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# SYNTHESIS OF SOME PERFLUORO-ORGANOMETALLIC TYPES [$R_f$—M]

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## Contents

## 1. Introduction

Perfluoroorganometallic compounds are useful and interesting for many applications and varied purposes.

Our special interest in organic compounds containing a metal and a plurality of fluorine atoms goes back a few decades. At that time we were exploring synthetic procedures for the preparation of compounds of uranium suitable for isotope separation [1]. Later developments were concerned with the extension of procedures for the preparation of some perfluoro-organometallic types. These involved $R_f$—M species in which R was alkyl or aryl, and M was MgX, Li, Cu (as well as some other metals, and metalloids such as Si). The search here is for improved routes to $R_f$—M compounds for synthesis of transition metal complexes; for phosphorus and bismuth types; for highly thermally stable species; and for catalysts and polymers.

## 2. Perfluoroalkyl-organometallic compounds

### *(a) $R_f$—MgX and $R_f$—Li*

Over the years there have appeared in the literature numerous reports dealing with splendid developments on the preparation and synthetic applications of perfluoroalkyl Grignard [2-20] and $R_f$—Li [21-31] reagents. As an evidence of the uncommonly large number of methods (general and special) for the preparation of most types of organometallic compounds up to 1954 see a review published about two decades ago [32].

The literature coverage here with the $R_f$—M species can only be token in nature. Additional references are to be found in components of ref. 10; and, particularly, in some of the books and reviews listed at the end of the concluding section of references.

Aided by the significant studies of many, over a long period, we have helped to improve techniques for the preparation of $R_fM$ species by employing the somewhat standard procedure of the halogen—metal exchange [33]. Another route is novel and relatively recent in development. This grew out of our earlier work on the cleavage of the C—$SiMe_2H$ unit by R—M compounds to convert a series of perhaloaryldimethylhydrosilanes to the corresponding perhaloaryl—MgX and, particularly, the perhaloaryl—lithium [8] compounds.

#### *(1) Halogen—metal exchange*

A generalized reaction is:

$$R_f\text{—I} + \text{RMgX} \rightarrow R_f\text{—MgX} + \text{RI}$$

The yields of $R_f$—MgX are essentially quantitative with either EtMgBr or PhMgBr, and many other hydrocarbon Grignard reagents may be used with nearly equal success. However, the reaction can be significantly affected by experimental conditions. For example, the quality of the $C_8F_{17}I$ was found to have a pronounced effect. Using $C_8F_{17}I$, which had not been distilled recently (the material contained dissolved iodine as evidenced by the violet color) the yield was 64-66% (using a 10% excess of EtMgBr). When freshly distilled and colorless $C_8F_{17}I$ was used, the yield rose to 94-100% [10].

The nature of X in $R_f$—X can be quite important; and the general order of effectiveness is $R_fI > R_fBr \gg R_fCl$. Hitherto the iodides have been generally used, and there appears to be no report of an exchange of a perfluoroalkyl chloride to the corresponding Grignard reagent. Our actual chlorine—MgBr exchange in one reaction was merely 4.5%. In a generalized reaction, a 10% excess of EtMgBr is used, and the reaction is completed in less than 30 minutes at —78°, with THF as the solvent. In our preliminary work [10] we observed that

$Et_2O$ was an extremely poor solvent, when $ClSiMe_3$ was a characterizing, yield-measuring compound, because of the essential absence of reaction between $R_f$—MgX with $ClSiMe_3$.

*(2) Cleavage of C—SiMe₂H by R—M*

The general reaction for this novel and effective procedure is:

$$R_fSiMe_2H + RMgX \text{ (or RLi)} \rightarrow R_f\text{—MgX (or —Li)} + RSiMe_2H$$

The EtMgBr and n-BuMgBr reactions used to prepare the $R_fMgX$ were carried out in THF. Cleavage is very poor in $Et_2O$; and an 80/20 THF/HMPA mixture is a superior solvent for the cleavage. The yield was improved with a moderate excess of the cleaving RM reagent, and this may possibly be associated with an equilibrium reaction.

