Published in final edited form as:

European J Org Chem. 2012 October 1; 2012(30): 5897–5901. doi:10.1002/ejoc.201200867.

Tandem Aldol Condensation – Platinacycle-Catalyzed Addition Reactions of Aldehydes, Methyl Ketones and Arylboronic Acids

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Abstract

Tandem aldol condensation of aldehydes with methyl ketones followed by anionic four-electron donor-based (Type I) platinacycle-catalyzed addition reactions of arylboronic acids to form β -arylated ketones is described. Good to excellent yields of β -arylated ketones were obtained for the tandem reactions of aromatic/aliphatic aldehydes, methyl ketones and arylboronic acids, and moderate yields were observed for the tandem reaction with α , β -unsaturated aldehydes as the aldehyde source.

Keywords

Tandem Reaction; Aldol Condensation; Addition Reaction; Platinacycle; Arylboronic Acids

Introduction

Over the past decade, transition metal-catalyzed addition reactions of arylboronic acids with α , β -unsaturated ketones have emerged as useful tools for organic synthesis.^{1,2} While impressive success including high enantioselectivities has been achieved for this type of addition reactions, the prepurified α , β -unsaturated ketones were used. Although α , β -unsaturated ketones can be “readily” obtained from the aldol condensation of aldehydes and/or ketones, the use of prepurified α , β -unsaturated ketones apparently posed some limits: they’re less available than aldehydes/ketones and require an extra purification/separation step from widely available aldehydes/ketones. During our study of transition metal-catalyzed addition reactions of arylboronic acids with carbonyl-containing compounds,^{3,4} we became interested in combining such transition metal-catalyzed addition reactions with the formation of α , β -unsaturated ketones in a sequential or tandem fashion.^{5–7} We reasoned that achieving such sequential/tandem reactions would minimize the effort for the preparation of α , β -unsaturated ketones because prepurification for such ketones is eliminated, and may also expand the α , β -unsaturated ketone substrate scope. In this context, we have recently documented the sequential aldol condensation of aldehydes with methyl ketones followed by Rh(I)- or anionic four-electron donor-based (Type I) palladacycle **1** (Figure 1)^{8,9}-catalyzed addition reaction to access β -arylated ketones (Scheme 1).^{10,11} We found that with palladacycle **1** or Rh(I)/diene complex as the catalyst, the reaction of aldehydes, methyl ketones and arylboronic acids could be realized in a sequential fashion,¹⁰ but not in a tandem fashion due to the fast palladacycle **1**- or Rh(I)/diene-catalyzed 1,2-addition reaction of arylboronic acids with aldehydes. Because tandem reactions, in which

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Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ejoc.xxxxxxxx>.

Supporting Information: Characterization data and copies of ¹H and ¹³C NMR spectra of the tandem reaction products.

reaction materials are loaded altogether, are operationally more convenient than sequential reactions, it was of interest to us to realize such reactions in a tandem fashion. Based on our previous study that Type I platinacycle **2**¹² (Figure 1) -catalyzed 1,2-addition reaction of aldehydes with arylboronic acids occurred slower than that with Type I palladacycles as catalysts,^{3a} we surmised that that it might be possible to realized the reaction of aldehydes, methyl ketones and arylboronic acids in a tandem fashion by using platinacycle **2** as the 1,4-addition reaction catalyst.^{3a,11c} Herein, we report our successful realization of such tandem aldol condensation followed by Type I platinacycle **2**-catalyzed addition reactions.

