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THE PREPARATION AND CHARACTERIZATION OF TRI-N-PROPYL-, TRI-ISOPROPYL- AND TRIVINYLGALLIUM*

J. P. OLIVER and L. G. STEVENS†
Department of Chemistry, Wayne State University
Detroit 2, Michigan

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Abstract—The preparation of three triorganogallium compounds is described in detail. The reaction of divinyl- and diallylmercury with gallium metal has been found to occur readily at room temperature unlike dialkylmercury compounds which require elevated temperatures before reaction occurs.

The compounds prepared have been characterized by their infra-red spectra, vapour-pressures, and melting points; and also, by the reactions with acid solution, iodine, trimethylamine, and ammonia.

Cryoscopic measurements show trivinylgallium exists as the dimer and a structure is postulated for this molecular species. The two tripropylgallium compounds are shown to be monomeric in the vapour state.

THE preparation of trialkylgallium compounds was first reported in 1932 by DENNIS[1] and by RENWANZ[2]. Trimethyl- and triethylgallium etherates were obtained from the reaction of the appropriate Grignard reagent on a solution of gallium trichloride in ether. Two methods were soon devised for the preparation of the ether free compounds; these methods are described by the following equations:

$$3HgR_2 + 2Ga \rightarrow 2GaR_3 + 3Hg$$
$$2GaCl_3 + 3ZnR_2 \rightarrow 2GaR_3 + 3ZnCl_2.$$

Both reactions were originally reported to form trialkylgallium compounds only when heated to reflux temperatures.[1,3] Recently divinylmercury has been reported to react with gallium metal at room temperature to produce ethylene and a vinylmetallic compound[4] A more complete study has shown that trivinylgallium is produced by this reaction.[5]

The exchange reaction

$$3AlR_3 + GaCl_3 \rightarrow GaR_3 + 3AlR_2Cl$$

has also been used for the preparation of trialkylgallium compounds but has not been described in detail.[6]

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† This work was taken in part from the Ph.D. Thesis of L. G. Stevens, Wayne State University, 1962.

[1] L. M. DENNIS, and W. PANTODE, *J. Amer. Chem. Soc.* **54**, 182 (1932).
[2] G. RENWANZ, *Ber. Dtsch. Chem. Ges.* **65 B**, 1208 (1932).
[3] C. A. KRAUS and F. E. TOONDER, *Proc. Nat. Acad. Sci.* **19**, 292 (1933).
[4] F. E. BRINCKMAN and F. G. A. STONE, *J. Inorg. Nucl. Chem.* **11**, 24 (1959).
[5] J. P. OLIVER and L. G. STEVENS, *J. Inorg. Nucl. Chem.* **19**, 378 (1961).
[6] J. EISCH and H. GILMAN, *Advances in Inorganic Chemistry and Radiochemistry*, (Edited by H. J. EMELEUS and A. G. SHARPE) Vol. 2, pp. 61–103. Academic, New York (1960).

The work so far cited provides several excellent procedures for the preparation of organogallium compounds, there is, however, little information concerning the physical and chemical properties of compounds other than trimethyl- and triethylgallium.[(7–9)]

The current interest in the catalytic activity of the Group III trialkyls, i.e., those of boron and aluminium, has lead us to undertake an exploration of the physical and chemical properties of simple triorganogallium compounds in the hope that they may prove useful in this area of research. This paper constitutes a report on the preparation of two previously unreported compounds, tri-n-propyl- and tri-isopropylgallium and a brief characterization of them by some of their physical and chemical properties, as well as a more complete discussion of the preparation and properties of trivinylgallium.

EXPERIMENTAL AND RESULTS

Apparatus. All reactions were carried out in standard high vacuum apparatus or under a nitrogen atmosphere being kept free of oxygen and water as required by the reactivity of these compounds. Further, this was required when handling trivinylgallium because of its vile and clinging odour and by the toxicity of the organomercury compounds.

Materials. The gallium and gallium trichloride used were reagent grade obtained from Fairmount Chemical Company. The di-n-propylmercury, di-isopropylmercury, and divinylmercury were synthesized by the reaction of an excess of the appropriate Grignard reagent with mercuric chloride.

A minor modification of this procedure found useful in this laboratory was to dissolve the mercuric chloride in tetrahydrofuran. The solution was then added through a dropping funnel to the Grignard reagent; thus eliminating the soxhlet extractor normally used. This procedure was found useful in the preparation of these mercury compounds. The mercury compounds were purified by repeated fractional distillation and identified by vapour-pressure. The infra-red spectra were taken and showed that no ether was retained in the mercury compounds.

