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REDUCTIVE DEOXYGENATION OF ALCOHOLS VIA ESTERS WITH TRIPHENYLSILANE UNDER NEUTRAL CONDITIONS

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Treatment of carboxylic esters derived from alcohols with triphenylsilane in the presence of a radical generator at 140 °C gave the corresponding hydrocarbons in good yield.

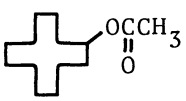
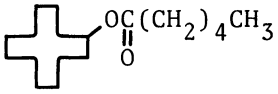
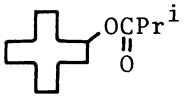
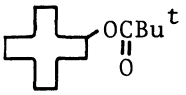
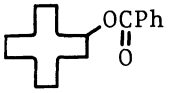
Reductive deoxygenation of alcohols, especially secondary alcohols, to hydrocarbons under neutral conditions is very important, since the reaction has been used in a modification of sugars which were widely utilized as antibiotics or chiral templates.[1] Generally, the reductive deoxygenation of secondary alcohol is difficult, though the reduction of primary or tertiary alcohol can be readily accomplished.[2] Although numerous attempts to achieve the reductive deoxygenation via various intermediates such as xanthate,[2] chloroformate,[3] etc.[4] have been done, the effective deoxygenation via esters which were more easily prepared from alcohols has been scarecely known.[5] We wish to report here an efficient transformation of esters to hydrocarbons using commercially available triphenylsilane.

We observed that the esters reacted with triphenylsilane(4 equiv.) in the presence of di-t-butylperoxide(DTBP)(1 equiv.) as a radical generator at 140 °C for 12 h to give the corresponding hydrocarbons (Table 1).

$$\mathrm{R'COOR} \xrightarrow[\Delta]{\mathrm{Ph_3SiH\ /\ DTBP}} \mathrm{RH}$$

The best results were obtained in the case of acetate(run 1) as ester compared with the other esters such as isobutyrate(run 3), pivalate(run 4), or

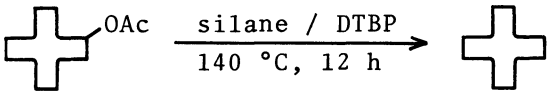
Table 1.

Run	Ester	Product	Yield/%	GLC yield/%
1			82	95
2			81	—
3			70	—
4			64	—
5			69	71
6	$n\text{-}C_{12}H_{25}OCCH_3$ (O)	$n\text{-}C_{12}H_{26}$	67	78
7	$PhCH_2C(Me)_2OCCH_3$ (O)	$PhCH_2CH(Me)_2$	43	54
8	$PhCH_2CH_2CH(Me)OCCH_3$ (O)	1-Phenylbutane	75	—
9	$n\text{-}C_8H_{17}CH(n\text{-}C_4H_9CH_2)OCCH_3$ (O)	Tetradecane	88	—

benzoate(run 5), which seemed to be prevented from the attack of silyl radical (see Scheme 2) due to their steric hindrance. As for alcoholic moiety, the yield of the reduction product decreased in the following order; secondary(run 1, 8, 9)

>primary(run 6) >tertiary alcohol(run 7). The fact that the reduction of secondary acetate proceeds almost quantitatively suggests that the direct transformation of acetylated sugar to deoxy sugar is promising.

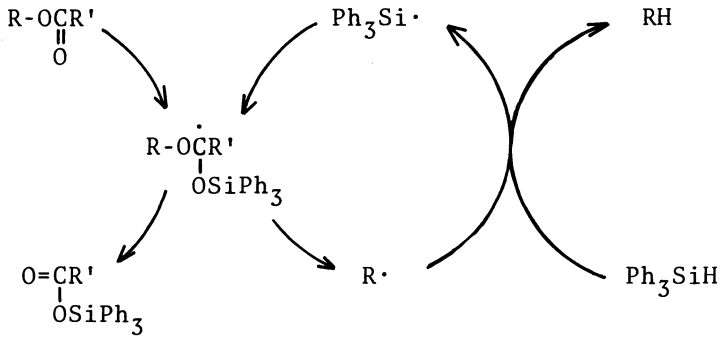
In this reaction, the choice of silane compounds is important. Thus, the reductive deoxygenation of cyclododecylacetate using tripropylsilane or diphenylmethylsilane instead of triphenylsilane gave poor yield as shown in Scheme 1.



silane	yield(GLC)/%
Pr_3SiH	18
Ph_2MeSiH	14

Scheme 1.

It was necessary to employ the excess of triphenylsilane(4 equiv.) to obtain the high yield, since the dimerization of silyl radical occurred competitively.[6] We found also that the use of catalytic amounts of DTBP(0.1 equiv.) gave similar results, although prolonged reaction time (≈24 h) was necessary.[7] However, neither azobisisobutyronitrile(AIBN) nor benzoylperoxide(BPO) could initiate the reaction. The plausible reaction mechanism is shown in Scheme 2.



Scheme 2.

A typical procedure is as follows. A mixture of cyclododecylacetate(400 mg, 1.77 mmol), triphenylsilane(1.84 g, 7.07 mmol) and DTBP(258 mg, 1.77 mmol) was heated at 140 °C for 12 h. Cyclododecane was isolated from the reaction mixture by silica gel column chromatography(hexane) in 82% yield.

As described above, the present reaction offers a new method for the effective deoxygenation of secondary alcohols to hydrocarbons under neutral conditions. Transformation of acylated sugars to deoxy sugars using this method will be reported in near future.

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6) Indeed, hexaphenyldisilane was isolated from the reaction mixture.

7) Treatment of cyclododecylacetate with triphenylsilane(4 equiv.) and DTBP(0.1 equiv.) at 140 °C for 24 h gave cyclododecane in 83% yield(GLC).

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