Pharmaceuticals Research Division for the authentic sample of compactin and Professor Clayton H. Heathcock for comparison spectra. We also thank Dr. Steven Fleischman for carrying out some of the molecular mechanics calculations.

Registry No. 1, 73573-88-3; 4, 86031-03-0; (±)-10, 43119-22-8; 11, 108712-85-2; (±)-12, 108712-86-3; (±)-13, 108712-87-4; (±)-14, 108712-88-5; (±)-15, 108813-29-2; (±)-16 (isomer 1), 108712-89-6; (±)-16 (isomer 2), 108813-30-5; (±)-17 (isomer 1), 108712-90-9; (±)-17 (isomer 2), 108813-31-6; (±)-18 (isomer 1), 108712-91-0; (±)-18 (isomer 2), 108813-32-7; (±)-19, 108712-92-1; (±)-20, 108813-33-8; (±)-21, 108814-46-6; (±)-22, 108712-93-2; (±)-23, 108712-94-3; (±)-24, 108813-34-9; (±)-25, 108712-95-4; (±)-26, 108712-96-5; (±)-27, 108712-97-6; (±)-28, 108712-98-7; (±)-29, 108712-99-8; 30, 108713-00-4; (±)-31, 108713-01-5; (±)-32, 95218-60-3; 34, 108713-02-6; (±)-35, 108712-46-5; (±)-37, 108712-47-6; (±)-37 (methyl epimer), 108712-48-7; (±)-38, 108712-49-8; (±)-38 (pivalate), 108712-50-1; (±)-42, 108712-52-3; (±)-42 (pivalate), 108712-51-2; (±)-42 (methyl epimer), 108813-28-1; (±)-43, 108712-54-5; (±)-43 (sulfate), 108712-53-4; 45, 108712-55-6; 47, 108712-64-7; 49, 108712-57-8; 49 ($PhSO_2$ deriv), 108712-56-7; 49 (aldehyde), 108712-58-9; 49 (aldoxime), 108712-59-0; 50, 108712-60-3; 51, 108712-61-4; 52, 108712-62-5; (±)-53, 108712-67-0; (±)-2-*epi*-53, 108712-68-1; (±)-53 (8-MOM ether), 108712-69-2; (±)-53 (8-$OCMe_3$ ether), 108712-70-5; (±)-53 (8-*t*-$BuMe_2Si$ ether), 108712-71-6; (±)-53 (1-*t*-$BuMe_2Si$, 8-$OCMe_3$ ether), 108712-72-7; (±)-54, 108712-73-8; (±)-2-*epi*-54, 108712-74-9; (±)-55, 108712-75-0; (±)-2-*epi*-55, 108712-76-1; 56, 108712-63-6; 59, 108712-66-9; 59 (8-alcohol), 108712-65-8; 60, 108713-03-7; 60 (lactol), 108743-01-7; (±)-A (R^1 = *t*-$BuPh_2Si$, R^2 = MOM), 108712-77-2; (±)-A (R^1 = *t*-$BuPh_2Si$, R^2 = Me_3CO), 108712-79-4; (±)-A (R^1 = *t*-$BuPh_2Si$, R^2 = *t*-$BuMe_2Si$), 108712-81-8; (±)-A (R^1 = *t*-$BuMe_2Si$, R^2 = Me_3CO), 108712-83-0; (±)-B (R^1 = *t*-$BuPh_2Si$, R^2 = MOM), 108712-78-3; (±)-R (R^1 = *t*-$BuPh_2Si$, R^2 = Me_3CO), 108712-80-7; (±)-B (R^1 = *t*-$BuPh_2Si$, R^2 = *t*-$BuMe_2Si$), 108712-82-9; (±)-B (R^1 = *t*-$BuPh_2Si$, R^2 = Me_3CO), 108712-84-1; (±)-THPO$(CH_2)_2$CHO, 89922-81-6; $(CH_3CH_2CH(CH_3)CO)_2O$, 1519-23-9; *trans*-$CH_3CH{=}CHCH_2OH$, 504-61-0; (*S*)-$CH_3CH_2CH(CH_3)CO_2H$, 1730-91-2.

