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BRIEF COMMUNICATIONS

Synthesis of Zinc Dialkyls from Zinc and Alkyl Bromides

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Abstract—Zinc dialkyls with linear radicals were prepared from zinc and alkyl bromides in the presence of stimulating systems based on a transition metal derivative and an organometallic compound capable of reducing the transition metal derivative under the reaction conditions.

Zinc alkyl compounds are widely used in laboratory studies and industry as starting compounds in inorganic, organic, and organometallic synthesis and as catalysts for polymerization of unsaturated compounds [1–7]. However, one of the major application fields of alkyl derivatives of nontransition metals and zinc is preparation of materials for electronics [7–22].

A procedure for preparing diethylzinc in 92% yield, involving reaction of zinc powder with ethyl bromide, was proposed in [23]:

$$\mathrm{Zn + AlkBr \rightarrow AlkZnBr}, \qquad (1)$$

$$\mathrm{2AlkZnBr \rightarrow Alk_2Zn + ZnBr_2}. \qquad (2)$$

Stage (1) is performed in the liquid phase under atmospheric pressure without solvent at 38–45°C in the presence of catalytic amounts of stimulating systems whose necessary components are a transition metal derivative and an organometallic compound (OMC). The latter should be capable of reducing the transition metal derivative under the reaction conditions. Disproportionation of alkylzinc bromide (2) with simultaneous distillation of dialkylzinc in a vacuum is performed in the same vessel at elevated temperature under isothermal conditions, or with a more sophisticated temperature schedule. This procedure eliminates the labor-consuming procedure for preparing a zinc–copper couple, the use of relatively expensive ethyl iodide, and the uncontrollable induction period in the first stage. Among a broad range of tested stimulating systems based on a transition metal derivative and an OMC (some of them are listed in patent [23]), the system copper(I) iodide–ethylzinc bromide showed high performance in synthesis of diethylzinc. However, attempts to use this system for preparing dipropyl- and dibutylzinc resulted in low yields of zinc dialkyls. Therefore, we carried out a study aimed at extending the synthetic potential of the procedure for preparing zinc dialkyls.

It is known [2, 3] that organic halides can react with OMCs. This is a complex process, and its mechanism is not still fully understood; the reactions are often accompanied by exchange, hydride reduction, and dehydrohalogenation of the organic halide. As a result, a complex mixture of products is usually formed. The reaction catalysts are commonly transition metals or their derivatives. Hence, it could be expected that the most probable reasons for low yields of dipropyl- and dibutylzinc in the preliminary experiments are side reactions of the initial alkyl bromides with the forming mono- and diorgano derivatives of zinc, yielding a mixture of hydrocarbons and zinc bromide. The other possible side reactions [reduction of copper(I) iodide with organozinc compounds or their thermal decomposition] can hardly be responsible for the poor yields of zinc dialkyls. Indeed, even complete reduction of the catalytic amounts of copper(I) iodide as a component of the stimulating system can decrease the yield of zinc dialkyl only to approximately 93%. The insignificant effect of thermal decomposition of zinc dialkyls on their synthesis follows, e.g., from the approximately equal yields of diethyl-, dipropyl-, and dibutylzinc (78–86%) in their synthesis by Noller's procedure from a zinc–copper couple and equimolar mixtures of the corresponding alkyl iodides and alkyl bromides under conditions similar to those of our experiments [1]. If this is the case, then, if unchanged alkyl bromide or a solid residue containing a transition metal and its derivative is removed from the reaction mixture before thermal disproportionation of alkylzinc bromide, the selectivity of zinc dialkyl synthesis must increase considerably.

Our experiments showed that the selectivity of synthesis of alkylzinc bromides at $T \leq 50°C$ is very high: The reaction mixtures contained only unchanged initial compounds (zinc and alkyl bromide) and alkylzinc bromide. The release of gaseous products was monitored with a gas meter connected to the reactor, and was insignificant. However, the conversion of alkyl halides in 4–8 h was as low as 50–80%. Subsequent thermal disproportionation of alkylzinc bromides with simultaneous vacuum distillation of zinc dialkyls from such reaction mixtures resulted in low yields of zinc dialkyls. The results of two of such experiments (nos. 1 and 3) are listed in the table. Removal of unchanged alkyl bromides from the reaction mixtures by vacuum distillation at temperatures below 50°C prior to thermal decomposition noticeably increased the yield of zinc dialkyls. Also, we found that, in the absence of other components of the reaction mixtures, the alkyl bromides in hand do not react with the corresponding organozinc compounds under the experimental conditions. Therefore, as expected, when the solid residue was removed from the reaction mixture prior to disproportionation, the yield of zinc dialkyls also increased (see table, run nos. 2 and 4). Since 5–15% of the formed organozinc compounds always remains in the reactor after the final stage of synthesis, our results show that, in the absence of alkyl bromides or substances catalyzing reaction of organic halides with OMC, disproportionation of alkylzinc bromides into zinc dialkyls is highly selective.

