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Capture of *In Situ* Generated Diazo Compounds or Copper Carbenoids by Triphenylphosphine: Selective Synthesis of *trans*-Alkenes and Unsymmetric Azines *via* Reaction of Aldehydes with Ketone-Derived *N*-Tosylhydrazones

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Abstract: Copper(II) acetylacetonate-catalyzed Wittig olefination reactions of aldehydes with ketone-derived *N*-tosylhydrazones are reported. A series of tosylhydrazones was investigated and our results showed that the carbon number of the alkyl chain influences the *E*-selectivity of the alkenes greatly. Alkenes could be obtained in moderate yields and excellent *E*-selectivity when the carbon numbers were up to two. Under metal-free conditions, triphenylphosphine was able to capture the *in situ* generated diazo compounds and the corresponding unsymmetrical azines were formed in good yields.

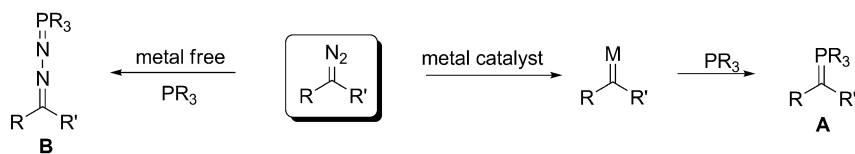
Keywords: alkenes; diazo compounds; *N*-tosylhydrazones; unsymmetrical azines; Wittig reactions

Diazo compounds have a long history and have attracted much attention due to their wide applications in organic synthesis.^[1] Among the various important applications, Wittig olefination plays an important role. The generation of free ylide **A** (Scheme 1), which could subsequently react with aldehydes or ketones to form the corresponding alkenes, has been extensively studied.^[2] Many kinds of metal catalysts have been developed to catalyze this reaction, such as

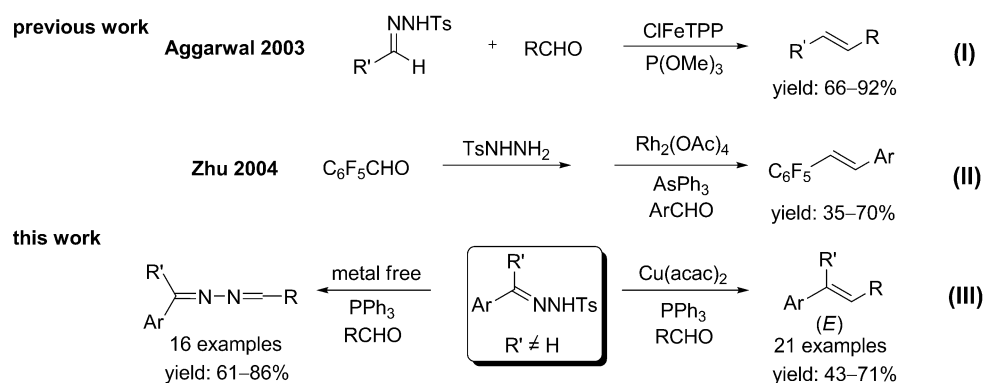
Mo,^[3] Re,^[4] Fe,^[5] Rh,^[6] Ru,^[7] Co,^[8] Cu,^[9] Ir.^[10] It was also reported that in the absence of a metal catalyst, phosphazine **B** would be formed as an intermediate which can react with aldehydes to form azines (Scheme 1).^[3,4d,7g]

However diazo compounds without an electron-withdrawing group are usually unstable and thus difficult to handle, which significantly limits the scope of this type of reaction. *N*-Tosylhydrazones, which can be utilized as safe diazo precursors, have been used in organic synthesis for a long time.^[11] In the past several years, rapid progress has been made in tosylhydrazone-participated cross-coupling reactions and X–H (X = C, O, S, N, P) insertion reactions.^[12]

The method of generating diazo compounds *in situ* from tosylhydrazones looks as if it is an ideal way to make up for the shortcomings of the diazo compounds without an electron-withdrawing group. But less attention has been paid to the Wittig olefination using tosylhydrazones. To the best of our knowledge, only two examples were reported. In 2003, Aggarwal and co-workers^[13] reported a ClFeTPP-catalyzed Wittig reaction of aldehyde-derived tosylhydrazones with aldehydes (Scheme 2, **I**). The alkenes were formed in high yields and high *E*-selectivity. In 2004, Zhu and co-workers^[14] described a straightforward method for the synthesis of *trans*-pentafluorophenyl-containing alkenes from aldehydes in moderate to good yields using Rh(OAc)₂ as catalyst (Scheme 2, **II**).



