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# A novel reduction reaction for the conversion of aldehydes, ketones and primary, secondary and tertiary alcohols into their corresponding alkanes

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**Abstract**—A novel one-pot reaction has been developed for the reduction of aldehydes, ketones and primary, secondary and tertiary alcohols into their corresponding alkyl function. This is also the first reported method which can efficiently reduce primary, secondary, or tertiary alcohols, without affecting carbon–carbon double bonds, into their corresponding alkyl function in high yields. The reduction utilises either diethylsilane or *n*-butylsilane as the reducing agent in the presence of the Lewis acid catalyst tris(pentafluorophenyl)borane.

The reduction of aldehydes, ketones and alcohols to a methyl function is a useful and widely reported synthetic pathway. In the case of ketones and aldehydes, multistep reduction procedures using reagents such as hydrazine in basic polyethylene glycol,[1–3] amalgamated zinc in a hydroxylic solvent containing HCl,[4] electrolytic reduction[5] and diphenylsilane at high temperatures[6] have been shown to be quite effective. Single step reductions of a carbonyl function to a methyl group have also been reported using polymethylhydrosiloxane,[7] triethylsilane[8,9] and triphenylsilane[10] in the presence of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$). Similarly, the reduction of alcohols to alkanes has also been reported via a range of procedures including acetic acid/HI,[11] mixed hydrides from $AlCl_3$ and $LiAlH_4$,[12] and photochemical reduction.[13] However, different reagents/methods are needed depending on whether the substrate is a primary, secondary or tertiary alcohol. For instance, the reduction of primary alcohols to hydrocarbons has been reported using $HSiEt_3$ in the presence of catalytic amounts of $B(C_6F_5)_3$, however, this reagent was unable to reduce secondary and tertiary alcohols to alkanes.[14,15] Primary and secondary acyclic alcohols can be reduced to alkanes using sodium borohydride once they have been activated by triphenylphosphonium anhydride.[16] In addition, aliphatic primary alcohols can be converted into hydrocarbons by condensation with samarium at low temperatures at about 80–90 K.[17] Secondary alcohols and tertiary alcohols were converted into their corresponding hydrocarbons by hydrogenation in the presence of $Ni/Al_2O_3$ catalyst at 190 °C.[18] Catalytic hydrogenation of alcohols to hydrocarbons in the presence of Pd/C was used after first converting the alcohols into ureas using diamines.[19] Chlorodiphenylsilane in the presence of the catalyst, indium trichloride, has been shown to directly reduce benzylic alcohols, secondary alcohols and tertiary alcohols into their corresponding alkanes.[20] In most of these cases, however, carbon–carbon double bonds are also reduced along with the target carbonyl/alcohol. In this work, we report the direct reduction of primary, secondary and tertiary alcohols, aldehydes and ketones to alkanes using either *n*-butylsilane (*n*-BS) or diethylsilane (DES) as reducing agents.

The proposed reaction mechanism for the reduction of alcohols by *n*-BS is presented in Figure 1. Table 1 contains a list of the alcoholic substrates studied, ordered by class. The ability of *n*-BS and DES to reduce primary alcohols is illustrated with the reduction of phenylmethanol **1**, and octadecanol **2**, using 2 equiv of *n*-BS or

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*Keywords*: Reduction; Aldehydes; Ketones; Alcohols; DES: diethylsilane; *n*-BS: *n*-butylsilane; $B(C_6F_5)_3$: tris(pentafluorophenyl)borane.

