α, ω -Diarylalkanes

Iridium-Catalyzed Reactions of ω-Arylalkanols to α,ω-Diarylalkanes**

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 α,ω -Diarylalkanes are attractive materials for chromophores and have been employed in fluorescent probes.^[1] Extensive spectroscopic investigations of their excimers, such as biradicals of α,ω -diarylalkanes, have therefore been performed.^[2] α,ω -Diarylalkanes are now also in demand as ligands for metal complexes,^[3] precursors of cyclophanes/calixarenes,^[4] polymerization initiators,^[5] and as agents for improving the viscosity index of lubricants, especially in high-temperature nuclear-radiation-resistant hydraulic fluids.^[6] In addition, α,ω -diarylalkanes are important model compounds for elucidating the mechanism of coal liquefaction.^[7] Conventionally, α,ω -diarylalkanes have been synthesized by coupling Grignard reagents with a, w-dihaloalkanes,^[8] Friedel-Crafts acylation of arenes using $ClOC(CH_2)_nCOCl$ in $AlCl_3$ with a subsequent reduction,^[9] Na-mediated Wurtz-Fittig reactions of aryl bromides and α,ω -dibromoalkanes,^[10] and by reduction of the corresponding ketones and α,β -enones.^[11] However, these existing methods have major drawbacks: they are multistep reactions, have narrow substrate scope, and/or produce stoichiometric amounts of metal salts as waste. The development of a facile, versatile, and waste-minimizing method for preparing α,ω -diarylalkanes from easily accessible chemicals is therefore highly desirable with regard to atom economy.

It is well known that Ir and Ru complexes serve as efficient catalysts for hydrogen transfer from alcohols to aldehydes^[12] and this catalysis has been used in α alkylations of carbonyl and related compounds,^[12,13] and β alkylations (Guerbet reaction) of alcohols.^[12,14] Furthermore, Ir, Ru, and Rh complexes are known to show efficient catalytic activity in the decarbonylation of aldehydes.^[15]

Herein, we report a novel general synthetic method for producing α, ω -diarylalkanes **2** from ω -arylalkanols **1** by dehydrogenation/ β -alkylation (step 1) and a subsequent dehydrogenation/decarbonylation (step 2), either by a direct one-step method (Scheme 1, route A) or a sequential twostep method (Scheme 1, route B). This reaction provides a simple, versatile, and clean route to α, ω -diarylalkanes from easily available alcohols.

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- [**] This work was supported by a Grant-in-Aid for Scientific Research (MEXT), the Strategic Project to Support the Formation of Research Bases at Private Universities (2010-2014), matching fund subsidy from the MEXT, and the Kansai University Research Grants: Grantin-Aid for Encouragement of Scientists, 2011.
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201104452.



Scheme 1. Preparation of α, ω -diarylalkanes (2) from 1. cod = 1,5-cyclooctadiene, dppe = 1,2-bis(diphenylphosphino)ethane.

2-Phenylethanol (1a) was used as a model substrate to investigate the reaction conditions for the direct one-step synthesis of α,ω -diarylalkanes from ω -arylalkanols (Scheme 1, route A; Table 1). The reaction of 1a (2 mmol) in the presence of a catalytic amount of $[(Cp*IrCl_2)_2]$ (1 mol%; Cp*=1,2,3,4,5-pentamethylcyclopentadienyl) and *t*BuOK (40 mol%) in *p*-xylene (0.5 mL) at 120°C for 4 hours gave 1,3-diphenylpropane (2a) in 81% yield with high selectivity, along with a small amount (5%) of toluene (4a; Table 1, entry 1).

Table 1: Ir-catalyzed reaction of 2-phenylethanol (1 a) under various reaction conditions.^[a]

\bigcirc	OH Ir catalyst Base Solvent		+) +
1a	120 °C, 4 h	2a	3	a	4a
Entry	Ir catalyst	Base [mol%]	Yield [%]		
			2a	3 a	4a
1	$[(Cp*IrCl_2)_2]$	<i>t</i> BuOK (40)	81 (79)	trace	5
2	$[{IrCl(cod)}_2]$	tBuOK (40)	4	8	2
3	$[{IrCl(coe)_2}_2]$	tBuOK (40)	trace	5	9
4	$[{Ir(OH)(cod)}_2]$	tBuOK (40)	2	11	5
5 ^[c]	IrCl ₃ ·3 H ₂ O	tBuOK (40)	6	15	trace
6	$[(Cp*IrCl_2)_2]$	NaOEt (40)	51	n.d. ^[d]	3
7	$[(Cp*IrCl_2)_2]$	КОН (40)	62	5	3
8	$[(Cp*IrCl_2)_2]$	K ₂ CO ₃ (40)	trace	trace	3
9	$[(Cp*IrCl_2)_2]$	tBuOK (20)	22	n.d. ^[d]	2
10	$[(Cp*IrCl_2)_2]$	tBuOK (30)	42	n.d. ^[d]	2
11	$[(Cp*IrCl_2)_2]$	tBuOK (70)	63	n.d. ^[d]	27
12 ^[e]	$[(Cp*IrCl_2)_2]$	tBuOK (40)	59	n.d. ^[d]	7
13 ^[f]	$[(Cp*IrCl_2)_2]$	tBuOK (40)	24	n.d ^[d]	2

