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## Synthesis of 2,2,2,-Trichloroethyl Aryl- and Vinyldiazoacetates by Palladium-Catalyzed Cross-Coupling

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**Abstract:** An efficient and convenient synthesis of 2,2,2trichloroethyl (TCE) aryl- and vinyldiazoacetates was achieved by palladium-catalyzed cross-coupling reactions between TCE diazoacetates and aryl or vinyl iodides. The broad substrate scope allows for rapid and facile formation of TCE aryl- and vinyldiazoacetates, which recently have emerged as versatile reagents for rhodium-carbene chemistry.

Diazo compounds are among the most frequently used precursors for transition-metal-catalyzed carbene reactions.<sup>[1]</sup> When decomposed by transition-metals, diazo compounds are transformed to highly electrophilic metal-carbenes, which can undergo a variety of useful transformations, including C-H insertion, cyclopropanation, ylide formation, and various cycloadditions.<sup>[1]</sup> Particularly noteworthy are donor/acceptor rhodium-carbenes, generated from dirhodium the tetracarboxylate-catalyzed decomposition of aryldiazoacetates because they exhibit excellent reactivity and selectivity in various transformations.<sup>[2]</sup> Recently, the trichloroethyl (TCE) aryldiazoacetates have emerged as versatile reagents because the resulting carbenes react more cleanly than other ester derivatives and enable the functionalization of substrates that were generally considered unreactive or would have otherwise reacted unselectively.[3,4]

With the greater popularity of trichloroethyl (TCE) diazoacetates and more evidence that they are robust reagents in rhodium-carbene chemistry, a general and efficient route for their synthesis is required (Scheme 1). Classically, aryldiazoacetates are synthesized from the corresponding arylacetates by the Regitz diazo transfer reaction (Scheme 1, **A**).<sup>[5]</sup> In the case of the formation of TCE diazoacetates, the safe diazo transfer reagent, *p*-acetamidobenzenesulfonyl azide (*p*-ABSA),<sup>[6]</sup> does not give high yields, and instead, the more reactive and less stable *o*-nitrobenzenelsulfonyl azide must be used. <sup>[3b]</sup> Furthermore, if the aryl group has electron-donating substituents such as methoxy, the diazo transfer reaction is ineffective even with *o*-nitrobenzenesulfonyl azide.<sup>[7]</sup>

C–H functionalization represents an area of considerable research interest,<sup>[8,9]</sup> and it has recently been applied to the synthesis of diazo compounds.<sup>[10]</sup> Wang and co-workers recently developed a palladium-catalyzed C–H functionalization strategy

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for the synthesis of ethyl aryldiazoacetates from aryliodides and ethyl diazoacetate (Scheme 1, **B**).<sup>[10a-c]</sup> We envisioned that the strategy could also be applied to the synthesis of TCE aryldiazoacetates (Scheme 1, **C**) and thus, circumvent the problems of the diazo transfer reactions for generating these compounds.

A: Synthesis of TCE aryldiazoacetate by traditional diazo transfer reaction





B: Ethyl aryldiazoacetates by Pd-catalyzed C–H functionalization (Wang and coworkers)



C: New synthetic route to 2,2,2-trichloroethyl aryldiazoacetates

$$R + H + H + O = O CE + O CE$$

Scheme 1. New synthetic route to TCE aryldiazoacetates.

For the palladium-catalyzed coupling to be a useful method for the synthesis of TCE aryldiazoacetates, a practical method would be needed to access the staring material, TCE diazoacetate **4**. The known procedure for its preparation is not amenable to large-scale synthesis.<sup>[11]</sup> This was achieved by adapting a reported procedure for the synthesis of 2,2,2-trifluoroethyl diazoacetate.<sup>[12]</sup> Condensation of 2,2,6-trimethyl-4*H*-1,3-dioxin-4-one (**1**) with trichloroethanol to form the acetoacetate **2**, followed by diazo transfer reactions with *p*-ABSA to form **3** and hydrolysis/decarboxylation generated **4** in 75% overall yield over three steps (eq. 1). This reaction was carried out at up to 120 mmol scale.



The optimal conditions for the cross-coupling were first explored using 1-bromo-4-iodobenzene as the standard substrate. Under the reaction conditions reported by Wang and co-workers (Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%)/Ag<sub>2</sub>CO<sub>3</sub> (10 mol%)), variable yields (42-83%) of the coupling product **6a** were obtained. Attempts at using other palladium and ligand combinations were unsuccessful. The standard Wang conditions use both palladium and silver salts and both of these metal salts could potentially catalyze the decomposition of diazo compounds.<sup>[13]</sup> The possibility that the variable yields were caused by product decomposition was investigated by means of ReactIR experiments: When the diazo product **6a** was treated with

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palladium tetrakis(triphenylphosphine) (5 mol%) for 4 h, it underwent decomposition. After an induction period of about 2 h, **6a** decomposed rapidly and was virtually all consumed after 4 h. In contrast, when an additional 10 mol% of triphenylphosphine was added to the mixture, the decomposition of **6a** was greatly retarded. Consequently, the cross coupling reactions were repeated using an additional 10 mol% of triphenylphosphine and under these conditions, **6a** was generated in 89% yield with consisted yields between runs.

