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Reduction by Tributyltin Hydride of Carbonyl Compounds Adsorbed on Silica Gel: Selective Reduction of Aldehydes

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Recently, we became interested in photochemically initiated reductions of adsorbed organic substrates by tributyltin hydride and were surprised to observe the rapid and efficient reduction of carbonyl groups adsorbed on dried silica gel, *but in the dark.*[2] This note describes investigations of these reactions and reveals the synthetic utility of tributyltin hydride reductions under these conditions.

Tributyltin hydride is one of the more readily available[3] and least reactive organotin hydrides.[4] In the absence of catalysts it will readily reduce strongly electrophilic species such as carbonium ions,[5] isocyanates,[6] isothiocyanates,[6] and carbonyl groups bearing powerful electron-withdrawing functions.[4] It also reacts spontaneously with alkyl iodides and bromides.[4] If radical initiators are present [e.g., ultraviolet light, azobis(isobutyryl)nitrile], then alkyl chlorides, aryl halides, esters, ketones, and other functional groups can also be reduced,[4,8–10] although elevated temperatures are often required. However, we found that in the presence of a cyclohexane slurry of dried silica gel, tributyltin hydride cleanly reduced aldehydes and ketones to give high yields of the corresponding alcohols (Table I). Sulfoxides, nitro groups, esters, arylnitriles, and alkyl, aryl, and benzylic chlorides were not effectively reduced. Attempted reduction of phenyl benzoate gave some phenol, but a blank reaction in the absence of tributyltin hydride gave the same result, indicating that the product arose from silicolysis of the ester on the silica gel. The fact that the silica gel had been activated to remove water and the failure to isolate any benzoic acid suggest that the phenol is displaced from the ester by hydroxyl end groups on the silica gel to give a benzoylated silica. Diphenylmethyl benzoate was also not reduced, and in this case no evidence for ester dissociation was observed.

Attempted reduction of an epoxide, that of *trans*-stilbene, led to the product of acid-catalyzed opening of the epoxide followed by pinacol rearrangement and reduction of the resulting carbonyl group. This was confirmed by a blank reaction where stilbene epoxide was treated with a cyclohexane slurry of dried silica gel; 2,2-diphenylacetaldehyde was isolated as the only major product.

With the exception of strained ketones such as norcamphor, the rate of reduction of carbonyl groups was found to be in the order aldehydes > dialkyl ketones > aralkyl ketones > diaryl ketones (Table I). When equimolar mixtures of aldehydes and ketones were treated with 1 equiv of tributyltin hydride in the presence of silica gel, selective aldehyde reduction was achieved (Table II).

Relatively few reagents are available for the selective reduction of aldehydes in the presence of ketones; tetrabutylammonium cyanoborohydride,[11] lithium aluminum tri-*tert*-butyloxyhydride,[12] sodium triacetoxyborohydride,[13] lithium di-*n*-butyl-9-borabicyclo[3.3.1]nonane,[14] diisopropylcarbinol on alumina,[15] and samarium diiodide[16] are ones which have been reported. Excluding the last of these reagents, a comparison has shown[15] that while all are capable of reducing an aldehyde in the presence of a *methyl* ketone, only diisopropylcarbinol on alumina has the ability to distinguish between a cyclohexanone and an aliphatic aldehyde. Tributyltin hydride in the presence of dried silica gel is superior to these reagents in its selectivity (Table II). Since this work was

Table I. Reduction of Organic Functional Groups by Excess Tributyltin Hydride on Dried Silica Gel at Room Temperature

substrate	product	isolated yield, %	minimum reaction time, h
norcamphor	norborneol (*exo* + *endo*)	$69^{a,b}$	0.5
3-cholestanone	3-cholestanol (α + β)	$89^{a,c}$	2
methyl naphthyl ketone	1-(β-naphthyl)ethanol	$91^{a,d}$	4
benzophenone	diphenylmethanal	94^{a}	6
benzaldehyde	benzyl alcohol	81^{a}	1
octanal	1-octanol	90^{a}	1
nitrobenzene	aniline	$<5^{a,e}$	24
trans-stilbene epoxide	1,2-diphenylethanol	82^{a}	6
phenyl benzoate	phenol	trace^{e}	72
diphenylmethyl benzoate		0^{e}	24
1-chloro-2-phenylethane		0^{e}	48
diphenyl sulfoxide		0^{e}	18
benzyl chloride		0^{e}	24
phenyl bromide		0^{e}	24
benzonitrile		0^{e}	24

[a] Average of at least two determinations. [b] 92% endo by VPC (20% Carbowax 20M on Chromosorb W, 100 °C, 7 ft) and ^{1}H NMR assay (average of at least two determinations); reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave 89% endo. [c] 89% β, computed from isolated yields of α and β isomers after separation by TLC and crystallization (average of at least two experiments); reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave 85% β. [d] Reduction with $Bu_3SnH/ZnCl_2/Et_2O$ solution gave a 77% yield of the alcohol. [e] Starting material recovered unchanged.

