

## ULTRASONIC IRRADIATION IN ONE-POT SYNTHESIS OF TRIETHYLALUMINUM ETHERATE AND ITS CONVERSION INTO OTHER ORGANOMETALLIC COMPOUNDS

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### Summary

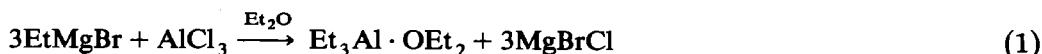
A mixture of ethyl bromide, aluminum and magnesium powders was irradiated with ultrasound and ethylaluminum sesquibromide(I) formed at room temperature. As soon as diethyl ether was introduced into the reaction medium, ethylmagnesium bromide (II) was formed in situ and subsequently treated with I to give the etherate of triethylaluminum (III, TEA · OEt<sub>2</sub>) in satisfactory yield (82%) and purity (98%). III, thus obtained, could react with triethyl borate or zinc chloride to give triethylborane (90%) and diethylzinc (82%) respectively.

### Introduction

Triethylaluminum (TEA) has been well known as a synthetic reagent [1-5] and practical catalyst in polymerization [6-8]. Many works concerning the preparation of triethylaluminum have been reported [9-14]. However, the pyrophoricity of this compound limits its application in the laboratory.

Triethylaluminum reacts readily with some electron-donating ligands to form complexes [14-15], in which the electrophilicity of the Al atom is lowered, most of the adducts formed, lost their pyrophoric nature. In other words, all these compounds are less dangerous to handle than TEA. This property simplified their use in the laboratory.

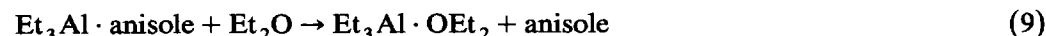
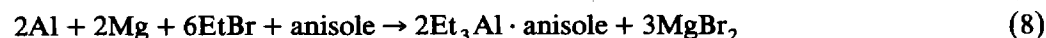
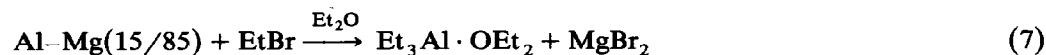
Triethylaluminum etherate may be prepared according to the procedure of Hurd [16], by treating anhydrous aluminum trichloride with ethylmagnesium bromide in ether (eq. 1).



Baker et al. [15] obtained triethylaluminum etherate after the reaction of ether with triethylaluminum, which was prepared according to Grosse's method [17] (eq. 2-4).



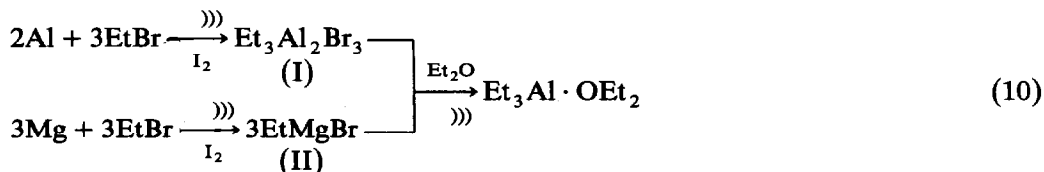
TEA · OEt<sub>2</sub> can also be synthesized from Al-Mg alloy (containing 11-15% Al) and ethyl bromide in ether [18-19] (eq. 5-7), or when a mixture of magnesium and aluminum powders are allowed to react with ethyl bromide and anisole thereby obtaining the triethylaluminum anisole complex. This was converted into triethylaluminum etherate, when its anisole ligand was exchanged with diethyl ether at high temperature (eq. 8-9) [20].



Except when a specified Al-Mg alloy is used, all the methods for preparing triethylaluminum etherate are multi-step syntheses.

Ultrasonic irradiation has been known to facilitate certain organic reactions, especially those of a heterogeneous nature [21-34]. Recently, we found ultrasonic irradiation to be a facile and effective method for synthesizing triethylborane [35] and trimethylaluminum [36]. Kuchin et al. [37] and Brown et al. [38] also proved that the synthesis of organoaluminum and organoborane compounds were efficiently promoted with ultrasound.

