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SYNTHESIS OF ALKYL PERFLUOROALKYL KETONES REACTIONS OF ALLYL PERFLUOROALKANOATES WITH ACYL CHLORIDES IN THE PRESENCE OF PALLADIUM(0)

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SUMMARY

The reactions of fluorocarbanions derived from palladium(0) mediated decomposition of allyl esters of fluoroalkylether acids, $R_fCO_2CH_2CH=CH_2$ ($R_f=C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)$, n=0,1), with acyl chlorides yielded enol esters of hemifluorinated ketones, $RR'C=C(R_f)OCOCHRR'$, n=0, **4**; n=1, **5**, plus a very small amount of the ketones $R_fCOCHRR'$, n=0, **6**; n=1, **7**, or allyl ketones, $R_fCOCHRCH_2CH=CH_2$, **8**, with a small amount of diallyl ketones, $R_fCOCR(CH_2CH=CH_2)_2$, **9**, depending on the reaction conditions employed. Esters **4**, **5** could be converted to ketones **6**, **7** in excellent yields with concentrated sulfuric acid.

INTRODUCTION

The synthesis of fluoroalkyl containing ketones has offered a useful transformation for the introduction of fluoroalkyl groups to organic molecules. During the past decade, considerable progress in this area of research has been made by Tamborski et al [1-6]. However, except for the preparation of aryl fluoroalkyl ketones [2,7,8], organometallics were generally involved in such preparations [9]. Recently, we have reported [10] that treatment of the $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2R$ type esters with LiCl/HMPA complex led to facile decarboalkoxylation and the forma-

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tion of fluorocarbanions of the type $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)^-$ which, upon trapping with aroyl chlorides, gave aryl perfluoroalkyl ketones in fair yields. Nevertheless, an attempted preparation of alkyl fluoroalkyl ketones met with little success. The interaction of solvent(HMPA) with acyl chlorides might be responsible for this failure[11]. During the course of our investigation, we observed that the above aryl fluoroalkyl ketones could also be prepared by treating the corresponding allyl esters with catalytic amounts of tetrakis(triphenylphosphine)palladium (0) in the presence of YC_6H_4COCl [12]. Since the palladium(0) catalyzed reaction could be conducted without any solvent, difficulties arising from the consumption of acyl chlorides by the solvent were open to be solved. Herein we describe a convenient way to obtain alkyl perfluoroalkyl ketones and their O-acylated and C-allylated derivatives via palladium catalyzed decomposition of the esters $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2CH_2CH{=}CH_2$ (n=0,1).

RESULTS AND DISCUSSION

The initial attempts to prepare hemifluorinated ketones **6**, **7** directly by the reaction of acyl chlorides with the esters $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2CH_2CH{=}CH_2$ (n=0, 1) in the presence of Pd(0) were found to be unsatisfactory. For example, when a 1:1.3 molar ratio of the allyl esters and acyl chlorides was treated with a catalytic amount of Pd(0) at 95°C , ca. 50% yields of **4**,**5** were obtained as the main products. The expected ketones **6**,**7** were separated only in very small amounts(ca. 3%).

$$C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2CH_2CH{=}CH_2 + RR'CHCOCl \xrightarrow{Pd(PPh_3)_4}$$

n=0, 1
n=1, **2**

3a-e

$$RR'C{=}C(R_f)OCOCHRR' + R_fCOCHRR' + R_fH \qquad (1)$$

n=0, **4a,b,d** n=0, **6a,b,d**
n=1, **5a-d** n=1, **7a-e**

a: R=H, R′=CH_3; b: R=H, R′=C_2H_5; c: R=H, R′=C_3H_7; d: R=H, R′=C_4H_9; e: R=R′=CH_3

Table 1 illustrates the dominating formation of perfluoroalkyl substituted alkenyl esters over hemifluorinated ketones. But in the case of R=R′=CH_3(Entry 8)the main product is ketone **7e** rather than enol ester **5e**.

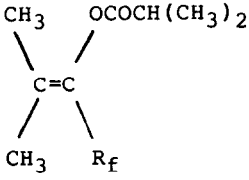
TABLE 1

Reactions of $C_3F_7O[CF(CF_3)CF_2O]_nCF(CF_3)CO_2CH_2CH=CH_2$ with acyl chlorides in 1:1.3 molar ratio[a]

Entry	n	RR′CHCOCl	t(h)	Product(yield, %)[b]			
				Enol ester	b.p.(°C)	Ketone	b.p.(°C)
1	1	**3a**	4	**4a**(64.9)	157	**6a**(<1)	-
2	1	**3b**	3	**4b**(56.9)	188	**6b**(2.5)	98
3	1	**3d**	4	**4d**(66.2)	239	**6d**(3.1)	116
4	2	**3a**	3.5	**5a**(60.6)	177	**7a**(2.5)	147
5	2	**3b**	3	**5b**(60.5)	211	**7b**(1.5)	161
6	2	**3c**	4	**5c**(58.1)	241	**7c**(2.4)	173
7	2	**3d**	4	**5d**(59.1)	264	**7d**(3.0)	192
8	2	**3e**	3	**5e**(0.00)	-	**7e**(78.1)	159

[a] a 3mol% $Pd(PPh_3)_4$ was employed ; [b] isolated yield based on $R_fCO_2CH_2CH=CH_2$, $R_f=C_3F_7O[CF(CF_3)CF_2O]_nCFCF_3$.

