

ORGANOMAGNESIUM COMPOUNDS FROM MAGNESIUM AND ALKYL HALIDES
IN HYDROCARBON MEDIUM*

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THE preparation of alkyl magnesium halides from magnesium and alkyl halides in hydrocarbon medium in the absence of ether and other catalysts of Grignard reaction may be of considerable synthetic interest. In spite of a number of works in this field,^{1,2} no systematic investigation of the interaction of alkyl halides and magnesium in a purely hydrocarbon medium has yet been carried out to estimate the yields of organomagnesium compounds and to elucidate the optimum conditions of the reaction. The lack of such data and the somewhat ambiguous literature on this subject have led to a widespread view that with ether and other catalysts being absent the synthesis of organomagnesium compounds does not proceed readily and cannot be considered of practical value.

Carrying on our investigation of non-catalysed synthesis of organomagnesium compounds³ we have studied the reactions of primary alkyl halides C₁ to C₁₀ and benzene halides with magnesium in hydrocarbon medium. We used fine magnesium turnings and isoöctane, dodecane, and tetraline as solvents. The optimum synthetic conditions and the yields of organo-

* Translated by A.L. Pumpiansky, Moscow.

¹ M.S. Kharash and O. Reinmuth, Grignard Reactions of Nonmetallic Substances. New York (1954).

² O. Bryce-Smith and G.F. Cox, J. Chem. Soc. 1175 (1961).

³ L.I. Zakharkin, O.Yu. Okhlobystin and B.N. Strunin, Izv. Akad. Nauk SSSR, Otdel. Khim. Nauk 2254 (1961).

TABLE 1

Experiment no.	Alkyl halide	Solvent	Temp. (°C)	Yield (%)
1	CH ₃ I	dodecane	120	40-50
2	C ₂ H ₅ Br	dodecane	100	50
3	C ₂ H ₅ I	dodecane	80	79
4	C ₃ H ₇ Cl	iso ^o ctane	100	83
5	C ₃ H ₇ Br	iso ^o ctane	100	84
6	C ₃ H ₇ I	iso ^o ctane	80	91
7	C ₄ H ₉ Cl	iso ^o ctane	80	85
8	C ₄ H ₉ Br	iso ^o ctane	80	93
9	C ₄ H ₉ I	iso ^o ctane	80	95
10	C ₅ H ₁₁ Cl	iso ^o ctane	100	81
11	C ₅ H ₁₁ Br	iso ^o ctane	100	92
12	C ₅ H ₁₁ I	iso ^o ctane	100	93
13	C ₆ H ₁₃ Cl	iso ^o ctane	100	86
14	C ₆ H ₁₃ Br	iso ^o ctane	100	93
15	C ₆ H ₁₃ I	iso ^o ctane	100	95
16	C ₇ H ₁₅ Br	iso ^o ctane	100	86
17	C ₇ H ₁₅ I	iso ^o ctane	100	92
18	C ₈ H ₁₇ Cl	iso ^o ctane	100	87
19	C ₈ H ₁₇ Br	iso ^o ctane	100	91
20	C ₈ H ₁₇ I	iso ^o ctane	100	95
21	C ₉ H ₁₉ Cl	iso ^o ctane	100	83
22	C ₉ H ₁₉ Br	iso ^o ctane	100	89
23	C ₉ H ₁₉ I	iso ^o ctane	100	90
24	C ₁₀ H ₂₁ Cl	iso ^o ctane	100	81

TABLE 1 - continued

Experiment no.	Alkyl halide	Solvent	Temp. (°C)	Yield (%)
25	C ₆ H ₅ Cl	dodecane	170	85
26	C ₆ H ₅ Br	dodecane	170	94
27	C ₆ H ₅ I	tetraline	170	86
28	C ₄ H ₉ Cl	without solvent	80	70
29	C ₄ H ₉ Br	without solvent	80	75
30	C ₄ H ₉ I	without solvent	80	71

magnesium compounds are summarized in Table 1.

In all instances the same amount of magnesium (0.55 g atom), alkyl halide (0.5 mole) and hydrocarbon (300 ml) were used. The reaction was initiated by heating magnesium with 2-3 ml of alkyl halide until the latter started boiling (2-3 min) and then the alkyl halide solution in hydrocarbon was gradually added. The process took 3-5 hr. All runs were carried out in nitrogen.

It will be seen from Table 1 that the yields of organomagnesium compounds are on the whole not inferior to those in ether solution. There is, however, some difference in the readiness of the reaction of various alkyl halides. That is, lower alkyl halides (methyl, ethyl) react less readily than do higher ones (C₃ and upwards). This necessitates external heating, whilst alkyl halides, beginning from butyl, react readily with warming up. Phenyl halides react only under drastic conditions. Organomagnesium compounds produced from higher alkyl and benzene halides are markedly soluble in hydrocarbon medium, lower alkyl magnesium halides give rise to suspensions. Both exhibit chemical properties similar to those of usual Grignard reagents.