

## Iron-Catalyzed $\beta$ -Alkylation of Alcohols

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**S** Supporting Information

**ABSTRACT:**  $\beta$ -Branched alkylated alcohols have been prepared in good yields using a double-hydrogen autotransfer strategy in the presence of our diaminocyclopentadienone iron tricarbonyl complex Fe1. The alkylation of some 2-arylethanol derivatives was successfully addressed with benzylic alcohols and methanol as alkylating reagents under mild conditions. Deuterium labeling experiments suggested that both alcohols (2-arylethanol and either methanol or benzyl alcohol) served as hydrogen donors in this cascade process.

The  $\beta$ -alkylation of alcohols belongs to the challenging family of carbon-carbon bond-forming reactions. The preparation of  $\beta$ -alkylated alcohols usually involves a threechemical-step process, i.e., first the oxidation of the alcohols, then alkylation of the ketone or aldehyde with alkyl halides or pseudohalides via the deprotonation with a strong base, and finally the reduction of the alkylated ketones/aldehydes. While this procedure is often used in laboratories, such an approach is associated with the formation of wastes and the handling of hazardous chemicals.<sup>1</sup> In the past decade, in order to develop more sustainable strategies, the borrowing hydrogen strategy or hydrogen autotransfer processes have been designed for the construction of C-C and C-N bonds.<sup>2,3</sup> The main advantages of this technology are the use of easily available alcohols as alkylating agents and the generation of water as a unique side product. Not only platinum, but also Earth-abundant, metalbased complexes have been reported for these methods.<sup>2,3</sup> Among the various C-C bond formation reactions, the Guerbet reaction led to the dimerization of primary alcohols via such  $\beta$ -C(sp<sup>3</sup>) alkylation.<sup>4</sup> However, the cross-dehydrogenative coupling reaction between two different primary alcohols remains underdeveloped (Scheme 1).<sup>5,6</sup> This reaction could be an exciting alternative to the hydroformylation/hydrogenation sequence of  $\beta_{,\beta}$ -disubstituted alkenes. The favorable outcome of such a cross-dehydrogenative coupling reaction relies on the different reactivities of the two alcohols. Benzylation of 2arylethanols was initially documented by Ramon in 2012 in the presence of a recyclable impregnated iridium oxide on magnetite at 110 °C for 4 days<sup>5b</sup> and later on by Manojveer and Johnson using the well-known ruthenium complex  $RuCl_2(PPh_3)_3$  as catalyst in refluxing toluene for 24 h (Scheme 1).<sup>5a</sup>  $\beta$ - Methylation of 2-arylethanols using the hydrogen autotransfer technology has also been elaborated, although the dehydrogenation of methanol is higher in energy compared to ethanol and higher alcohols. Methylation could be carried out in homogeneous catalysis either via a dual ruthenium catalysis, namely with the two ruthenium complexes Ru-Macho and Shvo's complex,<sup>6a</sup> or in the presence of a single ruthenium







complex (Ru–Macho–BH<sub>3</sub>)<sup>6b</sup> at elevated temperatures (Scheme 1). Heterogeneous catalysis could also be applied, and the iridium nanocluster,<sup>6c</sup> as well as platinum on carbon,<sup>6d</sup> have been engaged in this hydrogen autotransfer reaction.

While the establishment of economically viable processes advocated the replacement of noble-metal based complexes by nonprecious ones, reports on such cascade reactions involving borrowing hydrogen process are still scarcely mentioned in the literature.<sup>7,8</sup> Following our current research on the hydrogen autotransfer technology,<sup>9</sup> we detail in this work the  $\beta$ alkylation of alcohols catalyzed by the diaminocyclopentadienone iron tricarbonyl complex **Fe1**, enabling the synthesis of  $\beta$ branched benzylated or methylated alcohols from methanol,

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Scheme 2. Layout of the Iron-Catalyzed Double Hydrogen Autotransfer Alkylation



Table 1. Optimization of the Reaction Conditions.<sup>a</sup>

	он .	+ OH 5 equiv.	<b>Fe</b> (2 mol <u>NaOH (10 m</u> base (1 equiv.), te	%) ol %) emp., time	ОН
entry	Fe	base	temp. (°C)	time (h)	conv. <sup>b</sup> (%)
1	Fe1	K <sub>3</sub> PO <sub>4</sub>	90	24	28
2	Fe1	K <sub>3</sub> PO <sub>4</sub>	90	48	32
3	Fe1	K <sub>3</sub> PO <sub>4</sub>	110	48	49
4	Fe1	Na <sub>2</sub> CO <sub>3</sub>	110	40	26
5	Fe1	K <sub>2</sub> CO <sub>3</sub>	110	40	19
6	Fe1	$Cs_2CO_3$	110	40	49
7	Fe1	NaOMe	110	40	32
8	Fe1	NaO <sup>t</sup> Bu	110	40	91 (76) <sup>c</sup>
9	Fe1	KO <sup>t</sup> Bu	110	40	82
10	Fe2	NaO <sup>t</sup> Bu	110	40	71
11	Fe3	NaO <sup>t</sup> Bu	110	40	5
12	Fe4	NaO <sup>t</sup> Bu	110	40	3