Reluctance to form ester **5e** might be attributed to the steric bulk of the following structure.



Hemifluorinated ketones with other structures could be obtained by treating the fluorinated enol esters **4,5** with concentrated sulfuric acid.

$$\mathbf{4,5} \xrightarrow{\text{conc.}H_2SO_4} R_fCOCH_2R \qquad (2)$$

It can be seen from equation (1) that the formation of the ketones requires one mole of acyl chlorides while the formation of the alkenyl esters requires two moles of acyl chloride. In consideration of the stoichiometry, it seems that if a smaller amount of acyl chloride were used, the yields of the ketones **6,7** would increase. It turned out from the experiment that no appreciable change in the yields of ketones **6**, **7** was observed with the change of the molar ratio of allyl esters **1**, **2** to acyl chlorides **3**(1:1.3 to 1:1). It is interesting to note that the separation of the reaction mixture afforded other products (**8**) in addition to **4,5** and **6,7**. Physical measurements showed the existence of an allyl group in these compounds.

$$\mathbf{1} + \underset{\mathbf{3c}}{C_4H_9COCl} \xrightarrow{Pd(0)} \underset{\mathbf{6c}}{R_fCOC_4H_9} + \underset{\mathbf{4c}}{C_4H_9COOC(R_f)=CHC_3H_7} + \underset{\mathbf{8c}}{R_fCOCH(C_4H_9)CH_2CH=CH_2} \qquad (3)$$

If an excess of allyl esters in respect to acyl chlorides was used(e.g. **1:3a,d**=1:0.7), diallyl ketones **9a, d** were isolated in addition to the allyl ketones **8a, d** and enol esters **4a,d**; but the hemifluorinated ketones disappeared completely from the products.

$$\mathbf{1} + \underset{\mathbf{3a,\ d}}{RCH_2COCl} \xrightarrow{Pd(0)} \underset{\mathbf{4a,\ d}}{RCH_2COOC(R_f)=CHR} + \underset{\mathbf{8a,\ d}}{R_fCOCHRCH_2CH=CH_2} + \underset{\mathbf{9a,\ d}}{R_fCOCR(CH_2CH=CH_2)_2} \qquad (4)$$

Further increase in the molar ratio of allyl esters to acyl chlorides even resulted in the disappearance of enol esters **4** and the dominant formation of diallylated ketones **9** together with a small amount of allyl ketones **8** (see Table 2).

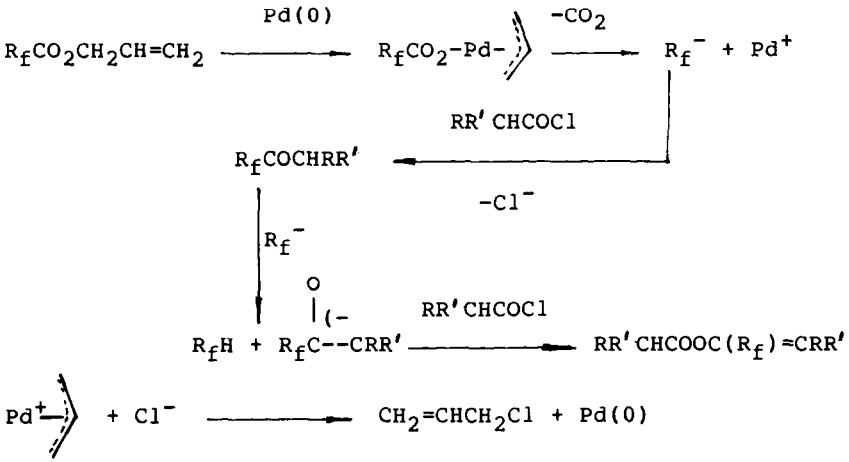
TABLE 2

Distribution of the products at different ratios of the reactants($R_fCO_2CH_2CH=CH_2$[a] : $RR'CHCOCl$)[b]

molar ratio (1 : 3)	Product(yield[c]) enol ester	b.p. (°C)	ketone	b.p. (°C)	allyl ketone	b.p. (°c)	diallyl ketone	b.p. (°C)
1 : 1.0	**4c**(51.5)	213	**6c**(2.16)	107	**8c**(11.4)	155	**9c**(<1)	-
1 : 0.7	**4a**(4.0)	157	**6a**(<1)	-	**8a**(9.2)	132	**9a**(33.8)	183
1 : 0.7	**4d**(4.3)	239	**6d**(<1)	-	**8d**(12.7)	163	**9d**(30.2)	208
1 : 0.6	**4a**(<1)	-	**6a**(0)	-	**8a**(5.6)	-	**9a**(55.2)	-
1 : 0.6	**4d**(<1)	-	**6d**(0)	-	**8d**(2.6)	-	**9d**(59.3)	-
1 : 0.7	**4e**(<1)	-	**6e**(<1)	-	**8e**(75.7)	156	**9e**(0)	-

[a] $R_f=C_3F_7OCF(CF_3)$; [b] a 3mol% of Pd(0) was used as catalyst; [c] isolated yield based on acyl chlorides.

