

ULTRASONIC IRRADIATION IN THE SYNTHESIS OF TRIMETHYLALUMINUM FROM METHYL IODIDE VIA METHYLALUMINUM SESQUIIODIDE

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Summary

Methyl iodide and aluminum powder were irradiated with ultrasound to form methylaluminum sesquiodide, which was then treated with triethylaluminum to give trimethylaluminum in satisfactory yield (86%) and purity (95%).

Introduction

The reactions between alkyl halides and aluminum are the basis of the classical and oldest method for the synthesis of organoaluminum compounds [1,2]. This method for the synthesis of organoaluminum compounds has been used in the preparation of alkylaluminum halides [3,4] (eq. 1) or trialkylaluminums [5,6]. The ease of this reaction depends on the nature of the solvents and the method of activation of the aluminum metal.

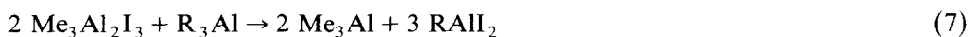


In addition to this method (eq. 2), there exist many other methods to synthesize the trimethylaluminum, eq. 3 [7] and eq. 4 [8].



Recently, Eidt et al. [9] reported the synthesis of trimethylaluminum from alkyl redistribution between trialkylaluminum and methylaluminum sesquiodide (eq.

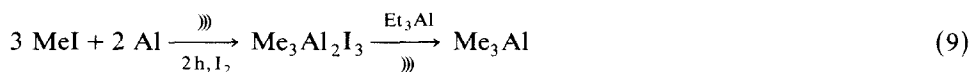
5–7). The trimethylaluminum was also prepared differently by Diefenbach from methyl iodide and triethylaluminum [10–12] (eq. 8).



Generally, the method involving methyl halides and aluminum metal requires a long reaction time (over 12 h). Diefenbach's redistribution method (eq. 8) required 18 h and a high temperature. Eidt's process [9,13] (eq. 5–7) not only took 12 h to complete the reaction, but also required preparation of a packed column with a length of 60–90 cm for distillation, which needed much time to purify the product.

Ultrasonic irradiation has been known to facilitate certain organic reactions, especially those of a heterogeneous nature [14–27]. However, very few works [28–30] about ultrasonic irradiation in the synthesis of organometallic compounds of Group III metals have been reported thus far.

Previously [31], we described that the ultrasonic irradiation could be used as a facile and effective method to synthesize triethylborane from ethyl bromide, aluminum powder and triethyl borate. In this study, we have extended the ultrasonic irradiation to promote the reaction between methyl iodide and aluminum powder in the presence of iodine at room temperature. Methylaluminum sesquiodide was first formed as an intermediate which was treated with triethylaluminum giving trimethylaluminum (eq. 9).



The first heterogeneous step of the reaction was complete within 2 h at room temperature. Methylaluminum sesquiodide, without isolation, was then redistributed with triethylaluminum to give trimethylaluminum.

Results and discussion

The detailed mechanism of the sonochemistry is not completely 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 [32].

Previously [31], we found that external heating during irradiation had no influence on the initiation of the reaction in the EtBr–Al system. In this study, we describe the effect of the temperature on the initiation of the MeI–Al system (see Table 1). The results indicate that the ultrasonic reaction occurs to form methylaluminum sesquiodide, in contrast to the fact that it does not take place at this temperature using the magnetic stirring method. The results also show that the external heating has some influence on the initiation of the reaction. The yields of methylaluminum sesquiodide slightly increased when the external temperature was raised. The reason for this phenomenon could be explained because the reaction rate

TABLE 1

THE EFFECT OF REACTION TEMPERATURE (Amounts of reactants used: MeI, 250 mmol; Al, 183 mmol; I₂, 2.5 mmol)

Type of reaction	Temperature (°C)	Time (h)	Yield of Me ₃ Al ₂ I ₃ ^a (%)
ultrasonic	room temp.	2	66.7
ultrasonic	room temp.	2	91.2 ^b
ultrasonic	room temp.	3	96.4 ^b
ultrasonic	40	2	81.7
ultrasonic	50	2	81.0
stirring	room temp.	2	0
stirring	40	2	20.6
stirring	50	2	44.8
stirring	50	4	84.3