<sup>*a*</sup>General conditions: 2-phenylethanol (0.5 mmol), Fe (2 mol %), NaOH (10 mol %), base (1 equiv), benzyl alcohol (2.5 mmol), <sup>*i*</sup>BuOH (1 mL). <sup>*b*</sup>Conversions were determined by <sup>1</sup>H NMR analysis of the crude mixture. <sup>*c*</sup>Yield based on purified product.

benzyl alcohols, and 2-arylethanols under mild reaction conditions (Scheme 2).

Initially, for the optimization of the reaction conditions, alkylation of phenylethanol (1 equiv) with benzyl alcohol was chosen as the model reaction (Tables 1 and S1).

A perusal of the literature revealed four main modes of activation for the iron–carbonyl complexes: (i) a photolytic activation under UV irradiation,<sup>10a</sup> (ii) the use of Me<sub>3</sub>NO,<sup>11,12</sup> (iii) Hieber's protocol in basic conditions,<sup>9a,b,10b</sup> and (iv) thermal activation.<sup>9d,13</sup> The first three methods can be used with complexes Fe1, Fe3, and Fe4, while Fe2 is thermally activated at 70 °C. A short examination of the temperature, in the presence of Fe1 as catalyst, benzylic alcohol (5 equiv), and NaO<sup>t</sup>Bu (1 equiv) as base in *tert*-butyl alcohol (1 mL) showed that the  $\beta$ -benzylation of 2-arylethanol 1a was achieved at 110 °C with good conversion (Table 1) and good isolated yield (76%, entry 8, Table 1). Any modifications of these conditions impeded the yields (Tables 1 and S1). Decreasing the amount of benzyl alcohol led to lower conversions (entries 1-3, Table S1). No reaction occurred without iron complex or base. A noticeable reduction of the conversion in 1a was noted when other bases or a substoichiometric amount of NaO<sup>t</sup>Bu was utilized (entries 3-9, Table 1). Gratifyingly, complex Fe2 can also be introduced without any preactivation (NaOH or Me<sub>3</sub>NO was not required),  $^{9d,13}$  although the conversion was lowered to 71% in 1a (entry 10, Table 1). Finally, other related

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<sup>a</sup>General conditions: 2-arylethanol (0.5 mmol), Fe1 (2 mol %), NaOH (10 mol %), NaO<sup>t</sup>Bu (1 equiv), benzyl type alcohol (2.5 mmol), <sup>t</sup>BuOH (1 mL) at 110 °C for 40 h. <sup>b</sup>Yield was based on purified product.

iron-carbonyl complexes ( $Fe3^{14}$  and  $Fe4^{15}$ ) provided almost no alkylation product (entries 11 and 12, Table 1).

With these optimized conditions in hand, a survey of the scope of this unprecedented iron-catalyzed benzylation was initiated first with several 2-arylethanol compounds and benzyl alcohol (Scheme 3). 2-Naphthylethanol (a more sterically hindered aromatic system) did not prevent the reactivity, and the corresponding alcohol 1d was isolated in 65% yield (Scheme 3). Various electron-withdrawing groups (such as CF<sub>3</sub> and F) within the aromatic fragment and heterocyclic structures (such as unprotected indole, thiophene, or thiazole) were tolerated, and the corresponding 2-benzylated alcohols **1b,c** and **1e-g** were isolated in moderate to good yields (38-76%, Scheme 3). Various substituted benzyl alcohols were then introduced as alkylating reagent, and the corresponding substituted propanol derivatives 1h-n were isolated in 29-74% yield (Scheme 3). Again, electron-donating and electronwithdrawing substituents, and heterocyclic fragments as well, were tolerated. No alkylation of the nitrogen atom in pyridine, indole, and thiazole was noticed.

To emphasize the synthetic viability of our protocol, the benzylation of 2-phenylethanol was performed on a 5 mmol scale. The corresponding 2,3-diphenylpropanol **1a** was isolated in 75% yield. Despite many efforts, alkylation of aliphatic alcohols remains unsuccessful.