[a] Reaction conditions: 1a (2 mmol) was treated with Ir catalyst (1 mol%) and base (20–70 mol% based on 1a used) in *p*-xylene (0.5 mL) at 120°C for 4 h. [b] Yields were determined by GC using pentadecane as the internal standard. The number in parenthesis shows the yield of the isolated product. [c] Ir catalyst (2 mol%) was used.
[d] Not detected by GC. [e] Reaction was performed without solvent.
[f] Reaction was performed at 100°C. coe = cyclooctene.

With regard to the selection of an Ir catalyst, $[(Cp*IrCl_2)_2]$ gave the highest catalytic performance, in both activity and selectivity (Table 1, entry 1). Other Ir complexes, which are used as efficient catalysts in hydrogen-transfer processes, such as $[{IrCl(cod)_2}_2]$, $[{IrCl(coe)_2}_2]$, $[{IrCl(cod)_2}_2]$, and $IrCl_3$,^[12-14] resulted in low yields of **2a** (< 6 %); 1,3-diphenyl-1-propene (**3a**; 5–15 %) and toluene (**4a**; < 9 %) were formed as by-products (Table 1, entries 2–5).

In the present reaction, the choice and amount of base markedly influenced the reaction efficiency. Among the bases examined, tBuOK (40 mol%, based on the amount of **1a** used) gave the best yield and selectivity for the formation of **2a** (Table 1, entry 1). Other bases such as NaOH and KOH resulted in moderate yields of **2a**, and K₂CO₃ was an inert base in this transformation (Table 1, entries 6–8). The use a larger amount of base (70 mol%) resulted in the formation of a considerable amount of the undesired **4a** (Table 1, entry 11). The reactions performed without a solvent or at a lower temperature (100 °C) resulted in low yields of **2a** (Table 1, entries 12 and 13).

As mentioned above, the yield and selectivity of 2a were the best when the reaction was performed under the reaction conditions shown in Table 1, entry 1. However, when the reaction of 1a was performed in the presence of 1,7octadiene, as a hydrogen acceptor, under the modified reaction conditions shown in [Eq. (1)] (at 160 °C in mesitylene), 3a was obtained as a major product.



Under the optimized reaction conditions shown in Table 1, entry 1, the reactions of various 2-arylethanols (**1a**-**g**), bearing electron-donating and electron-withdrawing groups on the phenyl ring, were carried out to afford the corresponding 1,3-diarylpropanes (**2a**-**g**) in good yield and high selectivity (Table 2). The formation of the α,ω -diaryl-alkanes **2** from **1** proceeded smoothly by a direct one-step method (Scheme 1, route A) when 2-arylethanols were used as the substrates (Table 2).

The reaction was markedly influenced by the alkyl chain length of **1**. The results of the reaction of 3-phenylpropanol (**1h**) under various reaction conditions are listed in Table 3. The reaction of **1h** under the reaction conditions shown in Table 1, entry 1 gave the desired α, ω -diarylalkane, 1,5-diphenylpentane (**2h**), in only 14% yield, and predominantly afforded a Guerbet-type β -alkylation product, β -(phenylmethyl)benzenepentanol (**5h**), in 82% yield (Table 3, entry 1).

With regard to the catalyst, $[(Cp*IrCl_2)_2]$ gave the best results for the formation of **5h**; the other selected Ir complexes showed low catalytic activity for the formation of both **2h** and **5h** under these reaction conditions (Table 3, entry 1 versus entries 2–5). With regard to the base, *t*BuOK, NaOEt, and KOH gave good results for the formation of **5h**,

Table 2: Ir-catalyzed reaction of 2-arylethanols 1 to α, ω -diarylpropanes 2 by direct one-step method (Scheme 1, route A).^[a]



[a] The reaction was performed under the reaction conditions in Table 1, entry 1. [b] Yields of the isolated product after purification. The yields of the by-products (**3** and **4**) under these reaction conditions were less than 5%, as detected by by GC.

