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ANOMALOUS REACTIONS OF ORGANOMAGNESIUM REAGENTS WITH PERFLUOROAROMATIC COMPOUNDS*

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SUMMARY

An investigation of the reactions of some perfluoroaromatic compounds with organomagnesium compounds has been made. It was found that the expected substitution products arising from simple nucleophilic reaction between a perfluoroaromatic and an organomagnesium compounds are not the only products formed during these reactions. The anomalous products formed apparently resulted from an intermediate metallation reaction. Decafluorobiphenyl (x moles) when allowed to react with ethylmagnesium bromide ($4x$ moles) afforded the expected 4-ethylnonafluorobiphenyl and 4,4′-diethyloctafluorobiphenyl and the anomalous 4-hydrononafluorobiphenyl, 4,4′-dihydrooctafluorobiphenyl and 4-ethyl-4′-H-octafluorobiphenyl. It has been shown that the intermediate organomagnesium compounds formed can be derivatized with trimethylchlorosilane to yield perfluoroaryltrimethylsilanes. The effect of changing stoichiometry of reactants on product distribution is discussed.

Perfluoroaromatic compounds are known to undergo ring fluorine substitution when allowed to react with a variety of nucleophiles (*e.g.*, CH_3ONa[1], RLi[2], C_6F_5ONa[3], C_6F_5SK[4], NH_3[5], RNH_2[5], etc.).

$$Ar_F + Nu^- \rightarrow Ar_FNu + F^- \qquad (1)$$

Appropriate ring substituents may compete to exclude the products of nucleophilic substitution. For example, organolithium and organomagnesium compounds react with bromopentafluorobenzene[6,7] and pentafluorobenzene[8] to produce the corresponding (pentafluorophenyl)organometallic compound. With the former, this occurs through a halogen–metal interconversion and with the latter, through a hydrogen–metal interconversion.

We have recently reported[7] an exception to the nucleophilic reaction of an organomagnesium compound with hexafluorobenzene (I). When diethylmagnesium (x moles) was allowed to react with hexafluorobenzene (x moles) in a tetrahydrofuran medium at room temperature, in addition to the expected alkylated product ethyl-

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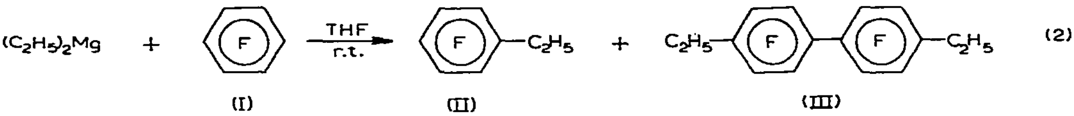
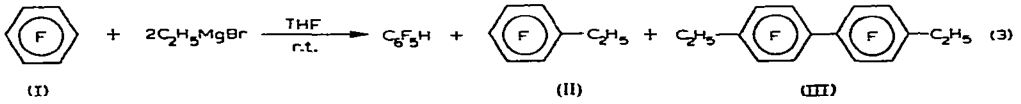
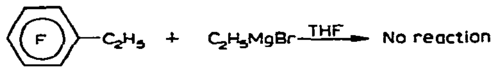
pentafluorobenzene (II), an appreciable yield of 4,4'-diethyloctafluorobiphenyl (III) (24%) was obtained.



To our knowledge, this was the second example of a perfluoroaromatic compound undergoing two different types of reactions with one nucleophilic reagent[8]. To explain the products of the reaction, we therefore suggested that besides the normal expected alkylated product (due to nucleophilic reaction) an intermediate pentafluorophenylmagnesium compound resulting from metalation of hexafluorobenzene (I) may have been formed. Such an intermediate organometallic compound could react further with the hexafluorobenzene (I) to produce decafluorobiphenyl (V). Subsequent reactions with the diethylmagnesium could account for the alkylated product observed. We now wish to report our further observations on the above mentioned anomaly.

A reexamination of the room temperature reaction of ethylmagnesium bromide with hexafluorobenzene (I)[8] in THF produced the expected normal product, ethylpentafluorobenzene (II) (73%), and the anomalous 4,4'-diethyloctafluorobiphenyl (III) (10%). Pentafluorobenzene, as previously reported[8], also was observed. Ethylpentafluorobenzene (II) failed to undergo any reaction with ethylmagnesium bromide thus indicating that it is not an intermediate in the formation of the anomalous product, 4,4'-diethyloctafluorobiphenyl (III).





If diethyl ether, rather than tetrahydrofuran, is used as the solvent, no apparent reaction occurs between ethylmagnesium bromide and hexafluorobenzene (I) within 24 h. However, in 1,2-dimethoxyethane (DME), the reaction between ethylmagnesium bromide* and (I) is nearly 90% complete (based on unreacted hexafluorobenzene) within 30 min at room temperature. The anomalous product, 4,4'-diethyloctafluorobiphenyl (III) is formed in only 6% yield and its yield does not increase with longer reaction time. Ethylpentafluorobenzene (II), formed initially as the major product in DME, is, however, slowly consumed to produce 1,4-diethyltetrafluorobenzene (IV). This substantiates our suggestion made above that ethylpentafluorobenzene (II) is not a precursor to (III).

We have previously shown[3] that decafluorobiphenyl is a more reactive substrate towards nucleophiles than hexafluorobenzene. In our present study, the reaction

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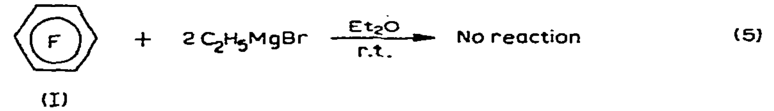
* A solution of C_2H_5MgBr prepared in dimethoxyethane was found to contain only 30% of the calculated amount of Br^- ion. See *experimental* section for details.



