

THE REACTION OF TRIALKYLBORANES WITH α -METHOXYVINYL LITHIUM

A NOVEL ROUTE TO DIALKYL METHYL CARBINOLS

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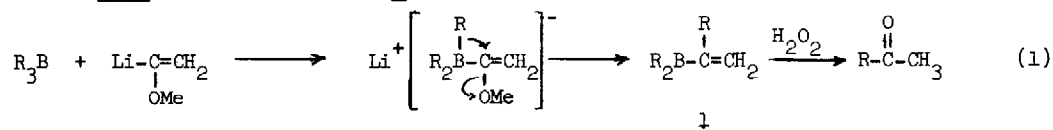
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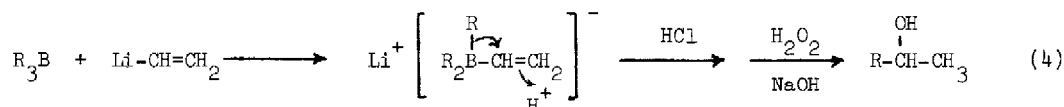
Trialkylboranes react rapidly with α -methoxyvinyl lithium (MVL) at -80°C to transfer one alkyl group from boron to carbon and displace the methoxy group. This leads to the formation of a lithium dialkylalkoxyvinylborate salt. This complex is extremely reactive towards protic media and treatment with dilute HCl leads to a second transfer reaction. Subsequent oxidation gives dialkylmethylcarbinols in excellent yields.

The recent use of MVL^{1,2} as an acyl carbanion equivalent led us to consider extending its utility by using trialkylboranes as alkylating agents³. Initial complexation followed by alkyl group transfer and displacement of the methoxy group was expected to lead to the anti-Markovnikov borane 1. Subsequent oxidation was expected to give methyl

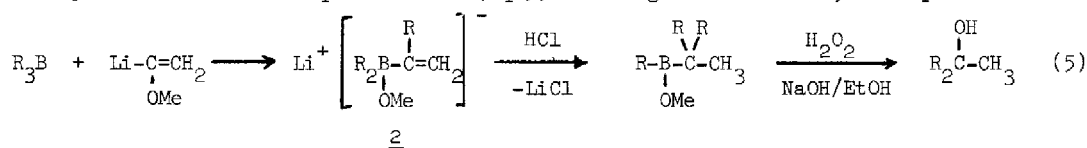


ketones (eq 1). Thus, treatment of tri-n-hexylborane with MVL followed by oxidation leads to an 82% yield of 2-octanone. However, attempts to extend this reaction to tricyclopentylborane lead to mixtures of dicyclopentylmethylcarbinol and methyl cyclopentylketone in a 1.4 to 1 ratio (eq 2). Other boranes gave similar results.

usually protonolyze to olefins⁵. Thus, we propose that the reaction of MVL with



trialkylboranes proceeds to give a lithium dialkylalkoxyvinylborate salt 2 which is extremely reactive towards aqueous media (eq 5). During the oxidation, the aqueous

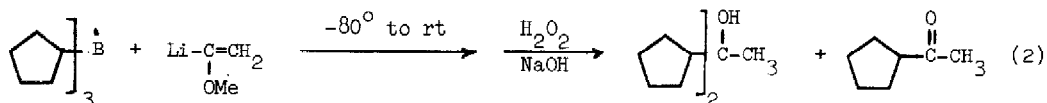


base catalyzes a transfer reaction in competition with the oxidation. Dilute acid is, as expected, more efficient in causing the second transfer and leads to good yields of the tertiary alcohols upon oxidation.

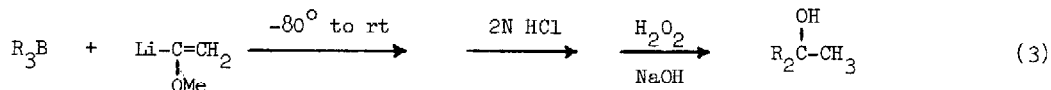
The rate of the second transfer reaction relative to oxidation appears to depend on the amount of steric strain present in the intermediate "ate" complex 2. When the alkyl groups on boron are relatively small (n-hexyl), the borane can be oxidized in good yield to the ketone. As the alkyl groups increase in size, steric strain in 2 increases causing the rate of transfer to become faster relative to oxidation.

The reactivity of what are essentially dialkylvinylboranes in the presence of lithium methoxide is somewhat surprising. We are actively investigating the reactions of these and other vinylboranes with a variety of electrophilic species.

The following procedure is representative. A dry 500 ml round bottom flask equipped with a septum inlet, reflux condenser and magnetic stirring bar is flushed with nitrogen. The flask is cooled to -80°C and 50 ml of THF followed by 6.20 ml (82.5 mmoles at -80°C) of methyl vinyl ether added⁶. Finally, 70.8 ml (75 mmoles) of t-butyl lithium is added. The flask is allowed to warm up and stirred until the yellow color disappears. The flask is cooled to -80°C again and 12.4 ml (50 mmoles) of tri-iso-butylborane added⁷. The solution is stirred for 10 min. while it warms to room temperature. To this solution is added 62.5 ml of 2N HCl. The solution is stirred for 30 min. then oxidized with 28 ml of 30% hydrogen peroxide and 62.5 ml of 3N sodium hydroxide using ethanol as a cosolvent. The mixture is heated under reflux for one hour,



In view of the anomalous reactivity of what we considered to be a vinylborane, we undertook a systematic investigation of this reaction. We quickly found the intermediate to be extraordinarily reactive towards protic media. Thus while treatment with base during the oxidation leads to mixtures of alcohols and ketones, treatment with 2N HCl for 30 min. followed by oxidation leads to excellent yields of dialkylmethylcarbinols (eq 3).



The results for a representative series of trialkylboranes are summarized in Table I.

Table I. The reaction of trialkylboranes with MVL for the synthesis of dialkylmethylcarbinols.

Trialkylborane ^a	Dialkylmethylcarbinol ^b	Yield ^c
R ₃ B, R=		%
<u>n</u> -Hexyl	Di- <u>n</u> -hexylmethylcarbinol	100
<u>iso</u> -Butyl	Di- <u>iso</u> -butylmethylcarbinol	94 (77) ^d
<u>sec</u> -Butyl	Di- <u>sec</u> -butylmethylcarbinol	92
Cyclopentyl	Dicyclopentylmethylcarbinol	87
Cyclohexyl	Dicyclohexylmethylcarbinol	94

a) 5 mmole of the borane added to 7.5 mmole of MVL at -80° ; allowed to warm to rt., treated with 2N HCl for 30 min., then oxidized in the usual manner with NaOH/EtOH/H₂O₂.

b) All compounds gave satisfactory spectral data or their physical properties agreed with the literature where available.

c) Yield by VPC.

d) Isolated yield.

The reactivity of the intermediates described herein is similar to the reactivity of lithium trialkylvinylborates. These salts have previously been reported to undergo transfer reactions in the presence of acid⁴ (eq 4), in contrast to vinylboranes which

extracted with petroleum ether, dried ($MgSO_4$), and the solvent removed under vacuum. Distillation through a short Vigreux column gives 6.06 g (77%) of 2,4,6-trimethyl-4-heptanol (di-iso-butylmethylcarbinol), bp 96-98 (28 mm), (lit.⁸ 94-96 (25 mm)).

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