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# Regioselective Reductive Hydration of Alkynes To Form Branched or Linear Alcohols

Le Li and Seth B. Herzon*

Department of Chemistry, Yale University, New Haven, Connecticut 06520, United States

Supporting Information

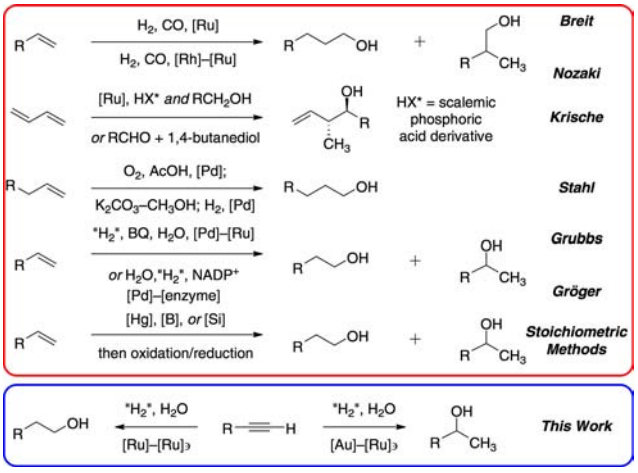
**ABSTRACT:** The regioselective reductive hydration of terminal alkynes using two complementary dual catalytic systems is described. Branched or linear alcohols are obtained in 75−96% yield with ≥25:1 regioselectivity from the same starting materials. The method is compatible with terminal, di-, and trisubstituted alkenes. This reductive hydration constitutes a strategic surrogate to alkene oxyfunctionalization and may be of utility in multistep settings.

The production of alcohols from hydrocarbon feedstocks is among the most important processes in the chemical industry.[1] Classical methods based on alkene oxyfunctionalization employ Brønsted acid catalysts[1] and generally provide the branched (Markovnikov) addition product for terminal alkenes. Recently, several powerful metal-catalyzed methods have been developed to prepare alcohols from alkenes (Scheme 1). These include tandem hydroformylation−reduction processes by Breit,[2] Nozaki,[3] and co-workers, a highly enantio- and diastereoselective hydrohydroxyalkylation of 1,3-dienes by Krische and co-workers,[4] an allylic oxidation−reduction sequence by Stahl and co-workers,[5] an oxidative hydration−reduction by Grubbs and co-workers,[6] and a chemoenzymatic method by Gröger and co-workers.[7] Despite these significant advances, stoichiometric approaches, such as hydroboration−oxidation or oxymercuration−reduction,[8] are often the methods of choice for complex substrates even though these processes require two steps and are not always highly regioselective.[9] Consequently, the development of additional regioselective, catalytic oxyfunctionalization reactions with broad functional group compatibility is desirable.

Recent advances in transfer hydrogenation[10] led us to consider the conversion of alkynes to alcohols under reducing conditions. Although alkynes retain many of the characteristics of alkenes, including reactivity orthogonal to that of heteroatom-based functional groups, alkyne-specific reaction pathways are known, potentially providing a handle for selectivity in polyunsaturated systems. Moreover, alkynes are readily introduced by a number of methods, including nucleophilic attack of metal acetylides to carbogenic electrophiles, metal-catalyzed cross-coupling reactions,[11] and carbonyl homologation reactions.[12]

The simplest method to effect reductive hydration would seem to involve the transformation of an alkyne to an aldehyde or ketone followed by in situ reduction. Although several catalysts are known to affect each individual step (see below), a number of challenges need to be addressed. For instance, most alkyne hydration processes are conducted under acidic conditions[13] while many transfer hydrogenation catalysts require basic activating agents.[10] Additionally, it has been reported that transfer hydrogenation catalysts may undergo irreversible deactivation in the presence of terminal alkynes.[14] Finally, competitive reduction of the alkyne could compromise the yield and/or selectivity.

