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# STUDIES ON FLUOROALKYLATION AND FLUOROALKOXYLATION. PART 24. MAGNESIUM-INDUCED SINGLE ELECTRON TRANSFER IN REACTIONS OF FLUOROALKYL IODIDES WITH ALKENES AND ALKYNES

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## SUMMARY

Magnesium metal catalyses the radical reactions of perfluoroalkyl iodides with alkenes and alkynes to give the corresponding adducts in high yields under mild conditions. The presence of 1,4-dinitrobenzene (p-DNB) or oxygen does not affect the reaction, but the reactions can be partially suppressed by hydroquinone and completely inhibited by 2-nitroso-2-nitropropane in DMF. In THF fluoroalkene is obtained in addition to the normal adducts, and the reaction could be inhibited by p-DNB. All these results seem to show that a radical mechanism is involved in non-ethereal solvents. However, both radical addition and fluoroalkyl Grignard reagent reactions are involved in THF. The formation of fluoroalkylmagnesium iodide is also found to proceed through a radical intermediate.

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## INTRODUCTION

It is well-known that magnesium is one of the most important elements in organic chemistry.By reaction with organic halides in ethereal solution Grignard reagents can be readily prepared which have been widely used in organic synthesis. Attempts have been made to introduce such useful reagents to fluorine chemistry [1], however, the application is still strictly limited because of its thermal instability [1,2]. The emphasis has been on the polar mechanism [3], although the formation of non-fluorinated Grignard reagents has been proved to proceed through radical intermediates and their reactions with carbonyl compounds are also known both through polar and single electron transfer (SET) processes [4,5]. On the other hand, some transition metals and their complexes, e.g. Cu(6a), Pd(0)(6b), Pt(0)(6c), Rh(I)(6d), Ni(6e), Fe(6f), Zn(6g), Ag(6h) etc.,have been found to catalyse the radical addition reactions of perfluoroalkyl iodides to carbon-carbon multiple compounds [6,7].However,previous reports describing the use of main group elements including magnesium for this kind of reaction have not appeared. It would be of interest if a possible radical intermediate could be used in fluoroorganic synthesis. As a continuation of the studies on the fluoroalkylation by metals [6], we here present the results of the addition reactions of perfluoroalkyl iodides to alkenes and alkynes catalysed by magnesium. The possible mechanism involving single electron transfer processes with or without the formation of Grignard reagents depending on the solvents used has also been discussed.

## RESULTS AND DISCUSSION

The fluoroalkylated adducts ,3, could be obtained in high yields by the reactions of fluoroalkyl iodides with alkenes in the presence of catalytic amounts of magnesium turnings or

TABLE 1

The reaction of 1 with alkenes and alkynes catalysed by Mg[a]

| Entry | RfI | alkenes / alkynes | 1:2 | t(h) | T°C | Conv(%)[b] | Products (%)[c] 3 | Products (%)[c] 4 |
|---|---|---|---|---|---|---|---|---|
| 1 | 1a | 2e | 1:1.5 | 10 | 80 | 82 | 88 | |
| 2 | 1a | 2e | 1:1.7 | 10 | 80 | 95 | 90[d] | |
| 3 | 1a | 2f | 1:2 | 10 | 80 | 78 | 85 | |
| 4 | 1a | 2f | 1:2 | 13 | 20 | 85.8 | 92[d] | |
| 5 | 1a | 2g | 1:1.5 | 10 | 60 | 82 | 78 | |
| 6 | 1a | 2j | 1:1.5 | 5 | 60 | 85.2 | 22.8 | 57.1[e] |
| 7 | 1a | 2i | 1:4 | 10 | 80 | 43.5 | 58.6[f] | 27.3 |
| 8 | 1a | 2h | 1:1.4 | 7 | 80 | 89.5 | 82.3 | |
| 9 | 1a | 6h | 1:2 | 10 | 80 | 88.5 | 90.2[g] | |
| 10 | 1a | 6f | 1:2 | 10 | 80 | 85.7 | 81.9[g] | |
| 11 | 1b | 2j | 1:1.5 | 5 | 60 | 76.2 | 17.5 | 52.5[e] |
| 12 | 1b | 2h | 1:2 | 10 | 80 | 89.7 | 89.5 | |
| 13 | 1b | 6f | 1:1.5 | 10 | 80 | 90.5 | 85.3[g] | |
| 14 | 1c | 2g | 1:2 | 10 | 50 | 72.5 | 73.6 | |

