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Abstract

Full Text

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Complexes in the Series of Aromatic Organozinc Compounds of the Class ArZnX

As was shown by a number of investigators and then once again noted by Blaise (^{1}), the direct reaction between halogen derivatives of the aromatic series and metallic zinc in the presence of various catalysts for the purpose of obtaining organozinc compounds does not occur. To obtain solutions of organozinc compounds, Blaise proposed a reaction between zinc halide salts in ether and organomagnesium compounds obtained by the Grignard method.

If, for synthetic purposes (^{2}) (for example, for obtaining ketones), this method of obtaining the initial organozinc compounds proved useful, it could hardly clarify the question of mixed organozinc compounds.

The complexity of the composition of the Grignard reagent itself, and, moreover, the presence in the latter of magnesium salts and their etherates, complicate the picture still further. It is therefore not surprising that, in an attempt to bring about the interaction of zinc chloride with phenylmagnesium bromide, when isolating from the solution a crystalline compound, Blaise (^{1}) arrived at a complex magnesium-zinc complex of the composition*:

$$(C_2H_5)_2O \cdot MgCl_2 \cdot (C_2H_5)_2O \cdot C_6H_5ZnBr$$

or

$$(C_2H_5)_2O \cdot MgClX \cdot (C_2H_5)_2O \cdot C_6H_5ZnCl.$$

However, as we have shown for the first time (^{3}), mixed organozinc compounds can be obtained on the basis of the disproportionation reaction in the form of their complexes with ether or dioxane. The method we developed for obtaining diarylzinc compounds through crystalline organolithium compounds (^{4}) made it possible to investigate the aromatic series quite broadly.

The complexes thus obtained in good yields—white crystalline substances—do not have a definite melting point. They are vigorously decomposed by water or alcohol, and with acid halides they readily form ketones.

The analysis for zinc was carried out by combustion in a quartz test tube with nitric acid, followed by ignition to zinc oxide.

Experimental Part

All syntheses and isolation of substances were carried out in an atmosphere of inert gas (nitrogen or argon) and in a medium of dry solvents.

The starting zinc diaryls were obtained by the method we developed through crystalline organolithium compounds (^{4}).

Preparation of crystalline etherates of general formula $ArZnX(C_2H_5)_2O$**.** After mixing solutions of diarylzinc

* Formulas in the authors' transcription.
** Or $Ar_2Zn \cdot ZnX_2 \cdot 2(C_2H_5)_2O$.

Table 1

Etherate	Yield, %	Analysis: found Zn	Analysis: found halide	Analysis: calculated Zn	Analysis: calculated halide
$C_6H_5ZnBr \cdot (C_2H_5)_2O$	70,5	21,9621,77	26,9727,35	22,08	26,96
$C_6H_5ZnJ \cdot (C_2H_5)_2O$	79,0	18,6319,16	36,6737,03	19,05	36,97
o-$CH_3C_6H_4ZnCl \cdot (C_2H_5)_2O$	55,1	25,0824,66	13,2713,00	24,60	13,35
o-$CH_3C_6H_4ZnBr \cdot (C_2H_5)_2O$	66,7	21,4021,40	26,2525,60	21,08	25,74
o-$CH_3C_6H_4ZnJ \cdot (C_2H_5)_2O$	82,6	18,5118,12	35,3335,55	18,30	35,52
n-$CH_3C_6H_4ZnCl \cdot (C_2H_5)_2O$	52,0	25,0124,81	13,7013,34	24,60	13,35
n-$CH_3C_6H_4ZnBr \cdot (C_2H_5)_2O$	72,5	21,1021,44	25,7626,05	21,08	25,74
n-$CH_3C_6H_4ZnJ \cdot (C_2H_5)_2O$	70,0	18,6618,41	35,1335,07	18,30	35,52
α-$C_{10}H_7ZnCl \cdot \frac{1}{2}(C_2H_5)_2O$	65,3	25,0924,91	13,4013,46	24,69	13,40
α-$C_{10}H_7ZnBr \cdot \frac{1}{2}(C_2H_5)_2O$	95,0	20,8220,71	25,4425,26	21,14	25,83
α-$C_{10}H_7ZnJ \cdot (C_2H_5)_2O$	61,9	16,8016,45	31,7031,93	16,63	32,27

Table 2

Dioxanate	Yield, %	Analysis: found Zn	Analysis: found halide	Analysis: calculated Zn	Analysis: calculated halide
$C_6H_5ZnJ \cdot C_4H_8O_2$	58,0	17,8017,90	35,1036,02	17,81	35,60
o-$CH_3C_6H_4ZnCl \cdot C_4H_8O_2$	77,6	23,9123,16	13,1013,20	23,36	12,68
o-$CH_3C_6H_4ZnBr \cdot C_4H_8O_2$	83,3	20,5320,05	24,5724,31	20,16	24,65
o-$CH_3C_6H_4ZnJ \cdot C_4H_8O_2$	86,0	18,0517,48	34,8034,01	17,62	34,18
n-$CH_3C_6H_4ZnCl \cdot \frac{1}{2}C_4H_8O_2$	71,0	28,1327,88	14,6214,55	27,71	15,04
n-$CH_3C_6H_4ZnBr \cdot \frac{1}{2}C_4H_8O_2$	75,0	23,0823,64	28,0328,16	23,32	28,50
n-$CH_3C_6H_4ZnJ \cdot C_4H_8O_2$	72,0	17,2017,23	34,6034,01	17,62	34,18

in an amount that is a multiple of one mole, in a minimal quantity of absolute ether sufficient for its dissolution, with a solution of the corresponding zinc halide salt (a multiple of 0,96–0,98 mole) in the same amount of absolute ether and, after distilling off two thirds of the ether, the precipitated white crystalline solid was filtered off, washed with cold ether, and dried in vacuum. In this case, obta-

the etherate of the corresponding mixed organozinc compound of sufficient purity, not requiring recrystallization for analysis.

All etherates are white crystalline substances, readily soluble in ether, dioxane, ethyl acetate, and pyridine, insoluble in benzene, hexane, carbon tetrachloride, and chloroform (Table 1).

Synthesis of crystalline dioxanates of the general formula $ArZnX \cdot C_4H_8O_2$. A solution of diarylzinc in a one-mole equivalent amount, in the minimum amount of absolute ether, was mixed with a solution of the zinc halide salt in an amount corresponding to 0.97–0.98 mole, in the same amount of absolute ether. The solution was allowed to stand for several hours, and then dry 1,4-dioxane was added (in a threefold excess, necessary for precipitation of the dioxanate). After removal of most of the solvent in vacuum, the precipitated white crystalline solid was filtered off, washed with cold petroleum ether, and dried in vacuum.

All dioxanates are white crystalline substances, soluble in pyridine, dioxane, absolute ether, and ethyl acetate, insoluble in benzene, hexane, and carbon tetrachloride (Table 2).

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