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Abstract

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NEW ORGANOCADMIUM COMPOUNDS OF THE CLASS Ar_2Cd AND THEIR DIOXANATES

In the present work the task was set of investigating the comparatively little-studied class of aromatic organocadmium compounds Ar_2Cd and their capacity for complex formation.

The only known representative of this class of compounds up to now has been diphenylcadmium, first obtained by A. N. Nesmeyanov and L. G. Makarova ([1]) in pure form by the action of cadmium bromide on phenyllithium in ether medium. Earlier, Gilpert and Grüttner ([2]), in an attempt to synthesize diphenylcadmium by the action of diphenylmercury on cadmium filings, obtained diphenylcadmium in a mixture with the initial organomercury compound and were unable to isolate it. Strohmeier ([3]), studying the properties of organometallic compounds of the second group of the periodic system, isolated small quantities of diphenylcadmium, suitable for physicochemical investigations, using organomagnesium compounds for its preparation. Thus, the synthesis of Ar_2Cd had been little developed and was carried out in a single example, while the question of the ability of organocadmium compounds to form complexes had not been touched upon at all.

By improving Strohmeier' s method, we succeeded for the first time in obtaining a series of new aromatic organocadmium compounds of the class Ar_2Cd, such as: di-*p*-tolylcadmium, di-*o*-tolylcadmium, di-*p*-chlorophenylcadmium (and also diphenylcadmium). It was also shown that organocadmium compounds of this class, when dissolved in 1,4-dioxane, form complexes, in all cases with one molecule of dioxane, and for di-*p*-chlorophenylcadmium with 1/2 molecule of dioxane.

The dioxanates, as well as the corresponding cadmium diaryls, are white crystalline substances, decomposed by water and by atmospheric oxygen. In the case of diphenylcadmium, di-*o*-tolylcadmium, and di-*p*-tolylcadmium, the dioxanates have definite melting points. On heating in vacuum the dioxanates lose a molecule of dioxane and give cadmium diaryls. The strength of the complex formed with dioxane depends on the nature of the aromatic radical of the organocadmium compound: thus, diphenylcadmium dioxanate loses dioxane on heating in vacuum to 80°, the dioxanates of di-*p*-tolylcadmium and di-*p*-

chlorophenylcadmium to 100°, and the dioxanate of di-*o*-tolylcadmium already at room temperature.

It was previously shown by us ([4]) that aliphatic organocadmium compounds R_2Cd, in reaction with cadmium halide salts, form RCdX. In the present work this was extended to the field of aromatic compounds as well. We found that, for example, in the interaction of diphenylcadmium with cadmium iodide, there occurs formation of the representative of a new class of aromatic organocadmium compounds not previously described anywhere, phenylcadmium iodide C_6H_5CdJ*.

Experimental part

All operations with organocadmium compounds were carried out in an atmosphere of inert gas (nitrogen or argon), in special apparatus ([5])

* Or $(C_6H_5)_2Cd \cdot CdJ_2$.

with dry solvents, the vacuum during drying or decomposition of the dioxanates was everywhere 2-3 mm.

Diphenylcadmium. To the Grignard reagent prepared from 12 g of magnesium (0.5 g-atom), 75 g of bromobenzene (0.48 mole) in 350 ml of ether, 42.5 g (0.156 mole) of anhydrous cadmium bromide are added in small portions (slight heating), and the contents of the flask are stirred thoroughly for one hour. To precipitate the magnesium salts formed, 110 ml of 1,4-dioxane are added, and after cooling to room temperature the reaction mixture is filtered with suction. Most of the solvent is distilled off from the filtrate in vacuo, finally heating on a water bath to 80°. The precipitate that separates is filtered with suction, washed with 10 ml of ether, then washed with cold petroleum ether and dried in vacuo. The diphenylcadmium obtained is recrystallized from ether. 12.8 g of substance were obtained (yield 30.8% of theory, calculated on the cadmium bromide taken), m.p. 174°. According to the literature data (1), the m.p. of diphenylcadmium is 173-174°.

$C_{12}H_{10}Cd$.	Found	% :	Cd	42.05;	42.32
	Calculated	% :	Cd	42.19	

Dioxanate of diphenylcadmium. Diphenylcadmium is dissolved in 1,4-dioxane and filtered. After removal in vacuo of most of the solvent, the white precipitate that separates is filtered with suction, washed with dry cold petroleum ether, and dried in vacuo.

$C_{16}H_{18}O_2Cd$.	Found	% :	Cd	32.15;	31.84
	Calculated	% :	Cd	31.72	

The diphenylcadmium dioxanate obtained melts within the range 59-66°. It is

soluble in the cold in dioxane, chloroform, and pyridine; on heating, in benzene, hexane, carbon tetrachloride, and ether.

When the dioxanate is heated on a water bath in vacuo to 80° for about 2–3 hours, the substance loses a molecule of dioxane and is converted into diphenylcadmium.

Phenylcadmium iodide. Into a flask (150 ml) fitted with a stirrer with a mercury seal, a reflux condenser, and an inlet for introducing nitrogen, 3 g (0.011 mole) of diphenylcadmium in 100 ml of ether are placed, and 4 g (0.010 mole) of dry cadmium iodide are added. After 3 hours of thorough mechanical stirring, the latter is converted into a lighter suspension of phenylcadmium iodide, which is filtered with suction, washed with ether, and dried in vacuo. 5.55 g of a white crystalline substance were obtained (yield 80.3%, calculated on the cadmium iodide taken). The phenylcadmium iodide obtained decomposes when heated in a sealed capillary under argon to 150°, without melting. It is insoluble in ordinary organic solvents.

