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1964

SovietRxiv

Abstract

Full Text

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PREPARATION OF ORGANOZINC COMPOUNDS OF THE TYPE R_2Zn IN THE AROMATIC, HETEROCYCLIC, AND ARALIPHATIC SERIES VIA THE GRIGNARD REAGENT

Organomagnesium compounds have been used relatively rarely in the synthesis of organozinc compounds of the type R_2Zn, and only in the aliphatic series ([1–4]). In the aromatic series, organomercury compounds ([5,6]) and organolithium compounds ([7,8]) have been used for this purpose. Thus, for example, the synthesis of diphenylzinc was carried out by the action of zinc chloride on an ethereal solution of phenyllithium ([7]). However, purification from the impurity of diphenyl required distillation in a high vacuum, which would present a number of difficulties in going over to higher zinc diaryls. On the other hand, the preparation of organozinc compounds by the action of zinc halide salts on crystalline organolithium compounds ([8]) required their preliminary preparation.

The use of organomagnesium compounds in the synthesis of organozinc compounds is of considerable interest, owing to the simplicity of the experiment and the possibility of using alkyl chlorides.

We have carried out the synthesis of aromatic, heterocyclic, and araliphatic organozinc compounds with the aid of organomagnesium compounds. For isolating them in pure form, we used a procedure described by us earlier for the synthesis of organocadmium compounds ([9]) and based on the precipitation of magnesium salts by dioxane according to Schlenk et al. ([10]).

In this way we obtained a series of organozinc compounds in the form of their dioxanates. The dioxanates of diphenyl-, di-*p*-tolyl-, di-*p*-biphenyl-, di-*α*-thienyl-, and dibenzylzinc were obtained. The yields of the organozinc compounds obtained were, in a number of cases, almost quantitative (di-*p*-biphenylzinc—93.3%, dibenzylzinc—88.6%). It should be noted that organozinc compounds of the heterocyclic series have not hitherto been obtained by anyone. An attempt to obtain dibenzylzinc with the aid of organomercury compounds ([6]) led only to the formation of dibenzyl.

We have shown for the first time that dioxanates of aromatic organozinc compounds, when heated in vacuo, lose a molecule of dioxane and are converted into pure zinc diaryls. All the compounds obtained are white crystalline powders, reacting vigorously with oxygen and moisture in the air; therefore all operations were carried out in a stream of inert gas in special apparatus.

Using di-*n*-butyl ether as the solvent for the Grignard reagent, we carried out the synthesis of aliphatic organozinc compounds; the yields of di-*n*-propyl-, di-*n*-butyl-, and diisobutylzinc reached 60%. Di-*n*-butyl ether as a solvent makes it possible to obtain organozinc compounds on a large-laboratory scale.

Experimental Part

Diphenylzinc dioxanate with the aid of the Grignard reagent. To the Grignard reagent obtained from 6 g of magnesium (0.25 g-atom) and 39.2 g of bromobenzene (0.25 mole) in 150 ml of dry ether, a solution of zinc chloride in ether is cautiously added dropwise. The addition of the zinc chloride solution is controlled by the Gilman test for the presence of the Grignard reagent. The Gilman test is negative when 10.14 g (0.074 mole) of zinc chloride has been added. The reaction mixture is heated for 2 hours on a water bath; after cooling, 150 ml of dry dioxane is added. The precipitate

filtered off and washed several times with dry ether. From the filtrate in vacuo, most of the ether and dioxane are distilled off. The precipitate that separates is filtered off, washed with cold petroleum ether, and dried in vacuo. This gives 14 g of diphenylzinc dioxanate. Yield 62.27%, calculated on zinc chloride; m.p. 113°.

Found, %: Zn 21.39, 21.71
$C_{16}H_{18}O_2Zn$. Calculated, %: Zn 21.27

Diphenylzinc from diphenylzinc dioxanate. On heating diphenylzinc dioxanate in vacuo at 60°, it loses a molecule of dioxane, being converted into pure diphenylzinc. M.p. 105°; according to the literature data (^{6}), m.p. 105–107°.

Found, %: Zn 30.18, 30.14
$C_{12}H_{10}Zn$. Calculated, %: Zn 29.82

Di-*p*-tolylzinc dioxanate via the Grignard reagent. By the procedure described above, from 6 g of magnesium (0.25 g-atom), 43 g (0.25 mole) of *p*-bromotoluene in 150 ml of dry ether, and 12.8 g (0.093 mole) of zinc chloride, 9.6 g (30.51%) of di-*p*-tolylzinc dioxanate are obtained, m.p. 144–145°.

Found, %: Zn 19.19, 19.23
$C_{18}H_{22}O_2Zn$. Calculated, %: Zn 19.51

Di-*p*-tolylzinc from di-*p*-tolylzinc dioxanate. On heating di-*p*-tolylzinc dioxanate in vacuo at 90°, it loses a molecule of dioxane, being converted into di-*p*-tolylzinc, m.p. 169–170°; according to the literature data (^{6}), m.p. 169–170°.