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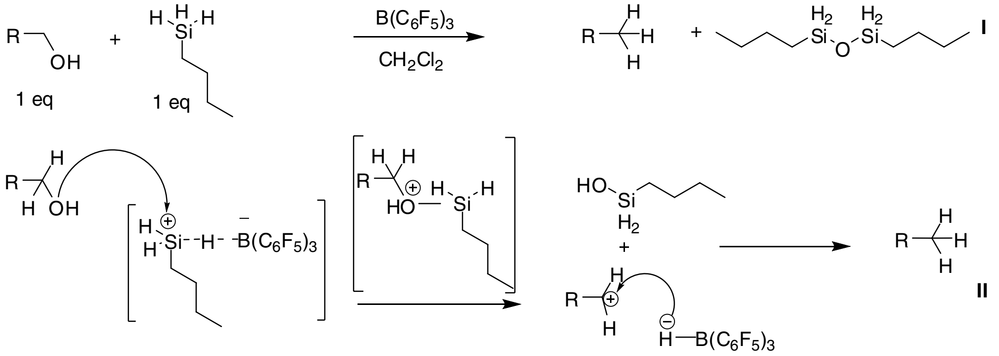
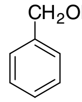
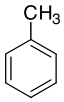
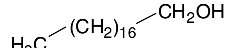
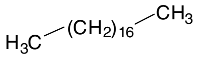
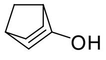
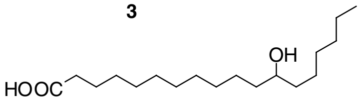
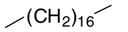
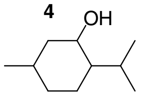
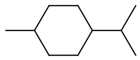
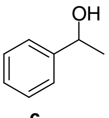
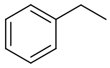
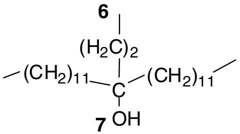
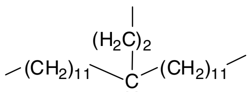
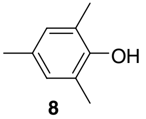
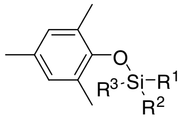
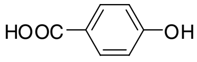
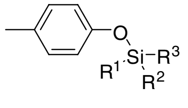
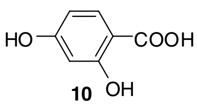
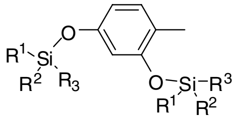


**Figure 1.** Reduction mechanism for alcohols.

**Table 1.** Reduction of alcohols and phenols using either *n*-butylsilane (*n*-BS) or diethylsilane (DES)

| Entry | Substrate | Product | GC yield (%) | |
|---|---|---|---|---|
| | | | *n*-BS | DES |
| 1 |  **1** |  | 97 | 41 |
| 2 |  **2** |  | 91 | 83 |
| 3 |  **3** |  | 81 | 54 |
| 4 |  **4** |  | 91 | 27 |
| 5 |  **5** |  | 97 | 34 |
| 6 |  **6** |  | 94 | 43 |
| 7 |  **7** |  | 72 | 17 |
| 8[a] |  **8** |  | 73 | 64 |
| 9[a] |  **9** |  | 67 | 48 |
| 10[a] |  **10** |  | 41 | 52 |

[a] $R^1 = R^2 = H$, $R^3 =$ butyl when using *n*-butylsilane and $R^1 = R^2 =$ ethyl, $R^3 = H$, when using diethylsilane as the reducing agent.

2 equiv of DES. Both substrates were converted to alkanes with either reagent. The reduction of secondary and tertiary alcohols is illustrated with the reduction of norbornen-2-ol **3**, 12-hydroxystearic acid **4**, 2-isopropyl-5-methylcyclohexanol **5** and 1-phenylethanol **6**. In the case of norbornen-2-ol **3**, it can be seen that the dou-

