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Organometallic Compounds of Group III. I. The Preparation of Gallium and Indium Alkyls from Organoaluminum Compounds[1a]

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Two new methods for preparing gallium and indium alkyls have been developed: (a) the transalkylation reaction between a gallium(III) or indium(III) halide (MX_3) and an aluminum alkyl; (b) the displacement reaction between the metal iso-butyl derivative and a higher olefin. In the former method it was found necessary to employ a $1:3$ ratio of $MX_3:AlR_3$ and to add three equivalents of KCl in order to obtain high yields of MR_3. Final purification of MR_3 from admixed AlR_3 was effected by preferential complexation of the AlR_3 with alkali fluorides. The second synthetic method ran smoothly with tri-iso-butylgallium and a typical olefin, 1-decene. However, although the reaction was attainable with tri-iso-butylindium and 1-decene also, the thermal instability of InR_3 at the necessary reaction temperature beclouded the preparative utility of this method for higher InR_3. The mechanism of the olefin displacement reaction is discussed in light of the thermal decomposition of $M[CH_2CH(CH_3)_2]_3$ itself.

The classic researches in organoaluminum chemistry by Ziegler and co-workers have been a forceful impetus in the postwar florescence of organometallic chemistry.[2] New synthetic methods for aluminum alkyls starting from olefins, aluminum metal and hydrogen make these compounds potentially the cheapest and most accessible organometallic reagents of commerce.[3] The newly discovered reactions of these aluminum alkyls range from their catalytic activity in olefin and diolefin polymerization processes to their stoichiometric use in the synthesis of long-chain alcohols and olefins from ethylene.[2] Among other uses, aluminum alkyls and alkylaluminum hydrides have demonstrated their utility in such diverse fields as the refining of aluminum,[4] the production of tetraethyllead,[5] the anti-Markownikoff hydration of α-olefins,[6] the hydride reduction of carbonyl compounds[7] and acetylenes[8] and the synthesis of boron alkyls[9] and boron hydrides.[10]

Because of the theoretical and practical significance of this novel organoaluminum chemistry, it became of interest to investigate the behavior of other Group III metal alkyls in the light of these findings. The object of the present study, delineated in this and succeeding papers, was to learn to what extent the chemistry of the little-known gallium alkyls and indium alkyls resembles that of aluminum alkyls. The first phase of the program consisted in finding suitable methods for preparing gallium and indium alkyls.

Previously, gallium alkyls had been prepared in a number of ways, such as: (a) the treatment of gallium(III) halides with Grignard reagents in ethereal solution[11,12]; (b) the displacement reaction between gallium metal and mercury alkyls in a solvent-free system[12–16]; (c) the reaction of gallium(III)

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[1] (a) This work constitutes a part of the results presented at the Organometallic Symposium, sponsored by the Cincinnati Section, A.C.S., October 29, 1958. (b) Department of Chemistry, University of Michigan, Ann Arbor, Michigan.

[2] *Cf.*, (a) K. Ziegler, Plenary Lecture: "Aluminum in Organic Chemistry," IUPAC, Zurich, Switzerland, July 21–27, 1955, as reprinted in *Experientia*, Supplement II; (b) K. Ziegler and co-workers, *Ann.*, **629**, 1–256 (1960).

[3] K. Ziegler, H.-G. Gellert, H. Lehmkuhl, W. Pfohl and K. Zosel, *Ann.*, **629**, 1 (1960).

[4] K. Ziegler and H.-G. Gellert, *Angew. Chem.*, **67**, 424 (1955).

[5] K. Ziegler and H. Lehmkuhl, *ibid.*, **67**, 424 (1955).

[6] K. Ziegler, F. Krupp and K. Zosel, *ibid.*, **67**, 425 (1955).

[7] K. Ziegler, K. Schneider and J. Schneider, *ibid.*, **67**, 425 (1955).

[8] G. Wilke and H. Müller, *Chem. Ber.*, **89**, 444 (1956).

[9] R. Köster, *Angew. Chem.*, **68**, 383 (1956).

[10] R. Köster and K. Ziegler, *ibid.*, **69**, 94 (1957).

[11] (a) J. Renwanz, *Ber.*, **65**, 1308 (1932); (b) C. A. Kraus and J. E. Toonder, *Proc. Natl. Acad. Sci.* (U. S.), **19**, 292 (1933) [*C. A.*, **27**, 2646 (1933)].

[12] L. M. Dennis and W. Patnode, *J. Am. Chem. Soc.*, **54**, 182 (1932).

[13] E. Wiberg, J. Johannsen and O. Stecher, *Z. anorg. allgem. Chem.*, **251**, 114 (1943).

[14] G. E. Coates, *J. Chem. Soc.*, 2011 (1951).

[15] A. W. Laubengayer and W. J. Gilliam, *J. Am. Chem. Soc.*, **63**, 477 (1941).

