

A novel reduction of polycarboxylic acids into their corresponding alkanes using *n*-butylsilane or diethylsilane as the reducing agent

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Abstract—A convenient one-pot reaction has been developed for the reduction of polycarboxylic acids on aliphatic and aromatic systems to their corresponding alkanes. The reduction utilises either diethylsilane or *n*-butylsilane as the reducing agent in the presence of the Lewis acid catalyst tris(pentafluorophenyl)borane.

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1. Introduction

In synthetic chemistry, the reduction of a carboxylic acid carbon to a methyl group is an important conversion. Carbonyl functions can be readily converted to a methylene group in a single-step by a variety of methods. However, the conversion of carboxylic acids into methyl groups usually requires a multi-step process. Typically, carboxylic acids are first converted to either aldehydes or alcohols, which are then subsequently reduced to a methyl group. Multi-step procedures for the reduction of aromatic carboxylic acid groups to methyl groups, without purification of the intermediates have been previously reported.¹ Recently, procedures for the reduction of aliphatic monocarboxylic acids to methyl groups in a one-pot reaction have also been reported.² To date, however, there is no established method for the conversion of di- and polycarboxylic acids into their corresponding alkanes via one-pot reduction. The method described here reduces di-carboxylic and polycarboxylic acids on both aliphatic and aromatic systems.

Silanes³ are mild reducing agents^{4,5} that have been commonly used in selective reductions.^{2,6–13} Silane reagents require either strong acid or Lewis acid catalysts in

order to become a hydride source. Tris(pentafluorophenyl)borane [$B(C_6F_5)_3$] is a convenient Lewis acid¹⁴ that has previously been used in conjunction with triethylsilane for the selective reduction of carbonyl and carboxylic functions to methylene/methyl groups.² However, this method was limited to aliphatic monocarboxylic acids and required the use of ammonium fluoride to cleave the silyl ethers formed with the aromatic carboxylic acids. When this method was applied to a di-carboxylic acid, the major product was a silyl ether rather than the corresponding alkane. In this work, we present a method for the successful reduction of both aliphatic and aromatic polycarboxylic acid functions to methyl groups using *n*-butylsilane or diethylsilane and tris(pentafluorophenyl)borane.

Several alkyl silanes, including triethylsilane (TES), dimethylethylsilane (DMES), diethylsilane (DES) and *n*-butylsilane (*n*-BS) in the presence of tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), were investigated in this study for the purpose of carboxylic acid reduction.

TES and DES were found to reduce straight chain di-carboxylic acids readily into their corresponding alkanes, however; alicyclic and aryl dicarboxylic acids were converted into their corresponding silyl ethers requiring 6 equiv of TES for each carboxylic acid group. HF or NH_4F can cleave these silyl ethers as already reported.² The ability of various silanes to reduce carboxylic acids was found to be dependent upon steric hindrance, thus the less sterically hindered silanes proved to be more efficient. TES and DMES were able to reduce straight chain

Keywords: Reduction; Polycarboxylic acids; TES: triethylsilane; DES: diethylsilane; DMES: dimethylethylsilane; *n*-BS: *n*-butylsilane; $B(C_6F_5)_3$: tris(pentafluorophenyl)borane.

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di-carboxylic acids. The length of reaction with DMES was less than that for TES reduction. This is because of the less bulky substituents on DMES. These studies encouraged the use of DES, with only two alkyl substituents on the silane, as a reducing agent. DES was successful in the reduction of di-carboxylic acids and polycarboxylic acids (Table 1) for which DMES was not. Although DES was able to reduce polycarboxylic acids, the yields were low and compounds, such as 1,2,3,4,5,6-hexacarboxylic acid cyclohexane **10** and 1,2,3,4,5,6-hexacarboxylic acid benzene **20**, did not yield any of the desired alkane products. Thus, the less sterically hindered *n*-BS was chosen as the reducing agent. *n*-BS was found to reduce di- and polycarboxylic acids to their corresponding methyl groups in high yields compared to diethylsilane (Table 1). The condition of the catalyst and the silane were found to be crucial to the reaction. If freshly prepared catalyst and silane were not used, considerably lower yields were observed.

The proposed reaction mechanism is described in Figure 1 and is based on the intermediate products observed during the reaction. Silanes are typically only considered to be hydride sources when substituted with bulky alkyl substituents; however, the silylation products formed indicate that silanes with less bulky substituents can also act as hydride sources **I**. The ability of *n*-BS to serve as a hydride source was tested with various other catalysts, such as palladium, platinum oxide, AlCl₃, BF₃·Et₂O, BBr₃, BCl₃ and rhodium. However, no conversion of polycarboxylic acids to the methyl groups was observed. *n*-BS and DES are effective reducing agents only in the presence of tris(pentafluorophenyl)borane, which is able to abstract the hydrogen even on *n*-BS. The siloxane formed is further condensed to form cyclotrisiloxanes and higher polymers in the presence of the polycarboxylic acids.

We have developed a simple, one-pot and direct reduction of aliphatic and aromatic mono-, di- and polycarboxylic acid moieties into the corresponding methyl group. This work also describes the application of the two reducing agents, *n*-BS and DES, in the field of synthetic chemistry.

