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Rapid Synthesis of Zwitterionic Phosphonium Benzoates by a Three-Component Coupling Involving Phosphines, Arynes and CO_2

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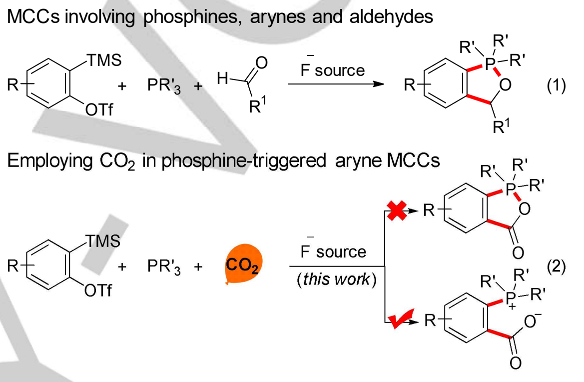
Dedication ((optional))

Abstract: *A mild and easy to perform multicomponent coupling involving phosphines, arynes generated from 2-(trimethylsilyl)aryl triflates, and* CO_2 *allowing the transition-metal-free synthesis of zwitterionic phosphonium benzoates has been developed. The reaction proceeds via the generation of 1:1 zwitterionic intermediates from phosphines and arynes followed by the interception with* CO_2 *to deliver the carboxylates in moderate to good yields instead of the anticipated benzooxaphosphol-3(1H)-ones.*

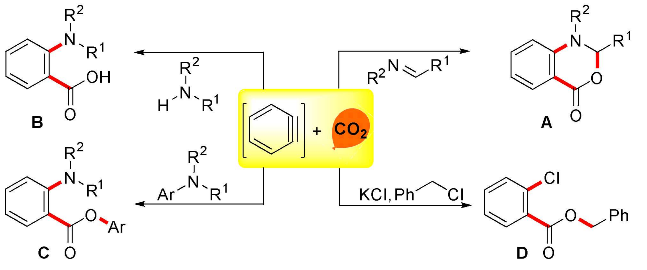
Introduction

A wide variety of 1,2-disubstituted benzene derivatives or benzo-fused heterocycles/carbocycles could be easily accessed employing multicomponent couplings (MCCs) using arynes as the aryl source.[1,2] In a typical aryne MCC, the nucleophiles having no acidic protons are added to the in situ generated arynes and the resultant aryl anion intermediate is intercepted with various electrophiles. The common nucleophilic triggers are isocyanides,[3] imines,[4] amines,[5] halides,[6] N-heterocycles such as (iso)quinoline, pyridine, aziridine etc.,[7] and solvents such as THF,[8] DMF,[9] DMSO etc.[10] The electrophilic third component usually employed are carbonyl compounds including CO_2. In the context of our interest in transition-metal-free aryne reactions,[2] in 2014, we have reported the use of phosphines as nucleophilic trigger in aryne MCCs using aldehydes as the third components for the synthesis of stable benzooxaphosphole derivatives (Scheme 1, eq 1).[11,12] Although a series of activated carbonyl compounds can trap the phosphine-aryne zwitterion, interestingly, the use of CO_2 as the third component for intercepting the phosphine-aryne zwitterion, to the best of our knowledge is unknown. We envisioned the trapping of phosphine-aryne zwitterions with CO_2 for the direct synthesis of analogous benzooxaphosphol-3(1*H*)-ones. Interestingly, under the reaction conditions, the zwitterionic phosphonium benzoates were formed instead of the anticipated benzooxaphosphol-3(1*H*)-ones (eq 2). Herein, we report the mild and operationally simple MCC of phosphines, arynes and CO_2 leading to the transition-metal-free synthesis of zwitterionic phosphonium benzoates.[13]



