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Hydrosilylation of Enones: Platinum Divinyltetramethyldisiloxane Complex in the Preparation of Triisopropylsilyl and Triphenylsilyl Enol Ethers

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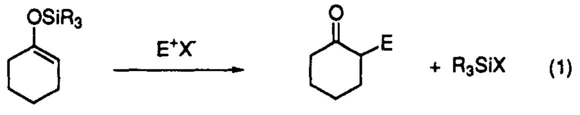
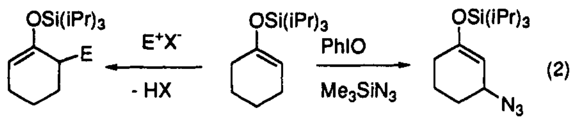
Summary: Enones are regioselectively converted to triisopropylsilyl and triphenylsilyl enol ethers in high yields using triisopropylsilane or triphenylsilane and platinum divinyltetramethyldisiloxane complex 1 (Karstedt's catalyst).

Silyl enol ethers have received considerable attention as synthetic intermediates over the past 20 years.[1] The most important role of these materials is as reactive intermediates for electrophilic α-substutution concurrent with nucleophilic desilylation (eq 1). Recently, Magnus has demonstrated broadened synthetic applications of triisopropylsilyl enol ethers;[2] the steric hindrance at silicon in such ethers suppresses desilylation and opens new and useful reaction pathways (eq 2).





A limiting factor in silyl ether chemistry is the frequent requirement for regiospecificity in the preparation of the silyl enol ethers; this requirement may not be met by simple base-promoted silylation of ketones. The direct and regiospecific preparation of silyl enol ethers from α,β-unsaturated carbonyl species can be accomplished using R$_3$SiH in the presence of a number of transition metal catalysts based on rhodium,[3] platinum,[4] or nickel.[5] Previously, no catalytic systems have been described which can accommodate a broad range of silanes (*e.g.*, triethyl to triisopropyl) in a convenient and high-yielding fashion. We wish to report an efficient and expedient method for the hydrosilylation of enones using the platinum divinyltetramethyldisiloxane complex 1 (Karstedt's catalyst),[6] which has proven to be effective for the preparation of the "bulkier" triisopropylsilyl and triphenylsilyl enol ethers (Figure 1 and eq 3). It has been suggested that the active form of catalyst 1 is colloidal in nature.[6a] Thus, exposing 1 to silane releases the active Pt(0) species which catalyzes the addition of silane to the enone providing the hydrosilylated product.[6a]

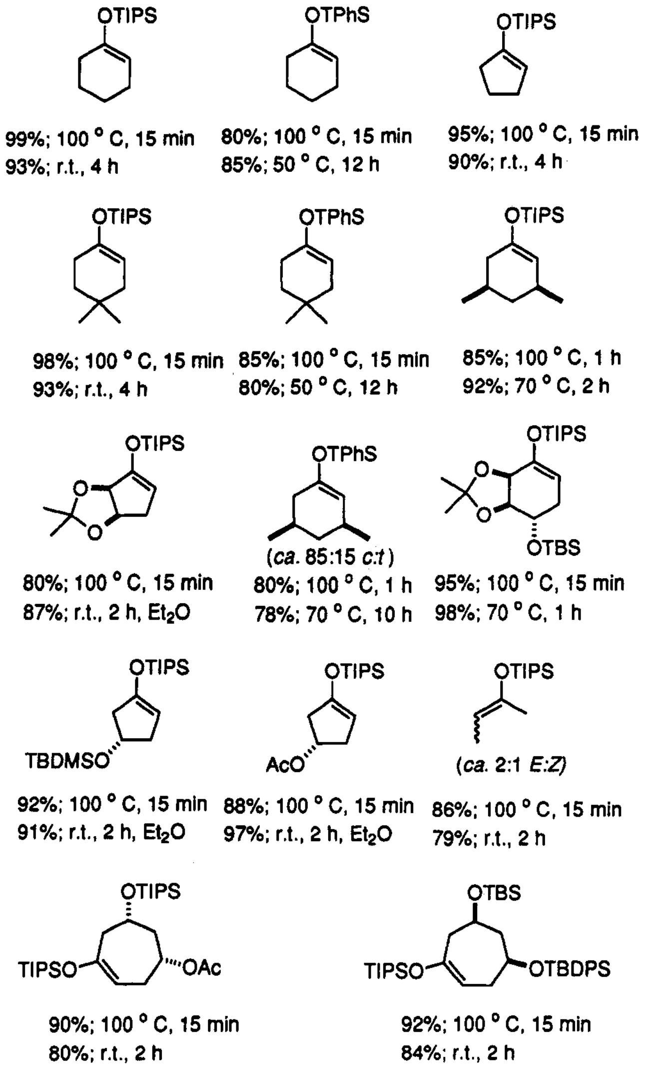
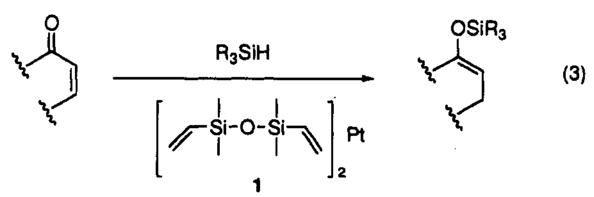


Figure 1. 1. Products of hydrosilylation of enones using 1 and (iPr)$_3$SiH or Ph$_3$SiH (eq 3). Two equiv of R$_3$SiH and one drop of catalyst 1 solution[6b] per 100 mg of substrate were commonly used.