Scheme 1. The generation of ylide **A** and phosphazine **B**.

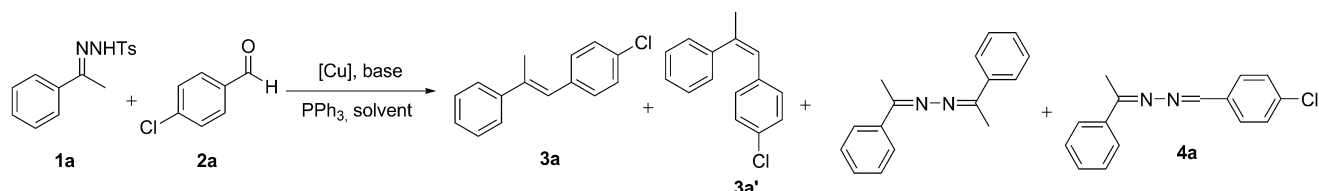


Scheme 2. Wittig reaction of *in situ* generated diazo compounds with aldehydes.

However, there are several problems remaining unsolved in this field. There was no report about Wittig olefination using ketone-derived tosylhydrazones

which may be due to the steric hindrance of the substrates. Therefore appropriate reaction conditions need be found to make this reaction work in reality.

Table 1. Reaction results of **1a** with **2a** in different reaction conditions.^[a]



Entry	Catalyst	Base	Solvent	<i>T</i> [°C]	<i>t</i> [h]	Product	Yield [%] ^[b]	<i>E</i> : <i>Z</i> ^[c]
1	CuI	K ₂ CO ₃	dioxane	90	12	3a + 3a'	49	85:15
2	Cu(acac) ₂	K ₂ CO ₃	dioxane	90	12	3a + 3a'	68	84:16
3	Cu(MeCN) ₄ PF ₆	K ₂ CO ₃	dioxane	90	12	3a + 3a'	34	87:13
4	CuCl ₂	K ₂ CO ₃	dioxane	90	12	3a + 3a'	28	82:18
5	Cu(OAc) ₂	K ₂ CO ₃	dioxane	90	12	3a + 3a'	24	92:8
6	Cu(acac) ₂	K ₂ CO ₃	DMF	90	12	3a + 3a'	64	84:16
7	Cu(acac) ₂	K ₂ CO ₃	toluene	90	12	3a + 3a'	51	89:11
8	Cu(acac) ₂	K ₂ CO ₃	CH ₂ ClCH ₂ Cl	90	12	3a + 3a'	39	82:18
9	Cu(acac) ₂	K ₂ CO ₃	DMSO	90	12	3a + 3a'	< 5	—
10	Cu(acac) ₂	K ₂ CO ₃	CH ₃ CN	90	12	3a + 3a'	52	83:17
11	Cu(acac) ₂	NaOH	dioxane	90	12	3a + 3a'	< 5	—
12	Cu(acac) ₂	Cs ₂ CO ₃	dioxane	90	12	3a + 3a'	61	83:17
13	Cu(acac) ₂	<i>t</i> -BuOLi	dioxane	90	12	3a + 3a'	80	80:20
14	Cu(acac) ₂	<i>t</i> -BuONa	dioxane	90	12	3a + 3a'	< 5	—
15	Cu(acac) ₂	<i>t</i> -BuOK	dioxane	90	12	3a + 3a'	51	82:18
16	Cu(acac) ₂	<i>t</i> -BuOLi	toluene	90	12	3a + 3a'	75	89:11
17	Cu(acac) ₂	<i>t</i> -BuOLi	dioxane	50	24	3a + 3a'	33	81:19
18	Cu(acac) ₂	<i>t</i> -BuOLi	toluene	50	24	3a + 3a'	36	88:12
19	Cu(acac)₂	<i>t</i>-BuOLi	toluene	90	10	3a + 3a'	75 (65^[d])	89:11
20 ^[f]	—	<i>t</i> -BuOLi	toluene	90	10	4a	80	—
21 ^[f]	—	<i>t</i> -BuOLi	dioxane	90	14	4a	91 (81 ^[e])	—