Table 3: Ir-catalyzed reaction of 3-phenylpropanol (1 h) under various conditions.^[a]



Entry	Ir catalyst	Base	Yield [%] ^[b]	
			2 h	5 h
1	[(Cp*IrCl ₂) ₂]	tBuOK	14	82 (79)
2	$[{IrCl(cod)}_2]$	tBuOK	trace	23
3	$[{IrCl(coe)_2}_2]$	<i>t</i> BuOK	n.d. ^[c]	17
4	[Ir(OH)(cod)] ₂	tBuOK	n.d. ^[c]	29
5 ^[d]	IrCl ₃ ·3 H ₂ O	tBuOK	n.d. ^[c]	30
6	$[(Cp*IrCl_2)_2]$	NaOEt	4	77
7	$[(Cp*IrCl_2)_2]$	КОН	11	62
8	[(Cp*IrCl ₂) ₂]	K ₂ CO ₃	n.d.	n.d.
9 ^[e]	$[(Cp*IrCl_2)_2]$	<i>t</i> BuOK	trace	89 (81)

[a] Reaction conditions : 1h (2 mmol) was treated with Ir catalyst (1 mol%) and base (40 mol%) in *p*-xylene (1 mL) at 120°C for 24 h. [b] Yields were determined by GC using hexadecane as the internal standard. The number in parenthesis shows the yield of the isolated product. [c] Not detected by GC. [d] Ir catalyst (2 mol%) was used. [e] 1,4-Dioxane (1 mL) was used as solvent by using a pressure tube.

but no reaction occurred using a weak base such as K_2CO_3 (Table 3, entries 6–8). On further investigation of the reaction conditions, the best yield and selectivity for the formation of **5h** were attained when the reaction was carried out in 1,4-dioxane as the solvent (Table 3, entry 9).

Based on the above results, we designed the preparation of α, ω -diarylalkanes 2 from ω -arylalkanols 1 that have longer

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Table 4: Ir-catalyzed selective reaction of ω-arylalkanols 1 to β-methylhydroxy-α,ω-diarylalkanes 5 (Scheme 1, route B, step 1).^[a]



[a] The reaction was performed under the reaction conditions shown in Table 2 entry 9. [b] Yields of the isolated product after purification.

alkyl chains. This preparation uses the sequential two-step method, which involves the isolation of β -methylhydroxy- α, ω -diarylalkanes **5** as intermediates (Scheme 1, route B). Therefore, compound **5** was initially prepared from **1** under the reaction conditions shown in Table 3, entry 9 (Table 4). Various ω -arylalkanols (**1h**–**k**) were smoothly converted under these reaction conditions and we successfully isolated the corresponding β -methylhydroxy- α, ω -diarylalkanes (**5h**–**5m**) selectively in pure form.

Next, optimization of the reaction conditions for the dehydrogenation/decarbonylation step (Scheme 1, route B, step 2), from **5** to the α,ω -diarylalkanes **2**, was performed using **5h** as a model substrate (Table 5). Initially, the reaction of **5h** was carried out in the presence of $[(Cp*IrCl_2)_2]$ catalyst (6 mol %) combined with a base (K₂CO₃, 20 mol %) at 160 °C. This resulted in the formation of the desired 1,5-diphenylpentane (**2h**) in low yield (35 %; Table 5, entry 1).

To date, intense attention has been paid to the Ir- and Rhcatalyzed decarbonylation of aldehydes.^[15] Recently, Tsuji and co-workers reported that [{IrCl(cod)}2] combined with diphosphine ligands provides an active catalyst for the decarbonylation of aldehydes.^[15a] Therefore, the [{IrCl-(cod)}2]/dppe catalytic system was employed in the reaction of 5h. Selective formation of 2h was observed, however, the yield was still not sufficiently high (Table 5, entry 2). After further investigations we attained the optimized reaction conditions, in which a combined [(Cp*IrCl₂)₂]/[{IrCl(cod)}₂]/ dppe catalyst system was used, and under these reaction conditions 2h was obtained in excellent yield (Table 5, entry 3). The choice of the phosphine ligand was also important and the best result was obtained when dppe was used as the ligand; other phosphine ligands such as PPh₃ and binap gave lower yields of 2h.

Using the $[(Cp*IrCl_2)_2]/[{IrCl(cod)}_2]/dppe$ combined catalyst system under the reaction conditions shown in Table 5, entry 3, various β -methylhydroxy- α,ω -diarylalkanes 5 were successfully converted into the desired α,ω -diarylalkanes **2** in good to excellent yields with high selectivity (Table 6).

