ORGANIC LETTERS

2000
Vol. 2, No. 8
1027−1029

An Efficient Pd-Catalyzed Route to Silyl Esters

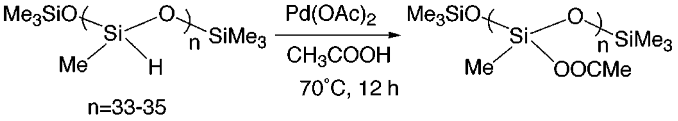
Moni Chauhan, Bhanu P. S. Chauhan, and Philip Boudjouk*

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

boudjouk@plains.nodak.edu

Received January 4, 2000

ABSTRACT



A one-step, highly selective catalytic route to silyl esters is reported. Commercially available silanes with Si-H functionality were converted to silyl or siloxy esters in the presence of $Pd(OAc)_2$ under mild reaction conditions. This protocol was found to be equally applicable for the modification of multiple silicon centers in one framework and lead to the corresponding polysilyl esters in high yields. A comparison of catalytic efficiency of $Pd(OAc)_2$ versus Pd on carbon was also undertaken.

Simple methods for the quantitative conversion of a variety of organic compounds into stable, easily isolable and identifiable silyl derivatives are required in organic synthesis.[1] The silylating agents generally used in the conversion of the carboxyl function to the silyl ester group are aminosilanes which require prolonged heating and continuous removal of ammonia or amine.[2] Other important methods to synthesize silyl esters are by heating chlorosilanes or alkoxysilanes with acetates or acetic anhydrides.[3] However, these processes are applicable under extreme reaction conditions and are accompanied by side products.

The utility of introducing functional groups on a polysiloxane backbone is well recognized, and modifying the existing ones is a continuous challenge. Organofunctional polysiloxanes couple the unique properties of polysiloxanes with the wide range of reactivities of carbon functional organic groups.[4] The degradation properties of polysilyl esters have received considerable interest in environmental and biomedical applications.[5] A few of the many applications of polysilyl esters are in the cotton textile industry to impact water repellency[6] as liquid cross-linkers, adhesion promoters, and as a source of silicon dioxide.[7] Polysiloxanes bearing silyl ester end groups have also been used as protection agents in anionic polymerization[8] and in photographic applications[9] and as viscosity reduction agents.[10] Although a wide range of transition metal catalysts have been reported for dehydrocoupling of OH-containing compounds with silanes,[11] there are only a few examples of COOH/SiH dehydrocoupling reactions.[12] We report herein a very simple, efficient, catalytic route for quantitative conversion of silanes

---

(1) Pierce, A. E. *Silylation of Organic Compounds*; Pierce Chemical Co.: Rockford, IL, 1968. Colvin, E. *Silicon in Organic Synthesis*; Butherworths: London, 1981. Haslam, E. *Tetrahedron* **1980**, *36*, 2409.

(2) Aizpurua, J. M.; Palomo, C.; Palomo, A. L. *Can. J. Chem*. **1984**, *62*, 336. Palomo, A. L. *An. Quim*.. **1981**, *77*(1), 35. Palomo, A. L.; Palomo, C. *An. Quim*. **1981**, *77*(*1*), 87. Palomo, C. *Synthesis*. **1981**, 809. Aizpurua, J. M.; Palomo, C. *Bull. Soc. Chim. Fr. II*. **1982**, 265.

(3) Mbah, G. C.; Speier, J. L. *J. Organomet. Chem*. **1984**, *271*, 77. Schuyten, H. A.; Weaver, J. W.; Reid, J. D. *J. Am. Chem. Soc*. **1947**, *69*, 2110. Sauer, R. O.; Patnode, W. *J. Am. Chem. Soc*. **1945**, *67*, 1548. Anderson, H. H.; Fischer, H. *J. Org. Chem*. **1954**, *19*, 1296.

(4) Chauhan, B. P. S.; Boudjouk, P. *Tetrahedron Lett*. **1999**, *40*, 4123. Arruda, A. F.; Campiglia, A. D.; Chauhan, B. P. S.; Boudjouk, P. *Anal. Chim. Acta* **1999**, *396*, 263.