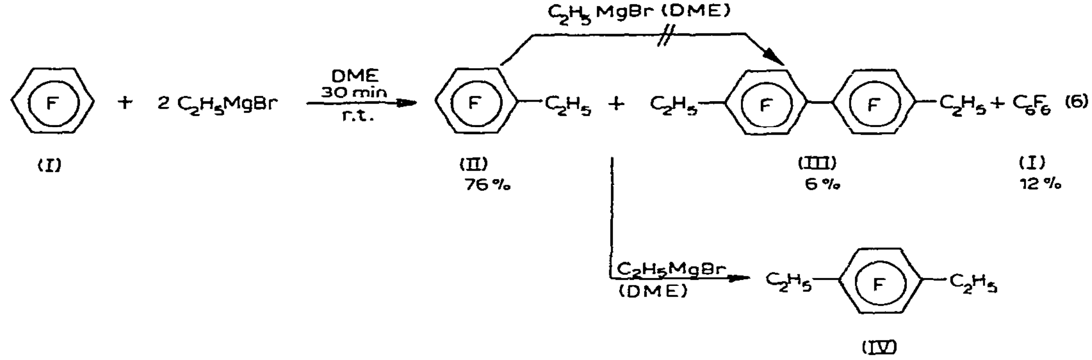
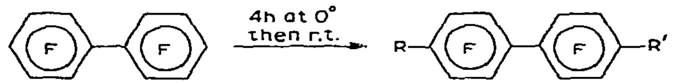


TABLE 1

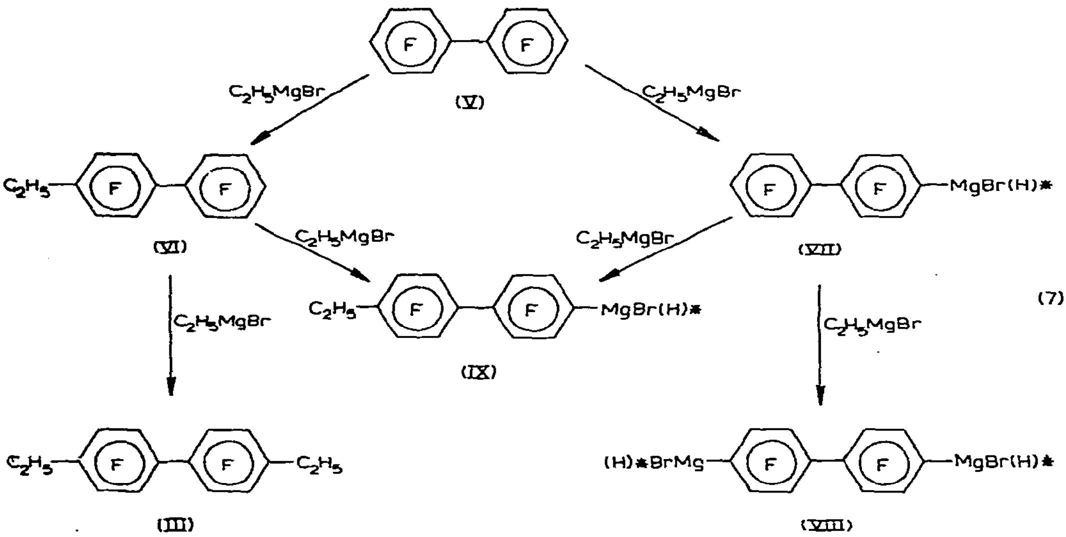
RESULTS OF THE REACTION: C_2H_5MgX +



C_2H_5MgX (moles)	X	$C_{12}F_{10}$ (moles)	Solv.	React. time (h)	Yields (%)					
					R = F R' = F	R = F R' = H	R = H R' = H	R = F R' = Et	R = H R' = Et	R = Et R' = Et
0.050	Br	0.0125	THF	0.5	28	9	0	56	0	9
				4	0	14	0	22	25	41
				24	0	0	10	0	45	45
0.025	Br	0.0125	THF	0.5	51	5	0	42	0	2
				4[c]	4	5	0	54	3	22
				24[c]	0	0	0	20	3	29
0.050[a]	Br	0.0125	THF	24[c]	0	0	3	0	37	47
0.025	C_2H_5	0.0125	THF	0.5	10	9	0	58	5	14
				4[c]	0	6	3	0	40	32
				24[c]	0	0	6	0	40	32
0.050	Br	0.0125	Et_2O	24	85	0	0	17	0	0
				48	76	0	0	27	0	0
				240	44	0	0	53	0	4
0.050	Br	0.0125	DME[b]	0.5[c]	0	0	0	0	13	80

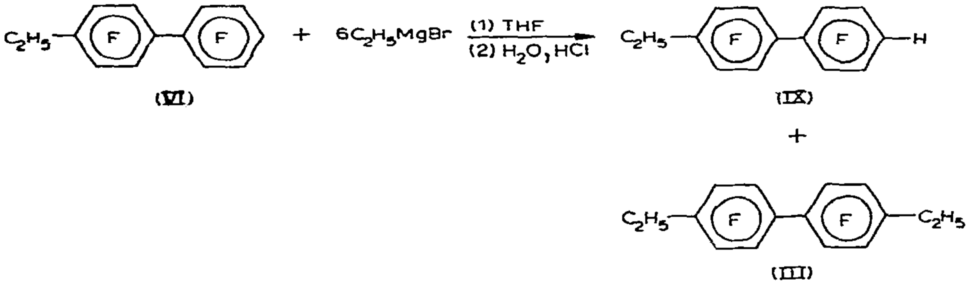
[a] Prepared from triple sublimed magnesium. [b] Entire reaction run at room temperature. [c] Insoluble material obtained.

