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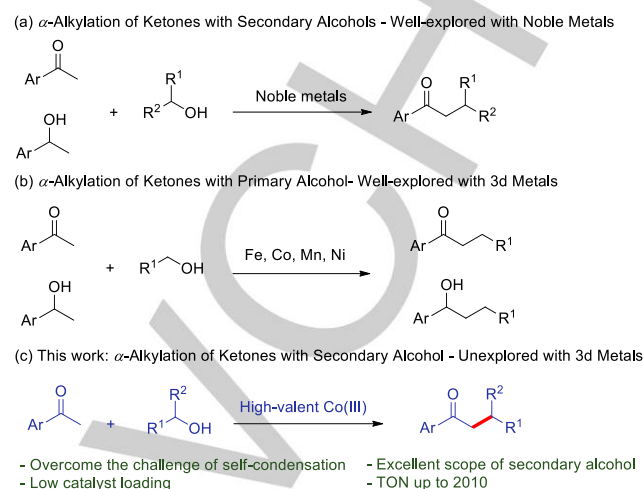
α -Alkylation of Ketones with Secondary Alcohols Catalyzed by Well-defined Cp*Co(III)-Complexes

Priyanka Chakraborty,^[a] Manoj Kumar Gangwar,^[a] Balakumar Emayavaramban,^[a] Eric Manoury,^[b] Rinaldo Poli^[b] and Basker Sundararaju*^[a]

Abstract: While α -alkylation of ketones with primary alcohols by transition metal catalysis is well-known, the same process with secondary alcohols is arduous and complicated by self-condensation. We herein demonstrate application of a well-defined high-valent cobalt(III)-catalyst for successful α -alkylation of ketones with secondary alcohols. A wide-variety of secondary alcohols, which include cyclic, acyclic, symmetrical and unsymmetrical, is employed as alkylating agents to produce β -alkyl aryl ketones.

Formation of C-C bonds in organic synthesis generally involves a multistep process entailing alkyl halides, organometallic coupling partners and other reducing agents, which generate copious amounts of waste.^[1] Development of atom-economical, environment-friendly and sustainable methods are more desirable than traditional alkylation reactions. In this context, the concept of "hydrogen borrowing" or "hydrogen auto-transfer process"^[2] has been tremendously exploited over the past decade or so. This process involves transition metal-catalyzed dehydrogenation of alcohols into carbonyl compounds, which are subsequently subjected to condensation *in situ* with carbonucleophiles to yield α,β -unsaturated carbonyl compounds followed by hydrogenation to afford C-alkylated ketones as the end products.^[3] The use of alcohols as alkylating reagents is preferred because of the cost, ready availability and environmental friendliness. The α -alkylation of ketones with primary alcohols has been well explored,^[4] but there are only a few reports documented for secondary alcohols as alkylating agents under noble metal catalysis (Scheme 1, a).^{[5],[6]} Traditionally, β -secondary alkylation of ketones has been achieved using strong bases, e.g., LDA, ^tBuLi, etc., and secondary alkyl halides. The reaction naturally produces large amounts of waste with appreciable selectivity.^[7] α -Alkylation of carbonyl compounds using primary alcohols has been widely investigated with 3d transition metals (Scheme 1, b).^{[8],[9]} It is worth mentioning that dehydrogenation of secondary alcohols is an

uphill process. To the best of our knowledge, no catalytic system based on base metals was previously reported for the α -alkylation of carbonyl compounds using secondary alcohols.



Scheme 1. Overview of α -alkylation of Ketones.

It is worth mentioning that Donohoe and co-workers reported the α -alkylation of ketones with secondary alcohols to form β -branched products using a Cp*Ir^{III} dimer; they have also addressed the issue of simultaneous self-condensation of the carbonyl substrate and the ketone derived from the alcohol by employing a sterically bulkier aryl ketone as the carbonyl substrate.^[5] Inspired by these results and by our on-going efforts to design inexpensive and sustainable processes under high-valent cobalt catalysis,^[10] we recently reported a well-defined Cp*Co^{III} complex for efficient dehydrogenation of secondary alcohols into the corresponding ketones and amines.^[11] Based on our earlier studies on dehydrogenation of secondary alcohols, we envisioned that Cp*Co^{III} catalytic system could be exploited for the α -alkylation of ketones with secondary alcohols to access β -alkyl ketones. We herein report our successful results of α -alkylation of carbonyl compounds with secondary alcohols by employing a well-defined and high-valent Cp*-Co(III) as the catalyst (Scheme 1, c).