**Scheme 1. Metal-Catalyzed and Stoichiometric Methods for the Formation of Alcohols from Unsaturated Hydrocarbons**



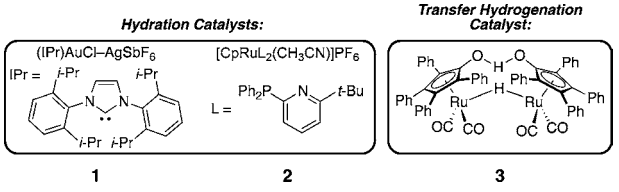




**Figure 1.** Selected precatalysts used in these studies.

Our studies began with an evaluation of the ability of alkyne hydration and transfer hydrogenation catalysts to effect the conversion of phenylacetylene (**4**) to *sec*-phenethanol (**5**) (Table 1). In addition to **5**, acetophenone (**6**), and isopropyl α-methylbenzyl ether (**7**) were formed. When Nolan's catalyst (**1**)[15] (Figure 1) and either $Ru(PPh_3)_3Cl_2$[16] or $(Cp^*IrCl_2)_2$[17] were employed (in the presence of potassium carbonate), <5% conversion of phenylacetylene (**4**) was observed, suggesting

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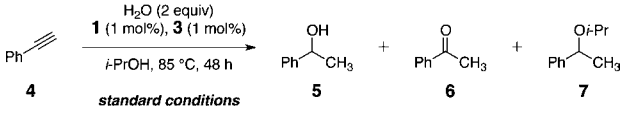
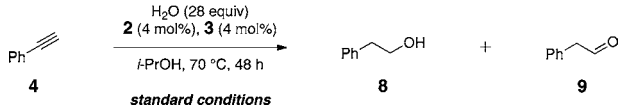
**Table 1. Optimization of the Markovnikov Reductive Hydration**[a]




| entry | deviation from standard conditions | yield (%)[b] 5 | 6 | 7 |
|---|---|---|---|---|
| 1 | 1 mol% $Ru(PPh_3)_3Cl_2$ + 10 mol% $K_2CO_3$ instead of **3** | 0 | 0 | 0 |
| 2 | 1 mol% $(Cp^*IrCl_2)_2$ + 10 mol% $K_2CO_3$ instead of **3** | 0 | 0 | 0 |
| 3 | standard conditions | 44 | 7 | 42 |
| 4 | 1 mol% $[Pt(C_2H_4)Cl_2]_2$ instead of **1** | 13 | 39 | 0 |
| 5 | 1 mol% $Hg(OTf)_2$ instead of **1** | 3 | 29 | 0 |
| 6 | 1 mol% $AgSbF_6$ instead of **1** | 3 | 33 | 0 |
| 7 | 4 equiv of $H_2O$ | 83 | 7 | 4 |
| 8 | 8 equiv of $H_2O$ | 81 | 6 | 9 |
| 9 | 17 equiv of $H_2O$ | 81 | 9 | 4 |
| **10** | **17 equiv of $H_2O$, 70 °C** | **85**[c] | **6** | **1** |

[a]1.0 mmol scale, [**4**] = 0.5 M (based on 2-propanol). [b]As determined by $^1H$ NMR analysis using an internal standard. [c]Isolated yield after purification. 30:1 branched/linear (**5**:**8**), as determined by $^1H$ NMR analysis of the unpurified product mixture.

**Table 2. Optimization of the Anti-Markovnikov Reductive Hydration**[a]

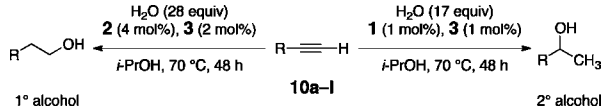



| entry | deviation from standard conditions | yield (%)[b] 8 | 9 |
|---|---|---|---|
| 1 | 1 mol% CpRu(dppm)Cl instead of **2**, 1 mol% **3** | 5 | 5 |
| 2 | 4 mol% CpRu(dppm)Cl instead of **2** | 15 | 11 |
| 3 | 4 mol% CpRu(dppm)Cl instead of **2**, 100 °C | 66 | <5 |
| 4 | 1 mol% **2**, 1 mol% **3** | 8 | 23 |
| 5 | standard conditions | 90 | <5 |
| **6** | **2 mol% 3** | **90**[c] | **<5** |
| 7 | 2 mol% **2**, 2 mol% **3** | 62 | <5 |
| 8 | 1 mol% **2**, 2 mol% **3** | 45 | 20 |

