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ULTRASONICS IN ORGANOBORANE CHEMISTRY. RAPID SYNTHESIS OF TRIORGANYLBORANES VIA A MODIFIED ORGANOMETALLIC ROUTE

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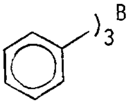
Abstract: A variety of triorganylboranes were prepared in a rapid and highly efficient manner, directly from organic halides, by a modified organometallic route employing ultrasound.

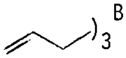
Prior to the discovery of hydroboration in ethereal solvents in our laboratories,[1] the practical methods for the preparation of triorganylboranes involved the reaction of an organometallic with boron esters or halides[2,3] (eq 1, 2).

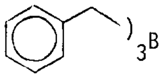
$$3\ R_2Zn + 2\ BCl_3 \longrightarrow 2\ R_3B + 3\ ZnCl_2 \qquad (1)$$

$$3\ RMgBr + B(OMe)_3 \longrightarrow R_3B + 3\ MgBrOMe \qquad (2)$$

However, a widespread application of such organometallic routes in organoborane syntheses has always been severely limited due to the ready availability of most triorganylboranes *via* facile hydroborations and also because of the need for the prior preparation of the organometallics (R_2Zn, RMgBr, etc.) in these methods. Nevertheless, the boron chemist's need for organoboranes containing groups not achievable *via* hydroboration (such as shown below) makes, even today, the use of organometallic routes indispensable.







Previously, ultrasound was utilized in many laboratories to accelerate a number of synthetically useful chemical reactions,[4-15] including the formation of several organometallic reagents. Although it was known that triorganylboranes could be prepared by the reaction of Grignard reagents with boron trifluoride-etherate,[2] the preparation of triorganylboranes directly from organic halides *via in situ* generation of the Grignard reagents in the presence of $BF_3 \cdot OEt_2$ (eq 3) has never been explored as a synthetic method.

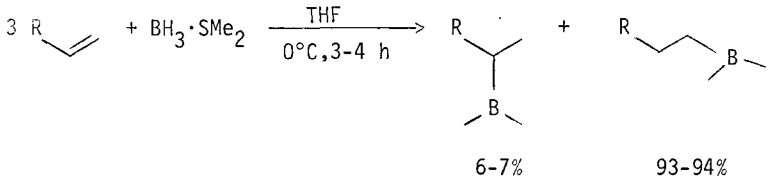
$$3\ RX \xrightarrow[OEt_2]{Mg, BF_3 \cdot OEt_2} R_3B \qquad (3)$$

In view of this, we decided to examine systematically the synthesis of triorganylboranes directly from organic halides (as shown above) with and without ultrasound. Indeed, triorganylboranes can be prepared in an exceptionally rapid and quantitative manner by the reaction of organic halides with a mixture of magnesium and $BF_3\cdot OEt_2$ under ultrasound (eq 4)

$$3\ RX \xrightarrow[\text{((((},Et_2O,15\text{-}30\ min]{Mg,BF_3\cdot OEt_2} \underset{90\text{-}100\%}{R_3B} \qquad (4)$$

Table I summarizes our results. The present procedure for the preparation of triorganylboranes has, in specific cases, significant advantages.

Symmetrical trialkylboranes, such as n-Pr_3B and n-Bu_3B, prepared *via* the hydroboration of 1-propene and 1-butene respectively with $BH_3\cdot SMe_2$, are contaminated with 6-7% by the undesired internal regioisomers[16] (eq 5). By the present procedure, n-Pr_3B and n-Bu_3B can be obtained in $\geq$ 99% purity in 15 minutes, starting from their corresponding alkyl halides.



(5)

The preparation of tricyclohexylborane by the hydroboration of cyclohexene with $BH_3\cdot SMe_2$ requires 24 h at 25°C in THF.[17] This highly hindered trialkylborane can be prepared in just 0.5 h from cyclohexylbromide using our modified organometallic procedure.

Triphenylborane, tri(α-naphthyl)borane, tribenzylborane and triallylborane are a representative class of organoboranes which cannot be prepared by hydroboration. These triorganylboranes can now be conveniently prepared in 15-30 minutes, directly from their respective halides, under ultrasound.

The following experimental procedure is representative for the preparation of triorganylboranes using ultrasound. The apparatus used in these experiments is as shown in Fig. 1.

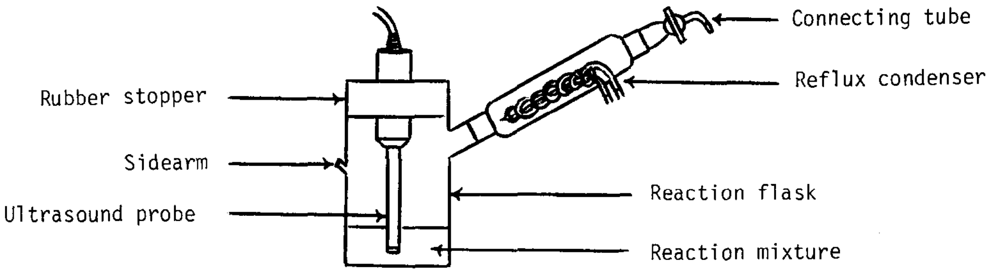
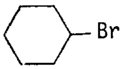
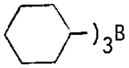
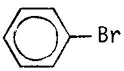
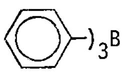
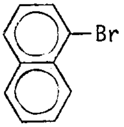
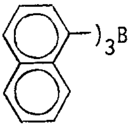
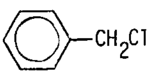
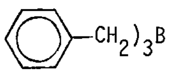
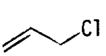
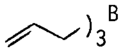


