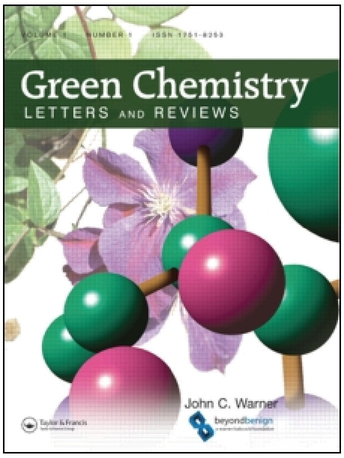


Green Chemistry Letters and Reviews
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t748292817

A greener organic chemistry experiment: reduction of citronellal to citronellol using poly(methylhydro)siloxane

Kathryn E. O'Brien[a]; Denyce K. Wicht[a]
[a] Department of Chemistry and Biochemistry, Suffolk University, Boston, MA, USA

To cite this Article O'Brien, Kathryn E. and Wicht, Denyce K.(2008) 'A greener organic chemistry experiment: reduction of citronellal to citronellol using poly(methylhydro)siloxane', Green Chemistry Letters and Reviews, 1: 3, 149 — 154

To link to this Article: DOI: 10.1080/17518250802512475

URL: http://dx.doi.org/10.1080/17518250802512475

Green Chemistry Letters and Reviews
Vol. 1, No. 3, September 2008, 149–154

Taylor & Francis
Taylor & Francis Group

ORIGINAL ARTICLE

A greener organic chemistry experiment: reduction of citronellal to citronellol using poly(methylhydro)siloxane

Kathryn E. O'Brien and Denyce K. Wicht*

Department of Chemistry and Biochemistry, Suffolk University, Boston, MA, USA

(Received 29 August 2008; final version received 29 September)

An undergraduate organic chemistry experiment based on literature reports in which the aldehyde functionality of citronellal is reduced to the primary alcohol is reported. The reducing agent, poly(methylhydro)siloxane (PMHS), is activated via a catalytic amount of fluoride. This polymeric reducing agent can be introduced as a safer, and thus, greener, alternative to sodium borohydride in the undergraduate laboratory setting, as PMHS is stable to air and water. The execution of this experiment requires standard organic chemistry techniques and the reduced substrate is analyzed via IR spectroscopy.

Keywords: reduction of aldehydes; poly(methylhydro)siloxane; PMHS; undergraduate organic laboratory curriculum; IR spectroscopy

Introduction

Recently, there have been significant efforts to develop college-level organic chemistry laboratory experiments that provide a context within which the laboratory instructor can introduce the theory and practice of green chemistry (*1*). To this end, efforts have been made to either modify traditional organic chemistry experiments or to develop entirely new experiments that illustrate specific green chemistry concepts, yet still teach students about organic chemistry reaction mechanisms and techniques (*2*). This article aims to add to this collective knowledge by describing a reported reduction reaction that has been adapted for the organic chemistry laboratory curriculum. Specifically, we report a laboratory experiment in which citronellal is reduced to citronellol using poly(methylhydro)siloxane (PMHS) and a catalytic amount of fluoride (*3*). To the best of our knowledge, this is the first adaptation of reported reduction chemistry involving PMHS and catalytic fluoride that has been designed specifically for pedagogical purposes.

Reduction chemistry is an important aspect of chemical transformations; in general terms, it allows a chemist to reduce the oxygen, nitrogen or halogen content and/or increase the hydrogen content of organic molecules (*4*). This particular topic is often introduced in the second semester of organic chemistry lecture, but effectively illustrating this chemistry in the laboratory is somewhat more difficult. One of the strongest reducing agents is lithium aluminum hydride ($LiAlH_4$); however, the high reactivity of this compound precludes its use in the undergraduate laboratory setting. A less reactive reducing agent is sodium borohydride ($NaBH_4$) and, accordingly, a number of organic chemistry experiments appropriate for the undergraduate laboratory using this reductant have been developed (*5*), although there are some hazards associated with the use of this reagent.[1]

PMHS, a silicone-based polymer which is a non-viscous, clear, colorless liquid at room temperature, has been demonstrated to be an effective reducing agent in organic transformations (Figure 1) (*6*). The use of this material in the laboratory is particularly attractive because it is stable to air and moisture, making it safe to store in the chemical stockroom and easy to weigh out on a top-loading balance on the bench top.[2] Furthermore, it is readily commercially available and inexpensive.[3]

