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A New Synthetic Route to Trimethylgallium

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Abstract—A new synthetic route to trimethylgallium was developed. It is based on preparation of gallium methyl derivatives by the Green reaction, followed by their alkylation with methyl Grignard reagent. The suggested procedure is well reproducible, with the yield of pure trimethylgallium exceeding 90%.

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Successful implementation of a process for preparing semiconductor epitaxial gallium arsenide structures, accomplished for the first time by Manasevit, gave an impetus to wide use of trimethylgallium as one of the main precursors for the production of A^3B^5 semiconductor structures, primarily of GaAs, GaN, and $Ga_xAl_{1-x}As$, by MOCVD (metalorganic chemical vapor deposition) [1, 2]. Today, the most widely used method for commercial production of high-purity trimethylgallium is the reaction of a Ga–Mg mixture or alloy with methyl iodide in ether, following the overall equation [3–5]

$$2Ga + 3Mg + 6CH_3I \rightarrow 2Ga(CH_3)_3{\cdot}L + 3MgI_2,$$

where $L = (C_2H_5)_2O$, $(n\text{-}C_4H_9)_2O$, $(i\text{-}C_5H_{11})_2O$, or THF.

This method is the simplest in implementation, because the starting compounds do not exhibit high reactivity toward the surrounding medium, oxygen, and moisture. However, practical experience revealed a number of significant drawbacks of this route to trimethylgallium, the main of which is the gallium aggregation (agglutination of fine metal particles) in the course of the reaction. This phenomenon was more pronounced at larger scales of the synthesis [6]. At the same time, the occurrence of a side reaction, dealkylation of the intermediate Grignard reagent with methyl iodide (Wurtz reaction), makes it necessary to take magnesium and methyl iodide in excess relative to the overall reaction stoichiometry [6, 7].

The goal of this study was elimination of the above drawbacks of the direct synthetic route to trimethylgallium with the aim to optimize the synthesis process and reduce the production cost. According to published data, agglomeration may be caused by rapid destruction of the oxide film on the gallium surface under the action of Grignard reagent [8]. To confirm this conclusion, we performed a synthesis of trimethylgallium by adding a mixture of gallium metal and methyl iodide to an ether solution of methylmagnesium iodide prepared in advance. In this case, the Ga agglomeration was 65%, and the target product yield did not exceed 10% [6].

Therefore, it seemed necessary to improve the direct method for preparing trimethylgallium by dividing it into two steps [9]. The first step involved a convenient procedure for preparing gallium methyl derivatives, developed by Green et al. [10]. This method consisted in ultrasonic activation of a mixture of gallium metal, iodine, and methyl iodide in a toluene solution. The mechanism of this reaction involved intermediate formation of highly reactive gallium monoiodide “GaI” whose further reaction with methyl iodide resulted in rapid dissolution of the metal with the formation of methylgallium diiodide as the only product (as stated by the authors):

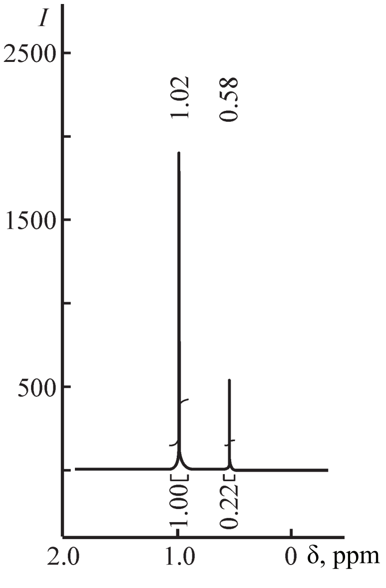
$$Ga + 0.5I_2 \xrightarrow{\text{Sonication}} \text{“GaI,”}$$

$$\text{“GaI”} + CH_3I \rightarrow CH_3GaI_2.$$

However, in the Green's procedure, methyl iodide is taken in a threefold excess relative to the reaction stoichiometry, which will inevitably lead to the subsequent occurrence of side dealkylation of the Grignard reagent and, as a consequence, to a decrease in the yield of the target product, trimethylgallium. Performing this reaction at equimolar reactant ratio did not lead to complete dissolution of the forming pale green "GaI" precipitate, whereas with 25% excess of methyl iodide the "GaI" dissolution was complete in 6 h. The need for taking methyl iodide in excess in this process is probably associated with the fact that the "GaI" formed in the reaction, according to data of several research teams [11, 12], is actually a mixture of different gallium sub-iodides with the prevalence of $[Ga]_2[Ga_2I_6]$.

As analytical data confirming the structure of the reaction product are lacking in Green's paper [10], we studied the composition of the compound obtained. For this purpose, the white crystalline substance isolated from the toluene solution was characterized by IR and ^{1}H NMR spectroscopy and by mass spectrometry.

