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NOTE

THE PREPARATION OF A GRIGNARD REAGENT FROM HEXAFLUOROBENZENE BY THE ENTRAINMENT TECHNIQUE

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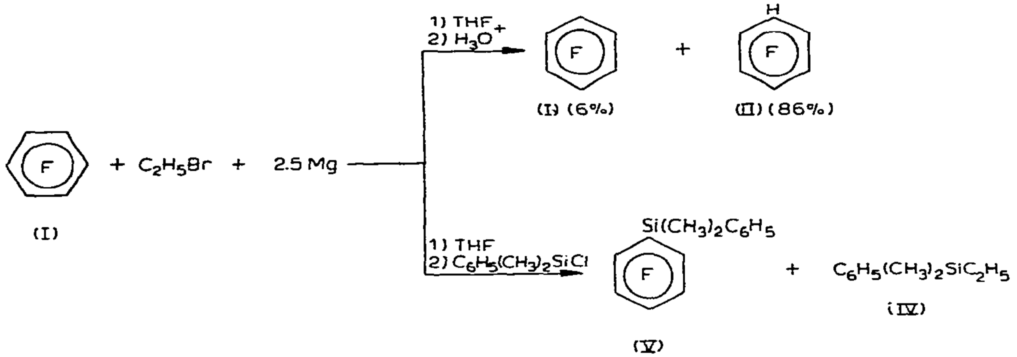
The preparation of the pentafluorophenyl Grignard reagent has been reported by a variety of techniques: from chloro-[1], bromo-[2], or iodopentafluorobenzene[3] in diethyl ether and from chloro-[4] and bromopentafluorobenzene[5] in tetrahydrofuran by conventional methods; from bromopentafluorobenzene and ethylmagnesium bromide in tetrahydrofuran (halogen–metal interconversion)[6] and from pentafluorobenzene and ethylmagnesium bromide in tetrahydrofuran (metalation reaction)[7]. More recently we have reported the unexpected metalation of hexafluorobenzene, to form a pentafluorophenylmagnesium compound, by using an ethylmagnesium bromide/cobalt(II) chloride system[8]. Heretofore, no one has reported concerning the direct reaction (success or failure) between magnesium and hexafluorobenzene. We wish now to describe the preparation of the pentafluorophenyl Grignard reagent from hexafluorobenzene and magnesium using the entrainment technique.

The entrainment method, although not widely employed, has been used to prepare Grignard reagents from organic halides that will not react with magnesium under the usual conditions[9]. A reactive organic halide (ethyl bromide has most often been used) is used as the "entrainer" to activate the magnesium surface which makes its reaction with the more inert halide possible. This is conveniently done by suspending magnesium with vigorous stirring in a diethyl ether solution of the unreactive halide and slowly adding the entrainer[10]. The use of ethyl bromide as the entrainer is handicapped in that one necessarily obtains a mixture of ethylmagnesium bromide as well as the desired Grignard reagent derived from the unreactive halide. This shortcoming has been avoided by using 1,2-dibromoethane as the entrainer[10]. The 1,2-dibromoethane reacts with magnesium but the resulting magnesium compound decomposes to ethylene and magnesium bromide as it is formed. One is thus left with a mixture of the desired Grignard reagent plus a molar quantity of magnesium bromide equal to that of the 1,2-dibromoethane employed (usually one mole of entrainer is used for each mole of inert halide). In this manner, Grignard reagents have been prepared from inert organic chlorides such as 1-chloronaphthalene and hexachlorobenzene[10].

Our application of this entrainment technique has been most successful in the synthesis of pentafluorophenylmagnesium compounds. When ethyl bromide (*x* moles) was used as the entrainer, hexafluorobenzene (I) (x moles) reacted with magnesium (2.5x g-atoms) in tetrahydrofuran to give, after hydrolysis, pentafluorobenzene (II) in 86% yield. Reaction of the organometallic reagent produced with phenyldimethylchlorosilane (III) yielded phenyldimethylethylsilane (IV) and phenyldimethyl(pentafluorophenyl)silane (V). When ethyl bromide (0.5x moles) was added to hexafluorobenzene (I) (x moles) and magnesium (2.5x g-atoms) in tetrahydrofuran, the yield of pentafluorobenzene (II) was only 47% after hydrolysis. There is then, clearly a requirement that a full equivalent of ethyl bromide be used to give nearly complete reaction of hexafluorobenzene (I) with magnesium.



