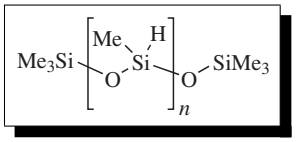
Polymethylhydrosiloxane



[9004-73-3]

InChI = 1/C9H30O4Si5/c1-14(10-15(2)12-17(4,5)6)11-16(3)13-18(7,8)9/h14-16H,1-9H3

InChIKey = INRLRTZQQOALFL-UHFFFAOYAM

(reducing agent often used in conjunction with metal catalysts or nucleophilic activators)

Alternate Names: PMHS; methylhydrogensiloxane polymer; methylhydrosilicone homopolymer; 1,1,1,3,5,7,7,7-octamethyltetrasiloxane (PMHS-dimer) [16066-09-4]; polymethylhydrosiloxane trimethylsilyl terminated [63148-57-2] and [178873-19-3]; and poly(dimethysiloxane-*co*-methylhydrosiloxane) (96% wt methylhydrosiloxane monomer units) [63148-57-2] are sold as 'PMHS'.

Physical Data: colorless free flowing liquid; average molecular weight 1500-2200 g mol^{-1} (supplier dependent); effective mass per hydride of 60 g mol^{-1}; d = 1.006.

Solubility: most ethereal, chlorinated, or hydrocarbon solvents as well as EtOH, i-PrOH, warm DMF, and warm NMP; insoluble in MeOH, DMSO, acetonitrile, and water.

Preparative Methods: hydrolysis of methyldichlorosilane followed by heating (60–150 °C) the resultant mixture of cyclic silanes in the presence of hexamethyldisiloxane generates the linear polysiloxane.[1]

Handling, Storage, and Precautions: stable to air and moisture; incompatible with strong acids, bases, or oxidants (forms hydrogen upon decomposition); generally considered non-toxic, however thorough toxicity studies have not been performed; skin/eye contact and inhalation should be avoided.

General. Polymethylhydrosiloxane (PMHS) is an easily handled, inexpensive, non-toxic, and mild reducing agent. Although relatively inert towards organic functionality, PMHS can transfer its hydride to a variety of metal catalysts (including Sn, Ti, Zn, Cu, and Pd) which can then participate in a wide range of reductions. Alternatively, when made hypercoordinate by the action of fluoride or other nucleophiles, PMHS can act directly as a reducing agent. PMHS is attractive as a substitute for more expensive or hazardous silanes or siloxanes and as the stoichiometric reductant in catalytic organotin-mediated processes. Applications of PMHS in organic synthesis have been detailed in several reviews[2] including an excellent treatise by Professor Nicholas J. Lawrence and co-workers (Cardiff/UMIST).[2a]

Synthesis of Alkyltin Hydrides. Perhaps the most widely recognized use of PMHS is in the synthesis of trialkyltin hydrides. In 1967, Hayashi et al.[3] established the PMHS reduction of organotin oxides (via Si-H/Sn-O σ-bond metathesis) as a preparative route to trialkyl- and dialkyltin hydrides (eq 1). This method obviates the need for highly reactive reducing agents like $LiAlH_4$.[4] The method is also amenable to in situ generation and reaction of organotin reagents,[2a] with the order of reactivity for organotin oxides towards PMHS is $Bu_2Sn(OEt)_2$ > Bu_3SnOEt > $(Bu_3Sn)_2O$ > Bu_2SnO > $(Ph_3Sn)_2O$ > $Bu_3SnOSiBu_3$. Complete conversion of $(Bu_3Sn)_2O$ to two equiv of Bu_3SnH typically requires elevated reaction temperatures (>80 °C), however Fu has shown that adding *n*-BuOH to the reaction mixture facilitates liberation of the second Bu_3SnH.[5]

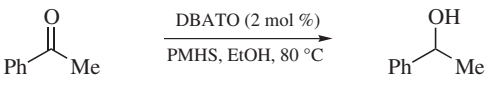
$$(Bu_3Sn)_2O \xrightarrow[\text{neat, }\Delta]{\text{PMHS}} \left[\begin{array}{l} Bu_3SnOSiR_3 \\ + \\ Bu_3SnH \end{array}\right] \xrightarrow[\text{neat, }\Delta]{\text{PMHS}} \underset{87\%}{Bu_3SnH} \quad (1)$$