Table II. Selective Carbonyl Reduction

carbonyl compounds[a]	% reduction[b]	reducing agent
benzaldehyde	97	tributyltin hydride[c] on silica gel
methyl naphthyl ketone	8	
n-octanal	99	tributyltin hydride[c] on silica gel
cyclohexanone	13	
n-decanal	84[d]	diisopropylcarbinol on alumina[d]
4-*tert*-butylcyclohexanone	13[d]	

[a] An equimolar mixture was used. [b] Determined by VPC and ^{1}H NMR spectroscopy; average of at least two experiments. [c] A slight excess of hydride was used. [d] From ref 15.

completed, two more reports concerning reagents capable of selective reduction of aldehydes have appeared.[17,18]

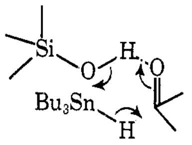
Experiments performed to investigate the mechanism of the reduction indicated that the reactions proceed via a hydride transfer mechanism analogous to complex metal hydride reductions.[19] Thus, the reductions were not inhibited by a radical scourge (2,6-di-*tert*-butylcresol), and only 1 equiv of tributyltin hydride was required, whereas radical-catalyzed tin hydride reductions utilize 2 equiv.[8] Furthermore, no reduction occurred in the presence of methanol or in the absence of silica gel, but it went inefficiently in the presence of dried basic alumina and proceeded well in the presence of zinc chloride. It would appear, therefore, that the function of the silica gel is largely that of a mild acid catalyst and serves to polarize the carbonyl group of the ketone sufficiently to allow reduction by the weakly nucleophilic hydride. This behavior is similar to that of sodium cyanoborohydride[19] and is consistent with the ability of tributyltin hydride to reduce highly electrophilic carbonyl groups without the aid of a catalyst.[7] Reduction in the presence of undried silica gel was not observed, presumably because of the hydrolysis of the tin hydride.

We have also demonstrated that tributyltin hydride does not undergo an exchange with the solid support to produce a "reducing silica gel" in an analogous manner to the formation of the "oxidizing alumina" obtained following treatment with a diacyl peroxide.[20] Treatment of dried silica gel with a cyclohexane solution of tributyltin hydride, filtration under an inert atmosphere, and treatment of the silica gel with a cyclohexane solution of a ketone gave no reduction, while the filtrate did reduce norcamphor if fresh, dried, silica gel was added.

Comparison of the stereochemistry of reduction of tributyltin hydride in the presence of a cyclohexane-dried silica gel slurry, by tributyltin hydride with zinc chloride dissolved in ether (a homogeneous system), and by common complex metal hydrides[21] (see footnotes *b*, *c*, and *d* in Table I) indicates that there is no steric effect upon the reaction due to surface adsorption on the silica gel and that it is apparently only acting as an acid catalyst. Catalysis of tributyltin hydride reduction by zinc chloride has been reported previously[22] but was not fully investigated. Our work shows that in terms of reaction rate it is more efficient than dried silica gel, but it suffers from the disadvantage that an aqueous workup is necessary to remove the zinc chloride and to destroy the zinc salts of the product alcohol, thus resulting in lower isolated yields.

The fate of the tributyltin moiety following carbonyl reduction was also examined. Treatment of a ketone (norcamphor) with approximately 1 equiv of tributyltin hydride in a silica gel–cyclohexane slurry followed by filtration and washing of the silica gel with ether gave the reduced ketone in high yield, but no tin-containing compounds were isolated when the filtrate and washings were evaporated, indicating that the latter were strongly bound to the silica gel. Displacement could not be effected by dry or moist ether or ethanol, but washing with an ethanol–acetic acid mixture allowed the isolation of tributyltin acetate, identical with a prepared authentic sample.

The isolation of tributyltin acetate along with the observations described above are consistent with, but do not require, a six-center reduction mechanism of type A to give



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stannylated silica gel and the alcohol. Alternatively, the initial formation of a tributyltin alkoxide and subsequent exchange with silanol groups may give the same products.

