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Herein, we report a Pd-catalysed alkoxy carbonylation of alkenes based on the use of a recyclable CO₂ reduction product, the crystalline and air-stable *N*-formylsaccharin, as a CO surrogate. The carbonylation proceeds under ambient conditions in an exceptionally complementary regioselective fashion yielding the desired branched products from styrene derivatives and valuable linear esters from alkyl-substituted alkenes.

Carbon monoxide constitutes the most versatile C1 building block for the construction of carbonyl compounds in homogeneously catalysed reactions.¹ Carbonylations of alkenes, such as hydroformylation² and alkoxy carbonylation³ play a central role in the production of bulk chemicals. However, their use in small laboratory synthetic applications is more rare, because of the toxicity of CO and advanced technical requirements. Therefore, the development of alternative ways to produce stoichiometrical amounts of CO in the reaction mixture is of considerable interest in synthetic organic chemistry.⁴

Thus, a number of CO surrogates have been applied in the carbonylation reactions of alkenes over the years. Most recent developments include the use of formates,⁵ formic acid,⁶ formaldehyde,⁷ alcohols⁸ and the greenhouse gas carbon dioxide.⁹ However, most transformations are performed under forcing conditions (temperatures >100 °C, high catalyst loading) and even if cheap, low-weight carbonylation reagents are used, the overall atom economy is deteriorated due to the employment of overstoichiometrical amounts of the CO surrogate. Moreover, the use of an internal alternative CO source often leads to deviations from the carbonylation mechanism causing changes in reactivity and selectivity.

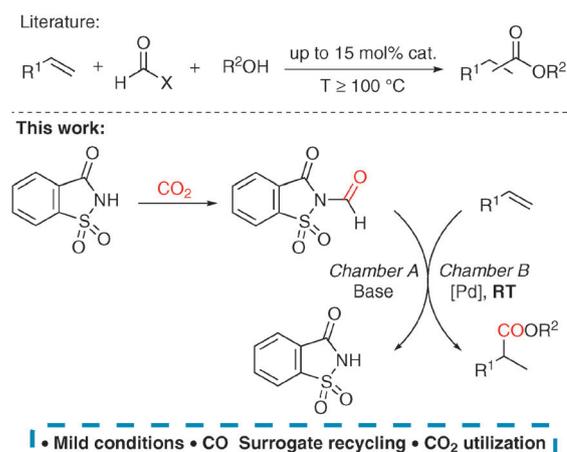
In order to overcome the flaws of the known CO surrogates used in alkene carbonylations, we have developed a methodology based on a separate CO production originally reported by Skrydstrup for the carbonylations of ArX compounds.¹⁰

A recyclable CO surrogate in regioselective alkoxy carbonylation of alkenes: indirect use of carbon dioxide†

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Palladium-catalysed alkoxy carbonylation¹¹ of styrene derivatives was chosen as a model reaction and the catalyst was optimized in order to operate under mild conditions and selectively produce branched esters. Thus, a unique catalytic system was developed, which is able to carbonylate alkenes at the room temperature with only 0.5 mol% catalyst loading and utilize *N*-formylsaccharin as a recyclable CO surrogate (Scheme 1).¹² Notably, our strategy allows for an indirect use of carbon dioxide as a C1 source. This approach to the reductive activation of CO₂ in two steps constitutes a useful alternative to the literature known methods, which usually suffer from harsh reaction conditions and low selectivity.

First, the setup for the *ex situ* generation of CO and simultaneous alkoxy carbonylation was investigated. The reactions were performed in two-chamber pressure tubes developed by Skrydstrup.^{10a} Carbon monoxide (max. 2.5 bar) was liberated from *N*-formylsaccharin (**1**) by treatment with a base in DMF at room temperature as previously described by Manabe and co-workers.^{12b,c} The type of the base is important by means of reproducibility and control of the decarbonylation. Therefore, the solid Na₂CO₃ was used due to a

