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A RADICAL DEOXYGENATION OF SECONDARY ALCOHOLS TO HYDROCARBONS BY USE OF TRIBUTYLTIN HYDRIDE

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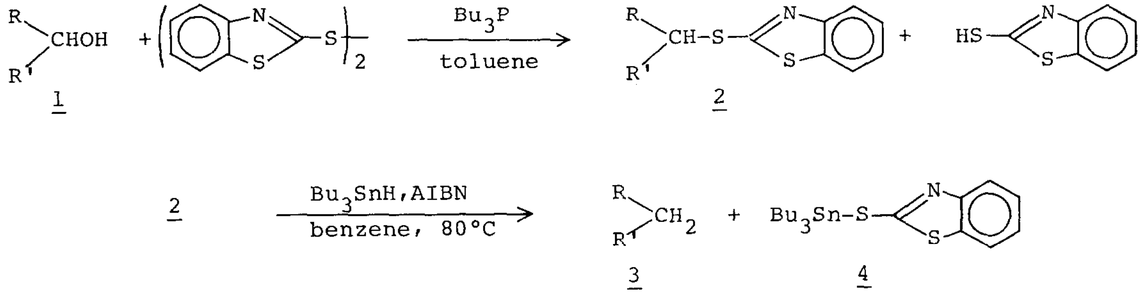
Abstract; Secondary alcohols 1 reacted with 2,2'-dibenzothiazolyldisulfide in the presence of tributylphosphine to give corresponding sulfides 2 in good yields. Sulfides 2 were subsequently desulfurized to hydrocarbons 3 with tributyltin hydride in radical conditions.

Ketones, carboxylic acids, and aldehydes can be reduced to alcohols with various reducing agents[1], but the reduction of the hydroxyl groups of alcohols to hydrocarbons seems to be not so easy, since alcohols are very stable toward common reducing agents. Therefore, it is necessary for the reduction with general methods to convert the hydroxyl groups to other functional groups[2]. On the other hand, some elegant methods for the replacement of hydroxyl groups of alcohols by hydrogen have been developed by Barton et al. through homolytic process[3]. These methods are effective to overcome the serious problems such as rearrangement. In a series of our study on radical process using tributyltin hydride[4], we wish to report here a facile radical deoxygenation of secondary alcohols.

Thus, we designed the strategy containing a couple of sulfurization and desulfurization outlined in the following scheme.



Namely, the alcohols 1 were transformed to benzothiazolylsulfides 2 by the combination of 2,2'-dibenzothiazolyldisulfide and tributylphosphine[5], and subsequently benzothiazolylsulfides 2, in which benzothiazolyl group worked as good leaving group in radical condition, were reduced with tributyltin hydride to corresponding hydrocarbons 3.

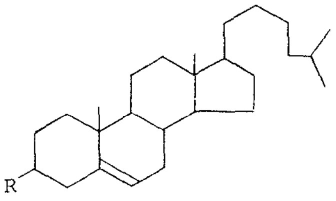
A typical experimental procedure is as follows. To a mixture of 2,2'-dibenzothiazolyldisulfide (3.82 g, 11.5 mmol) and diphenylethanol (1.63 g, 8.85 mmol) in toluene (30 ml) was added dropwise to a solution of tributylphosphine 2.86 ml, 11.5 mmol) in toluene (15 ml) in a period of 20 min. The reaction mixture was refluxed for 8 h. By the usual workup and purification by column chromatography on silica gel eluted by benzene 2b (2.71 g) was obtained in 92% yield. A mixture of 2b (0.71 g, 2.13 mmol) and tributyltin hydride (0.76 ml, 2.56 mmol) in benzene (6 ml) was refluxed for 5 h in the presence of a catalytic amount of azobisisobutyronitrile (AIBN). After removal of solvent under reduced pressure and purification by column chromatography eluted by benzene 0.34 g of 3b was afforded in 95% yield. The results are summarized in Table.

Reduction of benzothiazolylsulfides 2 proceeds smoothly to give corresponding hydrocarbons in good yield[6,7]. This method was applied to the alcohols 2f and 2g containing other functional groups. In those cases, protection of hydroxyl or carbonyl groups was not needed in the desulfurization step because of the neutral conditions.

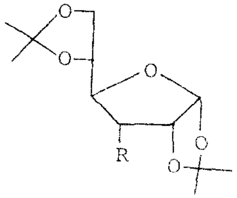
Furthermore, this reaction seems also applicable to the reduction of carbohydrates. Since, in general, many natural products are known as oxygenated or deoxygenated forms such as RNA and DNA, the potential utilities of our deoxygetation method is hifgly expected.

We applied to two cases i.e. cholesterol and sugar derivative, and could obtain the corresponding deoxygenated compounds, Cholest-5-ene 3h and deoxyglucofulanose derivative 3i in excellent yield.

Studies on this line and the applicayion to natural products are now in progress.