between decafluorobiphenyl (V) and ethylmagnesium bromide in tetrahydrofuran yielded a complex mixture of products (see Table 1). The composition of the reaction mixture varied with the stoichiometry of the reactants. Thus when ethylmagnesium bromide (4*x* moles) was allowed to react with decafluorobiphenyl (V) (*x* moles) in tetrahydrofuran, a nearly quantitative yield of a mixture of compounds was obtained. Besides the normal alkylation products, reduction products where fluorine was substituted by hydrogen, were observed. The possible competing reactions are summarized as follows:



(7)

By comparing product ratios (Table 1) at different reaction times, it can be seen that alkylation to produce 4-ethylnonafluorobiphenyl (VI) and 4,4′-diethyloctafluorobiphenyl (III) predominated in the early stages of reaction. Reduction products leading to the 4-hydrononafluorobiphenyl (VII), 4,4′-dihydrooctafluorobiphenyl (VIII) and 4-ethyl-4′-hydrooctafluorobiphenyl (IX) appeared during the later stages of the reaction once the alkylated products were formed. In order to gain further insight into the reaction scheme, 4-ethylnonafluorobiphenyl (VI) (x moles) was allowed to react with an excess of ethylmagnesium bromide ($6x$ moles). The reaction was complete within 4 h and produced a surprisingly high yield (83–96%) of the reduction product 4-ethyl-4′-hydrooctafluorobiphenyl (IX). Only 5–13% alkylation occurred to produce the 4,4′-diethyloctafluorobiphenyl (III).



(8)

In order to show that the reduction proceeded through an organometallic intermediate, as suggested in eqn. 7, the reaction mixture was treated with trimethyl-

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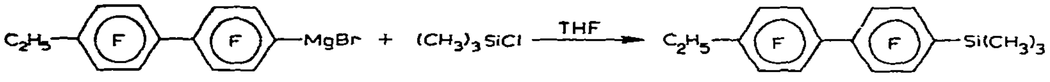
* After hydrolysis.

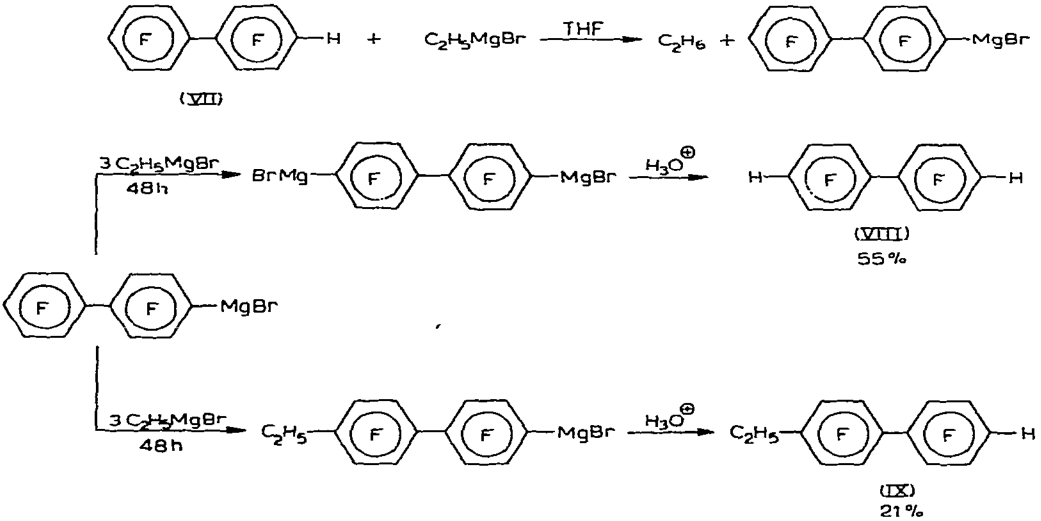
chlorosilane. Subsequent work up yielded the expected product, 4-ethyl-4'-(trimethylsilyl)octafluorobiphenyl (X):



(X)

(9)

A similar reduction of 4-hydrononafluorobiphenyl (VII) by ethylmagnesium bromide occurred. Thus after 48 h, the reaction between 4-hydrononafluorobiphenyl (VII) (*x* mole) and ethylmagnesium bromide (4*x* moles) produced a 55% yield of 4,4'-dihydrooctafluorobiphenyl (VIII), 21% of 4-ethyl-4'-hydrooctafluorobiphenyl (IX) and 9% unreacted starting material (VII).



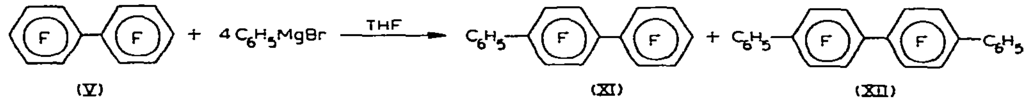
(10)

It can also be seen from Table 1, that the reaction products from decafluorobiphenyl and ethylmagnesium bromide made from either triply sublimed magnesium or ordinary Grignard grade magnesium were similar. Thus it appears unlikely that catalysis by impurities present in the magnesium are responsible for the reduction process.