[16] H. Gilman and R. G. Jones, *ibid.*, **62**, 980 (1940).

halides with zinc alkyls in a hydrocarbon solvent[11b,13]; (d) the alkylation of dialkylgallium halides with lithium alkyls.[17] The corresponding indium alkyls have been prepared according to methods a[18] and b[19,20] given above. In this work the feasibility of employing the more accessible aluminum alkyls as alkylating agents for other Group III metal halides was examined, since it has been shown that boron alkyls can be prepared in good yield from boron halides and aluminum alkyls.[21,22] The preparation of the key structural types, triethylgallium(I) and tri-isobutylgallium(II), from gallium(III) halides and the corresponding trialkylaluminum compounds was found to be an excellent synthetic procedure having certain interesting characteristics. First, as in other reactions of AlR_3, only one alkyl was "available" for alkylation; the stoichiometry of the reaction with $GaBr_3$ took the form

$$GaBr_3 + 3Al(C_2H_5)_3 \longrightarrow Ga(C_2H_5)_3 + 3Al(C_2H_5)_2Br \quad >80\% \qquad (1)$$

Secondly, the reaction of the aluminum alkyl with gallium(III) chloride instead gave about a 45% yield of the gallium alkyl, based upon the 1:3 reactant ratio in equation 1. This prompted the notion that one-half of the gallium halide was being bound up in a complex with the by-product, $Al(C_2H_5)_2Cl$. Hence, the following reaction scheme is proposed

$$GaCl_3 + 3Al(C_2H_5)_3 \longrightarrow Ga(C_2H_5)_3 + 3Al(C_2H_5)_2Cl \qquad (2)$$

$$GaCl_3 + 3Al(C_2H_5)_2Cl \longrightarrow Ga[Al(C_2H_5)_2Cl_2]_3 \qquad (3)$$

$$2GaCl_3 + 3Al(C_2H_5)_3 \longrightarrow \underset{\text{I}}{Ga(C_2H_5)_3} + \underset{\text{III}}{Ga[Al(C_2H_5)_2Cl_2]_3} \qquad (4)$$

The net reaction expressed by equation 4 is consistent with the observation that the residue of a reaction from which a 42% yield of I had already been obtained and which contained unreacted $Al(C_2H_5)_3$ and presumably III yielded upon addition of excess solid potassium chloride an additional 42% yield of I. This suggests that the KCl complexes preferentially with diethylaluminum chloride and hence frees the gallium chloride for complete alkylation

$$Ga[Al(C_2H_5)_2Cl_2]_3 + 3KCl \longrightarrow GaCl_3 + 3K[Al(C_2H_5)_2Cl_2] \qquad (5)$$

The existence of the complex III (or possibly lower complexes, such as $GaCl_3 \cdot Al(C_2H_5)_2Cl$ was tested by admixing gallium(III) chloride with three equivalents of diethylaluminum chloride and observing an exothermic reaction. The resulting solution distilled uniformly and completely under reduced pressure to yield a distillate containing approximately the proper amount of chlorine. Therefore, it was established that alkylation of gallium(III) chloride by trialkylaluminum was best done in the presence of potassium chloride to avoid such complexation

$$GaCl_3 + 3AlR_3 + 3KCl \longrightarrow GaR_3 + 3K[AlR_2Cl_2] \qquad (6)$$

Both triethylgallium and tri-isobutylgallium were obtained in yields of 90% by this method.

In the preparation of indium alkyls by this method the inclusion of potassium chloride in the reaction mixture proved essential to isolating any indium alkyl at all. Thus, treatment of indium(III) chloride with three equivalents of triethylaluminum (analogous to equations 1 and 2) gave upon distillation only $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$. Apparently, both indium(III) chloride and any triethylindium formed were complexed too strongly with diethylaluminum chloride to permit distillation of the triethylindium. Addition of potassium chloride again permitted a high yield of triethylindium. However, in the case of tri-isobutylindium the distilled product was approximately a 1:1 mixture of tri-isobutylindium and tri-isobutylaluminum, even in the presence of potassium chloride.

The final purification of the gallium alkyls and indium alkyls prepared in the above method from either traces or considerable quantities ($In(C_4H_9)_3$ case) of co-distilled aluminum alkyls was effected conveniently by redistillation of the products over solid alkali fluorides. The success of this technique is based upon the observation that galliumalkyls formed 1:1 complexes with potassium fluoride, but not discernibly with sodium fluoride.

$$Ga(C_2H_5)_3 + KF \longrightarrow K[Ga(C_2H_5)_3F] \qquad (7)$$

In comparison, indium alkyls gave no observable complexation with either alkali fluoride. Since aluminum alkyls form strong 1:1 complexes with both alkali fluorides,[23] gallium alkyls could be freed of AlR_3 traces by warming with powdered sodium fluoride and distilling. Indium alkyls, on the other hand, were separable from admixed aluminum alkyls by employing potassium fluoride in an analogous fashion. Thus the desired tri-isobutylindium could be obtained free of tri-isobutylaluminum in this manner.

The accessibility of the isobutyl derivatives of gallium and indium inspired a second novel synthesis of alkyl derivatives of these metals. It has been observed that aluminum alkyls undergo two principal types of reactions with olefins, namely, that of addition to the carbon-carbon double bond, as in ethylene[24,25]

$$AlR_3 + 3nCH_2{=}CH_2 \longrightarrow Al[(CH_2CH_2)_nR]_3 \qquad (8)$$

or that of displacement[26]

$$Al(CH_2CHR_2)_3 + 3CH_2{=}CHR' \longrightarrow Al(CH_2CH_2R')_3 + 3CH_2{=}CR_2 \qquad (9)$$

Since displacement is favored when straight-chain

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[17] H. P. A. Groll, U. S. Patent 1,938,179 [*C. A.*, **28**, 1053 (1934)].