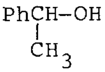
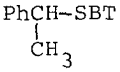
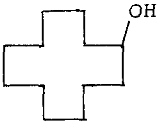
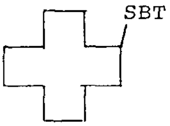
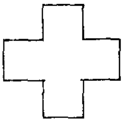
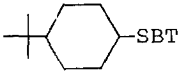
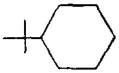
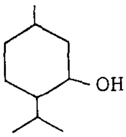
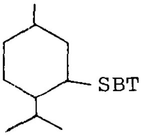
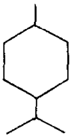
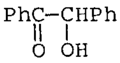
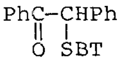
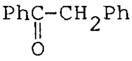
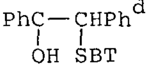
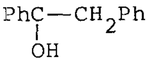


1h; R=OH
2h; R=SBT 87%
3h; R=H 98%



1i; R=OH
2i; R=SBT 87%
3i; R=H 89%

Table Preparation of sulfides 2 from secondary alcohols 1 and desulfurization of 2 by use of tributyltin hydride

	Alcohol 1	Sulfide 2	Yield (%)b)	Hydrocarbon 3	React time (h)	Yield (%)b)
a	 $\mathrm{Ph}\underset{\mathrm{CH_3}}{\underset{\mid}{\mathrm{C}}}\mathrm{H{-}OH}$	 $\mathrm{Ph}\underset{\mathrm{CH_3}}{\underset{\mid}{\mathrm{C}}}\mathrm{H{-}SBT}$ a)	90	$\mathrm{PhCH_2CH_3}$	1	90c)
b	$\mathrm{Ph_2CH{-}OH}$	$\mathrm{Ph_2CH{-}SBT}$	92	$\mathrm{Ph_2CH_2}$	5	95
c			78		14	89
d			58		4	87
e			92		4	67 (99)c)
f	 $\mathrm{Ph}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\underset{\mathrm{OH}}{\underset{\mid}{\mathrm{C}}}\mathrm{HPh}$	 $\mathrm{Ph}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\underset{\mathrm{SBT}}{\underset{\mid}{\mathrm{C}}}\mathrm{HPh}$	94	 $\mathrm{Ph}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}{-}\mathrm{CH_2Ph}$	5	94
g	————	 $\mathrm{Ph}\underset{\mathrm{OH}}{\underset{\mid}{\mathrm{C}}}{-}\underset{\mathrm{SBT}}{\underset{\mid}{\mathrm{C}}}\mathrm{HPh}$ d)	94	 $\mathrm{Ph}\underset{\mathrm{OH}}{\underset{\mid}{\mathrm{C}}}{-}\mathrm{CH_2Ph}$	3	99

a) BT=benzothiazole b) Isolated yield c) GLC yield d) Obtained by reduction of 2f with $\mathrm{NaBH_4}$

All new compounds obtained here had satisfactory spectral and analytical data. The structures of reduction products were fully confirmed by the comparison of the physical data with those of the authentic samples or reported data.

In conclusion, practical advantages of the present reduction method are as follows, (1) no side reaction such as rearrangement or disproportionation is observed in both sulfurization and desulfurization steps, (2) both of the reactions proceed smoothly under neutral conditions, and (3) yields of products are sufficiently high.

References and notes

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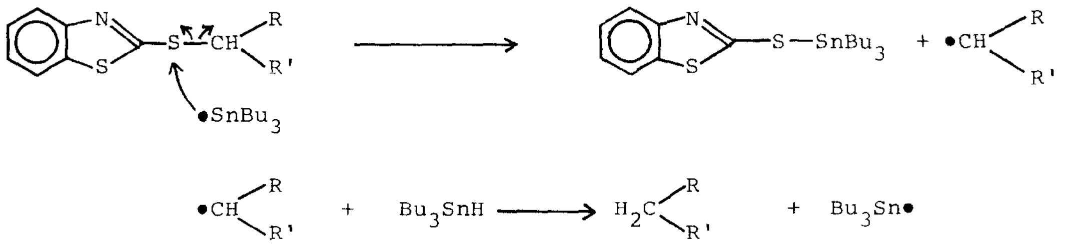
5. Original reaction was reported by Mukaiyama et al. Angew. Chem., Int. Ed. Engl., 15, 94 (1976). Other; I.Nakagawa, T.Hata, Tetrahedron Lett., 1409 (1975). K.H.M.Walker, Tetrahedron Lett., 4475 (1977).
6. It was reported that phenylselenides were reduced by tributyltin hydride, but phenylsulfides could not be reduced in the similar reaction conditions. D.L.J.Clive, G.Chittattu, C.K.Wong, J. Chem. Soc., Chem. Comm., 41 (1978). This suggests that the stability of alkyl radical or efficiency of leaving groups participates in the reactivity.
7. Thiostannane 4 could not be isolated in all cases because 4 was decomposed on silica gel column chromatography.
   Direct attack mechanism is considered as below based on the affinity of tin and sulfur atom.



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