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Microwave-Assisted One-Step Synthesis of Acetophenones *via* Palladium-Catalyzed Regioselective Arylation of Vinyloxytrimethylsilane

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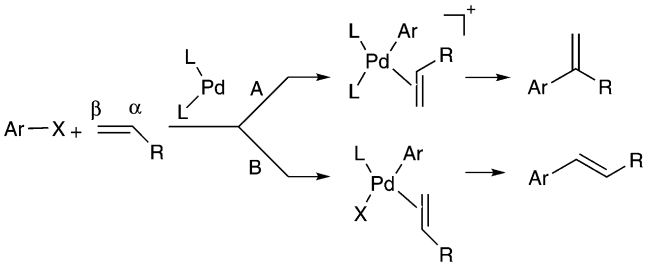
Abstract: The regiochemistry of the palladium-mediated arylation (Heck arylation) of enol ethers is sensitive to the structure of the enol ether, the arylating agent and the catalytic system. In this study, an effective and practical method was successfully developed for the synthesis of acetophenones with high regioselectivity under palladium-catalyzed conditions. A variety of acetophenones was readily prepared from aryl iodides in good to excellent yields under microwave irradiation in a single step. The key feature of our new protocol is the use of vinyloxytrimethylsilane as a highly regioselective acylation reagent.

Keywords: acetophenones; acylation reagents; Heck arylation; palladium; regioselectivity

Introduction

Acetophenones are widely used in the pharmaceutical, fragrance, dye, and agrochemical industries, and are common structural units of a variety of biologically active compounds.[1] Acetophenones are classically synthesized by Friedel–Crafts acylation catalyzed by Lewis acids.[2] However, the Friedel–Crafts acylation is neither effective for electron-deficient arenes nor sufficiently regioselective to introduce an acetyl group. Over the years, various Wacker-type reactions for the synthesis of acetophenones from styrenes have been reported. In these reactions, many catalytic systems have been developed, using solvents such as supercritical carbon dioxide (CO_2),[3] polyethylene glycol (PEG),[4] and ionic liquids;[5] phase-transfer catalysts;[6] reoxidants such as nitrous oxide[7] and *tert*-butyl hydroperoxide (TBHP);[8] metal catalysts such as Co,[9a,b] Rh,[9c] and Mn[9d] instead of Pd; and metal-free oxidation.[10] Besides, a number of palladium-catalyzed cross-coupling reactions have been developed to generate ketones.[11,12] Among these reported methods, the Pd-catalyzed Heck reaction of aryl halides with electron-rich olefin vinyl ethers is attractive due to its simplicity, tolerance of various functional groups and the easy availability of reagents.[13] Unfortunately, under normal Heck conditions, mixtures of α- and β-arylated products are typically obtained.[14,15] Thus, controlling the regioselectivity of this arylation process remains a challenge.

The problem of regioselectivity arises because there are two competing reaction pathways in the Heck reaction, as illustrated in Scheme 1.[13,14] In previous studies, Larhed,[14a,b] Hallberg[14] and Cabri[15] have improved the poor regioselectivity of this reaction by employing aryl triflates, adding stoichiometric silver or thallium salts. However, a significant drawback of this approach is that the use of silver raises the cost, thallium salts are toxic, and triflates are base sensi-



Scheme 1. The two competing pathways in the Heck reaction.

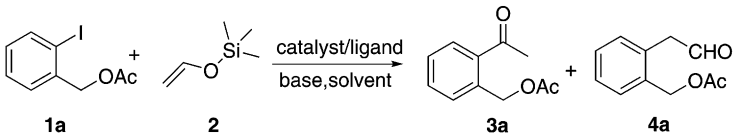
tive, thermally labile, and generally commercially unavailable. More recently, Hallberg[16] and Xiao[17] have developed effective methods to deal with the issue of regioselectivity with electron-rich olefins. The developed catalytic systems make use of solvents such as ionic liquids,[17a] and ethylene glycol (EG),[17b–e] and ligands such as 1,3-bis(diphenylphosphino)propane (DPPP),[16,17a,b,d,e] and 1,1′-bis(diphenylphosphino)ferrocene (DPPF).[17c,f] These methods can promote the ionic pathway A which leads to internal α-arylated vinyl ethers. Unfortunately, these reactions typically take hours or days to reach completion and valuable ligands such as DPPP are needed to achieve high regioselectivity. Furthermore, the α-arylated vinyl ethers need to be hydrolyzed in acid to generate acetophenones.