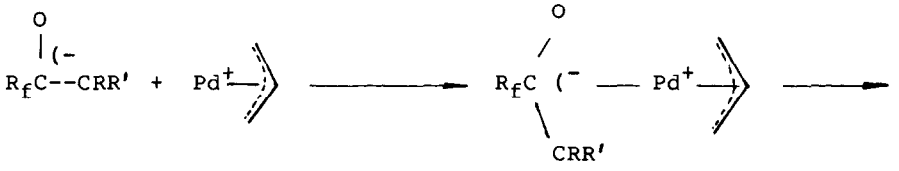
Similar to the perfluorocarbanion mechanism proposed for the reaction of allyl esters **1**, **2** with aroyl chlorides[12], the formation of both products **4**,**5** and **6**,**7** may be explained as follows(Scheme 1).



Scheme 1

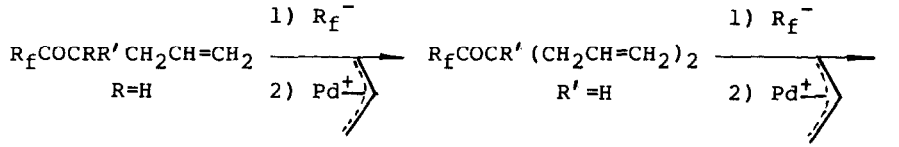
Insertion of Pd(0) to allyl esters led to the loss of carbon dioxide [10] and the formation of perfluorocarbanions $C_3F_7O[CF(CF_3)-CF_2O]_nCF(CF_3)^-$ which were trapped by acyl chlorides to give the hemifluorinated ketones **6**, **7**. The ketones thus formed immediately competed with acyl chlorides for fluorocarbanions, resulting in the formation of enolate anions. O-Acylation of the enolate anions afforded the perfluoroalkyl substituted enol esters **4**, **5**.

Allylation of enolate anions with (η^3-allyl)palladium complexes is a well established process [13]. In the light of the mechanistic consideration described in Scheme 1 it could be seen that there existed enolate anions and (η^3-allyl)palladium complexes as intermediates during the course of the reaction. If excess amounts of acyl chlorides were present, acylation of the enolate anions to form enol esters was favored, leaving the (η^3-allyl)palladium complex to be attacked by chloride ion to form allyl chloride. But if the concentration of acyl chlorides became so small that more and more enolate anions and the (η^3-allyl)palladium complex accumulated, the combination of the two species to form η^3-allyl palladium enolates which in turn converted to allylated ketones was a dominating process.



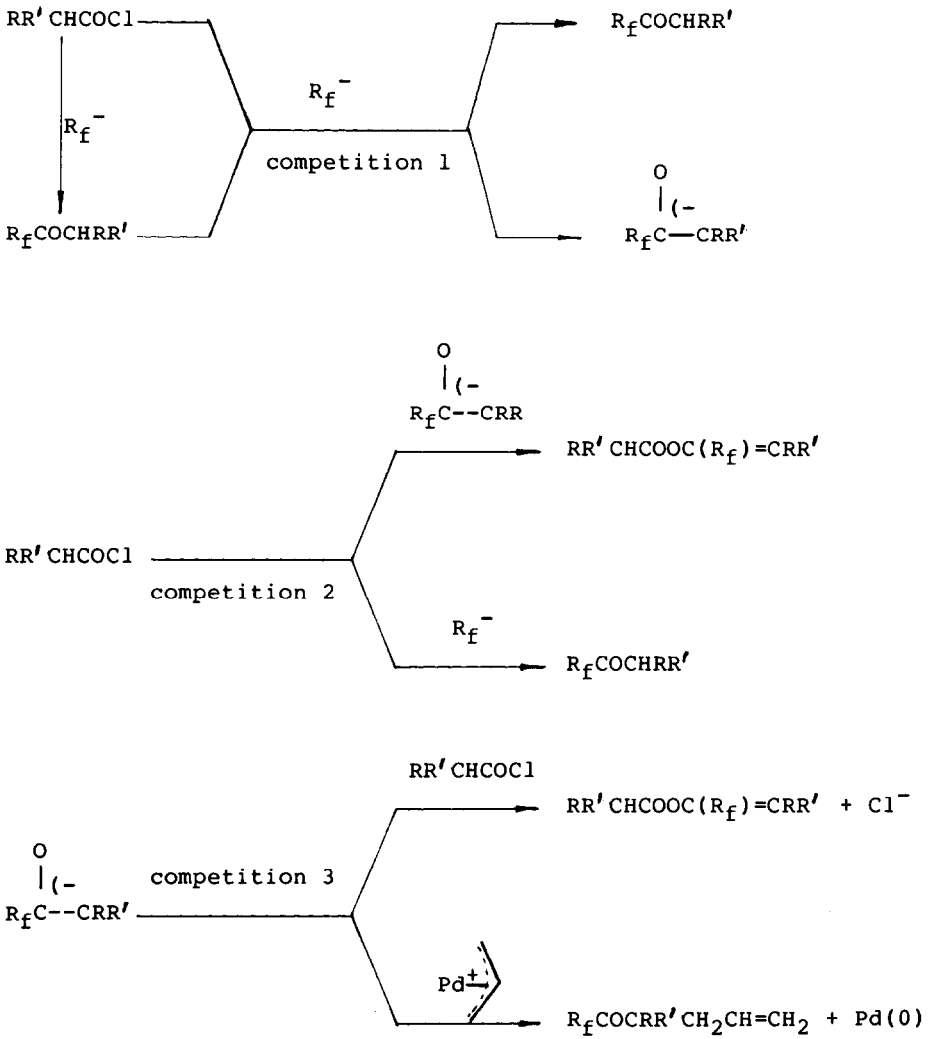
$$R_fCOCRR'CH_2CH{=}CH_2 + Pd(0) \qquad (5)$$