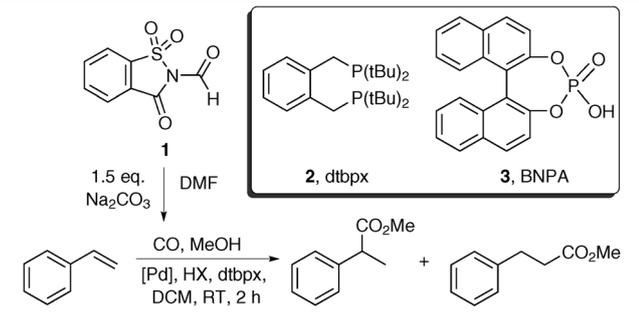


Scheme 1 Use of CO surrogates in alkoxy carbonylations of alkenes. Our work: indirect utilization of CO₂ as a C1 source under ambient reaction conditions using *N*-formylsaccharin as a CO transfer reagent.

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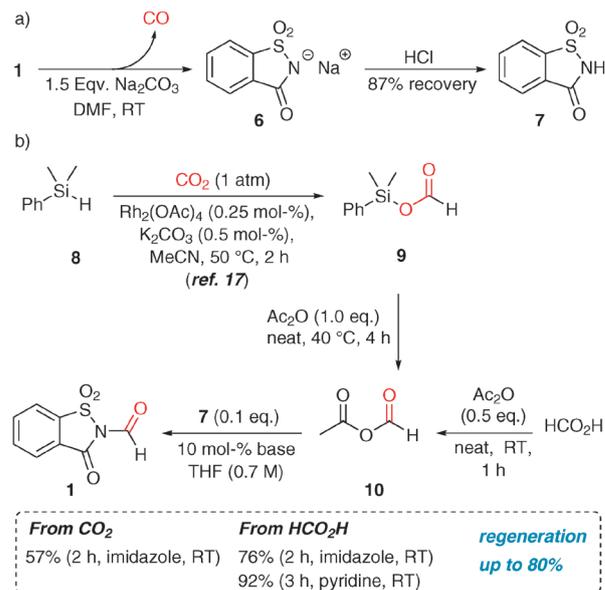
Table 1 Optimization of the methoxycarbonylation of styrene^a


Entry	Pd source	HX	pK _a (DMSO)	b : i ^b	Conv. ^b [%]	Yield ^b [%]
1	Pd(dba) ₂	<i>p</i> TsOH	7.1	71:29	27	9
2	Pd(dba) ₂	MsOH	1.6	69:31	28	6
3	Pd(dba) ₂	PhCOOH	11.1	51:49	21	2
4	Pd(dba) ₂	TFA	3.5	95:5	64	38
5	Pd(dba) ₂	3	3.4	88:12	57	56
6	Pd(acac) ₂	3	3.4	—	14	0
7	PdCl ₂	3	3.4	—	18	0
8	Pd(PPh ₃) ₄	3	3.4	93:7	11	1
9	Pd(OAc) ₂	3	3.4	92:8	16	2

^a Reaction conditions: chamber A: CO generation (max 2.5 bar): 1 (2.13 mmol, 449 mg), Na₂CO₃ (3.19 mmol, 340 mg) in DMF (1 mL); chamber B: styrene (1.00 mmol, 115 μL, 1 M solution), 1 : 3 MeOH : DCM (v/v), 0.5 mol% [Pd], 2 mol% dtbpx (20 μmol, 7.9 mg), 7.5 mol% HX, RT, 2 h. ^b Determined by quantitative GC-FID analysis of the crude reaction mixture.

slower reaction than with triethylamine. The choice of the carbonylation catalyst is based on the industrial production of methyl propionate from ethylene, which utilizes a palladium precursor and ligand dtbpx (2).¹³ Thus, the initial experiments using styrene and methanol as substrates were performed in order to identify the ideal catalyst and acid suitable for the carbonylation under room temperature and low pressure (Table 1). First, several acidic co-catalysts were tested. Interestingly, the most commonly used acids in this reaction such as *para*-toluene- and methanesulfonic acid caused low reactivity and moderate selectivity (Table 1, entries 1 and 2). So far, we don't know the reason for the difference between the conversion and the yield. The much weaker benzoic acid led to even lower yield and regioselectivity (Table 1, entry 3). Remarkably, use of acids with pK_a value in DMSO of 3.5 resulted in improved activity and high preference for the branched product. The reaction with TFA provided the esters **5aa** in moderate yield and high selectivity after 2 h reaction time (Table 1, entry 4). Higher yield and slightly lower selectivity were observed in the reaction with racemic BINOL-phosphoric acid (BNPA, 3), which was chosen for further studies (Table 1, entry 5).

