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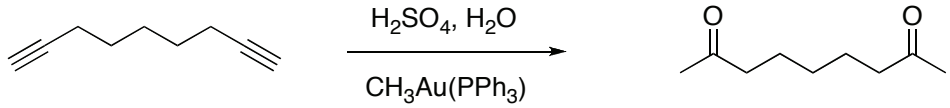
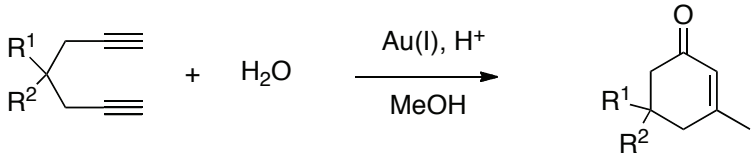
Discussion Addendum for: Au(I)-Catalyzed Hydration of Alkynes: 2,8-Nonanedione



Prepared by Teruyuki Hayashi.[1]

Original article: Eiichiro Mizushima, Dong-Mei Cui, Dilip Chandra Deb Nath, Teruyuki Hayashi,* and Masato Tanaka; *Org. Synth.* **2006**, *83*, 55.

The authors have applied hydration conditions for the reaction of 1,6-heptadiynes to form cyclohexenones.[2] Various substituents at the 4-position of 1,6-heptadiynes are tolerated to give 5-substituted 3-methylcyclohex-2-enones.

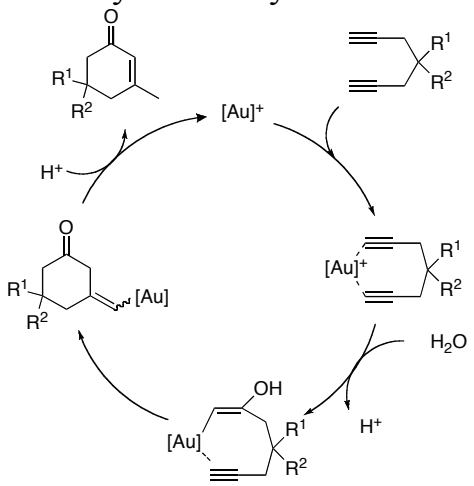


$(R^1, R^2) = (CO_2Me)_2, (CO_2Et)_2, (CO_2{}^iPr)_2, H_2, (OMe)_2, (OBn)_2, (CO_2H)_2, (POPh_2, CO_2Et), (H, CO_2Et), (Ph, CO_2Me), (Ph, CN)$

Scheme 1 Hydrative Cyclization of 1,6-Diynes

The formation of the six-membered ring instead of the dihydration is attributed to the elimination of the ring from the monohydrated intermediate

Figure 1 Catalytic Cycle of Hydrative Cyclization



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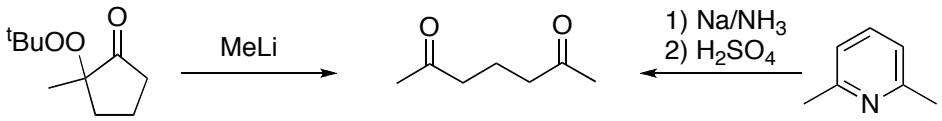
complex. A similar reaction has been reported in supported mercury-catalyzed hydration of 1,6-heptadiyne.[3]

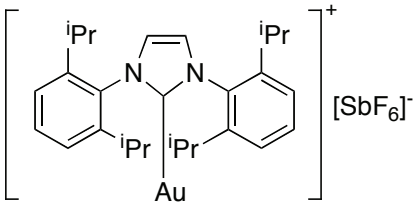
2,6-Heptanedione is prepared through reduction of 2,6-lutidine[4] or methylation of methylperoxycyclopentanone.[5]