In order to accomplish the conversion of hexafluorobenzene (I) to the corresponding Grignard reagent (III) without having the concurrent formation of another Grignard reagent (C_2H_5MgBr), we have examined the reaction of hexafluorobenzene (I) (x moles) and 1,2-dibromoethane (x moles) with magnesium (2.5x g-atoms) in tetrahydrofuran. However, in this case, the yield of pentafluorobenzene after hydrolysis was only 52%. An additional mole of 1,2-dibromoethane did raise the yield of pentafluorobenzene to 75%. This inferior capability of 1,2-dibromoethane as compared to ethyl bromide, as an entrainment agent to promote the reaction of hexafluorobenzene (I) with magnesium, was not anticipated since it has been reported that in diethyl ether they are of similar utility[10]. The reason for this difference as noted by us lies perhaps in our use of tetrahydrofuran as solvent. When 1,2-dibromoethane reacts with magnesium, a magnesium bromide–tetrahydrofuran complex which forms a very copious precipitate during the course of reaction results*. It is generally acknowledged that the role of the entrainer is to activate the magnesium surface by a cleaning action[9,10] and the formation of this insoluble complex and its precipitation on the magnesium surface would be expected to interfere with the process by which entrainment is said to succeed. This problem would not exist when ethyl bromide is used as the entrainer as the ethylmagnesium bromide thus formed is soluble in tetrahydrofuran. When sufficient tetrahydrofuran to dissolve all the magnesium bromide formed was used, only a 46% yield of pentafluorobenzene was obtained after hydrolysis. This low yield must be partly due to a dilution factor which makes the reaction less efficient, since under similar conditions using ethyl bromide as the entrainer, the yield of pentafluorobenzene (II) after hydrolysis also was reduced from that previously observed: from 86% to 67% yield.

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* At 30°, a saturated solution of magnesium bromide in tetrahydrofuran is reported to be 0.476 N[11].

It might be argued that the best approach would be to employ the very long addition times (up to 24 h) that have been employed to improve yields in the entrainment reaction[10]. However, this technique would not be applicable to our system as the pentafluorophenyl Grignard reagent will react with hexafluorobenzene (I) (within 24 h) to form perfluoropolyphenylene polymers.

The diethyl ether complex of magnesium bromide is a liquid and hence does not interfere with the entrainment process. Our attempts to take advantage of this by employing diethyl ether as a solvent for the preparation of the Grignard reagent from hexafluorobenzene (I) using 1,2-dibromoethane as the entrainment agent were unsuccessful. Under these solvent conditions, pentafluorobenzene was obtained, after hydrolysis, in only 3% yield. Use of a tetrahydrofuran/benzene solvent as the reaction medium resulted in solution of the magnesium bromide complex to a large extent, but pentafluorobenzene was obtained, after hydrolysis, in only 33% yield. The presence of benzene promotes the solubility of magnesium bromide but apparently serves to reduce the reactivity between hexafluorobenzene (I) toward activated magnesium.

Although we have demonstrated the ability of hexafluorobenzene (I) to react with magnesium in the presence of a suitable entrainer, we have not been able to reduce it to practical application. This would appear to require development of a method for using 1,2-dibromoethane in such a way as to render soluble the magnesium bromide formed without reducing the efficiency of the entrainment process.

EXPERIMENTAL

All entrainment reactions were carried out under an atmosphere of oxygen-free nitrogen. Tetrahydrofuran (THF) was freshly distilled from calcium hydride prior to use.

VPC analysis were carried out on an F&M Model 810 or F&M Model 700 Gas Chromatograph using an 11 ft. 15% polyphenyl ether on Chromasorb P. Ethylbenzene was used as an internal standard. Hexafluorobenzene was purchased from the Imperial Smelting Corporation, Ltd., Avonmouth, Bristol, England.