PMHS alone does not reduce triorganotin halides[6] (or amides[7]) and thus the Hayashi method is not readily applied to the preparation of Me_3SnH or other organotin hydrides for which the corresponding organotin oxides are not commercially available. However, PMHS in combination with a fluoride source can effect the reduction of trialkyltin chlorides, bromides, and fluorides (eq 2).[8] The PMHS/fluoride/R_3Sn–X combination is also applicable to in situ generation and reaction of organotin hydrides.[2a,8,9,10,11]

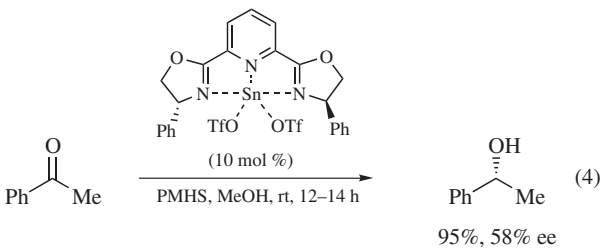
$$Bu_3SnCl \xrightarrow[\text{2.2 equiv. aq KF}]{\text{1.1 equiv. PMHS}} \underset{82\%}{Bu_3SnH} \quad (2)$$
$$\xrightarrow[\text{aq NaOH work-up}]{Et_2O,\ rt}$$

Reductions of C–O Bonds. A wide range of catalytic systems employing PMHS can reduce carbonyl groups. PMHS/$(Bu_3Sn)_2O$ does not efficiently reduce carbonyls, however slow addition of a ketone and PMHS to stoichiometric Bu_2SnO in toluene at 25 °C has been shown to be an efficient way of carrying out such reductions.[12]

Similar reductions can be made catalytic in tin by using dibutyltin dilaurate,[13] bis(dibutylacetoxytin) oxide (DBATO),[14] or polymer-supported organotins.[6] In some cases, these catalytic protocols have proven more successful than their stoichiometric counterparts (eq 3). However, enones suffer from competitive 1,4-reductions. Reductions using a chiral tin catalyst have recently emerged (eq 4), although the observed enantioselectivities are poor to moderate (0-58% ee).[15]



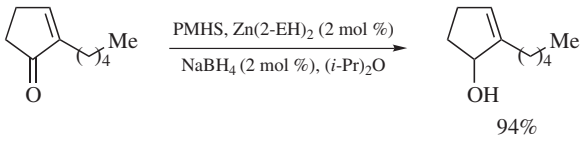
81% (3)



95%, 58% ee (4)

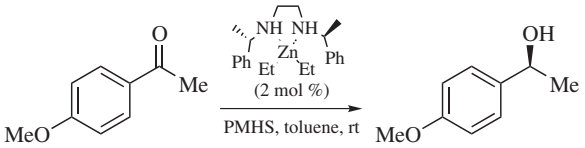
Mimoun et al. has extensively studied zinc catalysts in combination with PMHS. In order to effect the catalytic cycle, a co-catalyst

is necessary, usually $LiAlH_4$ or $NaBH_4$. The optimal [ZnH] combination appears to be 2-5 mol% Zn(2-ethylhexanoate)$_2$ (i.e. Zn(2-EH)$_2$), 2-5 mol% $NaBH_4$, and 1-2 equiv of PMHS.[16] Zinc-catalyst/PMHS allows for 1,2-reduction of saturated or α,β-unsaturated esters, aldehydes, and ketones (eq 5). It should be noted that in contrast to the organotin-mediated chemistry, these reactions initially afford the silyl ether, which is ultimately subjected to a separate hydrolytic work-up.



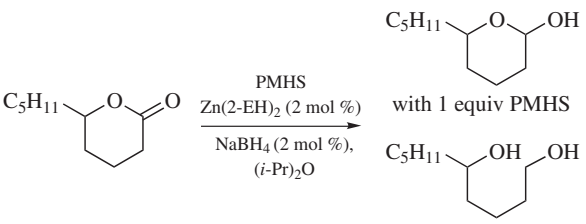
94% (5)

Zinc-mediated PMHS reductions have also been carried out enantioselectively.[17] Aromatic ketones afford alcohols in 64-81% ee (eq 6), while non-aromatic ketones are reduced less selectively (15-20% ee).