Nickel-, Palladium-, and Platinum-Catalyzed Reactions of Perfluoro- and Polyfluoroalkyl Iodides with Tertiary Amines

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The relative catalytic activities of Ni group metals in the reactions of perfluoroalkyl and polyfluoroalkyl iodides with tertiary amines to give enamines were compared, giving a reactivity order Ni > Pd > Pt, which parallels the order of the first ionization potential of the three metals. In comparing the Ni-catalyzed reaction of iodide **1** with tertiary amines containing zero to three methyl groups, it was found that in the case of trimethylamine only the reduced product **4** was formed, while the other three types of tertiary amines produced enamines (**19**, **21**, **23**) as well as **4**. The chemoselectivity of this reaction was studied. A mechanism is proposed for the reaction. Acid hydrolysis of (fluoroalkyl)enamines afforded enaminones or aldehydes depending upon the presence or absence of an alkyl group at the β-carbon.

It is well-known that fluoroalkyl halides (R_FX: R_F = perfluoro- or polyfluoroalkyl; X = Cl, Br, I), unlike the alkyl halides, are not able to form quarternary ammonium salts. Pullin et al.[1] reported that perfluoroalkyl halides react with tertiary amines to form 1:1 acceptor/donor adducts:

$$R_F{\cdots}I{\cdots}NR_3$$

Since then, few reports have appeared in the literature concerning this reaction.

Our discovery of the formation of enamines in the Pd-catalyzed reactions of perfluoro- and polyfluoroalkyl iodides with tertiary amines[2] led us to study this novel reaction in detail. The following is the general equation of this reaction

$$2R_FCF_2I + 3RCH_2CH_2NR^1R^2 \xrightarrow[n\text{-}C_6H_{14}]{ML_4} R_FCF_2C(R){=}CHNR^1R^2 + R_FCF_2H + 2(RCH_2CH_2)NR^1R^2{\cdot}HI$$

where R_F = $CF_3(CF_2)_n$, $ClCF_2(CF_2)_n$; R = H, alkyl; R^1, R^2 = alkyl; M = Ni, Pd, Pt; and L = PPh_3.

Results and Discussion

Relative Reactivities of the Catalysts. In a comparison of the relative activity of Ni group metals (Scheme I), it was found that in the reaction of iodide **1** with tri-

Scheme I

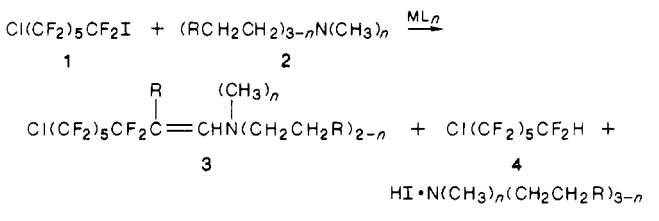

Table I. Relative Reactivities of the Catalysts in the Reactions of 1 with Various Amines

amine	catalyst	temp, °C/time,[a] h	yield,[b] % 3	4
$(CH_3CH_2)_3N$	$Ni(PPh_3)_4$	room temp/0.5	50	50
$(CH_3CH_2)_3N$	$Pd(PPh_3)_4$	60/0.5	50	50
$(CH_3CH_2)_3N$	$Pt(PPh_3)_4$	60/0.5	48	52
$(n\text{-}Pr)_3N$	$Ni(PPh_3)_4$	room temp/0.5	50	50
$(n\text{-}Pr)_3N$	$Pd(PPh_3)_4$	60/0.5	45	55
$(n\text{-}Pr)_3N$	$Pt(PPh_3)_4$	60/0.5	50	50
$(CH_3CH_2)_2NCH_3$	$Ni(PPh_3)_4$	room temp/0.5	35	65
$(CH_3CH_2)_2NCH_3$	$Pd(PPh_3)_4$	60/0.5	36	65
$(CH_3CH_2)_2NCH_3$	$Pt(PPh_3)_4$	70/2	tr	89
$(n\text{-}Pr)N(CH_3)_2$	$Ni(PPh_3)_4$	room temp/2	15	85
$(n\text{-}Pr)N(CH_3)_2$	$Pd(PPh_3)_4$	70/1	7	83
$(n\text{-}Pr)N(CH_3)_2$	$Pt(PPh_3)_4$	70/2	tr	90

[a] Conditions for complete reaction of 1. [b] Determined by ^{19}F NMR.