Few studies have focused on changing the substrate enol ethers to improve the regioselectivity of the arylation process. Silyl enol ether, as an electron-rich vinyl ether, has been used in many electrophilic addition reactions.[18] We therefore investigated vinyloxytrimethylsilane as an acetyl donor for the direct synthesis of acetophenones from aryl halides. Microwave heating has been shown to significantly expedite transition metal-catalyzed reactions in most cases.[19] In our protocol, we were able to restrict the reaction time to 2 h using microwave heating. The key feature of our new protocol is the use of vinyloxytrimethylsilane as a highly regioselective and novel acylation reagent to obtain acetophenones in a single step.

Results and Discussion

Using 2-iodobenzyl acetate **1a** and vinyloxytrimethylsilane **2** as the model substrates, we initially optimized the reaction conditions under microwave irradiation. A series of catalytic systems was screened including the catalyst/ligand, base, solvent and temperature (Table 1). No formation of **3a** or **4a** was observed with CuI as the catalyst and most of the starting material remained unchanged (Table 1, entry 1). Among the palladium catalytic systems (Table 1, entries 2–5), $Pd(OAc)_2/PPh_3$ was found to be the best in terms of isolated yield and regioselectivity of the Heck arylation. Substrate **1a** was completely arylated after 2 h to give exclusive α-substituted product **3a** in the presence of 1 mol% of $Pd(OAc)_2$ and 2 mol% of PPh_3 using Et_3N as the base in DMF at 100 °C heated by microwave (Table 1, entry 5). The β-substituted prod-

Table 1. Survey of the reaction conditions for the regioselective Heck reaction.[a]



1a **2** **3a** **4a**

Entry	Catalyst/Ligand	Base	Solvent	**3a**/**4a**[b]	Yield [%][c]
1	CuI	Et_3N	DMF	–	0
2	$Pd(OAc)_2$	Et_3N	DMF	>99/1	7
3	$Pd(PPh_3)_4$	Et_3N	DMF	>99/1	10
4	$PdCl_2(PPh_3)_2$	Et_3N	DMF	>99/1	86
5	$Pd(OAc)_2/PPh_3$	Et_3N	DMF	>99/1	87
6	$Pd(OAc)_2/PPh_3$	DBU	DMF	–	trace
7	$Pd(OAc)_2/PPh_3$	K_2CO_3	DMF	–	0
8	$Pd(OAc)_2/PPh_3$	Cs_2CO_3	DMF	–	0
9	$Pd(OAc)_2/PPh_3$	Et_3N	DMSO	>99/1	82
10	$Pd(OAc)_2/PPh_3$	Et_3N	CH_3CN	>99/1	56
11	$Pd(OAc)_2/PPh_3$	Et_3N		>99/1	30
12	$Pd(OAc)_2/PPh_3$	DMF/Et_3N = 1/1[d]		>99/1	59
13	$Pd(OAc)_2/PPh_3$	Et_3N	DMF/H_2O = 1/1	>99/1	0
14	$Pd(OAc)_2/PPh_3$	Et_3N	DMF/DMSO = 1/1	>99/1	89
15[e]	$Pd(OAc)_2/PPh_3$	Et_3N	DMF/DMSO = 1/1	>99/1	86
16[f]	$Pd(OAc)_2/PPh_3$	Et_3N	DMF/DMSO = 1/1	>99/1	78