Conclusions

We have demonstrated that silica gel catalyzed reduction of ketones and aldehydes by tributyltin hydride is a selective and high yield method with the advantage of mild nonbasic conditions and without the need of strong acidic workup to neutralize alkoxide salts. Reductions are performed simply and the products easily isolated in the pure state by elution off the silica gel. Most importantly, the method allows the reduction of aldehydes in the presence of ketones with a high degree of selectivity.

Experimental Section

Tributyltin hydride was prepared from tributyltin chloride by reduction with sodium borohydride in glyme.[3] The silica gel used was Baker column chromatography grade, 60–200 mesh, and it was activated by heating at 220 °C at a pressure of less than 1 mmHg for 20 h and stored in a desiccator until required. Cyclohexane was purified by passage through a column of alumina, and zinc chloride was freshly fused. All reactions were carried out under a dry, oxygen-free, nitrogen atmosphere.

General Procedure for Tributyltin Hydride Catalyzed Reduction. The compound to be reduced (1 mmol), silica gel (5 g), tributyltin hydride (1.2 mmol), and cyclohexane (20 mL) were stirred together until TLC indicated that the reaction was complete. The mixture was filtered, and the silica gel was washed first with cyclohexane to remove excess tributyltin hydride and then with ether. The ethereal washings were evaporated to yield the alcohol, which was purified by crystallization, or in the case of liquids by preparative TLC. All reduction products were identified by comparison with authentic samples. The results are given in Table I. In the case of ketones insoluble in cyclohexane, a more polar solvent can be used or the ketone can be preadsorbed onto the silica gel.

General Procedure for Zinc Chloride Catalyzed Reduction. To a freshly filtered, saturated, ethereal solution of zinc chloride (ca. 20 mL) was added the ketone (1 mmol) and tributyltin hydride (1.2 mmol), and the solution was stirred until TLC indicated that the reaction was complete. A white solid was precipitated as the reaction progressed. Following an aqueous workup procedure, the product was purified by crystallization. The results are given in Table I.

Selective Reduction of an Aldehyde in the Presence of a Ketone. Cyclohexanone and octanal or benzaldehyde and methyl naphthyl ketone (1 mmol of each) were stirred with tributyltin hydride (1.05 mmol) in cyclohexane (25 mL). Silica gel (10 g) was added, and after 2 h the mixture was filtered. The filtrand was washed with cyclohexane and then with ether, and the latter washings were carefully evaporated to give the product mixture. The relative amounts of cyclohexanone and octanal and their reduction products were determined by VPC (5% Carbowax 20M on Chromosorb P, 80 °C, 6 ft) using a calibration obtained with authentic mixtures. The relative amounts of benzaldehyde and methyl naphthyl ketone and their reduction products were determined from the ^{1}H NMR spectrum of the mixture. The results are given in Table II.

Isolation of Tributyltin Acetate. Norcamphor (2.5 mmol), tributyltin hydride (1 mmol), and silica gel (10 g) were stirred together in cyclohexane for 1 h. The mixture was filtered, and the silica gel was washed with ether to remove norborneol and excess norcamphor and then with acetic acid–ethanol (1:5). Evaporation of the ethanol–acetic acid washings gave the crude tributyltin acetate, which was recrystallized from petroleum ether (bp 60–80 °C) to give the pure product (79%), mp 84–85 °C, identical (mixed melting point and IR) with a prepared authentic sample.[23]

Registry No.—Norcamphor, 497-38-1; 3-cholestanone, 15600-08-5; methyl naphthyl ketone, 93-08-3; benzophenone, 119-61-9; benzaldehyde, 100-52-7; octanal, 124-13-0; nitrobenzene, 98-95-3; *trans*-stilbene epoxide, 1439-07-2; phenyl benzoate, 93-99-2; diphenylmethyl benzoate, 7515-28-8; 1-chloro-2-phenylethane, 622-24-2; diphenyl sulfoxide, 945-51-7; benzyl chloride, 100-44-7; phenyl bromide, 108-86-1; benzonitrile, 100-47-0; 1-(β-naphthyl)ethanol, 7228-47-9; diphenylmethanol, 91-01-0; benzyl alcohol, 100-51-6; 1-octanol, 111-87-5; aniline, 62-53-3; 1,2-diphenylethanol, 614-29-9; phenol, 108-95-2; cyclohexanone, 108-94-1; *n*-decanal, 112-31-2; 4-*tert*-butylcylohexanone, 98-53-3; tributyltin hydride, 688-73-3; tributyltin acetate, 56-36-0; *exo*-norborneol, 497-37-0; *endo*-norborneol, 497-36-9; 3α-cholestanol, 516-95-0; 3β-cholestanol, 80-97-7.