Scheme 1. Phosphine triggered aryne MCCs

The synthetic utility of CO_2 as a readily available and inexpensive one-carbon feedstock,[14] and as an electrophilic third component in aryne MCCs allows the straightforward method for the introduction of CO_2 group directly to the aryl ring. In 2006, Yoshida, Kunai and co-workers succeeded in incorporating CO_2 in aryne MCCs triggered by isocyanides for the synthesis of benzoxazinones derivatives **A** (Scheme 2).[4a] Later, the Yoshida group disclosed the synthesis of anthranilic acids **B** utilizing secondary amines as nucleophiles in aryne MCCs.[15] We have engaged isocyanides and aromatic tertiary amines as nucleophilic triggers in aryne MCCs for the incorporation of CO_2 leading to the synthesis of phthalimides and functionalized anthranilic acids **C** respectively.[16,17] Recently, Jiang and co-workers utilized inorganic chlorides as nucleophilic component in aryne MCCs for the synthesis of 2-chlorobenzoates **D**.[6b] It may be noted in this context that Cu-catalyzed CO_2 incorporation in aryne reaction has been uncovered by Kobayashi and co-workers for the synthesis of isocoumarin derivatives using terminal alkynes as the nucleophilic source.[18]



Scheme 2. Incorporation of CO_2 in aryne reactions

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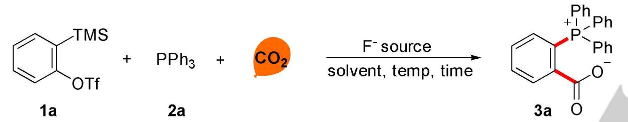
Results and Discussion

Inspired by our aryne MCCs triggered by phosphines for the synthesis of benzooxaphospholes,[11] the present study was initiated by the treatment of triphenylphosphine **2a** with the aryne generated from 2-(trimethylsilyl)aryl triflate **1a**[19] using KF as the fluoride source and 18-crown-6 as the additive under an atmosphere of CO_2 (balloon pressure) in THF at 25 °C. Under these conditions, the 2-(triphenylphosphonio) benzoate **3a** was formed in 84% yield (Table 1, entry 1).[20] Notably, the expected benzooxaphosphol-3(1*H*)-one was not formed under this condition. When the reaction was performed under the dilute conditions or heating conditions, the amount of **3a** formed was reduced (entries 2, 3). The additive 18-crown-6 was mandatory for the reaction as the reaction carried out without the additive did not afford **3a** (entry 4). Other commonly used fluoride sources such as CsF, TBAF (tetrabutyl ammonium fluoride) and TBAT (tetrabutylammonium difluorotriphenyl silicate) were found to be inferior for promoting this reaction (entries 5-8). Reducing the amount of 18-crown-6 from 2.4 equiv to 1.2 equiv resulted in the reduced formation of **3a** (entry 9). Moreover, the desired product **3a** was formed in less yield when the reaction was performed using excess phosphines (entry 10).

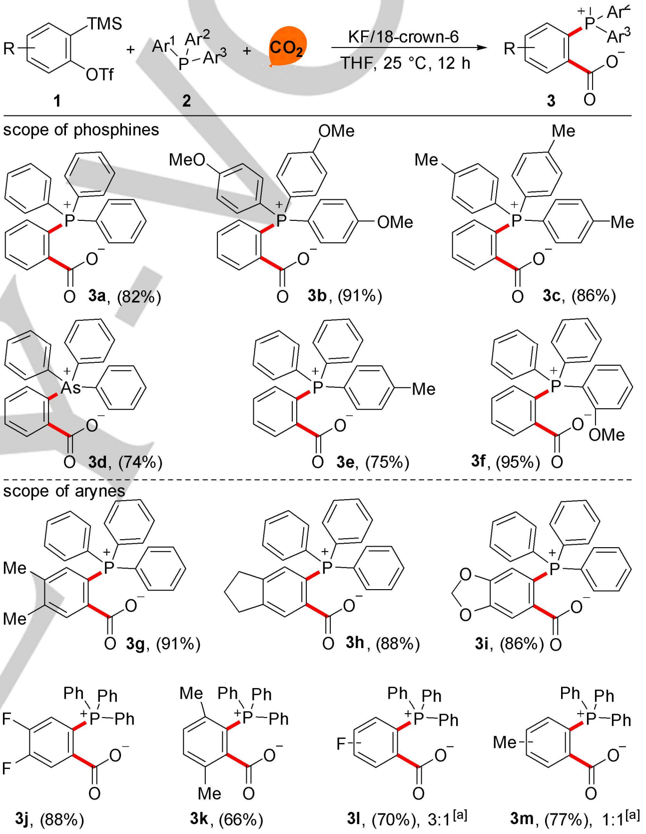
Table 1. Optimization of the reaction conditions[a]