ble bond was not affected during the reduction of the secondary alcohol. 12-Hydroxystearic acid **4** could be fully reduced to octadecane with 6 equiv of *n*-butylsilane. We have reported the conversion of carboxylic acids to alkanes using *n*-BS and DES in a previous paper.[21] Full reduction of 12-hydroxystearic acid **4** to octadecane could also be effected using 10 equiv of DES, albeit in lower yield. The other major product from this reduction was a silyl ether formed at the secondary alcohol. Higher yields of octadecane were obtainable by using a large (12 equiv) excess of DES. The reduction of tertiary alcohols is illustrated with the reduction of 13-propyl-hexacosane-13-ol **7**. Although *n*-BS was able to reduce this substrate in high yield, the yield of alkane using DES was low. Again, the use of a large excess of DES increased the yield to 68%. Both *n*-BS and DES produce silyl ethers when reacted with phenols as illustrated by the substrates 2,4,6-trimethylphenol **8**, 4-hydroxybenzoic acid **9** and 2,4-dihydroxybenzoic acid **10**.

The proposed mechanism for the reduction of aldehydes and ketones is presented in Figure 2. Table 2 contains a list of the carbonyl substrates studied, ordered by class. The reduction of aliphatic aldehydes is illustrated by the reduction of octanal **11** which was converted to octane in high yield. Similarly, the reduction of aromatic aldehydes both in the presence of electron donating groups, as in 4-methoxybenzaldehyde **12** and electron withdrawing groups, as in 4-nitrobenzaldehyde **13** were effected in high yield. The rate of reaction and yield of product did not appear to be affected by the electron donating/withdrawing properties of the substituents. Ketones were also successfully converted to alkanes. Further, the carbonyl carbons of 4-(2,6,6-trimethylcyclohex-2-enyl)but-3-en-2-one **14**, 4-(2,6,6-trimethylcyclohex-1-enyl)but-3-en-2-one **15**, hex-1-en-3-one **16** and 2-methyl-5-(prop-1-en-2-yl)cyclohex-2-enone **17** were readily reduced to methylenes without affecting the carbon–carbon double bonds. The aromatic ketones, benzophenone **18**, 3,4-dihydronaphthalen-1(2*H*)-one **19** and anthracen-9(10*H*)-one **20** were reduced to alkanes without difficulty.

In summary, although there are numerous reducing agents capable of converting alcohols, aldehydes and ketones to alkanes, to date, there has not been a mild reducing agent reported capable of converting all types of alcohol, be they primary, secondary, or tertiary to alkanes in a one-pot reaction and without affecting carbon–carbon double bonds. The method reported in this work is capable of reducing all the above functional groups to alkanes, even in the presence of carbon–carbon double bonds, in a single step and in very high yields.

An oven dried 25 mL round bottom flask was purged with nitrogen. Substrate (1 mmol) was weighed into the flask which was then closed with a septum and purged with argon. Catalyst ($B(C_6F_5)_3$, 5–10 mol %) was introduced via syringe as a freshly prepared solution in 5 mL of anhydrous dichloromethane. Stirring was continued for 10 min and then 1 equiv of *n*-butylsilane (99% pure) or diethylsilane (99% pure) was added for each alcohol group (2 equiv for each carbonyl group) present in the substrate. A static atmosphere of argon was established using an argon balloon. The reaction was stirred for about 0.5–10 h depending upon the number of alcohol/carbonyl functions present. The reaction progress was monitored by GC–MS. After complete conversion of the starting material, the reaction mixture was quenched with 0.1 mL of triethylamine. The crude

