

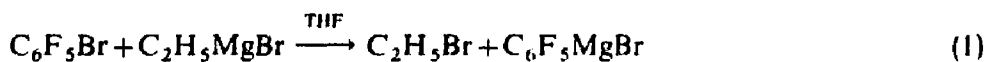
## NOTE

### Synthesis of some pentafluorophenylmagnesium compounds

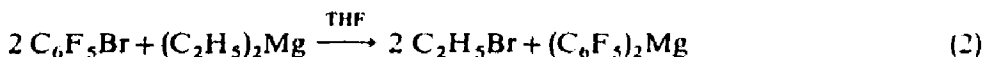
#### Discussion

The synthesis of pentafluorophenylmagnesium bromide has been accomplished previously by the conventional reaction between magnesium and bromopentafluorobenzene in diethyl ether<sup>1</sup>. We have also described its synthesis through the reaction between pentafluorobenzene and ethylmagnesium bromide (acid-base reaction)<sup>2</sup>. The reported synthesis of bis(pentafluorophenyl)magnesium (as a diethyl ether solution) was accomplished by a metal-metal interconversion between diphenylmagnesium and bis(pentafluorophenyl)mercury<sup>3</sup>.

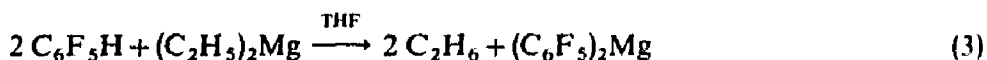
We now report efficient and more convenient alternative methods for the preparation of the pentafluorophenylmagnesium bromide and bis(pentafluorophenyl)magnesium. The formation of the former occurred exothermally via halogen-metal interconversion when bromopentafluorobenzene was added at room temperature to a THF solution of ethylmagnesium bromide. The exchange\* is complete in a few minutes. Hydrolysis of the reaction mixture produced a 98 % yield of pentafluorobenzene, indicating the rapidity and efficiency of this reaction. In a similar manner,



(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>Mg was prepared when a THF solution of bromopentafluorobenzene was added to a THF solution of diethylmagnesium. Hydrolysis of the resulting reaction mixture produced a 99 % yield of pentafluorobenzene. Alternatively, bis(pentafluoro-



phenyl)magnesium was prepared efficiently through the reaction between pentafluorobenzene and diethylmagnesium. Hydrolysis of the resulting magnesium compound would yield the starting material pentafluorobenzene. To test the efficiency



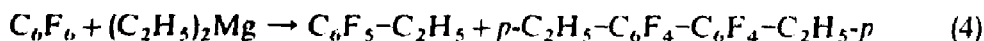
of the reaction, the reagent thus prepared was therefore treated with trimethylchlorosilane to produce (pentafluorophenyl)trimethylsilane<sup>6</sup> in an 86 % yield. A solution of this reagent, prepared via reaction (2), also was carbonated to produce after hydrolysis,

\* The ease of this exchange in the synthesis of C<sub>6</sub>F<sub>5</sub>MgBr stands in marked contrast to that of bromobenzene which itself does not undergo measurable exchange with amylmagnesium bromide in dimethoxyethane solution (a solvent which is reported to be more efficient for halogen-metal interconversions than is THF)<sup>4</sup>. However, perfluoroalkyl iodides have been previously shown to undergo quantitative metal-halogen interconversion with phenylmagnesium bromide<sup>5</sup>.

an 83% yield of pentafluorobenzoic acid. These reactions would indicate that both pentafluorophenyl groups of  $(C_6F_5)_2Mg$  have considerable reactivity.

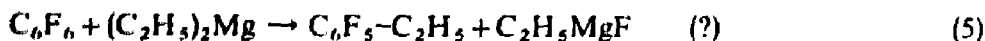
At room temperature, THF solutions of both magnesium reagents appear to be quite stable. For example,  $C_6F_5MgBr$  underwent no decomposition after 5 days, although a small amount of ethylpentafluorobenzene was observed. The formation of this product undoubtedly occurred through the reaction of the Grignard reagent with ethyl bromide. Similarly, a THF solution of  $(C_6F_5)_2Mg$  underwent no decomposition at room temperature over a two days period. However, at THF reflux temperature, solutions (of comparable concentration) of these reagents decomposed to produce an insoluble, white precipitate. The physical properties and infrared analysis of this material suggested the structure to be the polymeric polyfluorophenylene previously reported by Fear *et al.*<sup>7</sup> in their studies on the thermal decomposition of pentafluorophenylmagnesium bromide. The relative stabilities of the  $C_6F_5-Mg$  reagents, as indicated by their rates of decomposition appeared to be closely similar. After a 24 hours reflux period, 70% of  $C_6F_5MgBr$  was decomposed whereas  $(C_6F_5)_2Mg$  was 100% decomposed.