2. Experimental

A Shimadzu Gas Chromatograph 17A coupled with a QP5000 mass spectrometer was used for qualitative analysis. A Shimadzu Gas Chromatograph 17A with flame ionisation detector was used for quantitative analysis. In both cases the gas chromatograph was fitted with an SGE BPX-5 column (30 m × 0.25 mm i.d., 0.5 μm film thickness). An oven dried 25 mL round bottom flask was purged with nitrogen. Carboxylic acid (1 mmol) was weighed into the flask which was then closed with a septum and purged with argon. The catalyst (B(C₆F₅)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 2 equiv of *n*-BS (99% pure) or DES (99% pure) was added per carbonyl group (4 equiv for each carbox-

Table 1. Reduction of polycarboxylic acids on aliphatic and aromatic systems with *n*-butylsilane (*n*-BS) or diethylsilane (DES)

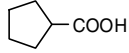

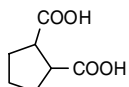

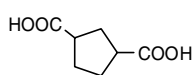

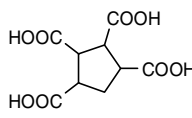
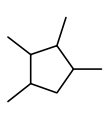
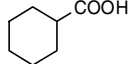

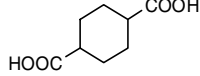
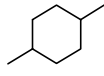
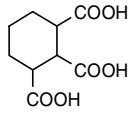
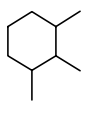
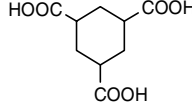
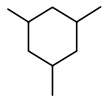
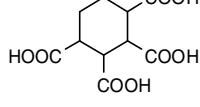
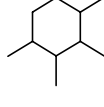
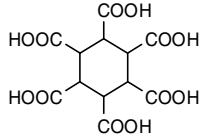
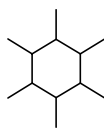
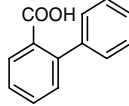
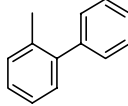
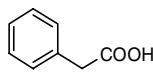
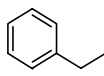
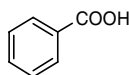

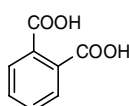
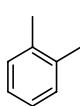
Substrate	Product	GC yield (%)	
		<i>n</i> -BS	DES
1 		73	87
2 		78	64
3 		87	79
4 		63	46
5 		87	82
6 		83	71
7 		52	34
8 		64	61
9 		57	37
10 		32	—
11 HOOC-(CH ₂) ₈ -COOH	H ₃ C-(CH ₂) ₈ -CH ₃	94	91
12 HOOC-(CH ₂) ₁₆ -COOH	H ₃ C-(CH ₂) ₁₆ -CH ₃	87	81
13 		74	59
14 		89	91
15 		89	69
16 		69	53

Table 1 (continued)

Substrate	Product	GC yield (%)	
		n-BS	DES
		83	71
		71	34
		65	41
		19	—

ylic acid) present in the substrate. A static atmosphere of argon was established using an argon balloon. The reaction mixture was stirred for about 6–20 h depending upon the number of carboxylic acids present. Light

was excluded for the duration of the reaction to prevent photolytic HCl production from the degradation of dichloromethane, which was found to hamper the reaction. 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 mixture was purified over silica gel with hexane as eluent or hexane/ethyl acetate (50:1).

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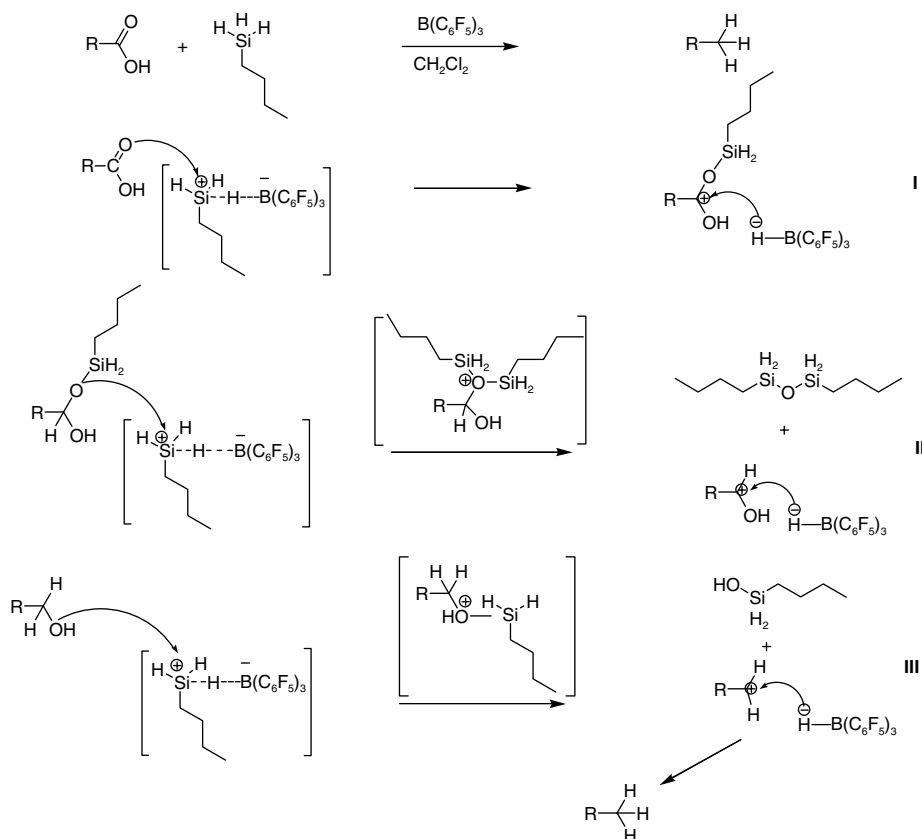


Figure 1. Proposed reduction mechanism.

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