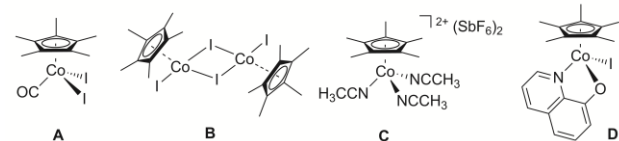
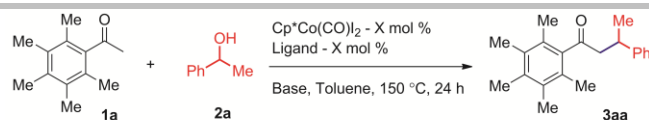
We began our investigations with 2,3,4,5,6-pentamethyl acetophenone (**1a**) and 1-phenylethanol (**2a**) as model reactants and by employing 10 mol% of Cp*Co(CO)₂ as the catalyst in the presence of ^tBuOK as the base in toluene (0.1 M). The reaction at 150 °C for 24 h led to the expected α -alkylated product **3aa** in 44% isolated yield (Table 1, entry 1). Encouraged by this result, other Cp*Co complexes, cf. Table 1, were screened, only to observe a marginal improvement (38 and 55%, entries 2 and 3, Table 1). Addition of a phosphine ligand such as PPh₃ or PCy₃ to the Cp*Co-monomer (**A**) yielded unsatisfactory results (32 and 59%, Table 1, entries 4 and 5).

Table 1. Results of Optimization of the Reaction^a

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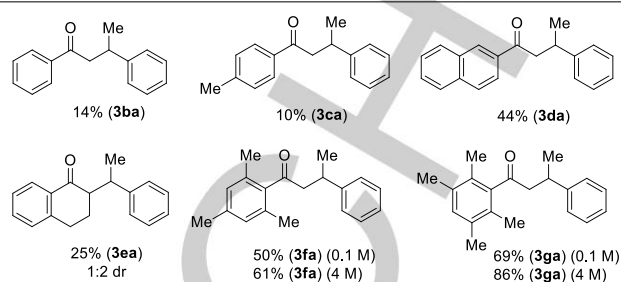
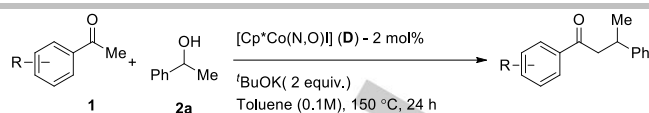


Entry	[Co] (mol %)	Ligand (mol %)	Yield(%) ^b
1	A (10)	-	44
2	B (10)	-	55
3	C (10)	-	38
4	A (10)	PPh ₃ (10)	32
5	A (10)	PCy ₃ (10)	59
6	A (10)	Pyridine (10)	n.r.
7	A (10)	2-hydroxypyridine (10)	72
8	A (10)	8-hydroxyquinoline (10)	77
9	D (2)	-	90
10	D (2)	-	62 ^c
11	D (2)	-	73 ^d
12	D (2)	-	74 ^e
13	D (2)	-	74 ^f
14	D (2)	-	95 ^g
15	D (2)	-	16 ^h

^[a] standard reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), [Co] (0.002–0.01 mmol), ^tBuOK (0.2 mmol) in toluene (0.1 M), at 150 °C for 24 h. ^[b] isolated yield.

^[c] ^tAmOH used as solvent. ^[d] Bu₂O used as solvent. ^[e] BuONa used as base. ^[f] 1.5 equivalent of base is used. ^[g] Conducted at 1 M concentration. ^[h] Performed at 130 °C. n.r. = no reaction.

