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Direct, Redox-Neutral Prenylation and Geranylation of Secondary Carbinol C−H Bonds: C4-Regioselectivity in Ruthenium-Catalyzed C−C Couplings of Dienes to α-Hydroxy Esters

Joyce C. Leung, Laina M. Geary, Te-Yu Chen, Jason R. Zbieg, and Michael J. Krische*

Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712, United States

Supporting Information

ABSTRACT: The ruthenium catalyst generated *in situ* from $Ru_3(CO)_{12}$ and tricyclohexylphosphine, PCy_3, promotes the redox-neutral C−C coupling of aryl-substituted α-hydroxy esters to isoprene and myrcene at the diene C4-position, resulting in direct carbinol C−H prenylation and geranylation, respectively. This process enables direct conversion of secondary to tertiary alcohols in the absence of stoichiometric byproducts or premetalated reagents, and is the first example of C4-regioselectivity in catalytic C−C couplings of 2-substituted dienes to carbonyl partners. Mechanistic studies corroborate a catalytic cycle involving diene−carbonyl oxidative coupling.

The ability to transform abundant feedstocks to value-added products in the absence of stoichiometric byproducts is a principal characteristic of a "process-relevant" method.[1] This attribute is exemplified by catalytic hydrogenation, which is applied across all segments of the chemical industry, including the manufacture of chiral pharmaceutical ingredients on scale[2] and alkene hydroformylation,[3] which may be viewed as the prototypical C−C bond-forming hydrogenation. As part of an effort aimed at the development of C−C bond-forming hydrogenations beyond hydroformylation, we have found that hydrogen transfer between primary alcohols and π-unsaturated reactants generates organometal−aldehyde pairs that combine to form products of carbonyl addition, enabling a departure from stoichiometric organometallic reagents in a range of C═X (X = O, NR) additions.[4]

Although primary alcohols participate in transfer hydrogenative C−C couplings to dienes[5,6] and other π-unsaturated reactants (allenes, enynes, alkynes and allylic acetates),[4] to date, secondary alcohols have proven uniformly unreactive, presumably due to the relatively low electrophilicity of the transient ketones that arise upon dehydrogenation. It was reasoned that the transfer hydrogenative coupling of related α-hydroxy esters and π-unsaturated reactants might be feasible, as the transient α-ketoester esters are highly susceptible to nucleophilic addition. However, dehydrogenation of α-hydroxy esters is challenging from both thermodynamic and kinetic standpoints. Here, we report that the ruthenium catalyst generated from $Ru_3(CO)_{12}$ and tricyclohexylphosphine promotes efficient redox-neutral C−C coupling of aryl-substituted α-hydroxy esters **1a**−**1f** to isoprene **2a** and myrcene **2b** with unique diene C4-regioselectivity to form products of carbinol C−H prenylation and geranylation, respectively (Figure 1).[5−21]

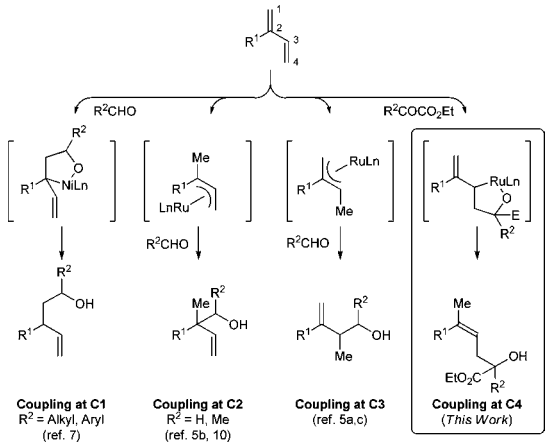

Figure 1. Regioselectivity in intermolecular metal-catalyzed C−C couplings of 2-substituted dienes to carbonyl partners. For catalytic intramolecular diene−aldehyde reductive couplings, see ref 10. For catalyzed and noncatalyzed stoichiometric generation of allylmetal species from dienes followed by carbonyl allylation, see refs 12−21.