The effect of stoichiometry can also be seen from Table 1. Reaction between ethylmagnesium bromide (2*x* moles) and decafluorobiphenyl (V) (*x* moles) produced approximately 50% yield of the ethylated products, 4-ethylnonafluorobiphenyl (VI) and 4,4'-diethyloctafluorobiphenyl (III) after 24 h. However, in addition to these products, there was a substantial amount of insoluble material produced. The infrared spectrum and wide melting point range (softens 265, melts 330°) suggested a mixture of alkylated perfluoropolyphenylenes (quarterphenyls or higher).

Table 1 also indicates that substituting diethylmagnesium for ethylmagnesium bromide does not appreciably alter the composition of the reaction products.

In an attempt to improve the yield of reduction products, by minimizing those of substitution, we have examined the reactions between decafluorobiphenyl and a series of organomagnesium compounds of varying structure and reactivity. Isopropylmagnesium bromide is known to be a poorer nucleophile than is ethylmagnesium bromide for reasons of steric hindrance. Use of such a reagent should minimize alkylation and hopefully increase reduction. However, the reaction between decafluorobiphenyl (V) and isopropylmagnesium bromide yielded a complex reaction mixture. Partial analysis by a combination of vapor phase chromatography and mass spectroscopy suggested the presence of alkylated products, reduced products and higher molecular weight polyphenylenes. No yield of reduction products could be determined from such a complex mixture. The reaction between phenylmagnesium chloride (or bromide) and decafluorobiphenyl (V) yielded only the substitution products 4-phenylnonafluorobiphenyl (XI) and 4,4'-diphenyloctafluorobiphenyl (XII). The reaction was very slow at room temperature as indicated by the fact that only 62% of the decafluorobiphenyl was consumed in 4 days. Finally, the reaction between methylmagnesium chloride and decafluorobiphenyl yielded 4-methylnonafluorobiphenyl (XIV), 4,4'-dimethyloctafluorobiphenyl (XV) and an unexpected product* bis(nonafluoro-4-biphenylyl)methane (XVI). No reduction products were detected. The latter compound XVI is believed to have been formed by the metalation of the monosubstituted product XIV by methylmagnesium chloride followed by subsequent reaction with decafluorobiphenyl.



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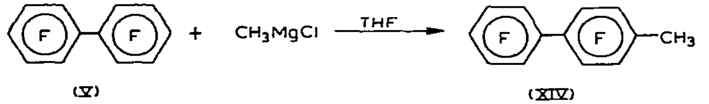

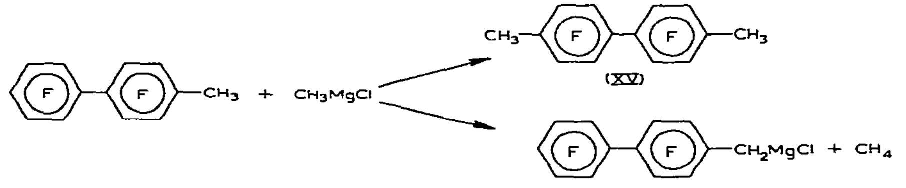

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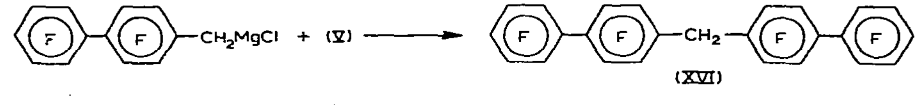

The above results indicate that the type of Grignard reagent has a definite effect on the yield of reduction products. Thus far, our studies indicate that ethylmagnesium bromide produces the highest yields of reduction products.

In an attempt to determine the origin of these anomalous reduction products, we have examined the reaction between ethylmagnesium bromide (6x moles) and 4-ethylnonafluorobiphenyl (VI) in more detail. We have previously mentioned that this compound (VI), produced the highest yield of the reduction product 4-ethyl-4'-

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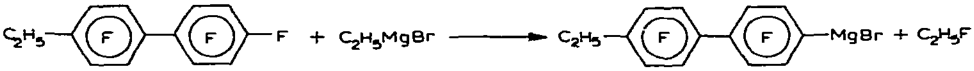
* More detailed information on this type of reaction will be presented at a later date.

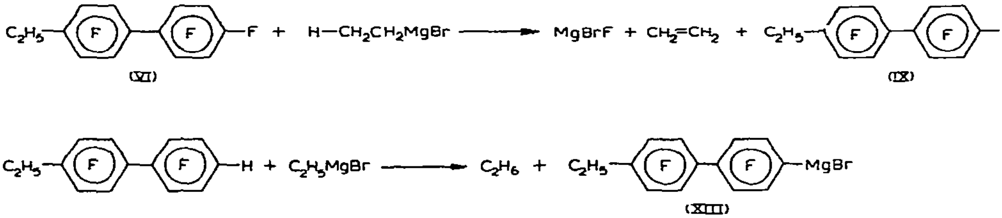
hydrooctafluorobiphenyl (IX) (83–96%). If in this reaction metalation occurred by a halogen–metal interchange, then ethyl fluoride would be one of the products.



(XI)

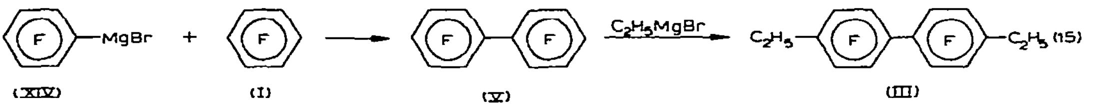
(13)

Analysis by mass spectroscopy of the evolved gases indicated the absence of ethyl fluoride but did show the presence of ethane and ethylene in nearly equal amounts as well as a trace of butane*. This led us to consider the possibility of reduction of the carbon–fluorine bond by hydride transfer from the β-carbon of ethylmagnesium bromide followed by the loss of fluoride ion. A mole of ethylene is produced in this manner. Reductions of carbonyl compounds by this type mechanism are well known[9]. In the presence of excess Grignard reagent, the acidic hydrogen is abstracted forming ethane and the organomagnesium reagent (XIII). Hydrolysis of (XIII) would lead to the observed 4-ethyl-4-hydrooctafluorobiphenyl (IX).



