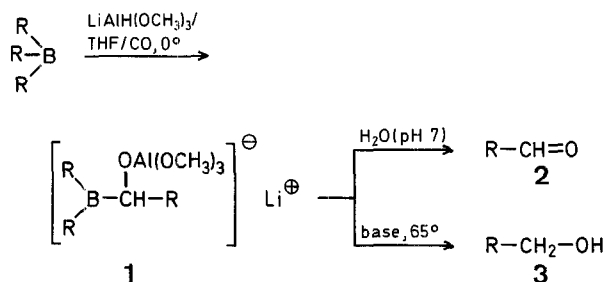


# Hydride-Induced Carbonylation of Trialkylboranes Followed by Treatment with Acid and Oxidation. A New Synthesis of Dialkylcarbinols under Mild Conditions

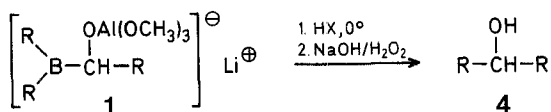
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Carbonylation of trialkylboranes using lithium trimethoxyaluminumhydride<sup>1,2</sup> provides an intermediate, presumably **1**, which can be easily converted to the corresponding one-carbon homologated aldehydes **2** or methylols **3**<sup>3,4</sup>.

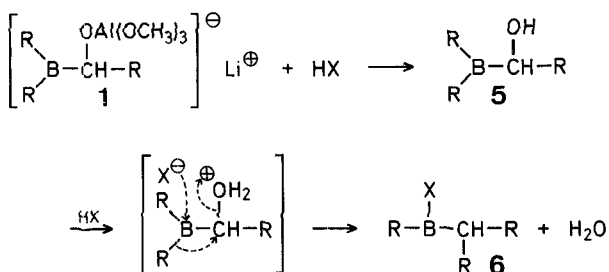


We wish to report that treatment of **1** with acid under very mild conditions causes migration of a second alkyl group from boron to carbon. Subsequent oxidation gives the corresponding dialkylcarbinols **4**.



The reaction appears to be quite general, proceeding satisfactorily for the representative trialkylboranes examined. Reaction conditions are extremely mild, and the successive steps are conveniently carried out in one flask without isolation of intermediates. Concentrated hydrochloric acid can generally be used to effect transfer of the second group. However, even acetic acid at 0° is sufficient to promote this transformation in most cases. The experimental results are summarized in the Table.

A possible mechanism is analogous to that of the  $\alpha$ -bromination transfer reaction<sup>5</sup>.



Acidification of **1** presumably gives the  $\alpha$ -hydroxyborane **5**. Protonation of **5** and subsequent nucleophilic attack at boron results in migration of an alkyl group with concomitant loss of water to form **6**, which is easily oxidized to give **4**.

The reaction conditions are quite mild relative to those of our previously reported method for conversion of trialkyl-

**Table.** Conversion of Olefins into Dialkylcarbinols via Carbonylation-Acidification-Oxidation of Trialkylboranes

Olefin	Amount of R <sub>3</sub> B [mmol]	Product	Acid	Yield [%] <sup>a</sup>	Physical data	Lit. values
ethylene	10	3-pentanol	CH <sub>3</sub> COOH	98		
1-octene	10	9-heptadecanol	HCl	78 <sup>b</sup>		
2-butene	10	3,5-dimethyl-4-heptanol	HCl	88	n <sub>D</sub> <sup>20</sup> : 1.4380	1.4378 <sup>10</sup>
	50		HCl	82 <sup>c</sup>		
isobutylene	10	2,6-dimethyl-4-heptanol	CH <sub>3</sub> COOH	81		
	10		HCl	84		
cyclohexene	10	dicyclohexylmethanol	CH <sub>3</sub> COOH	85	m.p. 62–64°	66° <sup>12</sup>
	10		HCl	86		
	50		HCl	80 <sup>c</sup>		
norbornene	10	bis[2-norbornyl]methanol	CH <sub>3</sub> COOH	40	m.p. 78–82°	
	10		HCl	87		
	50		HCl	85 <sup>c</sup>		

<sup>a</sup> Determined by G.L.C. except where otherwise indicated; G.L.C. conditions: 10% Carbowax 20M or OV-225 on Chromosorb W, 6 ft × 0.25 in.

