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Article

Aluminumoxyhydride: Improved Synthesis and Application as a Selective Reducing Agent

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Aluminumoxyhydride (HAlO) has been obtained by the reaction of aluminum hydride with the siloxane $(Me_2HSi)_2O$ or the stannoxane $(Bu_3Sn)_2O$ as an amorphous colorless insoluble powder. The highest-purity product resulted from the reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2HSi)_2O$. However, HAlO suspensions in tetrahydrofuran (THF) of sufficient quality for synthetic applications can be prepared from commercially available reagents with only minor precautions. A $LiAlH_4$ solution in THF was treated successively with Me_3SiCl and $(Me_2HSi)_2O$, followed by heating at 60 °C for 20 h. The resulting suspensions are 0.4–0.5 M in active hydride content and selectively reduce aldehydes and ketones to the respective alcohols in the presence of any other common nonprotic functional group.

Introduction

During the past 2 decades nonhydrolytic sol−gel procedures have become an important addition to the toolbox for the generation of metal oxides.[1,2] Some of the advantages include low reaction temperatures, homogeneous reaction mixtures, high surface area, and often very low hydroxyl contents. In this context, we have investigated dehydrosilylation as a route to high-surface-area aluminas.[3,4] Interestingly, the reaction between aluminum hydride and various methylsiloxanes did not go to completion but afforded the novel reactive solid aluminumoxyhydride (HAlO). This compound, which we have obtained as a nanosized amorphous solid, was found to be a mild reducing agent for cyclohexenone and Me_3SiCl.[3] Thin films of HAlO have also been generated by thermal decomposition of $(t\text{-BuOAlH}_2)_2$ on a metal surface in a chemical vapor deposition cold-wall reactor.[5] When a preliminary screening indicated that our nanosized HAlO might be very selective and tolerant to most nonprotic functional groups, we systematically investigated its reactivity. Here, we report the results of this study, discuss a variety of synthetic approaches to HAlO, and present a simple procedure for the synthesis of HAlO using readily available precursor chemicals.

Experimental Section

General Procedures. All work was performed under anaerobic and anhydrous conditions by using either modified Schlenk techniques or an Innovative Technologies or a Vacuum Atmospheres drybox. Solvents were freshly distilled under N_2 from sodium, potassium, sodium/potassium alloy, or calcium hydride and degassed twice prior to use or dispensed from an MBraun Solvent Purifier. Solid $LiAlH_4$, tetrahydrofuran (THF), or toluene solutions of $LiAlH_4$, Me_3SiCl, $(Me_2HSi)_2O$, $(n\text{-Bu}_3Sn)_2O$, $Me_2N(CH_2)_{11}CH_3$, and most organic substrates were obtained from commercial sources and used as received. $(n\text{-Bu}_3Sn)_2O$ was purified by vacuum distillation. $H_3Al{\cdot}NMe_3$[6] and isophorone oxide[7] were prepared according to literature procedures. Hydride contents were determined by hydrolysis of an aliquot with excess water and measurement of the amount of H_2 gas evolved. NMR spectra were recorded on a Varian Mercury 300 MHz, a Varian Unity Plus 400 MHz, a Bruker AMX 360, or a Bruker Avance 400 MHz spectrometer, and ^{1}H

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† Florida Institute of Technology.
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(1) Vioux, P. A. *Chem. Mater.* **1997**, *9*, 2292−2299.
(2) Lafond, V.; Mutin, P. H.; Vioux, A. *J. Mol. Catal. A* **2002**, *182−183*, 81−88.
(3) Fooken, U.; Khan, M. A.; Wehmschulte, R. J. *Inorg. Chem.* **2001**, *40*, 1316−1322.
(4) Liu, S.; Fooken, U.; Burba, C. M.; Eastman, M. A.; Wehmschulte, R. J. *Chem. Mater.* **2003**, *15*, 2803−2808.
(5) Veith, M.; Andres, K.; Faber, S.; Blin, J.; Zimmer, M.; Wolf, Y.; Schnöckel, H.; Köppe, R.; de Masi, R.; Hüfner, S. *Eur. J. Inorg. Chem.* **2003**, 4387−4393.
(6) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141−2144.
(7) Wasson, R. L.; House, H. O. *Org. Synth.* **1963**, *30−39*, 552−553.