Results and Discussion

Our study began with the condition screening for the tandem aldol condensation reaction of benzaldehyde with acetone followed by platinacycle **2**-catalyzed additions of *p*-tolylboronic acid. Toluene was chosen as the solvent and K₃PO₄ as the base for our study because they were identified as the best solvent and base in platinacycle **2**-catalyzed addition reactions of arylboronic acids with aldehydes.^{3a} As a temperature of 80 °C or higher was needed for platinacycle **2**-catalyzed addition reactions of arylboronic acids with aldehydes to occur efficiently,^{3a} we reasoned that carrying out the tandem reaction at a temperature of lower than 80 °C might suppress the 1,2-addition reaction of arylboronic acids with aldehydes. We thus began our study at 70 °C. We found although the desired tandem reaction product was observed to be only 31% of the reaction mixture, the moderate reaction conversion (31%) suggested that the platinacycle **2**-catalyzed addition reaction of *p*-tolylboronic acid with benzaldehyde indeed occurred very slowly (Table 1, entry 1). We speculated that the moderate conversion might be because the first step, the aldol condensation reaction step, occurred slowly. As K₃PO₄ is insoluble in toluene, we reasoned that the presence of water might facilitate the aldol condensation reaction, and the tandem reaction process. We thus tested to use water as the additive and found indeed the existence of a small amount of water significantly facilitated the tandem reaction (Table 1, entries 1–3). By using 7 equivalents of water as the additive, the tandem aldol condensation followed by platinacycle **2**-catalyzed addition reaction occurred efficiently, afford the β -arylated ketone as the major product (Table 1, entry 4). Further testing of other bases revealed that K₂CO₃, Cs₂CO₃ and KOH were more effective bases than K₃PO₄ for the tandem reaction. By using these bases, excellent conversions were observed, with the tandem aldol condensation-addition reaction product as the predominant product (Table 1, entries 6, 8, 10).

After indentifying the reaction condition, the scope of the tandem aldol condensation followed by Type I platinacycle **2**-catalyzed addition reaction was examined. Different aromatic aldehydes, methyl ketones and arylboronic acids were suitable starting materials for the tandem reaction and high yields were observed for all cases being tested (Table 2). The combination of aromatic aldehydes, methyl ketones and arylboronic acids permitted the access of a variety of β -aryl ketones including β -aryl ketones that have not been reported before, mainly because of the availability of such α,β -unsaturated ketones (Table 2).

We next examined aliphatic aldehydes as the aldehyde source for the tandem reaction, which could lead the formation of β -alkyl- β -aryl ketones. Aliphatic aldehydes are considered to be more problematic aldehydes than aromatic aldehydes for the tandem reaction because they may undergo a self-aldol condensation reaction under the reaction condition. Such possible self-aldol condensation reaction of aldehydes rendered β -alkyl α,β -unsaturated ketones much less available than β -aryl α,β -unsaturated ketones. We were particularly interested in accessing β -alkyl- β -aryl ketones that have not been reported before by using transition metal-catalyzed addition reactions, mainly because of the availability of their precursors, β -alkyl α,β -unsaturated ketones. We found aliphatic aldehydes were suitable starting materials, with the β -alkyl- β -aryl ketones being obtained in good yields

(Table 3), and the self-aldol condensation reaction was negligible. Thus, although β -alkyl α,β -unsaturated ketones are less available due to the self-aldol condensation of aliphatic aldehydes, our study provided an efficient route to a variety of β -alkyl- β -aryl ketones from readily available methyl ketones, aliphatic aldehydes and arylboronic acids.

α,β -Unsaturated aldehydes were also examined as the aldehyde source for the tandem reaction (Table 4). We found that by using KOH as the base, the tandem aldol condensation followed by 1,4-addition reaction occurred, but the reaction could not reach a complete conversion for the aldol condensation reaction products. A significant amount of the aldol condensation reaction product was observed even after lengthening the reaction time, increasing the amount of phenylboronic acid, or raising the reaction temperature. Such an observation might suggest that the δ,γ -double bond of the dienone likely served as a ligand to stabilize the Pt species after the 1,4-addition reaction of arylboronic acid with the dienone, which might hinder the regeneration of the Pt catalyst for the tandem reaction.

Conclusions

We have demonstrated that platinacycle **2**-catalyzed addition reactions of arylboronic acids with α,β -unsaturated ketones can be combined with the formation of α,β -unsaturated ketones, the aldol condensation reaction of aromatic and aliphatic aldehydes with methyl ketones, in a tandem fashion efficiently. A variety of β -arylated ketones can be obtained in good to high yields from readily available aromatic/aliphatic aldehydes, methyl ketones and arylboronic acids. Our future work will be directed to develop asymmetric version of such tandem reactions and other tandem/sequential reactions involving the addition reaction of arylboronic acids with aldehydes as part of the reaction sequence.

