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Pd/C-Catalyzed Carbonylative Esterification of Aryl Halides with Alcohols by Using Oxiranes as CO Sources

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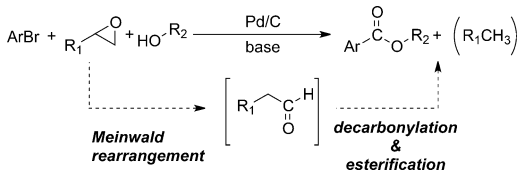
Abstract: A carbonylative esterification reaction between aryl bromides and alcohols, promoted by Pd/C and NaF in the presence of oxiranes, has been developed. In this process, oxiranes serve as sources of carbon monoxide by their conversion to aldehydes through a palladium-promoted Meinwald rearrangement pathway. Intramolecular versions of this process serve as methods for the synthesis of lactones and phthalimides.

Transition-metal-catalyzed carbonylation reactions are among the most useful and reliable processes for the preparation of esters.[1] The pioneering studies by Heck led to the development of the first palladium-catalyzed carbonylation reactions between alcohols, aryl halides, and carbon monoxide.[2] Because carbon monoxide gas is toxic and difficult to handle, many other one carbon carbonyl surrogates were applied in various transition-metal-catalyzed carbonylation reactions.[3] A remarkable transition-metal-catalyzed carbonylation involving ex situ generation of carbon monoxide from organic precursors, such as silacarboxylic acid,[4] acid chloride,[5] formic acid,[6] and carbon dioxide[7] was developed. However, these reactions require multistep and complex reaction setups (e.g., two-chamber reactor). Carbonylation involving in situ generation of carbon monoxide from carbonyl surrogates, such as chloroform,[8] formate,[9] formic anhydride,[10] aldehyde,[11] and alcohol,[12] has been also studied, and these reactions demand homogeneous catalysts (e.g., $Pd(OAc)_2$, $[\{Rh(CO)Cl(dppp)\}_2]$ and Ru_3CO_{12}), which require special phosphine ligands (e.g., dppp, DPEphos, Xantphos, and dtbpx).

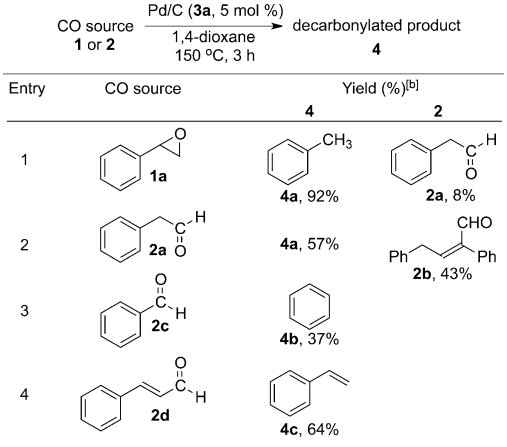
Recently, we reported a Pd/C-catalyzed carbonylative esterification reaction between alcohols and aryl chlorides, in which the alcohol serves the role of both the carbonyl source through dehydroxymethylation and the ether moiety of the ester.[13] During the course of recent studies targeted at the design of new ester-forming reactions, we observed that addition of an oxirane to a mixture of aryl bromide, alcohol, and Pd/C leads to the production of an alkane along with a cross-coupled ester (Scheme 1). We assumed that the oxirane involved in this process undergoes Meinwald rearrangement[14] to form an aldehyde, which serves as the carbon monoxide source.[15] To the best of our knowledge, this is the first example of an ester synthesis protocol, which utilizes oxirane as the carbonyl source.



Scheme 1. Carbonylative esterification strategy employing Meinwald rearrangements of oxiranes.

An investigation was conducted to determine if oxiranes function as suitable CO sources. The reaction of 2-phenyloxirane (**1a**) in the presence of Pd/C (**3a**, 5 mol%) in 1,4-dioxane was observed to produce toluene (**4a**) in 92% yield along with 8% of phenylacetaldehyde (**2a**) (Table 1, entry 1). This result suggests that carbon monoxide is generated in 92% yield in this process by decarbonylation of the intermediate aldehyde **2a**. However, when **2a** was directly subjected to the decarbonylation conditions, toluene (57%) along with a large amount (43%) of the aldol product **2b** was produced (entry 2). Other aldehydes, such as benzaldehyde (**2c**) and cinnamaldehyde

Table 1. CO production by decarbonylation of oxiranes and aldehydes.[a]



[a] Unless otherwise noted, reactions were carried out with CO sources **1** or **2** (0.2 mmol) and **3a** (5 mol%) in 1,4-dioxane (0.1 mL) at 150 °C. [b] All yields were determined by using GC analysis.