[a] catalysed by Mg turnings in DMF unless noted otherwise; Mg:1=40%:1; [b] determined by $^{19}F$ NMR; [c] isolated yield; [d] catalysed by Mg powder; [e] 5, Z:E=3:1; [f] trans:cis=1:2; [g]: 7, Z:E=2.5:1.

powder under mild conditions as illustrated in eq. 1. The representative examples are listed in Table 1.

$$\underset{1}{R_fI} + \underset{2}{RCH{=}CH_2} \xrightarrow{Mg} \underset{3}{R_fCH_2CHIR} + \underset{4}{R_fH} \qquad (1)$$

$R_f$: $Cl(CF_2)n$, n=4(a), 6(b), $FO_2S(CF_2)_2O(CF_2)_2$ (c)

2: R=$(CH_3)_2CHCH_2$(e), n-$C_4H_9$(f), n-$C_8H_{17}$(g), n-$C_5H_{11}$(h), cyclohexene(i)

When 2-methyl-butene-[1],($\underline{2}$j),was used in the reaction, the major product was fluoroalkylated alkenes, $\underline{5}$, instead of $\underline{3}$, together with a small amount of $\underline{4}$ (eq.2).

$$R_fI \; + \; \underset{\underline{2j}}{EtMeC{=}CH_2} \xrightarrow{Mg} \underset{\underline{5}}{R_fCH{=}CMeEt} \; + \; \underline{4} \qquad (2)$$

The reactions of perfluoroalkyl iodides with alkynes could also be catalysed by magnesium under the same conditions to give the corresponding adducts in high yields, which were shown to be the mixtures of E and Z isomers by $^{19}F$ NMR spectra (eq.3) (Table 1).

$$\underset{\underline{1}}{R_fI} \; + \; \underset{\underline{6}}{CH{\equiv}CR} \xrightarrow{Mg} \underset{\text{E \& Z}}{\underset{\underline{7}}{RCHI{=}CHR_f}} \qquad (3)$$

$R{=}n\text{-}C_4H_9(f),\ n\text{-}C_5H_{11}(h)$

The reactions occured readily in dimethylformamide (DMF), acetonitrile or acetone (Table 2). However, no products were formed in the absence of solvents. Magnesium powder seemed to be more efficient at catalysing the reaction than the turnings. As Table 1 shows, there was little effect on the reaction with variation of temperature from room temperature to 80°C. Variation in the amount of magnesium from catalytic amounts (40 mol%) to excess did not change the products and their ratios (i.e. $\underline{3}$:$\underline{4}$). The possibility by magnesium oxide and magnesium iodide of catalysis of the reaction, which might exist on the magnesium surface or be formed during the course of the reaction, were excluded by control experiments. Addition of single electron transfer scavenger, e.g. p-dinitrobenzene(p-DNB),to the reaction mixture or absence of pure nitrogen for protection, did not decrease the yield of the adducts. However, the reaction could be partially suppressed by hydroquinone and

