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Palladium-catalyzed olefination of *N*-tosylhydrazones as β-diazo phosphonate precursors with arylhalides

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Dedication ((optional))

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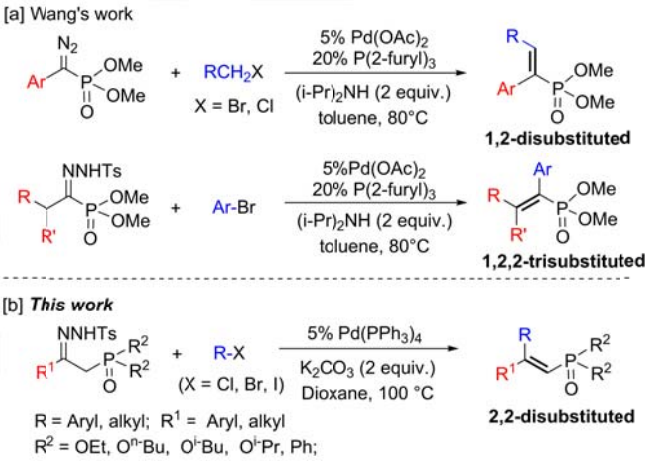
Abstract: An efficient palladium-catalyzed olefination of *N*-tosylhydrazones as *β*-diazo phosphonate precursors with aryl halides has been developed. 2,2-Disubstituted vinylphosphonates bearing versatile functional groups were easily accessed in moderate to excellent yields. Various aryl halides could be employed as the coupling partners, such as (hetero)arylbromides, aryliodides, and even arylchlorides. Moreover, with similar strategy (2,2-diphenylvinyl)diarylphosphine oxides can also be attained by the reaction of *N*-tosylhydrazones and aryl bromides. This protocol features easily available raw materials, simple reaction conditions, broad substrate scope as well as scale-up ability. Moreover, the potential application of this product was exemplified by further transformations.

Introduction

Main Text Paragraph.As an important family member of organic phosphates, substituted vinyl phosphates have been applied in the fields of pharmaceuticals, agricultural chemistry, and materials science due to their unique biological activity and chemical properties.[1] Furthermore, alkenylphosphates can also be very useful synthetic precursors, which can be variously transformed to provide pharmacologically active compounds and other functional molecules.[2,3] Therefore, the efficient stereoselective synthesis of alkenylphosphates is a significant objective for organic chemists. In the past decades, a variety of methods have been developed to access substituted vinylphosphates, mainly including transition-metal catalyzed Suzuki-type reaction,[4] Heck reactions of aryl halides with vinylphosphonates,[5] decarboxylative C–P coupling reaction,[6] nucleophilic addition of aryl alkynes with H-phosphine oxide,[7] dehydrogenative coupling of aryl alkenes or precursors with H-phosphine oxide,[8] and 1,2-aryl migration of diarylmethylated diazomethylphosphonates.[9] Although notable advances have been made, these methods usually encounter some drawbacks such as relatively harsh reaction conditions, narrow substrate scope, low yields of the products, the need to prepare prefunctionalized alkenylphosphonates or a stoichiometric amount of metal reagents, and poor regioselectivity. In addition, the methods for synthesizing 2,2-substituted vinylphosphonates are still limited. Therefore, it is still highly desirable to develop efficient and complementary strategies with mild reaction conditions and readily available reagents.

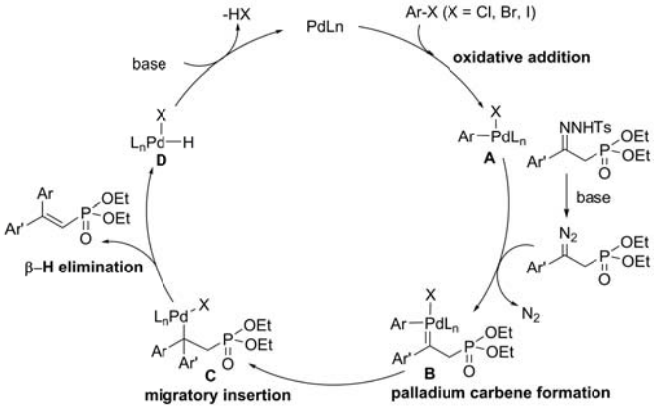


Scheme 1. Palladium-catalyzed coupling of α- or β-diazo phosphonates.