The fluoride activated uses of PMHS that have been described in the literature are the most amenable for undergraduate laboratory adaptation due to the fact that fluoride catalytically produces the hydride species that affects the reduction transformation (*6*, *7*). The addition of the PMHS, and thus the activation of the hydride species, is carefully controlled via standard organic chemistry techniques. In addition to giving students first-hand experience in the practice of

---

*Corresponding author. Email: dwicht@suffolk.edu

ISSN 1751-8253 print/ISSN 1751-7192 online

DOI: 10.1080/17518250802512475
http://www.informaworld.com

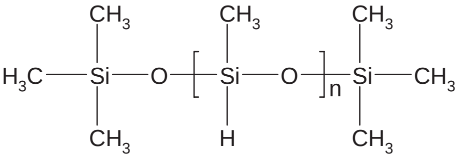


Figure 1. The structure of poly(methylhydro)siloxane (PMHS).

a reduction reaction, this experiment also provides the context within which the topic of polymers can be introduced, due to the polymeric nature of PMHS.

Green chemistry educational objectives

The goal of the project was to develop a specific experimental protocol that would be appropriate and economically feasible for educators to adopt as a part of the standard undergraduate green organic chemistry laboratory curriculum. The green chemistry concept that is clearly illustrated is the use of the safe, non-hazardous reagent PMHS in place of $LiAlH_4$ or $NaBH_4$. This hydride source is safer than either $LiAlH_4$ or $NaBH_4$ because the hydride activation is controlled via the addition of a catalytic source of fluoride.

Our choice of substrate was racemic citronellal (3,7-dimethyl-6-octenal), a non-toxic (*8*) natural product that can be derived from terpene feedstocks (*9*). Citronellal and citronellol are naturally occurring monoterpenes and have been found to be two of many of the chemical components in citronella oil, an essential oil used in personal care products and insect-repelling products (*10*). They instill a lemony scent to the products in which they are used and it is likely that students will be familiar with their use in citronella candles. The chemical reaction in which citronellal is converted to citronellol is shown in Scheme 1.

Mechanism

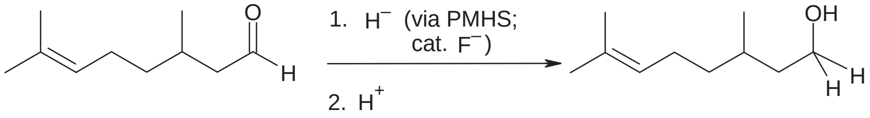
The mechanism for this reaction has been proposed (Scheme 2) (*7*). Presumably, the fluoride anion nucleophilicly activates a silicon atom of the PMHS polymer, forming a pentacoordinate silicate species, intermediate **A** (*11*). Transfer of the hydride to the carbonyl carbon forms a silyl ether (**B**) and the 1,3 intermolecular transfer of the fluoride nucleophile from the silicate to a silicon atom makes this reaction catalytic in fluoride.[4] The polymeric silyl ether remains intact until base-promoted methanolysis yields the alcohol product (**C**) and the polymeric silyl ether species (**D**). As the solvent is removed from the reaction mixture, the polymeric silyl ether **D** hydrolyzes in the presence of atmospheric moisture to give a polymeric silanol, which readily condenses with another silanol species to give an insoluble gel-like siloxane material (Scheme 3). The product can be extracted with an organic solvent and the insoluble by-product can be separated from the reaction mixture via filtration.