The examination of several palladium precursors revealed that best results were obtained using Pd(dba)₂ (Table 1, entries 5–9). Thus, we were able to find mild reaction conditions for the selective production of the branched ester **5aa** from styrene, which is in contrast to the literature-known carbonylations with the dtbpx ligand, which preferably provide the linear esters.^{5b,7e} A notable exception is the work of Tanaka, however only one example is given.^{11e}



Scheme 2 (a) Base-mediated decarbonylation of *N*-formylsaccharin. (b) Base-catalyzed *N*-formylation of **7**, where the formyl moiety either stems from formic acid or CO₂.

Recently, concerns emerged that compared to other lower-molecular weight CO surrogates, **1** only contains 13% CO relative to its molecular weight.^{7e} However, this problem can be alleviated by choice of an efficient recovery and regeneration process. The spent CO generation solution contains the sodium saccharinate (**6**), from which saccharin (**7**) can be precipitated in 87% yield by addition of HCl (Scheme 2). *N*-Formylsaccharin was synthesized by the formylation of **7** with the *in situ*-generated mixed anhydride **10** in the presence of 10 mol% of a base (pyridine or imidazole) in good yield with excellent chemoselectivity.¹⁴ This procedure can be used for a convenient synthesis of **1** at up to 20 g scale (92%).

We were additionally intrigued by the possibility to synthesize the CO surrogate from carbon dioxide, since its utilization as a C1 source in the synthesis represents one of the main goals and challenges of modern organic chemistry.¹⁵ However, the transformations of CO₂ usually require forcing reaction conditions. Therefore, we chose Rh-catalysed CO₂ hydrosilylation under mild conditions as a basis for our efforts.¹⁶ Thus, silyl formate **9** was prepared following the literature procedure and it was subsequently converted to the anhydride **10** quantitatively at 40 °C. This mixture was then employed to synthesize **1** under the aforementioned conditions, albeit in somewhat lower yields possibly due to the presence of PhMe₂SiOAc. In summary, this methodology allows for the capture of CO₂ as a solid CO surrogate by a hydrosilylation/transacylation/formamidation sequence.

With reliable procedures for the recycling of *N*-formylsaccharin and carbonylation in hand, we proceeded to investigate the scope and limitations of the catalytic system. First, the influence of the alcohol component on the overall reactivity and regioselectivity in the alkoxy carbonylation of styrene was tested (Table 2, entries 1–7). Isolated yields decreased from primary (**5aa**, **5ab**, **5af**; Table 2 entries 1–3 and 7) to secondary



Table 2 Alkoxy-carbonylation of substituted vinyl arenes^a

Entry	Ar	R	<i>b</i> : <i>l</i> ^b	Yield ^c [%]	Reaction	
					4a-4o	5aa-af, 5ba-oa, 5p
					Ar-CH=CH ₂	Ar-CH ₂ -CH ₂ -CO ₂ R + Regioisomer
					CO, ROH Pd(dba) ₂ , <i>rac</i> -BNPA, dtbpx, DCM, RT, 14 h	
1, 5aa	Ph	Me	88:12	76		
2, 5aa ^d	Ph	Me	87:13	80		
3, 5ab	Ph	Et	93:7	84		
4, 5ac	Ph	<i>i</i> Pr	90:10	15		
5, 5ad	Ph	<i>t</i> Bu	—	0		
6, 5ae	Ph	Cy	93:7	21		
7, 5af	Ph	Bn	82:18	79		
8, 5ba	3-Me-C ₆ H ₄	Me	91:9	92		
9, 5ca	3-OMe-C ₆ H ₄	Me	89:11	76		
10, 5da	4-Me-C ₆ H ₄	Me	91:9	55		
11, 5ea ^e	4- <i>t</i> Bu-C ₆ H ₄	Me	94:6	89		
12, 5fa	4-OMe-C ₆ H ₄	Me	93:7	97		
13, 5ga ^f	4-COOH-C ₆ H ₄	Me	77:23	21		
14, 5ha	4-NO ₂ -C ₆ H ₄	Me	—	0		
15, 5ia ^e	4-Cl-C ₆ H ₄	Me	92:8	90		
16, 5ja ^e	4-OAc-C ₆ H ₄	Me	93:7	43		
17, 5ka ^{e,g}	4-OAc-C ₆ H ₄	Me	86:14	57		
18, 5la	2-OMe-C ₆ H ₄	Me	64:56	66		
19, 5la ^e	2-OMe-C ₆ H ₄	Me	41:59	60		
20, 5ma ^h	2-OAc-C ₆ H ₄	Me	39:61	59		
21, 5na	2-Me-C ₆ H ₄	Me	50:50	5		
22, 5oa	2-CF ₃ -C ₆ H ₄	Me	—	0		
23, 5p ⁱ	2-OH-C ₆ H ₄	Me	—	16		