76% ee (6)

The zinc catalyst can also reduce lactones to their corresponding lactols or diols by using one or two equiv of PMHS, respectively (eq 7). Terminal primary epoxides are opened to the corresponding secondary alcohols (eq 8), while more substituted epoxides are unaffected. Employing Pd(OAc)$_2$(PPh$_3$)$_2$ or Cu(2-EH)$_2$ can reverse the normal 1,2- over 1,4-selectivity of enone reductions.



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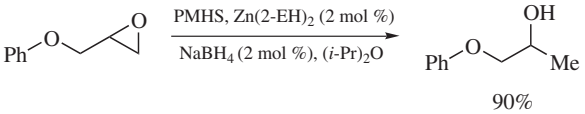
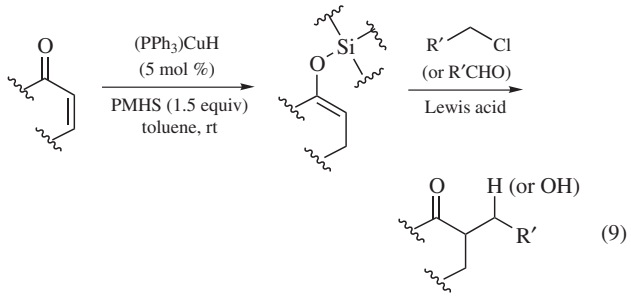


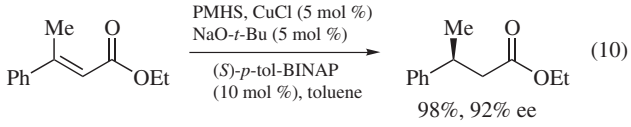
90% (8)

PMHS can also be used in conjunction with other copper catalysts to effect 1,4-reductions.[18] These reductions generate silyl enol ethers, which Lipshutz and co-workers have shown can be exploited in subsequent chemical events such as alkylations or condensations (eq 9). PMHS plus catalytic (PPh$_3$)CuH can also reduce saturated ketones and aldehydes in a 1,2-fashion.[19]



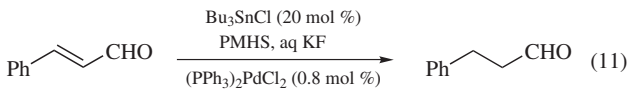
72–89% (9)

Enantioselective 1,4-reductions of conjugated esters with a PMHS, CuCl, BINAP mixture (eq 10) are high yielding and allow asymmetric construction of β-keto stereogenic centers (80-92% ee).[20]



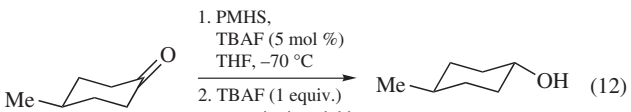
98%, 92% ee (10)

For selective 1,4-reduction of α,β-unsaturated aldehydes PMHS can be used in combination with aq KF, catalytic Pd(0), and 10 mol% Bu_3SnH (eq 11). It is useful to note that no reduction of the α,β-carbonyl compound occurs in absence of the tin halide and that no reduction of the resultant aldehyde was observed.[8]

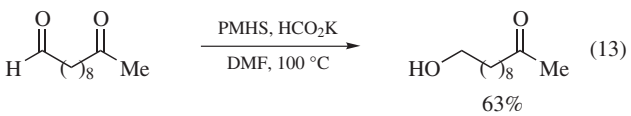


87% (11)

Hypercoordinate silicates formed by reaction of PMHS with KF, TBAF,[21,22] or other nucleophiles,[23] can reduce ketones, aldehydes, and esters (eq 12).[24] With proper nucleophile choice, aldehydes can be reduced selectively over ketones, and ketones over esters (eq 13). Halides, nitriles, nitro groups, and olefins survive these conditions, but enones often undergo both 1,2- and 1,4-reductions. PMHS is worse than other silanes for performing enantioselective reductions with chiral fluoride sources, affording alcohols in only 9–36% ee.[25]