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Improved Routes to Phenalene and Phenalanone. Alane, Borane, and Silane Reductions of Phenalenone

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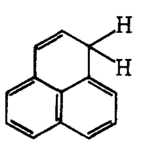
Phenalene (1) has enjoyed considerable attention from chemists because of its ability to generate an anion, neutral radical, and cation, all of which are aromatic and stable in solution.[1] Because earlier reported methods of making and isolating 1 and its precursors are generally tedious[2] and work in our laboratories required ready access to 1, we investigated ways of improving its yield and purification.



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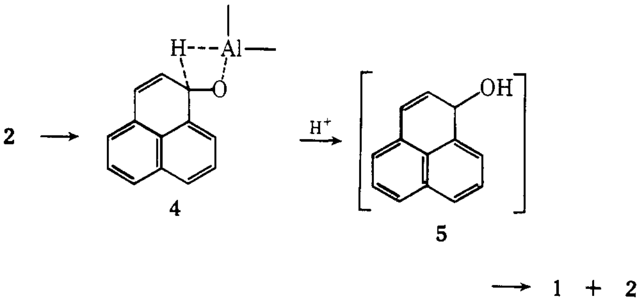
Recently, it was reported that LiAlH$_4$/AlCl$_3$ reduced phenalenone (2) to 1 and phenalanone (3).[3] The yields varied over a wide range, however, and were markedly affected by the purity of the LiAlH$_4$ and AlCl$_3$, the recommended procedure calling for newly opened bottles of these reagents. Furthermore, the isolation of 1 required large amounts of solvent and is often accompanied by oxidation of the very sensitive 1 on silica gel.

The active agents in the reduction of 2 to 1 by the LiAlH$_4$/AlCl$_3$ mixture were probably HAlCl$_2$ and H$_2$AlCl.[4] This suggested to us that diisobutylaluminum hydride (DIBAL-H) might also be effective in reducing **2**. We found that DIBAL-H will convert 2 to 1 in high net yields (>85%) and that 1 can be isolated easily in high purity from the product mixture. DIBAL-H is commerically available as a 1 M solution in hexane (Aldrich) and is handled conveniently and precisely by syringe technique. The reagent also has a long shelf-life, even after it has been sampled. These are distinct advantages over LiAlH$_4$/AlCl$_3$ mixtures.

The sensitivity of 1 to silica gel led us to try other solid supports, and we found that Florisil, a much more acidic absorbent than silica gel,[5] gave very satisfactory results. Phenalene is the first compound eluted from the column and is well separated from the only other product, phenalenone. Moreover, a shorter column and much less solvent are required than when we used silica gel. No significant decomposition of 1 during the chromatography was observed. Scaling up the reaction presented no handling problems, and yields were unchanged.

The production of 1 from 2 and DIBAL-H probably arises from a 1,2 addition of the metal hydride across the C=O bond. Hydrolysis of the resulting alkoxide would give phenalenol **5**, which is known to undergo a facile irreversible disproportionation to 1 and 2.[6] Consistent with this scheme is the fact that we recover ~50% of the amount of 2 that we start with regardless of reaction time and the number of equivalents of DIBAL-H used. Reaction times ranged from 4 h to 2 days, and ratios of metal hydride to 2 were varied from 1 to 5 equiv. The addition of aluminum powder or aluminum chloride as potential deoxygenating agents did not change the yield of 1.



We tried to intercept the disproportionation of 5 by using alcohols in large excess during workup. However, allyl alcohol, glyoxal, and benzoin did not alter the yield or product distribution. The report of successful hydrogenolysis of the magnesium alkoxides of allylic alcohols using complexes derived from adding *n*-propylmagnesium bromide[7] to bis(phosphine)nickel dichlorides suggested that 4 might be similarly reduced. This route also gave 1 and 2 when applied to 4. We also tried reductions of 2 using boranes and found that while BH$_3$·SMe$_2$ is useful for preparing cyclopropane from cyclopropenone,[8] mainly polymeric products are obtained when it is used with **2**. 9-Borabicyclononane, on the other hand, does give 1 in net yields of ~90% when stirred overnight at room temperature in THF.

We extended our studies to polymethylhydrosiloxane (PMHS)[9] and tetramethyldisiloxane (TMDS)[9] and found that

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