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(2) (a) Huang, Y. Z.; Zhou, Q. L.; Li, J. S. *Youji Huaxue* **1985**, 332. (b) Huang, Y. Z.; Zhou, Q. L. *Tetrahedron Lett.* **1986**, *27*, 2397.

0022-3263/87/1952-3552$01.50/0

ethylamine and tri-*n*-propylamine catalyzed by 0.5 mol % $M(PPh_3)_4$ (M = Ni, Pd, Pt) the Ni species possesses the highest reactivity as evidenced by the fact that it is able to catalyze the reaction at 0 °C or room temperature, while the other two metal complexes require higher temperatures (50–60 °C) to induce the reaction. Table I shows the results. Although different temperatures are required for the reactions with the various catalysts, the final yields of the enamines **3** (45–50% based on iodide) and the reduced products **4** (50%) are similar.

The relative reactivities of three kinds of catalysts in the reactions of **1** with diethylmethylamine and *n*-propyldimethylamine have been compared; the results are shown in Table I.

The relative catalytic activity of the three metal catalysts is in the order Ni > Pd > Pt, which parallels the order of the first ionization potentials of the metal (Ni 7.63, Pd 8.33, Pt 9.0 eV). The reactivity of $Ni(cod)_2$ is nearly the same as that of $Ni(PPh_3)_4$, and that of $Pd(dppe)_2$ is nearly the same as that of $Pd(PPh_3)_4$. $PdCl_2(PPh_3)_2$ is inactive. These observations indicate that the kind and the oxidation state of the metal in the complexes play an important role.

Mechanism. It was found that light is not needed in the reaction, initiators other than ML_n such as AIBN and peroxides do not initiate the reaction, and the reaction is completely inhibited on adding a free-radical scavenger, *p*-dinitrobenzene or hydroquinone. On the basis of these facts, in our previous paper we proposed a simple two-step mechanism.

$$R_FCF_2I + RCH_2CH_2NR^1R^2 \xrightarrow{Pd} RCH{=}CHNR^1R^2 + R_FCF_2H + HI$$

$$R_FCF_2I + RCH{=}CHNR^1R^2 \xrightarrow{Pd} R_FCF_2C(R){=}CHNR^1R^2 + HI$$

Here we suggest the more detailed mechanism shown in Scheme II.

Scheme II

$$R_FCF_2I + Pd \rightarrow R_FCF_2\cdot + \cdot PdI \quad (1)$$

$$R_FCF_2\cdot + RCH_2CH_2\ddot{N}< \rightarrow R_FCF_2^- + RCH_2CH_2\dot{N}^+< \quad (2)$$

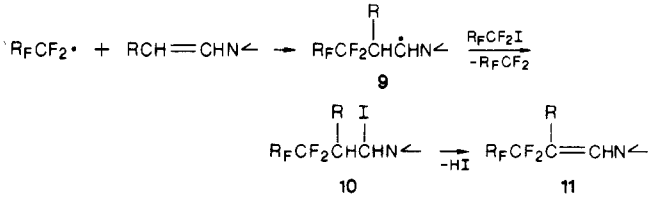
$$RCH_2CH_2\dot{N}^+< + R_FCF_2^- \rightarrow RCH_2\dot{C}H\ddot{N}< + R_FCF_2H \quad (3)$$

$$RCH_2\dot{C}H\ddot{N}< + \cdot PdI \rightarrow RCH{=}CH\ddot{N}< + HPdI \quad (4)$$

$$HPdI \rightarrow HI + Pd$$

Equation 1 involves the formation of the perfluoroalkyl radical $R_FCF_2\cdot$. It is well-known that perfluoroalkyl iodides undergo ready oxidative addition reactions with the Ni group metal complexes. Kochi,[3] Osborn,[4] and Parshall[5] and their co-workers have shown that the oxidative addition of active alkyl halides with d^{10} metal complexes might involve, at least in part, a single-electron transfer (SET) or a radical-chain process. However, owing to the reported stability of $R_FCF_2PdIL_n$[6] it seems unlikely that dissociation of a covalent complex can induce the observed reaction. In fact, an authentic sample of $R_FCF_2PdI(PPh_3)_2$ does not induce the reaction between **1** and a tertiary amine, even in the presence of excess PPh_3.

