Journal of Fluorine Chemistry, 39 (1988) 217–226

Received: September 28, 1987; accepted: January 11, 1988

STUDIES ON FLUOROALKYLATION AND FLUOROALKOXYLATION. PART 26. WILKINSON'S CATALYST-INDUCED ADDITION OF FLUOROALKYL IODIDES TO OLEFINS

Qing-Yun CHEN* and Zhen-Yu YANG

Shanghai Institute of Organic Chemistry, Academia Sinica
345 Lingling Lu, Shanghai (China)

SUMMARY

Addition of fluoroalkyl iodides to olefins in the presence of tris(triphenylphosphine)chlororhodium (I) in benzene or acetonitrile gives the corresponding 1:1 adducts in good yields. The reaction can be suppressed with p-dinitrobenzene (p-DNB) or di-t-butylnitroxide, and tetrahydrofuran derivatives are obtained from the reaction of fluoroalkyl iodides with diallyl ether. A radical chain-reaction mechanism induced by single electron transfer (SET) is proposed.

INTRODUCTION

Recently, several new methods for fluoroalkylation have been discovered which utilize transition metal salts or complexes as catalysts under mild conditions. Fuchikami and Ojima [1] and Werner [2] have reported that the addition of fluoroalkyl iodides to olefins or alkynes can be catalyzed by transition metal carbonyl compounds. We [3] have described the same reaction in the presence of copper in acetic anhydride, diglyme or acetonitrile. It was also found that fluoroalkylation of olefins and alkynes with fluoroalkyl iodides in the presence of palladium [4], platinum [5], iron [6], zinc[7], magnesium [8] and Raney nickel [9] occurs under mild conditions to give adducts in excellent yields. Herein, we wish to report the results of the reaction of fluoroalkyl iodides with olefins catalyzed by Wilkinson's catalyst.

0022-1139/88/$3.50

RESULTS AND DISCUSSION

Tris(triphenylphosphine)chlororhodium (I) is known as an effective catalyst for the homogenous hydrogenation of olefins and alkynes [10]. We found that it can also be used as a catalyst in the addition of fluoroalkyl iodides to olefins giving good yields of adducts under mild conditions.

$$\underset{\underline{1}}{R_fI} + \underset{\underline{2}}{CH_2{=}CRR'} \xrightarrow{RhCl(PPh_3)_3} \underset{\underline{3}}{R_fCH_2CIRR'}$$

R_f:$Cl(CF_2)_4$ (a),$F(CF_2)_4$ (b),$F(CF_2)_6$ (c),$Cl(CF_2)_6$ (d),$Cl(CF_2)_2$ (e)
$\underline{2}$: $n\text{-}C_5H_{11}CH{=}CH_2$(l), $(CH_2CH{=}CH_2)_2$(f), $n\text{-}C_6H_{13}CH{=}CH_2$(h)
$n\text{-}C_4H_9CH{=}CH_2$(i),$Me_2CCH_2CH{=}CH_2$(j),$O(CH_2CH{=}CH_2)_2$(m),$CH_2C{=}CMeEt$(g)

For example, when 4-chlorooctafluorobutyl iodide reacted with hept-l-ene in the presence of 1 mol% of $RhCl(PPh_3)_3$ in benzene at 90°C for 1.5h, the conversion was 84% and the selectivity was 93%. The reaction proceeded rather slowly at room temperature, and did not take place at 0°C. The optimal temperature was 80°C.

The Rh(I) complex-catalyzed addition of fluoroalkyl iodides to olefins shows higher chemical selectivity.When fluoroalkyl iodides reacted with olefins having an electron-donating group, such as 2-methylbut-l-ene, the conversion and yield were higher. But the reaction with olefins bearing an electron-withdrawing group, such as a (perfluoroalkyl)ethylene, did not take place under the same conditions. Fluoroalkyl iodides reacted with dienes, i.e. hexa-1,5-diene,to form only mono(fluoroalkylated) adducts. The reaction with nonterminal olefins, such as cyclohexene was slow and the conversion was also lower (30%) (Table).Fluoroalkyl bromides and chlorides did not react with olefins at 80 to 110°C.