When RLi compounds are used (in THF at —95°) to prepare $R_fLi$ the yields are higher than those obtained with RMgX as the cleavage reagents, reaching 88-100% with t-BuLi; then followed by n-BuLi which was more effective than MeLi. The $R_fLi$ prepared from t-BuLi was more stable than the preparations from n-BuLi and MeLi. Possibly, complexation might have contributed in part to the greater stability of $R_fLi$ compounds prepared via the cleavage reaction. The cleavage method is a useful and clean procedure for the preparation in good yields of $R_fLi$ types; whereas, $R_fMgX$ reagents are readily synthesized via halogen—metal exchange reactions.

The $R_fSiMe_2H$ starting compounds can be prepared conveniently and in good yields by the in situ reaction in THF:

$$R_fI \text{ (or Br)} + Mg + ClSiMe_2H \rightarrow R_fSiMe_2H + MgX_2$$

The halogen—metal exchange and the cleavage reaction were, where warranted, used in a series of comprehensive studies [10] for the preparation of a miscellany of types such as: $R_fM$, where $R_f$ is $C_6F_{13}$; $C_8F_{17}$; $C_{10}F_{21}$; $(CF_2)_6$; $(CF_3)_2CFO(CF_2)_n$, where $n = 2, 4, 6, 8$; $R_fCF{=}CF$; and $C_6F_5$.

Derivatization was generally carried out in THF by reaction with $ClSiMe_3$:

$$R_fMgX(Li) + ClSiMe_3 \rightarrow R_fSiMe_3 + MgX_2$$

This reaction was also used initially as a supplementary yield-determining procedure until we observed, as stated earlier, that it was of no value in $Et_2O$ (contrary to THF) for derivatization of $R_fMgX$ because of the essential absence of reaction with $ClSiMe_3$.

The following background material leading to the attractive method for the cleavage of perfluoroalkyl silanes as a synthetic tool for perfluoroalkylorganometallic species also provides additional items concerned with perfluoroarylorganometallic compounds described in Section 3.

A significant synthetic development came from earlier studies involving a series of perhaloarylmetallic compounds. (Perhalorayl)dimethylsilanes undergo a cleavage reaction with RLi compounds, under very moderate conditions, to produce (perhaloaryl)lithium derivatives in good yield [34]:

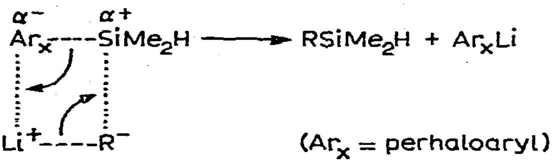
$$Ar_xSiMe_2H + RLi \rightarrow Ar_xLi + RSiMe_2H$$

A series of RLi compounds can be used to cleave the C—Si linkage to yield $C_6F_5Li$:

$C_6F_5SiMe_2H + BuLi \rightarrow C_6F_5Li + BuSiMe_2H$

Yields of $C_6F_5Li$ were determined by several procedures, including derivatization by compounds such as $ClSiMe_3$ and $CO_2$ to give the corresponding $C_6F_5SiMe_3$ and $C_6F_5COOH$.

The mechanism of the cleavage reaction can be visualized as a nucleophilic attack on the silicon atom, viz.:



Such a mechanism would be favored by electron-withdrawing groups (Cl, F) on the aryl nucleus which would increase the positive nature of the silicon atom. The absence of a cleavage reaction with $PhMe_2SiH$ may be attributed largely to a lack of the strongly electron-withdrawing halogens. The reaction proceeded instead to give the known $PhBuMe_2Si$ in 86% yield.

Bis(pentafluorophenyl)methylsilane reacts with primary alkyllithium and Grignard reagents to give high yields of the pentafluorophenylmetallic species [35]:

$(C_6F_5)_2SiMeH + 2RM \rightarrow 2C_6F_5M + R_2SiMeH$

where R = Me, n-Bu; M = Li and where R = Me, Et; M = MgX.

