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ULTRASONIC IRRADIATION IN THE SYNTHESIS OF TRIETHYLBORANE FROM ETHYL BROMIDE VIA ETHYLALUMINUM SESQUIBROMIDE

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Summary

Ethyl bromide and aluminum powder were irradiated with ultrasound to form ethylaluminum sesquibromide, which was then treated with triethyl borate to give triethylborane in satisfactory yield and purity. In comparison to other existing methods, ultrasonic irradiation seems to be a simple and effective process for the synthesis of organoboron compounds.

Introduction

Ultrasonic irradiation has been known to facilitate certain organic reactions especially those of a heterogeneous nature [1–14]. However, very few works [15] about ultrasonic irradiation in the synthesis of organometallic compounds of Group III metals have been reported thus far.

Triethylborane can be synthesized by treating ethyl halides (CH_3CH_2Cl or CH_3CH_2Br) with silane [16], metal hydrides [17], or boron halides [18–19]. It can also be prepared via Grignard reagent [20–23] or ethylaluminum sesquihalides [24–25].

In our investigation ultrasonic irradiation was used to promote the reaction between ethyl bromide and aluminum at room temperature. Ethylaluminum sesquibromide was first formed as an intermediate which was subsequently allowed to react with triethyl borate to give triethylborane.

$$3\underset{(1)}{CH_3CH_2Br} + 2Al \xrightarrow{)))} \underset{(2)}{(CH_3CH_2)_3Al_2Br_3} \xrightarrow{B(OCH_2CH_3)_3} (CH_3CH_2)_3B$$

In the first heterogeneous step of the reaction, sesquibromide **2** was formed when ethyl bromide **1** was irradiated with ultrasound in the presence of aluminum powder. The reaction was complete within 10–20 minutes at room temperature as indicated by the disappearance of ethyl bromide reflux. Compound **2** was allowed to react, without isolation and then with triethyl borate to give triethylborane.

TABLE 1

THE EFFECT OF REACTION TEMPERATURE (Amounts of reactants used: CH_3CH_2Br, 250 mmol; Al, 180 mmol; I_2, 2.5 mmol)

Temperature	Type of reaction	Initiation [a] time (min)	Completion [b] time (min)
room temp.	ultrasonic	12	19
36°C	ultrasonic	12	20
50°C	ultrasonic	11.5	21
room temp.	stirring	no reaction	
36°C	stirring	20	36

[a] Time required for the starting of reflux. [b] Time required for the ending of reflux.

Results and discussion

A detailed mechanism of sonochemistry is not known, but it is generally accepted that the phenomenon of cavitation is responsible for its chemical effects. The cavitation is due to the creation, growth, and impulsive collapse of gas vacuoles in solution by the sound field. This collapse generates transient hot-spots with local temperatures and pressures of several thousand K and hundreds of atmospheres [26]. External heating during irradiation has no influence on initiation of the reaction in this study, as shown by our results in Table 1. The results also show that the reaction with ultrasound occurs at room temperature, but the reaction does not take place at this temperature using the magnetic stirring method. When both reactions are performed at 36°C, the reaction time of the former is about half of that in the latter. The merits of this ultrasonic method are that the reaction time is shortened and can take place under milder conditions.

Quantity of I_2 initiator used

It is known that iodine can promote the formation of ethylaluminum sesquihalides [27]. To verify this in the process of ultrasonic irradiation we have systematically changed the quantity of iodine added to the reaction. A ratio of $I_2/EtBr = 20 \times 10^{-3}$ seems to be optimal for the formation of ethylaluminum sesquibromide as shown in Fig. 1.

The effect of EtBr / $B(OEt)_3$ ratio on yield of triethylborane

Since **2** reacted, as observed in our investigation, quantitatively with triethyl borate to give triethylborane, ethyl bromide could be considered de facto as the starting material for the preparation of this in the overall reaction. As shown in Table 2, yields of triethylborane were influenced by altering the EtBr/$B(OEt)_3$ ratio. A 20–30% excess of EtBr in mole ratio is favorable to the formation of triethylborane.

The effect of I_2 amount on yield of triethylborane

Since **2** had not been worked up prior to further conversion, I_2 added during the first step remained in the reaction and might affect the formation of triethylborane. Our results in Table 3 show, however, that the yield of triethylborane is independant from the amount of I_2 added.