Further enolization and allylation of the allyl ketones afforded diallyl and, in the case of R=R'=H, even the triallyl ketones.



$$R_fCO(CH_2CH{=}CH_2)_3 \qquad (6)$$

The results described above show that the yields of each kind of products are directly related to the molar ratio of the reactants. Direct preparation of such hemifluorinatd ketones is complicated not only by the fact that the ketones themselves compete with acyl chlorides for fluorocarbanions but also by the fact that the enolate anions derived from the first competition compete with fluorocarbanions for acyl chlorides which, in turn, compete with (η-allyl)palladium complexes for enolate anions.



Scheme 2

It is evident from competition 3 that C-allylation can be suppressed by O-acylation if an excess of acyl chlorides is present. From competition 1 one would assume that formation of the ketones **6, 7** is also favored so long as the relative concentration of acyl chlorides is much higher than that of the ketones **6, 7** being formed. In fact, it was found that increase of the molar ratio of acyl chloride **3b** to allyl ester **1** from 1:1.3 to 1:1.5 resulted in increase of the yield of ketone **6b** from 2% to 25%.

In summary, Pd(0) mediated decomposition of allyl perfluoroalkanoates was explored to accomplish the controlled synthesis of hemifluorinated ketones and the corresponding mono, di, triallylated ketones. Other catalysts are currently being investigated in this laboratory.

EXPERIMENTAL

General comments

Infrared spectra were recorded on a Perkin-Elmer model 683 and Shimadzu IR-40 infrared spectrophotometers. NMR spectra were obtained with an EM-360(60Hz) spectrometer;chemical shifts are reported in p.p.m. from external standards $(CH_3)_4Si(^1H)$ and CF_3COOH (^{19}F). Mass spectra were obtained on a GC-MS-4021 mass spectrometer. Analytical and preparative GLC were performed on a Shanghai Analytical Factory model 103 with a column packed with liquid oxaperfluoroalkylene triazine polymer or SE-30 on 100 mesh 102 support. Starting materials were purified according to standard procedures. All the reactions were carried out in a dry nitrogen atmosphere. The reaction apparatus was dried, assembled while hot, and flushed with dry nitrogen prior to introduction of the catalyst and reagents.

General procedure for the reactions of various acyl chlorides with allyl esters of perfluoroalkylether acids 1,2

Preparation of ester **5d** and ketone **7d**

To a 50mL three-necked flask equipped with a magnetic stirrer, a refluxing condenser and a gas inlet, were added 344 mg (0.3mmol) tetrakis(triphenylphosphine)palladium complex, 6.4g (12 mmol) allyl ester **2** and 2.0g(15 mmol) hexanoyl chloride. The reaction apparatus was connected to a dry ice-acetone trap and a gas accumulator. The mixture was stirred at ca. 95°C for 4h and 275mL(94.8%) carbon dioxide(identified by GC-MS analysis) was collected. The reaction mixture gave 1.8g(33.2%) $C_3F_7OCF(CF_3)CF_2O-CF(CF_3)H$ upon distillation. Flash chromatography followed by preparative GLC separation of the residual oil afforded 4.6g(59.1%) **5d** and 198mg(3.0%) **7d** (See Table 1). Analysis(5d): Found: C, 36.69; H, 3.28; F, 49.93. Required for $C_{20}H_{21}F_{17}O_4$ C, 37.04; H, 3.27; F 49.86%. IR(neat): 1782(C=O), 1683(C=C)cm^{-1}. ^{19}F NMR: 4.6(3F), 5.7 (2F), 5.8(2F, AB signal), 5.9(3F), 7.7(3F), 53.8(2F), 54.6(1F,d-t) 68.4(1F)ppm; ^1H NMR: 5.96(1H, t, C=CH), 2.21(2H, m), 2.05-1.60 (4H, m), 1.52-0.97(8H, m), 0.75-0.69(6H, m)ppm. MS(m/z, %): 649 (M^++1, 0.05), 629(M^+-19, 0.27), 185($C_3F_7O^+$, 1.81), 99($C_5H_{11}CO^+$, 100), 71($C_5H_{11}^+$, 25.37), 55($C_4H_7^+$, 13.19), 43($C_3H_7^+$, 21.97).

7d: Required for $C_{14}H_{11}F_{17}O_3$ C, 30.56; H, 2.02. Found: C, 30.58; H, 2.01%;IR(neat): 1764(C=O)cm^{-1}.^{19}F NMR:3.7(2F, AB signal), 4.9(3F), 5.5(2F), 5.9(3F), 6.3(3F), 54.1(2F), 59.6(1F, d-t) 68.9(1F)ppm. ^1H NMR: 2.60(2H, t, $COCH_2$), 1.63-0.95(6H, m), 0.75 (3H, t, CH_3)ppm. MS(m/z, %): 551(M^++1, 8.22), 550(M^+, 1.44), 169 ($C_3F_7^+$, 10.20), 99($C_5H_{11}CO^+$, 16.77), 71($C_5H_{11}^+$, 62.69), 69(CF_3^+, 32.48), 57($C_4H_9^+$, 38.75), 43($C_3H_7^+$, 60.12).

