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## Abstract

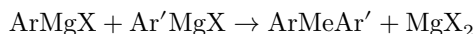
## Full Text

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# UNSYMMETRICAL AROMATIC ZINC- AND CADMIUM-ORGANIC COMPOUNDS OF THE TYPE $\text{ArMeAr}'$

Zhobe and Reich <sup>(1)</sup> were the first to attempt the synthesis of unsymmetrical zinc dialkyls. They attributed the failure of the experiment to the rapid symmetrization of the compounds formed. Later, Krause and Fromm <sup>(2)</sup> obtained a series of unsymmetrical zinc dialkyls and gave their physical constants, but indicated neither the yields nor the experimental details. Recently we <sup>(3)</sup> described in detail a method for the synthesis of unsymmetrical zinc dialkyls and for the first time prepared a series of unsymmetrical cadmium dialkyls not previously described in the literature. As for unsymmetrical zinc and cadmium diaryls, up to now they have not been known.

We have shown that in the reaction between mixed zinc- and cadmium-organic compounds and the corresponding Grignard reagent, unsymmetrical zinc and cadmium diaryls are formed according to the equation:

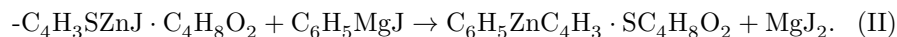
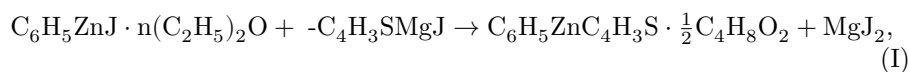


(where Me = Zn or Cd).

Since, for purification from impurities of magnesium salts, the latter were precipitated with 1,4-dioxane, all compounds were obtained in the form of their complexes with dioxane.

The dioxanates of phenyl- $\alpha$ -thienylzinc, benzyl- $\alpha$ -thienylzinc, and phenyl- $\alpha$ -thienylcadmium were synthesized.

Phenyl- $\alpha$ -thienylzinc dioxanate was obtained by two routes: by the action of phenylzinc iodide etherate on  $\alpha$ -thienylmagnesium iodide (I), and by the action of phenylmagnesium iodide on  $\alpha$ -thienylzinc iodide dioxanate (II):



In the first case the complex was formed with half a molecule of dioxane, in the second—with one molecule of dioxane.

The dioxanates of unsymmetrical zinc- and cadmium diaryls were white crystalline substances which reacted vigorously with moisture and atmospheric oxygen. None of the compounds had definite melting points, with the exception of the phenyl- $\alpha$ -thienylzinc complex with half a molecule of dioxane.

The dioxanates of  $\alpha$ -thienylzinc iodide,  $\alpha$ -thienylzinc bromide, and benzylzinc iodide, which served as our starting substances, were also obtained for the first time.

## Experimental Part

All operations for obtaining unsymmetrical zinc and cadmium diaryls were carried out in an argon atmosphere in special apparatus.

**Phenyl- $\alpha$ -thienylzinc dioxanate**,  $C_6H_5ZnC_4H_3S \times \frac{1}{2}C_4H_8O_2$ . Into a round-bottomed flask of 250 ml capacity, fitted with a stirrer with a mercury seal, a reflux condenser, and a dropping funnel, a suspension of 5.2 g (0.0155 mol) of phenylzinc iodide etherate in 50 ml of ether is placed, and 13.2 ml (4.5 g, 0.0192 mol) of a solution of  $\alpha$ -thienylmagnesium iodide is added. A gradual disappearance of the precipitate of zinc iodide etherate is observed. When the solution becomes clear, 25 ml of dry dioxane is added. The mixture is stirred for 30 min, the precipitate is filtered off (glass filter No. 4) and washed with ether. After removal from the filtrate

the greater part of the solvent has been distilled off, the precipitated white solid is filtered off, washed with cold petroleum ether, and dried in vacuo under nitrogen. This gives 3.1 g of phenyl- $\alpha$ -thienylzinc as a complex with one half molecule of dioxane. Yield 76.0%, calculated on phenylzinc iodide etherate. M.p. 128°. The substance is readily soluble in ether, chloroform, and dioxane, and is poorly soluble in benzene and petroleum ether even on heating.