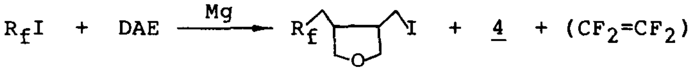
TABLE 2

Mg-catalysed reaction of 1 with alkenes in various solvents[a]

| Entry | $R_fI$ | alkene | solvent | t(h) | T(°C) | conv.[b] (%) | product (%)[c] 3 | 4 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| 15 | 1a | DAE | / | 15 | 80 | 0 | | | |
| 16 | 1a | DAE | $CH_3CN$ | 10 | 60 | 100 | | 5.0 | 88.5 |
| 17 | 1a | DAE | THF | 5 | reflux | 100 | 16.6[d] | 3.8 | 63.2 |
| 18 | 1b | DAE | THF | 5 | reflux | 100 | 13.8[d] | 8.2 | 70.7 |
| 19 | 1a | 2g | $CH_3COCH_3$ | 10 | reflux | 100 | 66.3 | 11.6 | |
| 20[e] | 1a | 2f | DMF | 8 | 60 | 100 | 78.2[f] | 10.5 | |
| 21[e] | 1a | 2f | THF | 10 | 60 | 87.3 | 55.4[f] | | 23.7[g] |

[a] catalysed by Mg turnings (40 mol%); ratio of 1:alkenes= 1:2; [b] determined by $^{19}F$ NMR; [c] isolated yield unless noted otherwise; [d] 9; [e] acetone was added (1:2:acetone= 1:2:2); [f] the yield was determined by $^{19}F$ NMR spectra; [g] $Me_2C(OH)R_f$,(10).

completly inhibited by 2-nitroso-2-nitropropane, (Table 3). Treatment of 1 with diallyl ether(DAE) gave the fluoroalkylated tetrahydrofuran derivatives (8) in high yield, (Table 3 and 4) [6,8]. The generation of tetrafluoroethylene (20%) indicated that $\beta$-fragmentation of the chlorotetrafluoroethyl radical intermediate might be involved [8]. in the reaction of 2-chlorotetrafluoroethyl iodide (1k) with DAE (eq.4).



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(4)

Rf: 1a, 1b, $CF_3(CF_2)_3$ (1d), $Cl(CF_2)_2$ (1k)

TABLE 3

Mg-catalysed reactions of 1a with alkenes in the presence of inhibitors[a]

| Entry | alkene | inhibitor | conv.(%)[b] (8) |
|---|---|---|---|
| 22 | DAE | $O_2$ or none | 100 |
| 23 | DAE | p-DNB(20%) | 93 |
| 24 | DAE | hydroquinone(10%) | 77.5 |
| 25 | DAE | $Me_2C(NO)NO_2$(100%) | 0 |
| 26 | 2e[c] | $Me_2C(NO)NO_2$(100%) | 0 |
| 27 | DAE[d] | p-DNB(10mol%) | 0 |

[a] in DMF at 80°C for 10h catalysed by Mg turnings; 1a:alkene= 1:1.5; [b] determined by $^{19}F$ NMR and GC; [c] catalysed by Mg powder. [d] in THF.

TABLE 4

The reaction of 1 with DAE catalysed by magnesium[a]

| Entry | $R_fI$[b] | t(h) | T(°C) | product(%)[c] 8 |
|---|---|---|---|---|
| 28 | 1a(1:2) | 9 | 60 | 89.3 |
| 29 | 1d(1:2) | 6 | 60 | 80.5 |
| 30 | 1b(1:2) | 8 | 60 | 83.6 |
| 31 | 1a(1:1.5) | 8 | 20 | 88.7 |
| 32 | 1k(1:2.5) | 8 | 50 | 67.0[d] |

[a] catalysed by Mg turnings in DMF; [b] ratio of 1:DAE; [c] isolated yield; [d] 20.1% of tetrafluoroethylene was also collected.

