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Formation and instability of an α-acetoxyborane

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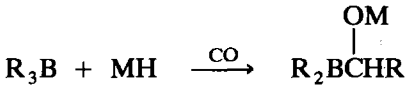
Abstract

The initial product from carbonylation of lithium triethylborohydride reacts with acetyl chloride, forming an α-acetoxyborane. This is unstable and rearranges slowly at room temperature or rapidly on heating, resulting in migration of a second ethyl group from boron to carbon. Subsequent oxidation affords 3-pentanol.

1. Introduction

Hydride-induced carbonylation of organoboranes [1,2] and carbonylation of trialkylborohydrides [3] are postulated to afford dialkylborylmethylates (I) formed by migration of one alkyl group from boron to carbon (eqn. (1)).



$$R_3B + MH \xrightarrow{CO} R_2B\overset{\overset{\displaystyle OM}{|}}{C}HR \qquad (1)$$

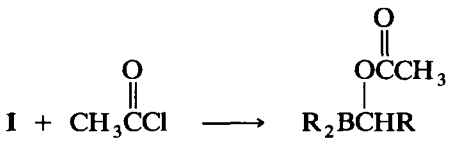
(I)

$MH = LiH, NaH, KH, LiAl(OCH_3)_3H,$

$LiAl[OC(CH_3)_3]_3H, KB[OCH(CH_3)_2]_3H$

Subsequently, I may be converted to various products: aldehydes [4], primary alcohols [4], dialkylmethanols [5], and homologated organoboranes [6].

As part of a program to study systematically the reactivity of I, examination of its reaction with acetyl chloride was undertaken. It was anticipated that this might lead to a method for preparing a novel class of compounds, the α-acetoxyboranes (II) (eqn. (2)).

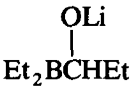


$$I + CH_3\overset{\overset{\displaystyle O}{\|}}{C}Cl \longrightarrow R_2B\overset{\overset{\overset{\displaystyle O}{\|}}{\displaystyle OCCH_3}}{\overset{|}{C}}HR \qquad (2)$$

(II)

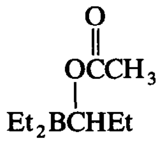
2. Results and discussion

Lithium triethylborohydride was chosen for this study. Carbonylation presumably leads to III (I, R = Et and M = Li), reaction of which with acetyl chloride might yield (1-acetoxypropyl)diethylborane, IV (II, R = Et).



$$Et_2B\overset{\overset{\displaystyle OLi}{|}}{C}HEt$$

(III)



$$Et_2B\overset{\overset{\overset{\displaystyle O}{\|}}{\displaystyle OCCH_3}}{\overset{|}{C}}HEt$$

(IV)

Carbonylation of the trialkylborohydride in tetrahydrofuran (THF) solution at room temperature was followed by addition of one molar equivalent of acetyl chloride. The solution turned pale green, then bright yellow, and a precipitate (presumably lithium chloride) formed. Oxidation using alkaline hydrogen peroxide and GLC analysis revealed a 52% yield of 3-pentanol. A small amount of propanal was also observed, but quantitative analysis was not performed due to the probability of side reactions such as the aldol condensation being promoted by the oxidation conditions.

Since III is known to give propanal upon oxidation [4] and since IV is similar in structure to III, the formation of propanal is consistent with conversion of III to IV. However, formation of 3-pentanol indicates partial rearrangement with migration of a second ethyl

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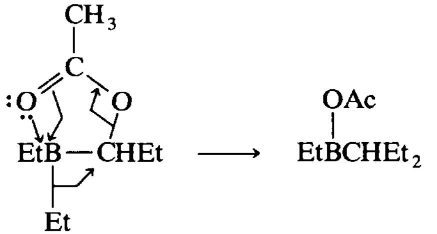
group from boron to carbon. Such a rearrangement may be rationalized in terms of a cyclic transition state involving Lewis acid–base interaction of the boron and carbonyl oxygen of **IV** (eqn. (3)). The acetoxyborane **V** accounts for 3-pentanol as an oxidation product.