^[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), catalyst (10 mol%), base (0.7 mmol), solvent (5 mL), PPh₃ (0.7 mmol), under an N₂ atmosphere.

^[b] Determined by GC or GC-MS, yield of *Z* + *E*.

^[c] Determined by GC or GC-MS.

^[d] Isolated yield of product **3a** based on aldehyde **2a**.

^[e] Isolated yield based on hydrazone **1a**.

^[f] Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), base (0.6 mmol), solvent (5 mL), PPh₃ (0.6 mmol), under an N₂ atmosphere.

Table 2. Olefinations with a range of aldehydes and *N*-tosylhydrazones.^[a]

$ \begin{array}{c} \text{R}^1 \\ \text{C}=\text{N}=\text{NHTs} \\ \text{R}^2 \end{array} + \text{R}^3\text{CHO} \xrightarrow[\text{toluene, 90 }^\circ\text{C, N}_2, 10 \text{ h}]{\text{Cu(acac)}_2, \text{PPh}_3, t\text{-BuOLi}} \begin{array}{c} \text{R}^1 \\ \text{C}=\text{C} \\ \text{R}^2 \end{array} + \begin{array}{c} \text{R}^1 \\ \text{C}=\text{C} \\ \text{R}^2 \end{array} $						
Entry	R ¹	R ²	R ³	Product	Yield of 3 [%] ^[b]	<i>E/Z</i> (3:3') ^[c]
1	Ph	Me	4-ClC ₆ H ₄	3a	65	89:11
2	4-ClC ₆ H ₄	Me	4-ClC ₆ H ₄	3b	51	78:22
3	2-thienyl	Me	4-ClC ₆ H ₄	3c	55	83:17
4	4-NCC ₆ H ₄	Me	4-ClC ₆ H ₄	3d	36 ^[d]	76:24
5	4-MeCO ₂ C ₆ H ₄	Me	4-ClC ₆ H ₄	3e	0 ^[e]	—
6	3-MeCONHC ₆ H ₄	Me	4-ClC ₆ H ₄	3f	0 ^[e]	—
7	Ph	Et	4-ClC ₆ H ₄	3g	71	99:1
8	Ph	Me	Ph	3h	52	90:10
9	Ph	Me	4-CF ₃ C ₆ H ₄	3i	43	89:11
10	Ph	Me	<i>n</i> -butyl	3j	49	60:40
11	Ph	Me	<i>n</i> -dodecyl	3k	50	64:36
12	4-MeOC ₆ H ₄	Me	4-O ₂ NC ₆ H ₄	3l	61	74:26
13	4-ClC ₆ H ₄	Et	4-ClC ₆ H ₄	3m	62	97:3
14	4-MeC ₆ H ₄	Et	4-ClC ₆ H ₄	3n	53	97:3
15	4-NCC ₆ H ₄	Et	4-ClC ₆ H ₄	3o	23 ^[d]	99:1
16	Ph	Et	Ph	3p	60	99:1
17	Ph	Et	4-CF ₃ C ₆ H ₄	3q	57	99:1
18	Ph	Et	2-thienyl	3r	55	98:2
19	Ph	Et	2-furyl	3s	45	99:1
20	Ph	Et	1-naphthyl	3t	60	99:1
21	Ph	<i>n</i> -propyl	4-ClC ₆ H ₄	3u	50	96:4
22	Ph	<i>n</i> -propyl	4-CF ₃ C ₆ H ₄	3v	51	99:1
23	Ph	<i>n</i> -butyl	4-ClC ₆ H ₄	3w	55	94:6

^[a] Reaction conditions: **1a** (0.6 mmol), **2a** (0.5 mmol), Cu(acac)₂ (10 mol%), *t*-BuOLi (0.7 mmol), toluene (5 mL), PPh₃ (0.7 mmol), under an N₂ atmosphere, 90 °C, 10 h.