Tri-n-propylgallium. The reaction of di-n-propylmercury with gallium metal was carried out using 11·1 mmole of $Hg(n\text{-}C_3H_7)_2$ with 7·43 mmole of gallium metal. This provided a very small excess of gallium metal. The reaction mixture was sealed into a glass tube and heated on a steam bath for 3 days, then cooled in ice-water with resultant solidification of the metal indicating that the reaction had not proceeded to a great extent. The reaction mixture was then heated at 150°C for 15 hr. The reaction products were transferred to the vacuum line for analysis and separation.

A small amount of gas which was noncondensable in liquid nitrogen was found, most likely, hydrogen. In addition, substantial amounts of propane and propylene were obtained. The remaining heavy material was used without further purification in the following experiments and constituted a yield of approximately 80 per cent.

The reaction of n-propylmagnesium bromide on gallium trichloride was also used to prepare tri-n-propylgallium.* This reaction proved less satisfactory, however,

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* This method for the preparation of tri-n-propylgallium has recently been reported in the literature, but no details of preparation were included.(10)

(7) G. E. COATES, *J. Chem. Soc.* 2003 (1951).

(8) G. E. COATES and R. G. HAYTER, *J. Chem. Soc.* 2519 (1953).

(9) G. E. COATES, *Organometallic Compounds* (2nd Ed.). J. Wiley, New York (1960).

(10) H. HARTMANN and H. LUTSCHE, *Naturwissenschaften* **48,** 601 (1961).

yielding a product difficult to separate from the ether which was used as a solvent. The acid hydrolysis, of the partially purified product, carried out as described below, gave a propane to gallium ratio of 2·9:1 for this product.

Tri-isopropylgallium. Due to the success of the metal exchange used in the preparation of the tri-n-propylgallium, this was the only procedure used in the preparation of tri-isopropylgallium. In a reaction tube 2·26 mmole of gallium metal was placed and 1·45 mmole of di-isopropylmercury was distilled into the tube. This was sealed off and heated in an oil bath at 150°C for 8 hr. The tube was then reattached to the vacuum line and products transferred into it for separation and analysis.

A considerable amount of hydrocarbons, consisting largely of propane and propylene were removed by fractional distillation. The purified product represented a 75 per cent yield of tri-isopropylgallium.

Trivinylgallium. Three different methods have been tried for the preparation of trivinylgallium. The first, the reaction of sodium vinyl and dimethylgallium chloride proved to give complex reaction products containing trace amounts of volatile gallium compounds. The second, the reaction of vinylmagnesium chloride with gallium trichloride in ether, provided small amounts of volatile gallium compounds which upon hydrolysis yielded ethylene. The low yields of these reactions, however, made them impractical.

The third method for the preparation of trivinylgallium was the reaction of divinylmercury with gallium metal. In this case divinylmercury was distilled into a reaction vessel containing an excess of gallium metal and the reaction carried out at room temperature. Best results were obtained when the reaction mixture was allowed to stand for 12 hr and then stirred with a magnetic stirrer in the presence of broken glass for approximately 4 hr. A typical reaction was carried out using 1·20 g of gallium metal and 3·86 g of divinylmercury. The purified product from this reaction weighed 1·31 g which represents a yield of 87 per cent based on the divinylmercury used in the reaction.

It should also be pointed out that when very carefully purified divinylmercury is used and all air and moisture is rigorously excluded, no ethylene is evolved during the course of the reaction as had previously been found.(5)

The product was purified by downward flow of the vaporized reaction products through a trap designed for fractional crystalization. This trap was maintained at −23°C allowing the trivinylgallium to crystallize on the sides of the tube, while, the divinylmercury drained into the bottom of the trap and could then be distilled away. Material purified in this manner contained no impurities detectable by mass spectrometry and was used in the subsequent reactions.

Triallylgallium has also been obtained by the reaction of diallylmercury under the conditions used for the preparation of trivinylgallium.* The details of this preparation and the properties of triallylgallium will be discussed in a subsequent paper.

Analysis. Samples of the gallium compounds were distilled from the vacuum line into weighted tubes, equipped with stopcocks and standard tapper joints, which were then reweighed providing an accurate method for determination of the sample size. Then the tube was reattached to the vacuum line and approximately 1 ml of either water or 6N hydrochloric acid was distilled into the vessel to hydrolyse the sample.