Cleavage of both pentafluorophenyl groups in $(C_6F_5)_2SiMeH$ proceeded rapidly under mild conditions to give a 92% yield with MeLi and an 86% yield with n-BuLi. However, with t-BuLi nucleophilic displacement of *para*-fluorines occurred predominantly. It is reasonable to assume that the steric bulk of the t-BuLi lessens its ability to cleave the Si—C bond and shifts attack mainly to the relatively more accessible *para*-fluorine atoms:

$$\begin{array}{l} (C_6F_5)_2SiMeH + t\text{-}BuLi \rightarrow \\ \quad (p\text{-}t\text{-}BuC_6F_4)_2SiMeH + p\text{-}t\text{-}BuC_6F_4Si(t\text{-}Bu)MeH + C_6F_5Li + LiF \\ \qquad\qquad (41\%) \qquad\qquad\qquad\qquad (24\%) \qquad\qquad (21\%) \end{array}$$

There was no evidence for any hydride displacement from silicon as occurs when many silicon hydrides are treated with organolithium or Grignard reagents.

Cleavage of one pentafluorophenyl group from silicon proceeds readily with a variety of Grignard reagents at 0° in THF or $Et_2O$/THF solvent mixture:

$(C_6F_5)_2SiMeH + RMgX \rightarrow C_6F_5MgX + C_6F_5Si(R)MeH$

$C_6F_5Si(R)MeH + RMgX \rightarrow C_6F_5MgX + R_2SiMeH$

Cleavage of the remaining pentafluorophenyl group was much more difficult, and was not observed in the case of i-PrMgCl. Ease of cleavage of (pentafluorophenyl)dimethylhydrosilane by Grignard reagents was shown to be in the order: MeMgCl > EtMgBr ≫ PhMgBr. This order may be indicative of the importance of steric hindrance in the cleavage of the Si—C bond.

Tris(pentafluorophenyl)silane, $(C_6F_5)_3SiH$ undergoes cleavage of the type shown by the homologous $(C_6F_5)_2SiMeH$ and $C_6F_5SiMe_2H$:

$$(C_6F_5)_3SiH + 3MeLi \rightarrow 3C_6F_5Li$$

Reaction with three equivalents of MeLi in ether at —50° gives 90% of $C_6F_5COOH$, subsequent to carbonation and acidification [36].

For general purposes, the $C_6F_5SiMe_2H$ is the best SiH compound to be used for this particular type of cleavage. A possible direct access to $R_f$—M types (where M is a metal or a metalloid), might [32] involve, as a substrate, a perfluoroalkane or a perfluorocycloalkane or alkenes related to such perfluoroalkanes.

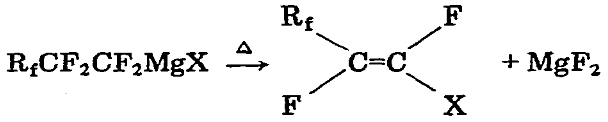
### *(b)* $(CF_3)_2CFO(CF_2)_nMgX(Li)$

In the in situ preparation [10] of $(CF_3)_2CFO(CF_2)_4SiMe_2H$, a satisfactory ratio of $(CF_3)_2CFO(CF_2)_4I$, Mg, and $ClSiMe_2H$ is 1/2/4; with the reaction temperature between —10 and 0°. General directions are given elsewhere in this article for the conversion of both $(CF_3)_2CFO(CF_2)_nI$ and $(CF_3)_2CFO(CF_2)_n$-$SiMe_2H$ to $(CF_3)_2CFO(CF_2)_nMgX(Li)$.

### *(c)* $R_fCF{=}CFMgX$

The thermal decomposition of perfluoroalkyl Grignard reagents ($R_fMgX$), formed from halogen—metal exchange with alkyl Grignard reagents, provides a good synthetic route to *trans*-1-haloperfluorovinyl compounds.

$$R_fCF_2CF_2I + RMgX \rightarrow R_fCF_2CF_2MgX + RI$$



$$R_fCF_2CF_2MgX \xrightarrow{\Delta} \underset{F\qquad X}{\overset{R_f\qquad F}{C{=}C}} + MgF_2$$