Experimental Section

General procedure for tandem aldol condensation followed by platinacycle **2**-catalyzed addition reactions of aromatic aldehydes, methyl ketones and arylboronic acids

To a vial containing aldehyde (0.25 mmol), arylboronic acid (0.5 mmol), base (K_2CO_3 , KOH or Cs_2CO_3 0.75 mmol) and platinacycle **2** (0.00125 mmol, 1.1 mg) were added ketone (0.2 mL), toluene (0.8 mL) and water (7 equiv). After the mixture was stirred at 70 °C for 6–8 hours, the reaction was quenched by adding 4 N HCl (2 mL) aqueous solution. The mixture was extracted with CH_2Cl_2 (3 $\times$ 15 mL). The organic layers were combined. After evaporation of the organic solvents, the residue was subjected to column chromatography [silica gel, ethyl acetate/hexane (v/v=1:20) as eluent] to afford the products.

General procedure for platinacycle **2**-catalyzed tandem reactions of aliphatic aldehydes, methyl ketones and arylboronic acids

To a vial containing aldehyde (0.25 mmol), arylboronic acid (0.5 mmol, 2 equiv), KOH (0.75 mmol, 3 equiv.) and platinacycle **2** (0.00125 mmol, 1.1 mg) was added ketone (0.2 mL) toluene (0.8 mL) and water (0.1 mL). After the mixture was stirred at 70 °C for 6 hours, the reaction was quenched by adding 4 N HCl (2 mL) aqueous solution. The mixture was extracted with CH_2Cl_2 (3 $\times$ 15 mL). The organic layers were combined. After evaporation of the organic solvents, the residue was subjected to column chromatography [silica gel, ethyl acetate/hexane (v/v=1:20) as eluent] to afford the products.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We gratefully thank the NSF (CHE0719311) and NIH (1R15 GM094709) for funding. Partial support from PSC-CUNY Research Award Programs is also acknowledged. We thank the Frontier Scientific for its generous gifts of arylboronic acids.

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Figure 1.
Anionic Four-Electron Donor-Based (Type I) Palladacycle **1** and Platinacycle **2**

Scheme 1.

Sequential Aldol Condensation-Transition Metal-Catalyzed addition of Aldehydes, Methyl ketones and Arylboronic Acids

Table 1

Tandem Aldol Condensation-Transition Metal-Catalyzed Reaction of Benzaldehyde, Acetone and Phenylboronic Acid ^a

Entry	Solvent	H ₂ O (equiv)	Base	Conv. (%) ^b	A/B ^b
1	Toluene	0	K ₃ PO ₄	31	31:64
2	Toluene	2	K ₃ PO ₄	52	65:35
3	Toluene	4	K ₃ PO ₄	69	77:23
4	Toluene	7	K ₃ PO ₄	73	92:8
5	Toluene	4	K ₂ CO ₃	72	80:20
6	Toluene	7	K ₂ CO ₃	95	99:1
7	Toluene	4	Cs ₂ CO ₃	87	97:3
8	Toluene	4	Cs ₂ CO ₃	94 ^c	99:1
9	THF	4	Cs ₂ CO ₃	67	99:1
10	Toluene	7	KOH	99 ^d	99:1
11 ^e	Toluene	7	K ₂ CO ₃	^f	-

^aReaction condition: aldehyde (0.25 mmol), *p*-toluolboronic acid (0.5 mmol, 2.0 equiv), solvent (0.7 mL), acetone (0.3 mL, 4 mmol), base (0.75 mmol, 3.0 equiv), 70 °C.^bBased on GC-MS analysis.^c15% of 1,5-diphenyl-1,5-di(*p*-tolyl)-3-pentanone was observed.^d5% of 1,5-diphenyl-1,5-di(*p*-tolyl)-3-pentanone was observed.^eNo platinumacycle 2 was used.^f4-Phenylbut-3-en-2-one was the product.