(3)

(IV) **(V)**

In an attempt to minimize rearrangement, the reaction was repeated with cooling to −78°C before addition of the acetyl chloride. Oxidation and GLC analysis revealed only 18% of 3-pentanol and a substantially larger amount of propanal.

The previous reaction, with cooling before addition of acetyl chloride, was repeated in order to characterize the products by NMR. After warming to room temperature, the THF solution was examined by ^{11}B NMR. There was a broad resonance at 11.9 ppm and a much less intense resonance at 54.3 ppm. The former, indicating considerable "ate" complex character, is attributed to **IV**; the latter, indicating a borinate, arises from developing **V**.

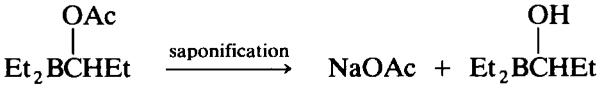
To facilitate examination by ^{1}H NMR, the THF solvent was removed using a water aspirator. The yellow solid remaining was treated with carbon tetrachloride, and the material that did not dissolve (presumably lithium chloride) was allowed to settle. Examination of the bright yellow supernatant liquid showed a triplet, 1H, at 4.0 ppm and an intense singlet, 3H, at 2.2 ppm. These resonances may be ascribed to the methine [7] and the acetate methyl group in **IV**.

After remaining at room temperature for 19 days, the carbon tetrachloride solution was again examined by NMR. ^{1}H NMR now showed that the 1H triplet at 4.0 ppm had disappeared. There was still an intense absorption attributed to acetyl methyl at 2.2 ppm, but all other peaks were in the range 0.6–1.8 ppm. This indicates no electron-withdrawing substituent in the α-position and is consistent with formation of **V**. These results are virtually identical to those obtained when a fresh carbon tetrachloride solution was heated to reflux.

^{11}B NMR after 19 days showed a broad resonance at 59.2 ppm and a less intense resonance at 8.4 ppm. Again, virtually the same results were obtained when a fresh carbon tetrachloride solution was heated. The former resonance is attributed to **V**; the species giving rise to the latter has not been identified.

To ascertain the extent of rearrangement, it was of interest to determine the yield of 3-pentanol upon oxidation after heating. Accordingly, lithium triethylborohydride was carbonylated and treated with acetyl chloride as before. The bright yellow solution was heated under reflux for 2 h, then oxidized; addition of sodium hydroxide changed the color to orange; it reverted to yellow on addition of hydrogen peroxide. The yield (GLC) of 3-pentanol was 79%. There was no propanal or 1-propanol, indicating that no **IV** remained after heating.

In a similar experiment, the solution was heated under reflux for 2.5 h with aqueous sodium hydroxide, then oxidized to give 81% 3-pentanol and 12% 1-propanol. A plausible pathway for the 1-propanol formation is shown in eqns. (4) and (5). The hydrolysis of (1-hydroxypropyl)diethylborane **(VI)** presumably occurs as in the same reaction of **III** [4]. Obviously, rearrangement (eqn. (3)) is faster than saponification.



$$\underset{\textbf{(IV)}}{\mathrm{Et_2B\overset{\overset{\displaystyle OAc}{|}}{C}HEt}} \xrightarrow{\text{saponification}} \mathrm{NaOAc} + \underset{\textbf{(VI)}}{\mathrm{Et_2B\overset{\overset{\displaystyle OH}{|}}{C}HEt}} \qquad (4)$$

$$\textbf{VI} \xrightarrow{\text{hydrolysis}} \text{1-propanol} \qquad (5)$$

This work shows that α-acetoxyboranes such as **IV** can be prepared. However, these are unstable, rearranging slowly at room temperature or rapidly on heating (eqn. (3)). Subsequent oxidation completes synthesis of the corresponding dialkylmethanol in good yield, but this is accomplished more economically using another method [5].

3. Experimental details

3.1. General comments

The techniques used for handling air- and water-sensitive materials are described elsewhere [8]. The automatic gasimeter [8,9] was a commercial model obtained from Delmar Scientific Laboratories, Inc., Maywood, IL. All glassware was dried at 140°C for at least 4 h, assembled hot, and cooled under a stream of prepurified nitrogen. The reaction flasks were fitted with sidearms capped with rubber septa.