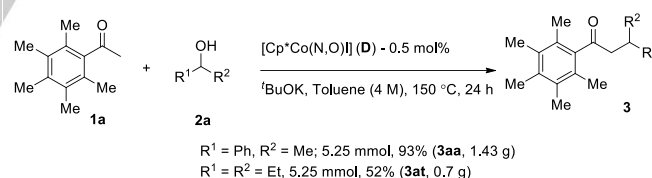
Further screening by employing σ -donor ligands such as pyridine also did not lead to any improvement in the product formation (entry 6). However, to our delight, 2-hydroxypyridine and 8-hydroxyquinoline led to remarkably better results with the latter affording the product in 77% yield (entries 7 and 8). The *in situ*-formed Cp*Co(N,O)I complex (**D**) was reported by us earlier^[11] for the acceptorless dehydrogenation of secondary alcohols. Hence, we pursued the screening using the well-defined cobalt catalyst **D**, but with a lower catalyst loading (2 mol%). Gratifyingly, the expected β -alkylated product **3aa** was isolated in 90% yield (entry 9). Use of other solvents and bases were found to be detrimental (entries 10–12). Incidentally, the yield of **3aa** dropped to 74% when the base loading was lowered from 2 to 1.5 equiv (entry 13). The product formation improved to 95% when the reaction was performed at 1 M concentration (entry 14). On the other hand, lowering the temperature to 130 °C gave only a 16% yield (entry 15). To gain further insights, control experiments were performed (See the SI for more informations).



Scheme 2. Effect of substituents on arenes.

With the optimized conditions at disposal, we explored the scope of various aryl ketones and the effect of sterics on the reactivity (Scheme 2). Unsubstituted aryl ketones led to poor yields due to self-condensation (**3ba–3da**). Tetralone as the ketone source was also less effective (**3ea**). However, the yields increased when the ortho-positions of the aromatic ketone were methyl-substituted (**3fa–3ga**), which highlights the necessity of crowding on the aromatic ring to preclude the substrate self-condensation.⁴

To demonstrate the practical applicability of this system, gram-scale reactions were tested for the synthesis of β -branched C-alkylated products as shown in Scheme 3. Pleasingly, the desired product **3aa** formed in 93% yield with only 0.5 mol% of catalyst loading and 1-phenylethanol (**2a**) as the alkylating agent. A gram-scale reaction conducted with 3-pentanol also provided the expected product **3at** in good yields (Scheme 3). In this case, lowering the catalyst loading to 0.05% led to a 33% yield (0.45 g or product **3at**), corresponding to a TON of 2010.

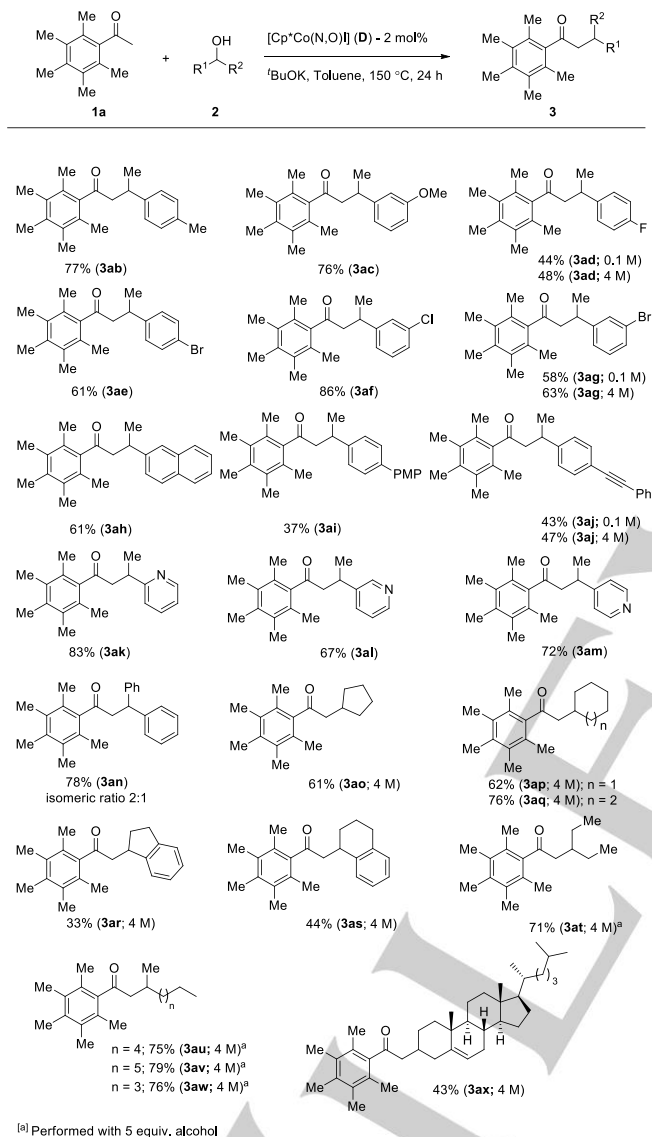


Scheme 3. Gram-scale synthesis.