Reaction of hexafluorobenzene (I) and ethyl bromide with magnesium in tetrahydrofuran

A THF (35 ml) solution of ethyl bromide (10.9 g, 0.10 mole) was added dropwise over 45 min to a THF (35 ml) solution of hexafluorobenzene (I) (18.6 g, 0.10 mole) and ethylbenzene (7.14 g, internal VPC standard) and Grignard grade magnesium (6.13 g, 0.25 g-atom). A few ml of the ethyl bromide solution was added to initiate reaction and then an ice/water cooling bath was employed to moderate the reaction after dropwise addition was started. During the early stages of the reaction, a bright yellow color developed but faded and a deep reddish brown color eventually prevailed. The ice/water bath was removed when the addition was completed. After 30 min additional stirring, VPC analysis of an aliquot sample that had been hydrolyzed in 4 *N* HCl and extracted with pentane, showed the presence of pentafluorobenzene (II) (86%) and hexafluorobenzene (I) (6%). Small amounts of other products were noted but not identified. To the remainder of the reaction mixture was added phenyldimethylchlorosilane (III) (35.0 g, 0.20 mole) in THF (15 ml). After 16 h, VPC analysis showed the presence of phenyldimethylethylsilane (IV) and phenyldimethyl(pentafluorophenyl)silane (V).

In a similar manner, ethyl bromide (10.9 g, 0.10 mole) in THF (125 ml) was added to hexafluorobenzene (I) (18.6 g, 0.10 mole), ethylbenzene (6.73 g, internal VPC standard) and magnesium (6.27 g, 0.26 g-atom) in THF (175 ml). The addition required 70 min. After 30 min additional stirring, VPC analysis after hydrolysis showed the presence of hexafluorobenzene (I) (27%) and pentafluorobenzene (II) (67%).

Reaction of hexafluorobenzene (I) and 1,2-dibromoethane with magnesium in tetrahydrofuran

In a manner similar to that described above, a THF (35 ml) solution of 1,2-dibromoethane (18.8 g, 0.10 mole) was added over 1 h to magnesium (6.13 g, 0.25 g-atom) and a THF (35 ml) solution of hexafluorobenzene (I) (18.6 g, 0.10 mole) and ethylbenzene (8.07 g). A bright yellow color was initially observed. During the addition, a copious white precipitate formed which did not dissolve on warming to room temperature. VPC analysis of an aliquot sample, after hydrolysis, showed the presence of hexafluorobenzene (I) (39%) and pentafluorobenzene (II) (52%). Other unidentified products were also present. When the reaction was repeated using sufficient THF to dissolve the white precipitate, no increase in the pentafluorobenzene yield was noted.

A similar reaction was run using 1,2-dibromoethane (37.61 g, 0.20 mole), magnesium (9.90, 0.40 g-atom), hexafluorobenzene (I) (18.61 g, 0.10 mole), ethylbenzene (8.02 g) and THF (70 ml). A thick, soupy mixture resulted to which was added additional THF (40 ml). VPC analysis of an aliquot sample after hydrolysis showed the presence of hexafluorobenzene (I) (8%) and pentafluorobenzene (II) (75%). Unreacted 1,2-dibromoethane and unidentified products were also observed.

Reaction of hexafluorobenzene (I) and 1,2-dibromoethane in other solvents

Repeating the above reaction in diethyl ether as the solvent yielded hexafluorobenzene (I) (96%) and pentafluorobenzene (II) (3%). No unreacted 1,2-dibromoethane was detected. In another experiment, use of a THF/benzene (55/30) solvent dissolved most of the white precipitate noted previously. VPC analysis of the hydrolyzed reaction mixture indicated hexafluorobenzene (I) (66%) and pentafluorobenzene (II) (33%).

The reaction of pentafluorophenylmagnesium bromide with hexafluorobenzene (I)

Pentafluorophenylmagnesium bromide was prepared from ethylmagnesium bromide (42 ml of a THF solution containing 0.052 mole) and bromopentafluorobenzene (12.4 g, 0.050 mole)[6]. To this was added hexafluorobenzene (9.3 g, 0.050 mole). During 24 h, considerable precipitate formed. VPC analysis of an aliquot sample taken at this time showed the presence of hexafluorobenzene (I) (82%, based on hexafluorobenzene added) and pentafluorobenzene (II) (7%, based on bromopentafluorobenzene added).

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