[a]0.25−1.0 mmol scale, [**4**] = 0.5 M (based on 2-propanol). [b]As determined by $^1H$ NMR analysis using an internal standard. [c]Isolated yield after purification. *sec*-Phenethanol (**5**) was not detected in the unpurified product mixture ($^1H$ NMR analysis).

that the two catalysts are incompatible under the reaction conditions (entries 1 and 2). Application of **1** and Shvo's catalyst (**3**)[18] led to a substantial increase in the yield of product **5** (44%); however, isopropyl $\alpha$-methylbenzyl ether (**7**) was also formed in 42% yield (entry 3). Interestingly $[Pt(C_2H_4)Cl_2]_2$,[19] mercury triflate,[20] and silver hexafluoroantimonate[21] selectively promoted the addition of water, but the yields of *sec*-phenethanol (**5**) were low (3−13%; entries 4−6). We found that the formation of isopropyl $\alpha$-methylbenzyl ether (**7**) using **1** and **3** could be suppressed by increasing the amount of water (entries 7−9). Under the optimized conditions, the temperature could be reduced to 70 °C to afford an 87% yield ($^1H$ NMR analysis; 85% isolated yield) of *sec*-phenethanol (**5**, entry 10). The ratio of the branched product *sec*-phenethanol (**5**) to the linear product phenethanol (**8**) was 30:1 under these conditions.

**Table 3. Scope of the Reductive Hydration Reaction**[a]




| entry[a] | substrate | yield **11a-l**[b] | yield **12a-l** (b/l)[b] |
|---|---|---|---|
| 1 | **10a** | **11a** 96% | **12a** 90% (58:1) |
| 2 | **10b** | **11b** 82% | **12b** 82% (47:1) |
| 3 | **10c** | **11c** 82% | **12c**[c] 80% (59:1) |
| 4 | **10d** | **11d** 95% | **12d** 95% (64:1) |
| 5 | **10e** | **11e** 84% | **12e** 81% (53:1) |
| 6 | **10f** | **11f** 84% | **12f** 90% (30:1) |
| 7 | **10g** | **11g** 80% | **12g**[c] 80% (59:1) |
| 8 | **10h** | **11h** 85% | **10h** 93% (45:1) |
| 9 | **10i** | **11i** 90% | **12i** 88% (51:1) |
| 10 | **10j** | **11j** 85% | **12j**[c] 84% (39:1) |
| 11 | **10k** | **11k**[d] 82% | **12k**[e] 75% (25:1) |
| 12 | **10l** | **11l**[f] 80% | **12l**[g] 81% (100:1) |

