==

Preparation of Organozinc and Organocadmium Compounds from the Metals and Alkyl Halides in the Presence of Stimulating Systems Based on a Derivative a Transition Metal and an Organometallic Compound

I. V. Eremeev, S. M. Danov, A. G. Skudin, and V. R. Sakhipov

Nizhni Novgorod State Technical University, Dzerzhinsk Branch, Dzerzhinsk, Nizhni Novgorod oblast, Russia

Abstract — Full and mixed alkyl derivatives of zinc and cadmium were prepared from these metals and organic halides in the presence of stimulating systems necessarily containing a transition metal derivative and an organometallic compound capable of reducing this derivative under the process conditions. Such stimulating systems make it possible to introduce selectively organic halides (iodides, bromides, chlorides) into the reaction with zinc and cadmium to obtain the corresponding mixed organometallic compounds.

Alkyl compound of zinc and cadmium are widely used in the preparative and industrial practice as initial substances for inorganic, organic, and organometallic syntheses and as catalysts for the polymerization of unsaturated compounds [1–4]. The production of materials for electronics is one of the most important applications of alkyl derivatives of these elements [5–12]. However, simple and highly efficient procedures of their synthesis are lacking. First of all, this concerns the preparation of high-purity organozinc and organocadmium compounds used in the production of materials for electronics [9–11]. At present, numerous methods for the synthesis of metal alkyl derivative are known. They can be divided into three groups: methods based on the direct alkylation of elements and their derivatives, and also those involving chemical transformations of full or mixed organometallic compounds by rearrangement or transformation of ligands under the action of various agents. From the viewpoint of obtaining high-purity organometallic compounds, the most promising is the so-called "direct synthesis" based on the alkylation of elements with organic halides. In particular, this is confirmed by the experimental studies of the impurity composition of alkyl compounds of nontransition elements depending on the method of their synthesis: the purest samples were obtained by the "direct synthesis" [13–15]. However, only electropositive alkali metals and magnesium readily react with alkyl halides. Various procedures for stimulating the process should be used to alkylate other elements, and nevertheless in many cases it is impossible to combine good results of the "direct synthesis" (high rate,

selectivity, possibility of using accessible and cheap alkyl chlorides or alkyl bromides) with its simplicity and efficiency. As a result, the most stimulation procedures either have a limited application area or are labor-consuming and uneconomical, or require solvents or significant amounts of chemical additions. As a result, the main potential advantage of "direct synthesis" in the production of high-purity organometallic compounds, namely, the possibility of using minimal number of chemicals which are the main source of impurities in the final product, is lost.

We have suggested a procedure for stimulating "direct synthesis" of organometallic compounds using systems whose necessary components are a derivative of a transition metal and an organometallic compound capable of reducing the transition metal derivative under the process conditions. Such systems appeared to be effective in the alkylation of a commercial zinc powder with ethyl bromide [16] [schemes (1) and (2)].

$$Zn + EtBr \longrightarrow EtZnBr, \qquad (1)$$

$$2EtZnBr \longrightarrow Et_2Zn + ZnBr_2. \qquad (2)$$
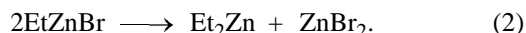
Therefore, the aim of this work was to examine the possibilities of this procedure for stimulating the "direct synthesis" of organometallic compounds, using the preparation of zinc and cadmium alkyl derivatives as an example.

Our experiments have shown that, in the presence of the above-mentioned stimulating systems, alkyl halides (iodides, bromides, chlorides) readily react

Synthesis of organozinc and organocadmium compounds by alkylation of zinc and cadmium with organic halides in the presence of stimulating systems consisting of a transition metal compound and an organometallic compound