Experimental procedure

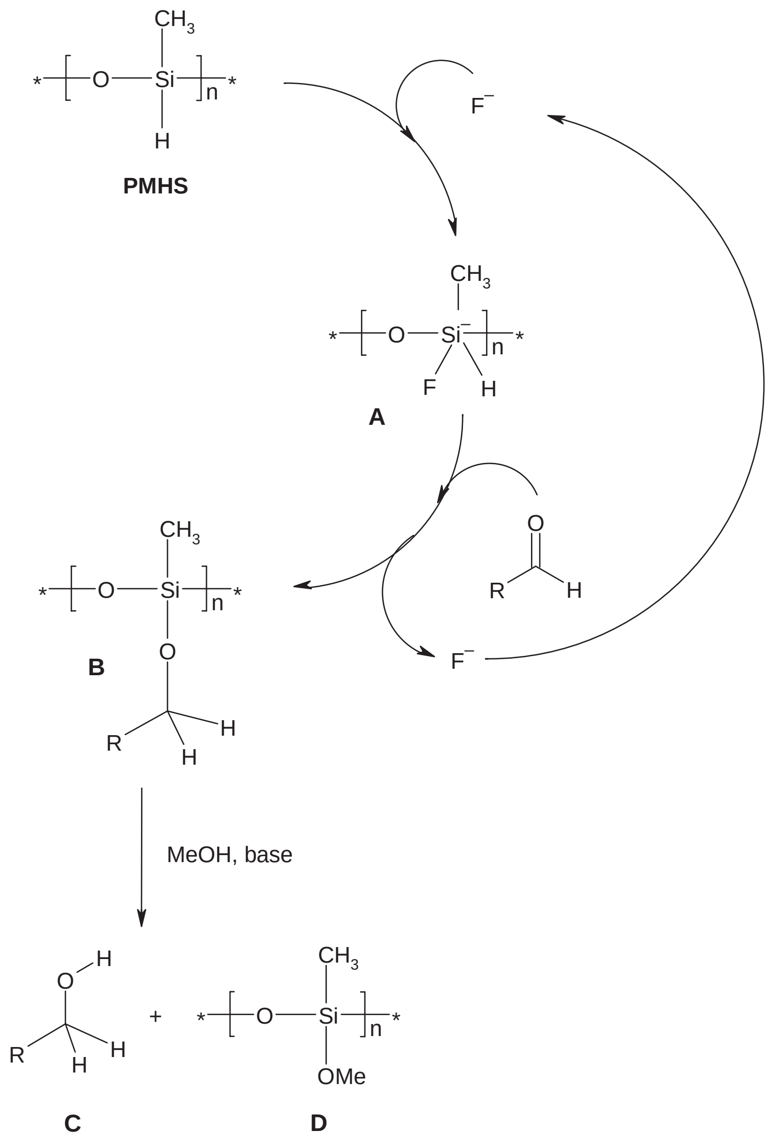
All reagents and solvents were purchased from commercial suppliers and used without further purification. The ^{1}H and ^{13}C NMR (nuclear magnetic resonance) spectroscopy data reported below were obtained using a 60 MHz Anastazi Fourier-transform nuclear magnetic resonance (FT NMR) spectrometer. The chemical shifts are reported in ppm (δ) downfield of tetramethylsilane (TMS). The IR (infrared) spectroscopy data reported below were obtained using a Perkin Elmer 1600 series IR spectrophotometer; all spectra were obtained from neat samples (NaCl plates). The typical two-week experimental procedure that the students are instructed to carry out in the lab is as follows.

Preparation of citronellol

Citronellal (1.0 g, 6.5 mmol), tetrabutyl ammonium fluoride (TBAF) (150 μL of a 1M solution in tetrahydrofuran (THF), 2 mol%), and THF (5 mL) were added to a 50 mL r.b. flask with a magnetic stir bar. The flask was fitted with a Claisen adapter and a separatory funnel. The reaction mixture was cooled with stirring in an ice bath. The separatory funnel was charged with PMHS (0.53 g of polymer with a reported hydride content of 1.59% by weight, 8.4 mmol of hydride, 1.3 mol equiv.) and THF (5 mL). The PMHS solution was added dropwise over a period of 15 min., during which time a mild effervescence was observed. If significant gelling of the silicone polymer was observed in the reaction mixture, the gel-like material was dissipated with vigorous stirring. The reaction mixture was allowed



Scheme 1. The reduction of citronellal to citronellol using poly(methylhydro)siloxane and a catalytic amount of fluoride.