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* Triallylgallium has also been prepared in this laboratory by the reaction of allyl Grignard reagent on gallium trichloride.

It was found that the aqueous hydrolysis was quite slow and did not go to completion in a reasonable time unless the lower portion of the reaction vessel was heated in a bath maintained at 100°C causing the reaction to take place under reflux conditions. Even then, it required 48 hr for complete hydrolysis of a sample of trivinylgallium. The acid hydrolysis is considerably more rapid in all cases, but required heating to drive the reaction to completion in less than a day. The complete reaction proceeds according to the equation:

$$GaR_3 + xH_2O + 3H^+ \rightarrow Ga(H_2O)_x{}^{3+} + 3RH.$$

The hydrolysis of tri-n-propyl- and tri-isopropylgallium was even more difficult to drive to completion requiring prolonged periods of heating in acid solution. The gas evolved during the hydrolysis was transferred to the vacuum line and its quantity determined in a standard volume. The results of the hydrolysis experiments are given in Table 1. The gallium analysis⁽¹¹⁾ was carried out by titration with potassium ferrocyanide while the evolved gases were identified by their infrared spectra.⁽¹²⁾ Ethylene was produced on the hydrolysis of trivinylgallium and propane was obtained from the two propyl derivatives. In all cases, the purity of the gas was determined by use of gas–liquid chromatography.

TABLE 1.—PRODUCTS FROM THE HYDROLYSIS OF THE ORGANOGALLIUM COMPOUNDS

Sample	Evolved gas (mmole) Calc.	Evolved gas (mmole) Found	Gallium (mmole) Calc.	Gallium (mmole) Found
Trivinylgallium				
23·4 mg (HCl)	0·465	0·461	0·155	0·146
42·5 mg (H_2O)	0·842	0·835	0·281	0·257
Tri-n-propylgallium				
72·5 mg (HCl)	1·092	1·105	0·364	0·356
Tri-isopropylgallium				
119·5 mg (HCl)	1·803	1·751	0·601	0·564

Reactions with halogens. In addition to the above analysis, samples of the tri-n-propyl- and tri-isopropylgallium were reacted with iodine and chlorine in an effort to further substantiate their structures by the production of the corresponding halogenated alkyls.

The reaction with iodine was performed by distilling a sample of either tri-n-propyl- or tri-isopropylgallium into a tube which was then attached to an apparatus containing iodine. This was so arranged that the iodine could readily be sublimed into the reaction vessel which was immersed in liquid nitrogen. When a known quantity of iodine had been sublimed into the reaction vessel, it was allowed to warm to room temperature and tipped so that the gallium compound could come in contact with the solid iodine. The gallium compounds dissolved the iodine giving a brown solution which was decolourized in 5–10 min when an excess of the gallium compound was present.

The resulting alkyl iodides which were produced in nearly quantitative yield were identified by their infra-red spectra and shown to be n-propyl iodide from tri-n-propylgallium and isopropyl iodide from tri-isopropylgallium, substantiating the formulation of the compounds.

(11) R. BELCHER, A. J. NUTTEN and W. L. STEPHEN, *J. Chem. Soc.* 2438 (1952).

(12) R. H. PIERSON, A. N. FLETCHER and E. GANTZ, *Analyt. Chem.* **28**, 1218 (1956).

Chlorine was also reacted with tri-isopropylgallium, but in this case the reaction did not proceed quantitatively to produce gallium trichloride and isopropyl chloride but produced isopropyl chloride as well as some other chlorinated products and a black residue. The reaction proceeded in this general fashion even when stoichemetric amounts of chlorine were added to tri-isopropylgallium, cooled with liquid nitrogen, and allowed to warm very slowly to room temperature.

Physical properties. The melting points of trivinyl- and tri-n-propylgallium and triallylgallium have been determined by the Stock method and are given in Table 2 with melting points of trimethyl- and triethylglallium for reference. The melting point of tri-isopropylgallium is below −100°C, but was not determined precisely.

TABLE 2.—MELTING POINTS OF SEVERAL TRISUBSTITUTED GALLIUM COMPOUNDS

Compound	m.p. (°C)
Trivinylgallium	9·0 ± 1°
Trimethylgallium[13]	15·70–15·9°
Triallygallium	72·0 ± 1°
Triethylgallium[13]	82·3°
Tri-n-propylgallium	85·2 ± 1°
Tri-isopropylgallium	Below −100°

The vapour-pressure of tri-n-propyl-, tri-isopropyl-, and trivinylgallium were determined over the temperature range 25–100°C and are given by the equation $\log_{10} P_{mm} = -A/T + B$. The values for A and B are given in Table 3; the calculated heats of vaporization are also included. The two tripropylgallium compounds were found to be stable over the temperature range used, however, trivinylgallium started to decompose at approximately 60°C to a brown oil and a mixture of hydrocarbons.