^a Reaction conditions: Chamber A: CO generation (max 2.5 bar): 1 (2.13 mmol, 449 mg), Na₂CO₃ (3.19 mmol, 340 mg) in DMF (1 mL); chamber B: styrene (1.00 mmol, 115 μL, 1 M solution), 1:3 ROH:DCM (v/v), Pd(dba)₂ (5.0 μmol, 2.9 mg), dtbpx (20 μmol, 7.9 mg), *rac*-BNPA (75 μmol, 26 mg), RT, 14 h. ^b Determined by GC-FID analysis of the crude reaction mixture. ^c Isolated yield. ^d DCE as solvent. ^e With Pd(dba)₂ (10.0 μmol). ^f The double ester was obtained. ^g 50 °C, deacetylated product (ArOH). ^h With 10.0 μmol Pd(dba)₂. ⁱ 5:95 MeOH:DCM (v/v), the lactone was obtained.

alcohols (**5ac**, **5ae**; Table 2 entries 4 and 6), while *t*BuOH provided no carbonylated product **5ad** (Table 2, entry 5), which is in agreement with the accepted mechanism of the reaction, according to which the final alcoholysis of the Pd-acyl complex is the rate-determining step.¹⁷

Next, the reactivity profile of various styrene derivatives in the methoxycarbonylation was examined (Table 2, entries 8–23). In general, *meta*- or *para*-alkyl and methoxy substituted styrene derivatives (Table 2, entries 8–12) gave high yields (up to 97%) with good to excellent branched-selectivity (89:11 to 94:6 *b*:*l*). The presence of an acidic function resulted in lower yield of **5ga** and selectivity, probably due to a combination of electronic effect and acidity (Table 2, entry 13). Also, the carboxylic acid group was esterified with methanol. While an alkene with a strongly electron-withdrawing nitro group was not converted at all (Table 2, entry 14), a styrene with a moderately electron-withdrawing chloride in the *para*-position provided the product in 90% yield and 92% branched selectivity (Table 2, entry 15). Lower yields of the desired product **5ja** and its deacetylated analogue **5ka** (ArOH) were obtained from *p*-acetoxy-substituted styrene (Table 2, entries 16 and 17).

Due to their steric hindrance, *ortho*-substituted styrenes (Table 2, entries 18–21) gave only moderate yields and selectivities of the corresponding products. Furthermore, the combination

of steric demand with electron-withdrawing properties led to no reactivity (Table 2, entry 22). It is noteworthy that 2-vinylphenol (**4p**) furnished the 5-membered cyclocarbonylated product **5p** even in the presence of MeOH, albeit in low yield (Table 2, entry 23). In some cases, reactions giving low yields were improved either by doubling the catalyst loading or increasing the reaction temperature to 50 °C.