The preparation of other compounds followed the same procedure. The results are listed below

4a: Yield, 64.9%. Analysis required for $C_{11}H_9F_{11}O_3$ C, 33.18; H, 2.28; F, 52.49. Found: C, 33.10; H, 2.20; F, 51.56%. IR(neat):

1787(C=O), 1688(C=C)cm^{-1} . ^{19}F NMR: 5.9(3F), 6.9(2F, AB signal), 7.6(3F), 53.8(2F), 55.0(1F)ppm. ^{1}H NMR: 6.17(1H, q, C=C-H), 2.42 (2H, q, $COCH_2$), 1.59(3H, d, $CHCH_3$), 1.28(3H, t, CH_2CH_3)ppm. MS (m/z, %): 400(M^+, 0.08), 399(M^+-1, 0.75), 385(M^+-19, 0.05), 69 (CF_3^+, 0.59), 57($C_2H_5CO^+$, 100).

4b: Yield, 56.9%. Analysis required for $C_{13}H_{13}F_{11}O_3$ C, 36.63; H, 3.08; F, 49.03 Found: C, 36.55; H, 3.01; F, 48.73%. IR(neat): 1788(C=O), 1689(C=C)cm^{-1}. ^{19}F NMR: 5.9(3F) 6.6(3F), 6.7(2F, AB signal), 53.9(2F), 54.9(1F, d-t)ppm. ^{1}H NMR: 5.93(1H, t, C=C-H), 2.27(2H, t, $COCH_2$), 2.20-1.18(4H, m), 1.00-0.75(6H, m)ppm. MS (m/z, %): 427(M^++1, 0.64), 407(M^+-19, 1.49), 169($C_3F_7^+$, 1.22), 71($C_3H_7CO^+$, 100), 69(CF_3^+, 2.18), 43($C_3H_7^+$, 39.27).

6b: Yield, 2.5%. Analysis required for $C_9H_7F_{11}O_2$ C, 30.35; H, 1.99; F, 58.68. Found: C, 30.36; H, 1.85; F, 58.52%. IR(neat): 1760(C=O)cm^{-1}. ^{19}F NMR:4.9(2F, AB signal), 6.3(3F), 6.4(3F), 54.0 (2F), 59.3(1F, d-t)ppm. ^{1}H NMR: 2.53(2H,t, $COCH_2$), 1.83-1.15(2H, m), 0.74(3H, t, CH_3)ppm.

4d: Yield, 66.2%. Analysis required for $C_{17}H_{21}F_{11}O_3$ C, 42.33; H, 4.40; F, 43.33. Found: C, 42.10; H, 4.45; F, 42.92%. IR(neat): 1786(C=O), 1685(C=C)cm^{-1}. ^{19}F NMR: 5.6(3F), 6.5(2F, AB signal), 7.3(3F), 53.3(2F), 54.8(1F, d-t)ppm. ^{1}H NMR: 5.9(1H, t, C=C-H), 2.27(2H, t, $COCH_2$), 1.70(2H, d-t, C=C-CH_2), 1.67-0.98(10H, m), 0.87-0.69(6H, m)ppm. MS(m/z, %): 483(M^++1, 0.51), 481(M^+-1, 0.09) 463(M^+-19, 1.34), 297(M^+-C_3F_7O, 6.99), 169($C_3F_7^+$, 1.98), 99 ($C_5H_{11}CO^+$, 100), 71($C_5H_{11}^+$, 48.74), 43($C_3H_7^+$, 61.74).

6d: Yield, 3.1%. Analysis required for $C_{11}H_{11}F_{11}O_2$ C, 34.38; H, 2.89; F, 54.40. Found: C, 34.65; H, 2.76; F, 54.94%. IR(neat): 1764(C=O)cm^{-1}. ^{19}F NMR: 4.7(2F, AB signal), 5.7(3F), 5.8(3F), 53.8(2F), 59.0(1F, d-t)ppm. ^{1}H NMR: 2.55(2H, t, $COCH_2$), 1.62-0.89(6H, m), 0.74(3H, t, CH_3)ppm. MS(m/z, %): 385(M^++1, 1.20), 384(M^+, 0.29), 383(M^+-1, 0.55), 365(M^+-19, 0.28), 199(M^+-C_3F_7O, 1.16), 169($C_3F_7^+$, 3.89), 99($C_5H_{11}CO^+$, 91.42), 71($C_5H_{11}^+$, 70.46), 69(CF_3^+, 24.23), 57($C_4H_9^+$, 10.86), 43($C_3H_7^+$, 100).

5a: Yield, 60.6%. Analysis required for $C_{14}H_9F_{17}O_4$ C, 29.80; H, 1.61; F, 57.25. Found: C, 29.71; H, 1.67; F, 57.18%. IR(neat): 1795(C=O), 1699(C=C)cm^{-1}. ^{19}F NMR: 4.5(3F), 5.8(3F), 5.9(2F), 6.6 (2F, AB signal), 7.6(3F), 53.7(2F), 55.0(1F, d-t), 68.6(1F)ppm. ^1H NMR: 6.10(1H, C=C-H), 2.35(2H, q, $COCH_2$), 1.51(3H, d, C=CH-CH_3), 1.07(3H, t, CH_2CH_3)ppm. MS(m/z, %): 565(M^++1, 11.37), 545 (M^+-19, 100).

