Dispersion of Rh/Cu in a Sol-Gel Matrix. Highly Chemo- and Stereoselective Catalyst for the Reduction of Alkynes to *Z*-Alkenes

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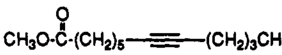
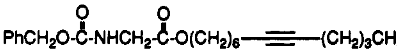
Summary: Treatment of hydrated $RhCl_3$ and $Cu(NO_3)_2$ in THF and H_2O with triethoxysilane affords a highly chemo- and stereoselective catalyst system for the reduction of alkynes to *Z*-alkenes while alkyl-NO_2, aryl-NO_2, *N*-carbobenzyloxy, hydroxy, ester, enoate, benzyloxy, alkyl bromide, aryl bromide, and enone moieties remain unaffected.

We previously described a method for the homogeneous dispersion of 15-Å Pd(0)-particles within sol-gel matrices by the reduction of $Pd(OAc)_2$ with triethoxysilane in aqueous reaction mixtures with concomitant growth of the silicon oxide host.[1] The Pd-containing gels were excellent stereoselective hydrogenation catalysts for the reduction of alkynes to *Z*-alkenes.[2] Unfortunately, the chemoselectivity of the Pd-containing gel was similar to that obtained with other standard Pd-catalyst systems such as the Lindlar hydrogenation catalyst.[3-5] Here we describe the use of a Rh/Cu mixed sol-gel system for the stereo- and highly chemoselective reduction of alkynes to *Z*-alkenes.

The reduction process involves the addition of triethoxysilane to a THF and H_2O solution of the alkyne, $RhCl_3$–$3H_2O$ (1 mol %), and $Cu(NO_3)_2$–$2.5H_2O$ (15 mol %).[6] The results of the hydrogenation reactions are summarized in Table I. Throughout the hydrogenations, we never observed reduction or regioisomerization of the alkene. Moreover, these hydrogenation results were consistent with $RhCl_3$ obtained from different distributors.

Table I. Reduction of Alkynes to *Z*-Alkenes Using Rh/Cu Dispersed in a Sol-Gel Matrix[a]

entry	alkyne starting material	*Z:E* alkene ratio[b]	% yield[c]
1	$CH_3(CH_2)_5{-}{\equiv}{-}(CH_2)_5CH_3$	8:1	83
2	$HO(CH_2)_2{-}{\equiv}{-}(CH_2)_4CH_3$	19:1	94
3	$HO(CH_2)_6{-}{\equiv}{-}(CH_2)_3CH_3$ 1	17:1	98
4	 $CH_3O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_5{-}{\equiv}{-}(CH_2)_3CH_3$	>20:1	84[d]
5	 $PhCH_2O\text{-}\overset{\overset{O}{\|}}{C}\text{-}NHCH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}O(CH_2)_6{-}{\equiv}{-}(CH_2)_3CH_3$	12:1	80
6	$O_2N\text{-}(CH_2)_6{-}{\equiv}{-}(CH_2)_3CH_3$	6:1	88

[a] The reductions used 1 mol % of $RhCl_3$–$3H_2O$ and 15 mol % of $Cu(NO_3)_2$ in a sol-gel matrix as described in ref 6. [b] Ratios determined by capillary GC and/or ^{13}C NMR analysis. See ref 11. [c] Isolated yields of the alkene product. [d] No exogenous H_2 source used and the reaction time was 9 h.

In an effort to further investigate the remarkable chemoselectivity, 7-dodecyn-1-ol (1) was mixed with an equimolar amount of a second potential substrate. Under the standard reaction conditions, none of the substrates shown in Figure 1 was reduced by the Rh/Cu catalyst system. In every case, (*Z*)-7-dodecen-1-ol was obtained in 80–99% yield in a *Z*/*E* ratio of 8:1 to 20:1.[12] *Thus, enones, enoates, alkyl bromides, aryl bromides, organonitro compounds, alcohols, N-cbz groups, and benzyl ethers are not reduced under the reaction conditions nor do they adversely affect*

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[1] Tour, J. M.; Pendalwar, S. L.; Cooper, J. P. *Chem. Mater.* **1990**, *2*, 648.

[2] (a) Tour, J. M.; Cooper, J. P.; Pendalwar, S. L. *J. Org. Chem.* **1990**, *55*, 3452. (b) Tour, J. M.; Pendalwar, S. L. *Tetrahedron Lett.* **1990**, *31*, 4719.

[3] For some heterogenous hydrogenation methods in organic synthesis, see: Rylander, P. N. *Hydrogenation Methods*; Academic Press: Orlando, FL, 1985.

