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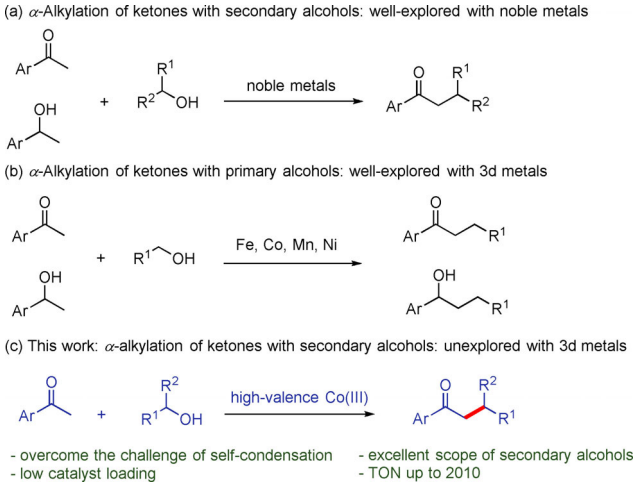
α-Alkylation of Ketones with Secondary Alcohols Catalyzed by Well-Defined Cp*Co^{III}-Complexes

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

Although 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. Herein a well-defined, high-valence cobalt(III)-catalyst was applied for successful α-alkylation of ketones with secondary alcohols. A wide-variety of secondary alcohols, which include cyclic, acyclic, symmetrical, and unsymmetrical compounds, was 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, environmentally friendly, and sustainable methods is more desirable than traditional alkylation reactions. In this context, the concept of "hydrogen borrowing" or "hydrogen autotransfer process"[2] has been tremendously exploited over the past decade. 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 their 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 by using strong bases (e.g., lithium diisopropylamide, *n*BuLi, etc.) and secondary alkyl halides. The reaction naturally produces large amounts of waste with appreciable selectivity.[7] α-Alkylation of carbonyl compounds by 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 with 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 by 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.[5c,d] Inspired by these results and by our ongoing efforts to design inexpensive and sustainable processes under high-valence 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 the 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 well-defined and high-valence Cp*-Co^{III} as the catalyst (Scheme 1 c).

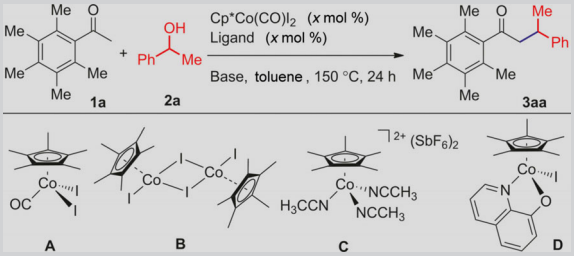
We began our investigations with 2,3,4,5,6-pentamethyl acetophenone (**1 a**) and 1-phenylethanol (**2 a**) as model reactants and by employing 10 mol% of Cp*Co(CO)I_2 as the catalyst in the presence of *t*BuOK as the base in toluene (0.1 M). The reaction at 150 °C for 24 h led to the expected α-alkylated produc-

[a] P. Chakraborty, Dr. M. K. Gangwar, B. Emayavaramban, Prof. B. Sundararaju
Department of Chemistry
Indian Institute of Technology Kanpur
Kanpur, Uttar Pradesh 208 016 (India)
E-mail: basker@iitk.ac.in

[b] Dr. E. Manoury, Prof. R. Poli
Fine CNRS, LCC (Laboratoire de Chimie de Coordination)
Université de Toulouse, UPS, INPT
205 Route de Narbonne
F-31077 Toulouse Cedex 4 (France)

Supporting Information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/cssc.201900990.

Table 1. Reaction optimization.[a]



