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Nanoporous Gold Catalyst for Highly Selective Semihydrogenation of Alkynes: Remarkable Effect of Amine Additives

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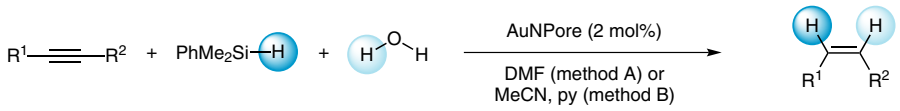
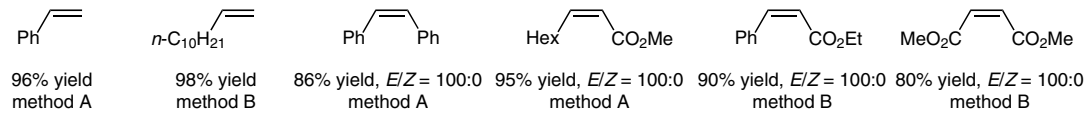
Nanoporous Gold Catalyst for the Selective Semihydrogenation of Alkynes



Selected examples:



96% yield
method A

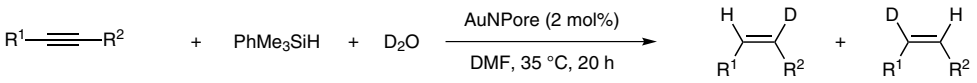
98% yield
method B

86% yield, *E*/*Z* = 100:0
method A

95% yield, *E*/*Z* = 100:0
method A

90% yield, *E*/*Z* = 100:0
method B

80% yield, *E*/*Z* = 100:0
method B



R^1 = Hex, R^2 = CO_2Me

80% yield, (4:1)

Significance: A nanoporous gold catalyst (AuNPore), which was prepared by dealloying a homogeneous $Au_{30}Ag_{70}$ alloy in nitric acid (70 wt%), catalyzed the semihydrogenation of alkynes with organosilanes and water as the hydrogen source to afford the corresponding alkenes. The reaction of phenylacetylene with $PhMe_2SiH$ and water in DMF proceeded in the presence of 2 mol% of AuNPore to give styrene as the sole product (method A: 35 °C, 3 h, 96% yield). 1-Dodecyne underwent the semihydrogenation efficiently in acetonitrile with 50 mol% of pyridine (method B: 80 °C, 8 h, 98% yield).

Comment: The catalytic ability of various catalysts was examined for the semihydrogenation of phenylacetylene: AuNPore (96%), AuCl (18%), $Au_{30}Ag_{70}$ alloy (0%), PdNPore (54%), and Pd/C (20%). The authors proposed the reaction pathway including the generation of the H^- on the AuNPore surface ($[AuNPore\text{-}H]^-$) and pyridinium cation ($[HPy]^+$) which subsequently react with the alkynes to form the corresponding *Z*-alkenes.

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Category

Polymer-Supported Synthesis

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semihydrogenation

alkynes

amines