[18] J. Runge, W. Zimmermann, H. Pfeiffer and D. Pfeiffer, *Z. anorg. allgem. Chem.*, **267**, 39 (1951).

[19] W. C. Schumb and H. I. Crane, *J. Am. Chem. Soc.*, **60**, 306 (1938).

[20] H. Gilman and R. G. Jones, *ibid.*, **62**, 2353 (1940).

[21] R. Köster, *Ann.*, **618**, 31 (1958).

[22] As described in the Experimental section, triethylgallium was prepared in one instance from gallium(III) bromide and diethylzinc. As the requisite zinc alkyl was obtained from zinc chloride and triethylaluminum, this suggested the direct alkylation of gallium(III) halide with organoaluminum compounds.

[23] K. Ziegler, R. Köster, H. Lehmkuhl and K. Reinert, *Ann.*, **629**, 33 (1960), report also the formation of 1:2 complexes of the type, $MF \cdot 2AlR_3$.

[24] K. Ziegler and co-workers, *Brennstoff-Chem.*, **33**, 193 (1952).

[25] K. Ziegler, H.-G. Gellert, K. Zosel, E. Holzkamp, J. Schneider, M. Söll and W.-R. Kroll, *Ann.*, **629**, 121 (1960).

[26] K. Ziegler, W.-R. Kroll, W. Larbig and O.-W. Steudel, *ibid.*, **629**, 53 (1960).

α-olefins react with aluminum alkyls the alkyl group of which is branched in the β-position, higher aluminum alkyls can be prepared by heating tri-isobutylaluminum and α-olefins at 100–110° and allowing the isobutylene to escape[2a]

$$\mathrm{Al[CH_2CH(CH_3)_2]_3 + 3CH_2{=}CHR \xrightarrow{\Delta} Al(CH_2CH_2R)_3 + 3CH_2{=}C(CH_3)_2\uparrow} \quad (10)$$

Boron alkyls also have been shown to undergo this type of displacement reaction at a convenient rate above 120.[27] Therefore, it was of interest to test the extension of this reaction to gallium and indium alkyls. By heating tri-isobutylgallium(II) with a slight excess of 1-decene, it was found that the isobutylene was evolved steadily in the temperature range of 155–160°. After the gas evolution had ceased, the excess 1-decene was pumped off to leave a residue of pure tri-*n*-decylgallium. Thus

$$\mathrm{Ga[CH_2CH(CH_3)_2]_3 + 3CH_2{=}CHC_8H_{17} \longrightarrow Ga(C_{10}H_{21})_3 + 3CH_2{=}C(CH_3)_2\uparrow} \quad (11)$$

the displacement reaction with olefins and II offers an excellent route to higher, non-distillable gallium alkyls.

The analogous reaction between tri-isobutylindium and 1-decene encountered the difficulty that at the temperature necessary for isobutylene evolution the indium alkyls were unstable. The evolved gas was largely isobutylene (83%), which indicates that a displacement had occurred.

$$\mathrm{In[CH_2CH(CH_3)_2]_3 + 3CH_2{=}CHC_8H_{17} \longrightarrow In(C_{10}H_{21})_3 + 3CH_2{=}C(CH_3)_2\uparrow} \quad (12)$$

The quantities of hydrogen (9.4%) and isobutane (7.6%) suggest that only a minor amount of the tri-isobutylindium itself underwent thermal decomposition during the heating period (*vide infra*). However, the fact that a large amount of indium metal (64%) was deposited during the reaction points to the subsequent thermal breakdown of tri-*n*-decylindium (*e.g.*, equation 13).

$$\mathrm{2In(CH_2CH_2{-}C_8H_{17})_3 \longrightarrow 2In\downarrow + (1\text{-}C_{10}H_{20}) + 3}n\text{-}\mathrm{C_{10}H_{22}} \quad (13)$$

$$\mathrm{In(CH_2CH_2{-}C_8H_{17})_3 \longrightarrow In\downarrow + 3(}l\text{-}\mathrm{C_{10}H_{20}) + 1^1/_2H_2} \quad (14)$$

A thermal breakdown as depicted in equation 14 is much less important due to the minor proportion of hydrogen evolved.

The ease with which isobutyl derivatives of Group III participate in the displacement reaction seems to decrease approximately in the order Al > B > Ga > In. To shed light upon the pathway of the displacement reaction with tri-isobutylgallium, the thermal dissociation of the latter compound was investigated. In addition to gallium metal itself, isobutylene and hydrogen were formed almost exclusively in about a 2:1 ratio (1.8:1.0) at a temperature of 155°. Thus, a decomposition scheme compatible with these data is

$$\underset{\text{II}}{\mathrm{Ga[CH_2CH(CH_3)_2]_3}} \xrightarrow{\Delta} \mathrm{Ga[CH_2CH(CH_3)_2]_2H + CH_2{=}C(CH_3)_2\uparrow} \quad (15)$$

$$\underset{\text{III}}{\mathrm{3Ga[CH_2CH(CH_3)_2]_2H}} \longrightarrow \mathrm{2Ga[CH_2CH(CH_3)_2]_3 + GaH_3} \quad (16)$$

$$\mathrm{GaH_3 \longrightarrow Ga + 1.5H_2} \quad (17)$$

$$\mathrm{Ga[CH_2CH(CH_3)_2]_3 \longrightarrow Ga + 1.5H_2 + 3CH_2{=}C(CH_3)_2} \quad (18)$$