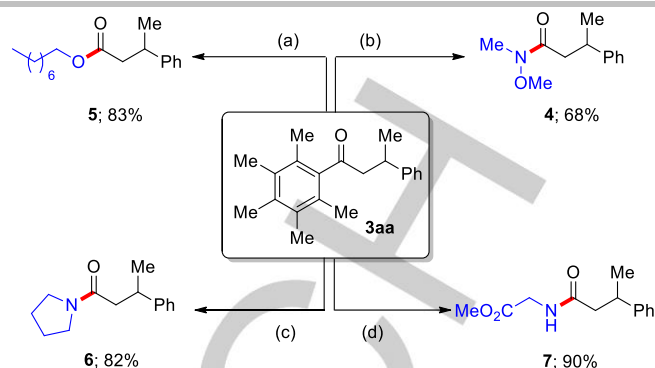
We then examined the scope of the alcohols, and a summary of the results is presented in Scheme 4. Various aromatic secondary alcohols bearing electron-donating substituents such as Me and OMe give the corresponding C-alkylated products in good yields (**3ab–3ac**). Aryl alkyl secondary alcohols with electron-withdrawing moieties such as F, Cl and Br afford moderate-to-good yields of the products (**3ad–3ag**) with the substituents unaffected. Naphthyl and *p*-methoxyphenyl methyl substituted alcohols provided the corresponding products in satisfactory yields (**3ah–3ai**). Furthermore, when the alcohol contained *p*-(phenylethynyl) substituent, the desired product was selectively obtained with the alkyne moiety intact (**3aj**). Surprisingly, heteroatom containing 2-, 3- and 4-pyridyl

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secondary alcohols were also effective in leading to the products without the catalyst being poisoned, and their corresponding (pyridin-2-yl)butanone derivatives were obtained in good yields (**3ak-3am**). Diphenylmethanol provided the corresponding alkylated products in a good yield. We further evaluated the reactivity of aliphatic alcohols under our conditions. To our delight, various cyclic secondary alcohols were found to react to afford the products in moderate-to-good yields (**3ao-3as**).



Scheme 4. Scope of secondary alcohols.



Scheme 5. Diversification of **3aa**. Reactions conditions: (a) (i) Br_2 (2 equiv.), CH_2Cl_2 , -17 °C, 15 min (ii) n-octanol (3 equiv.), rt, 20 h; 83% (after 2 steps). (b) (i) Br_2 (2 equiv.), CH_2Cl_2 , -17 °C, 15 min (ii) MeONHMe·HCl (2 equiv.), Et_3N (4 equiv.), rt, 20 h; 68%. (c) (i) Br_2 (2 equiv.), CH_2Cl_2 , -17 °C, 15 min (ii) pyrrolidine (3 equiv.), rt, 20 h; 82%. (d) (i) Br_2 (2 equiv.), CH_2Cl_2 , -17 °C, 15 min (ii) $NH_2CH_2COOCH_3$ ·HCl (2 equiv.), Et_3N (4 equiv.), rt, 20 h; 90%.

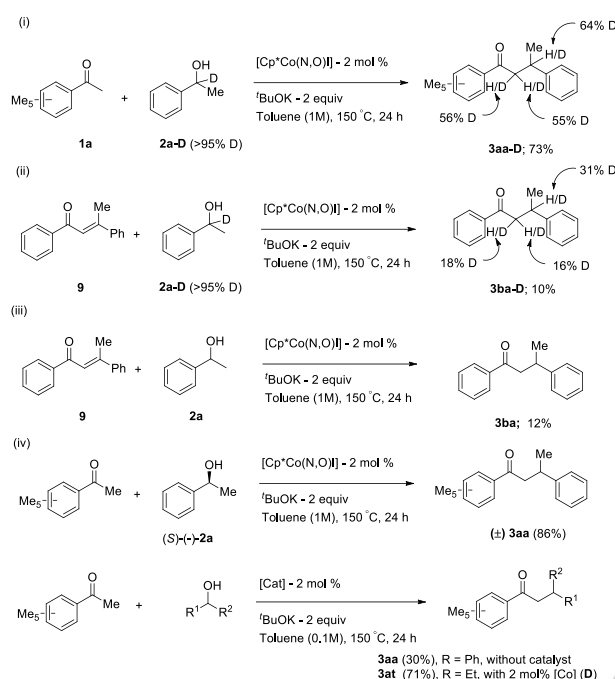
Finally, we investigated more challenging long chain acyclic aliphatic alcohols. It was found that excess amount of alcohol was necessary to achieve the desired products in respectable yields (**3at-3aw**). The developed methodology was also extended to the late stage functionalization of cholesterol with **1a**. The corresponding cholesterol derivative **3ax** was isolated in 43% yield.