In recent years, *N*-tosylhydrazones as a class of readily accessible and stable diazo precursors have been extensively used in organic synthesis.[10] In particular, a palladium-catalyzed cross-coupling reaction via diazo compound has been established as a powerful tool for the formations of carbon-carbon double bonds.[11] It is worth mentioning that Wang et.al demonstrated an efficient strategy on the synthesis of 1,2-disubstituted vinylphosphonates through the palladium-catalyzed coupling reaction of *α*-diazo phosphonates with benzyl or allyl halides. Moreover, with similar strategy 1,2,2-trisubstituted vinylphosphonates can also be attained by using *N*-tosylhydrazones as α-diazo phosphonates precursors (**Scheme 1a**).[12] Inspired by this work, we speculated 2,2-disubstituted phosphates should be achieved by employing easily available *β*-diazophosphonates as coupling partners to react with aryl halides in the presence of Pd-catalyst (**Scheme 1b**).

As shown in **Scheme 2**, the plausible pathway of palladium-catalyzed olefination involves four fundamental steps: 1) oxidative addition of the aryl halide to a Pd(0) complex to form aryl-palladium-halide complex A; 2) palladium carbene formation; 3) migratory insertion; and 4) *β*-hydride elimination. Besides, an important reason we tend to adopt such a strategy to construct 2,2-disubstituted phosphates is that the *β*-ketophosphonates used to prepare *β*-diazophosphonates precursors are readily available.[13] Moreover, condensation of *β*-

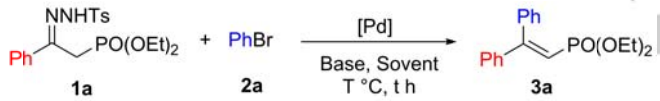
keto phosphonates with $TsNHNH_2$ gives the corresponding *N*-tosylhydrazones in good yields. As a part of our research interest in *N*-tosylhydrazones,[14] herein we described a Pd-catalyzed olefination reaction of *N*-tosylhydrazones as β-diazophosphonate precursors and aryl halides for the synthesis of 2,2-disubstituted phosphates and derivatives.



Scheme 2. A possible mechanism pathway.

Results and Discussion

Table 1. Optimization of reaction conditions.[a]