Scheme III



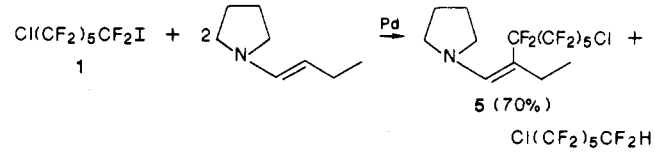
The second step (eq 2) involves the transfer of an electron from the nitrogen atom to form the aminium radical. This process resembles the electron transfers from nitrogen in the chemical oxidations,[7] photochemical oxidations,[8] and electrochemical oxidations[9] of amines, which have been well established. Abstraction of a proton from the α-carbon of the aminium intermediate by $R_FCF_2^-$ produces the reduced product **4** and the highly stabilized α-aminoalkyl radical (eq 3). Abstraction of a β-hydrogen atom by ·PdI finally produces an enamine and HPdI, which undergoes reductive elimination to regenerate the zerovalent metal catalyst. Another possibility is the abstraction of α hydrogen directly by $R_F\cdot$, if so, the reaction will not stop at one alkyl group in the case of a tertiary amine. This is in contradiction with the experimental facts.

An alternative to steps 3 and 4 is the sequence shown in eq 5 and 6. Evidence has been obtained for the formation of iminium ion intermediates and will be presented later.

$$RCH_2CH_2N^{\cdot+}< + \cdot PdI \rightarrow RCH_2CH{=}N^+< + HPdI \quad (5)$$

$$RCH_2CH{=}N^+< + R_FCF_2^- \rightarrow RCH{=}CH\ddot{N}< + R_FCF_2H \quad (6)$$

In order to prove that an enamine $RCH{=}CHNR^1R^2$ might be an intermediate in the reaction, the following reaction was carried out



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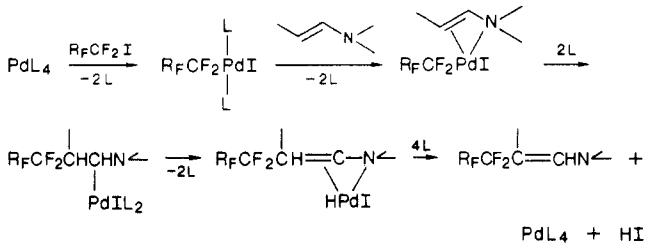
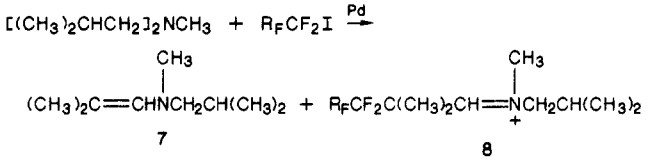
Scheme IV

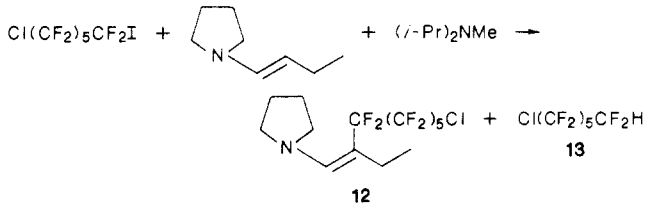


and it was observed that the ratio of **5** in the products increased to 93%, instead of lower than 50% of enamine formed starting from the tertiary amines. In addition, in the reaction of **1** with diisobutylmethylamine catalyzed by Pd, enamine **7** and the iminium ion **8** were formed, the latter being obviously the addition product of R_FCF_2I and enamine **7**. Acid hydrolysis of **8** afforded the corresponding aldehyde. Lewis et al.[8c,e] and Mann et al.[9a,b] have also shown that the photochemical and electrochemical oxidation of tertiary amines proceeds through the enamine intermediates.



Alternatively, the $R_FCF_2\cdot$ can interact with the enamine to form the stabilized polyfluoroalkyl-substituted free radical **9**, which reacts with R_FCF_2I to form **10** and a polyfluoroalkyl radical. Elimination of HI from **10** gives the enamine **11**[10] (Scheme III).