[4] For some homogeneous hydrogenation methods, see: James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

[5] For the use of other oxide-supported metal catalysts, see: (a) Lewis, L. N.; Lewis, N. *J. Am. Chem. Soc.* **1986**, *108*, 7228. (b) Sinfelt, J. H.; Via, G. H. *J. Catal.* **1979**, *56*, 1. (c) de Jongste, H. C.; Ponec, V.; Gault, F. G. *J. Catal.* **1980**, *63*, 395. (d) Anderson, J. R. *Structure of Metallic Catalysts*; Academic Press: New York, 1975. (e) Sinfelt, J. H. *Sci. Am.* **1985**, *253*, 90. (f) Ponec, V. *Adv. Catal.* **1983**, *32*, 149. (g) Sinfelt, J. H. *Bimetal. Clust. Catal.* **1977**, *10*, 15. (h) Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, J. *Catal. Rev. Sci. Eng.* **1988**, *30*, 161. (i) Breitscheidel, B.; Zieder, J.; Schubert, U. *Chem. Mater.* **1991**, *3*, 559.

[6] Triethoxysilane (2.5 mmol) was added to a solution of the alkyne (1 mmol), $RhCl_3$–$3H_2O$ (0.01 mmol), and $Cu(NO_3)_2$–$2.5H_2O$ (0.15 mmol), in a mixture of THF (5 mL) and H_2O (1 mL).[7] The reaction mixture darkened and was stirred[8] at room temperature. Molecular hydrogen was generated in situ (determined by mass spectrometry) from the hydrolysis of the Si–H linkage presumably by the known reaction of R_3Si–H compounds with HOR′ species in the presence of metal salts to form R_3Si–OR′ and H_2.[9] Thus, after the triethoxysilane addition, if the reaction mixture was sealed to prevent the escape of the generated H_2, the reduction was often complete within 24 h. However, to facilitate the reduction process, exogenous H_2 was slowly bubbled through the reaction mixture and the reductions were then usually complete in 2–4 h.[10] The mixture was then filtered through a 1-in. plug of silica gel and eluted with 1:1 ether/hexane. The filtrate was dried over anhydrous sodium sulfate and concentrated. The residue was redissolved in 1:1 ether/hexane and filtered as above to afford the alkene products. Upon completion of this simple filtration process, there were no other compounds detected by capillary GC or spectroscopic analysis.

[7] Tetraethoxysilane was purchased from HULS-Petrach or Aldrich and distilled prior to use. $RhCl_3$–$3H_2O$ and $Cu(NO_3)_2$–$2.5H_2O$ were purchased from Alfa/Johnson Matthey and Aldrich, respectively.

[8] The reaction mixture was stirred with a magnetic stir bar, and the gelation of the system is sufficiently slow so we never experienced difficulty in stirring.

[9] Sommer, L. H.; Barie, W. P., Jr.; Weyenberg, D. R. *J. Am. Chem. Soc.* **1959**, *81*, 251. Sommer, L. H.; Korte, W. D.; Frye, C. L. *J. Am. Chem. Soc* **1972**, *94*, 3463.

[10] The H_2 (balloon) was slowly bubbled directly through the reaction mixture via a glass capillary that was drawn from a Pasteur pipet. The reactions generally took 24 h or more if they were simply placed under 1 atm of H_2 rather than having the gas bubbled through the reaction mixture. The use of higher H_2 pressures was not investigated.

[11] In most cases, the two newly formed alkenyl protons were so similar in chemical shift that routine ^1H NMR coupling constants could not be used. The stereochemical assignments were based on the ^{13}C NMR shifts of the alkenyl carbons. When alkenyl carbons are flanked by methylenes, the *Z*-alkenyl carbons are ~0.5 ppm further upfield than the *E*-alkenyl carbons. This trend was consistent throughout all the compounds in Table I except entry 4 where no *E*-isomer was detected. For a presentation of this trend, see: Bremser, W.; Ernst, L.; Franke, B.; Gerhards, R.; Hardt, A. *Carbon-13 NMR Spectral Data. A Living com-Microfiche Collection of Reference Material*; Verlag Chemie: New York, 1979. Additionally, the 7-tetradecene obtained by this Rh/Cu method was identical to (*Z*)-7-tetradecene obtained by a Lindlar hydrogenation method.

[12] For the additives (1) 2-cyclohexen-1-one, (2) isophorone, (3) coumarin, (4) 1-bromooctane, (5) bromobenzene, (6) *m*-nitrotoluene, and (7) 1-(benzyloxy)octane, the GC yield of the remaining unsaturated additive, the GC yield of the alkene product, and the *Z*/*E* ratio of the alkene are, respectively, (1) 95%, 99%, 10.5:1; (2) 99%, 81%, 13:1; (3) 99%, 99%, 9:1; (4) 99%, 88%, 20:1; (5) 99%, 99%, 16:1; (6) 81%, 79%, 11:1; and (7) 99%, 95%, 20:1.