Table 2

Tandem Aldol Condensation-Platinacycle 2-Catalyzed Reaction of Aromatic Aldehydes, Methyl Ketones and Arylboronic Acids^a

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} + \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{O} + \text{ArB(OH)}_2 \xrightarrow[\text{Toluene/H}_2\text{O, Base, 70 }^\circ\text{C, 6 h}]{0.5 \text{ mol\% Platinacycle } \mathbf{2}} \text{Ar}-\text{C}(\text{O})-\text{C}(\text{O})-\text{R}' \end{array} $					
Entry	RCHO	R'COCH ₃	ArB(OH) ₂	Base	Yield (%) ^b
1				K ₂ CO ₃	86
2				K ₂ CO ₃	84
3				K ₂ CO ₃	81
4				K ₂ CO ₃	86
5				K ₂ CO ₃	87
6				K ₂ CO ₃	85
7				K ₂ CO ₃	86
8				K ₂ CO ₃	86
9				KOH	85
10				KOH	83
11				KOH	91
12				KOH	80
13				KOH	86
14				KOH	85

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \end{array} + \begin{array}{c} \text{O} \\ \parallel \\ \text{R}'-\text{C}-\text{H} \end{array} + \text{ArB(OH)}_2 \xrightarrow[\text{Toluene/H}_2\text{O, Base, 70 }^\circ\text{C, 6 h}]{0.5 \text{ mol\% Platiniacycle } \mathbf{2}} \begin{array}{c} \text{Ar} \text{ O} \\ \diagup \quad \diagdown \\ \text{R}-\text{C}=\text{C}-\text{R}' \end{array} $						
Entry	RCHO	R'COCH ₃	ArB(OH) ₂	Base	Yield(%) ^b	
15				KOH	87	
16				KOH	82 ^c	
17				KOH	84 ^c	
18				KOH	82 ^c	
19				KOH	91 ^c	
20				KOH	88 ^c	
21				Cs ₂ CO ₃	70	
22				Cs ₂ CO ₃	76	

^aReaction condition: aldehyde (0.25 mmol), arylboronic acid (0.5 mmol, 2.0 equiv), toluene (0.8 mL), ketone (0.2 mL, 1.7–2.7 mmol), H₂O (7 equiv), base (0.75 mmol, 3.0 equiv), 70 °C.

^bIsolated yield.

^cH₂O (13 equiv) was used.

Table 3

Tandem Aldol Condensation-Platinacycle **2**-Catalyzed Reaction of Aliphatic Aldehydes, Methyl Ketones and Arylboronic Acids^a

Entry	RCHO	RCOCH ₃	ArB(OH) ₂	Yield(%) ^b
1				80
2				76
3				74
4				77
5				83
6				80
7				78

^aReaction condition: aldehyde (0.25 mmol), arylboronic acid (0.5 mmol, 2.0 equiv), ketone (0.2 mL, 1.9–2.7 mmol), toluene (0.8 mL), H₂O (0.1 mL), KOH (0.75 mmol, 3.0 equiv), 70 °C.

^bIsolated yield.

Table 4

Tandem Aldol Condensation-Platinacycle 2-Catalyzed Reaction of α,β -Unsaturated Aldehydes, Acetone and Phenylboronic Acid^a

$ \begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{CH}=\text{CH}-\text{CHO} + \text{O}=\text{C}(\text{CH}_3)_2 + \text{PhB(OH)}_2 \end{array} \xrightarrow[\text{KOH}]{\text{Platinacycle 2 catalyst, Toluene, H}_2\text{O}} \begin{array}{c} \text{Ph} \quad \text{O} \\ \parallel \quad \parallel \\ \text{R}-\text{CH}=\text{CH}-\text{C}=\text{C}-\text{C}(\text{OCH}_3)_2 \quad (\text{C}) \\ + \\ \text{R}-\text{CH}=\text{CH}-\text{C}(\text{OCH}_3)_2 \quad (\text{D}) \end{array} $					
Entry	R	Cat. Loading	Temp.(°C)	Time	Yield (%) ^b
1	Ph	1 mol %	70	8 h	60 : 40
2	Ph	1 mol %	70	16 h	60 : 40
3	Ph	2 mol %	80	8 h	75 : 25
4	Ph	2 mol %	70	8 h	75 : 25 ^c
5	CH ₃	2 mol %	80	10 h	50 : 50 ^d

^aReaction condition: aldehyde (0.25 mmol), arylboronic acid (0.5 mmol, 2.0 equiv), toluene (0.8 mL), acetone (0.2 mL, 2.7 mmol), H₂O (13 equiv.), KOH (0.75 mmol, 3.0 equiv), 70 °C.^bIsolated yield of C.^c4 equiv of PhB(OH)₂ was used.^d2,4,7,9-Undecatetraen-6-one was observed as the aldol condensation product.