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REACTION OF PERFLUOROALKYL IODIDES WITH ALKENES INITIATED BY ORGANOPHOSPHINE AND RELATED COMPOUNDS

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SUMMARY

Perfluoroalkyl iodides reacted with alkenes in acetonitrile solution containing catalytic amounts of an organophosphine under mild conditions to give the corresponding adducts in moderate to high yields. Addition of hydroquinone to the reaction mixture suppressed the reaction. Diallyl ether reacted to afford tetrahydrofuran derivatives. These findings indicated that the reaction involved a free radical mechanism.

INTRODUCTION

The addition of perfluoroalkyl iodides to alkenes is one of the most important procedures for perfluoroalkylation [1]. It can be initiated by thermolysis, photolysis, peroxides and other radical initiators [2], various metal and metal complexes [3-5], metal salt-amine systems [6,7], sodium dithionate and related reagents [8,9] and triethyl borane [10]. In further searching of new type of electron donors in these electron transfer (ET) reactions, we found that organophosphines (R_3P) such as triphenyl phosphine, ethyl phosphite and related compounds can effectively initiate the addition of perfluoroalkyl iodides to alkenes in acetonitrile solution.

Triphenyl phosphine is a widely used reagent. It was able to transfer single electron to compounds such as chloranil [11], TCNQ [12] to form the corresponding radical ion pairs. It reacted with perfluoroalkyl halides to form the phos-

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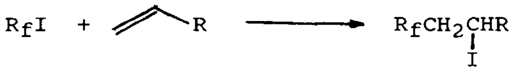
phonium salts by heating in acetonitrile [13], but there was no mention of the mechanism of the latter reaction. Herein, we wish to report the results of the reaction of perfluoroalkyl iodides with alkenes catalyzed by triphenyl phosphine or other related compounds. The possible mechanism involving single electron transfer process has also been discussed.

RESULTS AND DISCUSSION

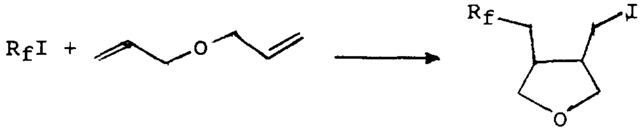
In the presence of catalytic amounts of triphenyl phosphine, perfluoroalkyl iodides reacted with terminal alkenes readily to form 1:1 adducts in moderate to good yields. The yields and reaction conditions were shown in Table 1.



1 **2**, R=n-C_4H_9 **4**, R=n-C_4H_9
3, R=n-C_6H_{13} **5**, R=n-C_6H_{13}

R_f = C_6F_{13}, a; $Cl(CF_2)_4$, b; $Cl(CF_2)_6$, c; $FSO_2(CF_2)_2O(CF_2)_8$, d; C_8F_{17}, e; $FSO_2(CF_2)_2O(CF_2)_2$, f.

The reaction of perfluoroalkyl iodides with diallyl ether gave the tetrahydrofuran derivatives 7, indicating a free radical pathway.

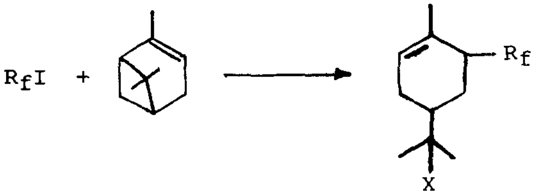


1 **6** **7**

On prolonged reaction time, the reaction could also be applied to disubstituted olefins such as cyclohexene

8 **9**

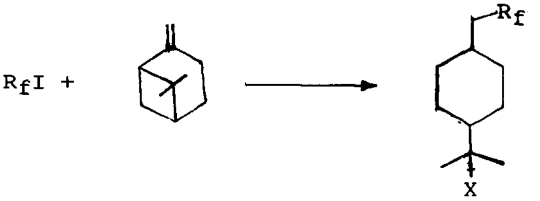
Perfluoroalkyl iodide 1f added to α-pinene **10** to give the rearrangement product **11**, which was reduced by Zn/EtOH to **12** for purification.



10

11, X=I
12, X=H

Similarly, perfluoroalkyl iodide 1b added to β-pinene **13**, followed by reduction with Zn/EtOH to give **15** as pure form.

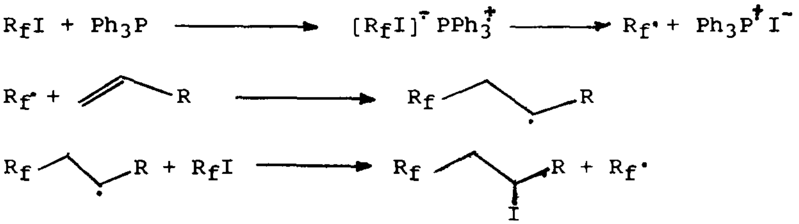


13

14, X=I
15, X=H

In the presence of 10% equiv. of hydroquinone, the above addition can be completely suppressed.