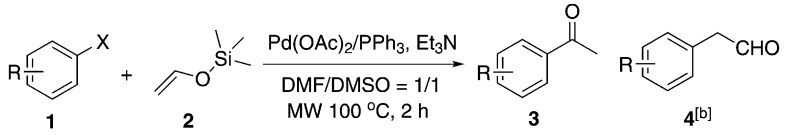
[a] Unless otherwise stated, all reactions were carried out under microwave irradiation using **1a** (0.36 mmol), **2** (0.72 mmol), catalyst (3.6 μmol), ligand (7.2 μmol) and base (1.08 mmol) in the indicated solvent at 100 °C for 2 h.
[b] Molar ratio of **3a**/**4a**. When product **4a** could not be detected, a value of >99/1 was assigned. The same applies for Table 2.
[c] Isolated yield.
[d] 1/1 refers to v/v.
[e] This reaction was carried out at 110 °C.
[f] This reaction was carried out at 90 °C.

uct **4a** was not isolated, suggesting that the ionic pathway A is operative with vinyloxytrimethylsilane **2** as the acylation reagent. The base additive plays an important role in the overall efficiency of the reaction. When we changed the base from Et_3N to other bases such as DBU, K_2CO_3, and Cs_2CO_3, yields decreased sharply (Table 1, entries 6–8). When an inorganic base was used, no product was observed (Table 1, entries 7 and 8). We then investigated the effects of different solvents on this reaction. DMSO was found to be another good choice, providing good yield and regioselectivity (>99/1) (Table 1, entry 9). Lower yields were obtained when reactions proceeded in acetonitrile, Et_3N, DMF/Et_3N (v/v = 1/1) and DMF/H_2O (v/v = 1/1) (Table 1, entries 10–13). The best result was obtained in DMF/DMSO (v/v = 1/1), where the product yield reached 89% while the regioselectivity remained excellent (Table 1, entry 14).

Lowering of the reaction temperature from 100 °C to 90 °C resulted in a decrease in product yield from 89% to 78%. When the reaction was carried out at 90 °C, the starting material **1a** was not consumed after 2 h. Besides, no significant increase in the yield of product **3a** was observed when the reaction temperature was raised to 110 °C (Table 1, entries 15 and 16).

With the optimized conditions in hand, we started to examine the substrate scope of this reaction. The arylation of **2** was undertaken with a variety of aryl halides under the optimum conditions. The results are summarized in Table 2. As can be seen, most of the reactions proceeded smoothly, leading to relatively clean products **3**. The neutral path B (Scheme 1) was completely suppressed using vinyloxytrimethylsilane **2** as the acylation reagent. The reaction can be equally applied to *ortho*-, *meta*-, and *para*-substituted iodobenzenes bearing electron-withdrawing or electron-

Table 2. Palladium-catalyzed regioselective synthesis of acetophenones from aryl halides and vinyloxytrimethylsilane.[a]



1 2 3 4[b]

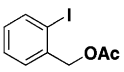
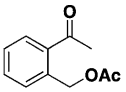
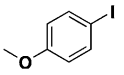
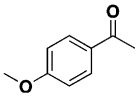
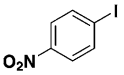
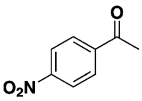
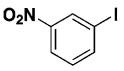
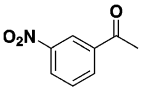
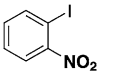
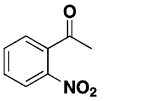
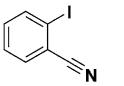
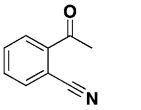
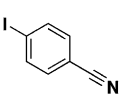
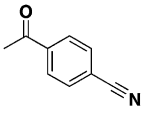
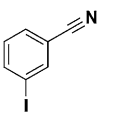
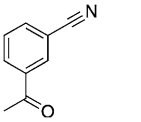
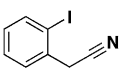
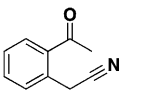
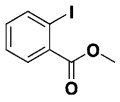
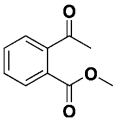
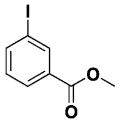
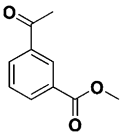
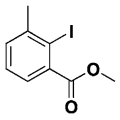
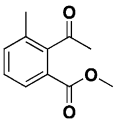
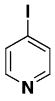
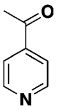
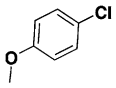
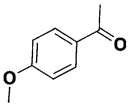
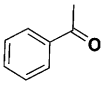
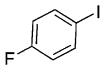
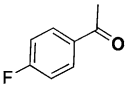
Entry	Substrate		Product		Yield [%][c]
1		**1a**		**3a**	89
2		**1b**		**3b**	84
3[d]		**1c**		**3c**	85
4		**1d**		**3d**	96
5		**1e**		**3e**	91
6		**1f**		**3f**	56
7[d]		**1g**		**3g**	90
8		**1h**		**3h**	85
9		**1i**		**3i**	92

