Journal of Fluorine Chemistry, *40* (1988) 129–137

F-ALKYLIRON(II) COMPOUNDS [1] *

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SUMMARY

F-Alkyliron tetracarbonyl iodides are convenient sources of terminal vinyl iodides by a simple pyrolytic technique. The precursors to the *F*-alkyliron tetracarbonyl iodides, an *F*-alkyl iodide and iron pentacarbonyl, can be used to generate *F*-alkyl radicals capable, for example, of *F*-alkylating benzene in moderate yield. Mechanisms for these transformations are proposed.

INTRODUCTION

Oxidative addition of trifluoromethyl and heptafluoropropyl iodides to iron pentacarbonyl is known to proceed readily at 65-70 °C with formation of the corresponding *F*-alkyliron tetracarbonyl iodides in good yield [2]. These adducts slowly lose CO when heated further at 70 °C to give dinuclear products, $[R_FFe(CO)_3I]_2$, but were shown to have C-Fe bonds which are stable at 70-80 °C. Pyrolysis at higher temperatures, however, resulted in α-elimination of fluorine in the special case of the trifluoromethyliron tetracarbonyl iodide, with tetrafluoroethylene and a minor amount of *F*-propene identified as volatile products. The heptafluoropropyliron compound **1**, on the other hand, was found to give only hexafluoropropene by an apparent β-fluorine elimination (eqs. 1 and 2).

$$CF_3I + Fe(CO)_5 \longrightarrow CF_3Fe(CO)_4I \longrightarrow [CF_3Fe(CO)_3I]_2 \longrightarrow CF_2=CF_2 \tag{1}$$

$$\begin{gathered} CF_3CF_2CF_2I + Fe(CO)_5 \longrightarrow \underset{\mathbf{1}}{CF_3CF_2CF_2Fe(CO)_4I} \longrightarrow \\ \underset{\mathbf{1a}}{[CF_3CF_2CF_2Fe(CO)_3I]_2} \longrightarrow CF_3CF=CF_2 \end{gathered} \tag{2}$$

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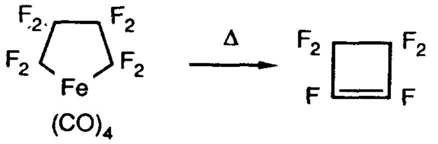
*Dedicated to Emeritus Professor W. K. R. Musgrave on the occasion of his 70th birthday.

0022-1139/88/$3.50

One example of coupling of fluoroalkyl residues other than difluorocarbene was reported [2]. The precursor in this case was the octafluoroferrocyclopentane **2**, in which coupling occurred between two carbon atoms attached to the same iron atom, an arrangement which clearly could facilitate coupling (eq. 3),



2

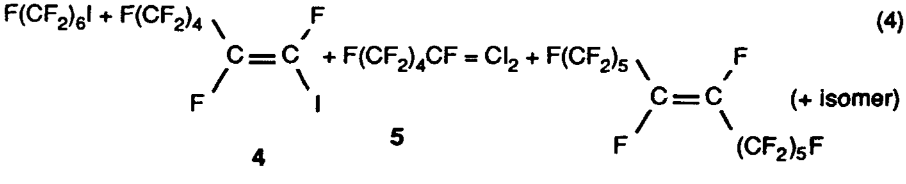
(3)

An interest in the use of readily available zero-valent transition metal compounds as reagents in organofluorine chemistry led to an examination of the chemistry of higher fluoroorganoiron(II) iodides.

RESULTS AND DISCUSSION

A crystalline adduct, assumed to be **3**, was easily obtained from *F*-hexyl iodide and iron pentacarbonyl at 65 °C. Pyrolysis of **3** occurred slowly at 100 °C and more rapidly at 140 °C to give a 25% yield of regenerated *F*-hexyl iodide, 10% of E-1-iodo-*F*-hexane-1 (**4**), and 10% of 1,1-diiodo-*F*-hexene-1 (**5**). A small amount of isomeric coupled products, *F*-dodecene-6 (**6**) and *F*-dodecene-5, was also obtained, with only traces at most of *F*-hexene-1 from straightforward elimination of β-fluorine (eq. 4).