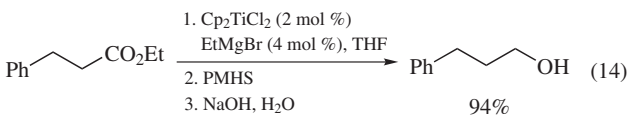
trans/*cis*
91:9 (12)



63% (13)

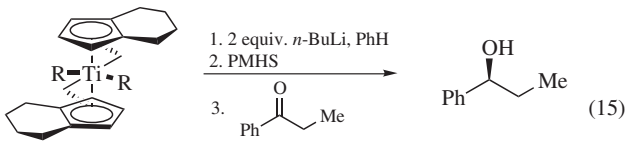
Buchwald and co-workers have developed a number of titanocene-based protocols involving catalytic Cp_2TiCl_2 activated

by EtMgBr or *n*-BuLi. PMHS converts the resultant titanium species into a titanium hydride, which can reduce ketones and esters (eq 14).[26] Conjugate hydride addition is rarely seen with α,β-unsaturated esters, however 4-10% of the 1,4-reduction products has been observed during reductions of enones. Again, it is the silyl ether that is initially formed in these reactions. Employing $Cp_2Ti(p\text{-}C_6H_4O)_2$ or Cp_2TiF_2 as the catalyst allows for the conversion of lactones to lactols.[27] Both Reding[28] and Breeden[29] have also found that Ti(O-*i*-Pr)$_4$ can catalyze the reduction of esters to primary alcohols. Importantly, alkynes, bromides, chlorides, epoxides, and nitro groups are compatible with this chemistry.



(14)

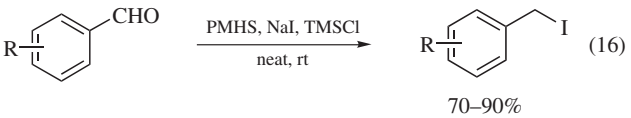
Halterman and co-workers[30] and Buchwald et al.[26b] have used chiral titanocenes to asymmetrically reduce aryl and α,β-unsaturated ketones with relatively high enantioselectivity (82-97% ee) (eq 15). However, electron-withdrawing groups about the aryl ring appear to be problematic, as are saturated ketones.



(15)

R = (*R,R*)-1,1'-binaphthyl-2,2'-diolate

In addition to carbonyl reductions, PMHS can also be used in deoxygenations. For example, PMHS, NaI, and TMSCl will generate benzyl iodides from benzaldehydes (eq 16). Unfortunately this solventless transformation does not work well with ketones or aliphatic aldehydes.[31] Fu and co-workers have shown that PMHS is instrumental in performing Barton-McCombie deoxygenations of thionocarbonates with only catalytic amounts of $(Bu_3Sn)_2O$ (eq 17).[5] Interestingly, dithiocarbonates do not respond uniformly well to similar conditions.[32]



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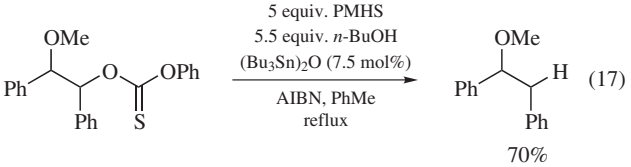
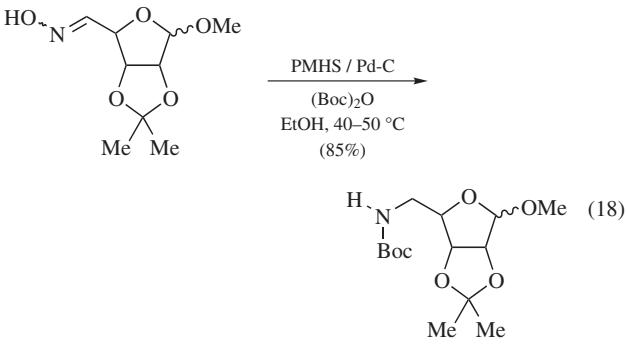


(17)

