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Abstract

Full Text

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ORGANOGALLIUM COMPOUNDS OF THE CLASS Ar_3Ga AND THEIR DIOXANATES

Organometallic compounds of gallium have so far been studied very little, especially those of the aromatic series, where only triphenylgallium is known. Gilman and Johnson ([1]) obtained the latter by the action of metallic gallium on molten diphenylmercury at 130° in good yield; however, the reaction required 75 hours of heating. Although the initial organomercury compounds of the class Ar_2Hg are quite accessible, on proceeding even to the nearest homologs the reaction in the melt would require considerably higher temperatures (for example, di-*p*-tolylmercury has m.p. = 238°) and probably an even longer process duration.

For the synthesis we used the reaction

$$3ArMgBr + GaCl_3 \rightarrow Ar_3Ga + 3MgClBr;$$

The usual decomposition of the reaction product with acid or water to separate Ar_3Ga from magnesium salts is not applicable here because of the instability of organogallium compounds toward water. In contrast to volatile aliphatic organogallium compounds, separation by fractional distillation is hardly feasible.

We made use of the Schlenk method, which we have repeatedly employed in work on organocadmium compounds ([2]). Magnesium salts precipitate from the ether–benzene solution in the form of a dioxanate; the dioxanate of triarylgallium remains in solution and can thus be isolated.

The yields of the dioxanates (calculated on gallium trichloride) are satisfactory (42–75%). They are white crystalline substances having definite melting points (with the exception of the dioxanate of tri-*m*-tolylgallium). An important property of theirs is that, on heating to 100° in vacuum (2–3 mm), they lose dioxane, passing into triarylgallium (the dioxanate of tri-*p*-tolylgallium is stable under these conditions).

Experimental Part

Because of the sensitivity of the compounds obtained to oxygen and atmospheric moisture, all operations with organogallium compounds were carried out in an atmosphere of inert gas (nitrogen or argon), in special apparatus, with dry solvents (vacuum usually 2-3 mm; throughout, 1,4-dioxane).

Dioxanate of triphenylgallium $(C_6H_5)_3Ga \cdot C_4H_8O_2$. A four-necked flask of 500 ml capacity, equipped with a stirrer with a mercury seal, a reflux condenser, and an opening for introducing nitrogen, is charged with 5.5 g (0.031 mole) of anhydrous gallium trichloride in 50 ml of benzene, and, with stirring, 24.83 g (0.137 mole) of Grignard reagent prepared by the usual method in ether from 6 g (0.25 g-atom) of magnesium is added (slight warming). The reaction mixture is thoroughly stirred for another hour at room temperature, after which 110 ml of dioxane is added to precipitate the magnesium salts formed. After cooling to room temperature, the reaction mass is filtered with suction and washed with benzene. Most of the solvent is distilled off from the filtrate in vacuum, at the end warming on a water bath to 80°. The precipitated solid is filtered off with cold petroleum ether and dried in vacuum at room temperature. 8 g of triphenylgallium dioxanate was obtained—yield 67%. After recrystallization from dioxane, triphenylgallium dioxanate has a melting point of 139-140°; it is soluble in the cold in dioxane, ether, chloroform, benzene, and carbon tetrachloride, and poorly soluble in hexane and petroleum ether, even on heating.

$C_{22}H_{23}O_2Ga$. Found, %: Ga 17.80; 17.89.
Calculated, %: Ga 17.93.

Triphenylgallium $(C_6H_5)_3Ga$. When the triphenylgallium dioxanate is heated in vacuum at 100° for 18-20 hours, the substance loses a molecule of dioxane. The triphenylgallium obtained has m.p. 164–165° (literature value 166° [1]). Solubility—as in the case of triphenylgallium dioxanate.

Found, %: Ga 23.07; 23.22.
$C_{18}H_{15}Ga$. Calculated, %: Ga 23.18.

Dioxanate of tri-*o*-tolylgallium $(o\text{-}CH_3C_6H_4)_3Ga \cdot C_4H_8O_2$. By the procedure described above, from 5 g (0.028 mole) of gallium trichloride in 50 ml of benzene and 24.9 g (0.127 mole) of the Grignard reagent, 5.1 g of tri-*o*-tolylgallium dioxanate with m.p. 127–128° is obtained (yield 42%). Solubility is analogous.

Found, %: Ga 16.38; 16.13.
$C_{25}H_{29}O_2Ga$. Calculated, %: Ga 16.18.

Tri-*o*-tolylgallium $(o\text{-}CH_3C_6H_4)_3Ga$. When tri-*o*-tolylgallium dioxanate is heated in vacuum at 100° for 18-20 hours, it loses a molecule of dioxane, giving tri-*o*-tolylgallium. After recrystallization from benzene the substance has m.p.

169–170°; it is readily soluble in dioxane, ether, benzene, chloroform, and carbon tetrachloride, and poorly soluble in hexane and petroleum ether.

Found, %: Ga 19.93; 19.96.
$C_{21}H_{21}Ga$. Calculated, %: Ga 20.34.

Dioxanate of tri-*p*-tolylgallium $(p\text{-}CH_3C_6H_4)_3Ga \cdot C_4H_8O_2$. From 8 g (0.0455 mole) of anhydrous gallium trichloride in 60 ml of benzene and 24.5 g (0.127 mole) of the Grignard reagent, 11.5 g of tri-*p*-tolylgallium dioxanate with m.p. 74–77° is obtained in the usual manner (yield 75%).

Found, %: Ga 16.15; 16.50.
$C_{25}H_{29}O_2Ga$. Calculated, %: Ga 16.18.

It is readily soluble in dioxane, ether, carbon tetrachloride, and chloroform; poorly soluble in benzene in the cold, but readily on heating; in petroleum ether it is poorly soluble even on heating.

When tri-*p*-tolylgallium dioxanate is heated in vacuum to 70°, it loses half a molecule of dioxane. The latter compound, after recrystallization from benzene, has m.p. 118–119°. Solubility is analogous.

Found, %: Ga 17.92; 18.14.
$C_{23}H_{25}OGa$. Calculated, %: Ga 18.03.

Dioxanate of tri-*m*-tolylgallium $(m\text{-}CH_3C_6H_4)_3Ga \cdot C_4H_8O_2$. From 2.8 g (0.016 mole) of anhydrous gallium trichloride in 50 ml of benzene and 13.4 g (0.069 mole) of the Grignard reagent, 4.9 g of tri-*m*-tolylgallium dioxanate is obtained by the procedure described above (yield 72%).

Found, %: Ga 16.51; 16.30.
$C_{25}H_{29}O_2Ga$. Calculated, %: Ga 16.18.

After recrystallization from dioxane, tri-*m*-tolylgallium dioxanate, when heated in a sealed capillary under nitrogen, decomposes above 300° without melting. It dissolves readily in dioxane, chloroform, and carbon tetrachloride; poorly in ether and benzene in the cold but readily on heating; poorly in hexane and petroleum ether even on heating.

Tri-*m*-tolylgallium $(m\text{-}CH_3C_6H_4)_3Ga$. When tri-*m*-tolylgallium dioxanate is heated in vacuum at 100°, it loses a molecule of dioxane, converting into tri-*m*-tolylgallium. The latter, when heated in a sealed capillary under nitrogen, decomposes above 200° without melting.

Found, %: Ga 20.23; 20.06.
$C_{21}H_{21}Ga$. Calculated, %: Ga 20.34.

It is readily soluble in dioxane, chloroform, benzene, and ether; poorly soluble in hexane and petroleum ether both in the cold and on heating.

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Note: Figure translations are in progress. See original paper for figures.