

p-Bis(diphenylhydrosilyl)benzene. A Useful Reagent for the
Deoxygenation of Alcohols via Acetates

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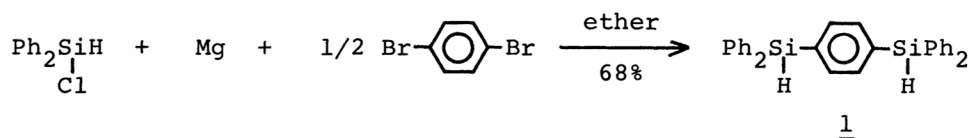
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Acetates which were derived from primary, secondary, and tertiary alcohols were deoxygenated to the corresponding hydrocarbons in high yield by p-bis(diphenylhydrosilyl)benzene under homolytic conditions.

Reductive deoxygenation of alcohols is of great interest in carbohydrate chemistry.¹⁾ Although numerous methods for the deoxygenation via various intermediates such as xanthate, chloroformate, etc. have been reported,^{2,3)} satisfactory methods via esters, especially acetates, which were more easily prepared from alcohols have been scarcely known.⁴⁾ Recently, we reported that triphenylsilane was an effective reagent for the deoxygenation of simple esters and acylated sugars.^{5,6)} However, the problems still remain in that the reaction needs rather excess triphenylsilane (4 equiv.), since the dimerization of triphenylsilyl radical occurred competitively, and the isolation of products from the reaction mixture is somewhat troublesome in some cases.

We wish to report that the use of p-bis(diphenylhydrosilyl)benzene 1 in place of triphenylsilane afforded more satisfactory results.

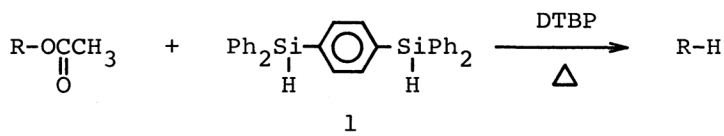
The reducing agent 1 was easily prepared by the reaction of diphenylchlorosilane with p-dibromobenzene and magnesium as shown in Scheme 1.⁷⁾



Scheme 1.

Using the reagent 1, we examined the deoxygenation of cyclododecyl acetate as a

representative ester in the presence of di-*t*-butyl preoxide (DTBP) as a radical initiator under various conditions. As the results, the deoxygenation proceeded

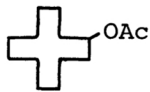

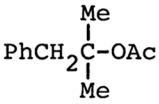
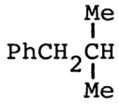
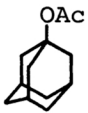

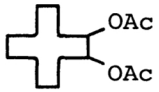

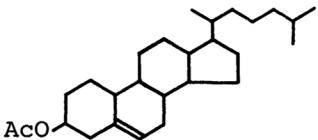
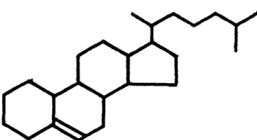


almost quantitatively even in the use of 1.5 molar equivalent of 1. And GLC analysis of this reaction mixture showed almost single product. These observations are rationalized by the bulkiness of 1. Thus, it seems that the side reactions (dimerization) of the silyl radical generated from 1 were suppressed owing to the steric interference between the radicals, and the silyl radical derived from 1 having a higher molecular weight compared with that from triphenylsilane gave the higher boiling by-products, if any formed, which might be easily separated from the product by distillation. Furthermore, TLC analysis of this reaction mixture showed that the desired product, cyclododecane, could be readily isolated from the reaction mixture, probably owing to increased number of polar groups in the by-products derived from reagent 1 having two reaction sites, as compared to the case of triphenylsilane reagent. The applications of this reaction to various acetates are summarized in Table 1 together with the yields on using triphenylsilane for comparison.

The generality of this reaction is indicated by the finding that primary, secondary, and tertiary acetates could be deoxygenated in high yield, though the yields on using triphenylsilane were relatively low in the cases of primary and tertiary acetates. It should be noted that the diacetate of 1,2-diol provided the corresponding hydrocarbon on treatment with the silane 1 (Run 6), although the deoxygenation of 1,2-diols via bis(thiobenzoates) using tin hydride gave cyclization products.⁸⁾ The somewhat lower yield in the case of cholesteryl acetate (Run 7) may be due to partial hydrosilylation of 1 to the internal double bond.⁹⁾

A typical reaction procedure is as follows; A mixture of 1 (880 mg, 2 mmol), cyclododecyl acetate (300 mg, 1.3 mmol), and DTBP (194 mg, 1.3 mmol) was sealed in a glass tube under a reduced pressure. After heating at 140 °C for 15 h, cyclododecane was isolated from the reaction mixture by silica gel column chromatography (hexane) in 89% yield.

Table 1.

Run	Ester	Product	Yield/% ^{a)}	
			A	B
1			89 (98)	82 (95)
2	$n\text{-C}_8\text{H}_{17}\text{CH}(\text{OAc})\text{C}_5\text{H}_{11}$	$n\text{-C}_{14}\text{H}_{30}$	70	88
3			71 (92)	43 (54)
4			85	
5	$n\text{-C}_{11}\text{H}_{23}\text{CH}_2\text{-OAc}$	$n\text{-C}_{12}\text{H}_{26}$	95 (100)	67 (78)
6			64 ^{b)}	
7			59	

a) Isolated yield (in parentheses GLC yield); A: using reagent 1, B: using Ph_3SiH .

b) Three mol of 1 and two mol of DTBP were used.

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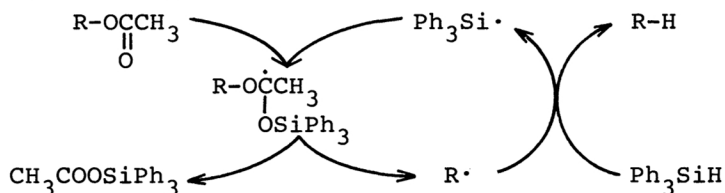
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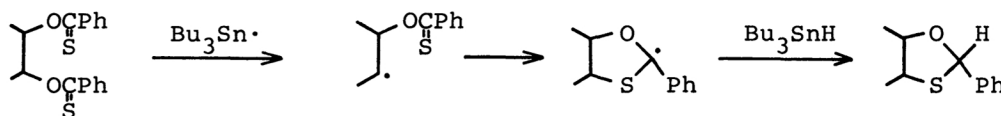
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