In the IR spectrum of the compound, there are absorption bands corresponding to stretching vibrations of C–H bond [ν_{as}(CH) = 2979, ν_s(CH) = 2913 cm^{-1}], to bending [δ_{as}(CH$_3$) = 1393, δ_s(CH$_3$) = 1200 cm^{-1}] and rocking [ρ(CH$_3$) = 745 cm^{-1}] vibrations of methyl groups, and to stretching vibrations of the Ga–C bond (540, 576, 610 cm^{-1}). The ^{1}H NMR spectrum shown in the figure suggests the presence of two groups of nonequivalent protons (two singlets at δ 1.02 and 0.58 ppm).



^{1}H NMR spectrum of the Green reaction product. (*I*) Intensity and (δ) chemical shift.

Comparison of the results obtained with published data [13–15] shows that the product of the Green reaction contains both methyl and dimethyl gallium derivatives. This conclusion is confirmed by mass-spectrometric analysis. For example, in the mass spectrum, along with the characteristic fragment ions originating from different methyl and iodo gallium derivatives, there are molecular peaks of methylgallium diiodide [$M^+(CH_3{}^{69}GaI_2)$ = 338, $M^+(CH_3{}^{71}GaI_2)$ = 340] and dimethylgallium iodide {$M^+[(CH_3)_2{}^{69}GaI]$ = 226, $M^+[(CH_3)_2{}^{71}GaI]$ = 228}. Thus, analysis shows that the product of the Green reaction is a mixture of methylgallium diiodide and dimethylgallium iodide. According to the ^{1}H NMR data, the major product is CH_3GaI_2 (mole fraction 90%).

Methyl Grignard reagent was prepared by the standard procedure [16] using dipentyl ether as solvent. Addition of a toluene solution of gallium methyl derivatives to the methylmagnesium iodide solution obtained leads to complete alkylation of the gallium derivatives with the formation of the corresponding trimethylgallium etherate. The use of high-boiling dipentyl ether in the suggested procedure allows the etherate decomposition to be performed in situ, with isolation of the final product by distillation at the reaction mixture temperature of 120–150°C.

The subsequent purification of the trimethylgallium distillate obtained in the synthesis to remove impurities of the starting compounds, methyl iodide and toluene, by fractional distillation allowed the target product to be isolated in 92% yield based on gallium metal taken for the synthesis. The ^{1}H NMR spectrum of the purified sample contains a strong singlet from trimethylgallium methyl protons at $\delta = -0.11$ ppm [17]; the content of organic impurities does not exceed 0.1%.

Thus, the suggested procedure allowed the drawbacks of the direct synthesis of trimethylgallium to be eliminated, which, in turn, allowed the target product to be prepared in a yield exceeding 90% and the amount of the starting substances used in the synthesis, magnesium and methyl iodide, to be decreased.

EXPERIMENTAL

As starting substances we used an ingot of gallium metal of grade 99.999, GOST (State Standard) 12797–67; magnesium powder of MFP-3 grade, GOST 6001–79;

crystalline iodine, GOST 4159–79; pure grade toluene, GOST 14710–78; chemically pure grade methyl iodide, TU (Technical Specification) 6-09-3988– 83; and pure grade dipentyl ether, TU 6-09-3496–78.

All the reactions were performed in a dry argon atmosphere. The starting reactants were purified and dried before the synthesis [18]. Dipentyl ether and toluene were distilled from sodium metal. Methyl iodide was dried over P_2O_5 and then distilled. Magnesium metal powder was dried in a vacuum at 150°C for 3 h.

As a source of ultrasonic radiation, we used a UZU-0.25 ultrasonic installation. The ^{1}H NMR spectra were recorded with a Bruker Avance 400 spectrometer operating at 400 MHz, with C_6D_6 as solvent. The IR spectra were recorded with an Infralyum FT-801 spectrometer in the range 480–3300 cm^{-1} using KBr windows.

The mass spectra were taken with a DSQ II quadrupole mass spectrometer. Samples were prepared by dissolving 10 μg of a test substance in 100 μg of molten 1,2,4,5-tetramethylbenzene (mp 79°C) with vigorous stirring. After cooling, 1 μg of the solid solution obtained was placed in the capillary tube of the direct inlet system, which was introduced into the ion source of the mass spectrometer via vacuum sluice. The electron impact (70 eV) positive ion mass spectra were recorded in the range *m*/*e* 35–800 in the course of heating the sample from 50 to 200°C.

Gallium methyl derivatives. A 0.5-L three-necked flask filled with argon and equipped with a high-speed power-driven stirrer and a reflux condenser was placed in an ultrasonic water bath with the water temperature $T \geq 30$°C. The flask was charged in an argon stream with 72.4 g (0.285 mol) of crystalline iodine, 44 mL (0.71 mol) of methyl iodide, 190 mL of toluene, and 40 g (0.57 mol) of gallium metal. The contents were vigorously stirred and treated with ultrasound. Within 20 s after switching on the ultrasonic generator, the initially violet solution became colorless, and a pale green precipitate formed. The solution temperature was maintained in the course of the reaction in the interval 40–50°C to prevent the decomposition of the iodine compounds. The subsequent ultrasonic treatment with stirring for 6 h led to complete dissolution of the precipitate and formation of a transparent pale yellow solution.