3.2. Materials

All materials were kept under an atmosphere of prepurified nitrogen in Teflon stopcock-protected ampoules. THF was distilled from lithium aluminum hydride. Acetyl chloride was distilled from calcium hydride. Lithium triethylborohydride was prepared as described previously [10].

3.3. Analyses

GLC analyses were carried out on a Hewlett-Packard 5752B chromatograph using 0.25 in OD columns 1.8 m long filled with 10% Carbowax 20M on 60/80 AW-DMCS Chromosorb W.

^{1}H NMR spectra were obtained using a Varian T-60 spectrometer.

^{11}B NMR spectra were recorded using a Varian XL-100-15 spectrometer (32.1 MHz) fitted with a Nicolet 1080 data acquisition system. All spectra were recorded in the CW mode and were signal averaged 4–25 scans. The spectra were referenced to boron trifluoride etherate (0 ppm) using either ^{2}H internal or ^{19}F external locks.

3.4. Carbonylation of lithium triethylborohydride

A dry 200-ml flask with magnetic stirring bar and septum inlet was attached to an automatic gasimeter and the system was flushed with nitrogen. The flask was immersed in a water bath and 6.71 ml of 1.49 M lithium triethylborohydride in THF (10.0 mmol) was introduced. After flushing the system with carbon monoxide, vigorous stirring was begun. Complete carbon monoxide absorption required 6–17 min. After absorption ceased, the system was flushed with nitrogen. The foregoing procedure was followed prior to (a)–(e) below.

3.5. Preparation, observation and reactivity of (1-acetoxypropyl)diethylborane (IV)

(a) Acetyl chloride (0.71 ml, 10 mmol) was added at 25°C. The solution turned pale green, then bright yellow and a precipitate (presumably lithium chloride) formed. After 1 h, 3.5 ml of 3 N aqueous sodium hydroxide and 4 ml of 30% hydrogen peroxide were added (**CAUTION**: exothermic!). After 1 h, 5 mmol (1.30 ml) of *n*-tetradecane was added as an internal standard; then 7.5 g of anhydrous potassium carbonate was added and dissolved. The THF layer was separated and dried over anhydrous magnesium sulfate, then powdered 3 Å molecular sieves. GLC analysis showed 5.2 mmol 3-pentanol, and propanal was observed in the trace.

(b) The flask was immersed in a dry ice–acetone bath at −78°C and acetyl chloride (0.71 ml, 10 mmol) was added. The solution turned pale green. After 20 min the cold bath was removed. The solution became bright yellow as it warmed. After 1 h, oxidation and GLC analysis were carried out as in (a). Only 1.8 mmol of 3-pentanol was found and considerable propanal was observed.

(c) The procedure of (b) was followed except the yellow solution was heated to reflux 2.5 h after addition of the sodium hydroxide, then oxidized. GLC analysis showed 1.2 mmol of 1-propanol and 8.1 mmol of 3-pentanol.

(d) The procedure of (c) was followed except heating to reflux was carried out before addition of sodium hydroxide. Oxidation and GLC analysis revealed 7.9 mmol of 3-pentanol and no 1-propanol or propanal.

(e) The procedure was as in (b). After reaching 25°C, the THF was removed using a water aspirator, 10 ml of carbon tetrachloride was added, and the insoluble solid was allowed to settle. ^{11}B NMR: 11.9 (s, br.); 54.3 (s, br., less intense). ^{1}H NMR: 4.0 (t, $J = 8$ Hz, 1H); 2.2 (intense s, 3H); 2.0 (weak s); 0.0–1.8 (complex group of peaks). After heating under reflux for 2 h, the solution was examined again. ^{11}B NMR: 59.3 (s, br); 9.6 (s, br., less intense). ^{1}H NMR: 2.2 (s); 0.6–1.8 (complex group of peaks). The NMR sample taken before heating showed spectra virtually identical to the latter set after 19 days at 25°C.

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