(5) Peppas, N. A.; Langer, R. *Science* **1994**, *263*, 1715; Langer, R. *Acc. Chem. Res*. **1993**, *26*, 537. Weinberg, J. M.; Gitto, S. P.; Wooley, K. L. *Macromolecules* **1998**, *31*, 15.

(6) Patrode, W. I. U.S. Patent 2,306,222, December 22, 1942. (b) Barry, A. J. U.S. Patent 2,405,988, August 20, 1946.

(7) Kendrick, T. C.; Parbhoo, B.; White, J. W. *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Chapter 21.

(8) Mormann, W.; Schwabe, A.; Sikora, R. *Makromol. Chem*. **1986**, *187*, 133. Morshima, Y.; Hashimoto, T.; Itoh, Y.; Kamachi, M.; Nozakura, S. *J. Polym. Sci., Polym. Chem. Ed*. **1982**, *20*, 299.

(9) Shirai, M.; Miwa, T.; Tsunooka, M. *Chem. Mater*. **1995**, *7*, 642 and references therein. Aoai, T. (Fuji Film Co. Ltd.) Eur. Pat. Appl. EP010599, January 9, 1985; JP Appl. 83/117 769, June 29, 1983.

(10) Greber, G.; Darms, R. Gen. Offen. DE 2206359 720907.

10.1021/ol005507t CCC: \$19.00

and siloxanes to corresponding esters. In addition, application of this approach to obtain polysiloxy esters is also disclosed.

In initial experiments, we reacted commercially available silanes with acetic acid and 1 mol % (by weight) of Pd$(OAc)_2$ catalyst in C_6D_6 solution (Scheme 1). Triethyl- and triethoxysilanes were readily converted to the corresponding silyl carboxylates in excellent yields. The reactions were monitored by ^{1}H and ^{29}Si NMR, which showed the disappearance of the Si-H signals and the appearance of a new signal in the ^{29}Si NMR for the product silyl ester. The orange-colored $Pd(OAc)_2$ solution in benzene turns black on addition of the silane. These suspended black particles are precipitated on completion of the reaction. The pure products were obtained by simple filtration of the catalyst. There was no reaction between acetic acid and silanes in the absence of $Pd(OAc)_2$ under the same reaction conditions.

Scheme 1. Conversion of Hydrosilanes to Silyl Esters

$$R_3SiH \quad + \quad R'COOH \xrightarrow[C_6D_6,\ RT]{Pd(OAc)_2\ (1mol\ \%)} R_3SiOCOR'$$

Entry	R_3SiH	R'COOH	Conditions	Yield
1	$R=C_2H_5$	$R'=CH_3$	RT, 6 h	98%
2	$R=C_2H_5$	$R'=C_6H_5$	reflux, 4 h	95%
3	$R= OC_2H_5$	$R'=CH_3$	RT, 4 h	98%

We first examined model monosiloxane 1,1,1,3,5,5,5-heptamethyltrisiloxane, $[CH_3SiH(OSiMe_3)_2]$ **1**, which is commercially available and closely related to the polysiloxanes of interest. The present catalytic process was found to be quite general. Thus **1** reacted successfully with a variety of acids under mild conditions to provide corresponding monosiloxy esters in good yields (Table 1).[13] With the exception of benzoic acid, which required 70 °C, all acids were silylated at room temperature.

The reactions were monitored by ^{1}H and ^{29}Si NMR. Reaction completion is indicated by the disappearance of the 4.76 ppm signal in the ^{1}H NMR and −36.6 ppm signal in the ^{29}Si NMR showing consumption of the Si−H bonds. A new set of signals for the central silicon atoms appears in the ^{29}Si NMR spectrum in the range of −57 to −66 ppm. As expected, there are only small variations in ^{29}Si NMR shifts for $OSiMe_3$ in the products (δ 7 to 10 ppm) from the starting siloxane (δ 8.9 ppm). When comparing the yields from different reactions, it is important to note that low yields were obtained in reactions from trichloro- and trifluoroacetic acids and methanesulfonic acid (entries 5−7, Table 1). To improve the efficiency of these reactions, we dried the reactant methanesulfonic acid by the standard procedure.[14] The acid was then treated with monosiloxane **1** under the same conditions except that the concentration was reduced by a factor of 6. The reaction was completed in 24 h, and the yield of the siloxy ester was quantitative (based on ^{1}H and ^{29}Si NMR). Thus, we assume that the yields in entries 5 and 6 can be improved in the same manner.