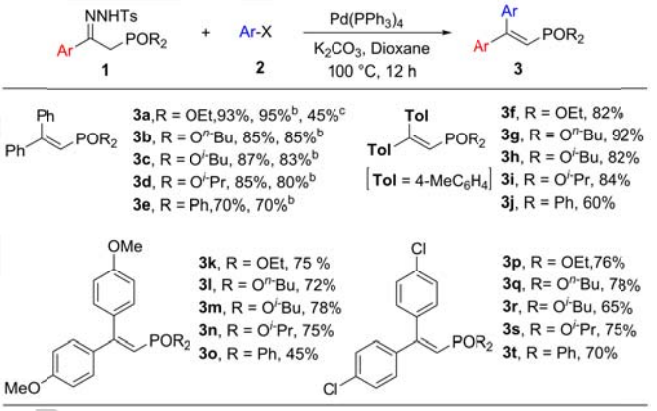


Entry	Catalyst	Base	Solvent	t (h)	Yield (%)[b]
1	$Pd(PPh_3)_4$	Na_2CO_3	Dioxane	5	25
2	$Pd(PPh_3)_4$	NaOH	Dioxane	5	26
3	$Pd(PPh_3)_4$	LiO^tBu	Dioxane	5	50
4	$Pd(PPh_3)_4$	K_3PO_4	Dioxane	5	70
5	$Pd(PPh_3)_4$	KOH	Dioxane	5	72
6	$Pd(PPh_3)_4$	Cs_2CO_3	Dioxane	5	75
7	$Pd(PPh_3)_4$	K_2CO_3	Dioxane	5	85
8	$Pd(PPh_3)_4$	K_2CO_3	THF	5	75
9	$Pd(PPh_3)_4$	K_2CO_3	DCE	5	50
10	$Pd(PPh_3)_4$	K_2CO_3	MeCN	5	65
11	$Pd(PPh_3)_4$	K_2CO_3	DMF	5	85
12	**$Pd(PPh_3)_4$**	**K_2CO_3**	**Dioxane**	**12**	**93**
13	$Pd(PPh_3)_4$	K_2CO_3	DMF	12	90
14[c]	$Pd(PPh_3)_4$	K_2CO_3	Dioxane	24	82
15[d]	$Pd(PPh_3)_4$	K_2CO_3	Dioxane	12	87

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), Base (2 equiv.)solvent (4 mL), 100 °C, under Ar atmosphere. [b] Isolated yields. [c] 80 °C. [d] K_2CO_3 (3 equiv.).

To assess whether the olefination process could be achieved, we chose the diethyl (2-phenyl-2-(2-tosylhydrazono)ethyl)phosphonate (**1a**, 0.2 mmol) and bromobenzene (**2a**, 0.24 mmol) as model substrates (Table 1). Initially, the reaction was performed in 1,4-dioxane (4.0 mL) at 100 °C for 5 hours under argon in the presence of $Pd(PPh_3)_4$ (5 mol%) as catalyst and Na_2CO_3 as base (2.0 equiv.). To our delight, the coupling reaction did occur and afford the desired coupling product 3a in 25% yield (entry 1). Encouraged by this result, we screened a series of bases (entries 2-7). The strong base NaOH did not show an influence on the yield (entry 2). Lithium tert-butoxide (LiO^tBu),[10,11] as a base commonly used in olefination reactions involving *N*-tosylhydrazones, did not show good results in this reaction (entry 3). In contrast, potassium and cesium salts showed good effects (entries 4-6), and K_2CO_3 turned out the best base to accomplish the transformation (entry 7, 85% yield). Subsequently, the effect of solvent was investigated (entries 8-11), and it was found that DMF also was an excellent solvent (entry 11, 85% yield) in terms of efficiency (entry 7). To our delight, the yield of product **3a** was dramatically raised to ≥90% with prolonged reaction time to 12 hours (entries 12 and 13). In addition, reducing the reaction temperature or increasing the amount of K_2CO_3 did not significantly improve the yield of the olefination (entries 14 and 15).

Table 2. Reaction of *N*-tosylhydrazones formed by *β*-ketophosphonates with aryl halides.[a]

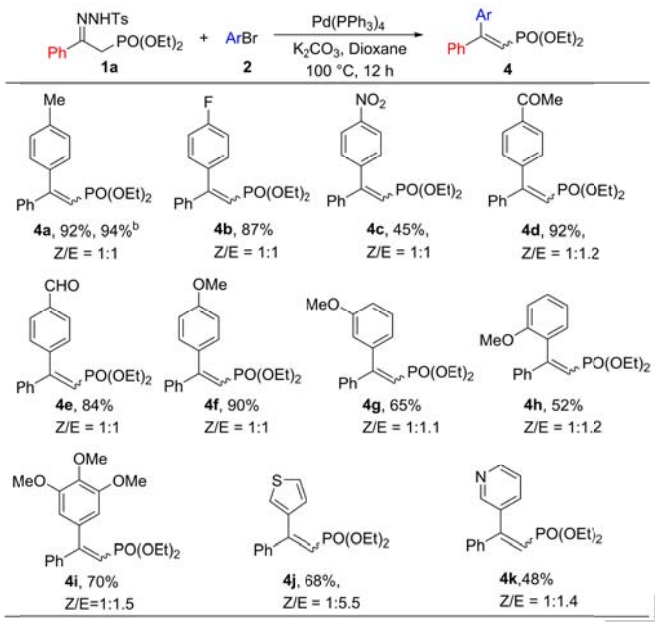


[a] Reaction condition: **1** (0.2 mmol), aryl bromide (**2a**, 0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (2 equiv.), 1,4-dioxane (4 mL), 100 °C, 12 h, under Ar atmosphere. Isolated yields. [b] PhI (**2b**, 0.24 mmol), [c] PhCl (**2c**, 0.24 mmol).

