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SYNTHESIS OF POLYFLUOROAROMATIC MAGNESIUM COMPOUNDS THROUGH THE EXCHANGE REACTION

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SUMMARY

A convenient synthesis for the preparation of various polyfluoroaromatic magnesium compounds through the magnesium–halogen exchange reaction is described. The reaction between ethylmagnesium bromide and chloride with various bromo- and chloropolyfluoroaromatic compounds provides the polyfluoroaromatic magnesium compounds usually in high yields. Anomalous instability of the (pentafluorophenyl)magnesium chloride is noted.

INTRODUCTION

Magnesium–halogen exchange reactions have been used in the past for the synthesis of perfluoroalkylmagnesium compounds. Pierce *et al.*[1] reported the synthesis of (n-heptafluoropropyl)magnesium iodide from the reaction between iodoheptafluoropropane and phenylmagnesium bromide while Sterlin *et al.*[2] reported the synthesis of (trifluorovinyl)magnesium iodide from the reaction between iodotrifluoroethylene and phenylmagnesium bromide. In our recent studies on highly fluorinated aromatic Grignards, we reported a convenient and high yield synthesis of C_6F_5MgBr[3] and p-$C_6F_5OC_6F_4MgBr$[4].

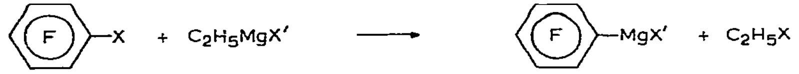
(1)

R = F or C_6F_5O

These latter observations indicated that a magnesium–halogen exchange reaction may be a general and more convenient method for synthesizing numerous and varied polyfluoroarylmagnesium compounds. We now wish to report the results of our further studies on the synthesis of such compounds.

RESULTS AND DISCUSSION

Table 1 summarizes the results of the magnesium–halogen exchange reactions.



(2)

X = I, Br, Cl, H ; X′ = Br or Cl

TABLE 1

y ARYL COMPOUND + x C_2H_5MgX

Aryl compound	X	Mole ratio (y/x)	% Grignard (time)	
			Mono	Di
C_6F_5I	Br	1/1	100 (1 min)	
C_6F_5Br	Br	1/1	96 (1 min)	
	Cl	1/1	96 (15 min)	
	Cl	1/1	0 (24 h)	
C_6F_5Cl	Br	1/1	85 (1 h)	
	Br	1/1	72 (24 h)	
	Cl	1/1	30 (15 min)	
	Cl	1/1	0 (24 h)	
C_6F_5H	Br	1/1	90 (1 h)	
	Br	1/1	96 (24 h)	
	Cl	1/1	65 (15 min)	
	Cl	1/1	50 (24 h)	
	Cl	1/1[a]	41 (24 h)	
$C_6F_4Br_2$ (*para*)	Br	1/1	90 (1 min)	
	Br	1/2	4 (15 min)	93 (15 min)
$C_6F_4Br_2$ (*meta*)	Br	1/1	95 (1 min)	
	Br	1/2	46 (15 min)	4 (15 min)
$C_6F_4Br_2$ (*ortho*)	Br	1/1	93 (1 min)	
	Br	1/2	84 (15 min)	14 (15 min)
C_5NF_5Br-4[b]	Br	1/1	96 (6 min)	

[a] An equivalent of C_2H_5Br was added to the fresh Grignard solution. [b] We like to acknowledge Drs. W. K. R. Musgrave and R. D. Chambers of the University of Durham, Durham, England for a generous sample of 4-bromo-tetrafluoropyridine.

The rate of exchange between ethylmagnesium bromide and the substituent X was found to be I ~ Br > H > Cl. With the aryl iodide and bromide the exchange is rapid and complete within 5 min after addition of ethylmagnesium bromide. The chloro and hydro derivatives, however, require approximately 1 h for maximum exchange. Synthesis of the mono Grignard reagents from the dibromotetrafluorobenzene derivatives (*o*-, *m*-, *p*-$C_6F_4Br_2$) was accomplished readily. Synthesis of the di-Grignard reagent from the same dibromotetrafluorobenzenes was applicable only to the *para* dibromotetrafluorobenzene which yielded the di-Grignard in at least a 90% yield. The *o*-dibromotetrafluorobenzene, however, produced primarily the *ortho* bromo Grignard in an 84% yield. Similar difficulties were experienced recently by us in attempts to prepare the *o*-dilithiotetrafluorobenzene[5] from *o*-dibromotetrafluorobenzene and two equivalents of n-butyllithium. The synthesis of the di-Grignard from the *m*-dibromotetrafluorobenzene was not possible under these conditions. The variety of products found in this reaction (at least five products were detected by VPC) indicated that the *meta* di-Grignard if formed is quite unstable. Grignard reagents other than benzene derivatives may be easily prepared by this method. (4-Tetrafluoropyridyl)magnesium bromide was readily prepared in a 96% yield.