All these results seem to indicate that the reaction may involve a free radical chain mechanism initiated by triphenyl phosphine as an electron donor, thus:



The solvent used seems to play quite an important role in determinating the course of the reaction. It was shown that acetonitrile was the most suitable solvent, whereas in DMF or THF, the reaction proceeded much slower and part of the perfluoroalkyl iodide was reduced to R_fH.

TABLE 1

Ph_3P - catalyzed reaction of R_fI with alkenes

R_fI	Alkene	Cat(mol%)	Time(h)	Product[a]	Yield(%)[b]
1a	**2**	20	4	**4a**	79
1b	**2**	20	4	**4b**	81
1c	**2**	20	4	**4c**	83
1d	**2**	20	3.5	**4d**	87
1b	**3**	25	4.5	**5b**	75
1c	**3**	25	4.5	**5c**	77
1a	**6**	15	6	**7a**	74
1b	**6**	15	6	**7b**	79
1c	**6**	15	6	**7c**	80
1e	**6**	15	6.5	**7e**	72
1b	**8**	20	8	**9b**	54
1c	**8**	20	8	**9c**	57
1f	**10**	20	12	**12f**	28
1b	**13**	20	10	**15b**	47

[a] All these reactions were carried out at 70-75°C.

[b] Isolated yield.

It was shown that various other trivalent phosphorous compounds such as triethyl phosphite can be used in place of triphenyl phosphine to initiate the addition of perfluoroalkyl iodides to alkenes (Table 2). But, tris(diethylamino)phosphine was different in that it caused mainly the reduction of perfluoroalkyl iodides into R_fH either in acetonitrile or in DMF or CH_2Cl_2. Obviously the high electron density on phosphorus atom in tri(diethylamino)phosphine may be responsible for such a difference [14].

We have further studied the same reaction using analogous group VA compounds, such as triphenyl arsine, various amines and hydroxyamine. The results showed that among these compounds, hydroxyamine was most promising. It initiated the addition reaction (Table 3), whereas in using diethylamine or triethylamine as initiator, the results were complicated by the simultaneous occurrence of several side reactions such as the elimination of HI from the adducts formed and the reduction of

TABLE 2

$(EtO)_3P$, Bu_3P - initiated reaction of R_fI with alkenes

R_fI	alkene	cat[a]	time(h)[b]	product	yield(%)
1b	**2**	$(EtO)_3P$	4	**4b**	75
1b	**6**	$(EtO)_3P$	6	**7b**	71
1b	**2**	Bu_3P [c]	6	**4b**	72
1b	**6**	Bu_3P [c]	6	**7b**	68

[a] 25 mol% of catalytic amounts of R_3P were used.

[b] All these reactions were carried out at 70-75 C.

[c] Added in portions at two hours' time interval.

TABLE 3

NH_2OH - initiated reaction of R_fI with alkenes

R_fI	alkene	time(h)	product	yield(%)
1b	**2**	5	**4b**	81
1b	**6**	5	**7b**	75

perfluoroalkyl iodides into R_fH. Triphenyl arsine can also initiate the addition reaction,but very slowly(^{19}F NMR monitoring).

Thus, results of the present work furnished some more readily available donor reagents useful in the initiation of the addition of R_fI to alkenes under mild condition and easily carried out with good yields either in anhydrous acetonitrile or in aqueous acetonitrile.

EXPERIMENTAL

All melting point were uncorrected. IR spectra were recorded on a Carl Diatomite IR-440 spectrometer. ^{19}F NMR spectra were recorded on a Varian EM-360L spectrometer at 60MHz using TFA as external standard. Chemical shifts in ppm were positive for upfield shifts. The values reported were δ F= δ TFA +76.8ppm. ^1H NMR spectra were recorded on a EM-360A instrument at 60MHz, using TMS as external standard. MS spectra

were obtained on a EM-4021 spectrometer. Triphenyl phosphine was recrystallized from ethanol. Column chromatography was performed on silical gel (10-40μ).

