0
9	MeOH (0.47)	>99	0
10	dioxane (0.64)	25	18[b]
11	dioxane (0.64)	40	24[c]

Reaction conditions: **1a** (0.4 mmol), $Co_2(CO)_8$ (0.01 mol), solvent (1 mL), 100 °C, 16 h. conversions and yields were determined by GC analysis. In the parentheses is the isolated yield. THF = tetrahydrofuran; MTBE = methyl tert-butyl ether. [a] The data of hydrogen-bond basicity are collected from ref. 23b. [b] 12-crown-4 ether (0.4 mmol) was added. [c] 18-crown-6 ether (0.4 mmol) was added.

Despite the hardness of accurate evaluating solvent effect by static DFT-based calculation,[25] we still carried out the theoretical computations considering the contribution from explicit solvation effects in the implicit solvation model SMD[26] to obtain more insights about $HCo(CO)_4$ dissociation to $[Co(CO)_4]^-$ anion and solvated proton as well as the oxetane activation by solvated proton in DME, THF and 1,4-dioxane solvents (detailed computational results see SI). We found that although $HCo(CO)_4$ dissociation to $[Co(CO)_4]^-$ anion and DME-solvated proton is endothermic in the solvation of DME, it is much more viable than in the solvation of 1,4-dioxane. By local energy decomposition with local pair natural orbital based coupled-cluster methods (i.e. DLPNO-CCSD(T)),[27] we found that the interaction between oxetane and DME-solvated proton fragments was stronger than between oxetane and 1,4-dioxane- or THF-solvated proton, which suggests the more effective oxetane activation by DME-solvated proton. Indicated by the results of control experiments and theoretical computation, the plausible mechanism was proposed (detailed mechanism and relevant discussion see SI).

In conclusion, we successfully developed a mild and highly efficient catalyst system for the carbonylative ring expansion of oxetane and thietane. Using $Co_2(CO)_8$ as the pre-catalyst, a wide range of oxetanes and thietanes were transformed into the corresponding γ-(thio)butyrolactone in good to excellent yields under syngas atmosphere. The utility of this carbonylation method in the construction of building block for drugs and intermediate for natural products has been demonstrated. The glycol-ether solvent plays a critical role in promoting $HCo(CO)_4$ dissociation to $[Co(CO)_4]^-$ and solvated proton, which respectively are the active carbonylation catalyst and Brønsted-acid-type oxetane/thietane activator.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: carbonylation • ring expansion • γ-butyrolactone • oxetane • solvent effect

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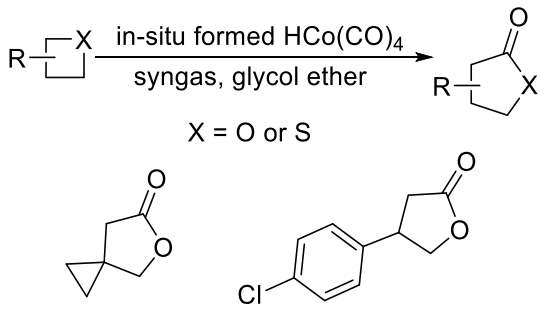

building blocks for Montelukast & Baclofen

Simple but useful: Solvated-proton-assisted cobalt-catalyzed carbonylative ring expansion of oxetanes or thietanes to γ-(thio)butyrolactones under syngas atmosphere has demonstrated its versatility in the synthesis of intermediates for pharmaceuticals and natural product. Glycol ether solvent plays an essential role in promoting the carbonylative conversion of the substrates.