With the optimized conditions in hand (**Table 1**, entry 12), we explored the substrate scope of the palladium-catalyzed olefination. As demonstrated in **Table 2**, a variety of *N*-tosylhydrazones formed by *β*-ketophosphonates reacted with aryl bromides smoothly to provide the corresponding olefination products (**3a–3d**, **3f-3i**, **3k-3n**, **3p-3s**) in 65-93% yields. In general, both electron-rich and electron-deficient groups (4-Me, 4-MeO, or 4-Cl) substituted *N*-tosylhydrazones or aryl bromides were suitable for this protocol, and the desired products were obtained in good to excellent yields. Moreover, the structure of the phosphate groups (POR_2, R = OEt, O^nBu, O^iBu, O^iPr) on the *N*-tosylhydrazones did not have a significant effect on the reactivity. In contrast, the reaction of *N*-tosylhydrazones with diphenylphosphine oxide group can also react with aryl bromides, giving the corresponding products (**3e**, **3j**, **3o**, and **3t**) in 45-70% yields. It is worth mentioning these (2,2-diarylvinyl)diphenylphosphine oxides could be easily reduced into (2,2-diarylvinyl)diphenylphosphane. This type of organophosphorus ligand has very promising applications in transition-metal catalyzed coupling reactions.[15] In addition, aryliodides could also be used for the reaction, and the corresponding products (**3a-3e)** could be obtained with good to

excellent yields. Notably, even chlorobenzene could take part in the olefination to provide the desired product **3a**, albeit with a relatively lower yield.

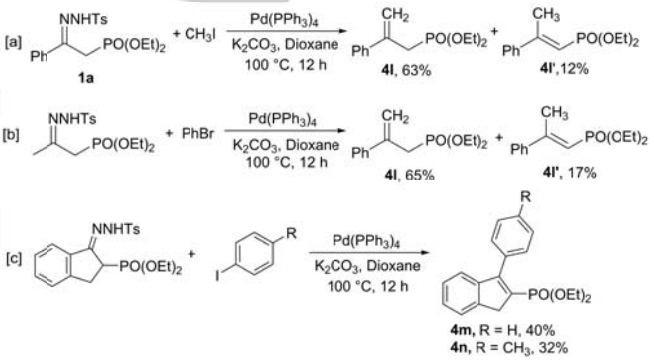
Table 3. Reaction of aryl halides with *N*-tosylhydrazone (**1a**) formed by diethyl (2-oxo-2-phenylethyl)phosphonate.[a]



[a] Reaction condition: **1a** (0.2 mmol), aryl bromide (**2**, 0.24 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (2 equiv.), 1,4-dioxane (4 mL), 100 °C, 12 h, under Ar atmosphere. Isolated yields. [b] PhI (0.24 mmol).

