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Preliminary communication

LOW-TEMPERATURE REACTION OF MAGNESIUM WITH FLUOROBENZENE

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Summary

The low-temperature reaction of magnesium with fluorobenzene has been investigated. Joint condensation of magnesium and fluorobenzene vapours at low temperatures quantitatively gave phenylmagnesium fluoride in one stage.

Organofluoro compounds can form Grignard reagents with difficulty. Alkylmagnesium fluorides were obtained in the presence of appropriate catalysts in ethers [1], but under these conditions fluorobenzene failed to react with magnesium. Signs of the formation of phenylmagnesium fluoride were discovered using highly reactive magnesium metal [2]. The compound has been obtained in pure form by the exchange reaction of diphenylmagnesium and boron trifluoride [3] but until now a one-stage method for formation of arylmagnesium fluorides in high yield did not exist.

We obtained unsolvated phenylmagnesium fluoride through the low-temperature reaction of magnesium and fluorobenzene. This reaction was performed by cocondensation of atomic magnesium and 50—300-fold excess of fluorobenzene onto a surface, cooled with liquid nitrogen according to the molecular beams method, for which the condensation rates of fluorobenzene were $0.4-4.5 \times 10^{16}$ molecules s^{-1} cm^{-2} and the condensation rates of magnesium $0.4-1.5 \times 10^{14}$ atoms s^{-1} cm^{-2}. Atomic magnesium was obtained by slow evaporation from a quartz crucible at 620—670 K.

Cocondensation of the reagents at 77 K resulted in the formation of chestnut coloured films. We could follow the reaction process by the disappearance of the original chestnut colour of the films upon heating. A visible reaction begins to proceed at about 190 K upon heating the film. At a magnesium/fluorobenzene ratio of 1/300 the film loses its colour completely before the melting point of fluorobenzene (231 K) is reached. Increase of the magnesium content in the mixture resulted in the decolourization of the film around the melting point of fluorobenzene. At a magnesium/fluorobenzene ratio higher than 0.01

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unreacted magnesium was traced after melting of fluorobenzene, i.e. the reaction did not proceed completely. This effect is probably due to the aggregation of atoms, which considerably reduce the activity of magnesium.

The low-temperature reaction of magnesium with fluorobenzene resulted in the formation of a white substance, which was easily decomposed by water with formation of benzene. The magnesium content in the reaction product determined by the method outlined in ref. 4 was about 23%, in agreement with the theoretical quantity for phenylmagnesium fluoride (20%). The yield of benzene varied from 50 to 100% of the theory depending on the ratio of initial reagents in accordance with the scheme:

$$C_6H_5F + Mg \rightarrow C_6H_5MgF \xrightarrow{H_2O} C_6H_6 + Mg(OH)F$$

Thus joint condensation of magnesium and fluorobenzene vapours at low temperatures allows obtainment of phenylmagnesium fluoride in a one stage process quantitatively.

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