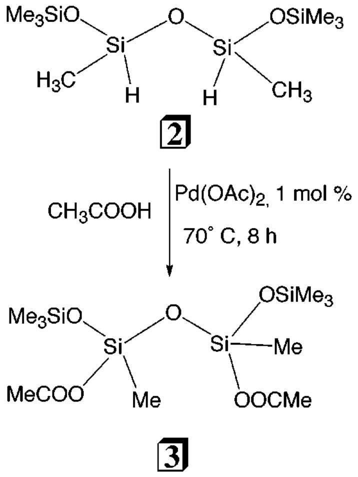
Table 1. Reaction of Monosiloxane **1** with Acids[a]

entry	substrate	reactn condns	^{29}Si NMR C_6D_6	yield, %[b]
1	CH_3COOH	rt, 8 h	−57.9, 10.0	90
2	HCOOH	rt, 2 h	−58.3, 10.7	99
3	PhCOOH	70 °C, 6 h	−57.1, 10.3	98
4	R''COOH[c]	rt, 3 h	−58.3, 10.4	85
5	CCl_3COOH	rt, 2 h	−65.8, 7.6	65
6	CF_3COOH	rt, 1 h	−65.2, 8.5	60
7	CH_3SO_3H	rt, 1 h	−65.5, 7.4	60

[a] In all cases the reactions were carried out in the presence of 1 mol % of $Pd(OAc)_2$ in C_6D_6 (0.50 mL) and 2 mmol of the acid and silane. [b] On the basis of the ^{1}H NMR spectrum. [c] R″ = $(OC_2H_5)_2POCH_2$.

Under typical reaction conditions, quantitative conversion of 1,1,1,3,5,7,7,7-octamethyltetrasiloxane **2** to the corresponding ester derivative was achieved by heating it with acetic acid at 70 °C for 8 h (Scheme 2). The reaction conditions remain the same, and the formation of the product was monitored by ^{1}H and ^{29}Si NMR.

Scheme 2: Synthesis of Oligosilyl Esters



After establishing the reaction conditions for esterification of model siloxanes, including their NMR signatures and

---

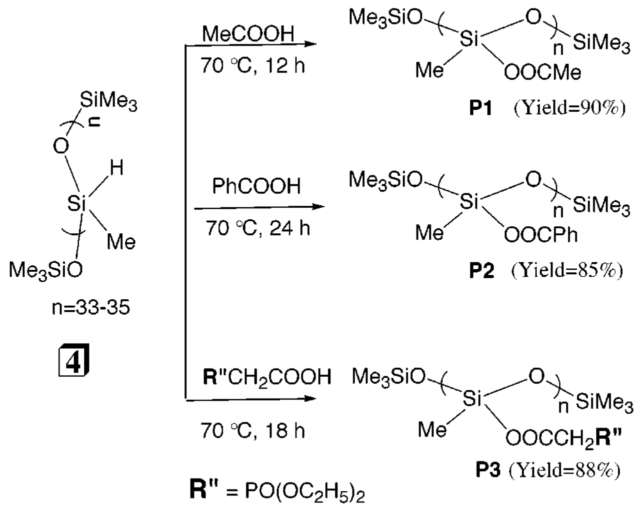
(11) Gauvin, F.; Harrod, J. F.; Woo. H. G. *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1998; Vol. 42.

(12) Schubert, U.; Lorenz, C. *Inorg. Chem.* **1997**, *36*, 1258.