For analysis, the reaction product was isolated from the toluene solution by distilling off the solvent in a vacuum.

Mass spectrum of the Green reaction product

m/*e*	Ion	I_{rel}, %
69, 71	$^{69}Ga^+$, $^{71}Ga^+$	40, 26
84, 86	$^{69}Ga(CH_3)^+$, $^{71}Ga(CH_3)^+$	4, 2
99, 101	$^{69}Ga(CH_3)_2^+$, $^{71}Ga(CH_3)_2^+$	15, 9
127	I^+	18
196, 198	$^{69}GaI^+$, $^{71}GaI^+$	24, 16
211, 213	$^{69}Ga(CH_3)I^+$, $^{71}Ga(CH_3)I^+$	100, 65
226, 228	$^{69}Ga(CH_3)_2I^+$, $^{71}Ga(CH_3)_2I^+$,	0.8, 0.5
254	I_2^+	0.9
323, 325	$^{69}GaI_2^+$, $^{71}GaI_2^+$	12, 8
338, 340	$^{69}Ga(CH_3)I_2^+$, $^{71}Ga(CH_3)I_2^+$	10, 6
437, 439, 441	$^{69}Ga_2(CH_3)_3I_2^+$, $^{69}Ga^{71}Ga(CH_3)_3I_2^+$, $^{71}Ga_2(CH_3)_3I_2^+$	0.05, 0.06, 0.02
450, 452	$^{69}GaI_3^+$, $^{71}GaI_3^+$	0.5, 0.3
549, 551, 553	$^{69}Ga_2(CH_3)_2I_3^+$, $^{69}Ga^{71}Ga(CH_3)_2I_3^+$, $^{71}Ga_2(CH_3)_2I_3^+$	0.03, 0.04, 0.01

IR spectrum (KBr), ν, cm^{-1}: 2979 [ν_{as}(CH)]; 2913 [ν_s(CH)]; 1393 [$\delta_{as}(CH_3)$]; 1200 [$\delta_s(CH_3)$]; 745 [$\rho(CH_3)$]; 610, 576, 540 [ν(Ga–C)]. ^{1}H NMR spectrum (C_6D_6, δ, ppm): 1.02 s (3H, CH_3GaI_2), 0.58 s [6H, $(CH_3)_2GaI$]. The mass spectrum is given in the table.

Methylmagnesium iodide. A 1-L three-necked flask filled with argon and equipped with a high-speed power-driven stirrer and a distillation headpiece was charged in an argon stream with 27.4 g (1.14 mol) of magnesium powder and 460 mL of dipentyl ether. To this mixture, 69 mL (1.11 mol) of methyl iodide was added dropwise over a period of 6 h. The temperature of the reaction mixture was maintained in the interval 40–45°C. After adding the whole amount of methyl iodide, the mixture was heated at 50–55°C for 1 h.

Trimethylgallium. A toluene solution of a mixture of methylgallium diiodide and dimethylgallium iodide was added dropwise to the methylmagnesium iodide solution over a period of 2 h. In the process, the temperature of the reaction mixture gradually increased. For complete methylation of the gallium alkyl derivatives, the contents were heated at 100–110°C for 5 h. In the course of heating, the color of the reaction mixture gradually changed from dark gray to white because of the formation of magnesium iodide. The first drops of trimethylgallium appeared in the reflux head of the distillation headpiece when the reaction mixture temperature reached 110°C. The subsequent increase in the temperature to 120°C led to intense refluxing in the reflux condenser at 60–80°C. At this temperature, we started to take off the product (a mixture of trimethylgallium with methyl iodide) with gradually raising the temperature of the reaction mixture. When the reflux temperature reached 110°C, the distillate takeoff was stopped. The amount of the crude product distilled off was 95 g.

Purification of trimethylgallium by fractional distillation. Further purification of the synthesis product was performed by fractional distillation at atmospheric pressure on a distillation column (height 300 mm, diameter 20 mm) packed with Nichrome spiral-prismatic Levin's packing (2 × 2 × 0.2 mm). We took off the distillate fraction with the vapor temperature of 55–56°C in an amount of 60.4 g (yield 92%). This fraction was collected into a preliminarily weighed stainless steel bellows cylinder. ^{1}H NMR spectrum (C_6D_6), δ, ppm: –0.11 s [9H, $Ga(CH_3)_3$].

CONCLUSION

A procedure was suggested for preparing trimethyl gallium with elimination of the side processes of gallium metal agglomeration and Grignard reagent dealkylation with excess methyl iodide, which, in turn, allows the final product yield as high as 92% to be achieved. The simultaneous decrease in the specific consumption of magnesium metal and expensive methyl iodide used in the synthesis allows the trimethylgallium production cost to be reduced.

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