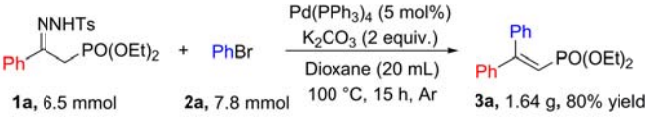
We next evaluated the scope of aryl and heteroaryl bromides for this olefination. Due to the difference of the di-substituted groups at the 2,2-position, the products have two configurations of Z and E, and the ratio is determined by ^{1}H NMR. As shown in Table 3, an array of substituents on the phenyl ring of arylbromides were well tolerated, and affording the desired products **4a-4k** in moderate to excellent yields. The substrates bearing an electron-donating group (4-Me and 4-OMe) at the para position of aryl bromides gave the desired products **4a** and **4f** in excellent yields (Z/E = 1:1). Moreover, aryl bromides with 4-fluoro, 4-formyl and 4-acetyl groups were transformed into their corresponding products **4b**, **4d**, and **4e** in excellent yields (Z/E = 1:1–1:1.2). 1-Bromo-4-nitrobenzene with a strong electron-withdrawing group as substrate was also tolerated in this transformation, albeit with moderate yield (Z/E = 1:1). In addition, 2- or 3-substituted methoxybromobenzene was also compatible with the current reaction conditions, affording the expected products **4g** and **4h** with 65% and 52% yields (Z/E = 1:1.1 and 1:1.2), respectively. Furthermore, 3,4,5-trimethoxybromobenzene was used as a substrate to participate in the reaction to give the product **4i** in 70% yield (Z/E = 1:1.5). Encouragingly, this reaction could be further extended into heteroaryl bromides. When 3-bromothiophene and 3-bromopyridine were used as partners in this reaction, the desired products **4j** and **4k** were obtained in 68% and 48% yields (Z/E = 1:5.5 and 1:1.4), respectively. Also, the reaction of methyl iodobenzene with **1a** can furnish an excellent yield, but the ratio of Z/E remains unchanged.

Interestingly, iodomethane as a substrate also participated the title reaction smoothly, delivering the product diethyl (2-phenylallyl)phosphonate **4l** in 63% yield with high selectivity, accompanied by a 12% yield of the product (*Z*)-diethyl (2-phenylprop-1-en-1-yl)phosphonate **4l'** (Scheme **3a**). When diethyl (*E*)-(2-(2-tosylhydrazono)propyl)phosphonate was selected as the substrate to react with bromobenzene, similar results could also be obtained (Scheme **3b**). These results indicated that the hydrogen on the methyl group preferentially underwent the *β*-H elimination compared to the hydrogen on the methylene group. Also, when diethyl (1-(2-tosylhydrazono)-2,3-dihydro-1*H*-inden-2-yl)phosphonate was used as the substrate, the olefination with aryl iodides also delivered the desired products **4m** and **4n** in 40% and 32% yields, respectively (Scheme **3c**).

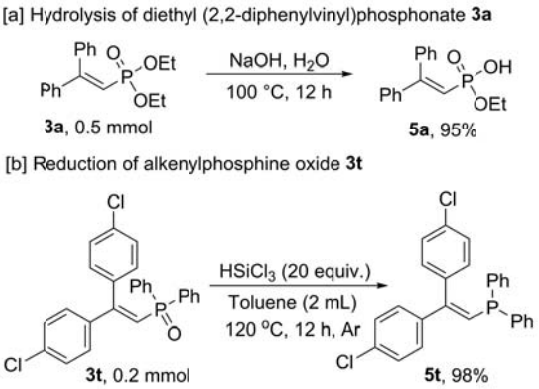


Scheme 3. The olefinations of *N*-tosylhydrazones with other substrates.

To demonstrate the practical application of this method, a gram-scale synthesis of **3a** was performed. Gratifyingly, the reaction could be conducted on a 6.5 mmol scale to provide 1.64 g of product **3a** in 80% yield (Scheme **4**).



Scheme 4. A gram-scale synthesis of **3a**.



Scheme 5. Derivatization reactions of **3a** and **3t**.

Synthetic transformations of products **3a** and **3t** were also conducted (**Scheme 5**). The product **3a** could be easily hydrolyzed to a monoester product ethyl hydrogen (2,2-diphenylvinyl)phosphonate **5a** in 95% yield by treatment with 10% aqueous NaOH (**Scheme 5a**). Additionally, in the presence of excess $HSiCl_3$, the product **3t** could be directly reduced into bis(4-chlorophenyl)(2,2-diphenylvinyl)phosphane (**5t**) with 98% yield (**Scheme 5b**). This type of organophosphorus ligand has very promising applications in transition-metal catalyzed coupling reactions.[15]

Conclusion

In summary, we have demonstrated an efficient $Pd(PPh_3)_4$-catalyzed olefination of *N*-tosylhydrazones as *β*-diazo phosphonate precursors with aryl halides, which constitutes a novel strategy to synthesize 2,2-disubstituted vinylphosphonates in moderate to excellent yields. Various aryl halides could be employed as the coupling partners, such as (hetero)arylbromides, aryliodides, and even arylchlorides. This transformation also could efficiently produce (2,2-diphenylvinyl)diarylphosphine oxides, which shows its eminent merits such as inexpensive $Pd(PPh_3)_4$ as catalyst, easily available *β*-diazo phosphonate precursors, broad substrate scope and facile scalability.