Table 1. Optimization of the reaction conditions.<sup>[a]</sup>

Br	N₂ 从O、CCI <u>a[Pd]</u>	Br (5 mol%), Ag <sub>2</sub> CO <sub>3</sub> (50 mol%)	
Υ Υ Η		NEt <sub>3</sub> , toluene, r.t.	
5a	4		6a <sup>12</sup>
entry	[Pd]	additional ligand	yield (%) <sup>[b]</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	-	42-83
2	Pd <sub>2</sub> (dba) <sub>3</sub>	dppe	[c]
3	Pd <sub>2</sub> (dba) <sub>3</sub>	Sphos	[c]
4	Pd <sub>2</sub> (dba) <sub>3</sub>	PCy <sub>3</sub>	[c]
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	PPh <sub>3</sub>	89

[a] Standard reaction conditions: aryl halide **5a** (1.0 mmol), TCE EDA **4** (1.3 mmol), NEt<sub>3</sub> (1.3 equiv), Ag<sub>2</sub>CO<sub>3</sub> (0.5 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), in 4 mL of toluene at room temperature for 4 h. [b] Isolated yield. [c] Trace amount of product.



*Figure 1.* ReactIR experiment. (Blue): **6a** in the presence of  $Pd(PPh_3)_4$  (5 mol%); (Red): **6a** in the presence of  $Pd(PPh_3)_4$  (5 mol%) and  $PPh_3$  (10 mol%). See supporting information for details.

The substrate scope of the reaction was then examined and the results are summarized in Scheme 2. A range of psubstituted phenyl derivatives with electron-withdrawing and electron-donating groups were tolerated (6a-m). The boron pinacolate group is compatible with this chemistry, generating 6n, which contains a useful synthetic handle for further manipulation. Particularly noteworthy is the ready access to the methoxy, acetamido and amino derivatives (6g, 6l and 6m) because the methoxy derivative 6g was not effectively formed in a diazo transfer reaction and amino derivatives have not been extensively utilized in the chemistry of donor/acceptor carbenes due to their inefficient synthesis. meta-Substituted derivatives such as halogen, methyl, and methoxy were also well tolerated (60-q), but ortho-substituted derivatives could not be prepared, suggesting that the reaction is sensitive to steric effects. TCE (Z)-styryldiazoacetate could also be synthesized by this method (6r). Both 3,5- and 3,4- disubstituted substrates were also compatible with this method (6s-t). Moreover, heterocyclic TCE diazoacetates could also be synthesized as illustrated by the



**Scheme 2**. Scope of aryl- and vinyl iodides. Standard reaction conditions: aryl halide **5a-y** (4.0 mmol), EDA (1.3 equiv), NEt<sub>3</sub> (1.3 equiv), Ag<sub>2</sub>CO<sub>3</sub> (0.5 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), in 16 mL of toluene at room temperature for 4 h. [a] The reactions were performed for 12 h. [b] Low conversion and no desired product.

diazoacetates (6v-z), with the pyridine and pyrimidine systems requiring longer reactions times.

Interestingly, the cross-coupling reaction of 2-iodopyridine **7** gave a cyclic pyridotriazole product **8** (eq 2). The formation of this product is proposed to go through the initial diazo formation, followed by a ring closing cyclization process.<sup>[5,14]</sup> This

thiophene-, benzothiazole-,

pyridine-, and pyrimidine-

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closed/open form equilibrium of pyridotriazoles was utilized in Rh-catalyzed transannulation by Gevorgyan and co-workers, <sup>[14]</sup> and our observation provides an alternative method for the preparation of pyridotriazoles.