In this study, ultrasonic irradiation was used to promote one-pot synthesis of triethylaluminum etherate from the mixture of ethyl bromide, magnesium and aluminum powders in the presence of iodine at room temperature. Ethylaluminum sesquibromide was formed as an intermediate within 30 min. Then, ethylmagnesium bromide was formed in situ by introducing diethyl ether into the reaction medium. The Grignard reagent reacts immediately with ethylaluminum sesquibromide already present in the reaction medium to give triethylaluminum etherate (eq. 10).



The etherate of triethylaluminum was treated with triethyl borate or zinc chloride to give triethylborane and diethylzinc, respectively.

## Results and discussion

The detailed mechanism of the sonochemistry has not been completely revealed, but it is generally accepted that the phenomenon of cavitation is responsible for this chemical effect. The work of Sehgal et al. [39] showed that the collapse of the cavities, induced by the sound field, generates transient hot-spots with local temperatures of several thousand K and pressures of several hundred atmospheres.

In our previous work [35], we found that with the application of ultrasound, the formation of ethylaluminum sesquibromide from ethyl bromide and aluminum powder, could be efficiently achieved within 20 min at room temperature. Similar results were expected, despite the extra magnesium turnings added to the reaction system. The ethylaluminum sesquibromide obtained, was treated with ethylmagnesium bromide to give triethylaluminum etherate in the same pot, after ether was introduced into the reaction medium.

The effect of ultrasound in the one-pot synthesis of triethylaluminum etherate is shown in Table 1. It shows that under ultrasonic irradiation triethylaluminum etherate is formed; whereas it is very difficult to bring it about at this temperature, when a magnetic stirrer is used. The result also shows that the more external heat ( $> 40^\circ\text{C}$ ) that is applied to the reaction medium and the shorter the reaction time (40 min), the less is the yield of the triethylaluminum etherate obtained. The reason for this is that if the reaction temperature is higher than the boiling point ( $> 40^\circ\text{C}$ ), the vapor pressure of ethyl bromide is increased, and hence cavitation is reduced. Decreasing the latter, would influence the effect of ultrasonic irradiation on the yield of triethylaluminum etherate. This result is in agreement with the work of Suslick et al. [40], who reported that decreasing the solvent vapor pressure increases the intensity of cavitation, and consequently the rate of sonochemical reactions. By

TABLE 1  
THE EFFECT OF ULTRASOUND (OR STIRRING) ON THE YIELD OF TEA·OEt<sub>2</sub><sup>a</sup>

Type of reaction	Temperature (°C)	Reaction time (min)	Isolated yield TEA·OEt <sub>2</sub> (%)
ultrasound <sup>b</sup>	r.t. <sup>c</sup>	40	57.3
ultrasound <sup>b</sup>	r.t. <sup>c</sup>	70	73.9
ultrasound <sup>b</sup>	r.t. <sup>c</sup>	100	76.2
ultrasound <sup>b</sup>	r.t. <sup>c</sup>	130	73.3
ultrasound <sup>b</sup>	r.t. <sup>c</sup>	40	74.6 <sup>d</sup>
ultrasound <sup>b</sup>	40	40	8.9
ultrasound <sup>b</sup>	40	70	77.7
ultrasound <sup>b</sup>	40	100	82.9
ultrasound <sup>b</sup>	50	40	1.4
ultrasound <sup>b</sup>	50	70	67.5
ultrasound <sup>b</sup>	50	100	75.0
stirring	r.t. <sup>c</sup>	40	0.5
stirring	r.t. <sup>c</sup>	70	1.3
stirring	r.t. <sup>c</sup>	130	1.4

<sup>a</sup> EtBr, 250; Al, 92; Mg, 163; I<sub>2</sub>, 2.5; Et<sub>2</sub>O, 750; mmol were used. <sup>b</sup> A 43 kHz ultrasonic cleaner was used. <sup>c</sup> Room temperature, 23–25°C. <sup>d</sup> Excepting this batch where soap-water was used as the wave-medium, for all other batches water was used as the wave-medium for ultrasonic irradiation, in this table.