where X = Cl, Br, I

Although many reports [2-20] in the literature deal with the preparation and synthetic applications of perfluoroalkyl Grignard reagents, only a little attention has been given to the thermal decomposition of these compounds. It has been reported that the products from the reaction of trifluoromethyl iodide with Mg/Hg are tetrafluoroethylene and fluorocarbon polymers [3]. A radical mechanism was suggested for the decomposition of perfluoropropylmagnesium iodide in ether in order to explain the formation of certain by-products ($C_3F_7H$, $CH_3CHO$, $C_3H_7CH(OH)CH_3$, etc.) [3]. Significant studies by Tatlow and co-workers have shown that perfluorobicyclo[2.2.1]heptan-1-ylmagnesium iodide (or bromide) has a greater thermal stability than non-bridgehead perfluoroalkyl Grignard reagents, and it has been suggested that this compound decomposes via transient bridgehead olefin or diradical formation [18, 19]. The decomposition of perfluoroisopropyl Grignard and lithium reagents gave perfluoropropene in high yield [7]. Our preliminary investigations [15] and work recently reported by others [17] have shown that a *trans*-1-bromoperfluorinated olefin is the major product from the thermal decomposition of certain perfluoroalkylmagnesium bromides in ether. An extensive and comprehensive paper to appear shortly [15b] describes in greater detail the nature and scope of this novel route to some *trans*-substituted fluorinated olefins.

These *trans*-1-haloperfluorovinyl compounds will lend themselves admirably to the preparation from them of unsaturated perfluoroalkylorganometallic reagents by simple halogen—metal exchange reactions using the splendid Tarrant [37b] procedure:

$$R_fCF{=}CFX + RM \rightarrow R_fCF{=}CFM + RX$$

Types like the $\alpha,\omega$-bis(bromovinyl)perfluorinated alkane (see, section 4(b)(5)) and the corresponding bis-organometallic compounds derivable from it may prove of particular interest in studies such as those concerned with polymers and transition metal complexes.

### (d) $(Li)XMg(CF_2)_nMgX(Li)$

Perfluorinated difunctional organometallic types have been reported, particularly by Tatlow and coworkers [18, 19] and by Johncock [26b].

We have prepared reactive 1,6-disubstituted perfluorohexanes via the reaction of 1,6-bis(dimethylhydrosilyl)perfluorohexanes with alkyllithium and with Grignard reagents [38]:

$$HMe_2Si(CF_2)_6SiMe_2H + RMgX \rightarrow XMg(CF_2)_6MgX + RSiMe_2H$$

$$HMe_2Si(CF_2)_6SiMe_2H + RLi \rightarrow Li(CF_2)_6Li$$

The 1,6-dilithioperfluorohexane which is presumably generated by the halogen—lithium exchange between an alkyllithium reagent and $Br(CF_2)_6Br$ is less thermally stable than the corresponding di-Grignard reagent. The 1,6-bis(bromomagnesium)perfluorohexane was also prepared in good yield by a halogen—metal exchange reaction.

Reaction of 1,6-bis(dimethylhydrosilyl)perfluorohexane with t-BuLi in THF at 95° followed by derivatization with $ClSiMe_3$ gave a 72% yield of $Me_3Si(CF_2)_6SiMe_3$. The Si—H bond remained intact as the co-product was $RSiMe_2H$ with no LiH or $R_xSiMe_2R'$ ($R'$ = Bu, t-Bu, etc.) detected. It is of interest to note that the organometallic species which resulted from reaction of $HMe_2Si(CF_2)_6SiMe_2H$ with an RLi reagent could be derivatized by $ClSiMe_3$ (at —95°) in much higher yield than the $Li(CF_2)_6Li$ which is presumably generated initially from reaction of $Br(CF_2)_6Br$ with an alkyllithium reagent.

The 1,6-bis(dimethylhydrosilyl)perfluorohexane was prepared in good yields by an in situ reaction in THF at —40° using either Mg or Li [34]:

$$Br(CF_2)_6Br + ClSiMe_2H + Mg \rightarrow HMe_2Si(CF_2)_6SiMe_2H$$

In the precursory in situ reactions it was found desirable to very carefully dry the glassware by heating for 24 hours at 120° in order to obtain consistently high yields.

In earlier work [39], there is a report on the preparation of $Me_3Si(CF_2)_4SiMe_3$ and of $Me_3Si(CF_2)_6SiMe_3$ from the corresponding $\alpha,\omega$-dibromoperfluorobutane and $\alpha,\omega$-dibromoperfluorohexane by in situ reactions using Mg or Li, $ClSiMe_3$, at —70 to —50° in THF.

## 3. Perfluoroaryl-organometallic compounds

The most widely used perfluoroaryl group is pentafluorophenyl. There are numerous procedures for the introduction of this $C_6F_5$ moiety. One of the better and highly versatile synthetic approaches is that involving $C_6F_5$—M types. Of these the reagent of choice is probably the moderately reactive $C_6F_5MgCl$ [40]. The attractiveness of $C_6F_5MgCl$ is associated, in part, with the low cost of $C_6F_5Cl$, and also that another organometallic compound is not needed to prepare the $C_6F_5MgCl$.

