Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

A new and convenient method of preparing alkyl and aryl fluoro Grignard compounds. The reaction of magnesium alkyls and aryls with metal fluorides

E.C. ASHBY and J.A. NACKASHI
School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)

(Received June 29th, 1970)

We recently reported the first successful preparation of alkylmagnesium fluoride in high yields involving the reaction of alkyl fluorides with magnesium in the presence of appropriate catalysts[1]. This approach even though successful has two disadvantages: (1) some alkyl fluorides are not readily available and (2) phenylmagnesium fluoride could not be prepared.

We would now like to report the first successful preparation of alkyl- and aryl-magnesium fluorides in high yields involving the utilization of organometallic exchange reactions. For example, dialkyl- and diarylmagnesium compounds have been found to react readily with boron trifluoride etherate in THF at room temperature to form the fluoro Grignard compounds in high yields.

$$3\ R_2Mg + BF_3 \cdot Et_2O \xrightarrow{THF} 3\ RMgF + R_3B \qquad (1)$$

Identification of the alkyl- and arylmagnesium fluoride involves elemental analyses (C—Mg/Mg/F = 1/1/1), observation of infrared absorption bands in the C—Mg stretching region*, and the presence of appropriate chemical shifts in the NMR spectra characteristic of C—Mg compounds.

Methylmagnesium fluoride was prepared in 80% yield by the reaction of dimethylmagnesium and boron trifluoride etherate in THF.

$$3\ Me_2Mg + BF_3 \cdot Et_2O \xrightarrow{THF} 3\ MeMgF + Me_3B \qquad (2)$$

During the addition of $BF_3 \cdot Et_2O$ to Me_2Mg, a precipitate was formed which was filtered from solution. Residual boron detected in the solution was removed by concentrating the solution to a solid followed by filtration and washing of the solid with hexane. This solid redissolved in THF and exhibited a C—Mg/Mg/F molar ratio of 1.0/1.1/1.0 by elemental analysis. The NMR spectrum of the solution exhibited a singlet at δ — 1.71 characteristic

---

*The C—Mg stretching frequency of alkyl Grignard compounds in THF has been cited between 500 and 535 cm^{-1} and for aryl Grignard compounds in THF the C—Mg stretching absorption has been cited[2] between 368 and 382 cm^{-1}. The following tentative assignments for the fluoro Grignard compounds prepared in this work are as follows: CH_3MgF (530 cm^{-1}), C_2H_5MgF (480 cm^{-1}), PhMgF (400 cm^{-1}).

of methylmagnesium fluoride prepared previously from methyl fluoride and magnesium in THF[1] (Me_2Mg in THF exhibits a singlet at $\delta - 1.76$). It was observed that the mode and rate of addition of reagents are important in the yield of methylmagnesium fluoride. When neat boron trifluoride etherate was diluted in THF and added slowly to a stirred solution of dimethylmagnesium in THF, high yields of methylmagnesium fluoride resulted. This successful mode and rate of addition of reagents is presumably due to the fact that less magnesium fluoride would be expected when boron trifluoride etherate is added slowly to excess dimethylmagnesium. This explanation is substantiated by the observation that precipitate formation does not occur until a large portion of the diluted boron trifluoride is added to the dimethylmagnesium. It was also observed that the addition of neat boron trifluoride to dimethylmagnesium in a time period of 30 minutes resulted in the formation of significantly larger amounts of precipitate and a subsequently lower yield of the desired methylmagnesium fluoride.

Two reactions were examined concerning the preparation of ethylmagnesium fluoride: (1) the reaction of diethylmagnesium with boron trifluoride etherate and (2) the reaction of diethylmagnesium with diethylaluminum fluoride.

$$3\ Et_2Mg + BF_3 \cdot Et_2O \xrightarrow{THF} 3\ EtMgF + Et_3B \qquad (3)$$

$$Et_2Mg + Et_2AlF \xrightarrow{THF} EtMgF + Et_3Al \qquad (4)$$

Ethylmagnesium fluoride was prepared by the slow addition of boron trifluoride etherate in THF to a solution of diethylmagnesium. No precipitate was formed in the reaction, and the ethylmagnesium fluoride was isolated by solvent removal, washing of the resulting solid with hexane and redissolving of the solid in THF. The ethylmagnesium fluoride in solution exhibited a molar ratio of 1/1.1/1.2 (C—Mg/Mg/F), its NMR spectrum showed a quartet centered at $\delta -0.65$ (Et_2Mg in THF shows a quartet centered at $\delta - 0.77$) and the solution was shown by flame test to be void of any boron containing impurity.

Diethylaluminum fluoride (50% in heptane) was added to diethylmagnesium in three different solvent systems: THF, hexane and benzene. In all three cases it was not possible to obtain ethylmagnesium fluoride free of aluminum impurities. This result could possibly be due to the formation of a complex between $(C_2H_5)_3Al$ and C_2H_5MgF which is difficult to separate from C_2H_5MgF.

$$(C_2H_5)_2Mg + (C_2H_5)_2AlF \rightarrow C_2H_5MgF + (C_2H_5)_3Al \rightarrow FMgAl(C_2H_5)_4 \text{ or } C_2H_5MgAl(C_2H_5)_3F \qquad (5)$$

Recently we have shown that similar complexes do exist as equilibrium mixtures[3]

$$C_2H_5MgAl(C_2H_5)_3H \leftrightarrows HMgAl(C_2H_5)_4 \qquad (6)$$

The direct preparative route proved to be unsuccessful in the preparation of phenylmagnesium fluoride; however, phenylmagnesium fluoride was prepared in 74% yield by the reaction of boron trifluoride etherate in THF with diphenylmagnesium. A white solid formed during the reaction was removed by filtration leaving a boron free solution with a C—Mg/Mg/F ratio of 1.0/1.0/0.76. The NMR spectrum of the solution exhibited a complex, aromatic multiplet with the absorption of highest intensity being centered at δ 6.79. The absorption of highest intensity for the aromatic multiplet of Ph_2Mg is exhibited at δ 6.98.

Equations representing the course of this reaction are as follows:

$$3\ Ph_2Mg + BF_3 \rightarrow 3\ PhMgF + Ph_3B \tag{7}$$

$$3\ PhMgF + Ph_3B \rightarrow FMgBPh_4 + 2\ PhMgF \tag{8}$$

Thus the maximum yield in this reaction is expected to be 66%. The observed yield was 74% which is still consistent with a combination of eqns. 7 and 8 to describe the system.

Hexylmagnesium fluoride was prepared in low yield by the reaction of boron trifluoride etherate with a diethyl ether solution of dihexylmagnesium. No precipitate formed in the reaction. The solution was concentrated to a viscous oil which dissolved in hexane. Several methods of separation of hexylmagnesium fluoride from trihexylborane were attempted, however, only a small quantity of product could be isolated. The molar ratio of C–Mg/Mg/F for the isolated product was 1.1/1.0/1.2.

A further examination of various organometallic exchange reactions involving other metal fluorides such as SnF_4, SiF_4 etc. is in progress in an attempt to expand the number of applicable, facile reactions leading to the preparation of alkylmagnesium fluorides.

REFERENCES

1 E.C. Ashby, S.H. Yu and R.G. Beach, *J. Amer. Chem. Soc.*, 92 (1970) 433.
2 R.M. Salinger and H.S. Mosher, *J. Amer. Chem. Soc.*, 86 (1964) 1782.
3 Suresh C. Srivastava and E.C. Ashby, *Inorg. Chem.*, in press.