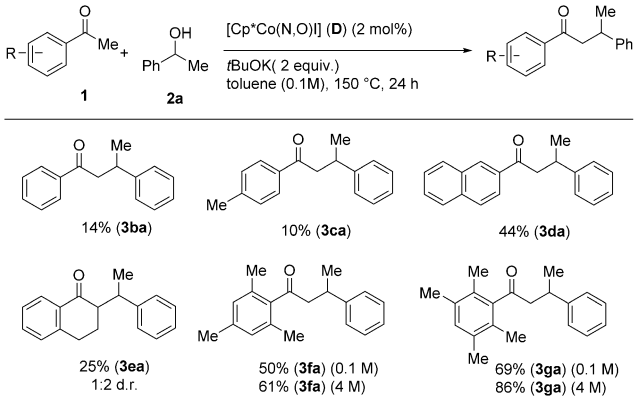
Entry	[Co] [mol%]	Ligand [mol%]	Yield[b] [%]
1	**A** (10)	–	44
2	**B** (10)	–	55
3	**C** (10)	–	38
4	**A** (10)	PPh_3(10)	32
5	**A** (10)	PCy_3 (10)	59
6	**A** (10)	pyridine (10)	n.r.
7	**A** (10)	2-hydroxypyridine (10)	72
8	**A** (10)	8-hydroxyquinoline (10)	77
9	**D** (2)	–	90
10	**D** (2)	–	62[c]
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), *t*BuOK (0.2 mmol) in toluene (0.1 M), at 150 °C for 24 h. [b] Isolated yields. [c] *t*AmOH used as solvent. [d] Bu_2O used as solvent. [e] *t*BuONa used as base. [f] 1.5 equiv. of base used. [g] Conducted at 1 M concentration. [h] Performed at 130 °C. n.r. = no reaction.

t **3aa** in 44% isolated yield (Table 1, entry 1). Encouraged by this result, we screened other Cp*Co complexes, only to observe a marginal improvement (38 and 55%, entries 2 and 3). Addition of a phosphine ligand such as PPh_3 or PCy_3 to the Cp*Co-monomer (**A**) yielded unsatisfactory results (32 and 59%, entries 4 and 5).

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, 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 by 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 was found to be detrimental (entries 10–12). Incidentally, the yield of **3aa** dropped to 74% if the base loading was lowered from 2 to 1.5 equiv. (entry 13). The product formation improved to 95% if the reaction was performed at 1 M concentration (entry 14). In contrast, lowering the temperature to 130 °C gave only a 16% yield (entry 15).

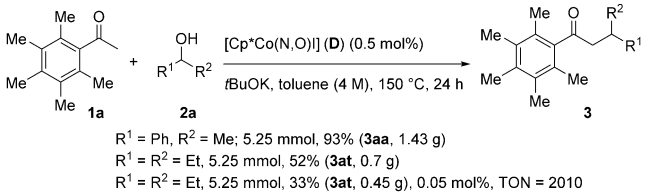
With the optimized conditions at our disposal, we explored the scope of various aryl ketones and the effect of steric hindrance on the reactivity (Scheme 2). Unsubstituted aryl methyl ketones led to poor yields owing to self-condensation (**3ba**–



Scheme 2. Effect of substituents on arenes. d.r. = diastereomeric ratio.