TABLE 3.—VAPOUR-PRESSURE AND HEATS OF VAPORIZATION FOR TRIVINYL-, TRI-N-PROPYL-, AND TRI-ISOPROPYLGALLIUM FOR THE EQUATION ($\log_{10} P_{mm} = -A/T + B$)

	A	B	ΔHvap. kcal/mole
Trivinylgallium	3790	12·12	17·4
Tri-n-propylgallium	2567	8·510	11·7
Tri-iso-propylgallium	2560	8·637	11·7

Molecular weights. The gas phase molecular weights of tri-n-propyl- and tri-isopropylgallium were determined and found to be within experimental error of the molecular weight of the monomer, calc. 198·99. Repeated efforts to determine the gas phase molecular weight of trivinylgallium resulted in failure due to its low vapour-pressure and its tendency to undergo polymerization. Cryoscopic measurements in cyclohexane, however, clearly show that this compound exists as a dimer in solution, calc. mol. wt. 301·72. The average molecular weight determined from three independent experiments was 302.

Infra-red spectra. The infra-red spectra of trivinyl-, tri-n-propyl- and tri-isopropylgallium are recorded in Table 4. These spectra were taken in carbon tetrachloride solution using a Beckman I.R. 4 Spectrophotometer.

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(13) E. WIBERG, T. JOHNNSEN and O. STECHER, *Z. Anorg. Chem.* **251**, 114 (1943).

TABLE 4.—INFRA-RED SPECTRA OF SEVERAL ORGANOGALLIUM COMPOUNDS

$Ga(C_2H_3)_3$ (cm^{-1})		$Ga(nC_3H_7)_3$ (cm^{-1})		$Ga(iC_3H_7)_3$ (cm^{-1})	
3013	*m*	2936	*s*	2935	*s*
2935	*m*	1464	*m*	2857	*s*
2909	*m*	1425	*w*	1468	*m*
1394	*s*	1379	*w*	1385	*m*
1264	*w*	1333	*w*	1162	*w*
1042	*m*	1063	*s*	1122	*m*
1017	*s*	1022	*w*	1063	*w*
981	*m*	982	*m*	988	*w*
952	*s*			959	*m*
				875	*w*

Reaction with air. The 5 per cent carbon tetrachloride solutions used for the infra-red measurements were opened to the air. No immediate reaction appeared to take place, however, between 30 and 60 min later the solutions of the tripropylgallium compounds became cloudy. After standing overnight a white crystalline precipitate formed. Trivinylgallium reacted more slowly requiring several hours of exposure to the atmosphere before any cloudiness appeared and one to two days for complete precipitation of a white crystalline material. These products are now under investigation but have not yet been rigorously identified.

Reactions with ammonia and Trimethylamine. A known amount of ammonia or trimethylamine was distilled into tubes containing weighted samples of the gallium compounds. The tubes were then closed off, warmed to room temperature for several minutes and cooled with a dry-ice–acetone bath. The tubes were then reopened to the vacuum line and the excess reactant distilled away and measured. In all cases, the initial uptake of amine corresponds to the formation of 1:1 addition compound. All of these products were liquid at room temperature and the vapour pressures were less than 1 mm at 25°C.

The trimethylamine compounds were quite stable toward hydrolysis or reaction with the atmosphere, as were the ammonia adducts. However, the ammonia addition compounds slowly decomposed at room temperature with evolution of hydrocarbon and the formation of a new gallium compound.

DISCUSSION

All of the physical and chemical data support the assignment of the formulas of tri-n-propylgallium and tri-isopropylgallium. In particular these structures are supported by the formation of the corresponding iodides from the reaction of iodine with the compound in question. Also the infra-red spectra of the parent compounds are compatible with this assignment.(14) The considerable amount of decomposition which occurred in the preparation of both tri-propylgallium compounds leads one to suspect that rearrangement might have occurred and the infra-red spectrum does not rule out this possibility. However, as noted earlier, the essentially quantitative formation of the corresponding alkyl iodides from these compounds demonstrates that little rearrangement took place.

(14) L. J. BELLAMY, *The Infra-red Spectra of Complex Molecules*, J. Wiley, New York (1954).