In the presence of an olefin, *e.g.*, 1-decene, the di-isobutylgallium hydride formed in equation 15 does not accumulate but adds promptly to the olefin (equation 19). The unsymmetrical type, $\mathrm{R_2GaR'}$, could then disproportionate to complete the reaction (equation 20)

$$\mathrm{Ga[CH_2CH(CH_3)_2]_2H + CH_2{=}CH{-}C_8H_{17} \longrightarrow Ga[CH_2CH(CH_3)_2]_2C_{10}H_{21}} \quad (19)$$

$$\underset{\text{IV}}{\mathrm{3Ga[CH_2CH(CH_3)_2]_2C_{10}H_{21}}} \longrightarrow \mathrm{2Ga[CH_2CH(CH_3)_2]_3 + Ga(C_{10}H_{21})_3} \quad (20)$$

Support for the rapidity of the addition shown in equation 19 is based upon the observed facility with which diethylgallium hydride adds to 1-decene at 80°.[28] Moreover, the resulting *n*-decyldiethylgallium is unstable to disproportionation into triethylgallium and tri-*n*-decylgallium above 100°,[28] analogous to the proposal in equation 20. Finally, it should be noted that both the thermal breakdown of tri-isobutylgallium (equations 15–18) and the olefin displacement reaction (equation 11) require a temperature of 150–160° to occur at a reasonable rate. All these observations taken together tend to indicate that the sequence of steps indicated in equations 15, 19 and 20 is important in the olefin displacement reaction with tri-isobutylgallium.

An alternative or competing pathway to be borne in mind for the postulated disproportionation of III (equation 16) and of IV (equation 20) is the step-wise elimination of isobutylene

$$\mathrm{Ga[CH_2CH(CH_3)_2]_2H \longrightarrow Ga[CH_2CH(CH_3)_2]H_2 + CH_2{=}C(CH_3)_2} \quad (21)$$

$$\mathrm{Ga[CH_2CH(CH_3)_2]_2C_{10}H_{21} \longrightarrow Ga[CH_2CH(CH_3)_2][C_{10}H_{21}]H + CH_2{=}C(CH_3)_2} \quad (22)$$

The iso-butylgallium dihydride could then lose isobutylene and decompose as in equation 17. The isobutyl-*n*-decylgallium hydride, on the other hand, could add to 1-decene and the isobutyldi-*n*-decylgallium in turn lose isobutylene. However, the greater ease with which the first isobutyl group is lost from $\mathrm{Al[CH_2CH(CH_3)_2]_3}$, compared with $\mathrm{Al[CH_2CH(CH_3)_2]_2H}$, and the greater stability of *n*-alkylaluminum derivatives to olefin elimination suggest that the processes in equations 16 and 20, producing the more thermally labile tri-isobutylgallium, would be more prominent.

Although the thermal decomposition of tri-isobutylindium at 125° seemed to take largely a course analogous to equation 18, (i-$\mathrm{C_4H_8}$:$\mathrm{H_2}$ = 2.85:1.0) the considerable proportion of isobutane (1.5) suggested the added occurrence of homolytic cleavage of In–C bonds in the sense of equation 13.

Finally, it should be mentioned that the thermal decomposition of these derivatives was accelerated markedly by the finely divided metal products of the reaction. This parallels the observations of many other workers[29,30] that metal hydrides

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[27] R. Köster, *Ann.*, **618**, 31 (1958).

[28] J. J. Eisch, unpublished studies.

[29] *Cf.* H. I. Schlesinger, H. C. Brown and G. W. Schaeffer, *J. Am. Chem. Soc.*, **65**, 1786 (1943), concerning the autocatalyzed decomposition of $\mathrm{Ga(BH_4)_3}$.

[30] K. Ziegler, H.-G. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 97 (1954).

undergo autocatalytic decomposition. The suggestion has been forwarded that the decomposition of diethylaluminum hydride by adventitious solid catalysts involves disproportionation to $Al(C_2H_5)_3$ and $(AlH_3)_x$ and the decomposition of the latter.[30] In the case of tri-isobutylgallium the effect of separated gallium metal may be to catalyze the reactions given in equations 16 and 17.[31]

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Experimental

General Experimental Techniques.—Although organogallium compounds are less moisture- and oxygen-sensitive than organoaluminum compounds, all traces of oxygen and active-hydrogen compounds were carefully excluded from preparative and purification operations. As an inert atmosphere either ultra-pure nitrogen or argon was employed for all reactions involving organometallic compounds. Thus, before use all reaction, distillation and storage vessels were evacuated and filled with the inert gas repeatedly.

For reactions conducted at the reflux temperature, it was found advisable to use either a copper-coil reflux condenser for water cooling or an ordinary glass condenser cooled with circulating kerosene. From the experience of the Max Planck Institut für Kohlenforschung such cooling avoids the possible explosive hydrolysis resulting from condenser breakage.

