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I. E. PALEEVA, N. I. SHEVERDINA, L. V. ABRAMOVA,

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Abstract

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I. E. PALEEVA, N. I. SHEVERDINA, L. V. ABRAMOVA,
Corresponding Member of the Academy of Sciences of the USSR K. A. KOCHESHKOV

CHEMICAL COMPOSITION OF "BLAISE' S REAGENT"

The name "Blaise' s reagent" denotes solutions of mixed organozinc compounds, which Blaise [1] obtained by the action of alkyl iodides on a "zinc-copper couple," using ethyl acetate as a catalyst, in toluene for primary alkyls or in saturated hydrocarbons (kerosene fractions) for compounds with secondary radicals. Solutions of aromatic organozinc compounds were formed, according to Blaise, by the action of zinc halide salts on a Grignard reagent. "Blaise' s reagent" subsequently found wide application in the synthesis of various kinds of ketones.

Blaise' s attempt [1] to isolate organozinc compounds of the aromatic series from solution led to the isolation only of a complex compound of complicated composition involving two metals: zinc and magnesium. In the aliphatic series such experiments were not carried out. Thus, the presence in "Blaise' s reagent" of organozinc compounds of definite composition remained unproved. Recently it has become possible to clarify this question, since mixed organozinc compounds, especially of the aromatic series, have been isolated in the disproportionation reaction [2,3]. In the aliphatic series, examples have also been described of the isolation of mixed organozinc compounds (ethylzinc iodide [4,5], perfluoropropylzinc iodide [6,7]).

Using the ability of mixed organozinc compounds to form crystalline complexes with 1,4-dioxane, we showed that compounds of the class $RZnX$ can be isolated from "Blaise' s reagent" in the form of complexes in both the aliphatic and the aromatic series. The yields in most cases reached 70–80%.

By the action of alkyl iodides on a "zinc-copper couple"in toluene or, respectively, heptane, the dioxanates of ethylzinc iodide, propylzinc iodide, and *iso*-butylzinc iodide were obtained; by the action of zinc halide salts on a Grignard reagent, the dioxanates of ethylzinc iodide, phenylzinc bromide, and phenylzinc iodide were obtained. At the same time, it was shown, using ethyl iodide and propyl iodide as examples, that when alkyl iodides act on a "zinc-copper couple"without solvent, mixed organozinc compounds are formed.

Experimental Part

Dioxanate of ethylzinc iodide $C_2H_5ZnJ \cdot C_4H_8O_2$. **Method 1—in solvent.** Into a round-bottomed three-necked flask of 500 ml capacity, fitted with a reflux condenser, stirrer, and an inlet for nitrogen, are placed 36 g of "zinc-copper couple" (32.4 g of zinc, 0.4953 mole), 39 g (0.25 mole) of ethyl iodide, 8 ml of ethyl acetate, 18 ml of dry toluene, and one crystal of iodine. The reaction mixture is cautiously heated on an oil bath. At a temperature of 78° (after 7-8 min) a vigorous reaction begins. After the spontaneous reaction has ended, the bath temperature is raised to 110°, and heating is discontinued. 18 ml of toluene are added; after cooling, the reaction mixture is filtered through a funnel with a No. 4 glass filter, washing with the greatest

amount of toluene. Add 40 ml of dioxane. Most of the solvent is distilled off in vacuo. The white precipitate that separates is suction-filtered (glass filter No. 3). It is washed with cold petroleum ether and dried in vacuo. This gives 61.4 g of ethylzinc iodide dioxanate. Yield 79.43%, calculated on ethyl iodide. The substance decomposes without melting in a sealed capillary under argon on heating to 180°. It is readily soluble in dioxane, ethyl acetate, dimethyl sulfoxide; poorly soluble in benzene, chloroform, and ether, even on heating.

Found %: Zn 21.07; 21.09; J 41.28; 41.07
$C_6H_{13}ZnJO_2$. Calculated %: Zn 21.14; J 41.02

Method 2—without solvent. Into a 250-ml round-bottom flask equipped with a stirrer with a mercury seal, a reflux condenser, and an inlet for nitrogen are placed 13 g of "zinc-copper couple" (11.7 g of zinc, 0.1788 mole) and 15.2 g (0.1 mole) of ethyl iodide. The reaction mixture is carefully heated until the spontaneous reaction begins (30-40 min). The reaction mixture is then heated until ethyl iodide ceases to flow down from the condenser. After cooling, 25 ml of ethyl iodide is added and the mixture is stirred for 20 min. The resulting solution is filtered (glass filter No. 3), and most of the ethyl iodide is distilled off in vacuo. The white precipitate that separates is suction-filtered, washed with cold petroleum ether, and dried in vacuo. This gives 14.6 g of ethylzinc iodide. Yield 67.8%, calculated on the ethyl iodide initially taken.

