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Decarboxylative Etherification of Aromatic Carboxylic Acids

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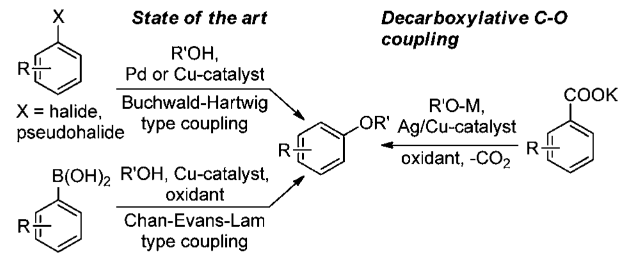
S Supporting Information

ABSTRACT: Decarboxylative Chan−Evans−Lam-type couplings are presented as a new strategy for the regiospecific construction of diaryl and alkyl aryl ethers starting from easily available aromatic carboxylic acids. They allow converting various aromatic carboxylate salts into the corresponding aryl ethers by reaction with alkyl orthosilicates or aryl borates, under aerobic conditions in the presence of silver carbonate as the decarboxylation catalyst and copper acetate as the cross-coupling catalyst.

The selective installation of alkoxy substituents at specific positions of aromatic rings is a synthetic transformation of fundamental importance, given the abundance of the aryl ether moiety in biologically active molecules and functional materials.[1,2] Traditional methods for the synthesis of aryl ethers via sp^2 C−O bond formation, e.g., nucleophilic aromatic substitutions of haloarenes or the Ullmann coupling of phenols with aryl halides, require rather harsh conditions unsuitable for the late-stage derivatization of functionalized molecules.[3]

Two reaction concepts have recently emerged that allow forming aromatic C−O bonds under mild conditions (Scheme 1). The Buchwald−Hartwig approach consists of coupling aryl halides with phenols or alcohols in the presence of a palladium catalyst and base.[4] Especially in the case of alcohols that can undergo β-hydride elimination at palladium catalysts, e.g., ethanol, highly complex ligand systems are necessary to achieve good yields.[5] Copper catalysts have a lower tendency to promote β-hydride elimination, but their activity extends only to costly aryl iodides and some activated aryl bromides.[6] The other strategy is the Chan−Evans−Lam coupling of boronic acids and phenols in the presence of amine base and copper(II) acetate, which is mostly used in stoichiometric amounts in combination with air or oxygen as the oxidant.[7,8] While publications focusing on preparative-scale reactions describe its application only to the synthesis of diaryl ethers, mechanistic studies by Stahl et al. reveal that this reaction may also be used to access alkyl aryl ethers.[9] It is a valuable alternative to the Buchwald−Hartwig coupling because it draws on a different starting material pool, although the use of boronic acids renders it rather costly.

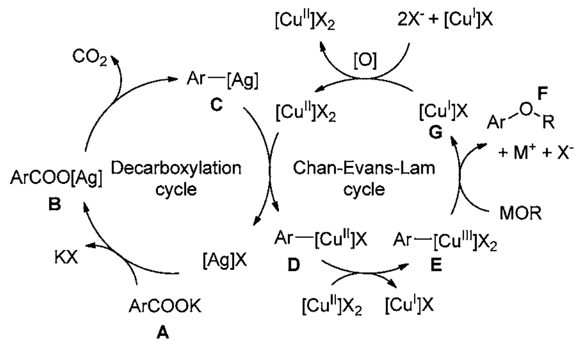
Scheme 1. Strategies for C(aryl)−O Bond Formation



Within recent years, a rapidly growing number of catalytic coupling reactions have been reported that make use of carboxylic acids as substrates.[10] The advantage of using carboxylates as leaving groups for regiospecific couplings is that aromatic carboxylic acids are available in great structural diversity. Since they are accessed via pathways that differ substantially from those leading to aryl halides or organometallic reagents, their substitution patterns are often complementary. In this context, catalytic decarboxylative coupling reactions have evolved into an efficient methodology for regiospecific C−C and C−heteroatom bond formation, allowing the expedient synthesis, e.g., of vinyl arenes,[11] biaryls,[12−14] aryl ketones,[15] thioethers,[16] haloarenes,[17] phosphine oxides,[18] ynamides,[19] or allyl compounds.[20]