The diverse applications of β -alkyl aryl ketone **3aa** into various carbonyl derivatives were shown in Scheme 5. Product **3aa** was first treated with Br_2 to cleave off the pentamethylphenyl group into Aroyl bromide, and the intermediate was subsequently trapped by various nucleophiles.^[5c] Addition of n-octanol yielded the corresponding ester **5** in 83% yield. Replacement of the alcohol with amines as nucleophiles afforded the corresponding amides **4**, **6** and **7** in good yields. Clearly, the sterically bulkier pentamethylphenyl group not only inhibited the self-condensation, but also facilitated the synthesis of diverse β -alkylcarbonyl derivatives.

To gain mechanistic insights, preliminary control experiments were carried out (Scheme 6). Deuterium labelling experiments were performed with **1a** and alcohol **2a-D** to validate the involvement of hydrogen borrowing methodology. Under standard conditions, the reaction yielded the product **3aa-D** in 73% yield, which exhibited 55-64% deuterium incorporation (Scheme 6 (i)). To further confirm our hypothesis, chalcone **9** prepared by self-condensation of acetophenone was also employed under standard conditions using **2a-D** as transfer hydrogenation reagent, providing the expected H/D scrambled product **3ba-D** with 16-31% deuterium exchange (Scheme 6 (ii)). These studies suggest that the transfer hydrogenation is reversible. Chalcone **9** and alcohol **2a** also yielded the product **3ba** under our catalytic system suggesting that the hydride source is derived from alcohol for the reduction step (Scheme 6 (iii)). Next, chiral (*S*)-(-)-1-phenylethanol was used as a coupling partner, leading to the formation of racemized product **3aa** in 86% yield, suggesting that the reaction proceeds through a dehydrogenation pathway as the chirality will be lost after dehydrogenation to ketone (Scheme 6 (iv)). Whereas the reaction with **2a**, carried out under the optimized

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conditions but without catalyst, produced **3aa** in ca. 30% yield and that with 3-pentanol (**2s**) did not proceed at all, using **D** as catalyst gave 71% yield of **3at** as shown in Scheme 6.



Scheme 6. Preliminary mechanistic investigations.

In conclusion, we have demonstrated the use of a phosphine-free, bench-stable and well-defined high-valent Co(III) catalyst for the α -alkylation of ketones using secondary alcohols. Steric crowding in the aryl moiety of aryl alkyl ketones was found to be important for prevention of self-condensation and to exemplify the synthetic utility and scope of the derived β -alkyl aryl ketones. Preliminary control experiments have been carried out to demonstrate the involvement of ‘hydrogen borrowing’ process. Further studies are currently pursued in our laboratory for isolation of Co-H intermediate and rationalization of mechanistic pathways through DFT calculations.

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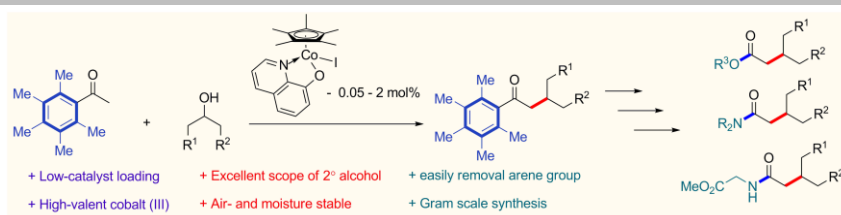
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A well-defined, air-stable Co(III)-catalyzed α -alkylation of ketones was achieved using secondary alcohols as alkylating agents.

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Well-defined Cp*Co(III)-catalyzed α -Alkylation Ketones with Secondary Alcohols