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Table 1. Reaction of HAlO with Carboxylic Acid Derivatives, Epoxides, and Nitrobenzene

entry	substrate	g (mmol)	HAlO, mmol/mL	HAlO, mmol	reaction time, h	reaction temp, °C	workup	product	mass, g (% yield)
1	benzoic acid	0.34 (2.8)	0.8	8.0	30	24	acidic	no reaction	
2	benzonitrile	0.41 (3.9)	1.0	7.9	130	60	acidic	no reaction	
3	diethyloxalate	0.35 (2.4)	0.3	5.0	22	60	acidic	no reaction	
4	maleic anhydride	0.14 (1.4)	0.6	5.8	60	60	acidic	no reaction	
5	4-methyl acetanilide	0.56 (3.8)	0.6	5.6	96	60	basic	no reaction	
6	*N*-methylpyrrolidinone	0.49 (4.9)	1.0	9.8	115	60	acidic	no reaction	
7	cyclooctene oxide	0.87 (6.9)	0.7	6.9	182	60	acidic	no reaction	
8	styrene oxide	0.30 (2.5)	0.5	4.9	30	60	acidic	1- and 2-phenylethanol	0.29 (95)
9	isophorone oxide	0.59 (3.8)	0.6	7.5	20	22	neutral	no reaction at epoxide group[a]	
10	nitrobenzene	0.81 (6.6)	1.0	19.6	95	60	basic	no reaction	

[a] For reduction of the keto group, see entry 18 in Table 2.

NMR chemical shift values were determined relative to the residual protons in C_6D_6 or $CDCl_3$ as an internal reference (δ 7.15 or 7.26 ppm). ^{13}C NMR spectra were referenced to the solvent signal (δ 128.0 or 77.0 ppm). IR spectra were recorded in the range 4000−400 cm^{-1} using a Nicolet Nexus 470 or a Nicolet Magna 550 FTIR spectrometer.

Reaction of $H_3Al{\cdot}NMe_3$ with $(Me_2HSi)_2O$ in the Presence of $Me_2N(CH_2)_{11}CH_3$. A solution of $H_3Al{\cdot}NMe_3$ (0.89 g, 9.9 mmol) in benzene (30 mL) was treated with $Me_2N(CH_2)_{11}CH_3$ (2.56 g, 12.0 mmol) and stirred for 30 min at room temperature. After a slight concentration of the solution under reduced pressure, $(Me_2HSi)_2O$ (1.59 g, 11.9 mmol) was added, and the reaction mixture was stirred at room temperature for 24 h. Because no visible change was observed, the clear colorless solution was heated at 60 °C for 16 h, during which time a fine colorless precipitate formed. The solid was collected on a glass frit, washed with hexanes (3 × 50 mL), and dried in vacuo. Yield: 1.15 g. FTIR (mineral oil, CsI plates): ν(Si−H) 2101 (w), ν(Al−H) 1885 (st), δ(Al−H) and ν(Al−O) 800 (vst) cm^{-1}. FTIR (KBr pellet): 2959 (st), 2927 (st), 2856 (m), ν(Si−H) 2114 (w), ν(Al−H) 1894 (st), 1480 (m), 1468 (m), 1261 (m), 1018 (st), 800 (vst) cm^{-1}. The volatile material was distilled off the filtrate, and the remaining clear colorless oil was identified as pure $Me_2N(CH_2)_{11}CH_3$ by ^1H NMR spectroscopy.