Experimental Section

Unless otherwise noted, all synthetic steps were performed under an Ar atmosphere using Schlenk tubes. The materials obtained from commercial sources were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Brucker Advance III HD 400 MHz spectrometer in $CDCl_3$ or CD_3OD solution. All chemical shifts were reported in ppm (*δ*) relative to the internal standard TMS (0 ppm). High-resolution mass spectra (HRMS) were acquired in electrospray ionization (ESI) mode using a TOF mass analyzer.

General procedure for the reaction of *N*-tosylhydrazones formed by *β*-ketophosphonates and bromobenzene.

A Schlenk tube (25 mL) was charged with *(E)*-(2-Aryl-2-(2-toluenesulfonyl)ethyl)phosphinate (**1**, 0.2 mmol), aryl bromide (**2**, 0.24 mmol), K_2CO_3 (0.4 mmol) and $Pd(PPh_3)_4$ (5 mol%) in 1,4-dioxane (4 mL) at room temperature under an argon atmosphere. Then the mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc (5 mL), and washed with saturated NaCl solution (5 mL), and the organic layer was separated. Then the aqueous layer was extracted with EtOAc (5 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude material was purified by column chromatography on silica gel to afford the final product **3** or **4**.

General procedure for gram-scale experiment.

A mixture of *N*-tosylhydrazone **1a** (6.5 mmol), PhBr **2a** (7.8 mmol), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (2 equiv.), and 1,4-dioxane (20 mL) were added into a Schlenk tube. The solution was stirred at 100 ºC for 15 h. After reaction completion, the reaction mixture was diluted with EtOAc (50 mL), and washed with saturated NaCl solution (50 mL), and the organic layer was separated. Then the aqueous layer was extracted with EtOAc (50 mL × 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give the final products **3a** (1.64 g, 80% yield).

Hydrolysis of diethyl (2,2-diphenylvinyl)phosphonate 3a

Diethyl (2,2-diphenylvinyl)phosphonate **3a** (0.5 mmol) was refluxed in 5 mL of 10% aqueous NaOH for 12 h. The solution was cooled to room temperature and acidified with 10% aqueous HCl. The water was evaporated, and the obtained solid was dissolved in chloroform. The organic phase was dried over anhydrous Na_2SO_4. Then the filtrate obtained after filtration was distilled to give the product **5a** as a white solid with a 95% yield.

Reduction of alkenylphosphine oxide 3t

(2,2-Bis(4-chlorophenyl)vinyl)diphenylphosphine oxide **3t** (0.2 mmol) and excess $HSiCl_3$ (20 equiv.) in toluene (2 mL) at room temperature under an argon atmosphere. Then the mixture was stirred at 120 °C for 12 h. After cooling to room temperature, the solution was added 10% aqueous NaOH carefully to quench unreacted $HSiCl_3$. Next, the mixture was diluted with water (10 mL) and extracted with ethyl acetate(10 mL× 3). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether/ethyl acetate = 150/1 as eluent to give the target product **5t** as white solid with 98% yield.

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Keywords: olefination • *N*-tosylhydrazone •*β*-diazo phosphonate • aryl halide • vinylphosphonate

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Entry for the Table of Contents

An efficient Pd-catalyzed olefination of *N*-tosylhydrazones as *β*-diazo phosphonate precursors with aryl halides was described. A series of 2,2-disubstituted vinylphosphonates and (2,2-diphenylvinyl)diarylphosphine oxides were easily obtained in moderate to excellent yields.

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