entry	F- source	solvent	temp (°C)	yield of **3a** (%)[b]
1	*KF/18-crown-6*	*THF*	*25*	*84(82)*
2[c]	KF/18-crown-6	THF	25	65
3	KF/18-crown-6	THF	50	59
4	KF	THF	25	<5
5	CsF	CH_3CN	25	<5
6	CsF	CH_3CN	80	<5
7	TBAF	THF	25	<5
8[d]	TBAT	toluene	25	69
9[e]	KF/18-crown-6	THF	25	59
10[f]	KF/18-crown-6	THF	25	61

[a] Standard conditions: **1a** (0.3 mmol), **2a** (0.25 mmol), CO_2 (balloon pressure), fluoride source (2.4 equiv), THF (1.0 mL), stirred for 12 h at 25 °C. [b] The yield determined using ^1H NMR of the crude product using CH_2Br_2 as an internal standard. Isolated yield in parenthesis [c] Reaction performed using 2.0 mL of THF. [d] The product was contaminated with TBAT as an impurity. [e] The reaction carried out using 1.2 equiv of 18-crown-6 instead of 2.4 equiv. [f] The reaction performed using 0.25 mmol of **1a** and 0.375 mmol of **2a**.

With the optimized conditions for the synthesis of zwitterionic phosphonium benzoates (Table 1, entry 1), the substrate scope of this reaction has been examined (Scheme 3). The unsubstituted PPh_3 worked well and reaction carried out using tris(4-methoxyphenyl) phosphine and tris(4-methylphenyl) phosphine resulted in the formation of the corresponding benzoate derivative in excellent yields (**3a-3c**). Moreover, triphenylarsine could be used as a nucleophilic trigger in the present reaction affording the zwitterionic arsonium benzoate **3d** in 74% yield. In addition, the monomethyl and monomethoxy substituted phosphines also worked well under the present conditions furnishing the desired products in good yields (**3e-3f**). Disappointingly, alkyl phosphines such as tri *n*-butyl/tri *n*-octyl phosphine did not afford the desired benzoate product under the optimized conditions. Interestingly, a series of electronically divergent arynes generated from the corresponding triflate precursors smoothly underwent the present three-component coupling to afford the target products in good yields (**3g-3k**). Furthermore, the unsymmetrical fluoro and methyl substituted arynes generated from the corresponding precursors delivered the products as an inseparable mixture of regioisomers in good yields (**3l, 3m**).



Scheme 3. Substrate scope of this reaction. General conditions: **1** (0.6 mmol), **2** (0.5 mmol), CO_2 (balloon pressure), fluoride source (2.4 equiv), THF (2.0 mL), stirred for 12 h at 25 °C. Isolated yield of products are given. [a] The regioisomer ratio was determined by ^1H NMR analysis of the crude reaction mixture.

All the zwitterionic phosphonium benzoates were characterized using the spectroscopic techniques. In the case of the compound **3a**, the structure was further confirmed by single crystal X-ray analysis (Figure 1).[21] The crystal of compound **3a** belongs to the monoclinic $P2_1/n$ space group containing one molecule of **3a** in the asymmetric unit along with a molecule of ethanol.[22] It is clear that the structure of **3a** is zwitterionic, wherein the carboxyl group of benzoic acid carries a negative charge and the phosphorus atom, which is bonded to four other atoms takes the positive charge. The distance between the carboxyl oxygen (O2) and the phosphorus atom (P1) is 2.413(1) Å. This clearly indicates that there is no bond between O2 and P1 in the solid state thus ruling out the formation of benzooxaphosphol-3(1*H*)-ones. The geometry at the phosphorus atom (P1) is tetrahedral. In the structure, the ethanol molecule is bonded to the carboxyl oxygen through O-H···O hydrogen bond.

