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Radical deoxygenation of alcohols via their trifluoroacetate derivatives with diphenylsilane

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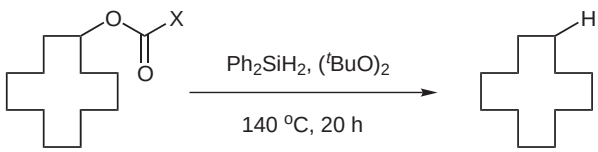
Abstract—Trifluoroacetate derivatives of alcohols can be used as precursors for the radical deoxygenation of alcohols with diphenylsilane. The reaction afforded high isolated yields of the deoxygenated products and neutral reaction conditions.

Reactions for the selective deoxygenation of alcohols are very important processes in organic synthesis, especially for the synthesis of biologically important molecules. Among various methods reported for the deoxygenation of alcohols, the radical deoxygenation of alcohols (Barton–McCombie reaction) is the most frequently used.[1] The Barton–McCombie reaction offers suitable reaction conditions that sensitive polyfunctionalized compounds can tolerate. The Barton–McCombie reaction has been a protocol for the selective deoxygenation of alcohols since it was reported.[2]

Although organotin hydrides are used commonly as radical hydrogen sources in the radical deoxygenation of alcohols, they have several drawbacks including toxicity and difficulty of removing the tin by-product from the desired products. There have been several research efforts to find alternatives to organotin hydrides such as silanes,[3] hypophosphorous acid,[4] dialkyl phosphites,[5] dialkylphosphine oxides[6] and phosphine-boranes.[7]

The radical deoxygenation of alcohols was accomplished via the reduction of their various thionocarbonyl derivatives. Among them, *S*-methyl dithiocarbonate,[2] phenyl thionocarbonate,[8] *p*-fluorophenyl thionocarbonate[6] and imidazolyl thionocarbonate[2,9] derivatives of alcohols are widely used due to their reactivity. However, the procedure for the preparation of *S*-methyl dithionocarbonate requires strong bases and the derivatizing reagents for the thionocarbonates such as phenyl chlorothionocarbonate, *p*-fluorophenyl chlorothionocarbonate and diimidazolyl thioketone are relatively expensive and unstable in moisture. Although carbonyl derivatives of alcohols can be prepared more readily, they are rarely used in the radical deoxygenation of alcohols.[10] We wish to

Table 1. Radical deoxygenation of carbonyl derivatives of cyclododecanol with diphenylsilane[a]



Entry	X	Yield (GC, %)
1	Ph	68
2	CH_3	75
3	^{t}Bu	65
4	Imidazolyl	69
5	OCH_3	3
6	OCH_2CH_3	5
7	CF_3	90
8[b,c]	CF_3	98
9[b,d]	CF_3	93

[a] A typical procedure was as follows unless noted otherwise: A mixture of carbonyl derivative of cyclodecanol (1 equiv.), diphenylsilane (4 equiv.) and di-*tert*-butyl peroxide (1 equiv.) was heated at 140°C. After 20 h the mixture was analyzed by GC.
[b] 5 Equiv. of diphenylsilane was used.
[c] The reaction time was 15 h.
[d] At 130°C.

Keywords: radical reactions; alcohols; deoxygenation; esters; reductions.