Analytical Methods.—The aluminum analyses on starting organoaluminum compounds were conducted according to a previously reported procedure.[32] The analyses for hydride content of AlR_3 reagents were kindly performed by Dr. Wilhelm Neumann,[33] using a modification of the procedure of Bonitz.[34]

The gallium analyses were performed according to three general procedures. In each case the analytical samples were taken according to techniques developed for organoaluminum compounds. Thus liquid samples were withdrawn by use of tared, partially evacuated glass ampoules and solids were transferred into small, glass-stoppered bottles. All transfers were conducted under an inert atmosphere.

The first gallium analytical procedure tried was the precipitation of gallium hydroxide. Thus the sealed ampoule of the gallium compound was crushed under ether and the resulting system treated with 6 *N* hydrochloric acid. The ether was evaporated and hydrolysis was completed by heating upon a steam bath for 1 hr. The cooled solution was filtered and the glass fragments remaining on the filter thoroughly washed. The filtrate was analyzed for gallium either by the method of Dennis and Bridgman[35] (precipitation with ammonium hydroxide and sodium sulfite) or that of Dennis and Patnode[36] (precipitation with ammonium hydroxide and hydrogen peroxide). However, satisfactory analyses could only be obtained by collecting the initially precipitated gallium hydroxide and concentrating the filtrate to complete precipitation. Moreover, the precipitate has a marked tendency to peptize upon washing; this effect was minimized by washing with very dilute ammonium nitrate solution in place of distilled water.

A second, more advantageous gallium procedure was the precipitation of gallium as its 8-hydroxyquinoline salt by treating the hydrolyzed gallium sample according to the directions of Geilmann and Wrigge.[37] This method was employed especially for halogen-containing organogallium compounds, because the third procedure (given below), involving heating with concentrated sulfuric acid, could occasion the loss of gallium as the volatile $(GaX_3)_2$ if the sample also contained halogen.

The most convenient procedure for gallium analysis was a modified procedure of Renwanz.[11a] In a tared crucible the ampoule containing the gallium sample was crushed under one milliliter of ether. The solution was carefully treated with 6 *N* sulfuric acid and the ether was evaporated. The residue was treated with 5–10 drops of concentrated sulfuric acid and carefully heated with a ring burner starting at the top of the crucible to evaporate the acid and decompose the sample. The residue was then ignited to gallium oxide, until constancy of weight was attained. Rapid weighing of the covered crucible was necessary, since the oxide was somewhat hydroscopic. The precision of duplicate analyses was within ±0.30%. The ampoule fragments did not interfere with accurate analysis.

In an analogous manner halogen-free indium compounds were analyzed by decomposition with sulfuric acid and ignition to the oxide.

The gas analyses reported in this study were obtained in most cases by mass spectrometry and in certain instances by vapor phase chromatography.

Starting Materials.—Anhydrous gallium(III) bromide, gallium(III) chloride and indium(III) chloride were obtained by the action of halogen on the metal. For bromine and gallium metal the reaction was conducted conveniently in an evacuated and sealed two-bulb glass apparatus. The bromine in slight excess in the one bulb was distilled slowly onto the gallium in the other bulb at such a rate that the reaction proceeded smoothly. Toward the end of the reaction the gallium(III) bromide was heated to keep it liquid and permit complete consumption of the metal. Finally, the $GaBr_3$-containing bulb was heated while the bromine bulb was cooled in a Dry Ice–acetone bath to distil away any excess bromine from the $GaBr_3$. The bulbs were separated by melting and sealing off the connecting tube between the bulbs. The gallium bromide was cream-colored to pale yellow.

A most advantageous preparation of gallium(III) chloride used in trialkylgallium synthesis consisted in placing the equivalent amount of gallium metal in a three-necked, round-bottom-flask of suitable size for the subsequent gallium halide–aluminum alkyl reaction. The flask was equipped with stoppers and a three-way stopcock. After flushing with nitrogen the flask was evacuated under high vacuum. Thereupon highly pure and dry chlorine gas was admitted slowly, so that the reaction was barely exothermic enough to keep the gallium(III) chloride in the liquid state. After all gallium metal traces had disappeared, the excess chlorine was removed by repeated evacuation and refilling with dry nitrogen. Indium(III) chloride was prepared in an analogous fashion.

The aluminum alkyls used in this study were obtained from commercial samples by careful fractional distillation.

Triethylgallium from Gallium(III) Bromide and Diethylzinc.—Diethylzinc was prepared by treating one molar equivalent of anhydrous zinc chloride[38] with two molar equivalents of triethylaluminum. A turbid solution was formed with little heat evolution. Fractional distillation of the mixture through a Vigreux column gave a 77% yield of colorless diethylzinc boiling at 24–25° under 17 mm. of pressure.

In a three-necked flask equipped with a nitrogen inlet, pressure-equalized dropping funnel and a copper-coil reflux condenser and provided with magnetic stirring were

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(31) The presence of mercury was found to exert a striking stabilizing influence on the thermal stability of gallium alkyls (*cf.* Experimental). This may be due to the mercury scavenging the finely divided metal particles by amalgamation and hence removing any catalytic activity. The use of mercury could thus serve to stabilize sensitive gallium compounds during their work-up and storage.

(32) K. Ziegler, *et al.*, *Ann.*, **589**, 91 (1954).

(33) W. P. Neumann, *ibid.*, **629**, 23 (1960).

(34) E. Bonitz, *Chem. Ber.*, **88**, 742 (1955).