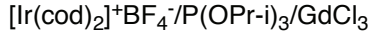
Scheme 2 Syntheses of 2,6-Heptanedione

α,ω-Diynes of C8 to C10 are dihydrated to give the corresponding diketones. Recently developed gold-carbene complexes,[6,7] as well as cationic iridium complexes with the aid of $GdCl_3$,[8] catalyze the reaction. Indium complexes also dihydrate α,ω-diynes of C9, C10, and C14 in the presence of diphenyldiselenide.[9]

Figure 2 New Dihydration Catalysts for α,ω-Diynes



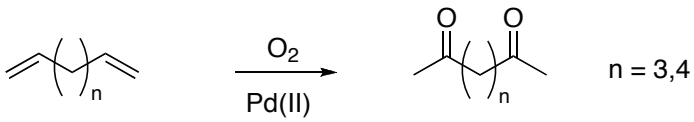
Ref. 6,7



Ref. 8

Ref. 9

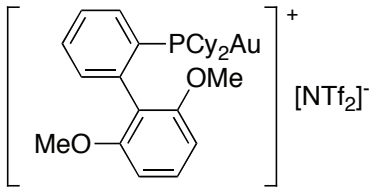
Wacker-type oxidation of α,ω-dienes should be an industrially better process to form the corresponding diketones. However, the selectivity and reactivity are not high enough, with the diketone selectivities of $Pd(OAc)_2$/molybdovanadophosphate system[10] being 40-60%. $PdCl_2$/*N,N*-dimethylacetamide system[11] gives the mixture of diketone and monoketone.



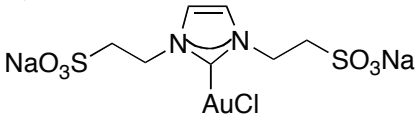
Scheme 3 Wacker-Type Oxidation of α,ω-Dienes

Recent progress in the catalysis of alkyne hydration utilizes cationic gold complexes,[6,7,12,13] gold-carbene complexes,[6,14,15] and water-soluble gold complexes.[16] The application of these catalyst systems to dihydration of diynes gives the diketones.

Figure 3 New Hydration Catalysts for Alkynes



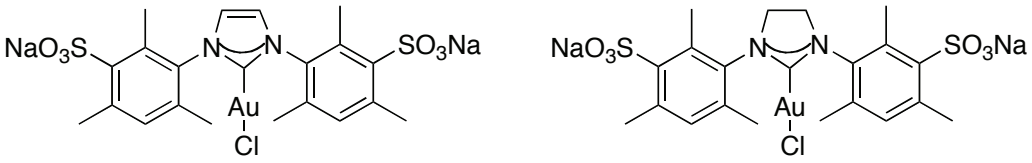
Ref. 13



Ref. 14

$(m\text{-}NaO_3SC_6H_4)_3PAuCCR$

Ref. 16



Ref. 15

For industrial application, heterogeneous catalysts are required. Those including $\{[NP(O_2C_{12}H_8)]_{0.85}[NP(OC_6H_4PPh_2)_2(AuPF_6)_{0.5}]_{0.15}\}$,[17] tin-tungsten mixed oxide,[18] and Hg(II)/silica[3] have been developed to have high activity and selectivity for the hydration of alkynes.

Neutral, metal-free hydration catalysis has been discovered by Abbott researchers.[19] They have reported that the hydration of alkynes proceeds with microwave irradiation in superheated water. On the other hand, graphene oxide has been reported to catalyze the reaction without metal components as an example of carbocatalysts.[20] These new systems have not been applied to the dihydration of diynes.

As for dihydration of α,ω-diynes, mononuclear gold complex systems with some Brønsted acids still seem the catalysts of choice at the present moment.

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Teruyuki Hayashi was born in Tokyo, Japan in 1949. He obtained B.Sc. at the University of Tokyo in 1973. He then joined National Institute of Advanced Industrial Science and Technology (AIST). He obtained his D.Sc. in 1982 from the University of Tokyo, was promoted to senior researcher in 1983, to group leader in 1994, and to deputy director in 2001. His research interests include invention of new catalytic methods for organic and/or material syntheses. Since 2008, he has been project professor at Department of Chemistry, the University of Tokyo.