A particularly helpful technique is the use of THF [41, 42]. We [42] have found that this Grignard reagent is formed in high yield from $C_6F_5Cl$ and Mg in THF at —10°. Addition of an initiator such as iodine or 1,2-dibromoethane is not required. On monitoring the preparation by GLC it was found that at 20, 30, 45 and 65 minutes after commencement, 80, 90, 95 and 99%, respectively, of the $C_6F_5Cl$ had been consumed. The yield of the Grignard reagent by titration in three separate preparations was 92, 95 and 99%. The THF solution of the Grignard reagent was brown to purple in color and gave Color Test I [43], although the malachite green color was slow (4 min) in developing.

Our next stage [44] was concerned with the applicability of the in situ technique. This was related to the preparation of pentafluorophenylcopper (or its complex) which was used in a series of reactions most [10] of which have been published. In the in situ reactions, the $C_6F_5Cl$ (0.1 mol), Mg (0.11 mol) and copper(I) halide (0.12 mol) were stirred at room temperature in THF (120 ml) until the onset of reaction was indicated by a darkening of the mixture. The reactions were then rapidly cooled to the desired reaction temperature, and stirred until GLC indicated that the concentration of the $C_6F_5Cl$ was 1% or less of its initial value. The derivatizing agent was then added, and the mixture stirred for 3 hours at reaction temperature. The reaction mixture was allowed to reach room temperature before customary work-up in the case of $C_6F_5COMe$ preparations from MeCOCl; or refluxed for 48 hours in the preparation of $C_6F_5C{\equiv}CC_6F_5$ from $CBr_2{=}CHBr$. The most convenient in situ conditions compatible with reasonable yields, are bath temperatures of —10 to 0°, and stirring for 3 hours.

The in situ preparation enjoys some advantages over the two-stage synthesis:

$$C_6F_5Cl + Mg \rightarrow C_6F_5MgCl$$

$$C_6F_5MgCl + CuCl \rightarrow C_6F_5Cu$$

Two advantages are the greater convenience and the reduction of time. Another is the actually slightly higher yield of $C_6F_5COMe$ than previously obtained in a two-stage process when a copper halide was added to the preformed $C_6F_5MgCl$. Incidentally, the yields can be improved somewhat by using copper(I) iodide, and also by running the reaction at —30° for 6 hours.

## 4. Reaction of polyhalogenated compounds with some organometallic compounds

### *(a) Some differences between n-BuLi and t-BuLi*

t-BuLi reacts with $C_6F_6$ to give only 1,4-di-(t-butyl)tetrafluorobenzene in very high yield (91.6%) [45]:

$C_6F_6$ + t-BuLi → 1,4-t-$Bu_2C_6F_4$

Whereas, n-BuLi under corresponding conditions gives the mono, bis, tris, and tetrakis compounds:

$C_6F_6$ + n-BuLi → n-$BuC_6F_5$ + 1,4-n-$Bu_2C_6F_4$ + 1,2,4-n-$Bu_3C_6F_3$ + 1,2,4,5-n-$Bu_4C_6F_2$

### *(b) Reactions of α,ω-dihaloperfluoro compounds with some RMgX and RLi compounds [46]*

#### *(1) $ICF_2CF_2I$*

Reaction with one equivalent of EtMgBr (or EtMgCl) at —95° gave $F_2C{=}CF_2$ very rapidly as the sole product by $^{19}F$ NMR.

#### *(2) $I(CF_2)_3I$*

Reaction with two equivalents of either EtMgCl or PhMgBr at —78° showed that an exchange reaction occurred rapidly as evidenced by the formation of EtI or PhI. However, $^{19}F$ NMR failed to show any recognizable signals, and the pale yellow film inside the NMR tube indicates that polymerization may have been involved.