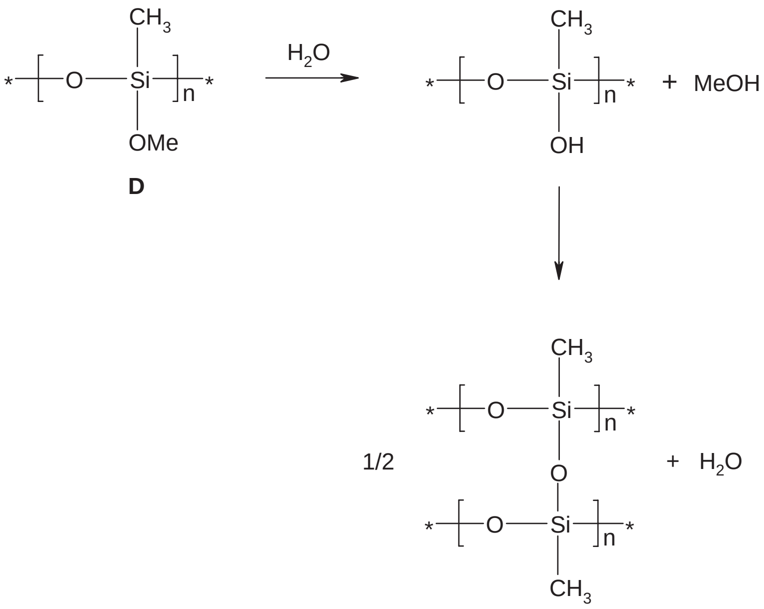


Scheme 2. The proposed mechanism for the reduction of an aldehyde to a primary alcohol with PMHS and a catalytic amount of fluoride.

to warm to room temperature and stirred until the reaction was complete as evidenced by the disappearance of citronellal via thin layer chromatography (TLC) (silica gel, eluted with 4:1 hexanes/ethyl acetate, visualized with iodine). Unreacted PMHS and the polymeric silyl ether have an approximate R_f value of 0.93 under these conditions; the R_f of the starting material is 0.81. Finely ground NaOH (0.1 g, 2.5 mmol) was dissolved in methanol (5 mL) and carefully added dropwise to the reaction mixture. The reaction mixture was heated at reflux for 30 min. to consume any unreacted Si–H species and promote the methanolysis of the silyl ether. The solvent was removed by simple distillation until the siloxane residue thickened and eventually gelled. The gelled siloxane was broken up with a spatula and stored in the reaction flask for a week at room temperature. The solid siloxane material was swelled in 10 mL pentane, filtered, and washed with an additional 10 mL pentane. The collected filtrate was dried over $MgSO_4$, filtered, and the organic solvent was removed on a rotary evaporator to give 0.61 g (60%) of crude citronellol.

Characterization of citronellol

The crude product was characterized by ^1H NMR ($CDCl_3$), ^{13}C NMR (neat), and IR (neat, NaCl) spectroscopy. ^1H NMR (δ): 5.1 (t, 1H, $J_{HH} = 6.5$ Hz, $(Me)_2C{=}CH$), 4.7 (s, 1H, OH), 3.6 (t, 2H, CH_2OH), 1.9 (m, 2H, $(Me)_2C{=}CHCH_2$), 1.6 (s,



Scheme 3. The hydrolysis of a silyl ether in the presence of adventitious water followed by the condensation of two silanol functional groups to give an insoluble silicone-based species.

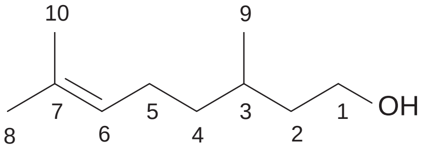


Figure 2. The structure of citronellol with carbons denoted for reference to assigned ^{13}C NMR chemical shifts.

3H, *trans* $(\mathit{Me})_2\mathrm{C}=\mathrm{CH}$), 1.5 (s, 3H, *cis* $(\mathit{Me})_2\mathrm{C}=\mathrm{CH}$), 1.5–1.1 (overlapping m, 5H, $\mathrm{C}\mathit{H_2}\mathrm{C}\mathit{H}(\mathrm{Me})\mathrm{C}\mathit{H_2}$), 0.9 (d, 3H, $J_{HH}=5$ Hz, $\mathrm{CH}(\mathit{Me})$). ^{13}C NMR (δ) (Figure 2): 130.4 (C7, $(\mathrm{Me})_2\mathit{C}=\mathrm{CH}$), 125.3 (C6, $(\mathrm{Me})_2\mathrm{C}=\mathit{C}\mathrm{H}$), 60.3 (C1, $\mathit{C}\mathrm{H_2OH}$), 40.2 (C2, $\mathit{C}\mathrm{H_2CH_2OH}$), 37.7 (C4, $=\mathrm{CHCH_2}\mathit{C}\mathrm{H_2}$), 29.6 (C3, $\mathit{C}\mathrm{H(Me)}$), 25.8 (C5 and C8, $=\mathrm{CH}\mathit{C}\mathrm{H_2}$ and *trans* $(\mathit{Me})_2\mathrm{C}=\mathrm{CH}$), 19.8 (C9, $\mathrm{CH}(\mathit{Me})$), 17.5 (C10, *cis* $(\mathit{Me})_2\mathrm{C}=\mathrm{CH}$). IR ($\mathrm{cm}^{-1}$): 3332 (broad, O–H), 2962, 2925, 2871, 1452, 1377, 1270, 1119, 1058, 1012.