The cross-coupling process could be applied to other ester derivatives that are useful in rhodium-carbene chemistry. Specifically, besides 2,2,2-trichloroethyl, 2,2,2-trifluoro, 2,2,2-tribromo, and trimethylsilylethyl aryldiazoacetate could also be synthesized with this cross-coupling strategy (Table 2).<sup>[3a, 15]</sup>

Table 2. Test of different esters.<sup>[a]</sup>

Br +		Pd(PPh <sub>3</sub> ) <sub>4</sub> (5 mol%), h <sub>3</sub> (10 mmol%), Ag <sub>2</sub> CO <sub>3</sub> (50 mol%	Br CO <sub>2</sub> R
	Ő	NEt <sub>3</sub> , toluene, r.t.	N <sub>2</sub>
5a	9a-c		10a-c
entry	R	product	yield (%) <sup>[b]</sup>
1	TCE	6a	89
2	TFE	10a	58
3	TBE	10b	53 <sup>[c]</sup>
4	TMSE	10c	87

[a] Standard reaction conditions: aryl halide **5a** (4.0 mmol), diazoacetates **9a-c** (1.3 equiv), NEt<sub>3</sub> (1.3 equiv), Ag<sub>2</sub>CO<sub>3</sub> (0.5 equiv), Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol %), and PPh<sub>3</sub> (10 mol %) in 16 mL of toluene at room temperature for 4 h. [b] Isolated yield. [c] 10 mol% of Pd(PPh<sub>3</sub>)<sub>4</sub> and 20 mol % of PPh<sub>3</sub> were used.

The synthetic utility of the transformation was further demonstrated by functionalizing aryl and vinyl iodides derived from estrone. These reactions afforded the corresponding diazo products **13** and **14** in 71% and 25% yield respectively (Scheme 3). The relatively low yield (25%) for the generation of **14** is presumably another indication that the cross-coupling reaction is not very tolerant of sterically demanding iodides.



Scheme 3. Application to estrone derivative

The cross-coupling reaction generated a number of novel diazo compounds that had not been previously applied to enantioselective rhodium-catalyzed reactions. Therefore, some of the most interesting ones were evaluated in the cyclopropanation of styrene using the recently developed catalyst Rh<sub>2</sub>(S-p-PhTPCP)<sub>4</sub> (Scheme 4).<sup>[15a]</sup> The reactions of TCE aryldiazoacetates with p-morpholine and p-Bpin on the phenyl ring gave the desired cyclopropanation in good yields with high levels of enantioselectivity (16a-b). The 3,5-dichlorosubstituted TCE diazoacetate yielded the cyclopropane in 85% yield with 85% ee (16c). Additionally, heterocycles such as benzothiazole, thiophene and pyrimidine were tolerated as the aryl group of the TCE diazoacetates (16d-f). Cyclopropanes were obtained in moderate yields (85-65%) with excellent levels of enantioselectivity (99-85%). The asymmetric induction with the heterocyclic diazo esters is much improved over previous results of cyclopropanation with the corresponding methyl esters



Rh<sub>2</sub>(*R*-*p*-PhTPCP)<sub>4</sub>

**Scheme 4.** Test of new diazo compounds in cyclopropanation reactions. The reactions were carried out with  $Rh_2(S-p-PhTPCP)_4$  (0.5 mol %) and styrene (2.0 equiv) in dry dichloromethane, followed by addition of a solution of diazo compounds **6** (1.0 equiv) in dichloromethane under argon over 2 h at room temperature. [a] The reaction used 1 mol % of  $Rh_2(S-p-PhTPCP)_4$ .

To conclude, a general and efficient route for the synthesis of 2,2,2-trichloroethyl (TCE) aryl-, heteroaryl-, and vinyldiazoacetates was achieved by palladium-catalyzed crosscoupling of the corresponding iodides and diazoacetate. The successful development of this process required addition of further phosphine ligand to the reaction mixture to avoid decomposition of the diazo product. The ready access of the diazo compounds will enhance the range and flexibility of the donor/acceptor metallocarbene chemistry.

#### **Experimental Section**

General Procedure for the palladium-catalyzed cross-coupling reaction:  $Pd(PPh_3)_4$  (231 mg, 0.2 mmol, 5 mol%), PPh<sub>3</sub> (106 mg, 0.4 mmol, 10 mol%), aryl iodide (4.0 mmol, 1.0 equiv), Ag<sub>2</sub>CO<sub>3</sub> (550 mg, 2.0 mmol, 0.5 equiv) were suspended in toluene (16 mL) under argon, followed by addition of NEt<sub>3</sub> (0.73 mL, 5.2 mmol, 1.3 equiv) and 2,2,2-trichloroethyl 2-diazoacetate (1.13 g, 5.2 mmol, 1.3 equiv). The resulting reaction was stirred at room temperature for 4 h and then filtered through a short path of silica gel, eluting with ethyl acetate. The filtrates were concentrated and the residue was purified by column chromatography to give the products.

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**Keywords:** 2,2,2,-trichloroethyl aryldiazoacetates • crosscoupling • palladium • donor/acceptor carbenes • asymmetric cyclopropanation

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COMN2UCATIONEt<sub>3</sub>, toluene, rt

Pd(PPh<sub>3</sub>)<sub>4</sub>, PPh<sub>3</sub>, Ag<sub>2</sub>CO<sub>3</sub>

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