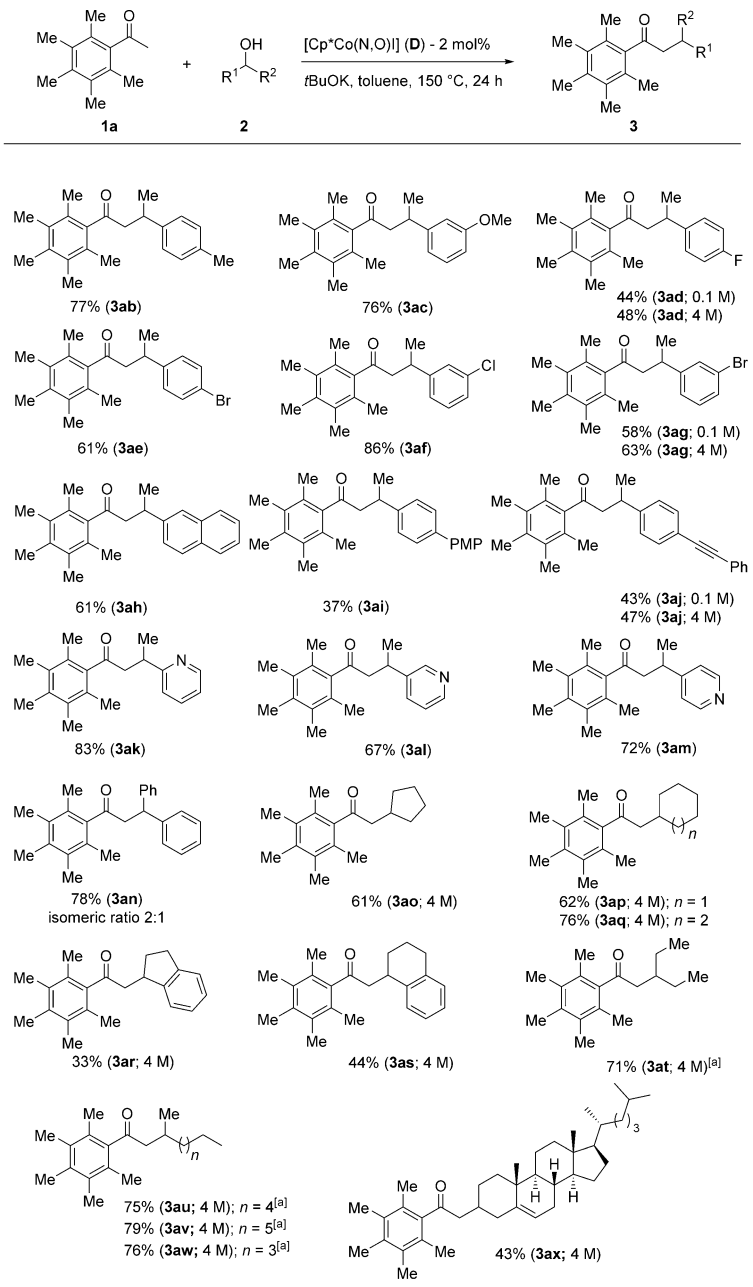
3da). Tetralone as the ketone source was also less effective (**3ea**). However, the yields increased if the *ortho*-positions of the aromatic ketone were methyl-substituted (**3fa**, **3ga**), which highlights the necessity of crowding on the aromatic ring to preclude substrate self-condensation.[4]

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 33% yield (0.45 g of product **3at**), corresponding to a turnover number (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 gave 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 remaining unaffected. Naphthyl- and *p*-methoxyphenyl methyl-substituted alcohols provided the corresponding products in satisfactory yields (**3ah**, **3ai**). Furthermore, if the alcohol contained a *p*-(phenylethynyl) substituent, the desired product was selectively obtained with the alkyne moiety intact (**3aj**). Surprisingly, heteroatom-containing 2-, 3-, and 4-pyridyl secondary alcohols were also effective in leading to the



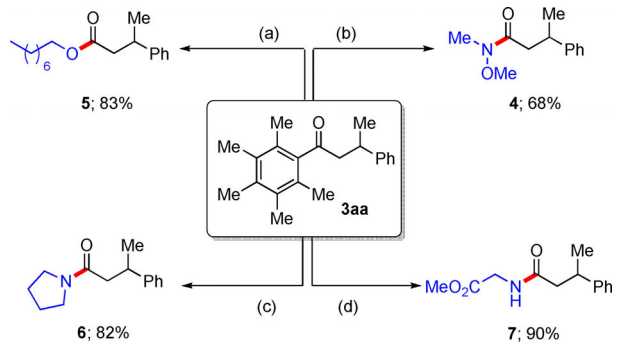
Scheme 4. Scope of secondary alcohols. [a] Performed with 5 equiv. alcohol.

desired products without catalyst poisoning, and their corresponding (pyridin-2-yl)butanone derivatives were obtained in good yields (**3 ak**–**3 am**). 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 afford the products in moderate-to-good yields (**3 ao**–**3 as**). 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 (**3 at–3 aw**). The developed methodology was also extended to the late-stage functionalization of cholesterol with **1 a**. The corresponding cholesterol derivative **3 ax** was isolated in 43 % yield.