Reaction of $H_3Al{\cdot}NMe_3$ with $(n\text{-}Bu_3Sn)_2O$. A solution of $H_3Al{\cdot}NMe_3$ (1.34 g, 15.0 mmol) in benzene (60 mL) was treated dropwise with $(n\text{-}Bu_3Sn)_2O$ (8.94 g, 15.0 mmol) at room temperature. The mixture warmed slightly upon stannoxane addition, and a fine colorless precipitate formed immediately. The mixture was stirred at room temperature for another 16 h. The solid was collected on a glass frit, washed with hexanes (3 × 30 mL), and dried in vacuo. Yield: 1.26 g. Because the ^1H NMR spectrum of a suspension of this solid still showed a significant amount of impurities, mainly $n\text{-}Bu_3SnH$, the solid was stirred in hexanes (50 mL) for 20 h, followed by filtration and drying in vacuo. This purified solid contained only minor amounts of $(n\text{-}Bu_3Sn)_2$ according to ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. FTIR (mineral oil, CsI plates): ν(Al−H) 1885 (st), δ(Al−H) and ν(Al−O) 800 (vst) cm^{-1}. Removal of the solvents from the combined filtrates and washing afforded a colorless liquid (7.60 g), which was identified as a mixture of $n\text{-}Bu_3SnH$ and $(n\text{-}Bu_3Sn)_2$ using ^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectroscopy.[8]

HAlO from $LiAlH_4$. Method A. Me_3SiCl (1.18 mL, 1.08 g, 10.0 mmol) was added via syringe to a solution of $LiAlH_4{\cdot}2THF$ (1.0 M, 10 mL, 10 mmol) in toluene at room temperature to give an immediate formation of a fine colorless solid (LiCl). The solid was allowed to settle, the supernatant liquid was decanted, $(Me_2HSi)_2O$ (1.94 mL, 1.48 g, 11.0 mmol) was added via syringe, and the mixture began to turn cloudy after 30 min. The reaction mixture was stirred overnight to give a colorless suspension. The solid was collected on a glass frit, washed with hexanes (3 × 50 mL), and dried in vacuo. Yield: 0.35 g. FTIR (mineral oil, KBr plates): ν(Si−H) 2110 (m), ν(Al−H) 1900 (st) cm^{-1}. The active hydride content of this solid was determined as 21.6 mmol/g (cf. 22.7 mmol/g for pure HAlO).

Method B. A solution of $LiAlH_4$ (1.0 M, 12 mL) in THF was diluted to 24 mL, and Me_3SiCl (1.53 mL, 1.30 g, 12.0 mmol) was added via syringe at room temperature. After 30 min, $(Me_2HSi)_2O$ (2.50 mL, 1.88 g, 14.0 mmol) was added via syringe, and the mixture began to turn cloudy after 30 min. The reaction mixture was refluxed for 20 h. The active H content of the suspension was determined as 0.42 mmol/mL. The solid was collected on a glass frit, washed with hexanes (2 × 50 mL), and dried in vacuo. Yield: 0.98 g. FTIR (mineral oil, KBr plates): ν(Si−H) 2286 (m), ν(Al−H) 1877 (st) cm^{-1}. The active hydride content of this solid was determined as 7.8 mmol/g.

DAlO from $LiAlD_4$. DAlO was prepared analogously to HAlO starting from a THF solution (15 mL) of $LiAlD_4$ (0.45 M, 6.7 mmol). Yield: 0.50 g. The active hydride content of the suspension was 0.45 mmol/mL and that of the isolated solid 9.2 mmol/g. FTIR (mineral oil, KBr plates): ν(Si−H) 2105 (m), ν(Al−H) 1882 (m), ν(Al−D) 1375 (st) cm^{-1}.

Reaction with Excess Disiloxane. A solution of $LiAlH_4$ (1.0 M, 6 mL) in THF was diluted to 12 mL, and Me_3SiCl (0.77 mL, 0.65 g, 6.0 mmol) was added via syringe at room temperature. After 30 min, $(Me_2HSi)_2O$ (4.4 mL, 3.35 g, 25.0 mmol) was added via syringe, and the mixture began to turn cloudy after 30 min. The reaction mixture was refluxed for 22 h. The active H content of the suspension was determined as 0.18 mmol/mL. The solid was collected on a glass frit, washed with hexanes (2 × 50 mL), and dried in vacuo. Yield: 0.64 g. FTIR (mineral oil, KBr plates): ν(Si−H) 2283 (m), ν(Al−H) 1875 (st) cm^{-1}. The active hydride content of this solid was determined as 1.3 mmol/g.