^[b] Isolated yield of **3** based on aldehydes.

^[c] Determined by GC-MS or ¹H NMR.

^[d] The yield was determined by GC-MS.

^[e] Messy products were obtained and the desired products were not detected by GC-MS.

Since copper(I) salts can catalyze the olefination of aldehydes with diazo reagents,^[9] we think that copper catalysts may also catalyze the olefination reaction of aldehydes with tosylhydrazones.^[15] On the other hand, PPh₃ was reported to be able to capture the diazo compounds forming phosphazine **B** (Scheme 1). If the *in situ* generated diazo compounds could also be captured by PPh₃ successfully, a simple and efficient way to synthesize unsymmetrical azines would be possible, which are not easy to synthesize by literature methods.^[16] In a continuation of our work on the development of new synthetic applications based on tosylhydrazones,^[17] here we report the results of our attempt in achieving these goals (Scheme 2, **III**).

Our study started with the CuI-mediated reaction of acetophenone-derived tosylhydrazone (**1a**) with 4-chlorobenzaldehyde (**2a**) and PPh₃ using K₂CO₃ as base at 90 °C in dioxane. With 0.1 equiv. of CuI, the corresponding alkenes (**3a** + **3a'**) were formed in 49% yield with an *E/Z* ratio of 85:15 (Table 1, entry 1). Inspired by this result, we decided to optimize this reac-

tion. Optimization of the copper catalysts (Table 1, entries 2–5) revealed that Cu(acac)₂ was the best which resulted in an increase in yield to 68%. A variety of solvents (Table 1, entry 6–10) and bases (Table 1, entries 11–16) were then screened. Among the bases tested, *t*-BuOLi gave the best result. As to the solvent, dioxane or toluene are superior to other solvents tested. When we decreased the temperature to 50 °C, the yield dramatically decreased to only 33% and 36% (Table 1, entries 17 and 18). Under optimized conditions, 10 h were needed to complete the reaction (Table 1, entry 19). When using P(OMe)₃, P(OEt)₃ or P(*O*-*i*-Pr)₃ instead of PPh₃, the yield was low (< 10%).

In the absence of a copper catalyst, we were delighted to find that PPh₃ was able to capture the diazo compound generated *in situ* from acetophenone-derived tosylhydrazone (**1a**), and the desired product **4a** was formed in 80% yield (Table 1, entry 20). After optimization of the solvent and reaction time, the

yield increased to 91% and the product was isolated in 81% yield (Table 1, entry 21).

With the optimized Wittig olefination reaction conditions in hand, scope of the reaction was then studied. By using tosylhydrazones derived from 1-(4-chlorophenyl)ethanone, 1-(thiophen-2-yl)ethanone and 4-acetylbenzonitrile, moderate yields were obtained, the *E*-selectivity depends on the aldehydes used. Using 4-chlorobenzaldehyde, benzaldehyde or 4-(trifluoromethyl)benzaldehyde as the substrate, a good *E*-selectivity was obtained (Table 2, entries 1–4, 8 and 9). When tosylhydrazones derived from 4-acetylphenyl acetate and *N*-(3-acetylphenyl)acetamide were used, the desired product alkenes were not detected by GC-MS (Table 2, entries 5 and 6). When aliphatic aldehydes such as butyraldehyde and dodecanal were used, moderate yields were obtained but the *E*-selectivity was low (Table 2, entries 10 and 11). When propiophenone-derived tosylhydrazone was used, we were delighted to find that the *E*-selectivity increased greatly and the *E/Z* ratio was up to 99/1 (Table 2, entry 7).^[18,19]