Discussion

The reduction of citronellal to citronellol using PMHS as the reducing agent and TBAF as the source of the catalytic nucleophile has been reported (*3b*). We have modified the reported procedure slightly in order to ensure that students can execute the experiment and isolate and analyze (IR spectroscopy) the product in two consecutive laboratory periods. The original paper reports the use of TBAF in THF to activate the hydride species of PMHS, followed by a potassium fluoride promoted silyl ether cleavage that occurs with vigorous stirring over four hours at room temperature. We have modified the work-up and isolation slightly to avoid the use of a stoichiometric amount of fluoride. A sub-stoichiometric amount of sodium hydroxide is dissolved in methanol and this solution is added directly to the reaction mixture to consume any unreacted Si–H species and promote the methanolysis of the silyl ether. The solvent is removed from the reaction mixture via simple distillation and the by-product solidifies as the siloxane concentration increases in the distilling flask. The solid siloxane residue is swelled in organic solvent to extract the citronellol product, the siloxane material is filtered, and the crude liquid product is isolated after removal of the solvent from the filtrate via rotary evaporation.

Students that executed this experiment in a second semester organic laboratory course successfully characterized the crude product by IR spectroscopy and compared the IR data to that of the starting aldehyde and PMHS. Most simply, by identifying the carbonyl stretch at 1727 cm^{-1} in the IR spectrum of citronellal and noting the absence of this absorption in the IR spectrum of their product, coupled with the appearance of the characteristic O–H absorption at 3332 cm^{-1}, students were able to provide evidence for the reduction reaction.

The use of PMHS as the reducing agent allows students to collect additional analytical data on the reagent used in this experiment that might not be possible with an inorganic-based reducing agent like $NaBH_4$. For example, some students correctly identified the Si–H stretch in the IR spectrum of PMHS at 2168 cm^{-1} and pointed out that formation of the gelled siloxane material is consistent with the transfer of the hydride to the carbonyl carbon of citronellal. In addition, some instructors may encourage students to compare the frequency of the Si–H absorption (2168 cm^{-1}) to the C–H absorption (2967 cm^{-1}) in the IR spectrum of PMHS and rationalize the significant frequency shift based on the relationship between frequency and mass as defined by Hooke's law.

For students that have already been introduced to NMR techniques in the laboratory, the ^1H and ^{13}C NMR spectra of the crude product and citronellal can also be obtained and together used to provide additional analytical evidence for a successful reduction reaction. The resonance for the aldehydic proton in ^1H NMR spectrum of citronellal ($\sim$10 ppm) can be compared to the signal for the aliphatic protons bonded to the carbon of the alcohol functionality in the crude product (3.6 ppm, triplet, $J_{HH} = \sim 6$ Hz). For more advanced students, DEPT (distortionless enhancement by polarization transfer) experiments can be used to identify the methyl, methylene, and methine carbons in both citronellal and the crude product. Importantly, there are three CH_2 carbons in citronellal observed at 50, 37, and 25 ppm in the DEPT(135) experiment, while there are four CH_2 carbons in citronellol observed at 60, 40, 38, and 25 ppm in the DEPT(135) experiment (*12*). Given that in both ^{13}C NMR spectra of citronellal and citronellol the signals for a methyl carbon and a methylene carbon resonate at the same chemical shift (25 ppm), it might be difficult for students to interpret the standard proton-decoupled ^{13}C spectrum of each compound, *a priori*. These overlapping signals only become apparent as the result of the DEPT experiments for each compound.

Conclusion

This experiment demonstrates that PMHS and a catalytic amount of fluoride can be used as an effective reducing agent in the undergraduate organic laboratory setting. Specifically, students convert the aldehyde functionality of citronellal to the primary alcohol, yielding citronellol and analyze the product by IR spectroscopy. The use of the non-hazardous reducing agent PMHS, coupled with the natural product substrate make this an attractive experiment to use as part of a green organic chemistry laboratory curriculum. The use of this experiment can facilitate green chemistry discussions around alternative reagents and alternative feedstocks. Additionally, because the hydride functionality of PMHS is activated via a catalytic amount of fluoride, discussions around inherently safer chemistry for accident prevention can be introduced by comparing this mode of reactivity to that of $LiAlH_4$ or $NaBH_4$.

