Tetrahedron Letters,Vol.26,No.18,pp 2187-2190,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

Ultrasonics in Organoborane Chemistry. A Novel and Powerful Method for Rapid Hydroboration

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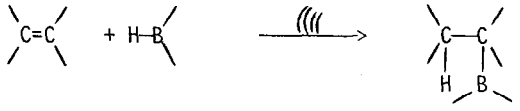
Abstract: Ultrasound enhances remarkably the rates of certain hydroborations which are slow under normal conditions.

Organoboranes are highly valuable intermediates in organic syntheses.[1] Most organoboranes are readily available *via* facile hydroboration of the desired olefins. However, the preparation of some important organoboranes involve slow hydroborations, requiring either long reaction periods,[2,3] or prolonged heating.[4-7] Recently, ultrasound has been utilized in many laboratories to accelerate a number of synthetically useful reactions.[8-18] We therefore explored the possibility that ultrasound might significantly enhance the rates of such slow hydroborations (eq 1).

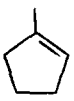
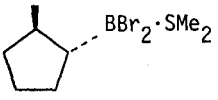
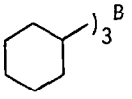
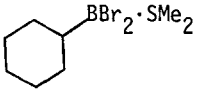
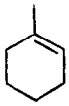
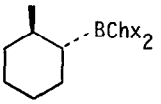
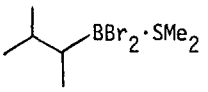
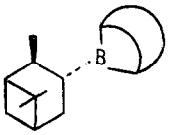
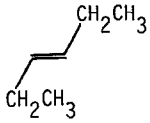
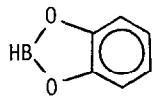
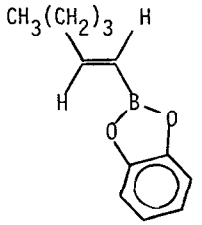


(1)

Indeed, we discovered that ultrasound dramatically enhances the rates of many slow heterogeneous hydroborations and has a relatively modest accelerating effect on slow homogeneous hydroborations. These results are summarized in the Table.

The importance of alkyldibromoboranes in organic syntheses is well established.[19] Alkyldibromoboranes are usually prepared by hydroboration of alkenes with $HBBr_2 \cdot SMe_2$. Unfortunately, these hydroborations are relatively slow and require 5-12 h at room temperature or 4-6 h at 40°C in CH_2Cl_2.[4,5] The application of ultrasound achieves these hydroborations in 1-2 h at 25°C. Thus, the hydroboration of 1-methylcyclopentene with $HBBr_2 \cdot SMe_2$, which requires 5 h at 25°C (or 4 h at 40°C), can be completed in 1 h with ultrasound. The hydroboration of *trans*-3-hexene with

Table. A Comparison of the Results of Hydroboration Obtained Upon the Application of Ultrasound and in the Absence of Ultrasound

Olefin	Hydroborating Agent	Product	Reaction Conditions[a] Literature Procedure[b]	Reaction Conditions[a] 25°C, Ultrasound	% Yield[c]
	$HBBr_2 \cdot SMe_2$		25°C, CH_2Cl_2, 5 h 40°C, CH_2Cl_2, 4 h	(((, CH_2Cl_2, 1 h	99
	$H_3B \cdot SMe_2$		25°C, THF, 24 h	(((, THF, 1 h[d]	98
	$HBBr_2 \cdot SMe_2$		25°C, CH_2Cl_2, vs[e] 40°C, CH_2Cl_2, 6 h[f]	(((, CH_2Cl_2, 1 h[f]	99
	$HBChx_2$		25°C, THF, 48 h	(((, THF, 1 h[d]	99
	$HBBr_2 \cdot SMe_2$		25°C, CH_2Cl_2, 5 h 40°C, CH_2Cl_2, 4 h	(((, CH_2Cl_2, 1 h	98
			25°C, THF, vs[e] 65°C, THF, 12 h 65°C, neat, 5 h	(((, THF, 3 h[g] (((, neat, 1 h[d]	 99
	$HBBr_2 \cdot SMe_2$	$CH_3CH_2CHCH_2CH_2CH_3$ $BBr_2 \cdot SMe_2$	25°C, CH_2Cl_2, 12 h 40°C, CH_2Cl_2, 6 h	((, CH_2Cl_2, 2 h	97
$CH_3(CH_2)_3C{\equiv}CH$			25°C, neat, 24 h	(((, neat, 6 h[g]	96

[a]All reactions were done at 1.0 *M* concentration. [b]References 2-7. [c]Determined by gas chromatography. [d]Heterogeneous reactions. [e]vs: very slow, incomplete reactions. [f]10 mol % of BBr_3 employed. [g]The bath temperature was maintained at 25°C by adding cold water.

$HBBr_2 \cdot SMe_2$, which requires 12 h at 25°C (or 6 h at 40°C), can be completed in 2 h under the influence of ultrasound. Similarly, the results obtained in the hydroboration of other representative olefins with $HBBr_2 \cdot SMe_2$ under ultrasound conditions are summarized in the Table.

More significant rate enhancements were observed in the case of heterogeneous hydroborations. The preparation of tricyclohexylborane by the hydroboration of cyclohexene with $BH_3 \cdot SMe_2$ in THF involves the prior formation of insoluble dicyclohexylborane and a slow subsequent reaction of the solid with a third mole of the olefin. This reaction requires 24 h at 25°C. However, under the influence of ultrasound, the reaction is complete in 1 h. Even more strikingly, the hydroboration of 1-methylcyclohexene with Chx_2BH in THF at 25°C, which requires 48 h for completion, can be achieved in 1 h using ultrasound.

Alpine-borane®, a highly useful chiral reagent[20] for the asymmetric reduction of α,β-acetylenic ketones and other prochiral carbonyl compounds, is generally prepared by the hydroboration of (+)- or (-)-α-pinene with 9-BBN either in THF (65°C, 12 h)[6] or under neat conditions (65°C, 5 h).[7] The reaction is very slow and incomplete at 25°C. However, using ultrasound, the same hydroboration can be achieved in 1 h under neat conditions.

Finally, the hydroboration of 1-hexyne with catecholborane, which requires 24 h at 25°C (under neat conditions), takes only 6 h under the influence of ultrasound.

The following experimental procedure is typical. Into a 100-ml flask fitted with a reflux condenser and connecting tube and flushed with N_2, the desired olefin (10 mmol), internal standard (5 mmol), and alkene (10 mmol), were introduced and the flask immersed into the water of the ultrasonic bath cleaner (5" x 9" x 4"; 50/60 Hz; 125 watts). This has been switched on 5 min prior to use. The reaction was followed by ^{11}B NMR and oxidized according to known procedures.[21] The alcohols were analyzed by GC to determine the yield.

Ultrasonics promise the hope of a new and powerful technique in organoborane chemistry. We continue to explore the full scope of this technique in the future.

ACKNOWLEDGEMENT

We wish to thank the National Science Foundation for the financial support of this research.

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(Received in USA 14 February 1985)