The reaction of fluoroalkyl iodides with styrene in the presence of a Rh(I) complex in benzene gave only non-volatile amorphous solids (the conversions of iodides was ~40%).The ^{19}F NMR spectra showed clear indication of attachment of a fluoroalkylated group to carbon. This phenomenon is quite similar to that observed in the analogous reactions catalyzed by copper [3].

TABLE

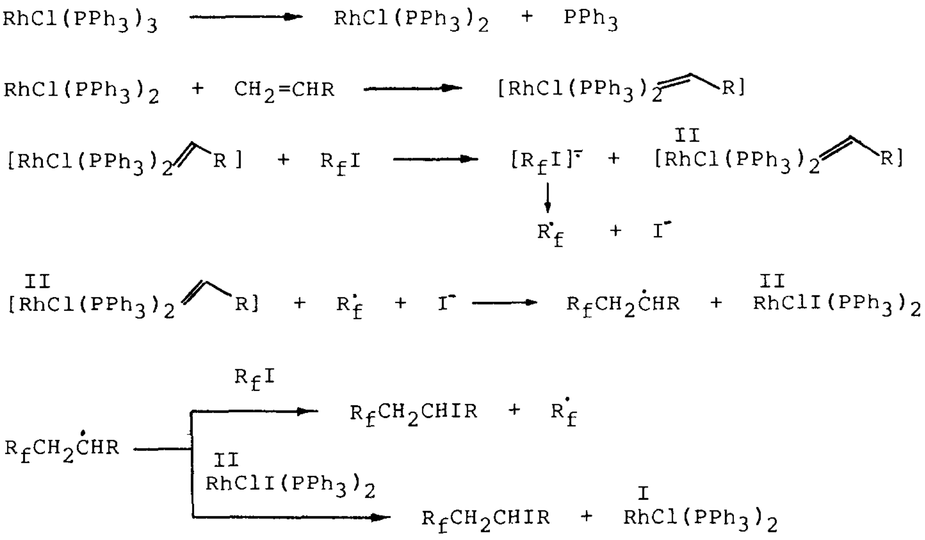
Fluoroalkyl iodides treated with olefins in the presence of $RhCl(PPh_3)_3$[a]

R_fI	Olefin	t(min)	Conv.(%)[b]	Adduct(%)[c]
1a	2l	90	84	92
1a	2l	205	81	91
1a	2i	205	80.0	86.5
1a	2i	205	80[d]	92
1a	2i	205	50[e]	90.5
1a	2i	205	7.8[f]	95
1a	2f	270	60	81
1a	2g	120	100	92
1a	2h	90	95	93
1a	2m	60	85	82
1b	2i	180	81	89
1b	2e	150	95	81
1b	2f	240	50	84
1c	2g	150	86	88
1d	2g	90	85	93
1d	2j	240	65	80
1e	2g	240	67	68
1e	2m	150	86	80

[a] In benzene at 80°C; R_fI:Olefin:Rh(I)=1:4:1%; [b] determined by ^{19}F NMR; [c] isolated yield; [d] in CH_3CN; [e] 20 mol% of p-DNB was added; [f] 2 mol% of $(t\text{-}Bu)_2NO$ was added.

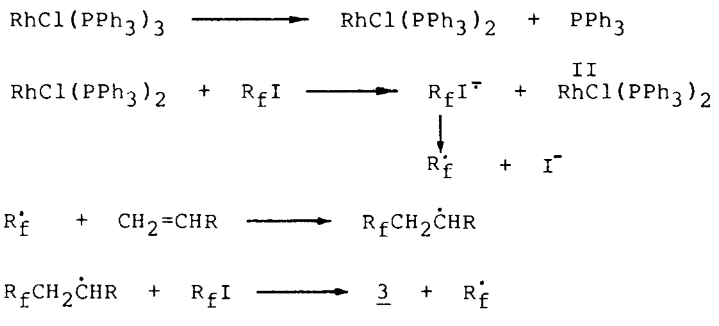
It is well-known that ring closure in the exo-mode from a hex-5-enyl radical is an excellent probe for elucidating mechanism [3]. Reaction of fluoroalkyl iodides with diallyl ether (DAE) afforded a tetrahydrofuran derivative. Addition of a free radical inhibitor, e.g. di-t-butylnitroxide, to the reaction mixture suppressed the reaction. For example, when 4-chlorooctafluorobutyl iodide reacted with hept-1-ene in the presence of 1 mol% $RhCl(PPh_3)_3$ and 2 mol%

di-t-butylnitroxide (relative to fluoroalkyl iodide) at 80°C for 205 min, the conversion was only 7.8% (see Table). These results seem to show that the mechanism may involve a single electron transfer process as shown in Scheme 1.