7a: Yield, 2.5%. Analysis required for $C_{11}H_5F_{17}O_3$ C, 26.00; H, 0.99; F, 63.56. Found: C, 25.89; H, 0.92; F, 64.43%. IR(neat): 1762(C=O)cm^{-1}. ^{19}F NMR: 4.1(3F), 4.3(2F, AB signal), 5.3(2F), 5.5 (3F), 53.3(2F), 59.1(1F, d-t),68.2(1F)ppm. ^1H NMR: 2.47(2H, q, $COCH_2$), 1.03(3H, t, CH_3)ppm. MS(m/z, %): 389(M^+-C_2F_5, 0.03), 223 (M^+-$C_3F_7OCFCF_3$, 0.87), 169(CF_3^+, 14.17), 57($C_2H_5CO^+$, 100).

5b: Yield, 60.5%. Analysis required for $C_{16}H_{13}F_{17}O_4$ C, 32.44; H, 2.22; F, 54.53. Found: C, 32.18; H, 1.99; F, 54.69%. IR(neat): 1791(C=O), 1696(C=C)cm^{-1}. ^{19}F NMR: 4.7(3F), 5,9(2F), 6.1(3F), 6.5 (2F, AB signal), 7.8(3F), 54.0(2F), 54.9(1F, d-t), 68.8(1F)ppm. ^1H NMR: 5.85(1H ,t, C=C-H), 2.11(2H, t, $COCH_2$), 1.89-1.23(4H, m), 0.85-0.62(6H, m)ppm. MS(m/z, %): 593(M^++1, 0.18), 573(M^+-19, 0.16), 71($C_3H_7CO^+$, 100), 69(CF_3^+, 2.63), 43($C_3H_7^+$, 7.18).

7b: Yield, 1.5%. Analysis required for $C_{12}H_7F_{17}O_3$ C, 27.60; H, 1.35; F, 61.85. Found: C, 27.20, H, 1.24, F, 62.61%. IR(neat): 1762(C=O)cm^{-1}. ^{19}F NMR: 4.6(2F, AB signal), 5.2(3F), 6.1(2F), 6.4 (3F), 6.7(3F), 54.0(2F), 59.5(1F, d-t), 68.7(1F)ppm. ^1H NMR: 2.70 (2H, q, $COCH_2$), 1.51(2H, m), 0.89(3H, t, CH_3)ppm. MS(m/z, %): 503 (M^+-19, 0.81), 185($C_3F_7O^+$, 7.35), 71($C_3H_7CO^+$, 100), 43($C_3H_7^+$, 94.05).

5c: Yield, 58.1%. Analysis required for $C_{18}H_{17}F_{17}O_4$ C, 34.85; H, 2.77; F, 52.07. Found: C, 34.78; H, 2.74; F, 52.53%. IR(neat): 1793(C=O), 1697(C=C)cm^{-1}. ^{19}F NMR: 3.8(2F, AB signal), 4.0(3F), 5.1(2F), 5.3(3F), 7.1(3F), 53.2(2F), 54.2(1F, d-t), 67.9(1F)ppm. ^1H NMR: 5.99(1H, t, C=C-H), 2.39(2H, t, $COCH_2$), 1.91(2H, m), 1.58 -1.27(6H, m), 0.90-1.09(6H, m)ppm. MS(m/z, %): 621(M^++1, 0.44), 620(M^+, 0.03), 601(M^+-19, 1.35), 85($C_4H_9CO^+$, 100).

7c:Yield, 2.4%. Analysis required for $C_{13}H_9F_{17}O_3$ C, 29.12; H, 1.70; F, 60.24. Found: C, 28.75%; H, 1.71; F, 60.05. IR(neat): 1763(C=O)cm^{-1}. ^{19}F NMR: 3.6(2F, AB signal), 4.0(3F), 4.2(2F), 5.5 (3F), 5.7(3F), 53.1(2F), 58.5(1F, d-t), 67.9(1F)ppm. ^1H NMR: 2.61 (2H, t, COCH2), 1.74-1.04(4H, m), 0.83(3H, t, CH_3)ppm. MS(m/z,%): 537(M^++1, 1.56), 517(M^+-19, 0.22), 185($C_3F_7O^+$, 20,70), 169($C_3F_7^+$, 5.59), 85($C_4H_9CO^+$, 100), 69(CF_3^+, 52.07), 57($C_4H_9^+$, 2.74).

5e: Yield, 78.1%. Analysis required for $C_{13}H_7F_{17}O_3$ C, 27.60; H, 1.35; F, 61.85. Found: C, 27.48; H, 1.24; F, 61.76%. IR(neat): 1739(C=O), 1648(C=C)cm^{-1}. ^{19}F NMR: 3.9(2F, AB signal), 4.9(3F), 5.3(2F), 6.2(3F), 6.4(3F), 54.0(2F), 60.3(1F, d-t), 68.9(1F)ppm. ^1H NMR: 3.16(1H, m, COCH), 1.04(6H, d, CH_3)ppm. MS(m/z, %): 522 (M^+, 2.50), 503(M^+-19, 0.45), 169($C_3F_7^+$, 8.67), 71($C_3H_7CO^+$, 67.92), 69(CF_3^+, 21.43), 43($C_3H_7^+$, 74.85).