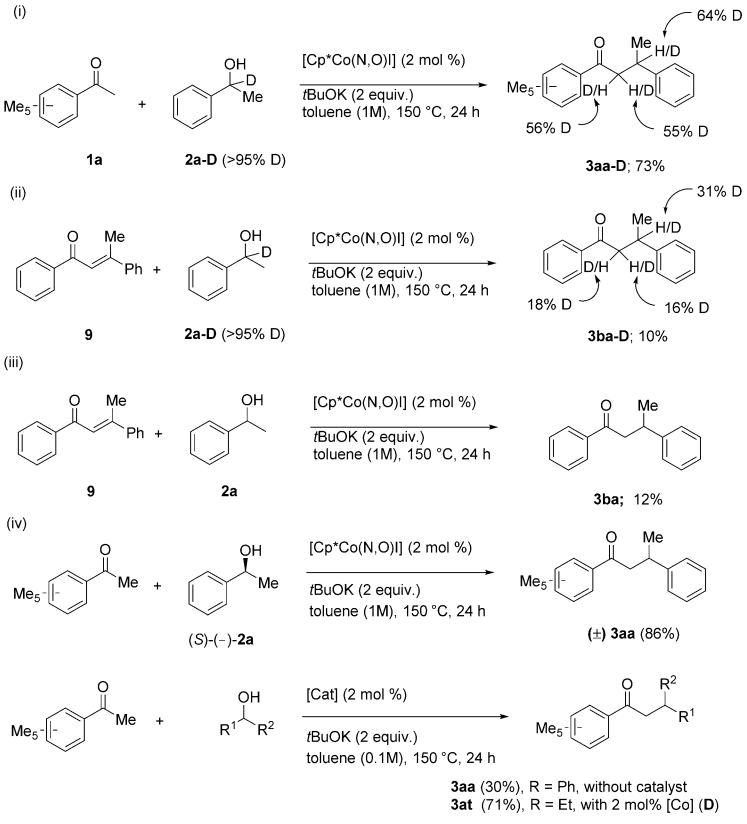
The diverse applications of β-alkyl aryl ketone **3 aa** into various carbonyl derivatives are shown in Scheme 5. Product **3 aa** was first treated with Br_2 to remove the pentamethylphenyl group as aroyl bromide, and the intermediate was subsequently trapped by various nucleophiles.[5c] Addition of *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 performed (Scheme 6). Deuterium-labelling experiments were performed with **1 a** and alcohol **2 a-D** to validate the involvement of hydrogen-borrowing methodology. Under standard conditions, the reaction yielded the product **3 aa-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 with **2 a-D** as transfer-hydrogenation reagent, providing the expected H/D-scrambled product **3 ba-D** with 16–31 % deuterium exchange [Scheme 6 (ii)]. These studies suggest that the transfer-hydrogenation step is reversible. Chalcone **9** and alcohol **2 a** also yielded the product **3 ba** 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 the racemized product **3 aa** in 86 % yield, suggesting that the reaction proceeds through a dehydrogenation pathway because the chirality will be lost after dehydrogenation to the ketone [Scheme 6 (iv)]. Whereas the reaction with **2 a**, performed under the optimized conditions but without catalyst, produced **3 aa** in approximately 30 % yield and the reaction with 3-pentanol (**2 s**) did not proceed at all, using **D** as catalyst resulted in 71 % yield of **3 at**, as shown in Scheme 6.

In conclusion, we have demonstrated the use of a phosphine-free, bench-stable, and well-defined high-valence Co^{III} catalyst for the α-alkylation of ketones with 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 performed to demonstrate the involvement of the "hydrogen borrowing" process. Further studies are currently pursued in our laboratory for isolation of the Co–H intermediate and rationalization of mechanistic pathways through DFT calculations.



Scheme 5. Diversification of **3 aa**. 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%.



Scheme 6. Preliminary mechanistic investigations.

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Conflict of interest

The authors declare no conflict of interest.

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*P. Chakraborty, M. K. Gangwar, B. Emayavaramban, E. Manoury, R. Poli, B. Sundararaju**

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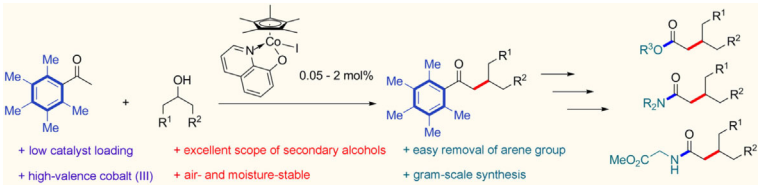
α-Alkylation of Ketones with Secondary Alcohols Catalyzed by Well-Defined Cp*Co^{III}-Complexes



Secondary success: A well-defined, air-stable, Co^{III}-catalyzed α-alkylation of ketones is achieved by using secondary alcohols as alkylating agents. A wide-variety of secondary alcohols, which include cyclic, acyclic, symmetrical, and unsymmetrical compounds, is employed as alkylating agents to produce β-alkyl aryl ketones.