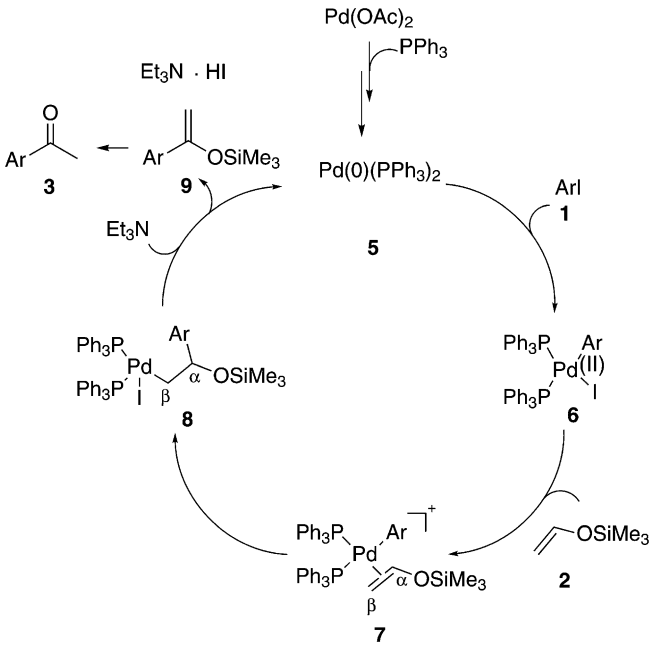
Table 2. (Continued)

Entry	Substrate		Product		Yield [%][c]
10		**1j**		**3j**	75
11		**1k**		**3k**	71
12		**1l**		**3l**	80
13		**1m**		**3m**	82
14		**1n**		**3n**	86
15		**1o**		**3o**	72
16		**1p**		**3p**	0
17		**1q**		**3q**	0
18		**1r**		**3r**	56
19		**1s**		**3s**	75

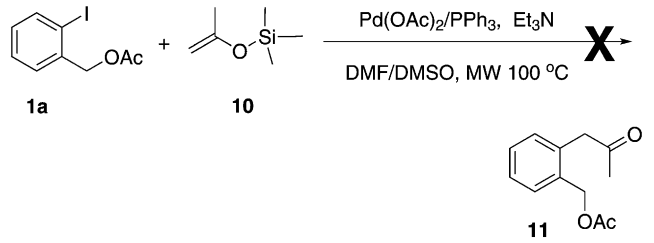
[a] Unless otherwise stated, all reactions were carried out under microwave irradiation using **1** (0.36 mmol), **2** (0.72 mmol), $Pd(OAc)_2$ (3.6 μmol), PPh_3 (7.2 μmol) and Et_3N (1.08 mmol) in DMF/DMSO (1:1) at 100 °C for 2 h.
[b] Compound **4** could not be detected.
[c] Isolated yield.
[d] Reaction using xantphos as ligand.

donating groups, such as $-NO_2$, $-CN$, $-CH_2OAc$, $-CH_2CN$, $-COOMe$, $-OMe$, $-Br$, and $-F$, all of which furnished the desired products in moderate to excellent isolated yields with excellent α/β ratios of >99/1 (Table 2, entries 1–11, 15, 19). The protocol also worked well for sterically hindered substrates, such as **1l** (Table 2, entry 12). The substrate of this efficient catalytic system could be extended to other heteroaryl halides, as demonstrated by substrates **1m** and **1n**, where the reactions were completed with excellent regioselectivity and good isolated yields (Table 2, entries 13 and 14). Furthermore, aryl bromide **1p** and aryl chloride **1q** were unreactive while 1-bromo-2-iodobenzene gave 2-bromoacetophenone **3o** under our standard reaction conditions, indicating that this catalytic system has good selectivity for iodobenzenes over bromobenzenes and chlorobenzenes (Table 2, entries 15–17).