Typical procedure for the reactions of allyl ester 1 with acyl chlorides at various molar ratios

Preparation of **8d** and **9d**

In a 50mL three-necked flask equipped with a magnetic stirrer, a refluxing condenser and a gas inlet was placed 348mg(0.3mmol) tetrakis(triphenylphosphine)palladium complex. The whole system was connected in series to a cold trap(dry ice-acetone) and a gas accumulator. To the flask were added 8.1g(22mmol) allyl ester **1** and 1.6g(12mmol) hexanoyl chloride through a syringe. The mixture was stirred at ca. 95°C until no more gas evolved(3h). Analysis of the contents of the cold trap by both GC and NMR(^1H, ^{19}F) spectroscopies indicated that a 65.1% yield of R_fH was obtained. Flash chromatography of the products on alumina oxide(petroleum ether as eluent) followed by preparative GLC separation gave 3.3g (59.3%) **9d** and 128mg(2.6%) **8d** (See Table 2). Analysis required for $C_{17}H_{19}F_{11}O_2$(**9d**): C, 43.97; H, 4.13; F, 45.01. Found: C, 43.85; H, 4.04; F, 44.91%. IR: 1745(C=O), 1657(C=C)cm^{-1}. ^{19}F NMR: 3.8(3F), 5.2(2F, AB signal), 5.6(3F), 53.4(2F), 56.9(1F, d-t)ppm. ^1H NMR: 5.73-4.82(6H, m, alkenyl-H), 2.38(4H, d), 1.58(2H, m), 1.39-0.91 (4H, m), 0.76(3H, t, CH_3)ppm. MS(m/z, %): 464(M^+, 0.31), 463(M^+-1, 1.95), 185($C_3F_7O^+$, 34.44), 109($C_8H_{13}^+$, 1.69), 57($C_4H_9^+$, 1.65), 43 ($C_3H_7^+$, 40.41), 41($C_3H_5^+$, 19.96).

8d: Analysis required for $C_{14}H_{15}F_{11}O_2$ C, 39.63; H, 3.57; Found: C, 39.24; H, 3.35%. IR: 1756(C=O), 1647(C=C)cm^{-1}. ^{19}F NMR: 4.7(2F, AB signal), 5.1(3F), 6.1(3F), 53.7(2F), 60.8(1F, d-t)ppm. ^{1}H NMR: 5.69-4.71(1H, m), 4.94-4.75(1H, m), 4.62-4.49(1H, m), 3.02-2.68(1H, m, COCH), 2.19-1.91(2H, m), 1.35-0.84(6H, m), 0.61 (3H, t, CH_3)ppm. MS(m/z, %): 425(M^++1, 3.74), 424(M^+, 0.35), 423 (M^+-1, 1.50), 405(M^+-19, 0.64), 185($C_3F_7O^+$, 32.15), 169($C_3F_7^+$, 1.19), 139($C_8H_{15}CO^+$, 22.56), 111($C_8H_{15}^+$, 34.35), 69($C_5H_9^+$, CF_3^+, 100), 57($C_4H_9^+$, 15.68), 41($C_3H_5^+$, 18.80).

The reactions of allyl ester 1 with other acyl chlorides at different molar ratios followed the same procedure as described above. Physical measurements of the new compounds are listed below.

4c: Analysis required for $C_{15}H_{17}F_{11}O_3$ C, 39.65; H, 3.78; F, 46.00. Found: C, 39.80; H, 3.79; F, 46.27%. IR(neat): 1791(C=O), 1695(C=C)cm^{-1}. ^{19}F NMR: 5.6(3F), 6.5(2F, AB signal), 7.3(3F), 53.9(2F), 54.8(1F, d-t)ppm. ^{1}H NMR: 6.05(1H, t, C=C-H), 2.32(2H, m, $COCH_2$), 1.84(2H, m, C=C-CH_2), 1.76-1.10(6H, m), 0.96-0.76(6H, m)ppm. MS(m/z, %): 455(M^++1, 0.85), 453(M^+-1, 0.13), 435(M^+-19, 0.80), 269(M^+-C_3F_7O, 19.74), 169($C_3F_7^+$, 2.77), 85($C_4H_9CO^+$, 100), 69(CF_3^+, 10.23), 57($C_4H_9^+$, 62.98).

6c: Analysis required for $C_{10}H_9F_{11}O_2$ C, 32.44; H, 2.46; F, 56.46. Found: C, 32.37; H, 2.34; F, 55.59%. IR(neat): 1766(C=O) cm^{-1}. ^{19}F NMR: 4.8(2F, AB signal), 6.0(3F), 6.1(3F), 53.8(2F), 59.3(1F, d-t)ppm. ^{1}H NMR: 2.52(2H, t, $COCH_2$), 1.63-0.90(4H, m), 0.70(3H, t, CH_3)ppm. MS(m/z, %): 371(M^++1, 1.12), 351(M^+-19, 0.15), 185($C_3F_7O^+$, 1.19), 169($C_3F_7^+$, 2.40), 85($C_4H_9CO^+$, 88.63), 69(CF_3^+, 15.85), 57($C_4H_9^+$, 100), 43($C_3H_5^+$, 27.75).

