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Platinum Oxide (PtO_2): A Potent Hydrosilylation Catalyst

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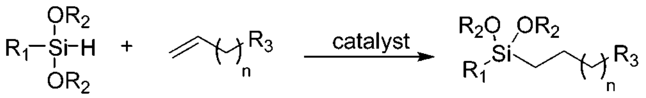
ABSTRACT



R_1, R_2 = alkyl
R_3 = $-NH_2$, -NHR, $-NR_2$, -CN, -COOR, -COOH, -COR, -OR, -epoxide...

Platinum oxide was found to be a versatile and powerful hydrosilylation catalyst upon a wide variety of functionalized alkenes and especially aminated alkenes. Moreover, highly reproducible results and easy removal make this new catalyst a useful tool for hydrosilylation reaction.

Silicones [poly(dialkylsiloxanes)] are of great interest both from the industrial[1] and the academic points of view. Two major processes are usually used to synthesize functionalized polysiloxanes: hydrosilylation of polyhydridosiloxanes and polymerization of functionalized alkoxysilanes.

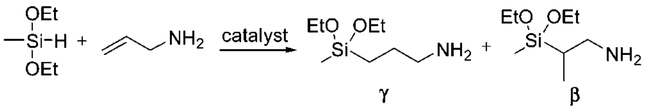
In both cases, the key step is the addition of hydridosilanes to unsaturated bonds, a topic that has been extensively reviewed.[2] Moreover, the hydrosilylation reaction is also of great importance for the synthesis of coupling agents,[3] reduction of carbonyl groups,[4] modification and cross-linking of polymers,[5] and the manufacture of silicon-organic copolymers.[6]

Although a large variety of catalysts are available for the synthesis of silanes and siloxanes via hydrosilylation, there is actually no efficient catalyst for hydrosilylation of aminated alkenes with alkyldialkoxysilanes.

Among all metal catalysts (Pd, Pt, Rh, ...), platinum-based catalysts are the most widely used. Speier's catalyst (i.e., $H_2PtCl_6 \cdot 6H_2O$) proved to be one of the most efficient, but during our investigations on substrates containing aminated functions, we noticed severe limitations as reported in the literature.[7]

Various platinum catalysts and conditions have been studied in the presence of methyldiethoxysilane and allylamine or allyldimethylamine in order to increase the efficiency of the conversion (Scheme 1).

Scheme 1



First, we examined the reactivity of allylamine in the presence of the most common hydrosilylation catalysts.

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(1) (a) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; p 437. (b) Eaborn, C.; Bott, R. W. In *Organometallic Compounds of the Group IV Elements*; MacDiarmid, A. G., Ed.; Dekker: New York, 1968; Vol. 1, p 105.

(2) (a) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 1999. (b) Marciniec, B.; Gulinski, J.; Urbaniak, W.; Kornetka, Z. W. *Comprehensive Handbook on Hydrosilylation*; Pergamon: Oxford, 1992. (c) Ojima, I. The Hydrosilylation Reaction. In *The Chemistry of Organic Silicon Compounds;* Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Vol. 1, Chapter 25, p 1479.

(3) Plueddemann, E. D. *Silane Coupling Agents*; Plenum Press: New York, 1982.

(4) (a) Felfoldi, K.; Kapocsi, I.; Bartok, M. *J. Organomet. Chem.* **1989**, *362*, 411. (b) For review, see: Brunner, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 897. (c) For review, see also ref 2c.

(5) (a) Brockmann, M.; Dieck, H.; Klaus, J. *J. Organomet. Chem.* **1986**, *301*, 2091. (b) Chujo, Y.; Ihara, E.; Ihara, H.; Saegusta, T. *Macomolecules* **1989**, *22*, 2040. (c) Friedmann, G.; Brossas, J. *Polym. Bull.* **1983**, *10*, 28.

(6) (a) Fang, T. R.; Kennedy, J. P. *Polym. Bull.* **1983**, *10*, 82. (b) Kennedy, J. P.; Carlson, G. M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 3551. (c) Friedmann, G.; Herz, J.; Brossas, J. *Polym. Bull.* **1982**, *6*, 252.

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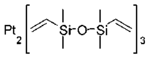
Table 1. Hydrosilylation of Allylamine with Methyldiethoxysilane in the Presence of Various Catalysts

Entry	Catalyst	Reaction time (h)	Ratio[a] (γ/β)	Yield[a] (%)
1	$H_2PtCl_6 \cdot 6H_2O$ in iPrOH	48	> 95/5	20-55
2	 (Karstedt catalyst)	24	> 95/5	50
3	Pt/C (10% Pt w/w)	24	> 95/5	> 95
4	PtO_2 (83.69% Pt w/w)	24	> 95/5	> 95

[a] Calculated on the basis of ^1H NMR spectrum.