Synthesized compound	Composition of initial reaction mixture, mol				Parameters of the synthesis of AlkMHlg (M = Zn, Cd)		Yield of AlkMHlg according to the analysis data, %	Yield of isolated compound, %[a]
	metal	organic halide	stimulating system	diethyl ether	T, °C	duration, h		
Me_2Zn	11.00 Zn	8.31 MeI	0.226 CuI; 0.150 $Me_3Al_2I_3$	–	42	12.0	–	90
Et_2Zn	3.06 Zn	2.44 EtBr	0.080 CuI; 0.170 EtZnBr	–	38–40	4.5	–	82
Pr_2Zn	0.77 Zn	0.66 PrBr	0.046 CuI; 0.047 EtZnBr	–	50	7.0	81	68[b]
Bu_2Zn	0.77 Zn	0.66 BuBr	0.046 CuI; 0.039 EtZnBr	–	50	8.0	78	66[b]
$C_8H_{17}ZnBr$[c]	0.31 Zn	0.25 $C_8H_{17}Br$	0.021 CuI; 0.030 EtMgI	1.1	35	48.0	61	45[d]
$C_{10}H_{21}ZnBr$	0.31 Zn	0.25 $C_{10}H_{21}Br$	0.021 CuI; 0.030 EtMgI	1.1	35	32.0	84	51[d]
BuCdI	0.30 Cd	0.25 BuI	0.010 CuI; 0.020 BuMgI	1.0	40	20.0	–	42
$C_7H_{15}CdI$	0.30 Cd	0.25 $C_7H_{15}I$	0.010 CuI; 0.020 BuMgI	1.0	40	20.0	–	48
$C_{10}H_{21}CdI$	0.30 Cd	0.25 $C_{10}H_{21}I$	0.010 CuI; 0.020 BuMgI	1.0	4	34.0	–	59

[a] Zinc alkyls were obtained by thermal disproportionation of AlkZnHlg. [b] Before AlkZnBr disproportionation, the liquid part of the reaction mixture was separated from the solid residue. [c] 2-Ethylhexylzinc bromide was synthesized from 2-ethylhexyl bromide. [d] Yield of the ketone isolated from the reaction of the synthesized AlkZnBr with acetyl chloride.

with zinc, and alkyl iodides and alkyl bromides, with cadmium. The results of the syntheses of certain full and mixed alkyl derivatives of zinc and cadmium in the presence of stimulating systems based on copper(I) iodide are shown in the table. Thus, the proposed procedure for stimulating the "direct synthesis" of organometallic compounds is highly efficient in the preparation of zinc and cadmium alkyl derivatives and is very simple in implementation.

The assumed mechanism of operation of the stimulating systems based on derivatives of transition metals and organometallic compounds can be illustrated by the following most important target stages. The heterogeneous reaction of a transition metal derivative and an organometallic compound proceeds on the surface of the transition metal derivative (which does not dissolve in the reaction mixture) to give a full alkyl compound of the transition metal. This stage is followed by the mass transfer of the transition metal alkyl compound onto the surface of the nontransition metal to be alkylated, decomposition of the transition metal alkyl compound on the surface of the nontransition metal with the formation of adsorbed transition metal atoms, insertion of the transition metal atoms into the carbon–halogen bonds of the organic halide with the formation of a mixed alkyl compound of the transition metal, decomposition of this compound with the formation of the alkyl radical and transition metal subhalide, reduction of

the transition metal subhalide with the nontransition metal with the formation of the corresponding surface halide of the nontransition metal and adsorbed atoms of the transition metal, and formation of the target mixed organometallic compound by the reaction of the alkyl radical and the surface halide of the nontransition metal.

It should be emphasized that these stages by no means reflect the whole set of processes that take place under the conditions of the "direct synthesis" of organometallic compounds in the presence of the stimulating systems under consideration. The mechanism of operation of the stimulating systems and the influence of the nature of the components on their activity and selectivity will be considered in more detail in a series of subsequent papers.

EXPERIMENTAL

In the work we used PTs-10-grade zinc [TU (Technical Specifications) 48-4015-1/0-81] and pure-grade cadmium [TU (Technical Specifications) 6-09-02-40086]. Grignard reagents were synthesized according to [17]. Heptyl iodide, 2-ethylhexyl bromide, and decyl iodide were synthesized from the corresponding alcohols and hydrogen halides [18]. A solution of methylaluminum sesquiiodide in methyl iodide was obtained from PA-1 grade aluminum and methyl iodide. Ethylzinc bromide was synthesized from zinc powder and ethyl bromide in the presence of the

stimulating system copper(I) iodide–ethylzinc bromide by the previously developed procedure [16]. The resulting solution of ethylzinc bromide in ethyl bromide was separated from unchanged zinc, and ethyl bromide was distilled off in vacuum. The resulting crystalline ethylzinc bromide was dissolved in the corresponding alkyl bromide for the subsequent use in the stimulating system. The other substances were of the grade required for their use in reactions. Alkyl halides were dried in a vacuum desiccator over calcium chloride and distilled directly before introducing into the reaction. Diethyl ether was dried over metallic sodium and distilled before use. The organometallic compounds were synthesized as indicated in the table.