$$F(CF_2)_6I + Fe(CO)_5 \xrightarrow{65\ ^\circ C} \underset{\mathbf{3}}{F(CF_2)_6Fe(CO)_4I} \xrightarrow{140\ ^\circ C}$$



4 **5** **6**

(4)

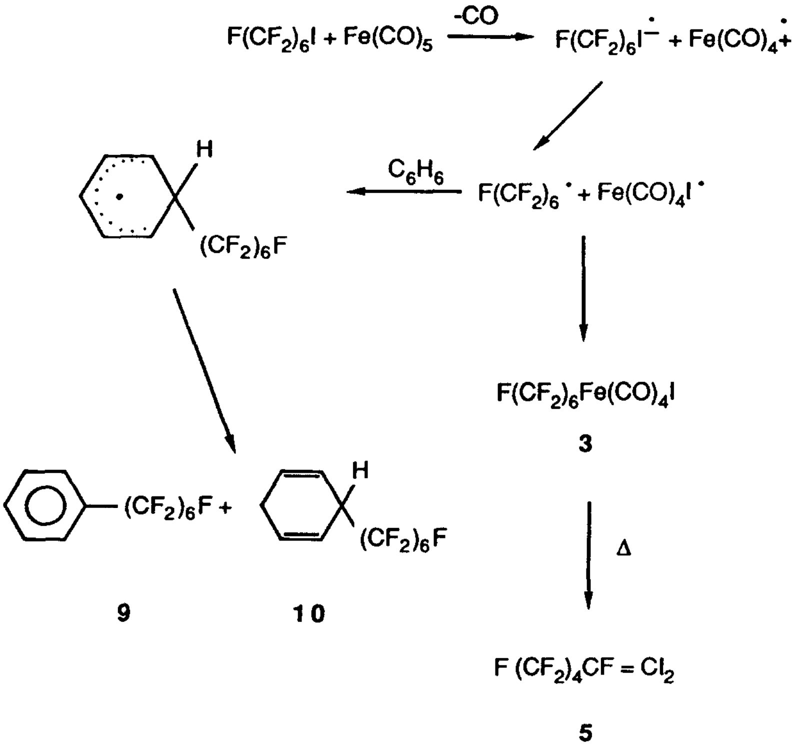
These results diverge from those reported for pyrolysis of the related straight-chain *F*-propyl compound **1**. Possibly the earlier workers isolated only the most volatile product and discarded higher-boiling iodides.

An α,ω-diiodide was shown to give diadducts similar to those from the monoiodides. Reaction of 1,4-diiodo-*F*-butane with excess iron pentacarbonyl at 65-70 °C quickly gave so much solid adduct that portions of benzene were added to facilitate mixing. Analysis of the product corresponded to that of structure **7** with some added loss of CO suggested. Further heating at 65-70 °C under vacuum resulted in loss of only one molecule of CO to give dimeric compound **8** (eq. 5), related in structure to **1a**. Vacuum pyrolysis of **8** gave only small amounts of many volatile products; in contrast to the behavior of **2**, little if any *F*-cyclobutene was formed.

$$\begin{tikzcd} I(CF_2)_4I + Fe(CO)_5 \arrow[r] & \underset{\mathbf{7}}{IFe(CO)_4CF_2CF_2CF_2CF_2Fe(CO)_4I} \arrow[dl, "\Delta"'] \\ \underset{\mathbf{8}}{[IFe(CO)_4CF_2CF_2CF_2CF_2Fe(CO)_3I]_2} & \end{tikzcd} \qquad (5)$$

The successful use of benzene as a diluent for the latter stages of the iron carbonyl/1,4-diiodide reaction provided encouragement for reacting *F*-hexyl iodide with iron pentacarbonyl in benzene solution. When the reaction was carried out at 65-70 °C and the volatiles were transferred by heating the mixture at 25-100 °C (0.5 mm), the major product (35% yield) was *F*-(hexyl)benzene (**9**) containing 5-10% of dihydro derivative **10**. The only other product detected in appreciable amount was 4% of diiodide **5**.