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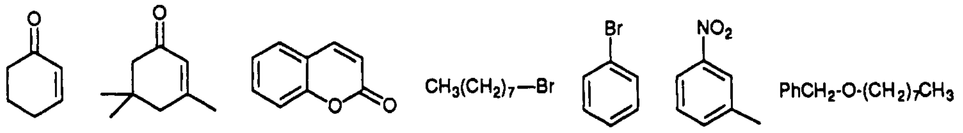

Figure 1.

the catalytic activity of this Rh/Cu system. Such a broad range of chemoselectivity in hydrogenation reactions is remarkable.[3-5]

The functionalities that cannot be tolerated under the reaction conditions are (1) aryl iodides because they deactivate the catalyst toward reaction with an alkyne, (2) terminal alkynes which also deactivate the catalyst, (3) 1-(trimethylsilyl)-1-alkynes which do not reduce cleanly to the alkene, and (4) terminal alkenes or propargylic alcohols because they undergo regioisomerization.

Several reaction conditions were studied to see the effect of using silanes in the absence of water so that no silicon sol or gel formation would occur. When the triethoxysilane reaction was executed on 7-tetradecyne (1 mol % $RhCl_3$, and 15 mol % $Cu(NO_3)_2$ in THF) in the absence of water, approximately 50% of the alkyne was hydrosilylated and 35% was converted to 7-tetradecene (4.8:1 Z/E ratio) after 24 h. Then, addition of water to the reaction mixture caused protodesilylation of the alkenyltriethoxysilane to afford a total of 71% yield of 7-tetradecene (3.5:1 Z/E ratio). If we used triethylsilane in place of triethoxysilane (1 mol % $RhCl_3$, and 15 mol % $Cu(NO_3)_2$ in THF) in the absence of water, approximately 50% of the alkyne was hydrosilylated and 30% was converted to 7-tetradecene (3.8:1 Z/E ratio) after 24 h. Then, addition of water to the reaction mixture caused protodesilylation of the alkenyltriethylsilane to afford a total of 60% yield of 7-tetradecene (3.6:1 Z/E ratio). In the absence of triethoxysilane, a mixture of $RhCl_3$ and $Cu(NO_3)_2$ in THF and water does not respond as a hydrogenation catalyst with exogenous H_2; thus, the silane is essential and the use of triethoxysilane under our standard reaction conditions proved to afford the highest yields and stereoselectivities.

We also screened other metal salts [$Al(NO_3)_3$, $Ti(OEt)_4$, $Zr(OEt)_4$, $Zr(O)(NO_3)_2$, $Ni(NO_3)_2$, $Cu(OAc)_2$, $Cu(SO_4)_2$] with $RhCl_3$ and noted that all of these metal salts dramatically changed the activity and the stereoselectivity of the reduction process; however, the $RhCl_3/Cu(NO_3)_2$ combination was optimal.

It is clear from powder X-ray diffraction (XRD) analysis of the xerogel (solvent free gel) that Cu(0) is present in the material. However, we were not able to detect any Rh(0) species even with more concentrated Rh samples; thus, we cannot presently determine whether this catalyst system is homo- or heterogeneous.[5a,13] A bimetallic system is indeed necessary since the reduction does not occur in the absence of either one of the two metals. Scanning electron micrographs (SEM) of the xerogel show only amorphous material. It was intriguing that while the Pd-containing xerogel[1] had an unusually large surface area (BET using N_2 adsorption at 77 K) of 852 m^2/g and a specific pore volume (N_2 pore volume filling) of 3.33 cc/g, the Rh/Cu material had a very small surface area of only 2.8 m^2/g and an undetectably low specific pore volume. Moreover, when resuspended in an aqueous THF solvent, the Rh/Cu xerogel was not an active hydrogenation catalyst in the presence of H_2.

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Supplementary Material Available: Detailed reduction procedures and spectroscopic data for the compounds listed in Table I (2 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) For some work on distinguishing between heterogeneous and homogeneous reactions, see: (a) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107. (b) Lyon, D. K.; Finke, R. G. *Inorg. Chem.* **1990**, *29*, 1784, 1789.

Rearrangements of 4-Alkynyl-, 4-Alkenyl-, and 4-Alkyl-4-hydroxy-3-methylenecyclobutenes

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Summary: Reported here are the thermal rearrangements of the 4-alkynyl- (1), 4-alkenyl- (7), and 4-alkyl-4-hydroxy-2-methyl-1-phenyl-3-benzylidenecyclobutene (11) to, respectively, the phenol 5, derived from the *p*-quinonemethide 4, the benzylidenecyclohexenone 10, and the acyclic dienone 14.

Generation of quinonemethides from methylenecyclobutenes, as represented by the transformation of 1 to 4, is unprecedented. However, a number of related transformations have appeared that suggest this to be a reasonable process. For example, many simple acyclic (Z)-1,2,4-heptatrien-6-ynes (enynylallenes) have been shown to undergo facile cycloaromatization to produce products formally derived from α,3-dehydrotoluene biradical intermediates.[1] Similar allene and biradical intermediates are envisaged to be involved in the rearrangement presented here. Another related analogy is the facile ring

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