In preliminary experiments, a range of ruthenium and iridium catalysts were assayed for their ability to promote the C−C coupling of racemic ethyl mandelate **1a** to isoprene **2a**. These attempts were completely unsuccessful or provided only trace quantities C−C coupling product or the α-ketoester, *oxo*-**1a**. Recently, however, Beller demonstrated that the catalyst generated from $Ru_3(CO)_{12}$ and $Cy_2P(CH_2)_2PCy_2$ in *tert*-amyl alcohol at 150 °C promotes the direct conversion of α-hydroxy amides to α-amino amides through dehydrogenation of the former.[22] While these conditions did not translate directly to the coupling of ethyl mandelate **1a** and isoprene **2a** (Table 1, entry 1), simply changing the solvent to THF and increasing the loading of ligand led to a 45% isolated yield of the *n*-prenylated hydroxy ester **3a** (Table 1, entry 2). Other bidentate phosphine ligands such as ferrocene-derived ligands DPPF, DiPPF, and BINAP-PCy_2 were assayed under these conditions; however, conversion to **3a** was not observed (Table 1, entries 3−5). In contrast, use of the simple monodentate phosphine ligand PCy_3 (12 mol%) under these conditions led to a 59% isolated yield of **3a** (Table 1, entry 6). A comparable isolated

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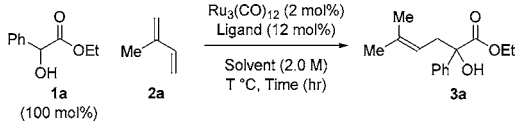
Table 1. Selected Optimization Experiments in the C−C Coupling of α-Hydroxy Ester 1a to Isoprene 2a[a]



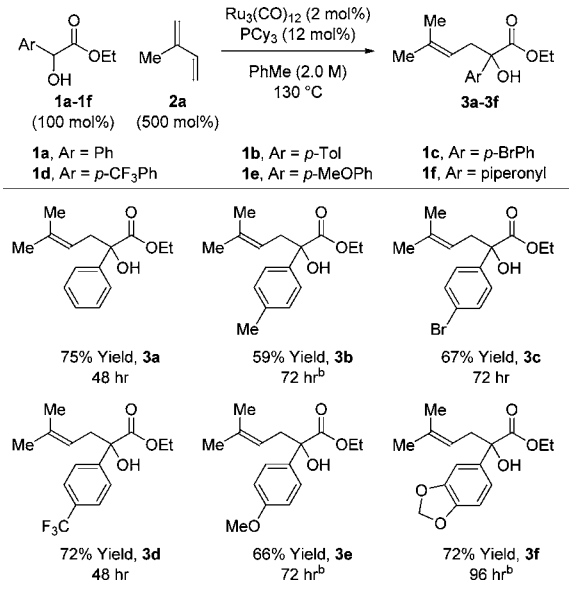
Entry	2 (mol%)	Ligand	Solvent (M)	T (°C)	Time (hr)	Yield%
1	400	$Cy_2P(CH_2)_2PCy_2$	*t*-AmOH (2.0)	150	48	<10[b]
2	400	$Cy_2P(CH_2)_2PCy_2$	THF (2.0)	150	48	45
3	400	DPPF	THF (2.0)	150	48	NR
4	400	DiPPF	THF (2.0)	150	48	NR
5	400	BINAP-PCy_2	THF (2.0)	150	48	NR
6	400	PCy_3	THF (2.0)	150	48	59
7	400	PCy_3	THF (2.0)	130	72	56
8	400	PCy_3	Dioxane (2.0)	130	72	60
9	400	PCy_3	DCE (2.0)	130	72	NR
10	400	PCy_3	PhMe (2.0)	130	72	68
11	400	PCy_3	PhMe (2.0)	130	72	68[c]
12	400	PCy_3	PhMe (1.0)	130	72	59
13	400	PCy_3	PhMe (0.5)	130	72	50
14	400	PCy_3	PhMe (2.0)	130	48	42
⇨15	**500**	**PCy_3**	**PhMe** (2.0)	**130**	**48**	**75**

[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further details. [b]$Cy_2P(CH_2)_2PCy_2$ (6 mol %). [c]Cy_3P (18 mol%).

yield of **3a** could be obtained at 130 °C by extending the reaction time (Table 1, entry 7). At this stage, different solvents were evaluated (Table 1, entries 8−10). By conducting the reaction in toluene, the *n*-prenylated product **3a** was obtained in 68% isolated yield (Table 1, entry 10). Variation of ligand loading did not improve the isolated yield of **3a** (Table 1, entry 11), nor did changes in concentration (Table 1, entries 12, 13). However, by decreasing reaction time and increasing the loading of isoprene (500 mol%), a 75% isolated yield of the *n*-prenylated product **3a** was obtained (Table 1, entry 15).