This mechanism could conveniently account for the absence of anomalous products in the reaction with phenylmagnesium halides and methylmagnesium chloride which do not possess a β sp^3 hydrogen attached to an sp^3 carbon atom.

In the case of hexafluorobenzene (I) and ethylmagnesium bromide, the organometallic intermediate (XIV), whose existence is indicated by the presence of pentafluorobenzene[8], could react further with starting material to produce decafluorobiphenyl (V) which is then alkylated to form the observed 4,4′-diethyloctafluorobiphenyl (III).



As an alternative to the hydride transfer mechanism, we have considered, after taking note of the highly colored nature of these solutions (deep blue to purple), the possibility of an electron transfer mechanism**. Such a transfer (or transfers) of an electron from the Grignard reagent to the perfluoroaromatic substrate would result in a radical anion or a dianion. Loss of fluoride (in the case of the dianion) would lead

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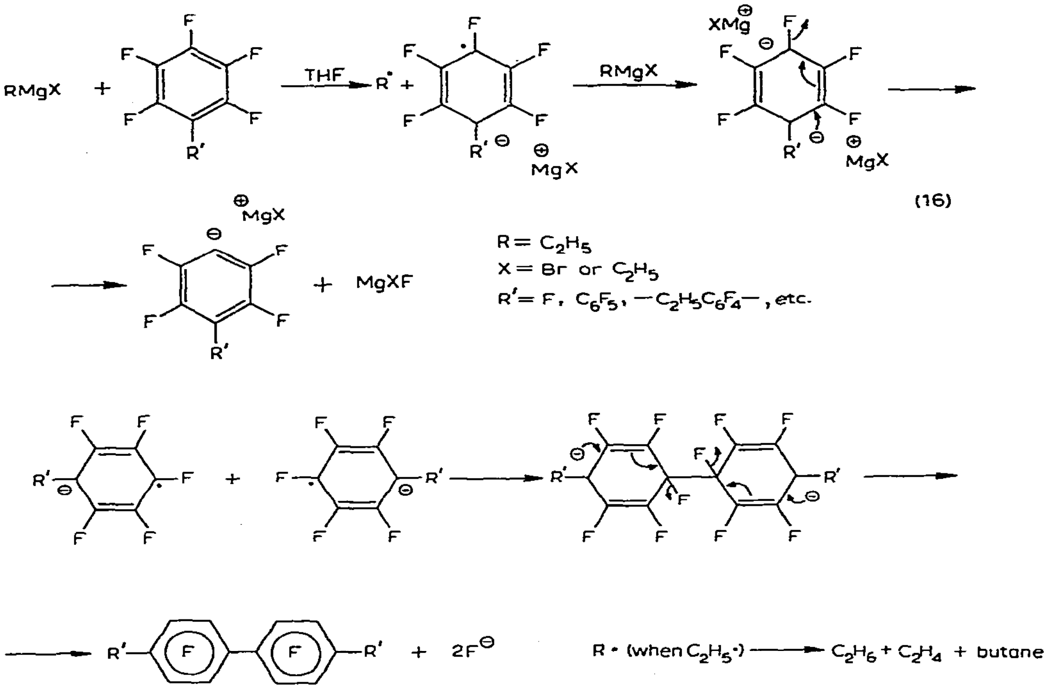
* The butane observed by mass spectroscopy could have arisen during the synthesis of ethylmagnesium bromide by Wurtz coupling of the Grignard reagent with unreacted ethyl bromide. Examination by mass spectroscopy of a simulated reaction (no perfluoroaromatic substrate) of ethylmagnesium bromide showed only a small amount of ethane. No butane could be detected.

** The ability of Grignard reagent to act as electron donor to aromatic systems has been previously noted[10,11].

to a simple perfluoroaromatic anion. In the case of ethylmagnesium bromide, the radical fragment could disproportionate to ethane and ethylene or couple to form butane. Higher molecular weight polyphenylenes could arise from the radical anion dimerization followed by loss of fluoride ion as shown.



(16)

These highly colored organometallic solutions have been investigated by electron spin resonance techniques in an attempt to observe the presence of radical anions. Positive results have not been obtained as yet.

The inconclusive results have not allowed us to exclude either of these mechanisms in the case of reactions of ethylmagnesium bromide with perfluoroaromatic substrates. We are, however, currently carrying out further investigations which, it is hoped, will allow such distinctions to be made.

Thus far, we have demonstrated that under certain conditions, perfluoroaromatic compounds can undergo metalation by certain Grignard reagents to yield as intermediates, organomagnesium species capable of further reactions. It is conceivable that under the proper conditions the concurrent alkylation of the fluoroaromatic may be minimized. If such is the case, then reduction of perfluorinated aromatics by certain Grignards may provide a synthesis procedure for producing useful perfluoroarylmagnesium intermediates directly from the more readily available perfluoroaromatic compounds.

EXPERIMENTAL

All organometallic preparations were carried out under an atmosphere of oxygen-free nitrogen. Tetrahydrofuran (THF) was freshly distilled from calcium hydride prior to use. 1,2-Dimethoxyethane (DME) was freshly distilled from lithium aluminum hydride. Nuclear magnetic resonance spectra were obtained using a Varian A56-60 spectrometer. Chemical shifts are reported in ppm from fluorotrichloromethane or tetramethylsilane as internal standards.