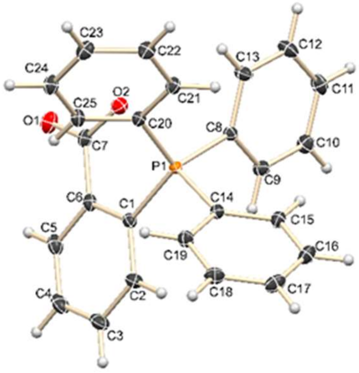
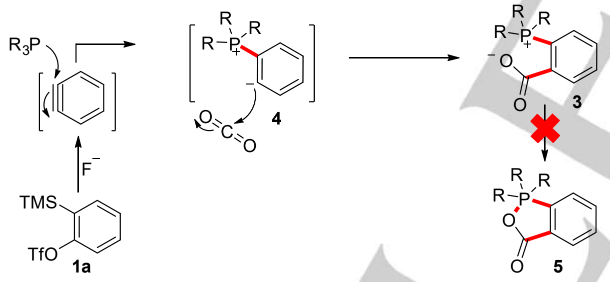


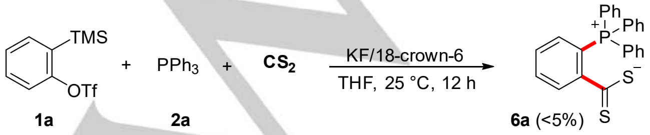
Figure 1. Crystal structure of **3a** (thermal ellipsoids are shown with 50% probability).

Mechanistically, the reaction proceeds via the fluoride induced generation of aryne from the precursor **1a** (Scheme 4). Nucleophilic attack of the phosphine to the in situ generated aryne could generate the aryl anion intermediate (1,3-zwitterion) **4**, which could be intercepted by CO_2 resulting in the formation of the desired carboxylate **3**. It is reasonable to assume that the zwitterionic benzoate **3** is less nucleophilic (enhanced stabilization of the carboxylate anion) for the addition to the phosphonium leading to the formation of the pentacovalent phosphorane **5**. Notably, in related reactions using aldehydes/activated carbonyls as third-components, the in situ generated alkoxide is more nucleophilic to add to the phosphonium to afford the benzooxaphospholes.[11]



Scheme 4. Plausible mechanism of the reaction

Encouraged by the trapping of phosphine-aryne zwitterion with CO_2, we then focused our attention on CS_2 as the third component. Disappointingly, the reaction performed using 2.0 equiv CS_2 under the optimized conditions did not afford the desired product **6a** (Scheme 5).[20] Instead, a mixture of tetraphenyl phosphonium triflate **12a** and unreacted PPh_3 were observed. The desired product was not formed even after using CS_2 as a solvent (1.0 mL) under the present conditions.[23]



Scheme 5. Envisioned reaction using CS_2

Conclusions

In conclusion, we have reported the transition-metal-free aryne three-component coupling triggered by phosphines using CO_2 as the third component. The reaction afforded the zwitterionic phosphonium benzoates under mild and operationally simple conditions instead of the envisioned benzooxaphosphol-3(1*H*)-ones. Mechanistically, the initially generated phosphine-aryne zwitterion was trapped by CO_2 to form the carboxylates in high yield in most cases. Given the potential application of phosphonium salts as ligands, reagents, ionic liquids and organocatalysts in organic synthesis, the zwitterionic phosphonium benzoates developed using the aryne strategy is likely to find important applications.[24] Further studies on related aryne MCCs are ongoing in our laboratory.

Experimental Section

General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. 25 °C Corresponds to the room temperature of the lab when the experiments were carried out. All aryne reactions were carried out under an atmosphere of CO_2 (balloon). THF was freshly purified by distillation over Na-benzophenone and was transferred under argon. 18-Crown-6 was recrystallized from dry CH_3CN, and KF was dried by heating at 110 °C for 12 h and left to cool under argon and stored in an argon filled glove-box. The 2-(trimethylsilyl)phenyl trifluoro methanesulfonate **1a** and the other symmetrical and unsymmetrical aryne precursors were synthesized following the literature procedure.[19b, 25] ^1H and ^{13}C NMR spectra were recorded on Bruker AV 200, 400, or 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm). Infrared spectra were recorded on a Bruker Alpha-E Infrared Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. HRMS data were recorded on Thermo Scientific Q-Exactive, Accela 1250 pump.