Reaction of HAlO with Organic Substrates. A solution of a substrate in THF was treated with a measured amount of a freshly prepared HAlO suspension (method B, above), and the resulting mixture was stirred at the desired temperature for 12 h or more. The progress of the reactions was monitored by determination of the hydride content of aliquots of the reaction mixture. The reaction mixtures were quenched with water, the precipitated aluminum salts were dissolved in acid or base, and the organic phase was separated. The aqueous phase was extracted with Et_2O, the combined organic phases were dried with $MgSO_4$, and the solvent was removed under reduced pressure to give the crude products. If needed, the products were purified using standard procedures. The identities of the products were established by ^1H NMR spectroscopy and occasionally mass spectrometry. Details are given in Tables 1 and 2 and

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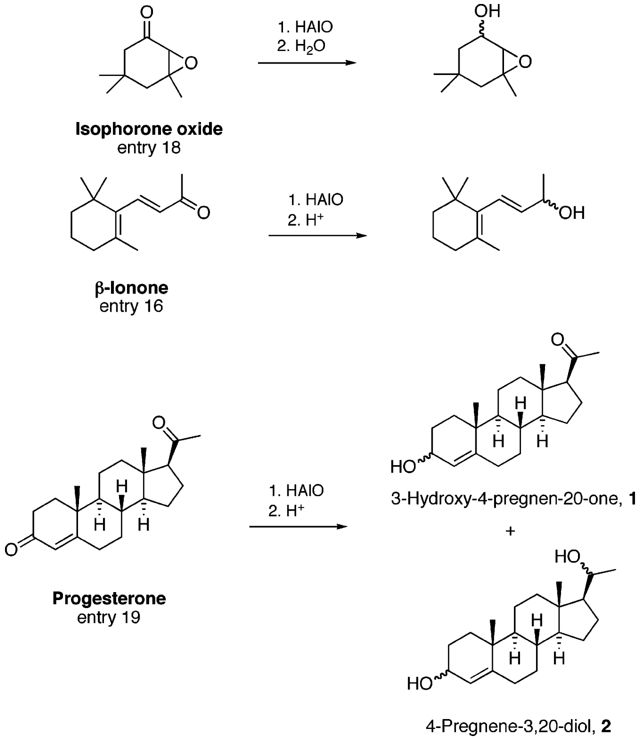
(8) Wrackmeyer, B. *Ann. Rep. NMR Spectrosc.* **1985**, *16*, 73−186.

Table 2. Reaction of HAlO with Aldehydes and Ketones

entry	substrate	g (mmol)	HAlO, mmol/mL	HAlO, mmol	reaction time, h	reaction temp, °C	workup	product	mass, g (% yield)
11	9-anthraldehyde	0.77 (3.8)	0.5	3.8	12	22	acidic	9-anthrol	0.55 (71)
12	cinnamaldehyde	0.40 (3.0)	0.4	6.0	12	25	acidic	cinnamyl alcohol	0.30 (77)
13	hexanal	0.48 (4.8)	0.6	4.8	5	26	acidic	1-hexanol	0.43 (86)
14	benzophenone	0.85 (4.7)	0.9	9.4	24	22	acidic	benzhydrol	0.78 (90)
15	2-heptanone	0.45 (3.9)	0.9	7.8	24	22	acidic	2-heptanol	0.33(71)
16	β-ionone	0.58 (3.0)	0.4	5.0	20	60	basic	β − ionol	0.40 (70)
17	2,4- pentanedione	0.15 (1.50)	0.4	4.5	20	60	basic	2,4-pentanediol	0.11 (71)
18	isophorone oxide	0.59 (3.8)	0.6	7.5	20	22	neutral	see Scheme 1	0.39 (66)
19	progesterone	0.31 (1.0)	0.6	1.2	20	22	acidic	see Scheme 1	[a]

[a] Crude yield: 03.1 g. See the experimental procedure.