Reductions of C–N Bonds. An ethanolic mixture of PMHS and Pd/C will reduce oximes (eq 18)[33] to amines and reductively open aziridines (eq 19).[34] Either (a) PMHS plus catalytic *n*-butyltin tris(2-ethylhexanoate) (eq 20)[35] or (b) PMHS plus $ZnCl_2$ reduces imines.[36] The PMHS/DBATO combination reduces azides,[37] while PMHS/Ti(O-*i*-Pr)$_4$ can be applied to reductive aminations (eq 21).[38] Asymmetric imine reductions via chiral titanium complexes and PMHS are also viable, but very substrate dependent with nonaromatic imines working best (69-99% ee vs. 6-97% ee for aromatic imines).[39]



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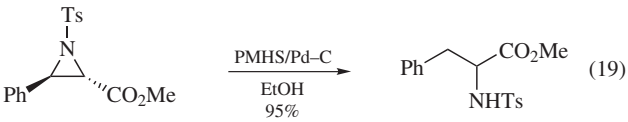

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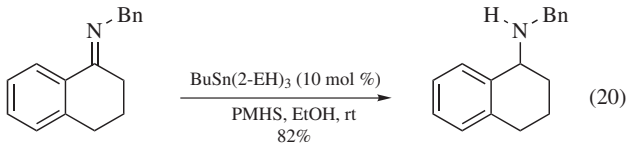

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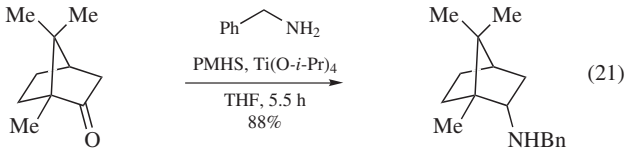
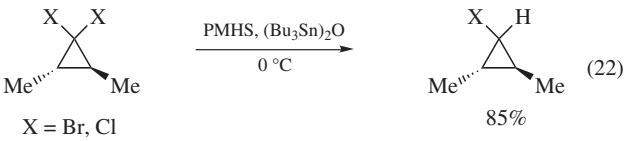


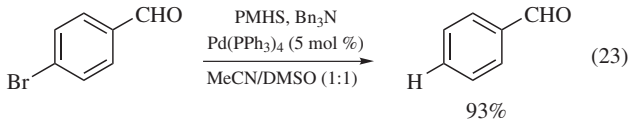
(21)

Reductions of C–X Bonds. Organotin hydrides generated in situ via PMHS reduction of Sn-O or Sn-X precursors easily reduce aromatic and aliphatic halides. These reactions can proceed either thermally or photochemically and have been used successfully to reduce geminal dihalides stepwise (eq 22).[12,40] Since organotin halides are the by-products of these reactions, the PMHS/fluoride/R_3Sn-X combination allows reactions to be carried out with catalytic amounts of tin.[8]



(22)

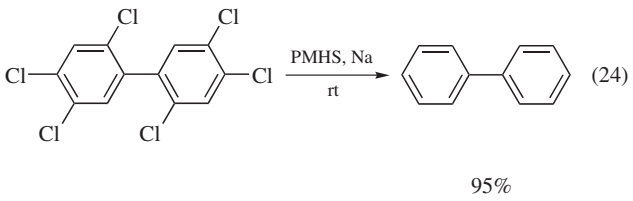
PMHS can be used directly as a hydride donor for the reduction of aryl and vinyl bromides or iodides along with α-halo ketones and acids provided the halide can be activated by Pd(0) (eq 23).[41]



(23)

The PMHS/Sn and PMHS/Pd protocols tolerate a wide range of organic functionality including alcohols, alkenes, carbonyls, and nitro groups, thus complementing $LiEt_3BH$, catalytic hydrogenation, and other means of effecting halide reductions.