(35) L. M. Dennis and J. A. Bridgman, *J. Am. Chem. Soc.*, **40**, 1547 (1918).

(36) L. M. Dennis and W. Patnode, *ibid.*, **54**, 182 (1932).

(37) W. Geilmann and F. W. Wrigge, *Z. anorg. u. allgem. Chem.*, **209**, 135 (1932); *ibid.*, **212**, 32 (1933).

(38) R. T. Hamilton and J. A. V. Butler, *J. Chem. Soc.*, 2283 (1932).

placed 100 ml. of dry pentane and 29.3 g. (0.095 mole) of gallium(III) bromide (poured in the molten state from the storage ampoule described above). Over a 90-minute period 18.2 g. (0.148 mole) of diethylzinc was slowly introduced. The mixture deposited a precipitate, presumably zinc bromide, with a marked heat evolution. After a 2 hr. reflux period the reaction suspension was centrifuged and the separated liquid phase was freed of pentane. Distillation of the residue yielded 10 g. (66%) of triethylgallium, b.p. 43–44° (16 mm.). A hydrolyzed sample of this product still showed the presence of trace amounts of zinc.[39]

Triethylgallium from Gallium(III) Bromide and Triethylaluminum. (a) **In a 1:1 Molar Ratio.**—Admixture of 13.5 g. (0.444 mole) of gallium(III) bromide in 50 ml. of dry hexane with 5.7 g. (0.05 mole) of triethylaluminum resulted in the exothermic formation of a turbid solution. After 1 hr. at reflux the hexane was drawn off under reduced pressure and the residue subjected to vacuum distillation. Under 256 mm. only about 0.5 ml. of distillate boiling from 57–63° was obtained. Lowering the pressure to 84 mm. and raising the bath temperature to 190° gave no further distillate.

(b) **In a 1:3 Molar Ratio.**—The residue from the distillation attempted above was dissolved in 50 ml. of dry hexane, and an additional 11.4 g. (0.10 mole) of triethylaluminum was introduced. Only a slight heat evolution was noted. After a 2 hr. reflux period the hexane was removed and the residue was fractionally distilled at 280 mm. of pressure. The colorless triethylgallium was collected at 106–108°, 5.6 g. (82%).

Triethylgallium from Gallium(III) Chloride and Triethyl aluminum. (a) **Without Potassium Chloride.**—Attempts to substitute the cheaper, more conveniently prepared chloride for the gallium(III) bromide led to markedly lower yields even when a 1:3 molar ratio was employed. Thus, treatment of 0.10 mole of gallium(III) chloride partially dissolved in 100 ml. of dry pentane with 42 ml. (0.30 mole) of triethylaluminum over a 30-minute period resulted in the exothermic formation of a clear solution. The solution was heated at the reflux temperature for 1 hr. and the solvent then evaporated. Distillation of the residue gave a 42% yield of triethylgallium, b.p. 108–110° (300 mm.). In a check run of the same size the yield of the gallium alkyl was 48%.

(b) **With Potassium Chloride.**—To the distillation residue of the preceding experiment were added 22.5 g. (0.3 mole) of finely ground potassium chloride (previously dried at 400°). The mixture was heated at 125° for 1 hr. with frequent shaking with the resulting formation of two liquid phases. Distillation yielded a further 42% yield of triethylgallium, b.p. 117–118° (320 mm.), for a total yield of 42 + 42% = 84%.

Complex Between Gallium(III) Chloride and Diethylaluminum Chloride in a 1:3 Molar Ratio.—To 2.5 g. (0.014 mole) of gallium(III) chloride was added 5.1 g. (0.042 mole) of diethylaluminum chloride. The temperature of the mixture rose to 70° as an almost colorless solution was formed. After 1 hr. of supplemental heating at 100° the liquid was distilled under reduced pressure. The distillate came over at 98–102° under 2.5 mm. of pressure with very little forerun or residue. This product contained 38.3% chlorine. (The complex $Ga[Al(C_2H_5)_2Cl_2]_3$ would contain 39.6% chlorine.) Repeated fractional distillation of this product yielded very pale yellow fractions which contained 37.1% and then 36.0% chlorine. This indicated a tendency of the complex to dissociate into its components at the temperatures necessary for distillation.

Preparative Procedure for Triethylgallium from Gallium(III) Chloride, Triethylaluminum and Potassium Chloride.—To a partial solution of 0.20 mole of gallium(III) chloride in 200 ml. of dry pentane was added 82 ml. (0.60 mole) of triethylaluminum over the course of 1 hr. After the exothermic reaction had subsided, the solution was heated at reflux for another hour. The pentane was removed under reduced pressure and the viscous liquid residue was transferred to a Claisen distillation flask under an inert atmosphere. Thereupon, 50 g. (0.67 mole) of finely ground and dry potassium chloride were introduced into the syrupy liquid. The mixture was heated at 100–110° for 1 hr. with thorough and frequent shaking. Two distinct liquid layers, the upper one of triethylaluminum and the lower one of the complex, $K[Al(C_2H_5)_2Cl_2]$, were formed. Upon distillation at 300 mm. the main fraction boiling at 108–110° provided an 89% yield of triethylgallium. The gallium content of this singly distilled product was 43.8 ± 0.1%. An emission spectrographic analysis of the total metal oxide obtained from the hydrolysis and ignition of this crude triethylgallium indicated the presence of less than 1% by weight of Al_2O_3.