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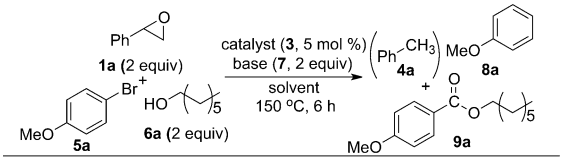
(**2d**), were found to be less efficient CO generators than **1a** under the reaction conditions (entries 3–4).

Based on these observations, 2-phenyloxirane was employed as the carbonyl source in studies aimed at optimizing the ester-forming process (Table 2). The results show that the reaction of 4-bromoanisole (**5a**) with 2-phenyloxirane (**1a**) and heptanol (**6a**) in the presence of Pd/C (**3a**) and NaF (**7a**) in 1,4-dioxane at 150 °C for 6 h generates heptyl 4-methoxybenzoate (**9a**) in 82% isolated yield (entry 1) along with toluene (**4a**, 77% GC yield) and a lesser amount of anisole (**8a**, 12% GC yield). Among various palladium catalysts tested, homogeneous catalysts, such as $[Pd(PPh_3)_4]$ and $Pd(OAc)_2$, do not promote the esterification reaction, whereas the process catalyzed by $[Pd_2(dba)_2]$ yields only 15% of the target ester **9a** (entries 3–5), implying that only a heterogeneous catalyst can be applied for this reaction. Among the various weak bases explored, such as NaF (**7a**), CsF (**7b**), Na_2CO_3 (**7c**), and $NaHCO_3$ (**7d**), NaF (**7a**) was found to be the optimal for this process (entries 1 and 6–8). Importantly, the reaction in which NaOH (**7e**) is the base gives only the homocoupling product (a biphenyl derivative, derived from **5a**) but none of the corresponding ester. Finally, 1,4-dioxane was found to be better solvent than those tested (CH_3CN, toluene, and $ClCH_2CH_2Cl$; entries 10–12).

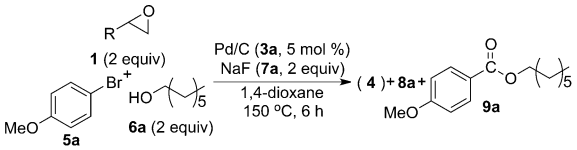
Table 2. Optimization of the carbonylative esterification reaction.[a]

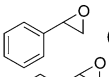
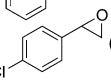


Entry	Catalyst	Base	Solvent	Yield [%]		
				4a[b]	8a[c]	9a[d]
1	Pd/C (**3a**)[e]	NaF (**7a**)	1,4-dioxane	77	12	82
2	Pd/C (**3b**)[f]	**7a**	1,4-dioxane	48	18	60
3	$[Pd(PPh_3)_4]$(**3c**)	**7a**	1,4-dioxane	0	0	0
4	$Pd(OAc)_2$ (**3d**)	**7a**	1,4-dioxane	0	0	0
5	$[Pd_2(dba)_3]$(**3e**)	**7a**	1,4-dioxane	20	10	15
6	**3a**	CsF (**7b**)	1,4-dioxane	40	48	48
7	**3a**	Na_2CO_3 (**7c**)	1,4-dioxane	49	69	31
8	**3a**	$NaHCO_3$ (**7d**)	1,4-dioxane	48	68	9
9	**3a**	NaOH (**7e**)	1,4-dioxane	50	0	0
10	**3a**	**7a**	CH_3CN	43	23	71
11	**3a**	**7a**	toluene	89	15	37
12	**3a**	**7a**	$ClCH_2CH_2Cl$	32	15	52

[a] Unless otherwise noted, reactions were carried out with **5a** (0.2 mmol), **1a** (0.4 mmol), **6a** (0.4 mmol), **3** (5 mol%), and **7** (0.4 mmol) in solvent (0.1 mL) at 150 °C. [b] GC yield based on **1a**. [c] GC yield based on **5a**. [d] Isolated yield based on **5a**. [e] 10% palladium on activated charcoal. [f] 10% palladium on carbon.