#### *(3) $I(CF_2)_4I$*

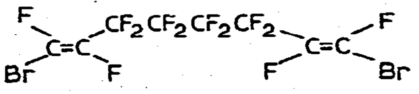
Here reaction occurred with two equivalents of EtMgBr (or PhMgBr) to give, perfluorocyclobutene, $\overline{CF_2CF_2CF{=}CF}$, as the only product observed. The yield was estimated to be ca. 85% by GC analysis and the formation of EtI (or PhI) was nearly quantitative. The reaction with one equivalent of PhMgBr at —78°, followed by hydrolysis after one hour, gave evidence for the $I(CF_2)_4MgBr$ species.

#### *(4) $I(CF_2)_6I$*

Two equivalents of EtMgX (X = Cl, Br, I) rapidly underwent an exchange reaction as evidenced by the quantitative formation of EtI. The isolated yield of perfluorocyclohexene, $\overline{CF_2(CF_2)_3CF{=}CF}$, was 69%.

#### *(5) $I(CF_2)_8I$*

The formation from $I(CF_2)_8I$ of the α,ω-bis(bromovinyl)perfluorinated compound (shown below) is another illustration that the course of these $I(CF_2)_nI$ reactions is dependent on both the chain length of the α,ω-diioperfluoroalkane, and the type of RM compound.

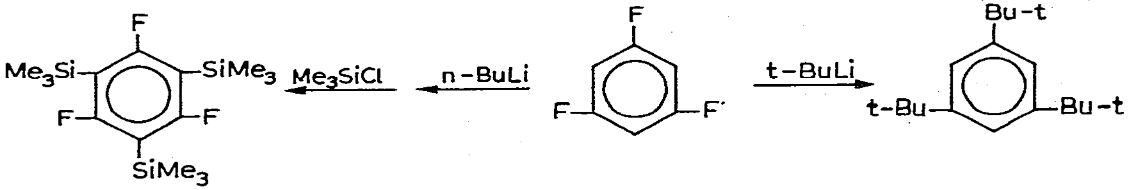


The reaction which led to this compound was very probably the thermal decomposition (occurring rapidly at ca. −10°) of the di-Grignard reagent, $BrMg(CF_2)_8MgBr$, formed in ether by the halogen—metal exchange reaction between $I(CF_2)_8I$ and RMgBr.

Such di-vinyl perfluorinated types, as well as organometallic and other compounds preparable from them, should prove attractive both in theoretical as well as in practical studies.

*(c) Polymetalated-perfluorobenzene via t-BuLi*

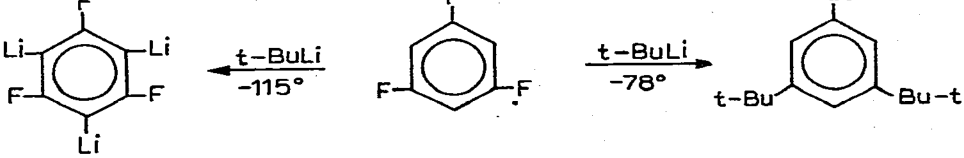
It has been found [47] that in reactions of 1,3,5-trifluorobenzene with t-BuLi, followed by treatment with $ClSiMe_3$, all three fluorine atoms are replaced to give 1,3,5-tri-t-butylbenzene in 72% yields with no apparent metalation products (other than those formed intermediately). With n-BuLi, under corresponding conditions, there is formed predominantly (after treating the intermediate trilithio compound with $ClSiMe_3$) 1,3,5-trifluoro-2,4,6-tris(trimethylsilylbenzene) as well as some products from partial metalations. The course of reaction is highly sensitive to experimental conditions, particularly temperature.



*(d) Pronounced temperature effect in reaction of 1,3,5-$C_6H_3F_3$ with t-BuLi*

As indicated earlier in this article, the preparation and reactions of some perfluorinated organometallic compounds are markedly influenced by reagents and reaction conditions. We have observed [48] a striking temperature effect in the reaction of 1,3,5-$C_6H_3F_3$ (I) with t-BuLi. From reaction of 4 equivalents of t-BuLi with I at −70° in a THF/pentane solvent mixture the predominant product was 1,3,5-tri-t-butylbenzene (II) in 72% yield.