Interestingly, when an ether-type solvent, *i.e.* tetrahydrofuran(THF), was used in the reaction, about 20% perfluoroalkene, $\underline{9}$, was obtained besides $\underline{3}$ and $\underline{4}$. This reaction can be inhibited completly by p-DNB (Table 2,3).

$$R_fI + \underline{2} \xrightarrow{\text{THF}} \underline{3} + \underline{4} + \underset{\underline{9}}{R_f{'}CF{=}CF_2} \qquad (5)$$

All these results, very similar to those obtained by using transition metals as catalysts (6,7) can be rationalized in terms of a radical chain process induced by magnesium through single electron transfer as follows(Scheme I):

$$\begin{tikzcd} & {[R_fI^{\bar{\cdot}}\ \ Mg^{+}]} \arrow[dr] & \\ R_fI + Mg \arrow[ur] \arrow[dr] & & {[R_f^{\bullet}\ \ IMg]} \\ & {[R_f\cdots I\cdots Mg]} \arrow[ur] & \end{tikzcd}$$

$$[R_f^{\bullet}\ \ IMg] \longrightarrow R_f^{\bullet} + MgI$$

$$MgI + R_fI \longrightarrow R_f^{\bullet} + MgI_2$$

$$R_f^{\bullet} + RCH{=}CH_2 \longrightarrow R_fCH_2\dot{C}HR \xrightarrow{\underline{1}} \underline{3}$$

$$R_f^{\bullet} + \text{'H'} \longrightarrow \underline{4}$$

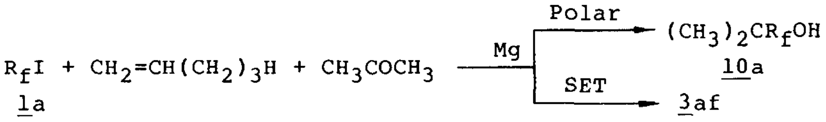
Scheme I

The appearence of perfluoroalkene, $\underline{9}$, in THF is difficult to explain by the above mechanism(Scheme I)[8] However, the formation of $\underline{9}$ may arise from the $\beta$-elimination of perfluoroalkylmagnesium halide as observed in the decomposition of the analogue in THF at room temperature by Tamborski and others [1, 2] (Scheme II).

$$[R_f^{\bullet}\ \ IMg] \xrightarrow{\text{THF}} R_fMgI \xrightarrow{-FMgI} \underset{\underline{9}}{R_f{'}CF{=}CF_2}$$

Scheme II

Then, the question we faced is whether the Grignard reagent was also involved in the above reactions when using the non-ether type solvents. The following facts seems to exclude such a possibility. First, no perfluoroalkenes were detected even if the reaction took place at 80°C. Second, no report for preparing Grignard reagents in non-ethereal solvents has appeared*. In fact,we found that no Grignard reagent was formed when phenyl bromide was treated with magnesium in DMF at 80°C for 24h. It was also found that perfluoroalkylmagnesium iodide does not react well with alkenes in THF to give the corresponding adducts. The lower yield of 9 indicated that the perfluoroalkyl radical may be trapped more easily by alkenes than by MgI to form the Grignard reagent, because the decomposition of perfluoroalkylmagnesium iodide would be rather faster at this temperature if it was formed. Thirdly, when acetone was added to the mixture to trap the possible perfluoroalkylmagnesium iodide in DMF, only the radical adduct,3, rather than the polar addition product, 10, was formed, indicating that the Grignard reagent was indeed not formed in non-ether type solvents (Table 2).



$$\underset{\underline{1}a}{R_fI} + CH_2{=}CH(CH_2)_3H + CH_3COCH_3 \xrightarrow{Mg} \begin{cases} \xrightarrow{\text{Polar}} \underset{\underline{10}a}{(CH_3)_2CR_fOH} \\ \xrightarrow{\text{SET}} \underline{3}af \end{cases}$$

However, if the reaction was carried out in THF, both polar and radical addition products, 10 and 3f, were obtained. Therefore, the more satisfactory explanation of all these results seems to be that the single electron transfer from magnesium to perfluoroalkyl iodides always readily occurs both in ethereal or non-ethereal solvents. In the presence of efficient radical trapping,the only fate for a radical generated by a SET process is trapping by alkenes or alkynes in the non-ethereal solvents.