Found %: Zn 29.80; 29.86; J 57.05; 57.20
C_2H_5ZnJ. Calculated %: Zn 29.55; J 57.33

Method 3—via the Grignard reagent. Into a 250-ml round-bottom flask equipped with a stirrer with a mercury seal, a dropping funnel, a reflux condenser, and an inlet for nitrogen are placed 10 g (0.055 mole) of a solution of ethylmagnesium iodide, and 17.7 g (0.055 mole) of a solution of zinc iodide in 50 ml of ether is carefully added dropwise. Slight warming and precipitation of a white solid are observed. The reaction mixture is stirred for four hours. Fifteen ml of dioxane is added. The precipitate that separates is suction-filtered; most of the solvent is distilled off from the filtrate, and the precipitate of ethylzinc iodide dioxanate is suction-filtered, washed with cold petroleum ether, and dried in vacuo. This gives 7.1 g, yield 41.4%, calculated on zinc iodide. In its properties the substance is analogous to the ethylzinc iodide dioxanate obtained by the other methods.

Found %: Zn 21.28; 21.49; J 41.32; 41.00

$C_6H_{13}ZnJO_2$. Calculated %: Zn 21.14; J 41.02

Propylzinc iodide dioxanate $C_3H_7ZnJ \cdot C_4H_8O_2$. **By method 1.** From 36 g of "zinc-copper couple" (32.4 g of zinc, 0.5 mole), 42.5 g of propyl iodide (0.25 mole), 8 ml of ethyl acetate, and 18 g of toluene, 66.5 g of propylzinc iodide dioxanate is obtained; yield 82.3%, calculated on propyl iodide taken. The substance softens, without melting, on heating in a sealed capillary to 64-67°. It is soluble in benzene, dioxane, ether, ethyl acetate, chloroform, and dimethyl sulfoxide. It is poorly soluble in carbon tetrachloride even on heating.

Found %: Zn 19.91; 19.78; J 39.45; 39.29

$C_7H_{15}ZnJO_2$. Calculated %: Zn 20.23; J 39.24

By method 2. From 18 g of "zinc-copper couple" (16.2 g of zinc, 0.2477 mole) and 42.3 g (0.25 mole) of propyl iodide, after addition of 40 ml of dioxane to the solution, 22.9 g of propylzinc iodide dioxanate is obtained, yield

28.34% based on the propyl iodide taken. In its properties the substance is analogous to the dioxane of propylzinc iodide obtained by other methods.

$C_7H_{15}ZnJO_2$.	Found, %:	Zn 20.57; 20.42;	J 38.93; 38.96
	Calculated, %:	Zn 20.23;	J 39.24

Dioxanate of isobutylzinc iodide-iso-$C_4H_9ZnJ \cdot C_4H_8O_2$. **By method 1.** From 36 g of "zinc-copper couple" (32.4 g of zinc, 0.4953 mole), 46 g of isobutyl iodide (0.25 mole), 8 ml of acetoacetic ester, and 18 ml of *n*-heptane, 49.6 g of the dioxanate of isobutylzinc iodide is obtained; yield 58.78%, based on the isobutyl iodide taken. On heating in a sealed capillary under argon the substance softens without melting at 70°. It is soluble in dioxane, ether, chloroform, and dimethyl sulfoxide. It is poorly soluble in benzene and carbon tetrachloride even on heating.

$C_8H_{17}ZnJO_2$.	Found, %:	Zn 19.46; 19.40;	J 37.69; 37.47
	Calculated, %:	Zn 19.39;	J 37.61

Dioxanate of phenylzinc bromide $C_6H_5ZnBr \cdot C_4H_8O_2$. **By method 3.** From 13.4 g (0.074 mole) of phenylmagnesium bromide and 16.6 g (0.074 mole) of zinc bromide in 50 ml of ether, 7.2 g of the dioxanate of phenylzinc bromide is obtained. Yield 31.48%, based on the initial zinc bromide. On heating in a sealed capillary under argon above 200°, the substance softens without melting. It is soluble in ether, dioxane, carbon tetrachloride, chloroform, ethyl acetate, and dimethyl sulfoxide.

$C_{10}H_{13}ZnBrO_2$. Found, %: Zn 20.90; 21.06; Br 25.96; 25.89
Calculated, %: Zn 21.08; Br 25.79

Dioxanate of phenylzinc iodide $C_6H_5ZnJ \cdot C_4H_8O_2$. **By method 3.** From 9.7 g (0.0425 mole) of phenylmagnesium iodide and 13.5 g (0.0422 mole) of zinc iodide in 50 ml of ether, 6.1 g of the dioxanate of phenylzinc iodide is obtained. Yield 40.36%, based on the zinc iodide taken.

$C_{10}H_{13}ZnJO_2$. Found, %: Zn 18.12; 18.31; J 35.49; 35.69; C 33.60; 33.63; H 3.62, 3.56
Calculated, %: Zn 18.30; J 35.50; C 33.58; H 3.64

n-Butylcadmium bromide n-C_4H_9CdBr. From 13.72 g (0.097 mole) of *n*-butylmagnesium bromide in 30 ml of ether and 23.2 g (0.097 mole) of cadmium bromide, 2.6 g of *n*-butylcadmium bromide is obtained. Yield 12.25%, based on the cadmium bromide taken.

C_4H_9CdBr. Found, %: Cd 44.89; 45.00; Br 31.74; 31.82
Calculated, %: Cd 45.09; Br 32.05

Physicochemical Institute
named after L. Ya. Karpov

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