Since pentafluorobenzene and bromopentafluorobenzene react with diethylmagnesium to produce  $(C_6F_5)_2Mg$ , it was of interest to determine whether diethylmagnesium would react with hexafluorobenzene to: (a) yield  $(C_6F_5)_2Mg$  by a fluorine-metal interconversion or (b) alkylate to yield ethylpentafluorobenzene\*. We have observed that when stoichiometric quantities of hexafluorobenzene and diethylmagnesium (THF solution) are allowed to react at room temperature, a 72% yield of ethylpentafluorobenzene is produced, with no indication of pentafluorobenzene. In addition to ethylpentafluorobenzene, 4,4'-diethyloctafluorobiphenyl also was obtained in 10% yield. When the reaction was repeated using a 2:1 excess of diethyl-



magnesium, a 60% yield of ethylpentafluorobenzene and a 24% yield of the biphenyl derivative, were obtained. The greater yield of the former indicates that diethylmagnesium preferentially alkylates. The presence of the latter however, indicates that some metallation is also occurring, but to a lesser extent. If metallation of a fluoraromatic compound is occurring, it would involve the reaction of a C-F bond. Formation of an organomagnesium compound via a C-F bond is unique. Further work in this laboratory is concerned with a more detailed investigation of this reaction.

One interesting aspect in the reactions between diethylmagnesium and hexafluorobenzene is that the formation of the fluoride ion from the substitution reaction corresponds to the stoichiometry of ethylmagnesium fluoride. The existence of such a



Grignard reagent was previously suggested by Dessy<sup>8</sup>, who reported the possibility of its synthesis through the reaction of magnesium fluoride with diethylmagnesium.

### Experimental

All organometallic preparations were carried out under an atmosphere of dry,

\* We have previously shown<sup>7</sup> that ethylmagnesium bromide alkylates hexafluorobenzene in THF to produce a 62% yield of ethylpentafluorobenzene.

oxygen-free nitrogen. Tetrahydrofuran was freshly distilled from sodium. VPC analyses were carried out on an F & M Model 810 gas chromatograph. An 11 ft., 15% polyphenylether on Chromosorb P column using helium carrier gas at about 125 cc/min was used. The temperature was programmed from 70° to 250° at 8°/min. All reactions (except carbonation) were standardized with ethylbenzene used as an internal standard.

*Preparation of ethylmagnesium bromide and diethylmagnesium.* Ethylmagnesium bromide was prepared from Grignard grade magnesium and ethyl bromide in THF. Diethylmagnesium<sup>9</sup> was prepared from diethylmercury and magnesium turnings in THF. The concentrations of the solutions were obtained using standard acid-base titrations and by derivatization with phenyldimethylchlorosilane<sup>10</sup>.

*Pentafluorophenylmagnesium bromide.* A solution of ethylmagnesium bromide (45 ml, 0.052 mole) in THF was cooled by an ice bath. To it was added dropwise a solution of bromopentafluorobenzene (12.35 g, 0.050 mole) and ethylbenzene (3.574 g, as internal standard). After the exotherm, the cooling bath was removed and the solution warmed to room temperature. Some precipitate was observed. This precipitate was found to be magnesium bromide (probably as an etherate of THF). An aliquot was removed, hydrolyzed with 4 *N* hydrochloric acid and extracted with pentane. The dried pentane extract was analyzed by VPC. The yield of the Grignard reagent was 98% as determined from the amount of pentafluorobenzene observed. The Grignard solution was stirred at room temperature for 5 days. VPC analysis indicated that 94% of active reagent still was present. A small amount of ethylpentafluorobenzene also was detected.

*Bis(pentafluorophenyl)magnesium.* In a manner similar to that described above, bromopentafluorobenzene (12.355 g, 0.050 mole) and ethyl benzene (3.001 g, as internal standard) were added in 15 ml of THF to diethylmagnesium (30 ml of a THF solution containing 0.025 mole). An aliquot was removed, hydrolyzed, extracted with pentane, dried and analyzed by VPC. Analysis for pentafluorobenzene indicated a 99% yield of  $(C_6F_5)_2Mg$ . The remainder of the reaction mixture was stirred at room temperature for 2 days. No decomposition of the reagent was observed by VPC analysis.

*Preparation of bis(pentafluorophenyl)magnesium.* In a manner similar to that described above, pentafluorobenzene (8.406 g, 0.050 mole) in 15 ml of THF was added over a 45 min period to diethylmagnesium (30 ml of a THF solution containing 0.025 mole). Trimethylchlorosilane (6.030 g, 0.055 mole) and ethylbenzene (5.293 g, as internal standard) dissolved in 15 ml of THF were slowly added. After it had been stirred at room temperature for 19 h, the reaction mixture was analyzed by VPC. An 86% yield of pentafluorotrimethylsilane<sup>9</sup> was obtained.