<sup>b</sup> The product contains 9% of an isomeric product arising from the 2-octyl groups present in the organoborane.

<sup>c</sup> Yield of isolated product; satisfactory analytical data obtained.

boranes to dialkylcarbinols<sup>6</sup>. This new procedure appears to offer an attractive alternative to syntheses employing acyl carbanion equivalents<sup>7</sup>.

All glassware was dried at 140° for at least 4 h before use. With the exception of carbonylations, all reactions were carried out under an atmosphere of prepurified nitrogen. During carbonylation, the reaction temperature must be maintained at 0° or below until after addition of the acid to avoid side reactions which lead to difficulties in product purification. Addition of the acid requires use of a syringe with a Teflon needle to avoid introduction of metal ions which catalyze the decomposition of hydrogen peroxide (Fenton's reaction).

### 3,5-Dimethyl-4-heptanol:

An automatic gasimeter<sup>8,9</sup> is assembled, using a 300-ml generator flask and a 500-ml reaction flask. In the generator flask is placed 95–98% sulfuric acid (150 ml) and the generator flask maintained at 90°. The buret is filled with anhydrous formic acid. The system is flushed with nitrogen and the reaction flask is immersed in an ice/water bath. The reactor is charged with tetrahydrofuran (30 ml) and borane: tetrahydrofuran (20.5 ml of a 2.55 molar solution, 50 mmol). To the solution, maintained at 0°, is added *cis*-2-butene (9.3 g, 165 mmol). The solution is stirred for 0.5 h to insure complete hydroboration. With stirring stopped, lithium trimethoxyaluminumhydride in tetrahydrofuran (78.2 ml of a 0.77 molar solution, 60 mmol) is added using a double-ended needle. The system is flushed with carbon monoxide by injecting formic acid (2 ml) into the sulfuric acid with a syringe. Carbonylation is initiated by vigorous stirring of the reaction mixture. Absorption of carbon monoxide at 0° requires about 40 min. The system is then flushed with nitrogen and concentrated hydrochloric acid (20 ml) is added. After 1 h, aqueous sodium hydroxide (120 ml of a 3 normal solution) is added, the solution is brought to 25°, and 30% hydrogen peroxide (20 ml) is added dropwise with caution (*exothermic reaction!*). Stirring is continued for 2 h. The reaction mixture is poured into water (150 ml). The mixture is extracted with pentane (200 ml), which is back extracted with water (3 × 150 ml) to remove 2-butanol and tetrahydrofuran. Removal of the pentane using a rotary evaporator gives pure 3,5-dimethyl-4-heptanol; yield: 5.95 g (82%); n<sub>D</sub><sup>20</sup>: 1.4380<sup>10</sup>; >99% pure by G.L.C.<sup>11</sup>.

### Dicyclohexylmethanol and Bis[2-norbornyl]methanol:

The procedures are essentially identical to that given above. Removal of cyclohexanol and *exo*-norborneol is accomplished by heating

at 0.2–0.3 torr. The cyclohexanol simply boils away leaving pure dicyclohexylmethanol; yield: 7.84 g (80%); m.p. 62–64° [Lit.<sup>12</sup>, 66°]. *Exo*-norborneol is sublimed into a cooled receiver, leaving pure bis[2-norbornyl]methanol; yield: 9.36 g (85%); m.p. 76–82°<sup>13</sup>; 99% pure by G.L.C.<sup>11</sup>.

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<sup>9</sup> A commercial model from Delmar Scientific Laboratories, Inc., Maywood, Illinois, was used for this study. An improved model is now available from Ace Glass, Inc., Vineland, New Jersey.

<sup>10</sup> Material 99% pure from Chemical Samples Company has n<sub>D</sub><sup>20</sup>: 1.4378. A value of 1.4283 given in *Dictionary of Organic Compounds* is apparently erroneous.

<sup>11</sup> G.L.C. conditions: 10% OV-225 on Chromosorb W; 6 ft × 0.25 in.

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<sup>13</sup> The wide melting point range is apparently due to a mixture of diastereomers.