Purification of this product was effected by heating it with about 10% by weight of finely powdered and ignited sodium fluoride for 1 hr. and then fractionally distilling under reduced pressure. The distillate was highly pure triethylgallium recovered in high yield. Emission spectrographic analysis indicated the presence of less than 0.1% by weight of Al_2O_3.

Anal. Calcd. for $C_6H_{15}Ga$: Ga, 44.44. Found: Ga, 44.47.

The procedure described above was employed successfully at least ten times on runs using 0.1 to 0.4 mole of gallium(III) chloride and resulting in yields of 83–90% of singly distilled triethylgallium. From the residue of $K[Al(C_2H_5)_2Cl_2]$ varying amounts of gallium metal (*ca.* 4%) were recovered as a metallic nugget.

Preparation of Tri-isobutylgallium.—In a manner analogous to the preceding procedure 0.20 mole of gallium(III) chloride in 200 ml. of dry pentane was treated with 149 ml. (0.60 mole) of freshly distilled tri-isobutylaluminum (di-isobutylaluminum hydride content of 0.61%). After subsequent heating and removal of the pentane the residue was treated with 50 g. of potassium chloride and the system heated in the usual fashion. Distillation under reduced pressure yielded as a main fraction 44.1 g. (92%) of tri-isobutylgallium, b.p. 67–69° (3 mm.), containing 29.28% gallium. Redistillation over solid sodium fluoride gave an analytically pure sample, d_{20}^{20} 0.94.

Anal. Calcd. for $C_{12}H_{27}Ga$: Ga, 28.92. Found: Ga, 28.76.

Triethylindium from Indium(III) Chloride and Triethylaluminum. (a) **Without Potassium Chloride.**—To a suspension of 41.3 g. (0.19 mole) of indium(III) chloride in 200 ml. of dry pentane was added 77 ml. (0.56 mole) of triethylaluminum over a period of 45 minutes. After the reaction mixture had cooled down, it solidified to an almost colorless mass. Upon removal of the pentane under reduced pressure the residue was subjected to vacuum distillation. At a bath temperature of 140–150° the solid mass melted and a colorless liquid distilled rapidly at 80–81° under 2 mm. of pressure. This product, upon redistillation, boiled at 100–112° under 3 mm. No flame test for indium could be obtained, but the product contained 23.2% aluminum and 19.5% chlorine. Since $Al(C_2H_5)_3$ contains 23.63% Al and $Al(C_2H_5)_2Cl$ contains 22.4% Al and 29.5% Cl, the product was apparently a mixture of the two.

Further vacuum distillation of the original reaction mixture yielded 6.0 g. of colorless liquid, b.p. 110–114° (4 mm.). Upon standing this distillate solidified partially. This product reacted vigorously with water and contained approximately 12% chlorine.

(b) **With Potassium Chloride.**—Treatment of 43.6 g. (0.20 mole) of indium(III) chloride in 200 ml. of dry pentane with 82 ml. (0.60 mole) of triethylaluminum gave a warm, colorless solution. Before cooling 70 g. (0.94 mole) of finely ground and ignited potassium chloride was introduced into the reaction system. After removal of the pentane the reaction residue was distilled under reduced pressure. The main fraction boiling at 95–105° under 17 mm. of pressure consisted of 36.0 g. (89%) of crude triethylindium. This product still contained 1.5% chlorine. Fractional redistillation of this product gave a main fraction boiling at 51–54° under 3 mm. (67% yield).

Anal. Calcd. for $C_6H_{15}In$: In, 56.83. Found: In, 56.72.

Tri-isobutylindium from Indium(III) Chloride and Tri-isobutylaluminum.—The addition of 149 ml. (0.60 mole) of tri-isobutylaluminum to a suspension of 43.6 g. (0.20 mole) of indium(III) chloride in 200 ml. of dry pentane over a period of 40 minutes resulted in only a slight evolution of heat. Upon refluxing for 1 hr. a turbid solution formed. The pentane was removed and 50 g. of powdered, dry potas-

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[39] H. Wendt and A. Brechlin in "Handbuch der Analytischen Chemie," Teil II, Band 2, Elemente der Zweiten Gruppe, Springer-Verlag, 1955, pp. 147–151.

sium chloride was introduced into the viscous liquid residue. Frequent shaking of the suspension while heating at 110° for 30 minutes did not cause the separation of any distinct liquid layers. Distillation under reduced pressure provided a main fraction of 50.3 ml., boiling at 78–83° under 2 mm. This fraction contained 35.1% indium, the total oxide all being calculated as indium(III) oxide. Redistillation of this product over 6 g. of dry, powdered sodium fluoride gave a forerun, 4 ml., b.p. 49–51° (1.5 mm.) and a main fraction, 35 ml., b.p. 51–54° (1.5 mm.). The latter fraction contained 32.1% indium (all calculated as indium(III) oxide). The very pale yellow color of the oxide indicated it was contaminated with aluminum oxide. The analysis corresponds approximately to a 1:1 molar ratio of $Al(C_4H_9)_3$:$In(C_4H_9)_3$.