We plan to continue to explore and improve this experiment. While the use of PMHS as a reducing agent is safer, we recognize that green chemistry implementation is a gradual and iterative approach toward the goal of truly benign chemistry and chemical processes. We feel that the pedagogical value of this experiment is important within the context of available laboratory experiments that illustrate reduction chemistry and, thus, the experiment as it has been successfully taught is reported here. Nonetheless, we hope to improve upon the current iteration of this laboratory exercise. We are exploring the use of other compounds that will promote the hydride activation and are less toxic.

Acknowledgements

This work was supported in part by a Summer Stipend Award granted by the College of Arts and Sciences Faculty Development Committee at Suffolk University. The authors would like to thank the students and faculty involved in the Organic Chemistry Laboratory courses taught spring 2007 at Suffolk University for their valuable contributions to this work.

Notes

1. The MSDS of sodium borohydride indicates that the solid is stable, however water, acid, or high temperature can liberate flammable hydrogen gas. In addition, it causes eye and skin burns.
2. The MSDS of poly(methylhydro)siloxane indicates that the polymer is stable under normal temperatures and pressures. It may cause skin and eye irritation.
3. Poly(methylhydro)siloxane (average M_n 1700–3200) was purchased from Sigma-Aldrich for $32.90 for 250 grams while reagent grade $NaBH_4$ is available for $52.70 for 100 grams. (May 2008.)
4. The 1,3-intermolecular fluoride transfer has been termed "zipper" catalysis by Drew and Lawrence et al., see references (*6*) and (*7*).

References

(1) (a) Kirchhoff, M.; Ryan, M.A., Eds.; *Greener Approaches to Undergraduate Chemistry Experiments*; American Chemical Society: Washington, DC, 2002; (b) Doxsee, K.M., Hutchinson, J.E. *Green Organic Chemistry: Strategies, Tools, and Laboratory Experiments*; Brooks/Cole: Pacific Grove, CA, 2004; (c) The Green Education Materials (GEMS) for Chemists Database. http://greenchem.uoregon.edu/gems.html (accessed May 2008).

(2) Some examples of recently published green organic chemistry experiments: (a) Nguyen, K.C.; Weizman, H. *J. Chem. Ed.* **2007,** *84,* 119–121; (b) Sereda, G.A.; Rajpara, V.B. *J. Chem. Ed.* **2007,** *84,* 692–693; (c) Gandhari, R.; Maddukuri, P.P.; Vinod, T.K. *J. Chem. Ed.* **2007,** *84,* 852–854.

(3) The reduction of citronellal to citronellol with poly(methylhydro)siloxane has been reported: (a) Chuit, C.; Corriu, R.J.P.; Perz, R.; Reye, C. *Synthesis* **1982,** 981–984; (b) Kobayashi, Y.; Takahisa, E.; Nakano, M.; Watatani, K. *Tetrahedron* **1997,** *53,* 1627–1634.

(4) Smith, M.B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure,* 5th ed.; John Wiley and Sons: New York, NY, 2001; pp. 1506–1507.

(5) (a) Baru, A.R.; Mohan, R.S. *J. Chem. Ed.* **2005,** *82,* 1674–1675; (b) White, L.L.; Kittredge, K.W. *J. Chem. Ed.* **2005,** *82,* 1055–1056; (c) Pohl, N.; Clague, A.; Schwarz, K. *J. Chem. Ed.* **2002,** *79,* 727–728; (d) Simek, J.W.; Tuck, T.; Bush, K.C. *J. Chem. Ed.* **1997,** *74,* 107–108.

(6) Lawrence, N.J.; Drew, M.D.; Bushell, S.M. *J. Chem. Soc., Perkin Trans. 1* **1999,** 3381–3391.

(7) Drew, M.D.; Lawrence, N.J.; Fontaine, D.; Sehkri, L; Bowles, S.A.; Watson, W. *Synlett* **1997**, 989–991.

(8) Gomes-Carneiro, M.R.; Felzenszwalb, I.; Paumgartten, F.J.R. *Mutation Res.* **1998,** *416,* 129–136.

(9) Swift, K.A.D. *Top. Catal.* **2004,** *27,* 143–154.

(10) Ritter, S. *Chem. and Eng. News.* **2006,** *84,* 42.

(11) Corriu, R.J.P.; Guerin, C.; Henner, B.J.L.; Wang, Q. *Organometallics* **1991,** *10,* 3574–3581.

(12) Bohlmann, F.; Zeisberg, R.; Klein, E. *Org. Magn. Reson.* **1975,** *7,* 426–432.