Found, %: Zn 26.20, 26.77
$C_{14}H_{14}Zn$. Calculated, %: Zn 26.43

Di-*p*-biphenylylzinc dioxanate via the Grignard reagent. By the procedure described above, from 6 g of magnesium (0.25 g-atom), 58.2 g (0.25 mole) of *p*-bromobiphenyl, 250 ml of ether, and 7 g (0.05 mole) of anhydrous zinc chloride, 22 g of di-*p*-biphenylylzinc dioxanate are obtained. Yield 93.3%, calculated on zinc chloride. Di-*p*-biphenylylzinc dioxanate is readily soluble in the cold in dioxane, chloroform, dimethyl sulfoxide; poorly soluble in ether, ethyl acetate, benzene, and petroleum ether. On heating it is readily soluble in ethyl acetate, poorly soluble in carbon tetrachloride. On heating in a sealed capillary, the substance decomposes without melting above 60°.

Found, %: Zn 14.29, 14.42
$C_{28}H_{26}O_2Zn$. Calculated, %: Zn 14.23

Di-*p*-biphenylylzinc from di-*p*-biphenylylzinc dioxanate. On heating di-*p*-biphenylylzinc dioxanate in vacuo at 45°, it loses a molecule of dioxane, being converted into di-*p*-biphenylylzinc. Di-*p*-biphenylylzinc, on heating in a sealed capillary under argon, decomposes without melting above 100°. It is readily soluble in the cold in benzene, dioxane, carbon tetrachloride, chloroform, ethyl acetate, and dimethyl sulfoxide; poorly soluble in ether; on heating it is poorly soluble in petroleum ether.

Found, %: Zn 17.56, 17.87
$C_{24}H_{18}Zn$. Calculated, %: Zn 17.61

Di-α-thienylzinc dioxanate via the Grignard reagent. By an analogous procedure, from 3 g of magnesium (0.125 g-atom), 20.5 g (0.126 mole) of α-bromothiophene in 125 ml of ether, and 6.96 g (0.051 mole) of anhydrous zinc chloride, 6.4 g (34.52%) of di-α-thienylzinc dioxanate are obtained, m.p. 150°. Di-α-thienylzinc dioxanate is readily soluble in the cold in dioxane, chloroform, ethyl acetate, and dimethyl sulfoxide; poorly soluble in benzene and ether; on heating it is readily soluble in benzene and ether.

Found, %: Zn 20.16, 20.75
$C_{12}H_{14}S_2O_2Zn$. Calculated, %: Zn 20.48

Di-α-thienylzinc from di-α-thienylzinc dioxanate. When di-α-thienylzinc dioxanate is heated in vacuum at 100°, it loses a molecule of dioxane, being converted into pure di-α-thienylzinc. On heating in a sealed capillary under argon, di-α-thienylzinc decomposes without melting above 150°; it is readily soluble in the cold in dioxane, chloroform, and dimethyl sulfoxide, poorly soluble in benzene, hexane, and ether, and soluble on heating in carbon tetrachloride and petroleum ether.

Found, %: Zn 28.39, 27.85
$\mathrm{C_8H_6S_2Zn}$. Calculated, %: Zn 28.27

Dibenzylzinc dioxanate via the Grignard reagent. By an analogous procedure, from 5.3 g of magnesium (0.22 g-atom) and 27.1 g (0.214 mole) of benzyl chloride in 240 ml of dry ether and 9.5 g (0.07 mole) of zinc chloride in 65 ml of ether, 20.7 g of dibenzylzinc dioxanate is obtained; yield 88.6%. Dibenzylzinc dioxanate is a white crystalline substance that reacts extremely vigorously with oxygen and atmospheric moisture and has no definite melting point. It is readily soluble in the cold in benzene, dioxane, ethyl acetate, and dimethyl sulfoxide, and poorly soluble in ether and petroleum ether, even on heating.

Found, %: Zn 19.60, 19.44
$C_{18}H_{22}O_2Zn$. Calculated, %: Zn 19.50

Di-*n*-butylzinc. To 56 g (206 ml, 0.5 mole) of a solution of *n*-butylmagnesium chloride in di-*n*-butyl ether ([11]), 23.5 g (0.24 mole) of zinc chloride dissolved in 100 ml of dry ether is added dropwise (the zinc chloride is first distilled under nitrogen from a quartz retort and ground in a chamber), at such a rate that the temperature of the reaction mixture does not rise above 45°. After completion of the addition, the Gilman Michler ketone test is negative. The reaction mixture is filtered under nitrogen (glass filter No. 4), the precipitate is washed with 100 ml of di-*n*-butyl ether, and the filtrate is subjected to fractional distillation in vacuum. Di-*n*-butylzinc is obtained in an amount of 25.4 g, b.p. 55–60° (4 mm). Yield 57.7%.

Di-*n*-propylzinc. To propylmagnesium bromide (24.3 g of magnesium, 1 g-atom; 84 g of propyl bromide in 100 ml of dry ether), 34.1 g (0.25 mole) of anhydrous zinc chloride is added. After the usual work-up and vacuum distillation, 19.6 g of di-*n*-propylzinc is obtained. Yield 53%, b.p. 41–44° (15 mm).

Diisobutylzinc. To the Grignard reagent prepared from 24.3 g (1 g-atom) of magnesium and 137 g (1 mole) of isobutyl bromide in 300 ml of di-*n*-butyl ether, 26.8 g (0.2 mole) of dry zinc chloride is added. The reaction mixture is heated at 70–80° for 3.5 h. After the usual work-up and distillation in vacuum, 21.7 g of diisobutylzinc is obtained (62.4%), b.p. 31° (2.5 mm).

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Received
24 XI 1963

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

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