VPC analyses were carried out on an F and M Model 810 or F and M Model 700 Gas Chromatograph using an 11 ft. 15% polyphenylether on Chromosorb P for reactions with hexafluorobenzene and a 6 ft. 10% Apiezon L on Chromosorb W for reactions with decafluorobiphenyl.

Preparation of organometallic reagents

Ethylmagnesium bromide was prepared from Grignard grade magnesium and ethyl bromide in THF and DME solutions. Preparation in DME was accompanied by copious precipitate formation. When an aliquot of the supernatant (total base concentration 1.35 *N*) was hydrolyzed in standard hydrochloric acid and then titrated with standard silver nitrate solution, using potassium chromate as an indicator, the concentration of bromide ion (total halide less standard HCl) was found to be 0.37 *N*. The precipitate is evidently an etherate of magnesium bromide.

Phenylmagnesium bromide and isopropylmagnesium bromide were prepared in THF from Grignard grade magnesium and bromobenzene and 2-bromopropane, respectively.

Diethylmagnesium was prepared from diethylmercury and magnesium turnings in THF solution.

The concentration of these solutions were determined by the technique described by Watson and Eastham[10]. However, a slight modification of the technique was required for THF solutions. Titration by a xylene solution of sec-butyl alcohol led to gelatinous precipitates which failed to give reproducible end points. If, however, anhydrous diethyl ether was added to the THF solution before titration, the precipitate formed was granular and did not appear to effect end point determination*.

Reaction of ethylmagnesium bromide in tetrahydrofuran with hexafluorobenzene (I)

Ethylmagnesium bromide (33 ml of a THF solution containing 0.050 mole) was added rapidly at room temperature to a mixture of hexafluorobenzene (I) (4.657 g, 0.025 mole) and ethylbenzene (1.621 g, as internal standard). After 24 h, an aliquot was withdrawn, hydrolyzed in aqueous hydrochloric acid, extracted with pentane and analyzed by VPC. Analysis indicated the presence of hexafluorobenzene (I) (19%), pentafluorobenzene (6%) and ethylpentafluorobenzene (69%). Another reaction using hexafluorobenzene (I) (4.649 g, 0.050 mole) and ethylmagnesium bromide (0.050 mole), after 7 days, showed the presence of ethylpentafluorobenzene[8] (II) (73%) and 4,4'-diethyloctafluorobiphenyl (III) (10%); m.p. 60–61°. (Found: C, 54.00; H, 2.81; mol.wt. by high resolution mass spectroscopy, 354. $C_{16}H_{10}F_8$ calcd.: C, 54.25; H, 2.85%; mol.wt., 354.)

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* Even this modification failed for solutions of diethylmagnesium, methylmagnesium chloride and phenylmagnesium chloride. The concentration of these reagents was determined by the method of House and Respess[12].

Reaction of ethylpentafluorobenzene (II) with ethylmagnesium bromide in tetrahydrofuran

Ethylmagnesium bromide (17 ml of a tetrahydrofuran solution containing 0.027 mole) was added at room temperature over 2–3 min to a solution of ethylpentafluorobenzene (II) (4.909 g, 0.025 mole) and ethylbenzene (2.159 g as internal standard) dissolved in THF (10 ml). After 48 h, analysis of an aliquot by VPC did not show the presence of 4,4′-diethyloctafluorobiphenyl (III). A small peak was observed and presumed to be (by retention time) 1,4-diethyltetrafluorobenzene.

Reaction of ethylmagnesium bromide in diethyl ether with hexafluorobenzene (I)

Ethylmagnesium bromide (35 ml of diethyl ether solution containing 0.050 mole) was added at room temperature to a solution of hexafluorobenzene (I) (9.292 g, 0.050 mole) and ethylbenzene (4.853 g, as internal standard) in diethyl ether (5 ml). Analysis by VPC of an aliquot taken after 24 h indicated no reaction had occurred.

Reaction of ethylmagnesium bromide in dimethoxyethane with hexafluorobenzene (I)

Ethylmagnesium bromide (40 ml of a DME solution containing 0.050 mole) was added at room temperature over a 10-min period to hexafluorobenzene (I) (4.65 g, 0.025 mole) and ethylbenzene (1.81 g as internal standard) in DME (10 ml). The reaction was slightly exothermic, the temperature reaching 50°. After 30 min, VPC analysis of an aliquot showed the presence of 4,4′-diethyloctafluorobiphenyl (III) (6%), ethylpentafluorobenzene (II) (76%) and hexafluorobenzene (I) (12%). On longer reaction time, the hexafluorobenzene (I) was consumed (0%, after 24 h) and ethylpentafluorobenzene (II) reacted further to form diethyltetrafluorobenzene (IV). (Found: C, 58.62; H, 5.12; mol.wt. by high resolution mass spectroscopy, 206. $C_{10}H_{10}F_4$ calcd.: C, 58.25; H, 4.89%; mol.wt., 206.) The ^{19}F NMR spectrum exhibited only one type of fluorine at 164 ppm ($CFCl_3$ internal standard). We presume the orientation to be *para* based on NMR analysis and considerable literature precedence for the preference of *para* attack by nucleophiles on monosubstituted pentafluorobenzenes. Longer reaction time did not increase the yield of 4,4′-diethyloctafluorobiphenyl (III).