The trivinylgallium has been characterized from its infra-red spectrum which clearly indicates the vinyl substituent(11,15) and from its quantitative hydrolysis to ethylene and Ga^{3+}. In addition, the nuclear magnetic resonance spectrum has been obtained and indicates that the three vinyl groups are equivalent.* A complete analysis of this spectrum will be given at a later date.

It is suggested from several different physical measurements that trivinylgallium exists as a dimer or higher polymer in liquid phase, in solution, and in the solid state. The evidence supporting this is as follows:

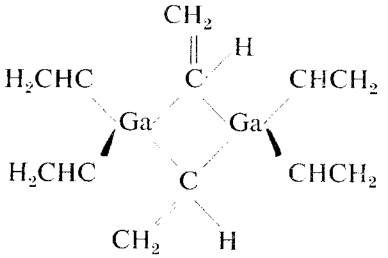
(1) Trivinylgallium has a very high melting point (−9°C) compared to triethylgallium (−82·3) but quite similar to that of trimethylgallium (−15·8).

(2) The vapour-pressure of trivinylgallium is considerably lower (0·8 mm ± 0·1 at 25°C) than that of triethylgallium (6·8 mm at 25°C).

(3) Cryoscopic measurements in cyclohexane indicate that the molecular weight is 302.

These data show conclusively that trivinylgallium exists as a dimer in solution and suggest that in the pure liquid and in the solid state it occurs as a dimer or more highly associated species. Unfortunately, little information is avaliable on the molecular structures of gallium compounds except that there is some evidence for association of trimethylgallium in the liquid state(17) and for the association of triethylgallium in benzene solution.(1) Comparing vapour-pressures and melting points of these two compounds with trivinylgallium provides strong circumstantial evidence for molecular association in both liquid and solid trivinylgallium.

The structure of the dimer is most likely similar to that known for the aluminium alkyls with the bridge bonding carbon atom



however, the possibility exists for the bonding to occur between the vacant *p*-orbital on the gallium and the π-electrons in the vinyl group. The present data does not allow a distinction to be made between these two possibilities.

* The equivalence of the three vinyl groups as demonstrated by n.m.r. is not anticipated from the proposed dimeric structure. However, this can be explained on the basis of a rapid equilibrium involving the exchange of the vinyl bridge groups with the terminal groups regardless of whether this equilibrium is inter- or intra-molecular. A similar equivalence of bridging and terminal alkyl groups has been demonstrated for the dimer of trimethylaluminum at ambient temperature.(16)

(15) (a) H. D. Kaesz and F. G. A. Stone, *Spectrochim. Acta* **15**, 360 (1959); (b) H. D. Kaesz and F. G. A. Stone, *Organometallic Chemistry*, *Amer. Chem. Soc.* Monograph No. 147 (Edited by H. Zeiss, p. 88–149 Reinhold, New York (1960).

(16) N. Muller and D. E. Pretchard, *J. Amer. Chem. Soc.* **82**, 248 (1960); S. Brownstein, B. C. Smith, G. Erlich and A. W. Lambengayer, *Ibid.* **82**, 1000 (1960); M. P. Groenewege, J. Smidt and H. de Vries, *Ibid* **82**, 4425 (1960).

(17) L. H. Long and J. F. Sackman, *Trans. Faraday Soc.* **54**, 1797 (1958).

Furthermore, it should be noted that there is a great disparity in the ease of preparation of the triorganogallium compounds from the corresponding mercury derivatives. In the case of the saturated hydrocarbons the reaction takes place only at elevated temperatures, while for the vinyl and allyl compounds reaction occurs readily at room temperature.

There are two possible explanations for this depending upon the mechanism of reaction. In the event of a radical reaction the ease of formation of the hydrocarbon free radical will be the determining step. This appears quite reasonable since the thermal decomposition of the mercury compound produces the corresponding free radical and reaction of the mercury compounds with gallium occurs near the decomposition point. The lack of radical rearrangement products makes this explanation somewhat dubious.

The second explanation can be given assuming that the reaction occurs between an electrophilic gallium atom and the carbon–mercury bond. In this case the polarity of the bond will influence the ease of reaction. This will increase greatly between the saturated mercury compounds and the unsaturated derivatives again providing a qualitative explanation in agreement with experiment. This explanation is further supported by work on other metal exchange reactions in which retention of configuration is observed, indicating a substitution mechanism.(15b) Neither of these explanations can be eliminated, however, until further work is carried out on gallium–mercury systems.

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