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Abstract

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ON THE PREPARATION OF ALKYLMAGNESIUM HALIDES FROM PRIMARY ALKYL HALIDES AND MAGNESIUM IN A HYDROCARBON MEDIUM

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The synthesis of organomagnesium compounds from alkyl halides and magnesium in a hydrocarbon medium, in the absence of ethers and other catalysts of the Grignard reaction, is of great interest for synthetic purposes. The information on this question available in the literature until recently has been fragmentary and, in many respects, contradictory. The first reports on the possibility of such a synthesis (^1-3), which appeared in the last century, now give rise to well-founded doubts, since, according to these data, heating lower alkyl halides with magnesium (or its amalgam) in sealed tubes leads to symmetrical compounds R_2Mg, which contradicts the data of all subsequent work. Kaur, in particular, (^2) described diethylmagnesium as a liquid, although in fact diethylmagnesium is a solid, infusible substance (^4). Grignard (^5) was unable to replace ether by hydrocarbon solvents—benzene, petroleum ether, etc.; and in a number of subsequent works, attempts to exclude ether from the Grignard synthesis were reduced to the search for other catalysts (^6). In 1904, Chelintsev reported the preparation of ethyl-, propyl-, and *n*-amyl-magnesium iodides, without indicating the yield, from the corresponding alkyl iodides and magnesium in xylene (^7). In lower-boiling solvents the reaction did not proceed, and for preparative purposes Chelintsev proposed using catalytic amounts of tertiary amines (^8).

The most systematic study of the interaction of alkyl halides with magnesium was undertaken in 1931 by Schlenk (^9). On shaking various alkyl halides with magnesium in sealed tubes in benzene at room temperature for two months, Schlenk obtained alkylmagnesium halides in widely fluctuating yields; in his opinion, the yields are determined by the nature of the alkyl group.

Spencer and co-workers ([10,11]) showed that, on heating in sealed tubes up to 270°, aryl halides and alkyl iodides with magnesium, in the absence of solvent, can give organomagnesium compounds. However, satisfactory results were obtained only for aryl halides, isoamyl and sec.-octyl iodides, whereas in the other cases decomposition products were obtained. Heating alkyl and aryl halides with magnesium at such high temperatures can hardly serve as a method for preparing alkyl-(aryl)-magnesium halides, since under these conditions their thermal

decomposition is inevitable (^12). Shorygin and co-workers (^13), who proposed a method for preparing arylmagnesium halides by heating metallic magnesium with aryl halides in an autoclave at 160°, reported in 1933 unsuccessful attempts to obtain organomagnesium compounds from magnesium and butyl, isoamyl, and *n*-octyl halides by boiling in toluene or without solvent (^14).

Thus, until recently, satisfactory results had been obtained only in the case of aryl halides and a small number of alkyl halides, and then under rather severe conditions (or with a very long duration of the process). Characteristically, the organomagnesium compounds obtained in this way, unlike ordinary Grignard reagents, were not assigned any serious preparative significance, and some of their simplest reactions (chiefly hydrolysis) were used only to prove their formation. This led to the widely

the widespread opinion that, in the complete absence of ether and other catalysts, the Grignard reaction—the synthesis of organomagnesium compounds—proceeds with difficulty and has no preparative significance.

Nevertheless, in 1958 two of the authors of the present work found that bromides and chlorides of *n*-butyl and isoamyl, contrary to the earlier data of Shorygin et al. ([14]), react readily and exothermically with magnesium in toluene or without solvent, giving the corresponding organomagnesium compounds in high yields ([15]). The latter were used for the synthesis of trialkylboranes. Independently of us, Bryce-Smith and Cox established that butyl iodide reacts with magnesium on heating in isopropylbenzene, giving the organomagnesium compound in good yield ([16]). These results were confirmed by Van Pho-sung, Dolgoplosk, and Erusalimskii ([17]). Later, Bryce-Smith and Cox showed that butylmagnesium halides and phenylmagnesium halides can be obtained in high yields (above 80%) in a number of hydrocarbon solvents (isopropylbenzene, tetralin, decalin) when working with a large excess of magnesium ([18]).