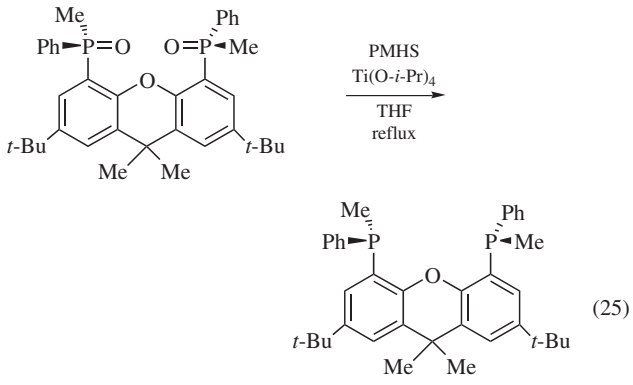
Finally, PMHS with sodium metal can be used to reduce aromatic chlorides (eq 24).[42]



(24)

Reductions of P–O Bonds. Phosphine oxides can be efficiently reduced to phosphines[43] using stoichiometric amounts of $Ti(O\text{-}i\text{-}Pr)_4$ and PMHS at 50 °C (vs. 250 °C without Ti[44]). The reduction proceeds via a *syn* hydrotitanation and goes with retention of configuration when the phosphine oxide is chiral (eq 25).[45] The PMHS/Ti reagent combination has also proven amenable to reaction with polymer supported materials.[46]

Miscellaneous Reductions. Carbon-sulfur bonds have been reduced using PMHS and $(Bu_3Sn)_2O$ with AIBN (eq 26).[47] PMHS can also serve as a substitute for hydrogen in Pd/C catalytic hydrogenations of aromatic nitro groups and various alkenes including those of α,β-unsaturated ketones and esters (eq 27). It is useful to note that electron-rich *trans*-alkenes are not reduced.[14] PMHS and catalytic $Pd(PPh_3)_4$ are superior to standard hydrogenation conditions for the reduction of acyl fluorides to their corresponding aldehydes (eq 28).[48]



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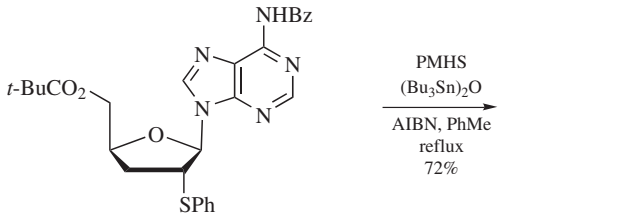

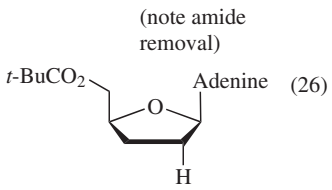

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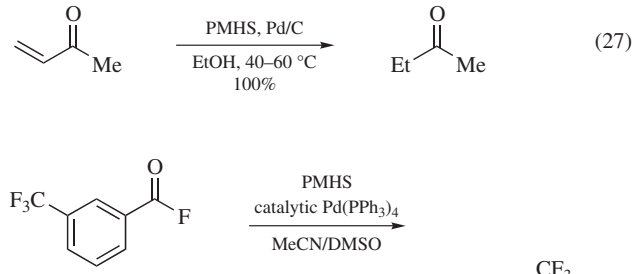

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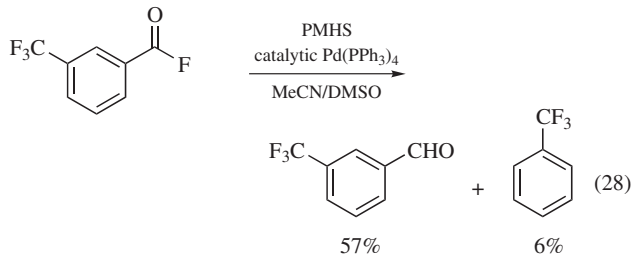
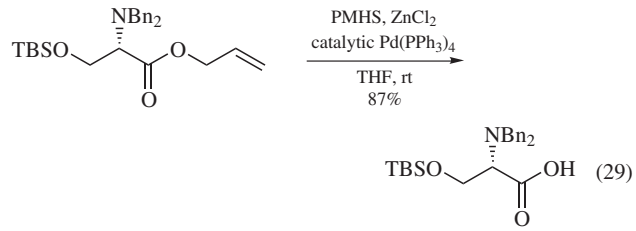


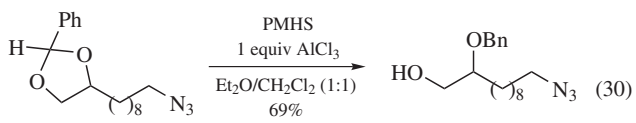
(28)