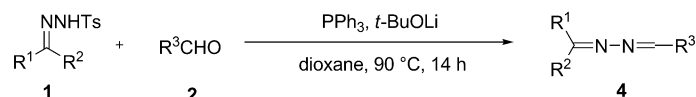
Inspired by this phenomenon, we studied the reactions of propiophenone-derived tosylhydrazone with different aldehydes, they all gave moderate yields and high *E*-selectivity (Table 2, entries 13–20). Finally, tosylhydrazones derived from 1-phenylbutan-1-one (the carbon number of the alkyl chain was up to 3) and 1-

phenylpentan-1-one (the carbon number of the alkyl chain was up to 4) were used, good yields and high *E*-selectivity were also obtained (Table 2, entries 21–23). Finally, tosylhydrazones derived from aliphatic ketones (cyclohexanone, cyclopentanone and 3-pentanone) were used, but no desired product was obtained which shows that the new method needs to be developed further to carry out this reaction.

Without the use of a copper catalyst, the reaction of tosylhydrazones, aldehydes and PPh₃ affords unsymmetrical azines in good yield. This method provides an easy and efficient way to synthesize a variety of unsymmetrical azines. A variety of electron-rich, electron-neutral, and electron-deficient aryl tosylhydrazones or aldehydes underwent the reaction smoothly to afford the desired products in good yields (Table 3, entries 1–18). When tosylhydrazones derived from aliphatic ketones (cyclohexanone, cyclopentanone and 3-pentanone) were used, no desired product was obtained.

A possible mechanism for the above reported reactions is depicted in Scheme 3. Initially, diazo compounds were formed *in situ* from the corresponding tosylhydrazones **1** under basic conditions. In the presence of a copper catalyst, the diazo compounds were converted to copper carbenoids which subsequently react with PPh₃ to form the free ylide **A**. Reaction of free ylide **A** with aldehydes gave olefination products.

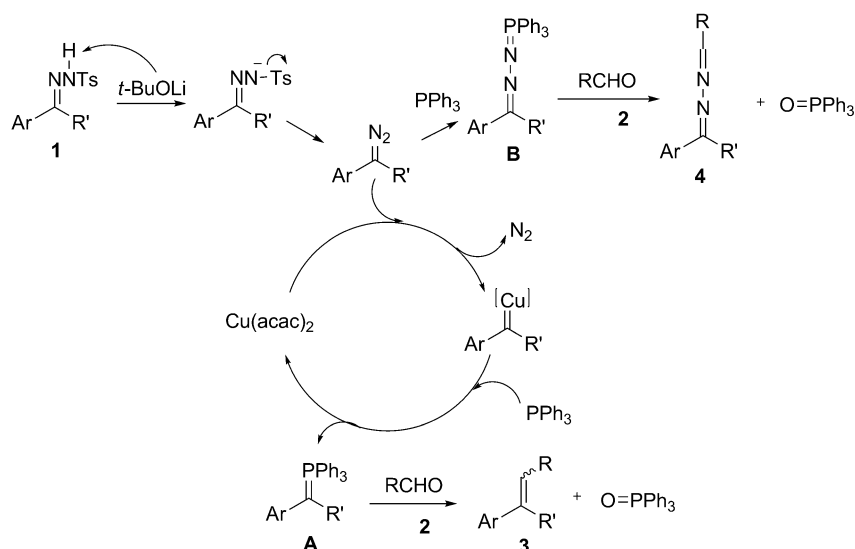
Table 3. Preparation of unsymmetric azines **4** from the reaction of **1**, **2**, and PPh₃.^[a]