The main fraction was now heated with 15 g. of powdered and ignited potassium fluoride for 0.5 hr., whereupon the fluoride dissolved and two distinct liquid layers were formed. Distillation removed the upper layer as a pale yellow liquid distillate, 23.6 g., b.p. 65–66° (2 mm.). This liquid contained 40.9% indium (bright yellow oxide) and constituted a 49.6% yield of tri-isobutylindium. Upon standing the pale yellow liquid became gray, due to the light-catalyzed deposition of indium metal. Final distillation over a fresh portion of potassium fluoride yielded a product showing the same analysis and light sensitivity. The deposition of indium suggested the presence of di-isobutylindium hydride traces. The somewhat high indium analyses support this assumption.

Anal. Calcd. for $C_{12}H_{27}In$: In, 40.12. Found: In, 40.74.

Displacement Reaction between Tri-isobutylgallium and 1-Decene.—A homogeneous mixture of 11.4 g. (0.047 mole) of tri-isobutylgallium and 26.0 g. (0.185 mole) of dry 1-decene (freshly distilled over sodium) was heated under argon for 26 hr. at 155 ± 2°, while the isobutylene evolved was collected in a mercury-filled gas buret. After this heating period 91% of the expected amount of olefin was evolved (Calcd. for $3C_4H_8$: 3.60 l. at 20° and 731 mm. Found: 3.21 l.). The colorless liquid residue was heated under a mercury diffusion pump vacuum (10^{-4} mm.) at 100° for 90 minutes, in order to remove the excess 1-decene. From the cold trap 6.2 g. of 1-decene (n^{20}_D 1.4205) were recovered; the calculated excess of olefin employed amounted to 6.0 g. The colorless distillation residue comprised almost a quantitative yield of tri-*n*-decylgallium.

Anal. Calcd. for $C_{30}H_{63}Ga$: Ga, 14.13. Found: Ga, 14.28.

Attempted Displacement Reaction Between Tri-isobutylindium and 1-Decene.—In an experiment analogous to the above procedure 4.2 g. (0.015 mole) of freshly distilled tri-isobutylindium and 7.4 g. (0.053 mole) of 1-decene were heated at 150 ± 2° (at lower temperatures the gas evolution was too slow). After 100 hr. 0.95 l. of gas (measured at 755 mm. and 21°) was collected. This gas consisted of isobutylene (83%), hydrogen (9.4%) and isobutane (7.6%). By careful filtration and washing of the reaction residue 1.07 g. (64%) of indium metal was recovered.

Thermal Decomposition of Tri-iso-butylgallium.—A 1.9 g sample of freshly distilled tri-iso-butylgallium (contained in a 5 ml. Schlenk tube, which was connected to a mercury-filled gas buret) was heated at 160 ± 2° for a period of 28 hr. a total volume of 146 ml. of gas (measured at 24° and 755 mm.) was collected. Ten minutes after the start of heating a gray solid appeared in the liquid gallium alkyl. This gallium metal precipitate appeared to accelerate the thermal decomposition: at the beginning of the heating period gas was evolved at a rate of 1 to 2 ml. per hour; at the end the gas evolution was at the rate of 5 to 6 ml. per hour. Mass spectrometric analysis of the evolved gas gave the composition: isobutylene, 64%; hydrogen, 35%; and isobutane, 0.8%. The gas buret stopcock had to be closed while the gallium alkyl was still warm, since isobutylene seemed to possess a considerable solubility in the undecomposed gallium alkyl. The observed mole ratio of isobutylene:hydrogen was 1.8:1.0. The deviation from 2:1 ratio suggests that even at 160° some isobutylene remained dissolved in the undecomposed gallium alkyl.

It was observed that the accidental presence of mercury inhibited the thermal decomposition of tri-isobutylgallium. For example, when 0.54 g. of tri-isobutylgallium was heated with 0.63 g. of mercury at 160 ± 2° for 74 hr., only 10 ml. of gas was evolved. A small amount of liquid collected in the mercury gas buret.

Thermal Decomposition of Tri-isobutylindium.—In an analogous manner 1.0 g. of tri-isobutylindium was heated at 125 ± 2° for 43 hr. The gas (117 ml., measured at 20° and 768 mm.) consisted of isobutylene (53%), isobutane (28%) and hydrogen (19%).

Behavior of Gallium and Indium Alkyls Toward Alkali Fluorides.—A suspension of 4.2 g. (0.027 mole) of triethylgallium and 0.56 g. (0.13 mole) of powdered and ignited sodium fluoride was heated with stirring at 100° for 5 hr. and finally at 145–155° for 2 hr. without any indication of solution or reaction. Only a slight gray tinge of the insoluble sodium fluoride indicated incipient thermal decomposition of the triethylgallium.

Similarly, heating triethylindium with the superior complexing agent, potassium fluoride, at 100° for 1 hr. gave no sign of complex formation.

However, when 3.08 g. (0.053 mole) of powdered and ignited potassium fluoride was heated with 9.1 g. (0.058 mole) of triethylgallium at 120° for ten minutes, a clear solution resulted. Upon cooling the liquid became a colorless crystalline mass. The excess triethylgallium was removed by pumping under a diffusion pump vacuum. The complex was found to melt at 75–79° and was readily soluble in warm benzene. The gallium analyses were performed according to the 8-hydroxyquinoline technique.

Anal. Calcd. for $C_6H_{15}GaKF$: Ga, 32.43. Found: Ga, 32.28.