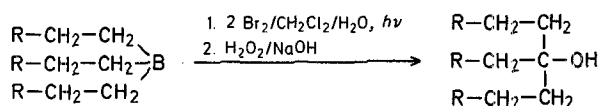


The Light-Induced Reaction of Hexyldialkylboranes with Bromine in the Presence of Water. A New and Convenient Synthesis of Tertiary Alcohols Including Those Containing Functional Substituents

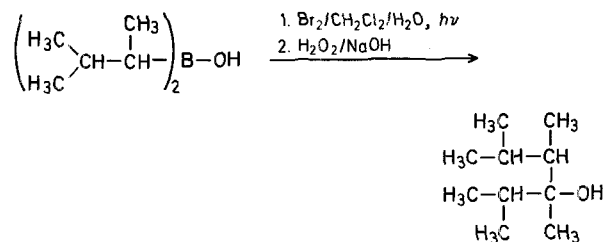
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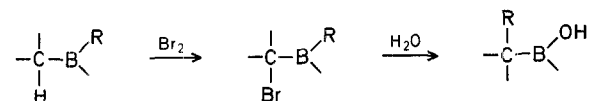
We previously reported that the light-induced bromination of trialkylboranes in the presence of water provides a new simple procedure for the union of three alkyl groups to produce tertiary alcohols¹.



The light-induced bromination of dialkylborinic acid in the presence of water also provides a convenient method for the combination of the two alkyl groups to produce highly substituted tertiary alcohols².



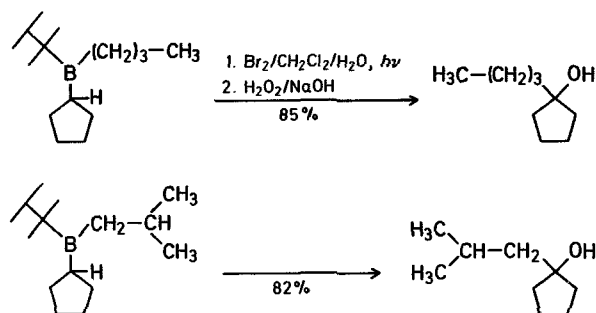
The light-induced reactions of bromine with organoboranes proceed through rapid α -bromination followed by a facile migration of an alkyl group from boron to carbon^{1,3}.



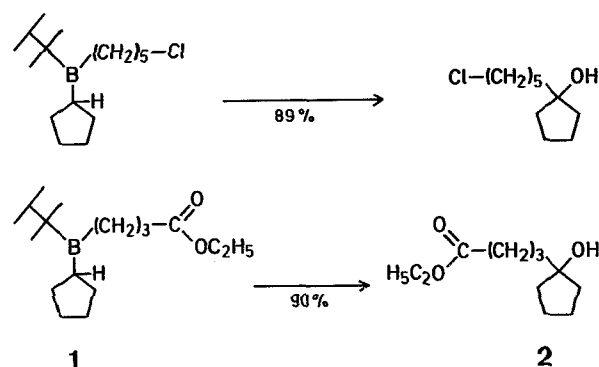
Symmetrical trialkylboranes and dialkylborinic acids were utilized in the initial investigation. Therefore, two or three identical alkyl groups were combined. If the union of two different groups were possible, the bromination-oxidation reaction of organoboranes would provide a major new route for the synthesis of carbon structures. This would be especially true if it were possible to include functional substituents in the alkyl groups.

Among the numerous unsymmetrical organoboranes that might be investigated, the thexyldialkylboranes appeared to be especially promising for the following reasons. They are readily available from olefins via stepwise hydroboration^{4,5}. Functional substituents in the olefins are readily accommodated⁵. Furthermore, the thexyl group does not contain any hydrogen atoms α to the boron atom. Finally, the migration of the bulky thexyl group is very sluggish⁵.

Representative thexylboranes were prepared. They react readily with bromine under the influence of normal laboratory light. Alkaline hydrogen peroxide oxidation of the products gave the corresponding alcohols in good yields.



Functionally substituted alcohols would also be obtained in excellent yields from the corresponding organoboranes.



These results are summarized in Table 1.

Interestingly, an excess amount of bromine (30 mmol) was required to obtain the maximum yield (90%) of 1-(3-ethoxycarbonylpropyl)-cyclopentanol (2) in the bromination of thexyl-(3-ethoxycarbonylpropyl)-cyclopentylborane (1) (10 mmol). When an equivalent amount of bromine (10 mmol) was used, 2,3-dimethyl-2,3-dibromobutane (3.2 mmol) was observed by G.L.C. analysis along with thexyl alcohol (4.4 mmol), cyclopentanol (4.6 mmol), and 2 (2.5 mmol)⁶. However, the bromination of thexyl-(10-methoxycarbonyldecyl)-cyclopentylborane (3) with one equivalent of bromine occurred in the normal manner to give, upon oxidation, an excellent yield of 1-(10-methoxycarbonyldecyl)-cyclopentanol. These results indicate that bromine attacked both the α (cyclopentyl) and the β (thexyl) tertiary hydrogens⁷ in 1, but only the α (cyclopentyl) tertiary hydrogen in 3. This loss of regiospecific nature of the α -bromination