Results are summarized in Table 1. All catalysts were tested under standard hydrosilylation conditions.[8] Equimolar amounts of silane and alkene are stirred with 100 ppm (i.e., 100 μmol per mole of silane) of catalyst at 85 °C in a sealed tube.[9] As a general trend, carrying out the reaction in a classical round-bottom flask led to lower yield and poor reproducibility.

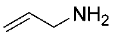
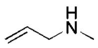
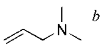
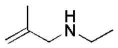
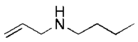
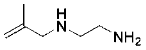
Speier's catalyst gave only moderate yields and low reproducibility probably as a result of poisoning of the catalyst by the amino function. Karstedt's catalyst (Table 1, entry 2), under similar conditions, gave identical and highly reproducible results. This could be attributed to the higher stability of the platinum complexes toward strong ligands.[10] Both catalysts gave γ and β regioisomers in over 95/5 ratios but in moderate yields.

Next, we tested heterogeneous catalysts, which are very little used for hydrosilylation reaction despite their easy removal from the reaction medium by simple filtration. First, Pt/C, which was described for hydrosilylation of alkynes,[11] in accordance with the early work of Wagner,[12] proved also to be very efficient under our standard conditions leading to more than 95% yield after 24 h. Then, PtO_2, which was to our knowledge never tested as a hydrosilylation catalyst, gave remarkable results similar to those observed for Pt/C.

These results prompted us to investigate PtO_2 further in order to evaluate its scope and limitations for other substrates containing amino functions.

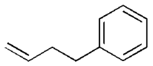
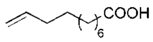
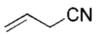
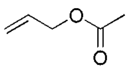
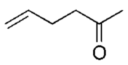
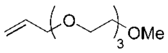
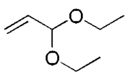
In Table 2, the performances of PtO_2 and Speier's catalyst are compared. As a general trend, PtO_2 led to total conversion

Table 2. PtO_2 vs $H_2PtCl_6 \cdot 6H_2O$ for Hydrosilylation of Aminated Alkenes with Methyldiethoxysilane in 24 h

Entry	Alkene	PtO_2		$H_2PtCl_6 \cdot 6\,H_2O$	
		Yield[a] (%)	Ratio (γ/β)	Yield[a] (%)	Ratio (γ/β)
1		> 95	> 95/5	30	> 95/5
2		> 95	44/56	0-30	> 95/5
3	 [b]	> 95	> 95/5	8-58	> 95/5
4		> 95	> 95/5	60-85	> 95/5
5		> 95	50/50	0	/
6		0	/	0	/

[a] Calculated on the basis of ^1H NMR spectrum. [b] Reactions run with Pt/C and $(Bu_4N)_2PtCl_6$ gave around 90% conversion of pure γ adduct.

Table 3. Hydrosilylation Conversion with Methyldiethoxysilane on Various Functionalized Alkenes

Entry	Alkenes	Yield[a] (%)
1		> 95
2		90[b]
3		90
4		85
5		> 95
6		95
7		> 95

[a] Yield calculated on the basis of ^1H NMR spectrum. [b] Ratio ω/ω-1 = 90/10, all others are >95/5

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(7) (a) Marciniec, B.; Gulinski, J.; Urbaniak, W.; Nowicka, T.; Mirecki, J. *Appl. Organomet. Chem.* **1990**, *4*, 27. (b) Ryan, J. W.; Speier, J. L. *J. Org. Chem.* **1966**, *31*, 2698. (c) Coy, D. H.; Fitton, F.; Haszeldine, R. N.; Newslands, M. J.; Tipping, A. E. *J. Chem. Soc., Dalton Trans.* **1974**, 1852.

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(9) **Procedure for 3-(diethoxy-methyl-silanyl)-1-acetoxy-propane:** 1.6 mL (10 mmol, 1 equiv) of methyldiethoxysilane and 1.08 mL (10 mmol, 1 equiv) of allyl acetate are stirred without solvent in a sealed tube under argon without any previous purification. Platinum oxide, PtO_2 (100 ppm equiv) is added, and the tube is sealed and heated at 85 °C during 20 h. After cooling to room temperature, the crude is filtered through activated charcoal with anhydrous ethanol. The filtrate is concentrated, dried under reduced pressure, and purified by vacuum distillation to afford the desired product in 80% yield. ^1H NMR (300 MHz, $CDCl_3$): δ 0.13 (s, 3H, CH_3-Si); 0.63 (m, 2H, $SiCH_2$); 1.22 (t, 6H, J = 7.1 Hz, OCH_2CH_3); 1.70 (m, 2H, $SiCH_2CH_2CH_2$); 2.05 (s, 3H, CH_3COO); 3.77 (q, 4H, J = 7.1 Hz, OCH_2-CH_3); 4.03 (t, 2H, J = 7.0 Hz, $SiCH_2CH_2CH_2$). ^{13}C NMR (50 MHz; $CDCl_3$): δ −5.0 (s); 9.9 (s); 18.3 (s); 20.9 (s); 22.2 (s); 58.1 (s); 66.6 (s); 170.0 (s). ^{29}Si NMR (59 MHz, $CDCl_3$ + $Cr(acac)_3$ 0.03 M): δ −5.5. IR (ATR, neat): ν (cm^{-1}) 2970−2880 (C−C); 1735.1 (C=O); 1230 ($SiCH_3$ δ); 1068.3 (Si−O); 942.0 (Si−O); 760.9 ($SiCH_3$ γ). MS (CI, NH_3): m/z 252 ($M + NH_4^+$); 235 ($M + H^+$); 189 ($M + H^+ - EtOH$). Bp = 72 °C/0.5 mbar.