*Preparation of pentafluorobenzoic acid.* A solution of  $(C_6F_5)_2Mg$  was prepared from diethylmagnesium (30 ml of a THF solution containing 0.025 mole) and bromopentafluorobenzene (12.355 g, 0.050 mole) as described above. Carbon dioxide was bubbled through the reaction for 3 h. The resulting *clear* solution was acidified with 4 *N* hydrochloric acid and extracted with diethyl ether. The diethyl ether was extracted with dilute sodium hydroxide, the aqueous layer acidified and again extracted with diethyl ether and dried. Removal of the solvent produced a solid, m.p. 95–102° (lit.<sup>11</sup> m.p. 103–104°), 83% yield. The infrared spectrum of this material was identical to that of an authentic sample of pentafluorobenzoic acid.

*Reaction of diethylmagnesium with hexafluorobenzene.* Hexafluorobenzene (4.654 g, 0.025 mole) and ethylbenzene (1.811 g, as internal standard) dissolved in THF (15 ml) were added to diethylmagnesium (30 ml of a THF solution containing 0.025 mole) at room temperature over a period of 2–3 min. The mixture was stirred for 24 h. Subsequently, VPC analysis of an aliquot sample, which had been hydrolyzed, extracted with pentane and dried, showed the presence of ethylpentafluorobenzene (60%), 4,4'-diethyloctafluorobiphenyl (24%), hexafluorobenzene (3%) and the absence of any pentafluorobenzene.

The reaction was repeated with stoichiometric quantities of the reactants, hexafluorobenzene (9.301 g, 0.050 mole), ethylbenzene (2.745 g as internal standard) and diethylmagnesium (30 ml of a THF solution containing 0.025 mole) (48 h at room temperature). VPC analysis of an aliquot treated as above showed the presence of ethylpentafluorobenzene (72%), 4,4'-diethyloctafluorobiphenyl (10%) hexafluorobenzene (15%) and no pentafluorobenzene.

*Thermal stability of  $C_6F_5-Mg$  reagents.* The thermal stabilities at reflux temperature in THF were determined by VPC analysis as described above. Solutions of the organometallic compounds were refluxed and aliquot samples were withdrawn periodically. At the end of 6 h, 80% of  $(C_6F_5)_2Mg$  (via  $C_6F_5Br$ ) and 75% of  $(C_6F_5)_2Mg$  (via  $C_6F_5H$ ) remained undecomposed. At the end of 18 h, 0% of the latter remained while at the end of 24 h, 30% of  $C_6F_5MgBr$  and 0% of  $(C_6F_5)_2Mg$  (via  $C_6F_5Br$ ) remained. The decomposed organometallics yielded an intractable material with no melting point up to  $360^\circ$ . The infrared spectrum of the material was similar to that of a polyfluorophenylene polymer previously reported.

*Nonmetallic Materials Division,  
Air Force Materials Laboratory,  
Wright-Patterson Air Force Base, Ohio (U.S.A.)*

WILLIAM L. RESPESS  
CHRIST TAMBORSKI

- 1 W. J. PUMMER AND L. A. WALL, *J. Res. Nat. Bur. Stand., A*, 63 (1959) 167; E. MILD, R. STEVENS AND J. C. TATLOW, *J. Chem. Soc.*, (1959) 166.
- 2 R. J. HARPER, E. J. SOLOSKI AND C. TAMBORSKI, *J. Org. Chem.*, 29 (1964) 2385
- 3 D. F. EVANS AND M. S. KHAN, *Chem. Commun.*, (1966) 67.
- 4 L. I. ZAKHARKIN, O. YU. OKILOBYSTIN AND K. A. BILEVITCH, *J. Organometal. Chem.*, 2 (1964) 309.
- 5 O. R. PIERCE, A. F. MEINER AND E. T. MCBEE, *J. Amer. Chem. Soc.*, 75 (1953) 2516.
- 6 C. TAMBORSKI, E. J. SOLOSKI AND S. M. DEC, *J. Organometal. Chem.*, 4 (1965) 446.
- 7 E. I. P. FEAR, J. THROWER AND M. A. WHITE, *19th Intern. Congr. Pure Appl. Chem.*, London, July, 1963.
- 8 R. E. DESSY, *Chem. Eng. News*, 38 (1960) (31) 42.
- 9 W. SCHLENK, *Ber.*, 64 (1931) 736.
- 10 H. O. HOUSE AND W. L. RESPESS, *J. Organometal. Chem.*, 4 (1965) 95.
- 11 E. NIELD, R. STEPHENS AND J. C. TATLOW, *J. Chem. Soc.*, (1959) 166.

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