The use of carboxylic acids in Chan−Evans−Lam-type couplings would be of substantial synthetic interest in view of the lower price and better availability of the starting materials.[21] We reasoned that decarboxylative Chan−Evans−Lam processes may be possible via the mechanistic concept outlined in Scheme 2. In the proposed decarboxylation cycle (Scheme 2, left), a transition-metal carboxylate forms via salt exchange and extrudes CO_2 to give an arylmetal species **C**. A transmetalation step connects this cycle with a Chan−Evans−Lam cycle in analogy to that proposed by Stahl et al. for the alkoxylation of

Scheme 2. Proposed Mechanism for a Decarboxylative Etherification Reaction



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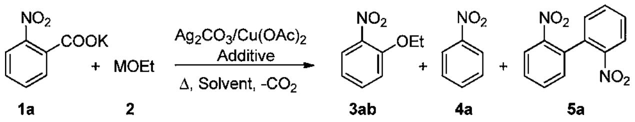
arylboronic esters.[9] The arylcopper(II) species **D** thus formed is oxidized to the Cu^{III} species **E**, which reacts with the *O*-nucleophile and reductively eliminates the aryl ether product **F**. It appeared plausible that $Cu(OAc)_2$, the cross-coupling catalyst used in standard Chan–Evans–Lam reactions, should be active also in this reaction variant. For the decarboxylation cycle, the use of Ag^I catalysts as used by Myers, Becht, Larrosa, and ourselves[11a,13,22] appeared to be more promising than of Cu^I phenanthroline complexes,[12b–d] because the latter would probably be converted to Cu^{II} under the strongly oxidizing conditions, thereby losing their activity.

In order to verify this mechanistic hypothesis, we investigated whether potassium 2-nitrobenzoate can be converted into 2-ethoxy-nitrobenzene by reaction with ethoxide derivatives in the presence of $Cu(OAc)_2$ as the Chan–Evans–Lam catalyst and Ag_2CO_3 as both the decarboxylation catalyst and stoichiometric oxidant (Table 1).

Table 1. Optimization of the Reaction Conditions[a]



entry	MOEt	additive[b]	temp (°C)	yield (%)		
				3ab	4a	5a
1	EtOH	–	120	0	62	0
2	NaOEt	–	120	0	tr.	0
3	$B(OEt)_3$	–	120	52	tr.	0
4	$Si(OEt)_4$	–	120	72	13	5
5[c]	$Si(OEt)_4$	O_2	120	68	15	4
6[c]	$Si(OEt)_4$	O_2	145	81	tr.	0
7[c]	$Si(OEt)_4$	BQ	120	0	62	0
8[c]	$Si(OEt)_4$	$K_2S_2O_8$	120	0	tr.	0
9[d]	$Si(OEt)_4$	O_2	145	24	23	14
10[c,e]	$Si(OEt)_4$	O_2	145	0	tr.	0

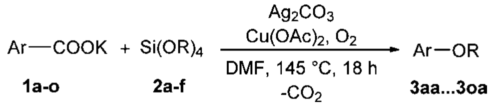
[a] Reaction conditions: 0.3 mmol potassium 2-nitrobenzoate, 1.2 equiv MOEt, 1 equiv Ag_2CO_3, 1 equiv $Cu(OAc)_2$, 2 mL solvent, 18 h. Yields determined by GC using *n*-tetradecane as internal standard. [b] 1 bar O_2 or 1 equiv *para*-benzoquinone (BQ) or 1 equiv $K_2S_2O_8$. [c] 25 mol % Ag_2CO_3. [d] Without Ag_2CO_3. [e] Without $Cu(OAc)_2$.