TABLE 2  
QUANTITY OF I<sub>2</sub> INITIATOR USED <sup>a</sup>

Frequency (kHz)	Reaction time (min)	I <sub>2</sub> /EtBr (×10 <sup>-3</sup> )	Isolated yield (%)
43	40	10	74.6
43	40	20	74.5
43	40	30	75.1
43	40	40	82.2
43	40	50	81.5
43	40	60	82.0

<sup>a</sup> EtBr, 250; Al, 92; Mg, 163; Et<sub>2</sub>O, 750; mmol were used.

extending the period of ultrasonic irradiation, the above-mentioned influence on the system disappeared, apparently owing to the competition between ultrasonic irradiation and thermal acceleration. For longer reaction times, the effect of the thermal acceleration would predominate. Table 1 also shows that prolonging the reaction time, slightly increases the yield of triethylaluminum etherate under ultrasonic irradiation, with water as the wave-medium. Furthermore, the yield of triethylaluminum etherate is greatly increased when soap-water is used as the wave-medium [41].

In our previous publication [35], we reported that a ratio of I<sub>2</sub>/EtBr = 20 × 10<sup>-3</sup> seems to be optimal for the formation of ethylaluminum sesquibromide in the Al/EtBr system. In the present study, however, the ratio could be different from the one above, because magnesium turnings were added to the reaction system. To verify this, the quantity effect of the iodine, initiator used, is listed in Table 2. The results show that larger amounts of iodine initiator (I<sub>2</sub>/EtBr = 40 × 10<sup>-3</sup>) are required for the formation of ethylaluminum sesquibromide in the Al/Mg/EtBr system.

Ostroski et al. [42] described that ultrasonic irradiation power had some effect on the emulsion polymerization of styrene. The results shown in Table 3 indicate that an increase in ultrasonic power has no effect on the yield of triethylaluminum etherate within the same period of reaction. The results shown in Table 4 indicate that a 40-min reaction time seems to be sufficient for the production of triethylaluminum etherate by this method.

Compared to the other existing methods for the synthesis of triethylaluminum etherate, the process described in this investigation showed distinct advantages, including the simplicity of one-pot reaction, a short reaction time, milder reaction conditions and inexpensive reactants.

TABLE 3  
THE EFFECT OF ULTRASONIC POWER ON THE YIELD OF TEA·OEt<sub>2</sub> <sup>a</sup>

Frequency (kHz)	Reaction time (min)	I <sub>2</sub> /EtBr (×10 <sup>-3</sup> )	Isolated yield of TEA·OEt <sub>2</sub> (%)
43	40	40	82.2
55	40	40	81.3
80	40	40	80.5

<sup>a</sup> EtBr, 250; Al, 92; Mg, 163; Et<sub>2</sub>O, 750; mmol were used.

TABLE 4  
THE EFFECT OF TIME ON THE YIELD OF TEA·OEt<sub>2</sub><sup>a</sup>

Frequency (kHz)	Reaction time (min)	I <sub>2</sub> /EtBr (×10 <sup>-3</sup> )	Isolated yield of TEA·OEt <sub>2</sub> (%)
43	30	40	77.3
43	40	40	82.2
43	70	40	81.0
43	100	40	83.1

<sup>a</sup> EtBr, 250; Al, 92; Mg, 163; Et<sub>2</sub>O, 750; mmol were used.

TABLE 5  
YIELDS OF TRIETHYLBORANE (%) PRODUCED FROM TEA, TEA·OEt<sub>2</sub> AND DIFFERENT BORATES<sup>a</sup>

Alkyl borates (RO) <sub>3</sub> B, R =	Me-	Et-	n-Pr-	i-Pr-	n-Bu-	i-Bu-
TEA	74.2	78.8	80.1	75.1	82.3	75.1
TEA·OEt <sub>2</sub>	65.0	90.0	82.1	57.0	69.0	67.0

<sup>a</sup> TEA, 110; TEA·OEt<sub>2</sub>, 110; Borates, 100; mmol were used.

TABLE 6  
YIELDS OF DIETHYLZINC (%) FROM DIFFERENT REACTANT RATIOS<sup>a</sup>

	TEA/ZnCl <sub>2</sub>			TEA·OEt <sub>2</sub> /ZnCl <sub>2</sub>		
	2.2	2.4	2.6	2.2	2.4	2.6
TEA	86.0	85.2	81.1			
TEA·OEt <sub>2</sub>				80.0	80.5	82.0

<sup>a</sup> ZnCl<sub>2</sub>, 50 mmol was used.