A commonly observed reaction path for facile generation of fluoroalkyl radicals from fluoroalkyl iodides and electron-rich reagents is initiated by one-electron transfer [3]. In the present case, this electron transfer followed by the usual shift of iodide anion should tend to generate the fluoroalkyl radical as an outer sphere complex with iron, thereby enhancing availability of the radical for reaction with a substrate such as benzene rather than for cage combination with the transition metal-based free radical. Reaction of the fluoroalkyl radical can therefore partition between the paths shown in Scheme I, the main path being addition to benzene.



Scheme I

Pyrolysis of neat solid **3** at 100-140 °C gave as one product 25% of *F*-hexyl iodide (*vide supra*), a reductive elimination product which may result from preliminary homolysis of the Fe-C bond. To the extent that the *F*-hexyl free radical is formed on pyrolysis and escapes the transition metal inner coordination sphere, it can be trapped by solvent benzene. When preformed **3** was refluxed in benzene, complete decomposition occurred within 13 hr at 80 °C. In addition to *F*-hexyl iodide, a 10% yield of monoiodide **4**, 17% of diiodide **5**, and only 4% of aryl derivative **9** were formed. So, as might be expected, reaction under these conditions disfavored attack on benzene relative to vinyl iodide formation.

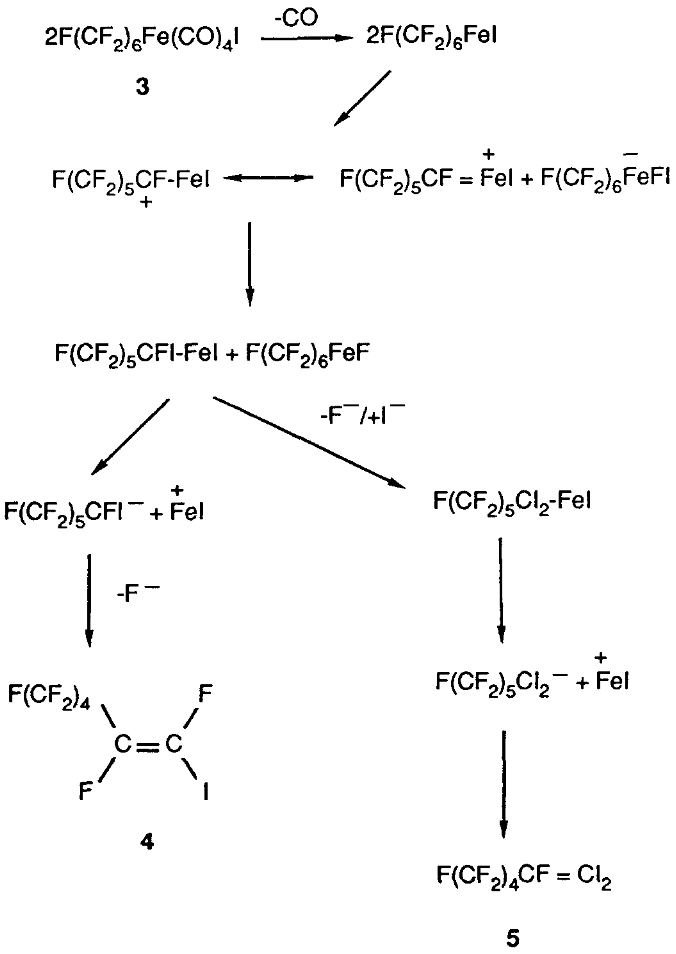
The use of iron pentacarbonyl/*F*-alkyl iodide mixtures to *F*-alkylate aromatics may have some utility. The ease of reaction and yield with the present procedure compare very favorably with the recently recommended use of preformed fluoroalkyliron(II) derivatives to accomplish the same transformation [4].