Table 3. Optimization of various oxiranes as carbonyl sources.[a]



Entry	Oxirane	Yield [%]		
		4[b]	8a[c]	9a[d]
1	 (**1a**)	77	12	82
2	 (**1b**)	84	9	60
3	 (**1c**)	-	16	0
4	 (**1d**)	-	10	0
5	 (**1e**)	-	27	11

[a] Unless otherwise noted, reactions were carried out with **5a** (0.2 mmol), **1** (0.4 mmol), **6a** (0.4 mmol), **3a** (5 mol%), and **7a** (0.4 mmol) in 1,4-dioxane (0.1 mL) at 150 °C. [b] GC yield based on **1**. [c] GC yield based on **5a**. [d] Isolated yield based on **5a**.

Moreover, aliphatic oxiranes, such as 2-methyloxirane (**1c**) and 2-butyloxirane (**1d**), do not participate in the ester-forming process (entries 3–4), and the reaction in which the sterically hindered analog 2,2-dimethyloxirane (**1e**) serves as the CO donor generates **9a** in only 11% yield (entry 5).

Based on the results described above, it is possible to propose the mechanism outlined in Figure 1 for the carbonylative esterification process. In this pathway, a palladium-catalyzed Meinwald-type rearrangement of 2-phenyloxirane (**1a**) occurs initially to generate phenylacetaldehyde (**2a**), which then rapidly undergoes a Pd^0-promoted decarbonylation to generate toluene (**4a**) and Pd^0–CO complex **10a**.[15g,16] In this event, aldol condensation of **2a** would be inefficient owing to its low concentration. An oxidative addition of 4-bromoanisole (**5a**) to **10a** affords acyl–Pd^{II}–Br intermediate **11a**, which reacts with

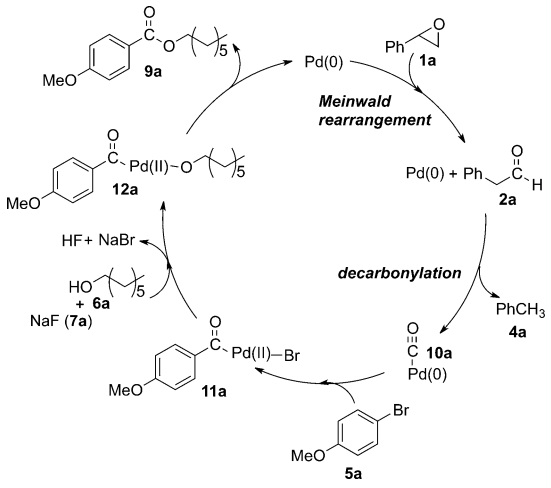
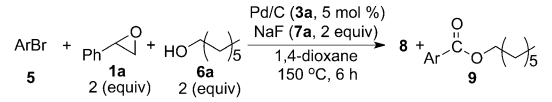


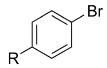
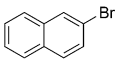
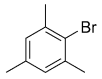
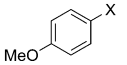
Figure 1. Proposed mechanism for the carbonylative esterification process.

heptanol (**6a**) to produce acyl–Pd^{II}–O–heptyl intermediate **12a**. This Pd complex then undergoes reductive elimination to generate ester **9a** along with the catalytically active Pd^0.

Next, the aryl halide substrate scope was explored. Esterification reactions of electron-neutral (bromobenzene (**5b**)), -donating (4-bromoanisole (**5a**)), and -withdrawing (4-bromobenzonitrile (**5c**)) group-substituted aryl bromides with heptanol proceed to give the corresponding esters in respective yields of 85, 82, and 62% (Table 4, entries 1–3). Hydroxyl (**5d**), *N*,*N*-dimethylamino (**5e**), chloro (**5f**), and acetyl (**5g**) functional groups are well tolerated under the esterification reaction conditions (entries 4–7). The reaction of polyaromatic analogue, 2-bromonaphthalene (**5h**), also gives a similar yield to that of bromobenzene (**5b**; entry 1 versus 8). Steric factors appear to influence the efficiency of the reaction. This is exemplified by the observation of the reaction of 2-bromo-1,3,5-trimethylbenzene (**5i**) under the optimal conditions, which generates ester **9i** in only 24% yield. Finally, the reactions of bromoarenes occur smoothly under the standard reaction conditions, whereas those of chloro- (**5j**) and iodoarene (**5k**) analogs are highly inefficient (entries 1, 10 and 11).[17]