Entry	R ¹	R ²	R ³	Product	Yield [%] ^[b]
1	Ph	Me	4-ClC ₆ H ₄	4a	81
2	4-ClC ₆ H ₄	Me	4-ClC ₆ H ₄	4b	73
3	4-MeOC ₆ H ₄	Me	4-ClC ₆ H ₄	4c	83
4	4-O ₂ NC ₆ H ₄	Me	4-ClC ₆ H ₄	4d	62
5	4-NCC ₆ H ₄	Me	4-ClC ₆ H ₄	4e	75
6	4-MeCO ₂ C ₆ H ₄	Me	4-ClC ₆ H ₄	4f	77
7	3-MeCONHC ₆ H ₄	Me	4-ClC ₆ H ₄	4g	79
8	Ph	Et	4-ClC ₆ H ₄	4h	71
9	4-MeC ₆ H ₄	Et	4-ClC ₆ H ₄	4i	68
10	4-NCC ₆ H ₄	Et	4-ClC ₆ H ₄	4j	77
11	Ph	Ph	4-ClC ₆ H ₄	4k	72
12	1-naphthyl	Me	4-ClC ₆ H ₄	4l	70
13	Ph	Me	Ph	4m	82
14	Ph	Me	4-MeOC ₆ H ₄	4n	67
15	Ph	Me	4-Me ₂ NC ₆ H ₄	4o	61
16	Ph	Me	4-O ₂ NC ₆ H ₄	4p	85
17	Ph	Me	2-thienyl	4q	80
18	Ph	Me	2-O ₂ NC ₆ H ₄	4r	86

^[a] Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), *t*-BuOLi (0.6 mmol), dioxane (5 mL), PPh₃ (0.6 mmol), under an N₂ atmosphere.

^[b] Isolated yield based on tosylhydrazones.



Scheme 3. Proposed pathway for the reactions of *N*-tosylhydrazones with aldehydes in the presence of PPh_3 .

Under metal-free conditions, the diazo compounds react with PPh_3 to form the intermediate **B** which reacts with aldehydes to form the corresponding unsymmetrical azines **4**.

In conclusion, we have developed an efficient copper(II) acetylacetonate-catalyzed Wittig olefination of aldehydes with ketone-derived *N*-tosylhydrazones. It was found that the alkyl chain of the tosylhydrazones influenced the *E*-selectivity of the alkenes greatly. When the carbon numbers of the alkyl chain were up to two, high *E*-selectivity could be obtained. We have also developed an efficient one-pot method for the synthesis of the unsymmetrical azines. Studies on further applications of this methodology are now in progress in our laboratory.

Experimental Section

$\text{Cu}(\text{acac})_2$ -Catalyzed Wittig Olefination Reaction of Ketone-Derived *N*-Tosylhydrazones with Aldehydes (**3a** as an Example)

A Schlenk tube with a magnetic stir bar was charged with hydrazone **1a** (172.8 mg, 0.6 mmol), **2a** (70.0 mg, 0.5 mmol), $\text{Cu}(\text{acac})_2$ (13.2 mg, 0.05 mmol), *t*-BuOLi (56.0 mg, 0.7 mmol), PPh_3 (183.4 mg, 0.7 mmol) and toluene (5 mL). The system was heated at 90 °C under an N_2 atmosphere with stirring for 10 h. The reaction mixture was then allowed to cool to ambient temperature, it was then diluted with 10 mL of ethyl acetate, and washed with brine (30 mL), water (30 mL), after which the organic layer was dried over Na_2SO_4 . After concentration under vacuum, the crude product was purified by column chromatography.

Metal-Free Reaction of *N*-Tosylhydrazones with Aldehydes toward Unsymmetrical Azines (**4a** as an Example)

A Schlenk tube with a magnetic stir bar was charged with hydrazone **1a** (144.0 mg, 0.5 mmol), **2a** (84.0 mg, 0.6 mmol), *t*-BuOLi (48.0 mg, 0.6 mmol), PPh_3 (157.2 mg, 0.6 mmol) and dioxane (5 mL). The system was heated at 90 °C with stirring for 14 h. The reaction mixture was then allowed to cool to ambient temperature, it was diluted with 10 mL of ethyl acetate, and washed with brine (30 mL), water (30 mL), after which the organic layer was dried over Na_2SO_4 . After concentration under vacuum, the crude product was purified by column chromatography.

Acknowledgements

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