However, when 3.15 equivalents of t-BuLi were slowly added to I at −115° in THF/pentane the yields of 1,3,5-$Li_3C_6F_3$ (III) in two independent reactions were 95 and 96% based on isolated yields of 1,3,5-trifluoro-2,4,6-tris-(trimethylsilyl)benzene after derivatization with $ClSiMe_3$. The chief contaminant was II (ca. 1%). It appears that at a temperature slightly below −115° the trilithio compound III may be formed in quantitative yield. The dramatic temperature effect upon the course of the reaction with t-BuLi was not apparent with n-BuLi. The enhanced metalating abilities of t-BuLi vs. n-BuLi have been attri-



(III) (I) (II)

buted to a greater tendency of the t-butyl anion to donate an electron to an aromatic system [49] and so give the more stable t-butyl radical. The pronounced difference in the reaction of I with t-BuLi vs. n-BuLi at —70° may be the result of an addition—elimination mechanism operative with t-BuLi at this temperature. The formation of the large amount of intractable pot residue with n-BuLi at higher temperature may be due to decomposition through a benzyne intermediate suggested for *o*-lithiofluorobenzene [50].

### *(e) Reaction of $Cl(CF_2)_3Cl$ with RLi compounds [51]*

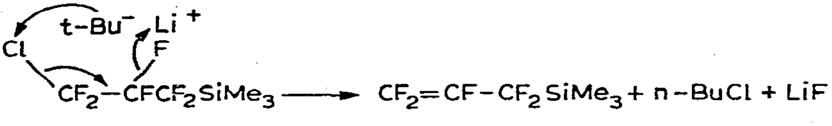
This section is treated separately from that of (b) (reactions with $\alpha,\omega$-dihaloperfluoroalkanes with RMgX and RLi compounds) because the types of reaction now reported with $Cl(CF_2)_3Cl$ would probably not take place to any significant extent with $Br(CF_2)_3Br$ and $I(CF_2)_3I$.

Although $Cl(CF_2)_3Cl$ appeared to be inert to Grignard reagents under mild conditions, reactions of one equivalent of MeLi, n-BuLi or t-BuLi in ether at low-temperature gave a rapid exchange reaction:

$$Cl(CF_2)_3Cl + RLi \xrightarrow[-110^\circ]{Et_2O} Cl(CF_2)_3Li + RCl$$

Subsequent addition of $ClSiMe_3$, $ClSiMe_2H$ or iodine, provided the 3-chlorohexafluoropropyl derivatives in high yields.

The stability of $Cl(CF_2)_3Li$ was not significantly affected by the addition of excess MeLi or n-BuLi; however, excess t-BuLi had some deleterious effect. This was determined by the use of derivatizing agents ($ClSiMe_2H$, $I_2$) that reacted rapidly at ca. —110° in ether with both $Cl(CF_2)_3Li$ and the excess RLi. When $ClSiMe_3$ was employed, in a reaction of $Cl(CF_2)_3Cl$ with two equivalents of n-BuLi, the major products were $CF_2{=}CFCF_2SiMe_3$ and $Me_3Si(CF_2)_3SiMe_3$. This would suggest that the second equivalent of n-BuLi reacted with $Cl(CF_2)_3SiMe_3$ in preference to coupling with $ClSiMe_3$ as the reaction mixture was slowly allowed to warm above —110°. In separate experiments it was shown that both $Cl(CF_2)_3SiMe_3$ and $ClSiMe_3$ react very slowly with n-BuLi at —110°. On the other hand, MeLi was completely unreactive to $Cl(CF_2)_3SiMe_3$, and readily coupled with $ClSiMe_3$ at this temperature. The coupling of t-BuLi with $ClSiMe_3$ has been shown to be unfavorable since metalation of a methyl group predominates [52]. If a $Li(CF_2)_3SiMe_3$ intermediate was involved in this reaction it was too unstable to be trapped by $ClSiMe_2H$ as no $HMe_2Si(CF_2)_3SiMe_3$ was obtained. Since it seems unlikely that $Li(CF_2)_3SiMe_3$ would be much less thermally stable than $Li(CF_2)_3Cl$, the reaction may have proceeded as depicted below:



### *(f) Possible course of reaction of $ClCF_2CF_2Cl$ with some RLi reagents*

In view of the low temperature reaction described in section (e):

$Cl(CF_2)_3Cl + RLi \rightarrow Cl(CF_2)_3Li$

there is the attractive possibility that the following reaction may occur under appropriate conditions:

$$ClCF_2CF_2Cl \xrightarrow[\text{low temp.}]{\text{an RLi or another RM compound}} ClCF_2CF_2M$$

Over the years numerous unsuccessful attempts have been made to prepare a species such as: $XCH_2CH_2MgX$.