Fig. 1. Apparatus used for experiments with ultrasound

Table I. Preparation of Trialkylboranes *via* a Modified Organometallic Route[a]:

$$3\ RX \xrightarrow[OEt_2]{Mg, BF_3\cdot OEt_2} R_3B$$

			Reaction Time		Yield (%)[c]	
Alkyl Halide	Product	(δ) ^{11}B Chem. Shift[b]	No Ultrasound (Et_2O,Reflux)	Ultrasound (Et_2O,(((,Reflux)	No Ultrasound (Et_2O,Reflux)	Ultrasound (Et_2O,(((,Reflux)
n-C_3H_7Br	$(n$-$C_3H_7)_3B$	86.7	2 h	15 min	98	100(92)[d]
n-C_4H_9Br	$(n$-$C_4H_9)_3B$	86.5	2 h	15 min	99	100
s-$C_5H_{11}Br$	$(s$-$C_5H_{11})_3B$	84.7	36 h	30 min	97	96
		81.3	24 h	30 min	90	99
		67.4	3 h	15 min	94	97(87)[e]
		72.7	24 h	30 min	91	93
		82.8	24 h	30 min	96	99[f]
		81.9	3 h	15 min	94	94[f]
n-$C_7H_{15}I$	$(n$-$C_7H_{15})_3B$	87.0	2 h	15 min	88	90

[a] All reactions were done at 0.25 *M* concentration in anhydrous ether. [b] ^{11}B chemical shifts of all compounds were taken in ether and are with reference to $BF_3\cdot OEt_2$ (δ 0 ppm). [c] Determined by oxidation and gas chromatographic analysis. [d] The yield of distilled product, bp. 54-56°C at 14 mm. [e] The yield of isolated solid, m.p. 144-146°C in sealed capillary under nitrogen. [f] Oxidized using trimethylamine-*N*-oxide (see reference 5).

Mg turnings (0.97 g, 40 mmol), a crystal of I_2, $BF_3 \cdot OEt_2$ (1.42 g, 10 mmol), *n*-undecane (0.78 g, 5 mmol) and anhydrous ether (34.5 ml) were taken into the reaction flask under N_2. The sonic disruptor (Model TSD-B-250, 250 watts, 20 KHz) was switched on (with timer switch on hold and output control at 5) and 1-bromopropane (4.31 g, 35 mmol) was next added dropwise over a period of 5 minutes. Decolorization of iodine was observed when approximately 0.5 ml of alkyl halide was added and ether began to reflux. The formation of *n*-Pr_3B was complete in 10 minutes, as evidenced by ^{11}B NMR. Ultrasound was then switched off and the magnesium salts allowed to settle. The clear ether layer was next transferred into another flask. The magnesium salts were washed once again with ether (20 ml) and the washings combined. Ether was then pumped off under vacuum, anhydrous tetrahydrofuran (10 ml) was added and the organoborane oxidized using alkaline H_2O_2.[18] By G.C. analysis, the yield of *n*-propanol and subsequently the yield of *n*-Pr_3B was established to be quantitative.

Very soon we shall report detailed experimental procedures for the preparation and isolation of various triorganylboranes by this modified organometallic route.

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REFERENCES AND NOTES

1. H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, 22, 1136 (1957).
2. N. Nesmeyanov and R. A. Sokolik, "Methods of Elemento-Organic Chemistry," North Holland, Amsterdam, 1967, Vol. 1.
3. W. Gerrard, "Organic Chemistry of Boron," Academic Press, London, 1961.
4. H. C. Brown and U. S. Racherla, *Tetrahedron Lett.*, 2187 (1985).
5. C. Petrier, J-L. Luche and C. Dupuy, *Tetrahedron Lett.*, 3463 (1985).
6. E. Lukevics, V. N. Gevorgyan and V. S. Goldberg, *Tetrahedron Lett.*, 1415 (1984).
7. A. M. Horton, D. M. Hollinshead and S. V. Ley, *Tetrahedron*, 40, 1737 (1984).
8. B. H. Han and P. Boudjouk, *J. Org. Chem.*, 47, 751 (1982).
9. B. H. Han and P. Boudjouk, *Tetrahedron Lett.*, 1643 (1982).
10. O. Repic and S. Vogt, *Tetrahedron Lett.*, 2729 (1982).
11. S. L. Regen and A. Singh, *J. Org. Chem.*, 47, 1587 (1982).
12. P. Boudjouk and B. H. Han, *Tetrahedron Lett.*, 3813 (1981).
13. B. H. Han and P. Boudjouk, *Tetrahedron Lett.*, 2757 (1981).
14. D. S. Kristol, H. Klotz and R. C. Parker, *Tetrahedron Lett.*, 907 (1981).
15. S. Raucher and P. Klein, *J. Org. Chem.*, 46, 3558 (1981).
16. H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, 88, 5851 (1966).
17. H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, 83, 3417 (1961).
18. H. C. Brown, G. W. Kramer, A. B. Levy and M. M. Midland, "Organic Syntheses via Boranes," Wiley-Interscience, New York, 1975.

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