(10) (a) Hitchcock, P. B.; Lappert, M. F.; Warhurst, N. J. W. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 438. (b) Karstedt, B. D. U.S. Patent 3,814,720, 1974.

(11) Chauhan, M.; Hauck B. J.; Keller L. P.; Boudjouk P. *J. Organomet. Chem.* **2002**, *645*, 1.

and highly reproducible results, whereas Speier's catalyst gave lower yields and weak reproducibility over several runs.

For allylbutylamine (entry 5), PtO_2 proved to give addition products in more than 95% yield, whereas Speier's catalyst induced no reaction. Noteworthy, however, is the difference in the ratios observed for both catalysts in the case of allylmethylamine (entry 2) (44/56 for PtO_2 and more than 95/5 for Speier's catalyst) and the equimolar mixture of regioisomers obtained for allylbutylamine (entry 5).

Although primary, secondary, and tertiary allylamines proved to be reactive, PtO_2 seems not to be a universal hydrosilylation catalyst as shown for chelating substrates such as diamino chelating alkenes (Table 2, entry 6).

To extend further the scope of PtO_2, we tested several other functionalized alkenes (Table 3).[13] Hydrosilylation gave high yields for all substrates whatever function (alkyl, acid, nitrile, ester, ketone, ether, or ketal) is present on the alkene.

While Speier's catalyst stays in the crude reaction mixture, PtO_2 can be filtered off. This is of particular interest for environmental issues: it allows reduction of heavy metal spill. However, since only a very small amount of PtO_2 is required to achieve total completion of the reaction, we never tried to recycle it.

Finally, 4-phenylbutene was engaged in a 400 g scale hydrosilylation reaction. Under similar conditions and after 24 h reaction, NMR analysis of the crude mixture revealed no significant differences with the small scale experiment (Table 3, entry 1).

In summary, PtO_2 proved to be a highly potent hydrosilylation catalyst compatible with a large range of functionalities including amino functions. Furthermore, the results are highly reproducible and the catalyst is conveniently removed by simple filtration, proving that altogether PtO_2 should become a useful hydrosilylation catalyst. Further studies are underway to expand the scope of the applications of the hydrosilylation reaction especially for substrates containing chelating bisamino groups.

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(12) (a) Wagner, G. H. U.S. Patent 2,632,013, 1953. (b) Wagner, G. H. U.S. Patent 2,637,738, 1953.

(13) **Procedure for 3-(diethoxy-methyl-silanyl)-propylamine:** 1.6 mL (10 mmol) of methyldiethoxysilane is reacted with 744 μL (10 mmol, 1 equiv) of allylamine using PtO_2, following the same procedure described for allyl acetate.[4] The desired product is obtained by vacuum distillation in 60% yield. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.10 (s, 3H, $\mathrm{Si}\mathit{CH}_3$); 0.62 (m, 2H, $\mathrm{Si}\mathit{CH}_2$); 1.21 (t, 6H, $J = 7.0$ Hz, $\mathrm{OCH_2}\mathit{CH}_3$); 1.51 (m, 2H, $\mathrm{SiCH_2}\mathit{CH}_2$-$CH_2$); 2.68 (t, 2H, $J = 7.2$ Hz, $\mathrm{SiCH_2CH_2}\mathit{CH}_2$); 3.80 (q, 4H, $J = 7.0$ Hz, $\mathrm{O}\mathit{CH}_2\mathrm{CH_3}$). ^{13}C NMR (75 MHz; $CDCl_3$): δ -5.2 (s); 10.6 (s); 18.1 (s); 27.0 (s); 44.9 (s); 57.7 (s). ^{29}Si NMR (59 MHz, $CDCl_3$ + $Cr(acac)_3$ 0.03 M): δ -5.0. IR (ATR, neat): ν (cm^{-1}) 3350 ($C{-}NH_2$ br); 2926 (C$-$C); 1262 ($SiCH_3$ δ); 1034 (Si$-$O); 956.2 (Si$-$O); 752.4 ($SiCH_3$ γ). MS (CI, NH_3): $m/z = 192$ ($M + H^+$). Bp = 105 °C/26 mmHg.