Pentafluorophenylmagnesium bromide has been prepared by at least three different procedures: (1) C_6F_5Br+Mg[6], (2) $C_6F_5H+C_2H_5MgBr$[7], (3) $C_6F_5Br+C_2H_5MgBr$[3]. The Grignard reagent prepared by procedure (3) is stable at room temperature for at least 4–5 days[3]. (Pentafluorophenyl)magnesium chloride prepared through the reaction between C_6F_5Cl and Mg, however, appears to be considerably less stable as an organometallic intermediate. Preparation of the organometallic in refluxing tetrahydrofuran (THF) solution produced only a polymeric material[8]. Recently, however, Jukes and Gilman[9] prepared the Grignard at $-10°$ in THF and reported that after a period of 16.5 h at room temperature at least 46.5% of the Grignard was still available for reaction with trimethylchlorosilane to yield the (pentafluorophenyl)trimethylsilane derivative. Using our ethyl Grignard exchange reaction we also have prepared what is believed to be C_6F_5MgCl. The extent of metalation was determined through the reaction of the Grignard reagent with phenyldimethylchlorosilane[3].

$$C_6F_5X+C_2H_5MgCl \rightarrow C_6F_5MgCl+C_2H_5X \tag{3}$$

$$C_6F_5MgCl+C_6H_5Si(CH_3)_2Cl \rightarrow C_6H_5Si(CH_3)_2C_6F_5 \tag{4}$$

Our studies have verified the relative instability of C_6F_5MgCl prepared through the exchange reaction of either C_6F_5Br or C_6F_5Cl with C_2H_5MgCl. The organometallic solution prepared by this method decomposed at room temperature within 24 h. However, the Grignard solution prepared from C_6F_5H and C_2H_5MgCl (in THF) decomposed approximately 50% under similar conditions. Addition of C_2H_5Br to a fresh Grignard solution prepared from C_6F_5H and C_2H_5MgCl did not affect the stability of the organometallic solution. No explanations can be advanced at this time for the relative instability of the C_6F_5MgCl as compared to the C_6F_5MgBr. Similarly, we cannot explain the apparent greater stability of the C_6F_5MgCl prepared from the C_6F_5H as opposed to that prepared from the C_6F_5Br or C_6F_5Cl. Although such differences in stability have been noted by us and others[8,9], they do not detract from the synthesis applicability of the organomagnesium compound provided it is used within a short time after its preparation.

EXPERIMENTAL

All organometallic reactions were carried out in an atmosphere of dry, oxygen-free nitrogen. Tetrahydrofuran was freshly distilled from sodium. VPC analyses were carried out on an F&M Model 700 gas chromatograph. A 12 ft., 15% polyphenylether (6 ring) on Chromosorb P column using helium carrier gas at about 80 cc/min was used. The temperature was programmed from 60° to 250° at 15°/min.

The following experimental description is typical of all the reactions carried out in this study.

Reaction of chloropentafluorobenzene and ethylmagnesium bromide

A THF (21.7 ml) solution of ethylmagnesium bromide (0.0282 mole) was added over 30 sec to a THF (30 ml) solution of chloropentafluorobenzene (5.71 g, 0.0282 mole) and n-decane (3.00 g, as an internal VPC standard) which was cooled with an ice bath and kept between 0–5°. An exothermic effect (20–25°) was noted from most metal–halogen exchange reactions involving bromine. The reactions of the chloro-and hydrofluoroaromatics were less exothermic. One to two ml samples for VPC analyses were withdrawn 1, 6, 15 min after addition of the ethyl-Grignard. After the 15 min sample was withdrawn, the reaction was allowed to warm to room temperature and wherever necessary 1 h and 24 h samples were then removed. The samples were hydrolyzed with dil. HCl and extracted with diethyl ether. All the products were characterized by VPC retention time with calibrated known samples.

In the case of the reactions between ethyl Grignard and the pentafluorobenzene, the extent of Grignard formation was determined by derivatizing the VPC aliquot samples with $C_6H_5Si(CH_3)_2Cl$ and determining by VPC analysis the amount of $C_6H_5Si(CH_3)_2C_6F_5$ formed[3].

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