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Selective Reduction Of Alkynes To Z-Alkenes Using Hydrosilane Functions Immobilized On Silica Gel

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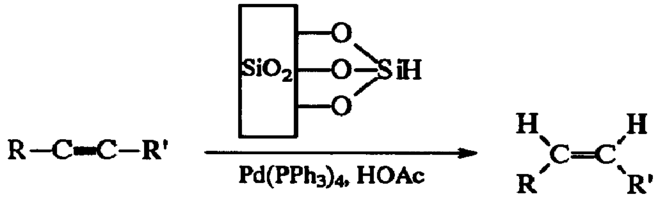
Abstract: **A solid reagent consisting of hydrosilane functions immobilized on the surface of silica gel was used in conjunction with acetic acid and tetrakis(triphenylphosphine)palladium(0) catalyst to effect the reduction of alkynes to *Z*-olefins. Simple filtration provides a convenient means for the reaction workup and isolation of products.**

Surface-supported or otherwise immobilized reagents are gaining increasing importance in organic chemistry because of a variety of advantages that they have to offer over their homogeneous counterparts.[1] Hydrides of tin, boron, and aluminum immobilized on solid polymeric supports are well known and their synthetic utility has been quite well exploited.[1] By contrast, corresponding immobilized hydrosilane functions are relatively unknown and their application in synthetic methodologies is scarce.[2] The use of hydrosilanes as versatile reducing agents has been well established under homogeneous conditions both in the presence or absence of catalysts.[3] We now wish to report that hydrosilane functions immobilized on silica gel may be used in conjunction with acetic acid and a Pd(0) catalyst system[4] for the facile and selective reduction of acetylenes to the corresponding *cis*-olefins (eq 1).



(1)

In a typical reaction a solution of 0.25 mmol of an acetylenic compound in 15 mL of CH_2Cl_2 was treated with a suspension of 2 mmol of the silica gel-immobilized hydrosilane functions[5] in the presence of 5 mol % of $Pd(PPh_3)_4$ and 2 mmol of acetic acid. The heterogeneous reaction mixture was stirred at room temperature for the indicated time, then filtered through a short pad of silica gel. The filtrate contained only the pure product and any remaining unchanged starting material. No further purification other than simple distillation or recrystallization was necessary.[6] The reactions were extremely clean, gave high yields, and demonstrated good *cis*-selectivity to the corresponding alkenes. The results are shown in the table.

Table. Reduction of Alkynes to Alkenes Using Silica Gel-Immobilized SiH Functions.

Entry	Substrate	Reaction Time, h	Product, % yield[a]	*Z*:*E*[b]
1	$CH_3CO_2C\equiv CCO_2CH_3$	2	98	24:1
2	$C_6H_5C\equiv CC_6H_5$	16	85[c]	8.5:1
3	$n\text{-}C_3H_7C\equiv CC_3H_7\text{-}n$	16	97	11.5:1[d]
4	$C_2H_5C\equiv CCH_2CH_2OH$	3	96	>99:1[e]
5	$C_6H_5C\equiv CC(C_6H_5)_2OH$	16	84[f]	10:1[g]
6	$n\text{-}C_{10}H_{21}C\equiv CH$	16	83[f]	-
7	$C_6H_5C\equiv CCO_2C_2H_5$	4	96	9:1
8	$n\text{-}C_4H_9C\equiv CSi(CH_3)_3$	16	-[h]	-

[a] All products were characterized using 400-MHz ^1H and 101-MHz ^{13}C NMR spectroscopy and/or GC/MS. Unless otherwise stated, yields were determined by GC analysis using dodecane as an internal standard. [b] Isomer ratios were found from 400-MHz ^1H NMR spectra and GC analysis. [c] Bibenzyl also obtained in 5% yield. [d] Ref. 7. [e] No *E* isomer detected. [f] Isolated yield. [g] Ref. 8. [h] Starting substrate recovered in 98% yield.

Overreduction to completely saturated product was not a problem except in the case of diphenylacetylene substrate (entry 2). In contrast to the effects produced by the Lindlar catalyst where azides undergo reductions at approximately the same rates as do alkynes, competitive reduction of an equimolar mixture of dodecyl azide[9] and dimethyl acetylenedicarboxylate (DMAD) using this reducing system produced a quantitative conversion of the alkyne to the alkene with a *Z:E* ratio of 96:4 (entry 1). The azide was recovered unchanged. Additional attempts to reduce the pure azide using these reaction conditions did not yield the amine but gave a nearly quantitative recovery of dodecyl azide (97%).

Competitive reduction of an equimolar mixture of 1-dodecene and DMAD gave the reduction product of the alkyne (principally dimethyl maleate) along with a quantitative recovery of unchanged 1-dodecene. This reducing system was also found to be selective for the partial reduction of an alkyne in the presence of an aromatic nitro group. This was shown by the selective reduction of DMAD to the corresponding alkene (*Z:E* = 96:4) in the presence of *m*-nitroacetophenone, which remained unchanged.

No reaction was observed when 1-trimethylsilyl-1-hexyne was subjected to this reducing system in the same manner as used for the other substrates indicated in the table (entry 8). In contrast to this, the use of triethylsilane in place of the silica gel-immobilized hydrosilane did result in the reduction of 1-trimethylsilyl-1-hexyne to a mixture of the corresponding alkenes in 84% yield.[6] Other alkynes bearing an adjacent terminal trimethylsilyl functional group have been reported to be reduced to the corresponding olefins by using acetic acid, 1,1,3,3-tetramethyldisiloxane (TMDS) and a Pd(0) catalyst.[4a] For example, phenyltrimethylsilylacetylene reacts very rapidly and the carbon-carbon triple bond may be reduced completely.[4a] Although the reason for the inability of the hydrosilane functions immobilized on the surface of silica gel to reduce 1-trimethylsilyl-1-hexyne has not been demonstrated in our case, one can imagine that there is a substantial dimensional steric difference between the immobilized hydrosilane functions and the mobile hydrosilanes such as TMDS and triethylsilane. Further investigations of the chemical nature of these immobilized hydrosilane functions are in progress.

In conclusion, the present method is a convenient one for reducing alkynes to *cis*-alkenes.[2e,f] We have demonstrated the effectiveness of hydrosilanes immobilized on the surface of silica gel as an attractive alternative reagent to mobile counterparts such as triethylsilane. The reactions are clean and the workup is extremely simple. Any silylated byproducts formed during the course of the reaction are apparently immobilized on the surface of the silica gel where they can be separated from the desired products by simple filtration. This work also demonstrates the use of a homogenous catalyst [$Pd(PPh_3)_4$] in a heterogeneous reaction system.

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5. Immobilization of monohydrosilane functions on the surface of silica gel was readily accomplished by treating a high surface area silica gel (e.g., Merck silica gel G, BET ca. 450 m^2g^{-1}) with $HSiCl_3$. The treated silica gel was then washed with MeOH and dried. The concentration of the hydrosilane functions bonded on the surface of silica gel was determined by treating the material with a known excess of aq. $AgNO_3$. Unchanged $AgNO_3$ was then precipitated as AgCl and estimated gravimetrically. The quantity of $AgNO_3$ consumed was equated to the amount of hydrosilane functions attached to the surface of the silica gel. For additional information see ref. 2d.

6. It was not possible to determine the value of *Z:E*. Both triethylsilyl acetate and hexaethyldisiloxane were identified as reaction products by GC/MS.

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