^a Yields were estimated by NMR. ^b 10% EtI added (based on MeI) as co-initiator.

of the MeI–Al system is far lower than that of the EtBr–Al system during ultrasonic acceleration. The added ethyl iodide could also promote the formation of sesquiodide in this study. In the thermal method, the formation of other alkylaluminum sesquihalides could be induced with methyl iodide [33], which contrasts with the result of our ultrasonic method herein.

It is known that iodine can promote the formation of ethylaluminum sesquihalide. To verify this we have systematically changed the quantity of iodine added to the reaction. A ratio of I₂/MeI = 10×10^{-3} seems to be optimal for the formation of methylaluminum sesquiodide as shown in Table 2.

Eidt et al. described that the formation of trimethylaluminum depended upon the stoichiometric amounts of methylaluminum sesquihalide and trialkylaluminum employed. Since the methylaluminum sesquiodide formed, without isolation, was allowed to react with triethylaluminum, methyl iodide could be considered as the starting material. In order to verify the influence of the relative amounts of triethylaluminum and methyl iodide on the trimethylaluminum formation, we also systematically changed the ratio of methyl iodide to triethylaluminum during the reaction. The results are shown in Table 3.

The yields of trimethylaluminum apparently decrease as the ratio of MeI to Et₃Al increases from 1.50 to 12.0. It is also indicated that a ratio of MeI/TEA = 1.50 seems to be optimal for the formation of trimethylaluminum using this method. The

TABLE 2

QUANTITY OF I₂ INITIATOR USED

I ₂ (mmol)	I ₂ /MeI ($\times 10^{-3}$)	Initiation time ^a (min)
0.5	2.0	no reaction
2.5	10.0	120
5.0	20.0	115
10.0	40.0	94

^a Time required for reaching the highest temperature of the medium.

TABLE 3
YIELDS OF PRODUCTS

MeI/TEA	MeI (mmol)	Al (mmol)	TEA (mmol)	Product (%) ^a			
				TMA	DMAI	DEAI	EADI
0.75	500	366	666	85			
1.50	500	366	333	86 (90) ^b		95 (94) ^b	
3.00	500	366	166	76	11.2		
6.00	500	366	83.3	65 (91) ^b	15.7		(97) ^b
12.00	500	366	41.6	62.5	22.5		93

^a TMA = Trimethylaluminum; DMAI = Dimethylaluminum iodide; DEAI = Diethylaluminum iodide; EADI = Ethylaluminum diiodide. ^b Data in parentheses were taken from ref. 9.

TABLE 4
COMPARISON OF B.P. AND NMR DATA WITH LITERATURE DATA

Product	Literature			This work		
	B.p. (°C/Torr)	¹ H	¹³ C	B.p. (°C/Torr)	¹ H	¹³ C
TMA	130/760		-7.28	66-68/100	-0.30	-7.0
DMAI	109-110/50			30-31/1	-0.01	-4.29
DEAI	118/4	$ \delta(\text{CH}_3) - \delta(\text{CH}_2) $ = 0.60		94-96/2	$ \delta(\text{CH}_3) - \delta(\text{CH}_2) $ = 0.63	C ¹ 5.02 C ² 9.47
EADI	158-160/4			137-138/2		C ¹ 10.17 C ² 9.03

TABLE 5
COMPARISON OF DIFFERENT METHODS FOR THE SYNTHESIS OF TRIMETHYL-
ALUMINUM (TMA)

