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STUDIES ON THE Pd CATALYZED REACTION OF PERFLUOROALKYL AND POLYFLUOROALKYL IODIDES WITH TERTIARY AMINES

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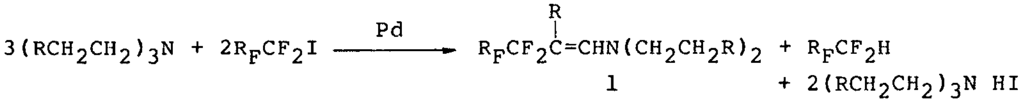
Abstract: Pd catalyzed reaction of perfluoroalkyl and polyfluoroalkyl iodides with tertiary amines gave enamines(**1**) which on acid hydrolysis afforded enaminones(**2**), or aldehydes(**3**).

So far as we know, no report appeared in the literature concernig the catalytic activation of saturated alphatic chain of tertiary amine to give enamine. Our preliminary communication gave a first example of Pd catalyzed reaction of perfluoroalkyl iodide with triethylamine affording perfluoroalkyl enamine.[1] We would like to report here the Pd catalyzed reaction of perfluoro- and polyfluoroalkyl iodides with a variety of tertiary amines.



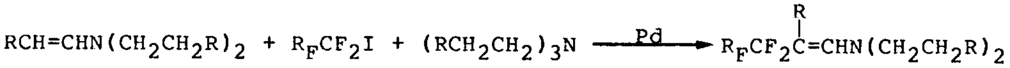
$$3(RCH_2CH_2)_3N + 2R_FCF_2I \xrightarrow{Pd} \underset{1}{R_FCF_2\overset{R}{\overset{|}{C}}=CHN(CH_2CH_2R)_2} + R_FCF_2H + 2(RCH_2CH_2)_3N\ HI$$

$R = H, CH_3, C_2H_5$
$R_F = CF_3(CF_2)_n$, $n=2,4$
$Cl(CF_2)_n$, $n=1,3,5,7$

The solvent chosen was crucial. Only in saturated hydrocarbon the reaction proceeded quite well. The most favorable reaction condition is heating the reaction mixture at 50-60°C for 0.5hr, and a catalytic amount (5mol%) of $Pd(PPh_3)_4$ is sufficient to carry out the reaction to completion. The conversion of the iodides reaches nearly to 100% (determined by ^{19}F NMR). The yields of **1** are shown in Table 1.

The reaction mechanism is most likely to be free radical in nature based upon that the reaction was completely inhibited on adding a free radical scavenger, p-dinitrobenzene or p-benzoquinone. We proposed that the reaction proceeds according to the following sequence.

$$R_FCF_2I + 2RCH_2CH_2N(CH_2CH_2R)_2 \xrightarrow{Pd} RCH{=}CHN(CH_2CH_2R)_2 + R_FCF_2H + (RCH_2CH_2)_3N\ HI$$



$$RCH{=}CHN(CH_2CH_2R)_2 + R_FCF_2I + (RCH_2CH_2)_3N \xrightarrow{Pd} R_FCF_2\overset{R}{C}{=}CHN(CH_2CH_2R)_2 + (RCH_2CH_2)_3N\ HI$$

1

Pd° may play the role of a free radical initiator since the reaction still occurred in the dark in the presence of $Pd(PPh_3)_4$, but did not occur by using $Pd(PPh_3)_2Cl_2$ instead of $Pd(PPh_3)_4$. The detailed mechanistic study is being pursued.