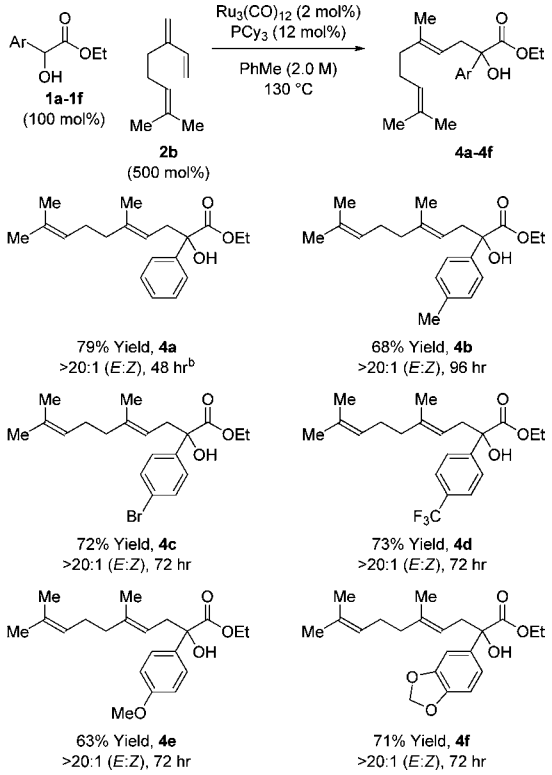
Under these optimal conditions, the redox-neutral C−C coupling of aryl-substituted α-hydroxy esters **1a−1f** and isoprene **2a** was explored (Table 2). In each case, the corresponding *n*-prenylated products **3a−3f** were isolated in good yield as single regioisomers. Alkyl-substituted α-hydroxy esters such as ethyl lactate provide low isolated yields of C−C coupling product using this first generation catalyst. However, analogous coupling reactions of aryl-substituted α-hydroxy esters **1a−1f** with myrcene **2b** were successful, delivering products of geranylation **4a−4f** with complete control of olefin geometry (Table 3). Thus, direct secondary carbinol C−H

Table 2. Prenylation of α-Hydroxy Esters 1a−1f via Ruthenium-Catalyzed Hydrohydroxyalkylation of Isoprene 2a[a]



[a]Yields are of material isolated by silica gel chromatography. See Supporting Information for further details. [b]Isoprene **2a** (600 mol%).

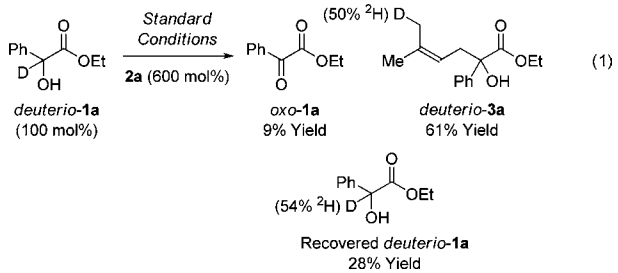
Table 3. Geranylation of α-Hydroxy Esters 1a−1f via Ruthenium-Catalyzed Hydrohydroxyalkylation of Myrcene 2b[a]



[a]As described for Table 2. See Supporting Information for further details. [b]Myrcene **2b** (400 mol%).

prenylation and geranylation is achieved under redox-neutral conditions in the absence of stoichiometric byproducts or premetalated reagents.[23] Reactions using 2,3-dimethylbutadiene, 1,3-pentadiene, and 3-methyl-1,3-pentadiene were attempted under standard conditions, but only trace quantities of product were observed.