In a typical procedure (Figure 1; entry 1) a solution of catalyst 1 (1 drop $\simeq$10 mg, 0.003 wt % Pt or 0.00015 mol % Pt)[6b] and triisopropylsilane (2 equiv, 0.47 mL, 2.0 mmol) were placed in a 5-mL round-bottomed flask equipped with a magnetic stirring bar and fitted with a rubber

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(1) (a) Brownbridge, P. *Synthesis* 1983, *1*, 85. (b) Poirier, J.-M. *Org. Prep. Proc. Int.* 1988, *20*, 317. (c) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981.

(2) (a) Magnus, P.; Mugrage, B. *J. Am. Chem. Soc.* 1990, *112*, 462. (b) Magnus, P.; Lacour, J. *J. Am. Chem. Soc.* 1992, *114*, 767.

(3) (a) Ojima, I; Kogure, T. *Organometallics* 1982, *1*, 1390. (b) Chan, T. H.; Zheng, G. Z. *Tetrahedron Lett.* 1993, *34*, 3095.

(4) (a) Barlow, A. P.; Boag, N. M.; Stone, F. G. A. *J. Organomet. Chem.* 1980, *191*, 39. (b) Rumin, R. *Ibid.* 1983, *247*, 351.

(5) Bourhis, R.; Frainnet, E.; Moulines, F. *J. Organomet. Chem.* 1977, *141*, 157.

(6) (a) Lewis, L. N.; Lewis, N.; Uriate, R. J. In *Homogeneous Transition Metal Catalyzed Reactions*; American Chemical Society: Washington, DC, 1992, pp 541–549. (b) Catalyst 1 can be purchased from United Chemical Technologies, Bristol, PA, as a 2–3% platinum solution in xylene.

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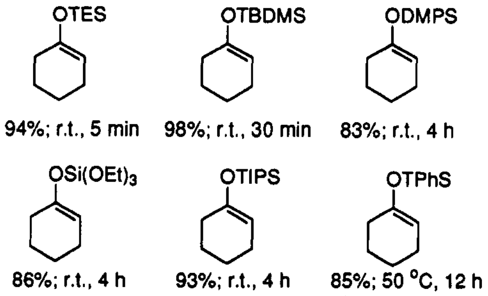

Figure 2. Products of hydrosilylation of cyclohexenone in the presence of catalyst 1. Conditions: 2 equiv of silane, 1 drop of catalyst solution. [b] DMPS = dimethylphenylsilyl, TES = triethylsilyl, TIPS = triisopropylsilyl, TPhS = triphenylsilyl, TBDMS = *tert*-butyldimethylsilyl.

septum. The mixture was stirred under argon for 15 min, and then 2-cyclohexen-1-one (100 mg, 1.0 mmol) was introduced *via* syringe[7] and the solution was stirred for 2 h. Excess silane was removed *in vacuo*,[8] and the resultant crude mixture was chromatographed using 20:1 petroleum ether/ethyl acetate to afford clean product **2a** (247 mg, 93%). No 1,2-hydrosilylated products were observed.[9]

A broad range of silanes can be used (Figure 2); their relative rates of reactivity are as follows: triethyl > *tert*-butyldimethyl ≫ dimethylphenyl, triethoxy, triisopropyl ≫ triphenyl.

Although most hydrosilylations could be carried out at room temperature, enones with β or γ substituents required elevated temperatures (70 °C) to provide complete conversion to their corresponding triisopropylsilyl enol ethers. Preparation of triphenylsilyl enol ethers required both elevated temperatures and longer reaction times. It should be noted that hydrosilylation of methyl vinyl ketone gave both possible isomers (*E*/*Z* 2:1). From 3,5-dimethyl-2-cyclohexen-1-one both cis and trans isomers are possible; in the case of triispropylsilane addition only cis product was observed whereas with *tert*-butyldiphenylsilane the product was ca. 85% cis and 15% trans.

To our knowledge no catalytic system has been reported for the preparation of triisopropylsilyl or triphenylsilyl enol ethers from any α,β-unsaturated carbonyl species. In our hands neither $(PPh_3)_3RhCl$ (Wilkinson's catalyst)[3a] nor $HRh(PPh_3)_4$[3b] was successful in the conversion of enones to their corresponding triisopropylsilyl enol ethers; the latter was recently reported as a catalyst in the preparation of dimethylphenylsilyl and triethoxysilyl enol ethers.[3b]

In summary, we have shown that Karstedt's catalyst can effect the conversion of enones to a variety of silyl enol ethers, including triisopropylsilyl and triphenylsilyl enol ethers, in high yields and under mild conditions. We are continuing to explore other applications of this and related chemistry.

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Supplementary Material Available: ^{1}H NMR (300 MHz) and ^{13}C NMR of all silyl enol ethers listed in this paper (36 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see current masthead page for ordering information.

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(7) At this point a variety of solvents can be introduced (*i.e.*, diethyl ether, toluene, benzene, acetone, or tetrahydrofuran).

(8) Except in the case of triphenylsilane which was separated chromatographically.

(9) For examples see: Ojima, I.; Donovan, R. J.; Clos, N. *Organometallics* **1991**, *10*, 2606.