Table 4. Aryl halides substrate scope of the reaction.[a]

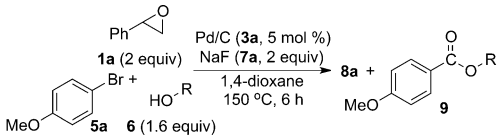


Entry	Aryl halide			Yield [%] 8[b]	9[c]
1[d]			(**5b**)	15 (**8b**)	**9b**, 85 (85)
2		R = OMe	(**5a**)	12 (**8a**)	**9a**, 88 (82)
3[d]		CN	(**5c**)	34 (**8c**)	**9c**, 66 (62)
4		OH	(**5d**)	14 (**8d**)	**9d**, 86 (67)
5[d]		$N(CH_3)_2$	(**5e**)	15 (**8e**)	**9e**, 85 (54)
6		Cl	(**5f**)	12 (**8f**)	**9f**, 88 (88)
7		$COCH_3$	(**5g**)	23 (**8g**)	**9g**, 77 (62)
8[e]			(**5h**)	20 (**8h**)	**9h**, 80 (79)
9			(**5i**)	0 (**8i**)	**9i**, 35 (24)
10		X = Cl	(**5j**)	1 (**8a**)	**9a**, 4
11[f]		I	(**5k**)	2 (**8a**)	**9a**, 0

[a] Unless otherwise noted, reactions were carried out with **5** (0.2 mmol), **1a** (0.4 mmol), **6a** (0.4 mmol), **3a** (5 mol%), and **7a** (0.4 mmol) in 1,4-dioxane (0.1 mL) at 150 °C. [b] GC yield based on **5**. [c] GC yield based on **5**, and isolated yields are given in parenthesis. [d] 1,4-dioxane (0.05 mL) was used. [e] Reaction was carried out with **5** (0.2 mmol), **1a** (0.6 mmol), **6a** (0.6 mmol), **3a** (5 mol%), and **7a** (0.4 mmol) in 1,4-dioxane (0.05 mL) at 150 °C. [f] Phenylacetaldehyde was obtained in 71% yield based on **1a**.

The participation of various alcohols in the esterification reaction was also probed. The reaction of 4-bromoanisole (**5a**) with aliphatic alcohols, such as octanol (**6b**) and methanol (**6c**), leads to the formation of octyl ester and methyl ester in 84 and 81% yield, respectively (Table 5, entries 1 and 2). Benzyl alcohol (**6d**) and phenol (**6e**) also serve as reactants, forming

Table 5. Alcohol substrate scope of the reaction.[a]



Entry	Alcohol		Yield [%] 8a[b]	9[c]
1	$CH_3(CH_2)_7OH$	(**6b**)	12	**9j**, 88 (84)
2[d]	CH_3OH	(**6c**)	17	**9k**, 83 (81)
3		(**6d**)	13	**9l**, 87 (53)
4[d]	Ph–OH	(**6e**)	35	**9m**, 65 (55)
5[d]		(**6f**)	38	**9n**, 62 (36)
6		(**6g**)	13	**9o**, 87 (54)
7		(**6h**)	0	**9p**, 0 (0)

[a] Unless otherwise noted, reactions were carried out with **5a** (0.2 mmol), **1a** (0.4 mmol), **6** (0.32 mmol), **3a** (5 mol%), and **7a** (0.4 mmol) in 1,4-dioxane (0.1 mL) at 150 °C. [b] GC yield based on **5a**. [c] GC yield based on **5a** and isolated yields are given in parenthesis. [d] 1,4-dioxane (0.05 mL) was used.

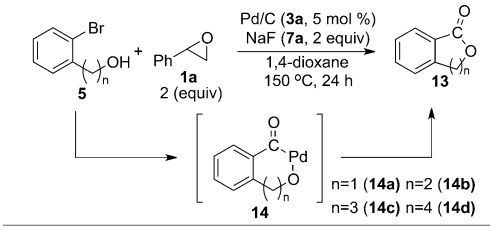
the corresponding esters in 53 and 55% yield, respectively (entries 3 and 4). The reaction of thiophene-substituted alcohol **6f** proceed to give the corresponding ester **9n** in a moderate 36% yield (entry 5). Steric effects also appear to influence the efficiency of the process as is reflected by the observation that secondary alcohol **6g** is less reactive than primary alcohol **6b** (entries 1 and 6), and that the tertiary alcohol **6h** does not participate in the process (entry 7).