The easy synthesis of fluorinated vinyl iodides reported here may also be useful, since vinyl iodides are frequently required as intermediates. The formation of vinyl iodides during pyrolysis of neat *F*-hexyliron tetracarbonyl iodide appears not to be the result of β-fluorine elimination to give *F*-hexene-1 followed by exchange of vinylic fluorine by iodide. A prototypical reaction of anhydrous FeI_2 with *F*-propene under pressure at 140 °C gave only a trace amount of $CF_3CF{=}CFI$. Preliminary exchange of α-fluorine for iodine in the *F*-alkyliron moiety could be favored, since fluoroorganometallics are known to be a class in which the α-fluorine is labelized, particularly with the assistance of Lewis acids [5], leading to carbenoid intermediates which can add a different halide ion. The ability of iron to expand its coordination shell readily could allow coordination of α-fluorine to iron with subsequent removal as fluoride anion. The resulting carbenoid cation should easily add iodide to form an α-iodo-*F*-alkyliron intermediate. Heterolysis then can form a relatively stable carbanion which would β-eliminate fluorine to give monoiodide **4**. Alternatively, the iodination could first be repeated, leading eventually to diiodide **5**. The proposed reaction path is illustrated in Scheme II, wherein removal of α-fluorine is depicted as an intermolecular process rather than an intramolecular fluoride shift.

EXPERIMENTAL [6]

Preparation of Pyrolysis of F-hexyliron(II) Tetracarbonyl Iodide (3) (n.c.)

A mixture of 49.0g (0.11 mol) of *F-n*-hexyl iodide and 14.6g (0.10 mol) of iron pentacarbonyl was blanketed with nitrogen and heated at 60-65 °C for one day, after which time CO evolution had essentially stopped. The small amount of volatiles present was removed at 25 °C (0.05 mm) to give red crystalline **3** as a residue. The solid **3** was heated under full pump vacuum from 90 °C to 140 °C over a 3-hour period while 31.1g of pyrolyzate collected in a -80 °C trap and traces only in a -196 °C trap. Fractionation gave a mixture, bp 110-115 °C, containing two main components. One was identified by GC and ^{19}F NMR as 12.4g (25%) of *F-n*-hexyl iodide. The coproduct was 4.1g (10%) of E-1-iodo-*F*-hexene-1 (**4**). IR (neat): 1675 cm^{-1} (C=C). NMR (CCl_4): ^{19}F ϕ -81.8 (m, 3F, CF_3), -106.1 (A branch of AB, d of t of t, J_{FF} 149.7, 26.9, 5.8 Hz, 1F, $=CFI$), -199.6 (d of d of t, J_{FF} 26.9, 14.2, 12 Hz, 2F, $CF_2C{=}$), -127.4 (m, 2F, CF_2), -129.4 (m, 2F, CF_2), -144.3 (B branch of AB, d of t of m, J_{FF} 149.7, 14.2 Hz, 1F, $CF_2CF{=}$). A second fraction, bp 51-56 °C (8.6 mm), 1.8g, was shown by GC and NMR to be a nearly equimolar mixture of coupled product **6** [7] and diiodide **5**. Further distillation gave 4.9g (10%) of 1,1-diiodo-*F*-hexene-1 (**5**) (n.c.) containing free iodine as an impurity, bp 61-63 °C (8.4



Scheme II

mm). The product was washed with aq. Na_2SO_3, dried and analyzed. IR (neat): 1605 (C=C), 1300-1100 cm^{-1} (CF). NMR (CCl_4): ^{19}F ϕ -64.3 (t of t of t, J_{FF} 10.6, 8.8, 3.8 Hz, 1F, $C\mathit{F}=$), -81.7 (t of t, J_{FF} 10.1, 2.3 Hz, 3F, $C\mathit{F}_3$), -110.3 (q of m, J_{FF} 11 Hz, 2F, $C\mathit{F}_2C=$), -123.5 (m, 2F, $C\mathit{F}_2$), -127.0 (m, 2F, $C\mathit{F}_2$). The ^{13}C NMR spectrum established the structure as containing both iodine atoms on the terminal carbon; NMR ($CDCl_3$): ^{13}C 146.8 (d of t, J_{CF} 268, 28 Hz, CF=), 117.4 (q of t, J_{CF} 288, 33 Hz, CF_3), 114 to 105 (multiplets, $2CF_2$), 1.0 (d, J_{CF} 37 Hz, $=\mathit{C}I_2$). Analysis indicated the presence of two atoms of I/molecule, although analytical purity was not established. Anal. Calcd. for $C_6F_{10}I_2$: I, 49.20 Found: I, 44.24.