C_6H_5CdJ.	Found	% :	Cd	35.15;	35.80;	J	40.02;	39.77
	Calculated	% :	Cd	35.54;		J	40.12	

Dioxanate of di-*p*-tolylcadmium. To the Grignard reagent prepared from 12 g of magnesium (0.5 g-atom), 86 g of *p*-bromotoluene (0.5 mole) in 350 ml of ether, 42.5 g (0.156 mole) of anhydrous cadmium bromide are added, and the mixture is stirred for 1 hour while heating on a water bath. After addition of 110 ml of 1,4-dioxane and cooling to room temperature, the precipitate is filtered with suction and washed with ether. Most of the solvent is distilled off in vacuo, finally heating on a water bath to 50°. The precipitate that separates is filtered with suction, washed with 10 ml of ether, then with cold petroleum ether, and dried in vacuo. The precipitate obtained is recrystallized from dioxane, giving 21.5 g of di-*p*-tolylcadmium dioxanate (yield 32.9%, calculated on the cadmium bromide taken).

$C_{18}H_{22}O_2Cd$.	Found	% :	Cd	28.97;	29.61
	Calculated	% :	Cd	29.39	

Dioxanate of di-*p*-tolylcadmium has a melting point of 54–56°, is soluble in the cold in dioxane, benzene, chloroform, pyridine, and, on heating, in ether and carbon tetrachloride; it is poorly soluble in hexane and petroleum ether.

Di-*p*-tolylcadmium. On heating dioxanate of di-*p*-tolylcadmium in vacuum at 100°, it loses a molecule of dioxane, being converted into di-*p*-tolylcadmium. The latter, when heated in a sealed capillary to 200°, decomposes without melting. The substance is soluble in chloroform and carbon tetrachloride, and poorly soluble in ether, benzene, toluene, and xylene.

$C_{14}H_{14}Cd$.	Found	% :	Cd 37.90; 37.94
	Calculated	% :	Cd 38.19

Di-*o*-tolylcadmium. To a Grignard reagent prepared from 12 g (0.5 g-atom) of magnesium and 86 g of *o*-bromotoluene (0.5 mole) in 350 ml of ether, 42.5 g (0.156 mole) of anhydrous cadmium bromide is added, and the contents of the flask are stirred for 1 hour while being heated on a water bath. After addition of 110 ml of 1,4-dioxane and cooling to room temperature, the solution is filtered off with suction and the precipitate is washed with ether. Most of the solvent is distilled off in vacuum, toward the end heating the bath to 80°. The precipitated solid is filtered off with suction, washed with 10 ml of ether and then with cold petroleum ether, and dried in vacuum. The resulting precipitate is recrystallized from dioxane, giving 24.5 g of substance with m.p. 115° (yield 53.3%, calculated on the cadmium bromide taken).

$C_{14}H_{14}Cd$.	Found	% :	Cd 38.31; 37.92
	Calculated	% :	Cd 38.19

Di-*o*-tolylcadmium is soluble in dioxane, benzene, carbon tetrachloride, ether, and pyridine, and poorly soluble in hexane and petroleum ether.

Dioxanate of di-*o*-tolylcadmium. Di-*o*-tolylcadmium is dissolved in dioxane and filtered. Most of the solvent is removed, and the precipitated white solid is filtered off with suction, washed first with cold petroleum ether (b.p. 80–120°), then with pentane, and dried for 20 min in a stream of nitrogen.

$C_{18}H_{22}O_2Cd$.	Found	% :	Cd 29.48; 29.34
	Calculated	% :	Cd 29.39

Dioxanate of di-*o*-tolylcadmium has m.p. 93–95°. It is readily soluble in dioxane, chloroform, ether, and pyridine, and poorly soluble in cold benzene, hexane, and petroleum ether.

On more prolonged drying (at room temperature) in a stream of nitrogen or in vacuum, dioxanate of di-*o*-tolylcadmium readily loses a molecule of dioxane, being converted into di-*o*-tolylcadmium (see above).

Dioxanate of di-*p*-chlorophenylcadmium. To a Grignard reagent prepared from 12 g (0.5 g-atom) of magnesium and 96 g (0.5 mole) of *p*-chlorobromobenzene in 350 ml of ether, 42.5 g (0.156 mole) of cadmium bromide is added, and the mixture is stirred for one hour while heated on a water bath. After addition of 110 ml of 1,4-dioxane and cooling, the contents of the flask are filtered off with suction and washed with ether. Most of the solvent is distilled off in vacuum, toward the end heating on a water bath to 40°. The precipitated white solid is filtered off with suction, washed with cold petroleum ether, and dried in vacuum. It is then recrystallized from dioxane,

the precipitate is washed with pentane and dried in a stream of nitrogen for 10–15 min. Yield 21 g (31.77%, calculated on the cadmium bromide taken).

$C_{14}H_{12}OCdCl_2$.	Found	% :	Cd 29.34; 29.44;	Cl 18.94; 18.95
	Calculated	% :	Cd 29.63	; Cl 18.72

Dioxanate of di-*p*-chlorophenylcadmium has a decomposition temperature of 185°; it is soluble in dioxane, pyridine, and acetic ester; insoluble in ether, benzene, chloroform, and hexane.

Di-*p*-chlorophenylcadmium. On heating dioxanate of di-*p*-chlorophenylcadmium in vacuum at 100°, it loses a molecule of dioxane,

passing into di-*p*-chlorophenylcadmium (decomposes on heating to 100°, without melting). The substance is soluble in dioxane and pyridine, insoluble in ether, benzene, chloroform, and hexane.

$C_{12}H_8CdCl_2$.	Found, %:	Cd	33.49;	33.67;	Cl 20.73; 20.69
	Calculated, %:	Cd	33.52		Cl 21.17

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