Although a detailed reaction mechanism for the present coupling reaction has not been fully confirmed at this stage, the above Ir-catalyzed transformation, exemplified by the conversion of 2phenylethanol (1a) to 1,3-diphenylpropane (2a), can be rationally explained by the following sequential pathway (Scheme 2). First, the Ir catalyst serves as a hydrogen acceptor from substrate 2a to give the aldehyde A and an Ir-hydride species. Then aldehyde A reacts by a base-catalyzed aldol condensation to give the unsaturated aldehyde **B** and water. Subsequently, B undergoes hydrogenation by the Irhydride complex to give the intermediate 5a (step 1). Hydrogen transfer from alcohol 5a then gives aldehyde C and an Ir-hydride complex. Then the C(O)-H bond of aldehyde **C** undergoes oxidative addition to the Ir complex, followed by extrusion of CO and β -hydrogen elimination, thus leading to the

Table 5: Ir-catalyzed reaction of β -(phenylmethyl)benzenepentanol (5 h) under various conditions (Scheme 1, route B, step 2).^[a]

	HO Ir catalyst Base mesitylene		2b
	5h		211
Entry	Ir-catalyst [mol%]	Ligand [mol%]	Yield of 2h [%] ^[b]
1 ^[c]	[(Cp*IrCl ₂) ₂](6)	none	35
2	[{IrCl(cod)} ₂](6)	dppe (12)	70
3	[(Cp*IrCl ₂) ₂](2)/[{IrCl(cod)} ₂](4)	dppe (8)	96(93)
4	[(Cp*IrCl ₂) ₂](2)/[{IrCl(cod)} ₂](4)	PPh3 (16)	54
5	[(Cp*IrCl ₂) ₂](2)/[{IrCl(cod)} ₂](4)	binap (8)	66
6 ^[d]	$[(Cp*IrCl_2)_2](2)/[{IrCl(cod)}_2](4)$	dppe (8)	94
7 ^[e]	$[(Cp*IrCl_2)_2](2)/[{IrCl(cod)}_2](4)$	dppe (8)	89

[a] Reaction conditions : **5 h** (1 mmol) was treated with Ir catalyst, ligand, and K_2CO_3 (20 mol%) in mesitylene (1.5 mL) at 160 °C for 24 h. [b] Yields were determined by GC using hexadecane as the internal standard. The number in parenthesis shows the yield of the isolated product. [c] In addition, 1,5-diphenyl-pentane and 2-benzyl-5-phenylpentanal were obtained in 9% and 4%, respectively. [d] *t*BuOK (20 mol%) was used as a base. [e] Cs₂CO₃ (20 mol%) was used as a base. binap = *rac*-2,2'-bis (diphenylphosphino)-1,1'-binaphthyl.

intermediate 1,3-diphenyl-1-propene (3a). Subsequent hydrogenation of 3a by the Ir-hydride would lead to the desired product 2a. Recently, Madsen and co-workers reported a mechanism, obtained by DFT studies, for the Rh-catalyzed decarbonylation of aldehydes.^[16] They reported that the decarbonylation of aldehydes involves a rapid oxidative addition into the C(O)–H, bond, followed by a rate-limiting extrusion of CO. In this case, the reaction using 2-arylethanols such as 1a would produce thermodynamically stable alkenes 3a, in which the double bond is conjugated with aryl groups,^[15a] thus resulting in the direct one-step



Table 6: Ir-catalyzed decarbonylation reaction of 5 to $\alpha, \omega\text{-diarylalkanol}$ 2. $^{[a]}$



[a] The reaction was performed under the reaction conditions shown in Table 5 entry 3. [b] Yields of the isolated product after purification.



Scheme 2. A plausible reaction pathway.

reaction being achieved by a facile decarbonylation/ β -hydrogen elimination step (step 2). Indeed, in the reaction of **1a**, no **5a** was detected at all (see Table 1). The reaction using aliphatic alcohols under these reaction conditions resulted in Guerbet-type dimer compounds, as we reported previously.^[14f,g]

In conclusion, we found a novel, efficient, and atomeconomical route to α, ω -diarylalkanes from easily accessible ω -arylalkanols. The reaction was achieved by a direct onestep method or a sequential two-step method, depending on the alkyl chain length of the ω -arylalkanol used. Further investigations with regard to the detailed reaction mechanism, scope, and applications of this reaction are currently in progress.

Experimental Section

A typical reaction was carried out as follows (Table 1, entry 1): **1a** (246 mg, 2.0 mmol) and *p*-xylene (0.5 mL) were added to a mixture of $[(Cp*IrCl_2)_2]$ (16 mg, 0.02 mmol) and *t*BuOK (90 mg, 0.8 mmol) under Ar in a schlenk flask. The reaction mixture was stirred at 120 °C for 4 h. The product (**2a**) was isolated by column chromatography (230–400 mesh silica gel, *n*-hexane) in 79% yield (157 mg).

Received: June 28, 2011 Published online: August 2, 2011

Keywords: β alkylation \cdot decarbonylation \cdot homogeneous catalysis \cdot iridium \cdot synthetic methods

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