Table 1 Yield of Enamines

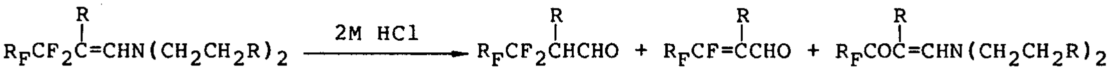
Iodide	Amine	Product	Yield(%)(^{19}F NMR)*
$CF_3(CF_2)_2CF_2I$	NEt_3	$CF_3(CF_2)_2CF_2CH{=}CHNEt_2$	45
$CF_3(CF_2)_4CF_2I$	NEt_3	$CF_3(CF_2)_4CF_2CH\text{-}CHNEt_2$	50
$Cl(CF_2)CF_2I$	NEt_3	$Cl(CF_2)CF_2CH{=}CHNEt_2$	45
$Cl(CF_2)_3CF_2I$	NEt_3	$Cl(CF_2)_3CF_2CH{=}CHNEt_2$	48
$Cl(CF_2)_5CF_2I$	NEt_3	$Cl(CF_2)_5CF_2CH{=}CHNEt_2$	50
$Cl(CF_2)_7CF_2I$	NEt_3	$Cl(CF_2)_7CF_2CH{=}CHNEt_2$	40
$Cl(CF_2)_5CF_2I$	$N(Pr\text{-}n)_3$	$Cl(CF_2)_5CF_2\underset{CH_3}{C}{=}CHN(Pr\text{-}n)_2$	50
$Cl(CF_2)_5CF_2I$	$N(Bu\text{-}n)_3$	$Cl(CF_2)_5CF_2\underset{C_2H_5}{C}{=}CHN(Bu\text{-}n)_2$	46

* Because of the instability of perfluoroalkyl enamine, its distillation is sufferred partial decomposition causing the decrease of the isolated yield.

Hydrolysis of enamine (**1**) at 40°C for 30 min afforded easily either enaminone (**2**) or aldehyde (**3**) accompanied by its dehydrofluorination product **4** depending upon whether alkyl group is present or not at β-carbon. The conversion of **1** reaches nearly to 100% and the yields of **2** or **3** are shown in Table 2.

$$R_FCF_2CH{=}CHN(CH_2CH_3)_2 \xrightarrow{2M\ HCl} R_FCOCH{=}CHN(CH_2CH_3)_2$$

2



$$R_FCF_2\overset{R}{C}{=}CHN(CH_2CH_2R)_2 \xrightarrow{2M\ HCl} R_FCF_2\overset{R}{C}HCHO + R_FCF{=}\overset{R}{C}CHO + R_FCO\overset{R}{C}{=}CHN(CH_2CH_2R)_2$$

3 **4**

major minor trace

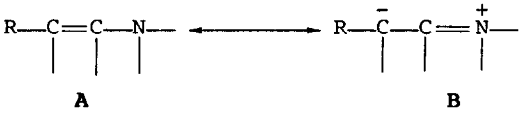
It is noteworthy that enaminone has been attracted much attention by organic chemists due to its multiple reactive centers.[2-4]

The behavior of the enamine structure can be ascribed to resonance by conjugation of the unshared pair of electrons of N atom with the π-electrons of the duoble bond:

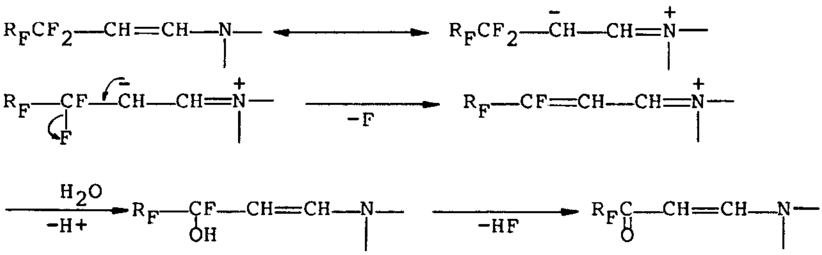
Table 2 Yield of Hydrolyzed products

Reactant	Product	Yield(%)*	m.p. or b.p(°C)
$CF_3(CF_2)_2CF_2CH=CHNEt_2$	$CF_3(CF_2)_2COCH=CHNEt_2$	92	30-32
$CF_3(CF_2)_4CF_2CH=CHNEt_2$	$CF_3(CF_2)_4COCH=CHNEt_2$	86	45-47
$Cl(CF_2)CF_2CH=CHNEt_2$	$Cl(CF_2)COCH=CHNEt_2$	95	20-21
$Cl(CF_2)_3CF_2CH=CHNEt_2$	$Cl(CF_2)_3COCH=CHNEt_2$	83	42-43
$Cl(CF_2)_5CF_2CH=CHNEt_2$	$Cl(CF_2)_5COCH=CHNEt_2$	95	50-52
$Cl(CF_2)_7CF_2CH=CHNEt_2$	$Cl(CF_2)_7COCH=CHNEt_2$	93	53-54
$Cl(CF_2)_5CF_2\underset{CH_3}{C}=CHN(Pr\text{-}n)_2$	$Cl(CF_2)_5CF_2\underset{CH_3}{C}HCHO$	69(91)	70-72/15 mmHg
$Cl(CF_2)_5CF_2\underset{C_2H_5}{C}=CHN(Bu\text{-}n)_2$	$Cl(CF_2)_5CF_2\underset{C_2H_5}{C}HCHO$	46(67)	68-70/8 mmHg