To probe the catalytic mechanism and gain insight into the origins of regioselectivity, deuterated *rac*-ethyl mandelate, *deuterio*-**1a**, was exposed to isoprene **2a** under standard conditions for redox-neutral C−C coupling (eq 1). Notably,



(1)

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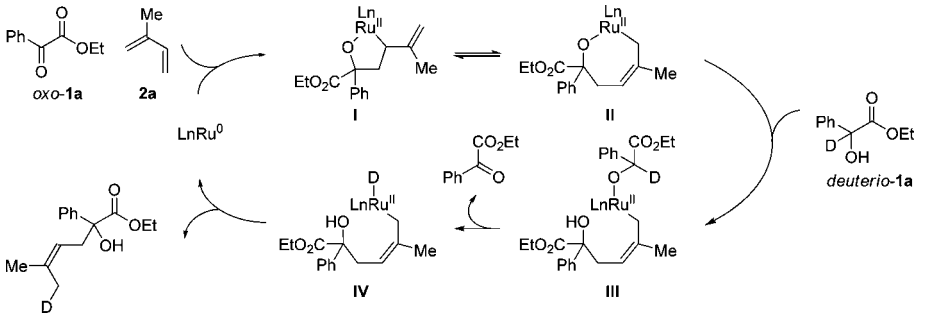
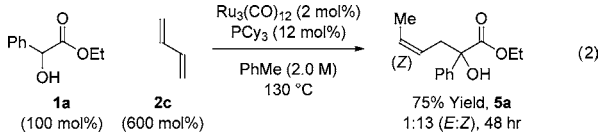
Scheme 1. Plausible Catalytic Mechanism for the Redox-Neutral C−C Coupling of *deuterio*-1a to Isoprene 2a



the *n*-prenylated adduct *deuterio*-**1a** incorporates deuterium exclusively at the *cis*-methyl group of the *n*-prenyl moiety (^{2}H 50%). Incomplete deuterium incorporation may be attributed to the reversible transfer of hydrogen between *deuterio*-**1a** and isoprene, as corroborated by deuterium loss in recovered *deuterio*-**1a** (^{2}H 54%). The regioselectivity and extent of ^{2}H incorporation were evaluated using ^{1}H and ^{2}H NMR spectroscopy. Also, recovered from this reaction in 9% yield is the α-ketoester, oxo-**1a**. Indeed, for many of the reactions reported in Tables 2 and 3 small quantities of the corresponding the α-ketoesters can be observed by thin layer chromatography or isolated by flash silica gel chromatography (typically <5% yield).

The regioselectivity of C−C coupling and deuterium incorporation is consistent with the indicated catalytic cycle, which involves diene−carbonyl oxidative coupling (Scheme 1). To further challenge this mechanistic hypothesis, the redox-neutral coupling of *rac*-ethyl mandelate **1a** and butadiene **2c** was performed under standard conditions. The product of C−C coupling **5a** is formed as (*Z*)-stereoisomer, which is consistent with the proposed oxidative coupling mechanism (eq 2).



In other hydrohydroxyalkylations we have developed, employing ruthenium(II) catalysts, mechanisms involving diene hydrometalation to form π-allylruthenium intermediates appear operative.[5] The present ruthenium(0) catalyst system is unique in its ability to promote both alcohol dehydrogenation *and* diene−carbonyl oxidative C−C coupling, as illustrated in the formation of oxametallacycle **I** (Scheme 1) and as found in related Pauson−Khand-type reactions of 1,2-diones.[23] As suggested by Beller's work[22] and our collective studies, the $Ru_3(CO)_{12}$/phosphine catalyst system also appears better at promoting alcohol dehydrogenations that require β-hydride elimination of electron-deficient carbinol C−H bonds, in comparison to ruthenium(II) catalysts.

In summary, the redox-neutral prenylations and geranylations reported herein represent the first examples of the transfer hydrogenative C−C coupling of secondary alcohols. Further, the C4-regioselectivity displayed by these processes is unique among catalytic diene−carbonyl C−C couplings. As corroborated by mechanistic studies (eqs 1 and 2), this unique regioselectivity is a consequence of a novel catalytic mechanism that links alcohol dehydrogenation and diene−carbonyl oxidative coupling. Direct prenylations and geranylations of secondary carbinol C−H bonds employing isoprene and myrcene, respectively, should facilitate access to diverse terpenoid natural products.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and spectral data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

mkrische@mail.utexas.edu

Notes

The authors declare no competing financial interest.

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