8a: Analysis required for $C_{11}H_9F_{11}O_2$ C, 34.57; H, 2.39; F, 59.70. Found: C, 34.92, H, 2.31; F, 59.68%. IR: 1758(C=O), 1650 (C=C)cm^{-1}. ^{19}F NMR: 4.3(2F, AB signal), 4.9(3F), 5.5(3F), 53.2 (2F), 59.9(1F, d-t)ppm. ^{1}H NMR: 5.53(1H, m), 4.99(1H,m), 4.76 (1H, m), 3.02(1H, m, COCH), 2.20(2H, m), 1.03(3H, d, CH_3)ppm.

MS(m/z, %): 383(M^++1, 4.18), 382(M^+, 0.42), 363(M^+-19, 0.39), 197($M^+-C_3F_7O^+$, 1.20),97($C_5H_9CO^+$, 33.42), 69($C_5H_9^+$, $CF3^+$, 83.29), 41($C_3H_5^+$, 100).

8c: Analysis required for $C_{13}H_{13}F_{11}O_2$ C, 38.06; H, 3.20; F, 50.94. Found: C, 37.93; H, 3.26; F, 51.38%. IR: 1755(C=O), 1646 (C=C)cm^{-1}. ^{19}F NMR: 4.3(2F, AB signal), 4.9(3F), 5.8(3F), 53.4 (2F), 60.4(1F, d-t)ppm. ^1H NMR: 5.90-5.26(1H, m), 5.00(1H, m), 4.77(1H, m), 3.05(1H, m, COCH), 2.26(2H, d-d, $C=C-CH_2$), 1.81-1.07 (4H, m), 0.82(3H, t, CH_3)ppm. MS(m/z, %): 411(M^++1, 6.35), 391 (M^+-19, 0.53), 169($C_3F_7^+$, 18.15), 125($C_7H_{13}CO^+$, 33.32), 97 ($C_7H_{13}^+$, 50.27), 41($C_3H_5^+$, 100).

9a: Analysis required for $C_{14}H_{14}F_{11}O_2$ C, 39.72; H, 3.34; Found: C, 39.61; H, 3.06%. IR: 1743(C=O), 1655(C=C)cm^{-1}. ^{19}F NMR: 3.2(3F), 4.9(2F, AB signal), 5.7(3F), 53.2(2F), 55.8(1F, d-t)ppm. ^1H NMR: 5.89-5.10(2H, m), 5.04(2H, m), 4.89-4.73(2H, m), 2.28(2H, t, $C=C-CH_2$), 1.21(3H, s, CH_3)ppm. MS(m/z, %): 423(M^+-1, 1.73), 422(M^+, 1.18), 421(M^+-1, 2.43), 403(M^+-19, 1.46), 137($C_8H_{13}CO^+$, 15.44), 109($C_8H_{13}^+$, 89.02), 69(CF_3^+, 26.19), 67($C_5H_7^+$, 100), 41 ($C_3H_5^+$, 65.85).

8e: Analysis required for $C_{12}H_{11}F_{11}O_2$ C, 36.37; H, 2.80; F, 52.75. Found: C, 36.52; H, 2.87; F, 53.10%. IR(neat): 1740(C=O), 1648(C=C)cm^{-1}. ^{19}F NMR: 3.6(3F), 4.5(2F, AB signal), 5.3(3F), 53.2(2F), 55.7(1F, d-t)ppm. ^1H NMR: 5.98-4.84(3H, m, alkenyl-H), 2.30(2H, d, $C=C-CH_2$), 1.25(6H, s, CH_3)ppm. MS(m/z, %): 397(M^++1, 0.16), 396(M+, 0.18), 169 ($C_3F_7^+$, 8.11), 111($C_6H_{11}CO^+$, 14.88), 83 ($C_6H_{11}^+$, 87.91), 69(CF_3^+, 48.75), 55($C_4H_7^+$, 100), 41($C_3H_5^+$, 75.43).

10: Analysis required for $C_{19}H_{15}F_{17}O_3$ C, 37.14; H, 2.47; F,52.58. Found: C, 36.88; H, 2.30; F, 52.64%. IR(neat): 1736(C=O), 1649(C=C)cm^{-1}. ^{19}F NMR: 2.1(3F), 3.5(2F), 4.1(3F), 5.1 (2F AB signal), 5.8(3F), 53.5(2F), 56.8(1F, d-t), 68.1(1F)ppm. ^1H NMR: 5.93-4.83(3H, m, alkenyl-H), 5.11-4.80(6H, m, alkenyl-H) ppm. MS(m/z, %): 614(M^+, 1.67), 573(M^+-41, 7.44), 169($C_3F_7^+$, 18.44), 163($C_{10}H_{15}CO^+$, 5.03), 69(CF_3^+, 33.38), 41($C_3H_5^+$, 100).

Representative transformation of enol esters **4** to hemifluorinated ketones **5**

The enol ester **4b**(1.0g, 2.3mmol)was allowed to mix with 1mL concentrated sulfuric acid at room temperature. Fractionates between 100°C-115°C were distilled from the mixture, washed with a 10% aqueous solution of $NaHCO_3$ and dried with Na_2SO_4.Comparison with an authentic sample(GC) indicates that a 86.6% (710mg) **5b** was obtained.

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