General Procedure for the Three-Component Coupling Involving Phosphines, Arynes and CO_2

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the KF (0.07 g, 1.2 mmol, 2.4 equiv), 18-crown-6 (0.317 g, 1.2 mmol, 2.4 equiv) and triarylphosphine **2** (0.5 mmol), in a glove-box. Then THF (2.0 mL) was added outside the glove-box under CO_2 atmosphere (balloon pressure) followed by addition of aryne precursor **1** (0.6 mmol, 1.2 equiv) and the reaction mixture was allowed to stir at 25 °C for 12 h. After 12 h, the solvent was evaporated and the crude residue was pre-adsorbed on silica gel and purified by flash column chromatography (DCM /MeOH = 90/10) on silica gel to afford the corresponding 2-(triaylphosphonio)benzoate **3** in moderate to good yields.

(Triphenylphosphonio)benzoate (3a)[26]

Following the general procedure, treatment of 2-(trimethylsilyl)phenyl trifluoromethanesulfonate **1a** (0.179 g, 146 μL, 0.6 mmol) and triphenylphosphine **2a** (0.131 g, 0.5 mmol), in the presence of KF (0.07 g, 1.2 mmol) and 18-crown-6 (0.317 g, 1.2 mmol) in THF (2.0 mL) at 25 °C in CO_2 atmosphere (balloon pressure) for 12 h followed by purification via silica gel flash column chromatography (DCM /MeOH = 90/10) of the crude reaction mixture afforded 2-(triphenylphosphonio)benzoate (**3a**) as a white solid (0.157 g, 82% yield). R_f (DCM /MeOH = 90/10): 0.53; **^{1}H NMR (400 MHz, CDCl$_3$)** δ 8.49 (s, 1H), 7.78 (t, J = 6.7 Hz, 1H), 7.45 (s, 4H), 7.37-7.34 (m, 12H), 6.94 (dd, J1 = 13.4 Hz, J2 = 7.9 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 166.2, 143.9 (d, J = 9.0 Hz), 136.5 (d, J = 14.9 Hz), 134.8 (d, J = 2.6 Hz), 132.4 (d, J = 9.2 Hz), 131.3, 130.7 (d, J = 14.9 Hz), 130.1 (d, J = 10.7 Hz), 129.06, 128.6 (d, J = 13.1 Hz), 122.19 (d, J = 114.3 Hz). **HRMS (ESI)** [M+H] + calcd for $C_{25}H_{20}O_2P$ 383.1195; found: 383.1195. **FTIR (cm^{-1})** 3385, 3019, 2253, 1795, 1625, 1567, 1483, 1216, 1100, 909, 834, 774.

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Keywords: arynes • multicomponent coupling • phosphines • carbon dioxide • zwitterions

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[22] The source of EtOH in the crystal is unclear at this stage. We believe that the MeOH used for the chromatographic separation of **3a** contains traces of EtOH, and this EtOH is trapped in the crystal.

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Entry for the Table of Contents

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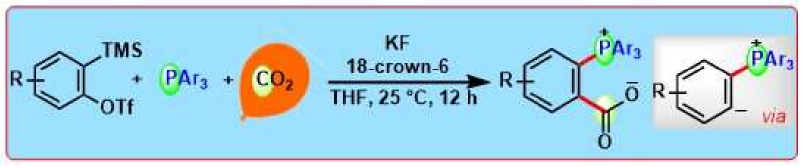

The multicomponent coupling involving phosphines, arynes and CO_2 allowing the transition-metal-free synthesis of zwitterionic phosphonium benzoates instead of the anticipated benzooxaphosphol-3(1*H*)-ones has been presented.

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Page No. – Page No.

Rapid Synthesis of Zwitterionic Phosphonium Benzoates by a Three-Component Coupling Involving Phosphines, Arynes and CO_2