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* In the presence of amine Grignard reagents can be prepared in hydrocarbon solvents (4a).

In an ethereal solvent (i.e.THF), both processes of radical and polar additions may occur simultaneously to give the corresponding adduct or the Grignard reagent, which means that the formation of perfluoroalkyl Grignard reagents might also involve radical intermediates similar to non-fluorinated ones. The fact that the reaction in THF could be completly inhibited by p-DNB , but not in DMF , seems to show that the solvent cage effect has appeared in this reaction [9].

## EXPERIMENTAL

All boiling points were uncorrected. GC spectra were measured on a Shanghai Model 103 with column packing with oxaperfluoroalkyltriazine polymer on 100 mesh 102 support. IR spectra were taken on a Shimedzu IR-440. NMR spectra (chemical shifts in ppm from external TMS for $^{1}$H NMR and from external TFA for $^{19}$F NMR, positive for upfield shifts) were recorded on a EM-360 NMR spectrometer at 60 MHz. Mass spectra were measured on MS-4021. Laser Raman spectra was taken on a JY-T 800. All solvents and reagents were purified prior to use and all reactions were carried out under an atmosphere of pure nitrogen. Both magnesium turnings or powder were commercial materials and without further activation.

### General Procedure

In a 50 ml three-necked flask, fitted with a magnetic stirrer, nitrogen inlet and condenser with a desiccator, were placed catalytic amounts of magnesium,alkene or alkyne and perfluoroalkyl iodide.After 10 ml of solvent was added at the desired temperature, the colour of the solution soon turned red-black.The conversion was monitored by $^{19}$F NMR while the mixture stirred.Magnesium could be recovered by filtration and the solution was washed by dilute hydrochloric acid, then extracted three times with diethyl ether.The combined extracts were washed with water,dried over anhydrous $MgSO_4$.Distillation gave the adducts 3 and 4 (the results are given in Table 1 ). The new products were identified by elemental analyses, IR, $^{1}H$ and $^{19}F$ NMR as well as Mass spectra. The others not listed below are known compounds [6].

3cg: b.p.122°C/3mmHg; $^{1}H$ NMR $\delta$ 4.3(m,1H), 2.1-0.93(m,19H)ppm; $^{19}F$ NMR $\delta$ -121.4(s,1F), 4.6(s,2F), 7.1(m,2F), 34.6(s,2F), 39.5 (m,2F) ppm; IR (film) 2995, 2950, 2800, 1460, 1380, 1340, 1300, 1245, 1200, 1150, 1110, 990, 820, 730 $cm^{-1}$; MS m/e :439, 397, 383, 119, 100, 85, 71, 69, 66, 57, 43; Analysis,Found, C,29.73, H,3.54, F,30.51, S,6.25; $C_{14}H_{20}O_{3}F_{9}S$, requires,C,29.68, H,3.53, F,30.21, S,5.65.

## The reactions of 1 with 2j catalysed by magnesium

To a three-necked flask was added magnesium powder (40% mol relative to 1 ) and DMF added 1a and 2j in ratio of 1:1.5 respectively. After stirring the mixture at 60°C for 5h, the conversion was determined by $^{19}F$ NMR. After workup, distillation gave the products ,3 and 5, with a small amounts of 4. The results are summarised in Table 1.

5aj: b.p. 58°C/1mmHg; IR (film) 2995, 2950, 2800, 1650, 1460, 1360, 1260, 1185, 1135, 1085, 1055, 985, 840, 785 $cm^{-1}$; Laser Raman: 1448, 1650, 1670 $cm^{-1}$; $^{1}H$ NMR $\delta$ 4.29(m,1/2H), 5.40(m, 1/2H), 2.7-2.1(m,2H), 1.47(m,3H), 0.81(m,3H) ppm; $^{19}F$ NMR $\delta$ -9.4(t,2F), 35.2(m,2F), 42.0(m,2F), 45.0(s,2F)ppm; MS m/e: 304, 306,305, 307, 119, 100, 91, 85, 87, 77, 69, 65, 59, 57, 55, 47, 43,43,41; Analysis, Found, C,34.94, H,3.14, Cl,11.04; $C_{9}H_{9}F_{8}Cl$, requires,C,35.47, H,2.96, Cl,11.66.