Found, %: C 53.11, 53.33; H 4.53, 4.52; S 11.58, 11.63;

Zn 24.14, 24.17

$C_{12}H_{12}ZnSO$ . Calculated, %: C 53.44; H 4.45; S 11.88; Zn 24.28

**Dioxanate of phenyl- $\alpha$ -thienylzinc**,  $C_6H_5ZnC_4H_3S \times C_4H_8O_2$ . From 6.1 g (0.0168 mol) of the dioxanate of  $\alpha$ -thienylzinc iodide in 100 ml of ether and 11.3 ml (3.5 g, 0.0154 mol) of phenylmagnesium iodide, by the analogous procedure, 4.7 g of phenyl- $\alpha$ -thienylzinc with one molecule of dioxane is obtained. Yield 88.5%, calculated on the initial dioxanate of  $\alpha$ -thienylzinc iodide. On heating in a sealed capillary under argon, the substance decomposes, with slight sintering, above 100°. It is readily soluble in dioxane, chloroform, ethyl acetate, and dimethyl sulfoxide. It is poorly soluble in cold benzene, ether, carbon tetrachloride, and petroleum ether. It is readily soluble in hot benzene.

Found, %: Zn 20.45, 20.47

$C_{14}H_{16}ZnSO_2$ . Calculated, %: Zn 20.86

**Dioxanate of  $\alpha$ -thienylbenzylzinc**,  $C_6H_5CH_2ZnC_4H_3S \times C_4H_8O_2$ . From 6.4 g (0.0172 mol) of the dioxanate of benzylzinc iodide in 100 ml of ether and 11.9 ml (3.22 g, 0.0167 mol) of  $\alpha$ -thienylmagnesium iodide, by the analogous procedure, 2.6 g of benzyl- $\alpha$ -thienylzinc is obtained as a complex with one molecule of dioxane. Yield 46.1%, calculated on the initial dioxanate of benzylzinc iodide. On heating in a sealed capillary under argon, the compound obtained sinters without melting and decomposes above 60°. The substance is soluble in the cold in all common organic solvents except hexane and ether.

Found, %: Zn 19.63, 19.97

$C_{15}H_{18}ZnSO_2$ . Calculated, %: Zn 19.98

**Dioxanate of phenyl- $\alpha$ -thienylcadmium**,  $C_6H_5CdC_4H_3S \times \frac{1}{2}C_4H_8O_2$ . In a 250-ml round-bottomed flask equipped with a stirrer with a mercury seal, a reflux condenser, and a dropping funnel, a suspension of 3.5 g (0.011 mol) of phenylcadmium iodide in 50 ml of ether is placed. Then 7.4 ml (2.6 g, 0.011 mol) of  $\alpha$ -thienylmagnesium iodide is added dropwise. The reaction mixture is stirred for 4 hours until the precipitate has completely disappeared, after which 25 ml of dry dioxane is added. After 20 min, the precipitated solid is filtered off (glass filter No. 4), the greater part of the solvent is distilled off from the filtrate in vacuo. The precipitated solid is filtered off, washed with cold petroleum ether, and dried in vacuo. This gives 0.9 g of phenyl- $\alpha$ -thienylcadmium as a complex with one half molecule of dioxane. Yield 25.7%, calculated on the initial phenylcadmium iodide. The substance is soluble in ether, chloroform, and dioxane, and is poorly soluble in hot benzene. On heating in a sealed capillary under argon it decomposes above 60°.