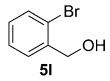
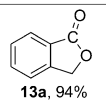
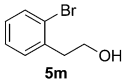
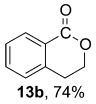
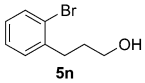
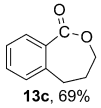
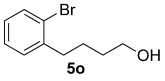
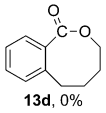
The intramolecular version of the carbonylative esterification reaction serves as a useful method for the preparation of lactones (Table 6).[18] For example, the reaction of 2-bromobenzyl alcohol (**5l**) with 2-phenyloxirane (**1a**) in the presence of **3a** and **7a** takes place to generate isobenzofuran-1(3H)-one (**13a**) in 94% yield (entry 1).[19] Likewise, 2-bromoaryl alcohols, such as 2-bromophenyl ethanol (**5m**) and 2-bromophenyl propanol (**5n**), also yield the respective isochroman-1-one (**13b**) and 4,5-dihydrobenzo[c]oxepin-1(3H)-one (**13c**) in high yields (entries 2–3). In contrast, the reaction with 4-(2-bromophenyl)butan-1-ol (**5o**) does not produce the expected 8-membered lactone **13d** (entry 4), and the yields of the lactone-forming reaction decreases as the ring size increases. This result demonstrates that the generation of six-membered palladacycle intermediate **14a** (Table 5) is most favorable.

Lactonization using styrene and *meta*-chloroperbenzoic acid (*m*CPBA) as a CO source instead of 2-phenyloxirane was also conducted [Eq. (1)]. The reaction of **5l** with styrene (**14a**) and *m*CPBA proceeds in the presence of **3a** and **7a** to generate **13a** in 94% yield. During the reaction, 2-phenyloxirane might be generated in situ by the reaction of styrene with *m*CPBA. 2-Bromophenyl ethanol (**5m**) was also efficiently converted to lactone **13b** in 92% yield.

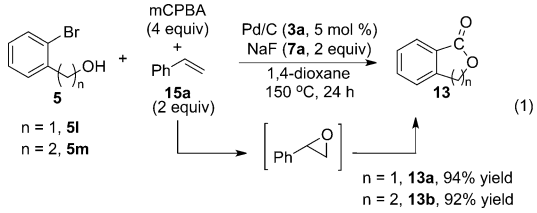
Finally, the intramolecular cyclization of 2-bromobenzamide (**5p**) with oxirane **1a** in the presence of **3a** and **7a** under the

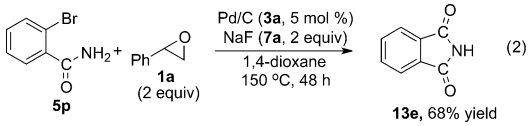
Table 6. Lactonization of various 2-bromoaryl alcohol[a]



Entry	Aryl halide	Yield (%)[b] 13
1[c]	 5l	 13a, 94%
2	 5m	 13b, 74%
3	 5n	 13c, 69%
4	 5o	 13d, 0%

[a] Unless otherwise noted, reactions were carried out with **5** (0.2 mmol), **1a** (0.4 mmol), **3a** (5 mol%), and **7a** (0.4 mmol) in 1,4-dioxane (0.1 mL) at 150 °C. [b] Isolated yield based on **5**. [c] 1,4-dioxane (0.05 mL) was used.





standard conditions was observed to generate phthalimide **13e** in 68% isolated yield [Eq. (2)].

In summary, we developed a new Pd^0-catalyzed carbonylative esterification reaction, which utilizes 2-phenyloxirane as a carbon monoxide source. Carbon monoxide, in the form of the Pd^0–CO complex, is generated in this process by a pathway involving sequential palladium-promoted Meinwald rearrangement to form phenylacetaldehyde and decarbonylation. The new protocol can be used to synthesize 5–7-membered lactones. A mixture of styrene and *m*CPBA can be also applied as an efficient CO surrogate. Other methods to bring about carbonylative esterification using oxiranes as carbon monoxide sources are currently under study in our group.

Acknowledgements

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Keywords: carbonylation · cross-coupling · cyclization · lactones · palladium

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