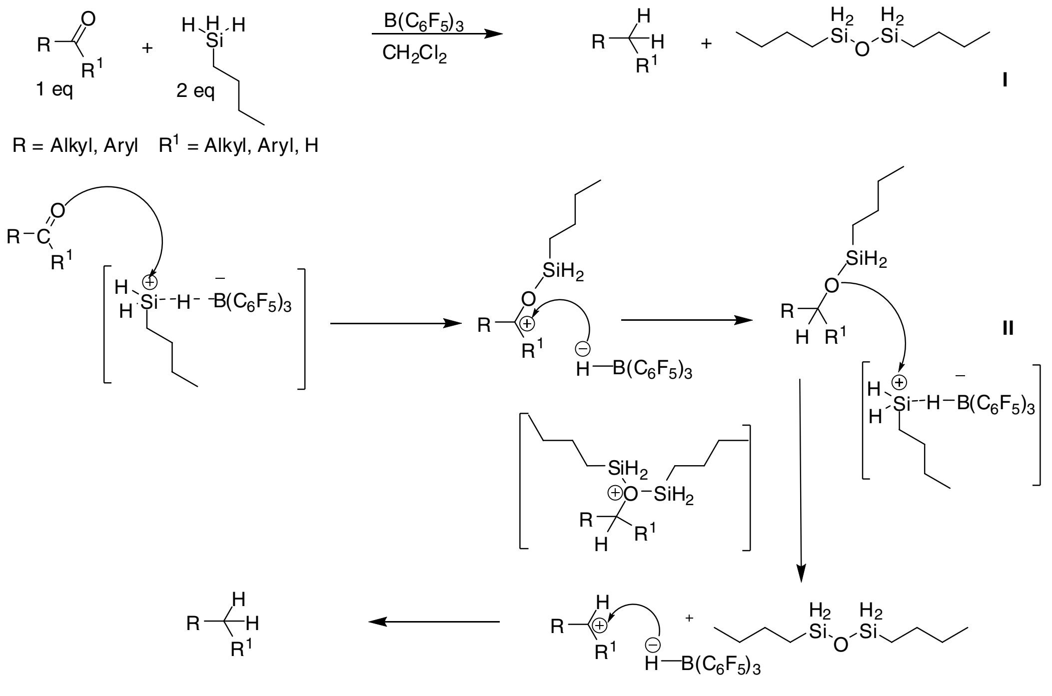
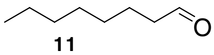
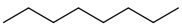
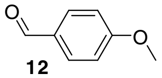
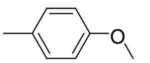
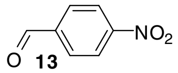
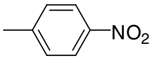
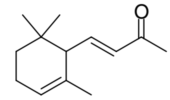
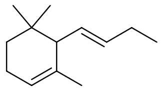
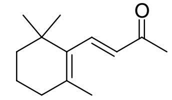
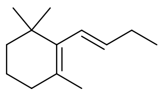
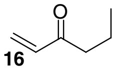
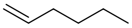
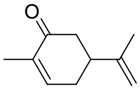
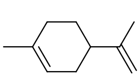
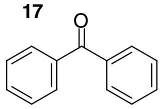
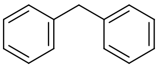
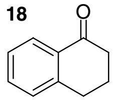
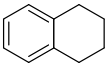
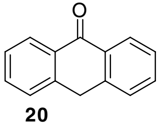
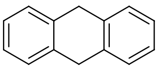


**Figure 2.** Reduction mechanism for aldehydes and ketones.

**Table 2.** Reduction of aldehydes and ketones using either *n*-butylsilane (*n*-BS) or diethylsilane (DES)

| Entry | Substrate | Product | GC yield (%) | |
|---|---|---|---|---|
| | | | *n*-BS | DES |
| 1 |  **11** |  | 79 | 81 |
| 2 |  **12** |  | 91 | 89 |
| 3 |  **13** |  | 87 | 71 |
| 4 |  **14** |  | 93 | 64 |
| 5 |  **15** |  | 85 | 78 |
| 6 |  **16** |  | 84 | 67 |
| 7 |  **17** |  | 73 | 86 |
| 8 |  **18** |  | 87 | 41 |
| 9 |  **19** |  | 87 | 41 |
| 10 |  **20** |  | 93 | 56 |

mixture was purified by silica gel flash column chromatography with hexane as eluent or hexane–ethyl acetate (50:1) to elute silyl ethers.

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