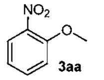
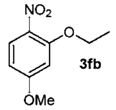
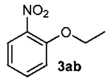
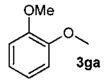
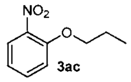
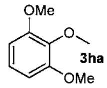
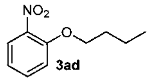
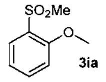
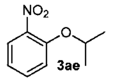
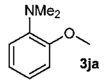
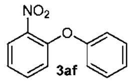
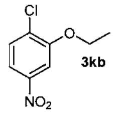
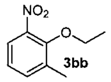
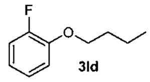
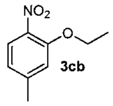
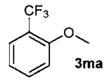
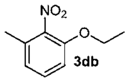
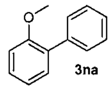
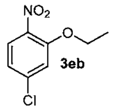
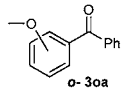
When ethanol was employed as the *O*-nucleophile in the presence of stoichiometric amounts of silver carbonate and copper acetate at 120 °C in DMF, the formation of nitrobenzene (**4a**) indicated that decarboxylation takes place but that the resulting aryl–metal intermediate undergoes protonolysis by the alcoholic OH group (Table 1, entry 1). For metal alkoxides, no reaction was observed (entry 2). However, we were pleased to see that the desired product formed in reasonable yields when using borate[23] or silicate esters[5c,24] as *O*-nucleophiles. Only small quantities of nitrobenzene and 2,2′-dinitro-1,1′-biphenyl (**5a**) were observed as side products (entries 3,4). The amount of silver carbonate could be reduced to substoichiometric amounts when performing the reaction under an oxygen atmosphere (entry 5). By increasing the reaction temperature to 145 °C, the yield could be improved to 81% using 25 mol % Ag_2CO_3 (entry 6). This is an excellent result for the introduction of an alkoxy group that is prone to competing β-hydride elimination reaction.[5]

Further investigations revealed that oxygen is the most effective oxidant (entries 5,7,8), DMF is the optimal solvent, minimizing protodecarboxylation, and that silver carbonate and copper acetate are the optimal catalyst precursors (see Table S1, Supporting Information (SI)). Control experiments revealed that the reaction is effective only in the presence of both catalyst metals. Using copper acetate alone, the yield dropped to 24%, and large amounts of side products were observed. With silver carbonate alone, the reaction did not proceed at all.

Having thus found an effective protocol for the decarboxylative etherification,[25] we next investigated its scope with regard to the *O*-nucleophile. As can be seen from Table 2, potassium 2-nitrobenzoate was successfully coupled with both linear (methyl, ethyl, propyl, butyl) and branched (isopropyl) orthosilicates. Aromatic silicates are harder to access, so we were pleased to find that the easily available triphenylborate is a suitable reagent for the introduction of phenoxy groups (**3af**). Further studies revealed that the new protocol is applicable to the full spectrum of aromatic carboxylates that are known to

Table 2. Scope of the Decarboxylative Etherification[a]



product	yield (%)	product	yield (%)
 **3aa**	85[b]	 **3fb**	84
 **3ab**	78	 **3ga**	78[b]
 **3ac**	84	 **3ha**	79[b]
 **3ad**	83	 **3ia**	73[b]
 **3ae**	81	 **3ja**	55[b]
 **3af**	48[c]	 **3kb**	58
 **3bb**	78	 **3ld**	73
 **3cb**	82	 **3ma**	46(58)[b,d]
 **3db**	73	 **3na**	55[b]
 **3eb**	68	 ***o*- 3oa** ***m*- 3oa'**	64(*o*-)[b] 29(*m*-)[b]