* Isolated yield, the figure in parenthesis denotes the yield determined by ^{19}F NMR



Hydrolysis of enamine, in general, affords carbonyl compound through imine intermediate.[5] However, when R group of the above formula is displaced by R_FCF_2 group, form **B** predominates due to the stabilization of anion, and the elimination of F ion occurs readily.[6] The following reaction sequence is thus proposed:



When both R_FCF_2 and alkyl group are present at β-carbon of enamine, doubtless, the electron-withdrawing action of R_FCF_2 will be partially counteracted, causing the stabilization of anion more or less unfavorable, therefore, the usual hydrolyzed product, aldehyde, is obtained.

EXPERIMENT

Typical procedure 1) **2(ω-chloro-dodecafluoro-n-hexyl)vinyl Diethylamine:** to 5 ml n-hexane were added 465 mg (1 mmol) $Cl(CF_2)_5CF_2I$, 200 mg(2 mmol) NEt_3 and 55 mg (0.05 mmol) $Pd(PPh_3)_4$. The reaction mixture was heated under N_2 at 60°C for 30 min with stirring. ^{19}F NMR showed that the conversion of $Cl(CF_2)_5CF_2I$ was 100%, and the yield of the product was 50% (from $Cl(CF_2)_5CF_2I$). After removal of the solvent and excess NEt_3, the residue was distilled with micro distillator, giving pure product (27%), b.p. 60°C/2mmHg, IR: (cm^{-1}) 1650(C=C), 1100-1300 (C-F); ^1H NMR: (CCl_4) 6.49(d, 1H, J_{HH}=13Hz), 3.90(m, 1H), 3.03(q, 4H, J_{HH}=7Hz), 1.06(t, 6H, J_{HH}=7Hz); ^{19}F NMR: (CCl_4 $FCCl_3$ ext) 65.5(t, 2F, J_{FF}=14Hz), 101.8 (m, 2F), 118.7(m, 2F), 119.8(m, 4F), 121.4(m, 2F); MS: m/z 433(M^+, 33.97%), 434(24.86), 435(13.25), 398(15.51), 148(100), 98(9.52), 85(18.63); Anal. Calcd for $C_{12}H_{12}ClF_{12}N$: C,33.25; H, 2.77; Cl,8.06; F,52.66; N,3.23. Found: C,33.06; H,2.70; Cl,7.86; F,52.70; N,3.16.

2) **2(ω-chloro-decafluoro-n-caproyl)vinyl Diethylamine:** 110 mg(0.25 mmol) of the above compound was treated with 2 ml of 2M HCl at 40°C for 0.5 hr. The reaction mixture was extracted several times with ether. The combined ethereal solution was dried with Na_2SO_4, After removal of the solvent, 98 mg (95%) of the product was chromatographed on silica gel (eluted with 3:1 benzene and ethyl acetate). Recrystallization with methanol gave pure product, m.p.50-52°C. IR: (cm^{-1}) 1670(C=O), 1580(C=C), 1100-1300(C-F); ^1H NMR: (CCl_4) 7.92(d, 1H J_{HH}= 12.5Hz), 5.28(d, 1H, J_{HH}=12.5Hz), 3.48(q, 2H, J_{HH}=7Hz), 3.32(q, 2H, J_{HH}=7Hz), 1.28(t, 3H, J_{HH}=7Hz), 1.23(t, 3H, J_{HH}=7Hz); ^{19}F NMR; ($CCl_4/FCCl_3$ ext) 66.1(t, 2F, J_{FF}=14Hz), 119.1(m,2F) 121.4(m, 6F); MS: m/z 411(M+, 17.42%), 412(14.77), 413(5.70), 376(10.17), 126(100), 85(5.05); Anal. Calcd for $C_{12}H_{12}ClF_{10}NO$: C, 35.00; H, 2.91; Cl,8.49; F,46.12; N,3.39; Found: C,35.16; H,2.90; Cl,8.14; F, 46.10; N,3.28.

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