Scheme 1. Selected HAlO Reductions



Scheme 1. The reduction of progesterone (entry 19) resulted in the formation of a mixture of seven compounds. A fraction of the mixture was separated by column chromatography, and the two major isomers were identified as 3-hydroxy-4-pregnen-20-one (**1**) and 4-pregnene-3,20-diol (**2**) in an approximate 6:1 ratio. **1**: eluted with 1:1 EtOAc/hexane, $R_f = 0.50$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.63 (s, CH_3, 3H), 1.05 (s, CH_3, 3H), 2.11 (s, CH_3, 3H), 4.14 (m, OHC*H*CH═C, 1H), 5.29 (s, C*H*═C, 1H). MS (DART): $M + H^+$, *m*/*z* 317.2726 (calcd 317.2475 for $C_{21}H_{33}O_2$); $(M + H^+) - H_2O$, *m*/*z* 299.2393 (calcd 299.2375 for $C_{21}H_{33}O_2$). **2**: eluted with 1:1 EtOAc/hexane, $R_f = 0.45$. ^{1}H NMR ($CDCl_3$, 400 MHz): 0.77 (s, CH_3, 3H), 1.05 (s, CH_3, 3H), 1.12 (d, CH_3, 3H), 4.15 (m, OHC*H*CH═C, 1H), 5.25 (s, OHCHC*H*═C, 1H). MS: $(M + H^+) - 2H_2O$, *m*/*z* 283.2434 (calcd 283.2426 for $C_{21}H_{31}$).[9]

Results and Discussion

HAlO Synthesis from Isolated $H_3Al{\cdot}NMe_3$. We have reported previously that the reaction of aluminum hydride $H_3Al{\cdot}NMe_3$ with 1,1,3,3-tetramethyldisiloxane $[(Me_2HSi)_2O]$ in a benzene solution at 60 °C for 20 h gave the most consistent yields of HAlO according to eq 1.[3]

$$H_3Al{\cdot}NMe_3 + (Me_2HSi)_2O \xrightarrow{C_6H_6,\ 60\ ^\circ C,\ 20\ h} HAlO + 2Me_2SiH_2 + NMe_3 \quad (1)$$

Using toluene or THF as the solvent did not significantly alter the appearance or the IR spectrum of the HAlO obtained. Only on one occasion did a toluene suspension become opalescent, suggesting particle sizes close to the wavelength of visible light. Given that soluble small particles generally display a higher reactivity than insoluble aggregates, we attempted to solubilize nanometer-sized particles by coating them with the long-chain aliphatic amine $Me_2N(CH_2)_{11}CH_3$. A solution of $H_3Al{\cdot}NMe_3$ in benzene was treated with 1.2 equiv of $Me_2N(CH_2)_{11}CH_3$, stirred for 30 min, concentrated slightly to remove some NMe_3, and finally treated with $(Me_2HSi)_2O$. However, a fine colorless solid was obtained after 16 h at 60 °C, analogous to the reactions without the long-chain amine. The mass of the solid powder was more than twice the amount expected for HAlO, and according to IR spectroscopy, this increase was due to $Me_2N(CH_2)_{11}CH_3$. The strong and sharp Al−H stretch was observed at its normal position at 1894 cm^{-1} accompanied by a weak Si−H absorption at 2114 cm^{-1}, resulting from residual silane (Me_2SiH_2) or siloxy groups ($-OSiHMe_2$). NMR spectra collected from samples suspended in C_6D_6 showed only hexane signals (used for washing) even after heating to reflux for a couple of minutes, suggesting that the amine is either bound tightly to the surface or encapsulated inside the HAlO particles. The clear and colorless filtrate contained only $Me_2N(CH_2)_{11}CH_3$ after removal of the volatile materials under reduced pressure. There was no indication of soluble amine-coated HAlO particles.