Synthesis of zinc alkyls. Copper(I) iodide and zinc were placed in a reactor equipped with a stirrer and a reflux condenser. The reactor was evacuated for 10 min and filled with thoroughly dried and deoxygenated argon. Then the organic halide and the organometallic compound of the stimulating system as a solution in the corresponding alkyl halide were added. The free end of the reflux condenser was closed with a calcium chloride tube. The first stage of the synthesis [synthesis of alkylzinc halide by scheme (1)] was carried out with vigorous stirring. After completion of this stage, the stirrer was taken out of the reaction mixture, the reactor was cooled to room temperature, the reflux condenser was replaced by a descending condenser, and the thermal disproportionation of the alkylzinc halide by scheme (2) with simultaneous vacuum distillation of the zinc dialkyl was carried out.

To obtain dipropyl- and dibutylzinc, the liquid part of the reaction mass was decanted from unchanged zinc after completion of preparation of alkylzinc bromide, and the solid residue was washed with several portions of the corresponding alkyl bromide. After each washing, the liquid phase was decanted from the solid residue. Then all portions of the wash liquid and the liquid part of the reaction mass were combined, the alkyl bromide was distilled off in a vacuum, and the alkylzinc bromide was subjected to the thermal disproportionation. The measured characteristics of the zinc dialkyls obtained agreed with the published data [1]. The yield of zinc dialkyls was calculated from the amount of the isolated product. The yield of alkylzinc bromides in the first stage of the synthesis was estimated from the content of zinc ions, which was determined by Na_2EDTA titration [19] of a sample of the reaction mixture (free from solid fragments) after hydrolysis of alkylzinc bromide and dissolution of the precipitated zinc hydroxide in an aqueous solution of hydrogen chloride.

Synthesis of alkylzinc- and alkylcadmium halides was carried out similarly to the first stage of the synthesis of zinc dialkyls. Alkylmagnesium iodides contained in the stimulating systems were added into the reactor as solutions in diethyl ether. After termination of the heating and stirring of the reaction mixture, the solution obtained was decanted from the solid residue, which was washed with diethyl ether (2×200 ml). The washing liquid was combined with the liquid part of the reaction mixture. In the case of the synthesis of alkylcadmiun iodides, the main part of diethyl ether was distilled off, 100 ml of heptane was added, and distillation of diethyl ether was continued. Then the distillation flask was cooled to –20°C, and the crystalline precipitate was separated from the liquid phase. The yield of alkylcadmiun iodide was calculated from the weight of the precipitate obtained, in which the cadmium content agreed with the calculated values.

The yields of 2-ethylhexyl- and decylzinc bromides were estimated in the same way as in the synthesis of zinc dialkyls. Furthermore, the resulting alkylzinc bromides without their isolation as pure compounds were brought into the reaction with acetyl chloride to obtain ketones [18]. The reaction was carried out at a temperature below 8°C by adding dropwise a solution of acetyl chloride (0.3 mol) in 50 ml of diethyl ether to a solution alkylzinc bromide. After adding acetyl chloride, the reaction mixture was stirred for 1 h, 40 ml of distilled water and 10 ml of sulfuric acid (2.3 M) were added, and the mixture was stirred for an additional 10 min. Then 100 ml of diethyl ether was added, and the oily layer was separated and washed with distilled water, sodium carbonate solution (0.5 M), and again water. After that, the resulting substance was dried in a vacuum desiccator over sodium sulfate, and the solvent was distilled off in a vacuum. The residue was crystallized from acetone on cooling to –17°C. The yields of ketones are given in the table. The ketones obtained were identified by ^1H NMR spectroscopy on a Tesla BS-487 instrument (80 MHz). The melting point of methyl decyl ketone agreed with the published data [20].

