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Abstract

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SYNTHESIS OF ORGANOMETALLIC COMPOUNDS VIA ORGANOMAGNESIUM COMPOUNDS IN AN ETHER-FREE MEDIUM

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Despite the very broad field of application of organomagnesium compounds, the interaction of alkyl halides with magnesium in the absence of special catalysts (ethers, amines, etc.) has been little studied and is not used for synthetic purposes. Although in a number of earlier works^(1-3) it was shown that organomagnesium compounds can be obtained from magnesium and alkyl halides without any catalysts, the principal method of work subsequently became the preparation and use of organomagnesium compounds in the form of their ethereal solutions. In a large number of studies the catalytic influence of ethers, amines, and other substances on the course of formation of organomagnesium compounds was specially investigated^(4). Since this influence appeared to be very considerable, the opinion arose that organomagnesium synthesis in the absence of these catalysts is unsuitable for preparative purposes, and that the very preparation of alkylmagnesium halides in the absence of ethers, amines, etc., proceeds with difficulty, if it proceeds at all.

Schlenk obtained alkylmagnesium halides by shaking magnesium with alkyl halides for two months; the yields of organomagnesium compounds depend substantially on the nature of the alkyl^(3).

Shorygin et al.^(5) found that the interaction of halobenzenes with magnesium in the absence of catalysts can be carried out at 160°. These same authors state that *n*-butyl chloride and isoamyl chloride do not react at all with magnesium when boiled in toluene or without a solvent^(6). With the exception of arylmagnesium halides, the preparation of organomagnesium compounds, according to all the cited works, appears difficult. The formation of alkylmagnesium halides was usually demonstrated by hydrolysis, and the magnesium alkyls obtained were not used for synthetic purposes.

We previously found that the interaction of alkyl metaborates with magnesium and the alkyl halides *n*-butyl and isoamyl in toluene can readily be carried out in the complete absence of Grignard-reaction catalysts^(7); the corresponding borotrialkyls are formed in the reaction. In this case, however, in principle a certain catalytic influence of the metaborate itself is not excluded, since, for example, the catalytic action of ethyl orthosilicate is known^(8). In studying the role of metaborate as a possible catalyst for the formation of an organomagnesium compound, we found that the cited work of P. Shorygin, V. Isagulyants, and A. Guseva^(6), referred to in the most widely used monographs on organomagnesium compounds, is entirely erroneous.

We discovered that both *n*-butyl chloride and isoamyl chloride react rapidly and readily with magnesium both without any solvent at all and in toluene or petroleum ether, forming the corresponding organomagnesium compounds. Other halogenated compounds also react with varying degrees of ease.

alkyls; moreover, for the reaction to begin it is usually sufficient merely to heat to 80–100°, after which the reaction proceeds with self-heating. The reaction proceeds especially readily with higher alkyls, beginning with butyl halide. Preliminary activation with iodine of the magnesium, used in the form of ordinary turnings or filings, is also not necessary. In this case alkyl halides, beginning with butyl, form organomagnesium compounds just as readily as in the presence of absolute ether. The reaction temperature is maintained within the range 80–150° by the rate of addition of the alkyl halide. External heating is necessary only when working with lower alkyls and to complete the process. If the synthesis is carried out without solvent, the organomagnesium compound is formed as a dry amorphous powder; in a hydrocarbon medium, its suspension is obtained. The formation of organomagnesium compounds $RMgX$, where $R = C_4H_9$ and higher, in hydrocarbons or without solvent proceeds so readily that, for the synthesis of various organoelement compounds, the usual procedure employing absolute ether has no advantages. Both the dry organomagnesium compound and its suspension in hydrocarbons readily enter into a radical–halide exchange reaction, as we have shown using the example of halides of boron, aluminum, mercury, silicon, tin, and antimony:

$$X_n + n\,RMgX \to R_n + n\,MgX_2.$$

In carrying out the process, two variants of the procedure are possible:

a) Magnesium, in the form of turnings or filings, is heated with a small amount of the corresponding alkyl halide until formation of the organomagnesium compound begins (as a white powder), after which either a hydrocarbon solvent is first added and then, gradually, the alkyl halide, or their mixture is added at once, or only the alkyl halide is added if the reaction is conducted without solvent. The halide of the element in question is then added to the resulting suspension of the organomagnesium compound, and the second stage of the process also, as a rule, proceeds exothermically.

b) The preparation of the organomagnesium compound and of the corresponding organometallic compound can be combined, and in this case the entire process is carried out in one stage. To magnesium that has

> begun to react with the alkyl halide, the hydrocarbon solvent, the alkyl halide, and the element halide are added simultaneously; in this case it is also possible to conduct the process without any solvent at all.

In a number of cases, products inaccessible by the usual organomagnesium synthesis can be obtained by means of the proposed method. For example, alkylation of aluminum halides with ethereal solutions of alkylmagnesium halides leads to stable etherates of aluminum trialkyls ([9]), from which the ether cannot be removed. However, interaction of aluminum chloride with magnesium alkyls obtained in the absence of catalysts leads to individual aluminum trialkyls. By this route we obtained, for example, triisoamylaluminum in 87% yield.

The organomagnesium compounds obtained by the method described are readily carboxylated, giving the corresponding carboxylic acids.

