An Improved Procedure for Preparation of *t*-Butyl Alcohol-O-*d*

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Alcohols in which the hydroxyl hydrogen is replaced by deuterium have been exceedingly valuable in mechanistic organic chemistry, particularly in the study of carbanions by base-catalyzed hydrogen–deuterium exchange.[1] The labeled alcohols are normally produced using D_2O as the source of deuterium which, because of its cost, must be used as the basis for meaningful yield calculations. The best procedures utilize both deuterium atoms of the D_2O molecule in some irreversible process, producing deuterium-free byproducts which are easily separated. Examples are the hydrolysis of alkoxysilanes[2,3] and carbonate[4] and orthoformate[5] esters. These procedures are applicable to primary and secondary alcohols but have not been available for tertiary alcohols presumably, because of the complications caused by competing eliminations.

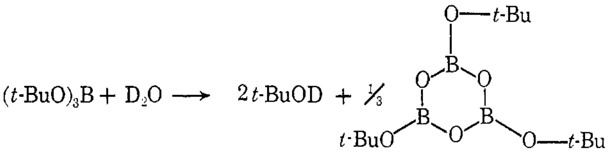
Traditionally, oxygen-deuterated tertiary alcohols have been prepared by direct exchange with D_2O.[6,7] This method is costly, time consuming, and, in the case of *t*-butyl alcohol, complicated by the water solubility of the alcohol. The alcohol and water must be separated after each exchange by distillation of the azeotropic mixture, which must eventually be dried. In our own laboratories we were, until recently, using saturated solutions of KF in D_2O to wash the alcohol and, although this gave a product of high deuterium content, it was only slightly less costly and time consuming than the distillation method.

Wolfe, Lee, and Campbell[8] have now published the first procedure using an ester hydrolysis. In theory, their basic hydrolysis of acetate and benzoate esters can produce 1 mol of alcohol for each mole of D_2O, 1 equiv being lost in the preliminary production of NaOD. In practice, the yield of alcohol, based on moles of D_2O used, was 5–9%. We would like to report a new procedure for the preparation of *t*-butyl alcohol-O-*d* from which molar yields (moles of alcohol × 100/moles of D_2O) of 75–150% have been obtained.

t-Butyl orthoborate can be obtained in good yield simply by refluxing boric acid in *t*-butyl alcohol–benzene with azeotropic removal of water.[9] Addition of D_2O to the ester gave *t*-butyl alcohol-O-*d*, which could be removed from the reaction mixture by distillation. In the presence of excess D_2O, the hydrolysis must be the simple reverse of esterification, from which a maximum molar yield of 82% could be expected if *t*-butyl alcohol was removed as the azeotrope, assuming that boric acid was dehydrated to give metaboric acid[10] (eq 1). In

$$(t\text{-BuO})_3B + 3.67D_2O \rightleftharpoons 3(t\text{-BuOD}\cdot 0.55D_2O) + DBO_2 \quad (1)$$

practice, a yield of 85% was obtained assuming an azeotropic composition of 36 mol % (13 wt %).[11] Hydrolysis in the presence of limited D_2O might be expected[12] to give the stoichiometry of eq 2. In theory



(2)

this could give up to 200% yield based on moles of D_2O. We have obtained a 150–175% yield using this modification.

Experimental Section

***t*-Butyl Orthoborate.**—This was prepared in yields of 75–80% by the procedure of Lippincott.[9]

Hydrolysis of *t*-Butyl Orthoborate Using Excess Deuterium Oxide.—The ester (362 g, 1.57 mol) was treated with deuterium oxide (94.5 g, 4.73 mol) under dry nitrogen.

The reaction mixture was heated cautiously with vigorous stirring until homogeneous and then refluxed for 5 hr. Simple distillation under nitrogen gave 345 g of the wet *t*-butyl alcohol-O-*d* (85% molar yield assuming azeotropic composition).

This was passed over a column of Linde 3A, 0.125-in. molecular sieves (170 g baked at 600° for 24 hr) and finally distilled from molecular sieves through a 1-m wire-spiral Dufton column to give 267 g (75% yield). Gc analysis on a 10 ft × 0.25 in. column of SE-30 on Chromosorb W at 100° showed only *t*-butyl alcohol. No significant (less than 0.005%) amount of *t*-butyl orthoborate could be found and nmr measurements on the neat alcohol showed only the single resonance of the *t*-butyl group and a small hydroxyl hydrogen peak expected for about 1% contamination by undeuterated alcohol. Combustion analysis for deuterium[13] showed 0.985 atom of D.

Hydrolysis of *t*-Butyl Orthoborate Using Limited Deuterium Oxide.—A mixture of the ester (97.8 g, 0.426 mol) and deuterium oxide (8.5 g, 0.43 mol) was vigorously stirred for 15 hr in a bath held at 92°. The bath temperature was slowly raised and 55.7 g of product collected, bp 81–82°, 172 mol % as pure *t*-butyl alcohol-O-*d*, 150 mol % as azeotrope. Drying and distillation as before gave a product showing 0.98 atom of D by nmr. It was found important that the temperature of the oil bath be kept below 130°. In one experiment, in which the temperature was allowed to go higher, a decomposition with vigorous gas evolution was observed and a product of lower deuterium content was obtained. Presumably elimination of isobutylene occurred.

In the normal reaction, the residue in the distillation flask solidified on cooling. The white, crystalline solid could be purified by recrystallization from hexane in a drybox, mp 66–69°. Its infrared spectrum showed peaks at 2980, 1474, 1370, 1365, 1250, and 1182 and 720 cm^{-1} as expected for *t*-butoxyboroxin.[14,15] A satisfactory analysis was not obtained, however, possibly owing to the hydrolytic instability of the compound.

Registry No.—*t*-Butyl alcohol-O-*d*, 3972-25-6.

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[11] L. H. Horsley, Ed., "Azeotropic Data," American Chemical Society, Washington, D. C., 1952, p 8. This reference lists the composition of the *t*-butyl alcohol–water azeotrope as 11.8 wt % or 35.5 mol % water. We have assumed that the mol % D_2O in a mixture of D_2O and *t*-butyl alcohol-O-*d* is also 35.5, leading to a calculated 12.8 wt % D_2O in the deuterated azeotropic mixture. The figure of 85% was obtained from the expression yield (345 g)(87.2%)/(75.1 g/mol)(4.73 mol) = 84.7%.

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