*(g) Synthesis of perfluorinated terminal olefins from perfluoroalkyl iodides and organometallic reagents*

A procedure which has been used to obtain perfluorinated terminal olefins is reactions of perfluoroalkyl iodides with Grignard or RLi reagents [53]:

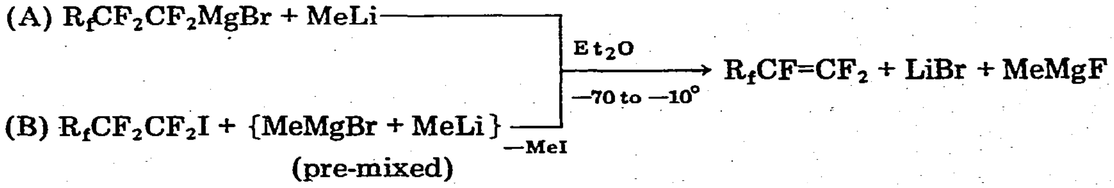
$$C_nF_{2n+1}CF_2CF_2I + RM \rightarrow C_nF_{2n+1}CF{=}CF_2 + RI + MF$$

Using appreciably higher homologous iodides, we sought to obtain good yields of perfluorinated olefins from n-$C_8F_{17}I$ and n-$C_{10}F_{21}I$ using alkyllithium reagents. High yields of olefin were isolated from the reaction of n-$C_3F_7I$ with MeLi [53]. Under similar conditions, we found that the yields of n-$C_6F_{13}CF{=}CF_2$ and n-$C_8F_{17}CF{=}CF_2$ were about 20% when one equivalent of MeLi or n-BuLi were used. Under our conditions, the high recovery of the starting perfluoroalkyl iodide (ca. 40%), and isolation of alkylated olefins (predominantly *trans*-$R_fCF{=}CFR$) were in agreement with the extent of halogen—metal exchange observed by Johncock [26]. When n-$C_{10}F_{21}I$ and MeLi were treated in a 2/1 ratio, n-$C_8F_{17}CF{=}CF_2$ was isolated in 66% yield. Under these conditions the halogen—metal exchange was essentially complete, and no alkylated olefins were formed.

The reaction of Grignard reagents with perfluoroalkyl iodides appears to be a somewhat disadvantageous general route to terminal perfluorinated olefins. Whereas perfluoroisopropylmagnesium bromide led to perfluoropropene in 70.5% yield [53], we have found that certain other perfluoroalkylmagnesium halides gave predominantly the *trans*-1-haloperfluorovinyl compounds when allowed to thermally decompose in ether (see section 2(c)).

Similar reactions in THF gave the terminal perfluoroolefin in somewhat variable, but generally moderate yield. Under considerably different conditions, MeMgCl has been treated with perfluoroalkyl iodides to give terminal perfluoroolefins in moderate yield along with lesser amounts of internal perfluoroolefins [53].

The use of MeLi in combination with MeMgBr provides an excellent method [51] for the synthesis of terminal perfluorinated olefins. Yields were ca. 90% by VPC and 60-80% on an isolated basis, with no contamination from internal isomeric olefins in the following procedures A-C:



$$\text{(A) } R_fCF_2CF_2MgBr + MeLi \xrightarrow[-70\text{ to }-10^\circ]{Et_2O} R_fCF{=}CF_2 + LiBr + MeMgF$$

$$\text{(B) } R_fCF_2CF_2I + \underset{\text{(pre-mixed)}}{\{MeMgBr + MeLi\}} \xrightarrow{-MeI} \xrightarrow[-70\text{ to }-10^\circ]{Et_2O} R_fCF{=}CF_2 + LiBr + MeMgF$$

$$(C)\ 2R_fCF_2CF_2I + \{MeMgBr + MeLi\} \xrightarrow[\substack{-70\ \text{to}\ 0^\circ \\ -2MeI}]{Et_2O} 2R_fCF{=}CF_2 + LiBr + MgF_2$$

Under these reaction conditions, the $R_fCF{=}CF_2$ formed does not react with any of the co-products including RMgX (X = Cl, Br, I).

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