Tetrahedron 64 (2008) 5815–5849

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report number 837

Gold-catalysed reactions of alcohols: isomerisation, inter- and intramolecular reactions leading to C–C and C–heteroatom bonds

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ARTICLE INFO

Article history:
Received 17 March 2008
Available online 8 April 2008

Keywords:
Gold
Alcohols
Catalysis
Rearrangement
Cyclisation

Contents

Abbreviations: aq, aqueous; bmim, 1-butyl-3-methylimidazolium; Bn, benzyl; cat., catalytic; Cy, cyclohexyl; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; de, diastereoisomeric excess; dr, diastereoisomeric ratio; ee, enantiomeric excess; equiv, equivalent; MOM, methoxymethyl; MS, molecular sieves; Boc, *tert*-butoxycarbonyl; PPTS, pyridinium *p*-toluenesulfonate; rt, room temperature; TBS, *tert*-butyldimethylsilyl; Tf, trifluoromethanesulfonyl; THP, tetrahydropyranyl; TIPS, triisopropyl; TMS, trimethylsilyl; TOF, turnover frequency; TON, turnover number; Ts, 4-methylphenylsulfonyl.

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doi:10.1016/j.tet.2008.04.018

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1. Introduction

Homogeneous catalysis by gold has emerged over the last 20 years. After the long-held assumption of the unreactivity of gold, a gold rush is occurring, as exemplified by the number of reports,[1] highlights[2] and reviews[1,3] on the Au-catalysed organic reactions that recently appeared. I have always been fascinated by the rich chemistry of alcohols under catalytic conditions[4,5] and, here, the aim is to give an overview of their reactions, except oxidations,[6] in the presence of Au catalysts. Such a topic has never been specifically reviewed. Recently, I reviewed the Pd-catalysed reactions of alcohols:[5] they require either a Pd^0 or a Pd^{II} catalyst, most of them involve β-H eliminations and, when mediated by Pd^{II} compounds, require oxidants to regenerate active Pd^{II} species from the Pd^0 that is produced in the course of the catalytic cycle.[7] In contrast, Au-catalysed reactions can often occur efficiently using gold salts of both stable oxidation states, i.e., Au^I and Au^{III}. Moreover, gold intermediates do not tend to undergo β-H eliminations and no reoxidant is required.

Since gold has high alkynophilicity, many reported Au-catalysed reactions of alcohols involve also alkynyl groups and begin by coordination of the C≡C bond to the catalyst. Other unsaturated functions can also participate in the reaction before that of the alcohol. Consequently, this review is organised by the type of substrate with, mainly, a chronological account of the reports.

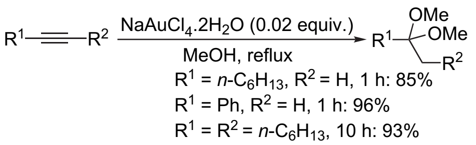
2. Formation of C–O bonds from the addition of exogenous alcohols to unrearranged unsaturated substrates

This section exclusively concerns processes in which the intermolecular addition of the alcohol to the substrate occurs prior to any intramolecular reaction. Other sections will contain examples of alcohol addition that proceeds after a gold-catalysed evolution of the substrate.

2.1. Alkynes

2.1.1. Using Au^{III} catalysts

In 1976, Thomas et al. disclosed that the reaction of aliphatic and aromatic alkynes with $HAuCl_4$ in refluxing methanol afforded the corresponding ketones as the main compounds, but also small amounts of the methyl vinyl ethers.[8] Fifteen years later, Fukuda and Utimoto, who apparently were not aware of the above Thomas study, reported the Au^{III}-catalysed acetalisation of alkynes in refluxing anhydrous MeOH (Eqs. 1 and 2).[9] In contrast, the use of a 1:10 mixture of H_2O/MeOH led, in most cases, to ketones, with no hydration occurring with a $gold^I$ catalyst such as $KAu(CN)_2$.[9] Fukuda and Utimoto have also observed that the treatment of alkynes with 1 equiv of a diol and catalytic amounts of $NaAuCl_4$, to produce cyclic acetals, was unsuccessful. Subsequently, the same team obtained α,β-unsaturated ketones with only traces of β-methoxy ketones from methyl propargyl ethers using aqueous methanol and catalytic $NaAuCl_4$ (Eq. 3).[10] In fact, Au^{III}-catalysed reactions of alkynes in aqueous methanol led, in most cases, to ketones.[10,11]



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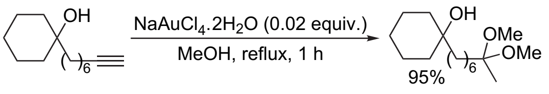

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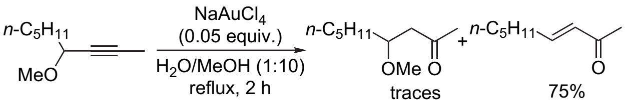

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