Table 1. The Bromination-Oxidation of Thexyldialkylboranes^a

Thexyldialkylboranes from olefins	Products ^b	Yield ^c %
1-butene, cyclopentene	1- <i>n</i> -butylcyclopentanol	85
<i>iso</i> -butene, cyclopentene	1- <i>iso</i> -butylcyclopentanol	82 (70)
1-hexene, cyclopentene	1- <i>n</i> -hexylcyclopentanol	94 (82)
1-butene, cyclohexene	1- <i>n</i> -butylcyclohexanol	51
5-chloro-1-pentene, cyclopentene	1-(5-chloropentyl)-cyclopentanol	89
ethyl 3-butenolate, cyclopentene ^{d,e}	1-(3-ethoxycarbonylpropyl)-cyclopentanol ^f	90 (72)
methyl 10-undecenoate, cyclopentene ^d	1-(10-methoxycarbonyldecyl)-cyclopentanol ^g	(75)

^a Organoborane (10 mmol) and bromine (11 mmol) were allowed to react in dichloromethane/water at 20–25°, and the resulting mixture was oxidized with alkaline hydrogen peroxide using ethanol as a co-solvent, unless otherwise indicated.

^b Structure assigned by comparison with an authentic sample or on the basis of analytical data and spectra. Thexyl alcohol, 2,3-dimethyl-2-butanol, was also produced (8–9 mmol), unless otherwise indicated.

^c By G.L.C. analysis, isolated yield in parentheses.

^d Bromine was added under the influence of a 150 W light bulb at 0–5°, and the resultant mixture was neutralized with aqueous NaOH then oxidized with NaOAc/H₂O₂ to avoid the hydrolysis of the ester group.

^e Excess bromine (30 mmol) was used.

^f 2,3-Dimethyl-2,3-dibromobutane (8.2 mmol) was obtained instead of thexyl alcohol.

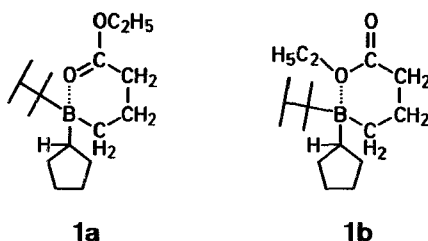
^g This alcohol underwent dehydration during distillation and the corresponding olefins were isolated.

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reaction could possibly be due to an intramolecular boron-oxygen coordination, which would be expected to occur quite favorably in **1** (**1a**, **1b**), but not in **3**.

In fact, the I.R. spectrum of **1** showed two absorptions in the carbonyl region (1645 , 1735 cm^{-1})⁸. Presently, it is not possible to state whether the loss of regiospecific attack is a reflection of the steric or electronic effect of the coordination.



1-*n*-Hexylcyclopentanol:

A dry 1000-ml flask, equipped with a septum inlet, thermometer well, pressure-equalizing dropping funnel, reflux condenser, and magnetic stirrer was flushed with dry nitrogen and maintained under a positive nitrogen pressure. The flask was cooled to $0-5^{\circ}$ and charged with dry tetrahydrofuran (200 ml) and a 2.90 *M* solution (71.5 ml) of borane (200 mmol of BH_3) in tetrahydrofuran. Thexylborane was formed by the dropwise addition of 2,3-dimethyl-2-butene (23.7 ml, 200 mmol). Stirring was continued for 1 hr at $0-5^{\circ}$ to ensure completion of the reaction. Cyclopentene (17.7 ml, 200 mmol) was added and allowed to react for 1 hr at $0-5^{\circ}$. Then 1-hexene (25 ml, 200 mmol) was added and the resulting mixture was stirred for 1 hr at $0-5^{\circ}$ followed by 1 hr at $20-25^{\circ}$. Tetrahydrofuran was removed at reduced pressure and replaced with dichloromethane (200 ml) and water (100 ml). Bromine (11 ml, 215 mmol) was then added at $0-5^{\circ}$ and the mixture was stirred at $20-25^{\circ}$ until the bromine color disappeared (~ 20 min). Sodium hydroxide (35 g, 870 mmol) was then added followed by ethanol (200 ml). Oxidation was accomplished by adding 30% aqueous hydrogen peroxide (66 ml) while maintaining a temperature below 10° . The reaction mixture was then heated to reflux ($\sim 42^{\circ}$) and maintained at reflux for 1 hr. After cooling, the aqueous layer was saturated with sodium chloride and the organic layer was separated, washed once with saturated aqueous sodium chloride, and dried with anhydrous potassium carbonate. The solvent was removed and the residue distilled in vacuo; yield: 27.8 g (82%); b.p. $83-84^{\circ}/2.4\text{ mm}$; n_D^{20} : 1.4582 (Ref.⁹, n_D^{25} : 1.4562).

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- ⁶ Ethyl 4-hydroxybutanoate was also produced. However, the precise yield was not determined because of the instability of the product upon G. L. C. analysis; H. C. BROWN, K. A. KEBLYS, *J. Org. Chem.* **31**, 485 (1966).
- ⁷ The attack of bromine at the β tertiary hydrogen would produce the corresponding β -bromoorganoborane, which would undergo β -elimination to give 2,3-dimethyl-2-butene and 3-ethoxycarbonylpropyl-cyclopentyl-boron bromide. The addition of bromine to this olefin would produce 2,3-dimethyl-2,3-dibromobutane.
- ⁸ The absorptions at 1645 cm^{-1} and 1735 cm^{-1} correspond to the structures **1a** and **1b**, respectively; L. A. DUNCANSON et al., *J. Chem. Soc.* **1958**, 3652.
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