Type of reaction	Reaction time (h)	Reaction conditions	Yield (%)	Reference
1. $3\text{MeI} + 2\text{Al} \xrightarrow[\text{TEA}]{\text{TEA}}$ TMA	2.5	room temp., ultrasonic	86	
2. $3\text{MeI} + 2\text{Al} \rightarrow \text{Me}_3\text{AlI}_3 \xrightarrow{\text{TEA}}$ TMA	6.5	100°C	90	9
3. $3\text{MeI} + 2\text{Al} \rightarrow \text{Me}_3\text{AlI}_3 \rightarrow \text{TMA}$	> 12	reflux	50	2, 34
4. $3\text{MeCl} + 2\text{Al} \xrightarrow{\text{Na}} \text{Me}_3\text{AlCl}_3 \rightarrow \text{TMA}$	25	autoclave	63	2
5. $\text{MeX} + \text{Al-Mg} \rightarrow \text{TMA}$	30	reflux 30-170°C	70-80	7
6. $\text{TEA} + \text{MeI} \rightarrow \text{TMA}$	18	room temp.	11	10-12
	18	92°C	95	
	18	room temp., catalyst	30	
7. $\text{MeI} + \text{Al} \xrightarrow{\text{Mg}} \text{Me}_2\text{AlI} \rightarrow \text{TMA}$	9	1. 100°C 2. 180-200°C	85	35
8. $\text{Na}[\text{AlMe}_2\text{F}_2] \rightarrow \text{TMA}$	1	250-300°C	88	36

second step of this one pot reaction belongs to the redistribution process. This is a chemical re-equilibrium reaction which consists of forming a mixture of methylaluminum sesquiodide and triethylaluminum. Although Eidt et al. suggested that the high efficient packed column (190 cm) would be beneficial to the above redistribution, we tried to use a packed column in different length for fractional distillation and discovered that a 30-cm packed column is good enough to perform redistribution by this ultrasonic method. A comparison of earlier reported boiling points and NMR data for the products with our results is shown in Table 4.

The process described in this study has distinct advantages compared to the other methods, which are shown in Table 5. The merits of this ultrasonic method lie in the simplicity of the one pot reaction, a short reaction time and mild reaction conditions. Neither expensive and complex filtration apparatus nor other solid-handling equipments are necessary in our experiments. We also find that the shorter packed column for distillation is sufficient and improves the excessive time for distillation used during Eidt's method.

In conclusion, this preparation of trimethylaluminum is far simpler for laboratory purposes than any previously used method.

Experimental

A laboratory ultrasonic cleaner (180 W, 43 kHz) manufactured by L & R company was employed. Commercial methyl iodide (Riedel-Dehaen, West Germany) and aluminum powder (150–250 mesh) were used. Triethylaluminum (purity 94%) was purchased from Nippon Aluminum Alkyls Ltd. Each experiment in the text is reproducible.

General procedure

All reactions were carried out under nitrogen. Stoichiometric amounts of methyl iodide, aluminum powder and iodine were introduced into a round-bottomed flask (250 ml) connected to a highly efficient condenser with ethanol at -20°C . The flask was then immersed in the water bath of the ultrasonic cleaner. Methylaluminum sesquiodide is formed completely within 2 h under ultrasonic acceleration. The medium became dark. Meanwhile, the corresponding amounts of triethylaluminum were dropped into the flask within 10 min. Upon completion of the addition of triethylaluminum, irradiation was continued with ultrasound for 30 min. Because an excess of aluminum was used, the final mixture contained black, unreacted aluminum.

Preparatory to vacuum distillation, the medium was worked up according to the general processes. The fractional column (3/4" i.d.) was packed with porcelain 6-mm Berl Saddles (Fisher Scientific Co.) 30 cm in length. Vacuum was slowly applied to the system until the pressure had decreased to 100 Torr. With constant pressure being kept, the reaction mixture was heated to reflux. The oil bath was maintained over the range $150\text{--}160^{\circ}\text{C}$. Trimethylaluminum was distilled from the reaction mixture, b.p. $66\text{--}68^{\circ}\text{C}/100$ Torr. The purity of trimethylaluminum was estimated by NMR and potentiometric titration. The iodide-containing compounds of the distillate was less than 4%, which could be improved to be less than 1%, if the crude distillate was proceeded once more with simple fractional distillation.

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