In the present work we have carried out a systematic study of the interaction of primary alkyl halides from C_1 to C_{10} and phenyl halides with magnesium in a hydrocarbon medium in order to determine the yields of organomagnesium compounds under these conditions. The results of the experiments are summarized in Table 1. The yields are given based on the halogenated alkyls taken into the reaction. In all experiments, 0.55 g-atom of magnesium was taken in the form of filings, 0.5 mole of alkyl or aryl halide, and 300 ml of hydrocarbon solvent. For comparison, Table 1 gives the yields of organomagnesium compounds obtained by Gilman et al. in ether ([19]). As can be seen from the data in Table 1, under the conditions found by us the yields of organomagnesium compounds, with the exception of methyl and ethyl derivatives, are not inferior to the yields of organomagnesium compounds obtained in an ether medium.

Table 1

Experiment No.	Alkyl halide	Solvent	Temp., °C	Yield, %	Yield in ether, %	Experiment No.	Alkyl halide	Solvent	Temp., °C	Yield, %	Yield in ether, %
1	CH_3J	Dodecane	120	40–50	–	16	$C_7H_{15}Br$	Isooctane	100	86	89
2	C_2H_5Br	Dodecane	100	50	93	17	$C_7H_{15}J$	Isooctane	100	92	–
3	C_2H_5J	Dodecane	80	79	–	18	$C_8H_{17}Cl$	Isooctane	100	87	–
4	C_3H_7Cl	Isooctane	100	83	–	19	$C_8H_{17}Br$	Isooctane	100	91	88.4
5	C_3H_7Br	Isooctane	100	84	92	20	$C_8H_{17}J$	Isooctane	100	95	–
6	C_3H_7J	Isooctane	80	91	–	21	$C_9H_{19}Cl$	Isooctane	100	83	–
7	C_4H_9Cl	Isooctane	80	85	91	22	$C_9H_{19}Br$	Isooctane	100	89	–
8	C_4H_9Br	Isooctane	80	93	94	23	$C_9H_{19}J$	Isooctane	100	90	–
9	C_4H_9J	Isooctane	80	95	85	24	$C_{10}H_{21}Cl$	Isooctane	100	81	–
10	$C_5H_{11}Cl$	Isooctane	100	81	–	25	C_6H_5Cl	Dodecane	170	85	–
11	$C_5H_{11}Br$	Isooctane	100	92	92	26	C_6H_5Br	Dodecane	170	94	94
12	$C_5H_{11}J$	Isooctane	100	93	–	27	C_6H_5J	Tetralin	170	86	–
13	$C_6H_{13}Cl$	Isooctane	100	86	–	28	C_4H_9Cl	Without solvent	80	70	91
14	$C_6H_{13}Br$	Isooctane	100	93	–	29	C_4H_9Br	Without solvent	80	75	94
15	$C_6H_{13}J$	Isooctane	100	95	–	30	C_4H_9J	Without solvent	80	71	85

* The experiment was conducted for 36 h.

In contrast to the reaction in ether, the interaction of alkyl halides with magnesium in a hydrocarbon medium proceeds at a sufficient rate only at a higher temperature (80–100°), and in the case of phenyl halides–at an even higher temperature (160–170°). Lower alkyl halides (methyl and ethyl), in accordance with the established views, react with magnesium with difficulty and only when heated externally, whereas alkyl halides (iodides, bromides, and chlorides), beginning with butyl and higher, react with magnesium very readily and with self-heating. In this case, in

under the temperature conditions we studied the reaction proceeds rapidly. Propyl halides occupy an intermediate position. In the case of phenyl halides, the thermal effect of the reaction is insufficient for its normal course, and some external heating is necessary. It should be noted that, unlike the reaction in ether, the preparation of organomagnesium compounds in a hydrocarbon medium requires stricter observance of the reaction conditions.

The yield of alkylmagnesium halide depends only slightly on the nature of the

halide in the haloalkane. For iodides the yields are somewhat higher than for bromides, and for bromides somewhat higher than for chlorides. In contrast to the Grignard synthesis in ether [20], with increasing length of the hydrocarbon chain in the haloalkane no decrease occurs in the yield of the organomagnesium compound. The lower alkylmagnesium halides are formed as suspensions; the higher ones are noticeably soluble in the hydrocarbon medium.