Scheme 1

The complex, $RhCl(PPh_3)_3$, dissociates in solution to form $RhCl(PPh_3)_2$ [11], which has a vacant site for olefin coordination. The complex then transfers its electron to the iodide to form a radical anion, which decomposes to produce a radical. An alternative explanation is that one electron transfer from $RhCl(PPh_3)_2$ to fluoroalkyl iodide occurs directly to yield the corresponding radical, which then adds to olefin to give the product (Scheme 2).



Scheme 2

Atom transfer(redox transfer) may be another possible mechanism [12] but is excluded by the following evidence: Addition of an SET scavenger, e.g.p-dinitrobenzene(p-DNB),to the reaction mixture decreased the conversion of fluoroalkyl iodide to 50% as compared with that of the control (see Table).

In order to distinguish the possible mechanisms (Scheme 1 and 2), further studies were carried out. According to Wilkinson [11] $RhCl(PPh_3)_3$ dissociates and then reacts with a strongly coordinating solvent(L), such as pyridine and acetonitrile, to give $RhCl(PPh_3)_2L$, which cannot catalyze the hydrogenation of an olefin at 25°C under one atmosphere pressure of hydrogen because no vacant site exists for an olefin to coordinate at. By analogy, one may argue that if olefin complexation is a preliminary step in the present reaction, reaction should not occur if acetonitrile is used as solvent. However, it was found that both the conversion and rate in CH_3CN were almost the same as those in benzene. Therefore, the reaction is likely to follow Scheme 2.

It is worth noting that in the reaction of 2-chlorotetrafluoroethyl iodide with olefins induced by a Rh(I) complex, a good yield of adducts was also obtained. No tetrafluoroethene was detected. The phenomenon is different from that in the reactions of 2-chlorotetrafluoroethyl iodide with olefins induced by enolate anion and AIBN[13], Cu[3] or $Na_2S_2O_4$[14], in which the yields of adducts were rather lower (20-40%). This has been interpreted in terms of the β-fragmentation of the 2-halotetrafluoroethyl radical [13,15]. In order to explain these results, the single electron transfer process and the consequent steps involving radical pairs may be suggested as follows:

$$\mathrm{RhCl(PPh_3)_3} + \mathrm{R_fI} \xrightarrow{\mathrm{-PPh_3}} \mathrm{[R_fI]^{\cdot -}[RhClI(PPh_3)_2]^{\cdot +}}$$

$$\mathrm{[R_fI]^{\cdot -}[RhClI(PPh_3)_2]^{\cdot +}} \longrightarrow \mathrm{[R_f^{\bullet}\ ][\overset{II}{Rh}ClI(PPh_3)_2]}$$

$$\mathrm{[R_f^{\bullet}\ ][\overset{II}{Rh}ClI(PPh_3)_2]} + \mathrm{CH_2{=}CHR} \longrightarrow \mathrm{[R_fCH_2\dot{C}HR][\overset{II}{Rh}ClI(PPh_3)_2]}$$

$$\mathrm{[R_fCH_2\dot{C}HR][\overset{II}{Rh}ClI(PPh_3)_2]} + \mathrm{PPh_3} \longrightarrow \mathrm{R_fCH_2CHIR} + \mathrm{RhCl(PPh_3)_3}$$

$$\mathrm{[R_fCH_2\dot{C}HR][\overset{II}{Rh}ClI(PPh_3)_2]} \longrightarrow \mathrm{R_fCH_2\dot{C}HR} + \mathrm{RhClI(PPh_3)_2}$$

$$\mathrm{R_fCH_2\dot{C}HR} + \mathrm{R_fI} \xrightarrow{\mathrm{RhClI(PPh_3)_2}} \underline{3} + \mathrm{[R_f^{\bullet}\ ][RhClI(PPh_3)_2]}$$

Scheme 3

$RhCl(PPh_3)_3$ transfers an electron to the fluoroalkyl iodide to form an ion pair, which decomposes to produce a radical pair. The radical pair reacts with olefin to generate a new radical pair, which abstracts iodine from $RhClI(PPh_3)_3$ to give the product or decomposes to give $R_fCH_2\dot{C}HR$.The resultant radical abstracts iodine from fluoroalkyl iodide to yield product. For easily polymerizable olefins the chain propagation process is much faster than the chain transfer,and hence a fluorine-containing polymer is obtained.