General procedure for reaction of ethylmagnesium compounds with decafluorobiphenyl (V)

A solution of the ethylmagnesium compound was added to a solution (in the same solvent as the organometallic reagent) of decafluorobiphenyl (V) and ethylbenzene (used as an internal standard) which had been cooled in an ice water bath. Sufficient solvent was used in dissolving standard and decafluorobiphenyl (V) to make the total volume of reaction 50 ml. After 4 h, the ice water bath was removed and for the remaining time, the reaction proceeded at room temperature. Aliquots were taken periodically, hydrolyzed in aqueous hydrochloric acid, and extracted with pentane. In all cases, the solutions developed deep bluish-purple colors. Experimental results are presented in Table 1.

Reaction of ethylmagnesium bromide with 4-ethylnonafluorobiphenyl (VI)

4-Ethylnonafluorobiphenyl* (VI) (1.04 g, 0.003 mole) and ethylbenzene

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* Unpublished studies, C. Tamborski and E. J. Soloski; prepared through the reaction between ethylmagnesium bromide and decafluorobiphenyl; m.p. 56–57°.

(0.515 g as internal standard) in THF (6 ml) was added over a period of 5 min to an ice cooled solution of ethylmagnesium bromide (12 ml of a THF solution, 0.017 mole). The reaction mixture turned a deep purple. VPC analysis of a hydrolyzed aliquot sample taken 4 h after addition showed the presence of 4-ethyl-4'-hydrooctafluorobiphenyl (IX), 84%, (Found: C, 51.74; H, 1.89; mol.wt. by high resolution mass spectroscopy, 326. $C_{14}H_6F_8$ calcd.: C, 51.55; H, 1.85%; mol.wt., 326.) and 4,4'-diethyloctafluorobiphenyl (III), 13%.

The reaction was repeated using ethylmagnesium bromide (12 ml of a THF solution containing 0.017 mole) and a THF solution of 4-ethylnonafluorobiphenyl (VI) (1.04 g, 0.003 mole) and ethylbenzene (0.712 g, as internal standard). A small gas trap was attached to the nitrogen exit line to allow sampling of effluent gases. After 4 h the gas trap was removed and analyzed by mass spectroscopy. In addition, an aliquot sample was removed from the reaction mixture and analyzed by VPC. This analysis indicated the presence of 4-ethyl-4'-hydrooctafluorobiphenyl (IX, 96%) and 4,4'-diethyloctafluorobiphenyl (III, 5%). Trimethylchlorosilane (2.20 g, 0.041 mole) was then added in THF (10 ml) and the reaction was allowed to warm to room temperature. After 16 h, the entire reaction was hydrolyzed with 4 *N* HCl and extracted with pentane. Analysis by VPC indicated the presence of a new component identified as 4-ethyl-4'-(trimethylsilyl)octafluorobiphenyl (X). No 4-ethyl-4'-hydrooctafluorobiphenyl (IX) remained. A sample of (X) was collected by VPC, mass spectrometer analysis measured *m/e* 398, calculated 398. The ^{1}H NMR spectrum exhibited a triplet at 0.29 ppm [J(H–o-F) 2 Hz] for $Si(CH_3)_3$, a triplet at 0.81 ppm (J 7 Hz) and a broad quartet at 1.73 ppm (for CH_3CH_2). The ^{19}F NMR showed multiplets at 128 ppm [o-F to $Si(CH_3)_3$], 140 ppm, and 146 ppm (o-F to CH_3CH_2).

The contents of the gas trap were analyzed by mass spectroscopy and indicated nitrogen, THF, ethane (11%), ethylene (8%) and butane ($<$ 1%). A blank analysis of the Grignard solution itself showed only the presence of a trace of ethane presumably from hydrolysis.

Reaction of 4-hydrononafluorobiphenyl (VII) with ethylmagnesium bromide

A THF solution (12 ml) containing 4-hydrononafluorobiphenyl[13] (VII) (3.163 g, 0.01 mole) and ethylbenzene (1.300 g as internal standard) was added over a 5 min period to ethylmagnesium bromide (28 ml of a THF solution containing 0.040 mole) which had been cooled by an ice-water bath. A deep purple color developed during the reaction. VPC analysis of an aliquot taken after 48 h showed the presence of 4-hydrononafluorobiphenyl (VII) (9%), 4,4'-dihydrooctafluorobiphenyl (VIII) (55%), 4-ethyl-4'-hydrooctafluorobiphenyl (IX) (21%), and a small amount of solid material (insoluble in THF) which was not further characterized.

Reaction of decafluorobiphenyl (V) with methylmagnesium chloride

Methylmagnesium chloride (19 ml of a THF solution containing 0.051 mole) was added over a 20-min period to a THF solution (31 ml) of decafluorobiphenyl (V) (4.18 g, 0.0125 mole) and ethylbenzene (1.68 g as internal standard) that had been previously cooled by an ice-water bath. A deep red color developed. After 4 h, the ice-water bath was removed. An aliquot was removed after 24 h and analyzed by VPC following hydrolysis with 4 *N* HCl. Only 2% decafluorobiphenyl (V) remained. Three major products were detected. Samples of each were collected from the same reaction run on a larger scale. The first product eluted was 4-methylnonafluorobiphenyl (XIV); m.p. 88–91°; mol.wt. by mass spectroscopy 330, calcd. 330. Its ^1H and ^{19}F NMR were the same as that of an authentic sample (see next experiment). The second product eluted was 4,4'-dimethyloctafluorobiphenyl (XV); m.p. 145–147°; mol.wt. by mass spectroscopy 326, calcd. 326. Its ^1H and ^{19}F NMR were the same as that of an authentic sample. The third product eluted is thought to be bis(nonafluoro-4-biphenylyl)-methane (XVI); m.p., 185–187°; mol.wt. by mass spectroscopy 644, calcd. 644. Its ^{19}F NMR exhibited fluorine resonances at 161.0 (multiplet), 150.3 (triplet), 141.0 (multiplet) and 137.7 (multiplet). Its ^1H NMR exhibited at 6.58 ppm a singlet resonance. Both the ^1H and ^{19}F NMR are consistent with the proposed structure.