General procedure

The following procedure for Ph_3P - initiated reaction of R_fI with alkene is typical: A mixture of 4.46 g (10 mmol) **1a**, 1.68 g (20 mmol) **2**, 0.52 g (2 mmol) triphenyl phosphine and 25 ml acetonitrile was stirred at 75°C for 4 hours.The solvent was distilled off under reduced **pressure.** The residue was purified through a short chromatographic column (eluent: petroleum ether) to give 4.1 g (79%) **4a**. All the known products were identified by comparison of their IR, ^1H and ^{19}F NMR, and mass spectra with the corresponding authentic specimens [5, 8,15,16]. Analytical data for new compounds are given below.

4a: ^1H NMR $\delta(CCl_4)$: 0.95 (3H, t, CH_3), 1.3-1.8 (6H, m,3 x CH_2), 2.4-3.3 (2H, m, CH_2CF_2), 4.2-4.6 (1H, m, CHI) ppm; ^{19}F NMR $\delta(CCl_4)$: 81.2 (3F, t, CF_3), 113.3 (2F, CF_2CH_2), 126.4 (2F, CF_2CF_3), 121.9-123.3 (6F, other 6F) ppm.; IR(neat): 2865-2960 (C-H), 1190 (C-F) cm^{-1}; m/e: 530 (M), 529 (M-1), 403 (M-I); Analysis, Found: C, 27.13, H, 2.32, F, 46.76%; $C_{12}H_{12}F_{13}I$, Calcd.: C, 27.20, H, 2.28, F, 46.59%.

4d: ^1H NMR $\delta(CCl_4)$: 0.96 (3H, t,CH_3), 1.3-1.85 (6H, m,3 x CH_2), 2.4-3.3 (2H, m, CH_2CF_2), 4.2-4.6 (1H, m, CHI) ppm; ^{19}F NMR $\delta(CCl_4)$: -45.8(1F, FSO_2), 82.3(4F, CF_2OCF_2), 112.1(2F, CF_2SO_2F), 113.0 (2F, CF_2CH_2), 121.5-124.8 (12F, m, other 12F) ppm; IR (neat): 2880-2990 (C-H), 1470 (SO_2F), 1190 (C-F) cm^{-1}; m/e: 811 (M+1), 809 (M-1), 684 (M+1-I); Analysis, Found: C, 23.58, H, 1.51, F, 48.96%; $C_{16}H_{12}F_{21}IO_3S$, Calcd.: C, 23.72, H, 1.49, F, 49.26.%.

7e: ^1H NMR $\delta(CHCl_3)$: 4.20-2.02 (m) ppm; ^{19}F NMR $\delta(CHCl_3)$: 81.3 (3F, CF_3), 113.6 (2F, CF_2CH_2), 126.3 (2F, CF_2CF_3), 121.8-123.3 (10F, other 10F) ppm; IR(neat): 2860-2890 (C-H), 1190 (C-F)

cm^{-1}; m/e: 644 (M), 517 (M-I); Analysis, Found: C, 26.06, H, 1.34, F, 51.48%; $C_{14}H_{10}F_{17}IO$, Calcd.: C, 26.09, H, 1.56, F, 50.15%.

Typical procedure for $(EtO)_3P$ - initiated reaction of R_fI with alkene

A mixture of 3.63 g (10 mmol) **1b**, 1.68 g (20 mmol) **2**, 0.42 g (2.5mmol) triethyl phosphite and 30 ml acetonitrile was stirred at 70-75°C for 4 hours. The solvent was distilled off under reduced pressure, the residue was purified through a short column (eluent: petroleum ether) to give 3.35 g **4b**, yield 75%.

Typical procedure for Bu_3P - initiated reaction of R_fI with alkene

A mixture of 3.63 g (10 mmol) **1b**, 1.68 g (20 mmol) **2**, 0.3 g (1.5 mmol) tributyl phosphine and 25 ml acetonitrile was stirred at 75°C. 2 hours later, another portion of tributyl phosphine was added to the mixture, and the reaction was continued for other 3 hours.The solvent was distilled off under reduced pressure, the residue was purified through a short chromatography column (eluent: petroleum ether) to give 3.2 g **4b**, yield 72%.

Typical procedure for NH_2OH - initiated reaction of R_fI with alkene

A mixture of 3.63 g (10 mmol) **1b**, 1.68 g (20 mmol) **2**, 5 ml aqueous hydroxyamine (prepared from the neutralization of 0.35 g hydroxyammonium chloride with 0.7 g potassium carbonate in 5 ml water), and 25 ml acetonitrile was stirred at 75°C for 6 hours. Then, 20 ml water was added to the mixture, and the mixture was extracted with ether, the ethereal solution was washed with water and dried with anhydrous $MgSO_4$. After removal of the solvent by distillation, the crude product was purified through a short chromatography column (eluent: petroleum ether) to give 3.6 g **4b**, yield 81%.

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