Finally, to strengthen the interest for this protocol and extend the scope of alkylating agent, methylation of 2arylethanol was then considered. Methylation catalyzed by



Figure 1. Proposed mechanism.



"General conditions: 2-arylethanol (0.5 mmol), Fe1 (2 mol %), NaOH (10 mol %), NaO'Bu (1 equiv), MeOH (0.5 mL), 'BuOH (1 mL) at 110  $^{\circ}$ C for 40 h. <sup>b</sup>Yield was based on isolated product.

# Scheme 5. Mechanistic Studies, Deuterium-Labeling Experiment



metal base complexes using the autotransfer hydrogen strategy has already been demonstrated for the alkylation of ketones, <sup>9a,16</sup> amines, <sup>9b,16d,17</sup> indoles, <sup>9c,16d</sup> and oxindoles. <sup>16d</sup> However, the  $\beta$ -methylation of alcohols with methanol as alkylating reagent remained underexplored.<sup>8</sup> A variety of 2arylethanols were engaged in this methylation after a rapid optimization of the reaction conditions (Scheme 4 and Table S2). Electron-donating groups (compounds 2b-c, 2e-h, 2n), electron-withdrawing substituents (compounds 2d, 2i, 2l-n), and heterocyclic aromatics (compounds 2f, 2j-k) were permitted, and the corresponding alcohols were obtained in 43–77% yield (Scheme 4). Ortho-substituted phenylethanol furnished the methylated alcohols 2e and 2m in lower yields, due to possible destabilizing steric interactions during the reduction step of the enal intermediate (intermediate V, Figure 1). Gratifyingly, pyridine, unprotected indole, and thiazole were not alkylated on the nitrogen atom, and the 2arylpropanols were obtained in 59-71% yield (Scheme 4).

As above with the benzylation reaction, the methylation of 2-phenylethanol was achieved on a larger scale (5 mmol), and the corresponding 2-phenylpropanol **2a** was isolated in 71% yield.

To gain more information on the mechanism and propose an acceptable mechanism, deuterium-labeling experiments were carried out (Scheme 5).

In deuterated methanol, the CD<sub>3</sub>-labeled 2-phenylethanol 2a was isolated in 68% yield (Scheme 5) and a deuterium incorporation ratio of D/H = 84/16. In other words, a 53/47 mixture of CD<sub>3</sub> and CD<sub>2</sub>H was observed by <sup>1</sup>H NMR spectroscopy analysis (Scheme 5 and Scheme S1). Deuterium was also introduced in the  $\alpha$ - and  $\beta$ -alcohol position. This chemical yield is as good as the nondeuterated methylation (Scheme 5). These experiments highlighted that both deuterated methanol and 2-phenylethanol are a source of hydride in the overall process.

Based on these observations and on our previous works on the borrowing hydrogen methodology,<sup>9</sup> the following mechanism can be proposed for the methylation of 2-arylethanol (Figure 1). According to previous reports,<sup>9b,10b</sup> the unsaturated iron species III could be formed from Fe1 via a decarbonylative activation in basic conditions followed by the formation and release of hydrogen (Figure 1). After coordination of either methanol or 2-phenylethanol leading to IV, a dehydrogenation afforded again the intermediate II and delivered either formaldehyde or 2-phenylethanal. As demonstrated by Casey and Guan with complex Fe3, this step might be reversible via an alcohol/carbonyl interconversion.<sup>18</sup> The 2phenylpropanal, resulting from the condensation of formaldehyde and the enolate, could then initially interact with the iron complex via intermediate V'. Its reduction via intermediate V and a concerted Michael-type additio,9d,13 could give the methylated aldehyde and the unsaturated intermediate III (Figure 1). The  $\beta$ -methylated alcohol (i.e., 2phenylpropanol) would be delivered after a second dehydrogenation step of either methanol or 2-phenylethanol, furnishing again the intermediate II, followed by the reduction of 2phenylpropanal (Figure 1). As mentioned above, steps VI-II and II-VII might be reversible. The same sequence could be also applied to the benzylation reaction with benzyl alcohol as alkylating agent.

In conclusion, we have disclosed an iron-catalyzed methylation and benzylation of 2-arylethanol. This alkylation process provided  $\beta$ -benzylated or  $\beta$ -methylated alcohols in moderate to high yields. Various functionalities, such heterocyclic fragments, can be introduced on the aryl ring. These results fulfill the criteria of atom-efficient procedures and pave the way to the synthesis of functionalized alcohols. This procedure also appears to be an alternative to the well-known hydroformylation—hydrogenation sequence.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b03171.

Preparation details, optimization conditions, and NMR spectra (PDF)

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The authors declare no competing financial interest.

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