Finally, we investigated the reactivity of other olefin types in the carbonylation with methanol or benzyl alcohol (Table 3). As expected, the linear product was formed exclusively from methyl methacrylate (**11**), albeit in moderate yield. A similar result was obtained with another geminally disubstituted alkene **16**. On the other hand, vinyl acetate (**12**) provided selectively the branched product, in contrast to similar catalyst systems using MsOH, where a maximal *b*:*l* ratio of 78:12 of the ester product was obtained.^{11e,18} In contrast, the transformation of *N*-vinylphthalimide (**15**) resulted in the formation of both regioisomers in 1:1 ratio. Interestingly, both β-methyl styrene (**14**) and allyl benzene (**13**) led to the same mixture of regioisomers. Only the benzylic and the terminal position were carbonylated in 1:1 ratio,

Table 3 Methoxy- or benzyloxy-carbonylation of various olefins^a

<p>11 → 21, 22 46% (<1:>99)^b 0.75 mol-% [Pd]; 51% (<1:>99)^b</p>	<p>12 → 23 32% (>99:<1)^b 1.0 mol-% [Pd]; 43% (>99:<1)^b</p>
<p>13 → 24 39% (50:50)^{c, d} 0.75 mol-% [Pd]</p>	<p>14 → 24 29% (50:50)^c</p>
<p>15 → 25 47% (46:54) 1.0 mol-% [Pd]; 82% (46:54)</p>	<p>16 → 26 34% (<1:>99) 0.75 mol-% [Pd]; 34% (<1:>99)^{d, e}</p>
<p>17 → 27, 28 53% (<1:>99) 1.0 mol-% [Pd]; 91% (<1:>99)^{b, e}</p>	<p>18 → 27, 28 39% (<1:>99) 1.0 mol-% [Pd]; 89% (<1:>99)^{b, e}</p>
<p>19 → 29 16% (<1:>99)</p>	<p>20 → 30 11% (<1:>99)^d</p>

^a Reaction conditions: chamber A: CO generation (max 2.5 bar): 1 (2.13 mmol, 449 mg), Na₂CO₃ (3.19 mmol, 340 mg) in DMF (1 mL); chamber B: alkene (1.00 mmol, 1 M solution), 1:3 MeOH:DCM (v/v), 0.5 mol-% Pd(dba)₂ (5.0 μmol, 2.9 mg), 2 mol-% dtbpx (20 μmol, 7.9 mg), 7.5 mol-% *rac*-BNPA (75 μmol, 26 mg), RT, 14 h. Isolated yields are given; the bracketed values refer to regioselectivities (*b*:*l*) measured by GC-FID analysis of the crude reaction mixture. ^b With BnOH:solvent (1:3). ^c Regioisomer ratios refer to the benzylic and terminal ester, respectively. ^d 0.75 mmol alkene. ^e 50 °C, DCE as solvent.



which demonstrates the competition between the minimization of steric clashes and the formation of a stabilized η^3 -benzyl-palladium species. Both terminal and internal aliphatic alkenes **17** and **18** were successfully transformed to the linear esters **27** (methyl) and **28** (benzyl), however higher catalyst loading and 50 °C was necessary to achieve complete conversion. The isomerization of the internal double bond and carbonylation of the terminal position was also observed in the case of oleic ester **19**, however the isolated yield of the diester was low. Lastly, we also examined the methoxycarbonylation of ethynylbenzene (**20**), but disappointingly a polymerization was taking place, which resulted in a low isolated yield of the unsaturated ester.

In conclusion, we have shown that *N*-formylsaccharin (**1**) is suitable for the *ex situ* generation of CO in Pd-catalysed hydroesterification reactions under mild reaction conditions. As opposed to an *in situ* CO generation approach, this ensures that the catalytic cycle of alkoxy-carbonylations remains unchanged. The carbonylation catalyst is based on a Pd(0) precursor, bidentate phosphine ligand and a moderately strong acid, which enable a highly regioselective transformation of styrene derivatives to the corresponding branched esters. Moreover, also aliphatic and functionalized alkenes were successfully carbonylated. Notably, we have shown that the atom economy drawback associated with the use of **1** can also be addressed by the external CO generation method, since it allows for a straightforward recovery of saccharin and its conversion to **1** with acetic formic anhydride. Furthermore, it was demonstrated that CO₂ can be transformed to a bench-stable CO surrogate in a single operation. With this proof-of-principle in hand, we are currently trying to develop a tandem procedure for the CO₂ utilization.

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