REFERENCES

1. Sheverdina, N.I. and Kocheshkov, K.A., *Metody elementoorganicheskoi khimii. Tsink, kadmii* (Methods of Organometallic Chemistry. Zinc, Cadmium), Nesmeyanov, A.N., Ed., Moscow: Nauka, 1964.

2. Harwood, J.H., *Industrial Application of the Organometallic Compounds,* London: Chapman & Hall, 1963.

3. *Comprehensive Organic Chemistry: The Synthesis and Reactions of Organic Compounds,* Barton, D. and Ollis, W.D., Eds., Oxford: Pergamon, 1979.

4. Erdik, E., *Tetrahedron,* 1987, vol. 43, no. 10, p. 2203.

5. *Osazhdenie plenok i pokrytii razlozheniem metalloorganicheskikh soedinenii* (Deposition of Films and Coatings by Decomposition of Organometallic Compounds), Razuvaev, G.A., Ed., Moscow: Nauka, 1981.

6. Zhuk, B.V., *Usp. Khim.,* 1985, vol. 54, no. 8, p. 1312.

7. *Primenenie metalloorganicheskikh soedinenii dlya polucheniya neorganicheskikh pokrytii i materialov* (Application of Organometallic Compounds to the Preparation of Inorganic Coatings and Materials), Razuvaev, G.A., Ed., Moscow: Nauka, 1986.

8. Efremov, A.A., Fedorov, V.A., and Grinberg, E.E., *Vysokochist. Veshch.,* 1988, no. 3, p. 5.

9. Bregadze, V.I., Golubinskaya, L.M., and Usyatinskii, A.Ya., *Metalloorg. Khim.,* 1988, vol. 1, no. 3, p. 517.

10. Galiullina, R.F., Sazonova, E.V., Rabinovich, A.M., Shnol', T.R., and Smirnov, A.S., *Metalloorg. Khim.,* 1991, vol. 4, no. 5, p. 1163.

11. Rubezhov, A.Z., *Metalloorg. Khim.,* 1992, vol. 5, no. 1, p. 7.

12. Vorotyntsev, V.M., *Vysokochist. Veshch.,* 1993, no. 2, p. 21.

13. Grishnova, N.D., Gaivoronskii, P.E., Donnikov, I.V., Moiseev, A.N., Salganskii, Yu.M., and Shushunov, N.V., *Vysokochist. Veshch.,* 1987, no. 1, p. 172.

14. Sharova, T.V., Leonov, M.R., and Feshchenko, I.A., *Zh. Prikl. Khim.,* 1990, vol. 63, no. 8, p. 1884.

15. Vorotyntsev, V.M. and Mochalov, G.M., Abstracts of Papers, *V Vsesoyuznaya konferentsiya po metalloorganicheskoi khimii* (V All-Union Conf. on Organometallic Chemistry), Riga, 1991, p. 354.

16. Eremeev, I.V., Danov, S.M., Gordeev, S.A., and Sakhipov, V.R., RF Patent 1775403, 1990, *Byull. Izobret.,* 1992, no. 42.

17. Ioffe, S.T. and Nesmeyanov, A.N., *Metody elementoorganicheskoi khimii. Magnii, berillii, kal'tsii, strontsii, barii* (Methods of Organometallic Chemistry. Magnesium, Beryllium, Calcium, Strontium, Barium), Nesmeyanov, A.N. and Kocheshkov, K.A., Eds., Moscow: Akad. Nauk SSSR, 1963.

18. Weygand, K. and Hilgetag, H.G., *Organisch-Chemische Experimentierkunst,* Leipzig: Johann Ambrosius Barth, 1964.

19. Charlot, G., *Les methodes de la chimie analytique. Analyse quantitative minerale*, Paris: Masson, 1965, 4th ed.

20. *Dictionary of Organic Compounds,* Heilbron, D. and Banbury, H.M., Eds., London: Eyre & Spottiswoode, 1953. Translated under the title *Slovar' organicheskikh soedinenii*, Moscow: Inostrannaya Literatura, 1949, vol. 2, p. 672.