Experimental Section

Tetra-*n*-butyltin. To 48.6 g (2 mol) of iodine-activated magnesium turnings was added, with stirring (under a nitrogen atmosphere), a mixture of 65.14 g (0.25 mol) of tin chloride and 185.14 g (2 mol) of *n*-butyl chloride. The addition was carried out at such a rate that the temperature of the exothermic reaction was maintained at 90–100°, after which the reaction mixture was heated to the same temperature for 1 hour. Tetra-*n*-butyltin was distilled directly from the reaction mass under vacuum. Obtained: 77 g of tetra-*n*-butyltin (90% of theory), b.p. 117° (1 mm); n_D^{20} 1.4750; d_4^{20} 1.0570. Literature data ([10]): b.p. 175–176°

(40 mm); n_D^{20} 1.4735; d_4^{20} 1.0559.

$C_{16}H_{36}Sn$. Found, %: H 10.62; 10.40; C 55.37; 55.11; Sn 33.80; 34.08
Calculated, %: H 10.45; C 55.35; Sn 34.19

Di-*n*-butyltin dichloride was obtained by a procedure analogous to that for the preparation of tetra-*n*-butyltin; 24.32 g (1 mole) of magnesium turnings, 65.14 g (0.25 mole) of tin tetrachloride, and 92.57 g (1 mole) of *n*-butyl chloride were taken. The yield of di-*n*-butyltin dichloride was 64 g (84% of theory), m.p. 43°, b.p. 135° (5 mm). Literature data (11): m.p. 43°.

$C_8H_{18}SnCl_2$. Found, %: H 5.66; 5.77; C 31.46; 31.30; Cl 22.92; 23.18
Calculated, %: H 5.97; C 31.62; Cl 23.34

Tri-*n*-butylgermanium chloride was obtained analogously. 48.64 g (2 moles) of germanium tetrachloride and 185.14 g (2 moles) of *n*-butyl chloride were taken. The yield of tri-*n*-butylgermanium chloride was 34 g (60% of theory), b.p. 104° (1 mm); n_D^{20} 1.4638; d_4^{20} 1.0252.

$C_{12}H_{27}GeCl$.	Found, %:	Cl 12.64; 12.44
	Calculated, %:	Cl 12.69

Tri-*n*-butylboron. To 29.18 g (1.2 moles) of iodine-activated magnesium turnings, with stirring in a stream of nitrogen, was added a solution of 118.08 g (1.2 moles) of *n*-butyl chloride in 250 ml of isooctane. The addition was carried out at such a rate that the solvent boiled gently. After the entire solution had been added, the reaction mixture was diluted with 300 ml of isooctane and heated at gentle reflux of the solvent for 2 hours. Then 23.5 g (0.2 mole) of boron chloride was added dropwise, the reaction mixture was heated for 1 hour, and, after removal of the solvent, tri-*n*-butylboron was distilled directly from the reaction mixture in vacuum. 31 g of tri-*n*-butylboron was obtained (85% of theory), b.p. 108° (12 mm), n_D^{20} 1.4230. Literature data (7): b.p. 61–63° (7 mm), n_D^{20} 1.4230.

***n*-Octylmercury chloride.** To 3 g (0.12 mole) of magnesium filings was added, with stirring in a stream of nitrogen, a solution of 26.7 g (0.11 mole) of *n*-octyl iodide in 50 ml of heptane. The addition was carried out with gentle boiling of the solvent. The reaction mixture was heated for 2 hours and then cooled with ice; with stirring, 20 g (0.074 mole) of sublimate was added in small portions, and the mixture was heated for 1.5 hours. The reaction mixture was filtered, and the precipitate was washed several times on the filter with 30 ml of boiling heptane. On cooling the filtrate, white crystals separated. After treatment with a solution of caustic potash in methanol and then with a saturated solution of potassium chloride, *n*-octylmercury chloride was obtained. Yield 21 g (81% of theory), m.p. 115°. Literature data (12): m.p. 115–115.5°.

Tri-*n*-butylstibine was obtained by a procedure analogous to that for the preparation of tri-*n*-butylboron, with the only difference that the magnesium turnings were not activated with iodine. 29.18 g (1.2 moles) of magnesium turnings, 125.7 g (1.2 moles) of *n*-butyl chloride in 450 ml of isooctane, and 45.63 g (0.2 mole) of antimony chloride were taken. The yield of tri-*n*-butylstibine was 43 g (73% of theory), b.p. 130° (12 mm). Literature data (13): b.p. 130° (12 mm).

Triisoamylaluminum was obtained analogously to the preceding compound. 60.8 g (2.5 moles) of magnesium turnings, 362.5 g (2.4 moles) of isoamyl bromide in 500 ml of heptane, and 53.34 g (0.4 mole) of anhydrous aluminum chloride were taken. After the reaction was carried out, the precipitate was centrifuged, and triisoamylaluminum was isolated from the resulting solution in vacuum. Yield 83 g (87% of theory), b.p. 152° (1 mm).

$C_{15}H_{33}Al$.	Found, %:	Al 10.94
	Calculated, %:	Al 11.22

Tetraphenyltin. To 29.2 g (1.2 moles) of iodine-activated magnesium turnings, with stirring (in a stream of nitrogen), was added a solution of 172.72 g (1.1

moles) of bromobenzene in 200 ml of decalin; the temperature was maintained
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was maintained at 160–170°. Then 39.08 g (0.15 mole) of tin chloride was added to the reaction mixture. The mixture was heated at 160–170° for 4 hours; 47 g of tetraphenyltin was isolated from the precipitate (yield 74% of theory), m.p. 225–225.5° (from benzene). Literature data [14]: m.p. 225°.

On carboxylation of the organomagnesium compounds obtained by the described method from isoamyl bromide, *n*-hexyl iodide, and *n*-octyl iodide, isocaproic, enanthic, and pelargonic acids were obtained, respectively, in yields of 30.9, 39, and 50.3% of theory.

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