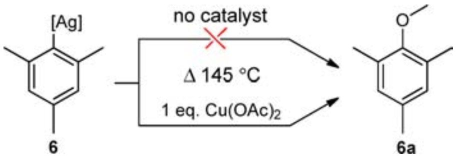
[a] Reaction conditions: 1.00 mmol benzoic acid potassium salt, 1.20 mmol $Si(OR)_4$, 0.25 mmol Ag_2CO_3, 1.00 mmol $Cu(OAc)_2$, O_2 balloon, 5 mL DMF, 145 °C, 18 h. [b] 5.00 mmol $Si(OMe)_4$ was used. [c] 1.20 mmol $B(OPh)_3$ was used. [d] ^{19}F NMR yield based on CF_3CH_2OH as an internal standard.

undergo silver-catalyzed decarboxylations. Thus, aromatic carboxylates with various electron-withdrawing and -donating groups in the ortho position were successfully converted.

The particular suitability of this method for the synthesis of ortho-functionalized aryl ethers makes it complementary to the traditional Buchwald−Hartwig and Chan−Evans−Lam reactions, for which only few examples of ortho-functionalized products have been reported.

In order to probe whether it is indeed the silver that mediates the decarboxylation and the copper that promotes the cross-coupling, some mechanistic experiments were conducted (Scheme 3). Preformed mesitylene silver (**6**),[26] an arylsilver species analogous to that which would form via decarboxylation of a silver carboxylate, was heated to 145 °C with Cu(OAc)$_2$ and Si(OMe)$_4$ in DMF under oxygen. The formation of the alkyl aryl ether **6a**[27] supports the proposed transmetalation from silver to copper.[28] In the absence of copper acetate no alkyl aryl ether was formed, suggesting that the cross-coupling can take place only at the copper.

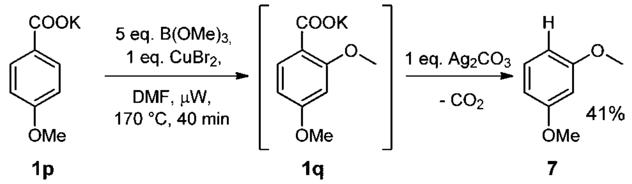
Scheme 3. Reaction of Arylsilver Species with Si(OMe)$_4$ in the Absence (top) and Presence (bottom) of Cu(OAc)$_2$



In all cases, the C−O bond formed regiospecifically in the position of the carboxylate group with the remarkable exception of compound **3oa**, for which 29% of the regioisomer (3-methoxyphenyl)(phenyl)methanone was observed as a side product. We suspected that this product may have formed via a carboxylate-directed[11a,29] ortho methoxylation with C−H activation,[30] followed by protodecarboxylation, analogously to a pathway described by Satoh, Miura, and Larrosa for C−C bond-forming reactions.[31] We went on to seek conditions under which this reaction mode would dominate. Indeed, when potassium 4-methoxybenzoate, which has a particularly low tendency to decarboxylate, was heated in a microwave reactor to 170 °C with B(OMe)$_3$ in the presence of CuBr$_2$ and Ag$_2$CO$_3$, 1,3-dimethoxybenzene (**7**) was formed in reasonable yield. Although significant catalyst development is still required to bring this reaction mode to synthetic maturity, our finding demonstrates that carboxylates can direct an alkoxylation not only into the ipso but also into the ortho position in aromatic rings. This opens up further opportunities for regioselective C−O bond formation (Scheme 4).

In conclusion, decarboxylative alkoxylation reactions have been developed as a first example of Chan−Evans−Lam-type couplings of aromatic carboxylic acids. They constitute a valuable synthetic entry to aryl ethers starting from widely available carboxylic acids. For carboxylates with a low tendency to extrude carbon dioxide, an alternative pathway consisting of ortho functionalization and protodecarboxylation has been shown to be functional, so that the ether group is installed in the ortho rather than the ipso position of the former carboxylate group. These findings set the stage for the development of a whole class of related decarboxylative C−heteroatom bond-forming reactions, e.g., decarboxylative aminations.

Scheme 4. Ortho-Directed Decarboxylative Methoxylation of Potassium 4-Methoxybenzoate



■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experiment details and spectral data for all compounds are provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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