The preparation of 4-*methylnonafluorobiphenyl* (*XIV*)

A solution of 4-hydrononafluorobiphenyl (15.80 g, 0.050 mole) in diethyl ether (150 ml) was cooled to −76°. Methyllithium (42 ml of a diethyl ether solution containing 0.050 mole) was added to form 4-lithiononafluorobiphenyl[8]. To this solution was added methyl iodide (10.73 g, 0.076 mole) in diethyl ether (50 ml). Analysis, by VPC, of an aliquot taken after 2 h indicated no reaction had occurred. At this point, THF (50 ml) was added and the reaction mixture allowed to warm slowly to room temperature. The entire reaction mixture was treated with 4 *N* HCl and extracted with diethyl ether. After drying ($MgSO_4$) and removal of solvent, a brown solid was obtained. This material was sublimed (70°/0.02 mm) to give a white solid. VPC analysis showed the presence of unreacted starting material ($\sim$10%) and one other product. Isolation (by preparative VPC) of this product afforded a white solid (m.p. 88–90°), 4-methylnonafluorobiphenyl (XIV). (Found: C, 47.30; H, 0.95. $C_{13}H_3F_9$ calcd.: C, 47.29; H, 0.92%.) Its ^{19}F NMR exhibited fluorine resonances at 162.4 (multiplet), 151.6 (triplet with further splitting), 142.8 (multiplet), 140.7 (multiplet) and 138.4 ppm (multiplet). Its ^1H NMR exhibited a triplet at 2.40 ppm [*J*(H–*o*-F) 2 Hz].

The preparation of 4,4'-*dimethyloctafluorobiphenyl* (*XV*)

Methyllithium (85 ml of a diethyl ether solution containing 0.102 mole) was added to a cold (0°) solution of decafluorobiphenyl (16.70 g, 0.050 mole) in diethyl ether (30 ml). After 30 min the ice-water bath was removed and the reaction stirred at room temperature for 3 h. At this time, the entire reaction mixture was hydrolyzed with 4 *N* HCl and extracted with diethyl ether. The extracts were dried ($MgSO_4$) and the solvent removed to give a brown solid. Sublimation of this material (90°/0.03 mm) yielded a white solid. Recrystallization from petroleum ether yielded 4,4'-dimethyloctafluorobiphenyl (XV); m.p. 145–147°. (Found: C, 51.65; H, 1.92. $C_{14}H_6F_8$ calcd.: C, 51.55; H, 1.85%.) Its ^{19}F NMR exhibited fluorine resonance at 143.4 (multiplet) and 140.6 ppm (multiplet). Its ^1H NMR exhibited a triplet at 2.38 ppm [*J*(H–*o*-F) 2 Hz].

Reaction of phenylmagnesium bromide and chloride with decafluorobiphenyl (*V*)

Phenylmagnesium bromide (35 ml of a THF solution containing 0.050 mole) was added over a 15-min period to a THF solution (15 ml) of decafluorobiphenyl (V) (4.187 g, 0.0125 mole) and ethylbenzene (1.938 g, as internal standard) that has been previously cooled in an ice-water bath. After 4 h, the ice-water bath was removed. An aliquot sample taken after 4 days, hydrolyzed in 4 *N* HCl, and analyzed by VPC showed the presence of decafluorobiphenyl (V) (38%) and one other component.

THF-insoluble material was also observed. A similar result was obtained with phenylmagnesium chloride and decafluorobiphenyl. The component detectable by VPC, was isolated; m.p. 200–201°. (Found: C, 55.14; H, 1.38; mol.wt. by mass spectroscopy, 392. $C_{18}H_5F_9$ calcd.: C, 55.12; H, 1.28; mol.wt., 392.) This corresponds to 4-phenylnonafluorobiphenyl (XI). The THF insoluble material was recrystallized from hot benzene to yield 4,4'-diphenyloctafluorobiphenyl (XII); m.p. 279–281°, calcd. 450. (Found: C, 63.92; H, 2.28; mol.wt. by high resolution mass spectroscopy, 450. $C_{24}H_{10}F_8$ calcd.: C, 64.01; H, 2.24%; mol.wt., 450.) Its ^{19}F NMR (in hot benzene) exhibited fluorine resonances at 143 (multiplet) and 1.39 ppm (multiplet). Its ^1H NMR exhibited a singlet resonance at 7.19 ppm.

Reaction of isopropylmagnesium bromide with decafluorobiphenyl (V)

Isopropylmagnesium bromide (60 ml of a THF solution containing 0.049 mole) was added over a 10-min period to a THF solution (10 ml) of decafluorobiphenyl (V) (4.190 g, 0.0125 mole) and ethylbenzene (1.568 g, as internal standard) that had been previously cooled in an ice-water bath. After 4 h, the ice-water bath was removed. A pale orange coloration developed slowly. After 3 days, an aliquot was removed, hydrolyzed in 4 *N* HCl and analyzed by VPC. Analysis showed the presence of decafluorobiphenyl (V) (43%) and a complex mixture of products. One of these products was 4-hydrononafluorobiphenyl (VII) (6%) by VPC retention time. Another component, isolated by VPC, was analyzed by a mass spectrometer, measured *m/e* 630, calculated for perfluoroquaterphenyl 630. Its VPC retention time was also identical to perfluoroquaterphenyl.

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