EXPERIMENTAL

All boiling points are uncorrected. Analytical GC spectra were performed on a Shanghai Analytical Factory model 103 with a column packed with oxa-perfluoroalkylene triazine polymer on 100 mesh Diatomite 102 support.The infrared spectra were recorded on a Carl Shimadzu IR-440 spectrometer. NMR spectra (chemical shift in ppm from external TMS for ^1H, and from TFA for ^{19}F NMR, positive for upfield shifts) were recorded on an EM-360 NMR spectrometer (60 MHz). Mass spectra were taken on Finnigan GC-MS-4021.

General procedure

The following procedure for the fluoroalkylation of olefins is typical: $RhCl(PPh_3)_3$ (46.3mg, 0.05 mmol), heptene-1 (2i), (1.0 g, 10.2 mmol), and 2 ml of benzene were placed in a Pyrex tube fitted with a screw cap and the atmosphere was replaced by nitrogen. 4-chlorooctafluoroiodobutane (1a), (1.8 g, 5 mmol) was introduced and the mixture was stirred at 80°C for 1.5 h. ^{19}F NMR spectra showed that the conversion was 84%. Distillation of the product in vacuum gave the adduct 3ai, 2.1g. All the products were identified by comparison of their b.p., ^{1}H and ^{19}F NMR, and mass spectra with the corresponding authentic compounds [16]. Analytical data for new compounds are given below.

3bi: b.p. 70 °C/7mmHg, ^{1}H NMR δ 2.25(m,1H), 2.13-1.50(m,2H), 1.70-0.90(m,9H); ^{19}F NMR δ 4.0(3F), 36.2(2F), 47.2(2F), 48.7 (2F); IR (neat): 2980, 2920, 1160, 1100, 950 cm^{-1}; m/e: 303, 127, 119, 69, 55, 44, 41; Analysis, Found: C, 28.1, H, 2,50, I, 29.58; $C_{10}H_{12}F_9I$, Calc. C, 27.92, H, 2.81, I, 29.51%.

3bf: b.p.84°C/15mmHg, ^{1}H NMR δ 4.7-5.8(m,3H), 4.18(m,1H), 1.5-3.0 (m,6H); ^{19}F NMR δ 3.8(3F),36.0(2F), 47.1(m,1F), 48.5(2F); IR(neat) 3020, 2950, 1640, 1230, 1135,880 cm^{-1}; m/e: 428, 301, 273, 81, 67, 41; Analysis,Found: C,28.24, H,2.33, F,39.81, I,30.06; $C_{10}H_{10}F_9I$, Calc., C, 28.05, H, 2.35, F, 39.94, I, 29.64%.

3cg: b.p.80-82°C/8mmHg; ^{1}H NMR δ 2.85(t,2H),2.07(s,3H),1.15(q,2H), 1.04(t,3H); ^{19}F NMR δ 4.0(3F),34.0(2F),44.5(2F),46.1(2F),49.3(2F); IR(neat): 2980, 2940, 1460, 1360, 1260-1120, 1070, 820 cm^{-1}; m/e: 389, 301, 119, 69, 65, 55, 43, 41; Analysis, Found, C, 25.94, H, 1.86, F,47.36, I, 23.93; $C_{11}H_{10}F_{13}I$, Calc., C, 25.60, H, 1.95, F, 47.86, I, 24.95%.

3dg: b.p. 107-108°C; ^1H NMR δ 2.94(t,2H), 2.15(s,3H), 1.71(q,2H), 1.07(t,3H); ^{19}F NMR δ -10.0(s,2F), 33.4(2F), 42.5(2F), 43.5(2F), 45.7(2F); IR(neat): 2980, 2920, 1210, 1150, 1120, 1070 cm^{-1}; m/e: 405, 407, 389, 127, 85, 75, 69, 61, 55, 41; Analysis, Found: C, 25.54, H,1.80, F,43.42; $C_{11}H_{10}F_{12}ClI$, Calc., C, 24.81, H, 1.89, F, 42.81%.