Six alkyl borates were chosen for reaction with triethylaluminum etherate or triethylaluminum. As shown in Table 5, the following orders of reactivity (depending upon the nature of alkyl groups in producing triethylborane) were observed: For TEA: n-Bu > n-Pr > Et > i-Bu ~ i-Pr ~ Me; for TEA·OEt<sub>2</sub>: Et > n-Pr > n-Bu > i-Bu > Me > i-Pr.

Greater steric hindrance of triethylaluminum etherate compared to triethylaluminum in the transmetallation state offers a satisfactory explanation for these results.

Different amounts of zinc chloride were treated with triethylaluminum and triethylaluminum etherate to obtain diethylzinc, as shown in Table 6. The reactivity of triethylaluminum etherate toward zinc chloride was slightly lower than with triethylaluminum. But simple preparation of triethylaluminum etherate by this method and its handling safety is more beneficial than triethylaluminum.

## Experimental

Three types of laboratory ultrasonic cleaners (180 W, 43 kHz), (440 W, 55 kHz), (320 W, 80 kHz) were used. Commercial zinc chloride (Wako Chemical Industrial

Ltd.), aluminum powder (150–250 mesh) and magnesium turnings were used. Alkyl borates were obtained from the reaction between  $B_2O_3$  and related alcohols [43]. Triethylaluminum (purity 94%) was purchased from Nippon Aluminum Alkyls Ltd.

#### *General procedures*

All reactions were carried out under nitrogen.

*Preparation of triethylaluminum etherate.* Stoichiometric amounts of ethyl bromide, aluminum powder, magnesium turnings and iodine were introduced into a round-bottomed flask (250 ml) connected to a highly efficient condenser containing alcohol at  $-20^\circ C$ . The flask was then immersed in the soap-water bath of the ultrasonic cleaner. Ethylaluminum sesquibromide was then formed to near completion within 30 min. The medium became dark, and an excess of dry ether (200% excess) was subsequently added within 10 min. Ethylmagnesium bromide was formed to completion during this period. Both ethylaluminum sesquibromide and ethylmagnesium bromide were caused to react in the same pot. After all the dry ether had been added, the medium was stripped of excess ether at atmospheric pressure.

Prior to vacuum distillation, the medium was worked up (by use of) the general procedures. Triethylaluminum etherate was distilled from the reaction mixture, b.p.  $75-76^\circ C/2.0$  Torr. Triethylaluminum etherate was identified by comparing its NMR spectrum with that of an authentic sample prepared directly from triethylaluminum and dry ether. The purity of triethylaluminum etherate was estimated by NMR and potentiometric titration. The bromide-containing compounds in the distillate compressed less than 2%.

*Preparation of triethylborane.* A stoichiometric amount of triethylaluminum etherate or triethylaluminum was introduced into a round-bottomed flask (250 ml) connected to a highly efficient condenser containing alcohol at  $-20^\circ C$ . The medium was stirred and heated to  $120^\circ C$  in an oil bath. Then a corresponding amount of an alkyl borate was added dropwise into the medium during 10 min, after which, the mixture was stirred for a further 20 min. The medium was worked up according to the general procedure for atmospheric distillation. Triethylborane was distilled from the reaction mixture, b.p.  $94-96^\circ C$ . The purity of the product (> 95%) was analyzed by gas chromatography (GC-model, HP-5880: column, 3% SE-30,  $1/8'' \times 6$  ft: carried gas, He; gas flow-rate, 30 ml/min; column temperature,  $80^\circ C$ ; injection temperature,  $100^\circ C$ ; detection temperature,  $200^\circ C$ ) and the boron-content ratio was determined by potentiometric titration.

*Preparation of diethylzinc.* A stoichiometric amount of oven-dried zinc chloride was introduced into a round-bottomed flask (250 ml) connected to a highly efficient condenser with ethanol at  $-20^\circ C$ . The corresponding amount of triethylaluminum or triethylaluminum etherate was dropped into the flask over 10 min at room temperature. The medium was stirred with a magnetic stirrer and heated (at  $100^\circ C$ ) for 1 h. The diethylzinc was distilled from the mixture, b.p.  $66-68^\circ C/100$  Torr. The crude distillate was contaminated with trace amounts of ether that had broken from the by-product, diethylaluminum chloride etherate, when triethylaluminum etherate was used as the reactant. The residual ether could be removed by simple atmospheric distillation. The purity of the product was established by NMR and potentiometric titration, which showed no chloride-containing compounds to be present.

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