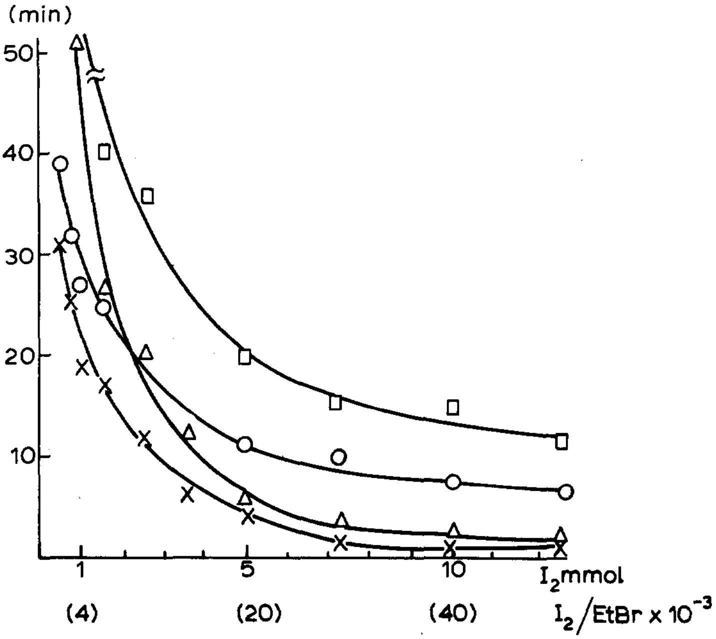

Fig. 1. Initiation time vs. I_2/EtBr at 36°C. Δ, initiation time with heating and stirring; □, completion time with heating and stirring; X, initiation time with ultrasonic irradiation; O, completion time with ultrasonic irradiation.

TABLE 2

THE EFFECT OF THE EtBr/B(OEt)$_3$ RATIO ON YIELDS OF TRIETHYLBORANE

EtBr/B(OEt)$_3$	TEB yield (%)	EtBr (mmol)	Al (mmol)	B(OEt)$_3$ (mmol)
3.0	52.7	500	363	167
3.3	60.2	550	399	167
3.6	88.0	600	435	167
3.9	90.0	650	471	167
4.2	89.1	700	507	167
4.5	91.4	750	543	167

TABLE 3

THE EFFECT OF THE AMOUNT OF I_2 ON THE YIELD TRIETHYLBORANE

(EtO)$_3$B (mol)	Al (mol)	EtBr (mol)	I_2 (mmol)	TEB yield (%)
0.166	0.476	0.65	1.0	87.5
0.166	0.476	0.65	2.5	90.0
0.166	0.476	0.65	5.0	90.3
0.166	0.476	0.65	7.5	87.9
0.166	0.476	0.65	12.5	88.8

TABLE 4

TEB PRODUCED FROM DIFFERENT ALKYL BORATES

Alkyl borates	TEB yield (%)
$(CH_3O)_3B$	65
$(EtO)_3B$	90
$(n\text{-}PrO)_3B$	56.5
$(i\text{-}PrO)_3B$	21.5
$(n\text{-}BuO)_3B$	58.5
$(i\text{-}BuO)_3B$	26.8

The effect of alkyl borates

Six alkyl borates were chosen for reactions with **2**. As shown in Table 4, the following order of their reactivities in accordance with the nature of alkyl groups were observed: EtO > CH_3O > n-PrO > n-BuO > i-BuO > i-PrO.

Steric hindrance of β-methyl groups in the transmetallation transition state offered a satisfactory explanation for these results. However, the reason why methyl borate is less reactive than ethyl borate is not completely clear. Further applications of this study are in progress.

Experimental

A laboratory ultrasonic cleaner (180W, 43KHZ) manufactured by L & R company was employed. Commerical ethyl bromide (Wako Chemical Industrial Ltd.) and aluminum powder (150–250 mesh) were used. Alkyl borates were obtained from the reaction between B_2O_3 and related alcohols [28]. Each experiment in the text was run two or three times and all data are reproducible.

General procedure

All reactions were carried out under nitrogen. Stoichiometric amounts of ethyl bromide, aluminum powder and iodine were introduced into a round-bottomed flask (250 ml) connected with a highly efficient condenser with alcohol at -20°C. The flask was then immersed in the water bath of the ultrasonic cleaner. Ethylaluminum sesquibromide would be formed completely when the spontaneously reflux ceased under ultrasonic acceleration. The medium was subsequently kept at room temperature and corresponding amounts of alkyl borate were added within 10 minutes. Triethylborane was distillated from the reaction mixture, b.p. 94–96°C. The purity of the product was analyzed by gas chromatography (GC-model, HP-5880; column, 3% SE-30, 1/8″ × 6 ft; carrier gas, He; gas flow rate, 30 ml/min. Column temperature, 80°C; injection temperature, 100°C; detection temperature, 200°C) and the boron content ratio was determined by potentiometric titration.

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