Preparation and Pyrolysis of F-Butane-1,4-bis(iron tetracarbonyl iodide) (7) (n.c.)

When 22.7g (0.05 mol) of 1,4-diiodo-*F*-butane and 36.5g (0.19 mol) of $Fe(CO)_5$ were heated at 65-70 °C for 30 min, formation of solid products made stirring difficult. Reaction was continued at 60-65 °C for a total of 10 hr with additions of 30 mL and later 20 mL of benzene to facilitate mixing. Removal of volatiles at 0.1 mm gave a solid orange residue which did not melt, but decomposed at 100-130 °C. A portion of the solid was triturated with methylene chloride, filtered off and dried under vacuum, giving a sample of diadduct **7** containing some impurity. IR (KBr): 2140, 2115, 2080 (coordinated CO), 1200-1100 cm^{-1} (CF). Anal. Calcd. for $C_{12}F_8Fe_2I_2O_8$: C, 18.25; F, 19.25; Fe, 14.15; I, 32.14 Found: C, 17.38; F, 19.06; Fe, 14.95; I, 32.15

Another sample of the crude product was heated in a sublimer at 65-70 °C (1-0.2 mm) for 20 hrs. No sublimable product appeared, and the off gases were indicated by IR to be CO with no fluorocarbon present. The residual product **8** now darkened on exposure to moist air. IR (KBr): 2150, 2020 (sh), 2090, and 2060 (coordinated CO), 1155, 1090 and 1020 cm^{-1} (CF). Anal. Calcd. for $C_{11}F_8Fe_2I_2O_2$: C, 17.35; F, 19.96; Fe, 14.67; I, 33.33 Found: C, 17.30; F, 19.79; Fe, 14.96; I, 33.02

Vacuum pyrolysis of **8** was carried out by heating a sample slowly from 100-210 °C. The pressure rose to 4 mm and then dropped while free iodine and small amounts of fluorocarbons were collected in a -80 °C trap and traces in a -196 °C trap. GC showed over 10 components to be present and the complex IR spectrum displayed prominent absorptions for Fe-CO, C=O, C=C and CF.

F-Hexyl Radical Formation in Benzene to Give F-(Hexyl)benzene (9)

A mixture of 14.6g (0.10 mol) of iron pentacarbonyl and 49.0g (0.11 mol) of *F*-*n*-hexyl iodide in 100 mL of benzene as solvent was stirred under nitrogen at 65-70 °C for 2 days, after which time CO evaluation was practically nil and red precipitate was present. Volatiles were transferred with the pot eventually at 100 °C (0.5 mm). Further heating to 160 °C (0.5 mm) gave a small amount of I_2, but little additional liquid product. Fractionation of volatiles removed at 25 °C afforded only benzene and 2.8g of **9** containing some **10**, bp 57 °C (5.6 mm). Fractionation of volatiles removed at 80-100 °C afforded 6.2g of a 70:30 mixture of **9/5**, bp 54-55 °C (5.2 mm), identified by IR and NMR, followed by 8.3g of **9** + **10**, bp 55 °C (5.2 mm) [8]. For **9** + **10**, IR (neat): 3070 and 3050 (unsat'd CH), 1605, 1500, and 1460 (aliph. and arom C=C), 1250-1150 cm^{-1} (CF). HPLC: single component with ca.