[a]0.5−1.0 mmol scale, [**10a–l**] = 0.5 M (based on 2-propanol). [b]Isolated yields after purification. Branched/linear ratios determined by $^1H$ NMR of unpurified product mixtures. For anti-Markovnikov reductive hydration, branched products were not detected. [c]0.5 mmol **10c**, **g**, or **j**, 34 equiv $H_2O$, 2 mol% Au(IPr)Cl, 2 mol% $AgO_2CCF_3$, and 2 mol% **3** (**10c**,**g**) or 4 mol% **3** (**10j**) in 2 mL 2-propanol. [d]0.2 mmol **10k**, 35 equiv $H_2O$, 5 mol% **2**, 2.5 mol% **3**, and 1.0 equiv PTSA in 0.5 mL 2-propanol, 80 °C, 12 h. [e]0.1 mmol **10k**, 170 equiv $H_2O$, 10 mol% Au(IPr)Cl, 10 mol% $AgO_2CCF_3$, 10 mol% **3**, and 1.0 equiv PTSA in 2 mL 2-propanol. [f]80 °C, 3 h. [g]0.2 mmol **10l**, 85 equiv $H_2O$, 5 mol% Au(IPr)Cl, 5 mol% $AgO_2CCF_3$, and 5 mol% **3** in 2 mL 2-propanol, 1:1 dr ($^{13}C$ NMR).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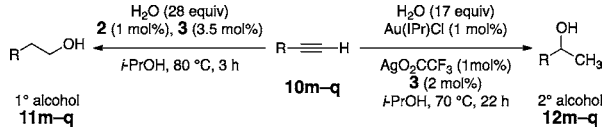
Our success with complex **3** led us to select this precatalyst for the anti-Markovnikov reductive hydration of phenylacetylene (**4**) (Table 2). Initial experiments employing CpRu(dppm)Cl[22] with **3** provided low to moderate yields of phenethanol (**8**) and phenylacetaldehyde (**9**) (entries 1–3). Using Grotjahn's catalyst (**2**)[23] (Figure 1) and **3** (1 mol% each) led to a 23% yield of phenylacetaldehyde (**9**) and an 8% yield of phenethanol (**8**) (entry 4). When the amounts of **2** and **3** were increased to 4 mol% (entry 5), phenethanol (**8**) was formed in 90% yield, and the yield of phenylacetaldehyde (**9**) was <5% ($^1$H NMR analysis). Decreasing the amount of **3** to 2 mol% was not detrimental to the yield (90% isolated yield of **8**; entry 6). However, further reducing the amount of either ruthenium catalyst led to lower yields of phenethanol (**8**) (45–62%; entries 7 and 8). Under the optimized conditions (entry 6), *sec*-phenethanol (**5**) was not detected ($^1$H NMR analysis).

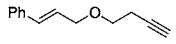
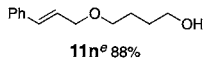
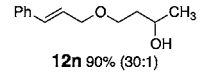
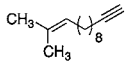
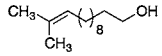
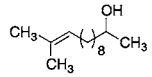
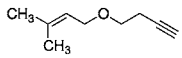
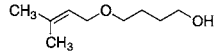
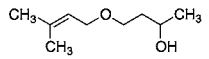
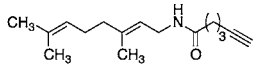
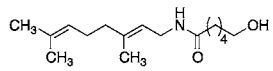
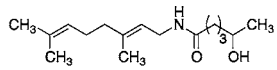
The scope of these reductive hydration reactions is shown in Table 3. Both aromatic and aliphatic alkynes gave high isolated yields of either branched or linear alcohol products (80–96%; entries 1–5). In the case of the electron-rich arylalkyne **10c**, use of silver trifluoroacetate instead of silver hexafluoroantimonate was necessary to suppress the formation of the secondary isopropyl ether in the Markovnikov reductive hydration. The current protocol is also compatible with common functional groups, including alcohols, carboxylic acids, imides, amides, and primary alkyl chlorides (80–93%; entries 6–10). Amines may also be employed, provided that an equivalent of acid [*p*-toluenesulfonic acid (PTSA)] is used to attenuate the basicity of the substrate (75, 82%; entry 11). 1,7-Octadiyne (**10l**) underwent double reductive hydration in 80 and 81% yield (linear and branched, respectively). In all cases, the anti-Markovnikov reductive hydration afforded a single regioisomer ($^1$H NMR analysis); the branched-to-linear selectivities in the Markovnikov reductive hydration were ≥25:1.