(13) In a preparative scale experiment, a mixture of palladium acetate (0.0336 g, 0.15 mmol) and acetic acid (0.855 mL, 15 mmol) in C_6D_6 (4.0 mL) was degassed by three freeze−pump−thaw cycles. Upon addition of 1,1,1,3,5,5,5-heptamethyltrisiloxane, $[CH_3SiH(OSiMe_3)_2]$ **1** (4.06 mL, 15 mmol), to the reaction mixture, gas evolution (presumably H_2) was observed in addition to a color change from yellow to black. The progress of the reaction was monitored by ^{1}H and ^{29}Si NMR. The Si-H signals at 4.76 ppm in the ^{1}H NMR and −36.28 ppm in the ^{29}Si NMR disappear and a new signal appears at −57.9 ppm in the ^{29}Si NMR for the acetate-substituted silicon center. After the completion of the reaction, the black turbid solution turned colorless and the catalyst precipitated as a black solid. The liquid

isolation techniques, we examined the catalytic activity of $Pd(OAc)_2$ to convert a polysiloxane backbone containing multiple Si−H centers to the corresponding polysiloxy esters (Scheme 3). Thus, poly(methylhydrosiloxane) **4** (containing 30−35 Si−H units) was treated with acetic acid in the presence of 1 mol % of $Pd(OAc)_2$ in benzene. The reaction went smoothly at 70 °C to give poly(acetoxymethylsiloxane) **P1** in 90% yield.

Scheme 3: Synthesis of Polysilyl Esters



Remarkably, even in the case of polymeric systems, we were able to monitor reaction progress by ^{29}Si NMR. The ^{29}Si NMR data clearly showed the disappearance of Si−H bonds at around −35 ppm and new multiple signals for acetate-substituted siloxane units centered at −58.6 ppm. The terminal $OSiMe_3$ groups are observed as one signal at 11.7 ppm. Complete substitution of Si-H groups to acetoxy groups was further confirmed by IR analysis (disappearance of the Si-H band at 2166 cm^{-1}). Similar results were obtained from reactions with benzoic acid and diethylphosphonoacetic acid to furnish the corresponding substituted polymers **P2** and **P3** in good yields (Scheme 3).

Interestingly, in all cases, the black solid catalyst left after removal of the product from reaction mixtures is recyclable with only a slight decrease in the reaction rate. For example, benzoic acid reacts with siloxane **1** at 70 °C to yield the corresponding ester in 6 h (entry 3, Table 1). After removal of the product, recharging the reaction vessel with starting materials led to 100% conversion to the same product in 30 h at 70 °C. This experiment led us to examine the catalytic activity of Pd-metal on carbon. We found that replacing $Pd(OAc)_2$ with Pd/C and using the same reaction conditions, treatment of triethylsilane or 1,1,1,3,5,5,5-heptamethyltrisiloxane **1** with acetic acid, led to the formation of the corresponding silyl esters in 60−65% yield. However, the Pd/C catalyst was not effective for the polymer **4**.

In conclusion, we have demonstrated that palladium acetate is an efficient catalyst for the high-yield synthesis of siloxy and polysiloxy esters under mild conditions. The catalyst can be recycled and is easily accessible. Thus, it offers significant advantages over $[Ph_3PCuH]$ which requires a multiple-step synthesis and is difficult to obtain in high purity.[15]

Acknowledgment. Financial support of the Air Force Office of Scientific Research through Grant F49620-99-1-0283 and the National Science Foundation through Grant 9874802 is gratefully acknowledged.

OL005507T

---

was removed by syringe and passed through a small silica gel column (eluent: benzene) under nitrogen to remove traces of the catalyst. 3-Acetoxy-1,1,1,3,5,5,5-heptamethyltrisiloxane (3.27 g, 78%) was obtained by evaporating the solvent under vacuum.

(14) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Reed Educational and Professional Publishing Ltd: 1996.

(15) Brestensky, D. M.; Huseland, D. E.; McGettigan, C.; Stryker, J. M. *Tetrahedron Lett.* **1988**, *29*, 3749.