On the basis of the above observations, a plausible mechanism for the selective formation of acetophenones **3** is proposed in Scheme 2. There is general agreement on the basic chemistry involved in Heck arylation of olefins.[17e,20] As in most palladium-catalyzed cross-coupling cases, the first step of the reaction is the reduction of the Pd(II) precursor to provide the active Pd(0) catalyst **5**. Then, aryl iodide with



Scheme 2. Proposed mechanistic pathway for the regioselective arylation of vinyloxytrimethylsilane.



Scheme 3. Attempted palladium-catalyzed arylation of **10**.

Pd(0) catalyst **5** forms the arylpalladium reagent **6** by oxidative addition, followed by formation of intermediate **7** with vinyloxytrimethylsilane **2**. The β-carbon of vinyloxytrimethylsilane **2** is the site of greatest electron density. Pd(II) inclines to form a bond with the β-carbon to give **8**. Finally, the collapse of **8** generates the α-substituted intermediate **9**, then affords product **3**.

Within this general scheme some regioselectivity and mechanistic details remain obscure. To gain further insight into the α-arylation mechanism using vinyloxytrimethylsilane, we performed additional experiments (Scheme 3). Under the same conditions, using silyl enol ether reagent **10** with the α-position blocked, product **11** was not observed. The result suggests that the α-position of vinyloxytrimethylsilane is the only site that can be arylated in this Heck reaction, which accounts for the high regioselectivity of our protocol.

Conclusions

In summary, we have developed an effective and practical protocol to generate acetophenones from aryl iodides using vinyloxytrimethylsilane as a highly regioselective and novel acylation reagent. This synthetic approach has a number of attractive features such as operational simplicity, a short reaction time, a single-step process, broad substrate scope, good yields and excellent regioselectivity. The new methodology reported in this work is complementary to those previously reported for the synthesis of important aromatic ketones, particularly Friedel–Crafts acylation, which is neither effective for electron-deficient arenes nor sufficiently regioselective to introduce an acetyl group.

Experimental Section

General Procedure for the Synthesis of 2-Acetylbenzyl Acetate (e.g., 3a)

A tube containing a stir bar was charged with aryl halide **1** (0.36 mmol), vinyloxytrimethylsilane **2** (0.72 mmol), $Pd(OAc)_2$ (3.6 μmol), PPh_3 (7.2 μmol), Et_3N (1.08 mmol) and DMF/DMSO = 1/1 (4 mL) at room temperature. The tube was placed in a microwave reactor. The mixture was stirred and heated at 100 °C. After 2 h, heating was stopped and the tube was cooled to room temperature. The reaction mixture was poured to 20 mL water, extracted with EtOAc (2 × 20 mL), and the combined organic layer was washed with saturated brine, dried over Na_2SO_4, filtered, and concentrated under vacuum. The aryl methyl ketone **3** was isolated out of the crude product by flash chromatography on silica gel (ethyl acetate/hexane = 1/40–1/4). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.79$ (d, $J = 7.5$ Hz, 1H), 7.52 (m, 2H), 7.43–7.37 (m, 1H), 5.45 (s, 2H), 2.61 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 200.76$, 170.58, 136.81, 136.31, 132.08, 129.70, 128.12, 127.58, 64.55, 28.91, 20.94; MS (ESI): $m/z = 191$ $[M-H]^-$; HR-MS (EI): $m/z =$ 192.0796, calcd. for $C_{11}H_{12}O_3$ M^+: 192.0786.

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