Significant efforts have been devoted to the selective oxyfunctionalization of polyolefins,[24] and the selective functionalization of an alkyne in the presence of one or more alkenes could provide an alternative solution to this problem. Toward this end, the reactivity of enynes was evaluated (Table 4). Alkynes incorporating terminal (entry 1), di- (entry 2), and trisubstituted alkenes (entries 3–5) were competent substrates for these transformations, forming the expected branched or linear alcohol products in good to excellent yields. In the Markovnikov hydration of enynes, the use of trifluoroacetate as the counterion provided higher product yields, presumably by attenuating acid-catalyzed decomposition pathways. For substrate **10m** bearing a monosubstituted alkene, careful optimization of the reaction parameters (catalyst loading, counterion, temperature, and concentration) was required to suppress isomerization[25] of the alkene.

Limitations of these dual catalyst systems include applications to substrates containing alkyl ester substituents, as these undergo transesterification with 2-propanol during the reaction, and acid-sensitive protecting groups (e.g., dioxolanes), which were found to be unstable toward hydrolysis. However, the acidic nature of the catalytic system may be exploited to effect a one-flask desilylation–hydration–reduction procedure (Scheme 2). Thus, exposure of trimethyl(phenylethynyl)silane (**13**) to the reductive hydration conditions formed the linear or branched alcohol product **8** or **5** directly (82 or 85% yield, respectively). As trimethylsilylacetylene is often used as a surrogate for acetylene itself, the direct reductive hydration of substrates incorporating protected alkynes should simplify multistep synthetic sequences.

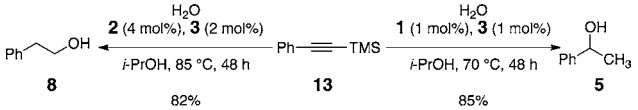
**Table 4. Site-Selective Reductive Hydration of Enynes**[a]




| entry | substrate | yield **11m-q**[b] / yield **12m-q** (b/l)[b] |
|---|---|---|
| 1 |  **10m** |  **11m**[c] 85%<br>  **12m**[d] 90% (70:1) |
| 2 |  **10n** |  **11n**[e] 88%<br>  **12n** 90% (30:1) |
| 3 |  **10o** |  **11o** 90%<br>  **12o** 85% (33:1) |
| 4 |  **10p** |  **11p**[e] 88%<br>  **12p**[f] 80% (31:1) |
| 5 |  **10q** |  **11q**[g] 85%<br>  **12q** 83% (57:1) |

[a] 0.25–1.0 mmol scale, [**10m–q**] = 0.25–0.50 M (based on 2-propanol). [b] Isolated yields after purification. Branched/linear ratios were determined by $^1$H NMR analysis of the unpurified product mixtures. For the anti-Markovnikov reductive hydration, branched products were not detected. [c] 9:1 mixture of **11m** and internal olefin isomers. [d] 3:1 mixture of **12m** and internal olefin isomers. [e] 0.5 mmol of **10n** or **10p**, 28 equiv $H_2O$, 4 mol% **2**, and 2 mol% **3** in 1 mL 2-propanol at 80 °C for 3 h. [f] 0.5 mmol of **10p**, 34 equiv $H_2O$, 2 mol% Au(IPr)Cl, 2 mol% $AgO_2CCF_3$, and 4 mol% **3** in 2 mL 2-propanol at 70 °C for 42 h. [g] 0.25 mmol of **10q**, 56 equiv $H_2O$, 8 mol% **2**, and 4 mol% **3** in 1 mL 2-propanol at 70 °C for 14 h.

**Scheme 2. Direct Conversion of 13 to 8 or 5**





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In summary, we have described the reductive hydration of terminal alkynes to form either branched or linear alcohols. The reaction conditions are compatible with a broad range of heteroatom-based functional groups. By the use of alkyne-specific reaction pathways, reaction at an alkyne is achieved in the presence of alkenes, which may provide a strategy for site-selective functionalization of polyunsaturated substrates.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed experimental procedures and spectral data ($^{1}H$, $^{13}C$, IR, and HRMS) for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION


### Corresponding Author

seth.herzon@yale.edu


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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