3ah: b.p. 120-122°C/8mmHg; ^1H NMR δ 4.28(m,1H), 3.16-2.40(m,2H), 1.60-0.90(m,13H); ^{19}F NMR δ -10.0(2F), 35.5(2F), 42.0(2F), 45.0 (2F); IR(neat): 2940, 2910, 2840, 1190, 1130 cm^{-1}; m/e: 347, 307, 305, 85, 71, 57, 43; Analysis, Found: C, 30.37, H, 3.37, F, 32.03; $C_{12}H_{12}F_{12}ClI$, Calc., C, 30.36, H, 3.54, F,31.09%.

3dj: b.p. 112-114°C/8mmHg; ^1H NMR δ 4.20(m,1H), 3.10-2.30(m,2H), 1.70-1.00(m,3H), 0.90(t,6H); ^{19}F NMR δ -9.6(2F), 34.8(2F), 42.6 (2F), 43.7(2F), 46.0(2F); IR(neat): 2940, 2910, 2850, 1470, 1370, 1200, 1140, 1120, 1080 cm^{-1}; m/e: 419, 421, 1127, 85, 69, 55, 44, 41; Analysis, Found:C,26.95, H,2.09, F,42.35; $C_{12}H_{12}F_{12}ClI$, Calc., C,26.37, H, 2.21; F, 41.71%.

3eg: b.p. 90-92°C/40mmHg; ^1H NMR δ 2.00(t,2H),2.20(s,3H), 1.77(q, 2H), 1.15(t,3H); ^{19}F NMR δ -6.5(2F), 33.0(2F); IR(neat): 2980, 2950, 1460, 1385, 1255, 1150, 1110, 1080, 950 cm^{-1}; m/e: 205, 207, 127, 91, 85, 69, 55, 41; Analysis, Found: C, 25.55, H, 3.03, F, 21.90; $C_7H_{10}F_4ClI$, Calc., C, 25.28, H, 3.03, F, 22.85%.

3em: b.p. 114-116°C/8mmHg; ^1H NMR δ 4.20-2.00(m); ^{19}F NMR δ -7.5 (2F),35.0(2F); IR(neat): 2950, 2850, 1435, 1255, 1210, 1150, 1080, 940 cm^{-1}; m/e: 361, 233, 235, 215, 203, 127, 73, 67, 43, 41; Analysis, Found: C,26.70, H,2.70, F, 20.34; $C_8H_{10}F_4ClIO$, Calc., C, 26.65, H, 2.80, F, 21.08%.

Experiments on inhibition of Rh(I)-complex catalyzed reaction of 4-chlorooctafluoroiodobutane with hept-1-ene by di-t-butylnitroxide or by p-dinitrobenzene

i) $RhCl(PPh_3)_3$ (23.3 mg,0.025 mmol),di-t-butylnitroxide,(7.3 mg, 0.05 mmol), hept-1-ene (0.5 g,5.1 mmol) and 1 ml of benzene were placed in a Pyrex tube fitted with a screw cap. The atmosphere was replaced by N_2, then 4-chloroperfluorobutyl iodide, 910 mg (2,51 mmol) was introduced, and the mixture was stirred at 80°C for 3.5 h. ^{19}F NMR spectral analysis showed that the conversion was 8%.

ii) $RhCl(PPh_3)_3$(23.3 mg, 0.0255 mmol), p-DNB(16 mg, 0.095 mmol), hept-1-ene (0.5 g, 5,1 mmol) and benzene (1 ml) were placed in a Pyrex tube fitted with a screw cap, and the atmosphere was replaced by N_2. 4-Chloroperfluorobutyl iodide (900mg, 2.5 mmol), was introduced and the mixture was stirred at 80°C for 3.5 h. ^{19}F NMR spectral analysis showed that the conversion was 56%.

ACKNOWLEDGEMENT

We would like to thank Professor Wei-Yuang Huang for his encouragement of this work. Thanks are also owed to the Chinese National Science Fund for support.

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