Thus, our study supports the above assumption concerning the reasons for the low yield of zinc dialkyls in their synthesis from zinc and alkyl halides in the presence of stimulating systems based on a transition metal derivative and an OMC. It should be noted that, to prepare high-purity zinc dialkyls, it is appropriate to use alkylzinc bromide formed in the first stage or the corresponding zinc dialkyl as the organometallic component of the stimulating system.

Synthesis of zinc dialkyls from zinc and alkyl bromides in the presence of the copper(I) iodide–ethylzinc bromide stimulating system

Run no.	Alk_2Zn	τ,[*] h	Yield, %	
			AlkZnBr by analysis	Alk_2Zn
1	Pr_2Zn	7	75	30
2	Pr_2Zn	7	81	68[**]
3	Bu_2Zn	4	52	0
4	Bu_2Zn	8	78	66[**]

[*] (τ) Time of AlkZnBr synthesis.

[**] The solid residue was removed from the reaction mixture prior to disproportionation of alkylzinc bromide.

EXPERIMENTAL

In our experiments, we used PTs-10 zinc powder [TU (Technical Specifications) 48-4015-1/0–81] and pure grade copper(I) iodide (TU 6-09-02-437–87). Pure grade alkyl bromides were dried over calcium chloride and distilled before use. Ethylzinc bromide was prepared from zinc powder and ethyl bromide in the presence of the copper(I) iodide–ethylzinc bromide stimulating system, as described in [23]. The resulting solution of ethylzinc bromide in ethyl bromide was separated from unchanged zinc, and excess ethyl bromide was distilled off in a vacuum. The remaining crystalline ethylzinc bromide was dissolved in an appropriate alkylbromide for subsequent use as a component of the stimulating system.

Synthesis of zinc dialkyls. A mixture of 8.76 g (0.046 mol) of copper(I) iodide and 50 g (0.765 mol) of zinc powder was vacuum-treated for 10 min, dry oxygen-free argon was passed, and alkyl bromide and a solution of ethylzinc bromide in the corresponding alkyl bromide were added. The total amount of alkyl bromide and the amount of ethylzinc bromide in the mixture were 0.66 and 0.04–0.05 mol, respectively. In the process, the reactor was protected from atmospheric moisture. Then the system was connected to a gas meter. The first stage was performed with stirring at 50°C. Then the stirring was stopped, the mixture was cooled to room temperature, and thermal disproportionation of alkylzinc bromide formed in the first stage was performed, with simultaneous vacuum distillation of zinc dialkyl. In certain experiments unchanged alkyl bromide was distilled off in a vacuum prior to disproportionation, or unchanged zinc was separated by decanting and washed with several portions of appropriate alkyl bromide. The liquid phase was separated by decanting after each washing. After combining all the liquid phases from washings and the liquid fraction of the reaction mixture, alkyl bromide was distilled off in a vacuum, and alkylzinc bromide was subjected to thermal disproportionation. The constants of the resulting dipropylzinc and dibutylzinc agreed with published data [1]. The yield of zinc dialkyls was determined from the amount of the isolated reaction products. The content of alkyl bromide in the reaction mixture was determined by GLC on a Tsvet-110 chromatograph after hydrolysis of alkylzinc bromide and extraction of alkyl bromide with toluene [24]. The yield of alkylzinc bromide in the first stage of the synthesis was evaluated from the content of zinc ions (EDTA titration [25]) after hydrolysis of alkylzinc bromide in a solid particle-free sample of the reaction mixture and dissolution of the resulting zinc hydroxide precipitate in aqueous HCl.

CONCLUSIONS

(1) Stimulating systems based on a transition metal derivative and an organometallic compound allow synthesis of zinc dialkyls with linear radicals in high yields from zinc and alkyl halides.

(2) In thermal disproportionation of alkylzinc halides, the reaction mixture should not contain significant amounts of the initial alkyl halides.

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