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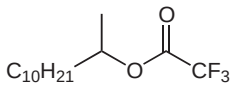
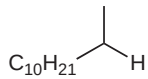
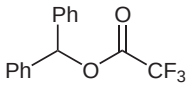
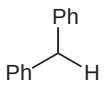
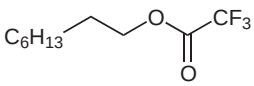
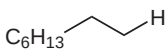
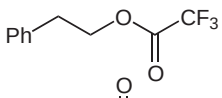
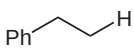
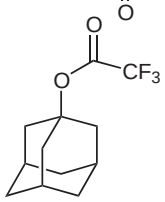
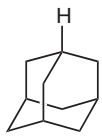
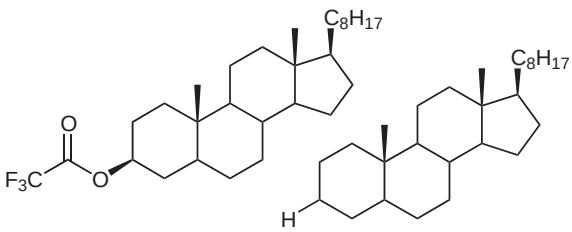
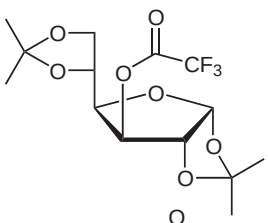
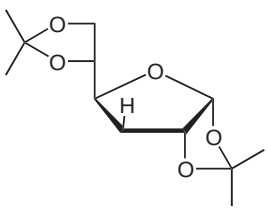
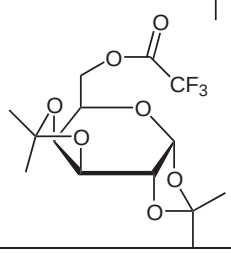
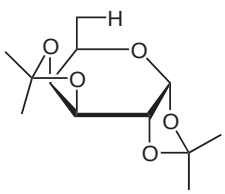
Table 2. Radical deoxygenation of various alcohols via their trifluoroacetate derivatives with diphenysilane[a]

Entry	Substrate	Product	Isolated Yield (%)
1			85
2			83
3			81
4			73
5			65
6			87
7			83
8			82

[a]A mixture of trifluoroacetate of alcohol (0.4 mmol, 1 equiv.), diphenylsilane (2.0 mmol, 5 equiv.) and di-*tert*-butyl peroxide (0.4 mmol, 1 equiv.) was sealed in an ampule under argon. After heating at 140 °C for 15 h, the deoxygenated product was isolated by column chromatography on silica gel.

report herein that the deoxygenation of alcohols can be accomplished efficiently via their trifluoroacetate derivatives with diphenylsilane.

Initially, the reaction of various carbonyl derivatives of cyclododecane with diphenylsilane in the presence of di-*tert*-butyl peroxide as the initiator was examined. The yields of cyclodecane were measured by GLC analysis and the results are summarized in Table 1. Ester derivatives of cyclododecanol afforded cyclododecane in moderate yields (entries 1–4), while the carbonate derivatives of alcohols gave a trace amount of cyclododecane along with the recovered starting material (entries 5 and 6). Among the carbonyl derivatives

we investigated, the trifluoroacetate of alcohol showed the most promising results. When the reaction of trifluoroacetate of cyclododecanol with diphenylsilane was carried out at 140°C in the presence of di-*tert*-butyl peroxide as the initiator in a sealed tube, cyclododecane was obtained in 90% yield with a small amount of the recovered starting material (entry 7). Finally, the reaction could be optimized to give 98% yield of cyclododecane (entry 8). Although a longer reaction time was required, the reaction was proceeded at 130°C (entry 9).

The reaction was applied to the deoxygenation of various alcohols. The results are summarized in Table 2. Secondary alcohols and even the primary alcohols were efficiently transformed into the corresponding hydrocarbons (entries 1–4). Tertiary alcohols afforded somewhat lower yields of the deoxygenated products (entry 5). The process could be used for the deoxygenation of steroids. Dihydrocholesteryl trifluoroacetate was converted into the corresponding hydrocarbon in 87% yield (entry 6). Selective deoxygenation of sugars is a very important tool for the modification of sugars that are widely used as antibiotics and chiral building blocks in organic synthesis.[11] The trifluoroacetates could be utilized for the preparation of deoxysugars. Trifluoroacetates of secondary alcohol of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose and primary alcohol of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose produced the deoxygenated product in 83 and 82% yield, respectively, under the conditions (entries 7 and 8). In summary, trifluoroacetate derivatives of alcohols can be used as precursors for the radical deoxygenation of various alcohols. They can be prepared without using toxic, expensive derivatizing reagents.

Acknowledgements

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