The organomagnesium compounds obtained by the method we developed are, in all their principal reactions, analogous in their chemical properties to the usual Grignard reagents (reaction with carbon dioxide, with carbonyl compounds, with inorganic compounds); we used them, in particular, to obtain a large number of diverse organoelement compounds [21].

Below is given a typical procedure for obtaining an organomagnesium compound from *n*-butyl chloride and magnesium in isooctane. 13.38 g (0.55 g-at.) of magnesium in the form of filings (obtained by milling) are placed in a four-necked flask equipped with an efficient stirrer, reflux condenser, dropping funnel, and thermometer. The magnesium is heated with a crystal of iodine (2–3 min., which somewhat softens the beginning of the reaction), then, in a nitrogen atmosphere, 2–3 ml of a solution of 46.28 g (0.5 mol) of *n*-butyl chloride in 200 ml of isooctane are added. Subsequent heating of the reaction mixture to boiling usually coincides with the beginning of the reaction, after which the apparatus is thermostated at 80°, and the entire solution of the alkyl halide is gradually added (2–4 hr, depending on the haloalkane). The resulting suspension of the organomagnesium compound is diluted with 100 ml of solvent and the mixture is heated at 80° for 1 hr. An aliquot portion of the mixture (5 ml) is taken for analysis [19], simultaneously determining the amount of unreacted magnesium from the quantity of hydrogen evolved upon treatment of the sample with acid. The excess acid is back-titrated, as usual, with 0.1 *N* NaOH solution.

Thus, the interaction of primary haloalkanes (C_3–C_{10}) with magnesium, carried out in hydrocarbon media in the complete absence of catalysts, is not inferior to the usual Grignard synthesis either in the yields of the organomagnesium compounds formed or in the duration of the process. Lower haloalkanes (and aryl halides) give the corresponding alkyl-(aryl)-magnesium halides under more severe conditions.

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CITED LITERATURE

1. W. Hallwach, A. Schafaric, Ann., **109**, 206 (1859).

2. A. Cahour, Ann. Chim., (3), **58**, 5 (1860); Ann., **114**, 227 (1860).

3. Ph. Löhr, Ann., **261**, 48 (1891).

4. H. Gilman, R. E. Brown, J. Am. Chem. Soc., **49**, 5045 (1930).

5. V. Grignard, Ann. Chim., (7), **24**, 433 (1901).

6. M. S. Kharash, O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, N. Y., 1954.

7. V. Chelnitsev, Ber., **37**, 4534 (1904).

8. V. Chelnitsev, Ber., **37**, 2081 (1904).

9. W. Schlenk, Ber., **64B**, 739 (1931).

10. J. F. Spencer, E. M. Stokes, J. Chem. Soc., **93**, 68 (1908).

11. J. F. Spencer, M. S. Crewdson, J. Chem. Soc., **93**, 1821 (1908).

12. E. Wiberg, R. Bauer, Ber., **85**, 593 (1952).

13. P. Schorigin, W. Issaguljanz et al., Ber., **64B**, 2584 (1931).

14. P. Schorigin, W. Issaguljanz, A. Gusseva, Ber., **66B**, 1426 (1933).

15. L. I. Zakharkin, O. Yu. Okhlobystin, Izv. AN SSSR, OKhN, 1959, 1135.

16. D. Bryce-Smith, G. F. Cox, J. Chem. Soc., 1958, 1050.

17. Van Fo-sun, B. A. Dolgoplosk, B. L. Erusalimskii, Vysokomolek. soed., **2**, 541 (1960).

18. D. Bryce-Smith, G. F. Cox, J. Chem. Soc., 1961, 1175.

19. H. Gilman, E. A. Zoellner, J. B. Dickey, J. Am. Chem. Soc., **51**, 1576 (1929).

20. H. Gilman, R. J. Vanderwal, Bull. Soc. chim. France, (4), **45**, 344 (1929).

21. L. I. Zakharkin, O. Yu. Okhlobystin, B. N. Strunin, Izv. AN SSSR, OKhN, 1961, 2254, DAN, **147**, No. 1 (1962).

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