6% of impurity (**10**) present. For **9**, NMR (CCl_4): ^1H δ 7.44 (m, arom, $C\mathit{H}$); ^{19}F ϕ -81.7 (t of t, J_{FF} 10.0, 2.5 Hz, 3F, $C\mathit{F}_3$), -111.5 (t of m, J_{FF} 15 Hz, 2F, $C\mathit{F}_2$-ø), -122.2 (broad m, 4F, $2C\mathit{F}_2$), -123.3 (m, 2F, $C\mathit{F}_2$), -126.8 (m, 2F, $C\mathit{F}_2$). For **10**, NMR (CCl_4): ^1H δ 5.98 (AA' branch d of m, J_{HH} 10Hz, 2H, $=C\mathit{H}$), 5.67 (BB' branch d of m, J_{HH} 10Hz, 2H, $=C\mathit{H}$), 3.57 (broad m, 1H, $C\mathit{H}$), 2.69 (m, 2H, $C\mathit{H}_2$), ^{19}F ϕ -81.7 (t of t, J_{FF} 10.0, 2.5 Hz, 3F, $C\mathit{F}_3$), -115.4 (t, J_{FF} 16Hz, of d, J_{HF} 15 Hz, of rough p, J_{FF} 4.5 Hz, 2F, $C\mathit{F}_2CH$), -120.9 (m, 2F, $C\mathit{F}_2$), -122.2 (m, 2F, $C\mathit{F}_2$), -123.3 (m, 2F, $C\mathit{F}_2$), -126.8 (m, 2F, $C\mathit{F}_2$). The NMR indicated about 10% of **10** to be present. Anal. Calcd. for $C_{12}H_5F_{13}$: C, 36.38; H, 1.27; F. 62.34 Found: C, 36.18; H, 1.26; F, 61.63

The reaction thus produced 15.2g (35%) of the aromatic derivative **9** containing some dihydro product **10**, and an appreciably lesser amount (2.1g, 4%) of diiodide **5**.

Thermolysis of Preformed 3 in Benzene

A mixture of 14.6g (0.10 mol) of iron pentacarbonyl and 49.0g (0.11 mol) of *F-n*-hexyl iodide was heated under nitrogen at 60-65 °C for one day. Volatiles (8 mL) were removed under vacuum at 25 °C, the residual solid was blanketed with nitrogen, and 50 mL of benzene was added. On heating to 70-80 °C, CO evolution became pronounced. The mixture was held at 80 °C for 13 hr, during which time CO evolution stopped and red solid precipitated, then was converted to light tan solid. Distillation of volatiles and GC analysis showed benzene (containing an indeterminate amount of $F(CF_2)_6I$) and 4g (10%) of monoiodide **4** as first fraction, bp 80 °C. Further fractionation afforded 10.5g of an 86/14 mixture of diiodide **5**/aryl compound **9**, bp 57-58 °C (6.4 mm), determined by NMR, so that 9.0g (17%) of diiodide **5** versus 1.5g (4%) of aryl derivative **9** was formed.

REFERENCES

1 (a) Contribution No. XXXX; (b) Dedicated to Professor W. K. R. Musgrave on the event of his 70th birthday.

2 R. B. King, S. L. Stafford, P. M. Treichel and F. G. A. Stone, J. Am. Chem. Soc., ***83***, (1961) 3604.

3 See A. E. Feiring, J. Org. Chem., ***48***, (1983) 347 for examples of known $S_{RN}1$ processes involving *F*-alkyl iodides and for leading references.

4 I. I. Gerus, Yu. L. Yagupol'skii, L. M. Yagupol'skii, Zh. Org. Khim, ***21(9)***, (1985) 1852 [C.A., ***105***, (1986) 190550m] report reactions of $R_FFe(CO)_4I/AgF$ or $R_FFe(CO)_4I/Hg(O_2CCF_3)_2$ with simple aromatics at 20-50 °C to give "moderate yields," e.g. 16%, of perfluoroalkylated aromatic. Interestingly, $(CF_3CF_2CF_2)_2Fe(CO)_4$ also *F*-propylated toluene at 110 °C in 21% yield.

5 (a) T. G. Richmond and D. F. Shriver, Organometallics, ***2***, (1983) 1061;
(b) D. L. Reger and M. D. Dukes, J. Organometall. Chem., ***153***, (1978) 67;
(c) T. G. Richmond and D. F. Shriver, Organometallics, ***3***, (1984), 305;
(d) A. M. Crespi and D. F. Shriver, Organometallics, ***4***, (1985) 1830.

6 IR spectra were recorded on 10% solutions unless otherwise indicated. NMR spectra were taken on 20% solutions with tetramethylsilane and trichlorofluoromethane as internal references. Downfield shift directions were taken as positive.

7 Identical ^{19}F NMR spectrum to that of a known mixture of isomers; detailed characterization to be published.

8 *F*-(Hexyl)benzene is a known compound whose synthesis is reported in ref. 3.