Found, %: C 45.59, 45.62; H 3.79, 3.70; S 10.02, 10.01; Cd 35.40, 35.42

$C_{12}H_{12}CdSO$ . Calculated, %: C 45.51; H 3.79; S 10.11; Cd 35.52

**Dioxanate of benzylzinc iodide**,  $C_6H_5CH_2ZnI \times C_4H_8O_2$ . 15.2 g (0.0453 mol) of the dioxanate of dibenzylzinc<sup>(4)</sup> is dissolved in 100 ml of dioxane, the resulting solution is filtered, a solution of 14.0 g (0.0438 mol) of zinc iodide in 75 ml of ether is added to the clear filtrate, and the solution is left to stand overnight. After the greater part of the solvent has been distilled off, the precipitated solid is filtered off, washed with cold petroleum ether, and dried in vacuo. This gives 27.3 g of the dioxanate of iodide ...

benzylzinc. Yield 83.83%, calculated with respect to the initial zinc iodide. The dioxanate of benzylzinc iodide, when heated in a sealed capillary under argon, sinters without melting at temperatures above 80°. The substance is soluble in dioxane, dimethyl sulfoxide, and ethyl acetate; poorly soluble in ether, benzene, hexane, and chloroform.

Found, %: Zn 17.48, 17.48; J 34.16, 33.75

$C_{11}H_{15}ZnJO_2$ . Calculated, %: Zn 17.62; J 34.18

If the reaction is carried out by dissolving the dioxanate of dibenzylzinc in ether and not adding dioxane, a complex of benzylzinc iodide with one-half molecule of dioxane is obtained in 92.6% yield. The substance, when heated in a sealed capillary under argon, decomposes above 150°. It is soluble in dioxane, ethyl acetate, and dimethyl sulfoxide; poorly soluble in ether, benzene, and chloroform even on heating.

Found, %: Zn 19.64, 20.35; J 39.27, 38.31  
 $C_9H_{11}ZnJO$ . Calculated, %: Zn 19.98; J 38.77

**Dioxanate of  $\alpha$ -thienylzinc iodide**,  $C_4H_3SZnJ \cdot C_4H_8O_2$ . Similarly, upon mixing a solution of 9.0 g (0.0281 mol) of the dioxanate of di- $\alpha$ -thienylzinc in 25 ml of ether and 50 ml of dioxane with a solution of 8.5 g (0.0266 mol) of zinc iodide in 50 ml of ether, after the usual workup 18.1 g of the dioxanate of  $\alpha$ -thienylzinc iodide is obtained. Yield 98.72%, calculated with respect to zinc iodide. The substance decomposes when heated in a sealed capillary under argon at 149°. It is soluble in dioxane, ethyl acetate, chloroform, and dimethyl sulfoxide; poorly soluble in hexane, benzene, and carbon disulfide.

Found, %: Zn 18.05, 18.07; J 34.69, 34.62  
 $C_8H_{11}ZnSJO_2$ . Calculated, %: Zn 18.00; J 34.92

**Dioxanate of  $\alpha$ -thienylzinc bromide**,  $C_4H_3SZnBr \times C_4H_8O_2$ . Similarly, from 2.8 g (0.0087 mol) of the dioxanate of di- $\alpha$ -thienylzinc in 50 ml of ether and 40 ml of dioxane and 1.6 g (0.0071 mol) of zinc bromide in 50 ml of ether, 4.1 g of the dioxanate of  $\alpha$ -thienylzinc bromide is obtained. Yield 91.2%, calculated with respect to zinc bromide. The substance decomposes, without melting, in a sealed capillary under argon above 80°. It is soluble in ether, dioxane, and dimethyl sulfoxide; poorly soluble in hot benzene.

Found, %: Zn 20.44, 20.67; Br 25.24, 25.42  
 $C_8H_{11}ZnSBrO_2$ . Calculated, %: Zn 20.67; Br 25.25

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 named after L. Ya. Karpov

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

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