PMHS has also proven useful in the removal of various protective groups. For example, PMHS and catalytic $Pd(PPh_3)_4$ in the presence of $ZnCl_2$ allow for the selective cleavage of allylic ethers, amines, or esters in the presence of PMB, benzyl, TBS and other ethers (eq 29).[49]



(29)

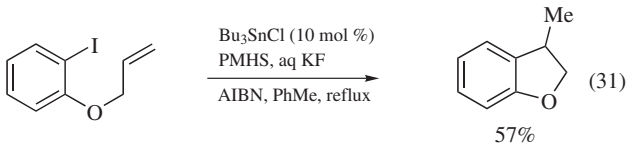
Benzylidenes acetals of 1,2- or 1,3-diols can be opened with PMHS and $AlCl_3$ to generate a mono-benzylated alcohol, where the benzyl group ends up at the most sterically hindered alcohol (eq 30).[50] Azides, esters, and TBS-protected alcohols are among the functional groups that tolerate these conditions.



(30)

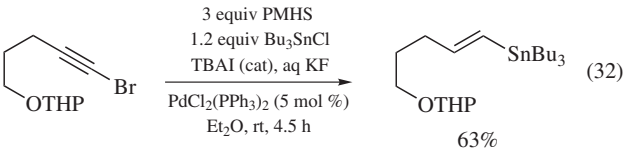
C–C Bond Forming and Related Reactions. In situ generated organotin hydrides can also be used in free radical C-C bond forming reactions. Terstiege and Maleczka have carried out such

reactions with catalytic amounts of tin via their PMHS/fluoride/R_3Sn-X method for generating R_3SnH (eq 31).[8]

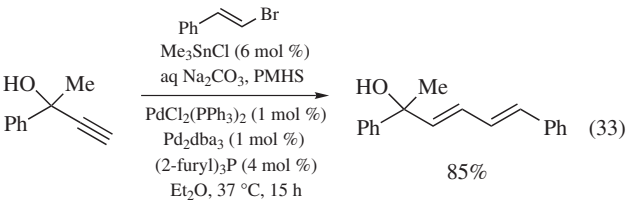


(31)

The same group has also used in situ generated R_3SnH in free radical and palladium-mediated hydrostannations of alkynes (eq 32).[9] This one-pot R_3SnH generation/Pd(0) hydrostannation protocol can also be coupled with an in situ Stille reaction. In such a sequence, PMHS can aid recycling of the tin by-product from the cross coupling, rendering the entire process catalytic in tin (eq 33).[10] Finally, in a testament to the thermal stability of PMHS, the stoichiometric R_3SnH generation/ hydrostannation/ Stille one-pot protocol can be carried out under microwave irradiation.[11]

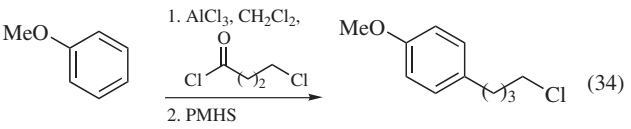


(32)

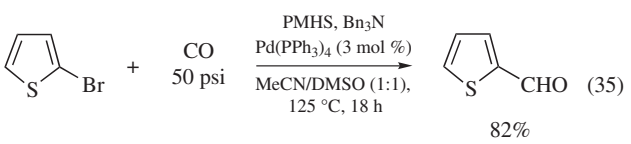


(33)

Several Friedel-Crafts processes have also exploited the reactivity of PMHS (eq 34),[51] and PMHS can serve as a substitute for R_3SnH in Pd(0)-mediated carbonylations (eq 35).[52]



(34)



(35)

Final Notes. The polymeric nature of PMHS can make GC analysis of reaction mixtures difficult, however Lopez et al. found that substituting PMHS-dimer [16066-09-4] for PMHS facilitates such analysis with little effect on reactivity.[5] In terms of purification, the insoluble gels that can form during the reaction or after hydrolytic work-up can clog filter paper and glass frits. It is usually possible to remove this material by passing it over a wide pad of silica gel. Alternatively, we have found that freezing the crude reaction mixture in benzene over night leads to a more granular and filterable PMHS waste product.

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