5bj: b.p.74°C/1.5mmHg; IR (film) 3000, 2995, 2800, 1675, 1555, 1470, 1440, 1260, 1210, 1155, 1120, 1090, 1000, 675 $cm^{-1}$; $^{1}H$ NMR $\delta$ 5.3(m,1/2H), 4.8(m,1/2H), 2.76-1.99(m,2H), 1.50(m,3H), 0.82(m,3H) ppm; $^{19}$F NMR δ -9.8(t,2F), 35.3(m,2F), 42.6(s,2F), 43.9(m,4F), 45.0(s,2F) ppm; MS m/e : 404, 406, 405, 407, 393, 385, 387, 349, 135, 137, 131, 119; Analysis, Found, C,31.99, H,2.23, F,55.99, Cl,8.80; $C_{11}H_9F_{12}Cl$,requires, C,32.36, H,2.22, F,56.37, Cl,8.78.

## The reaction of 1 with alkynes or DAE catalysed by magnesium

The experimental procedures are similar to those described above. The results are given in Table 1, 2, 3 and 4.

7ah: b.p.43°C/1.5mmHg; IR (film) 3010, 3000, 1900, 1685, 1480, 1200, 1135, 1105, 995, 855, 680 cm$^{-1}$; $^{1}$H NMR δ 6.02(m,1H), 5.40(m,1H), 1.92(m,2H), 1.11(m,6H), 0.72(m,3H)ppm; $^{19}$F NMR δ -10.3(t,2F), 29.3(m,cis,1/6 2F), 33.9(m,trans,5/6 2F), 41.8(t, 2F), 45.1(t,2F)ppm; MS m/e: 332, 334, 333, 335, 295, 293, 271, 273, 251, 253, 121, 101, 95, 90, 85, 87, 83, 81, 77, 70, 69, 61, 57, 56, 55, 43, 41; Analysis, Found, C,39.24, H,4.01, Cl, 10.35; $C_{11}H_{13}F_8Cl$, requires, C,39.20, H,3.91, Cl,10.68.

## Magnesium-catalysed reaction of 1 with alkenes in the presence of p-DNB and other inhibitors

To a mixture of magnesium (40% mol to 1),alkene in DMF,were added certain amounts of p-DBN (relative to Mg) and 1a at 80°C. The vigorously stirred solution was maintained at this temperature for 10h. The products were identified by $^{19}$F NMR and GC spectra. The results are given in Table 3.

## Magnesium-catalysed reactions of 1 with DAE in THF

To a solution of DAE in THF was added magnesium powder and 1. After refluxing the mixture for 5h, $^{19}$F NMR showed that the conversion was complete. Perfluoroalkene(9) was obtained in the ice-trap, which was identified by $^{1}$H, $^{19}$F NMR as well as GC spectra compared with authentic samples. Workup the residue gave the product 8. The results are given in Table 2.

## The reaction of 1 with alkene and acetone in THF induced by magnesium

To a solution of 3.6 g of 2f (40 mmol),2.3 g of acetone (40 mmol) in 20 ml of THF,were added 7.2 g (20 mmol) of 1a and 0.54 g of magnesium turnings. The vigorously stirred mixture was maintained at 60°C for 10h. $^{19}$F NMR and GC spectra analyses showed that 87.3% conversion was reached and the yield of 3af is 65.4%, 10a is 23.7% (They were compared with authentic samples).Distillation gave the products,3af and 10a, [10a, b.p. 50°C/10mmHg (lit.[10], 55°C/13mmHg)] (Table 2).

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