Because the reaction time for the preparation of HAlO with 10−12 h is relatively long, the potential of employing stannoxanes instead of siloxanes was investigated. The Sn−O bond is longer and weaker than the Si−O bond [1.940 Å in $(Me_3Sn)_2O^{10}$ vs 1.626(5) Å in $(Me_3Si)_2O^{11}$ and 276 kJ/mol for Me_3SnOEt^{12} vs 438 kJ/mol for $(Me_3Si)_2O^{12}$], and the compound bis(tributyltin)oxide $(Bu_3Sn)_2O$ is commercially available and air-stable. Furthermore, the presence of covalently bound $-OSnBu_3$ groups on the particle surface could

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(9) D'Incan, E.; Loupy, A.; Restelli, A.; Seyden-Penne, J.; Viout, P. *Tetrahedron* **1982**, *38*, 1755−1759.

(10) Vilkov, L. V.; Tarasenko, N. A. *Zh. Strukt. Khim.* **1969**, *10*, 1102.

(11) Barrow, M. J.; Ebsworth, E. A. V.; Harding, M. M. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2093−2099.

(12) Baldwin, J. C.; Lappert, M. F.; Pedley, J. B.; Poland, J. S. *J. Chem. Soc., Dalton Trans.* **1972**, 1943−1947.

enhance the particle solubility. The reaction of $H_3Al{\cdot}NMe_3$ with $(Bu_3Sn)_2O$ is fast and exothermic. A fine precipitate of HAlO was formed immediately after the stannoxane addition. Further stirring at room temperature did not lead to any obvious changes. Although the stannoxane reaction is significantly faster than the siloxane reaction, a major drawback is the difficulty of removing the byproducts Bu_3SnH and $Bu_3SnSnBu_3$ and occasionally unreacted stannoxane. Because of their high boiling points their removal requires repeated extraction with hexanes or ether. Even after three washings, these compounds can still be detected easily in C_6D_6 suspensions of the powder by ^1H NMR spectroscopy. The distannane $Bu_3SnSnBu_3$ is formed through base-catalyzed (NMe_3) decomposition of Bu_3SnH.[13] It should also be mentioned that an excess of stannoxane did not lead to the formation of Al_2O_3, an indication of the decreased reactivity of HAlO compared to other aluminum hydrides.

HAlO Synthesis from $H_3Al{\cdot}L$ Formed in Situ. The synthesis of crystalline $H_3Al{\cdot}NMe_3$ requires the use of vacuum lines and a drybox. To develop a synthetic procedure for HAlO that can be performed with only minor precautions in practically any synthetic laboratory, we have investigated several methods starting from commercially available $LiAlH_4$ solutions. It has been reported previously that clean and reactive THF solutions of H_3Al can be obtained by the careful addition of 100% sulfuric acid to a $LiAlH_4$ solution in THF.[14,15] Because the thought of adding a strong acid to $LiAlH_4$ may be disconcerting to many chemists, we investigated the potential of Me_3SiCl, which has been applied successfully in the synthesis of primary alanes $RAlH_2$ from the respective alanates $RAlH_3Li$.[16,17] Initial experiments were aimed at the isolation of HAlO and were thus conducted in benzene or ether to separate the LiCl side product. Generally, a suspension of purified $LiAlH_4$ in the presence of 2 equiv of amine was treated with Me_3SiCl at room temperature followed by filtration or decanting to remove the lithium chloride. The resulting $H_3Al{\cdot}NR_3$ solutions were then reacted with the siloxane $(Me_2HSi)_2O$ as described in the previous section to generate HAlO. However, this method suffered from the difficulty to generate suspensions of finely divided $LiAlH_4$, and the resulting HAlO generally was impure and had only relatively low contents of active hydride. Better results were obtained when a 1 M solution of $LiAlH_4{\cdot}2THF$ in toluene was employed. Under these conditions, HAlO was isolated in 95% yield.

For reductions of organic substrates, the presence of LiCl should not be a factor, and HAlO was generated in situ from a THF solution using a typical commercially available 1.0 M THF solution of $LiAlH_4$. Here, the LiCl byproduct is soluble and is eventually precipitated together with HAlO. Hence, the mass of the product isolated from this reaction is approximately twice that from the reactions that used $H_3Al{\cdot}NMe_3$ as the starting material or in which LiCl was separated prior to HAlO formation. In addition, the amount of Si−H groups remaining in this solid is somewhat higher than that in the HAlO obtained from LiCl free samples as shown in the IR spectra. Use of $LiAlD_4$ afforded DAlO with an Al−D stretching frequency with a value of 1375 cm^{-1} close to the value expected for a simple spring model (1330 cm^{-1}). The active hydride content of the suspensions varies depending on the reaction time, with reproducible results obtained after 20 h at 60 °C. Typically, 0.5 M $LiAlH_4$ solutions result in HAlO suspensions with active hydride concentrations of around 0.42−0.44 M, corresponding to a hydride yield of 84−88%. To ensure that there is no soluble hydride content, the solid HAlO/LiCl mixture was allowed to settle and the supernatant was hydrolyzed, yielding no H_2 gas. Prolonged refluxing (2−3 days) does not alter the hydride content. Use of a large excess of $(Me_2HSi)_2O$ eventually leads to the formation of a solid that has a significantly reduced hydride content, but its identity was not investigated in much detail. The IR spectrum of the isolated solid displays a reduced Al−H and an increased Si−H absorption.

Overall, this system has proven to be robust and simple enough for employment in a standard synthetic laboratory, and its reactivity toward 18 different organic substrates was investigated. Suspensions of HAlO were reacted with a variety of nonprotic organic substrates, and the results are listed in Tables 1 and 2 as well as in Scheme 1. HAlO is reactive only toward aldehydes and ketones, which were reduced cleanly to the corresponding alcohols. No reactions were observed with carboxylic acids (after deprotonation), esters, amides, anhydrides, nitriles, nitrobenzene, and epoxides even after prolonged refluxing. Among this group, only styrene oxide was eventually reduced after 30 h at 60 °C. Enolizable ketones were reacted with an extra 1 equiv of HAlO. Unfortunately, the regioselectivity of the HAlO reductions was rather poor. For example, in the reductions of isophorone oxide and styrene oxide, two isomers in close to 1:1 ratios were obtained, and 2,4-pentanediol was isolated as both the meso and racemic isomers in an approximately 1:1 ratio. On the other hand, progesterone was reduced primarily at the conjugated carbonyl function. The crude product consisted of several compounds, which were separated by column chromatography. The two main products, singly reduced 3-hydroxy-4-pregnen-20-one and doubly reduced 4-pregnene-3,20-diol, were found in an approximate 6:1 ratio. Single reduction at the acetyl group was not observed, and the double reduction product is most likely due to the use of a 20% excess of HAlO. Considering that HAlO consists of insoluble particles in the tens of nanometer range, the observed preference may be due to steric reasons. An inspection of progesterone models indicates the conjugated keto group to be more accessible.

Summary

HAlO can be obtained from crystalline $H_3Al{\cdot}NMe_3$ or, more conveniently, through in situ generated $H_3Al{\cdot}THF$ by

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(13) Davies, A. G. *Organotin Chemistry*; Wiley-VCH: Weinheim, Germany, 2004.

(14) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464−1472.

(15) Gorrell, I. B.; Hitchcock, P. B.; Smith, J. D. *Chem. Commun.* **1993**, 189−190.

(16) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694−6702.

(17) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611−5612.

reaction with a slight excess of 1,1,3,3-tetramethyldisiloxane. Through the latter procedure, a suspension of HAlO can be obtained in a straightforward manner in any synthetic laboratory, and its reactivity and selectivity match those of Li(*t*-BuO)$_3$AlH.[18] These HAlO suspensions selectively reduce aldehydes and ketones and are not affected by other nonprotic functional groups.

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(18) March, J. *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.