Another alternative is that the reaction might proceed via the mechanism shown in Scheme IV. In order to support our suggestion that the reaction proceeded according to Scheme III and not Scheme IV (like the Heck reaction) we carried out the following reaction:

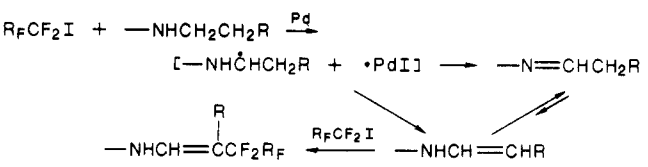


Yields were as follows: with no catalyst, 17% **12** and 10% **13**; with $R_FCF_2PdI(PPh_3)_2$, 18% **12** and 21% **13**; with $Pd(PPh_3)_4$, 70% **12** and 20% **13**.

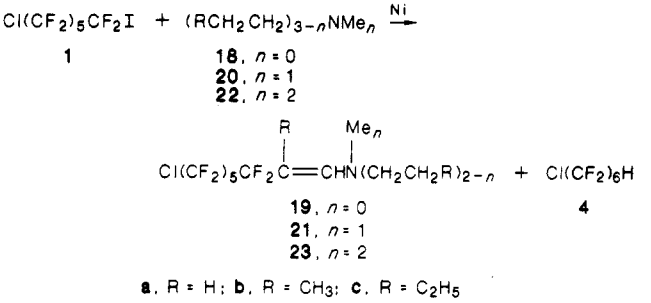
The results show that when $R_FCF_2PdI(PPh_3)_2$ was used, the yield of product **12** did not increase, as compared with the reaction in the absence of catalyst (this result differs from that reported in the literature,[10] which showed that ultraviolet light is necessary to induce the reaction). On the contrary, when $Pd(PPh_3)_4$ was used, the yield of **12** increased greatly. This suggests that it is likely that the reaction proceeds according to Scheme III.

Reactions with Secondary Amines. In the previous paper[2] we reported that the reaction of R_FCF_2I with secondary amines did not give $R_FCF_2CR{=}CHNHR^1$ when an excess of the secondary amine was used. When an excess of R_FCF_2I was allowed to react with diethylamine or di-*n*-butylamine, products **14** and **15** and **16** and **17** were formed, respectively (*based upon the amine used).

Scheme V



Scheme VI



Scheme VII

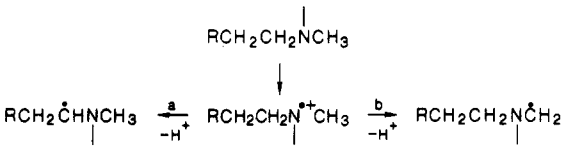
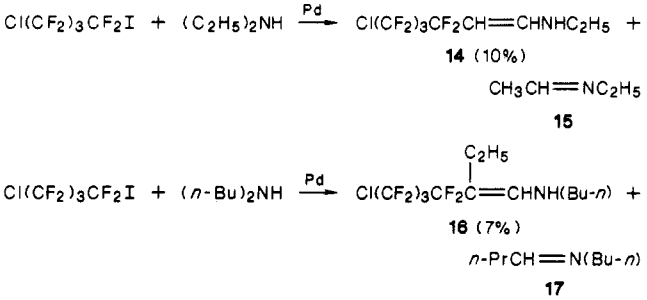


Table II. Reaction of Iodide 1 with Amines 18, 20, and 22

amine	R	yield, % 19[a]	21	23
a	H	50 (0.5)[b]	35 (1)	23 (2)
b	CH_3	50 (0.5)	36 (1.5)	15 (2)
c	C_2H_5	48 (0.5)	30 (2.5)	20 (2)

[a] Determined by ^{19}F NMR. [b] Time (hours) required for complete conversion of iodide **1** in parentheses.



These facts indicate that, in the cases of secondary amines, enamine and imine formed concurrently, and the former could easily be in equilibrium with the imine.[11] However, in the presence of an excess of the R_FCF_2I, the intermediate enamine is trapped (Scheme V).

Reactivity of Tertiary Amines. In comparing the catalyzed reaction of iodide **1** with tertiary amines containing zero to three methyl groups, it was found that in the case of trimethylamine only the reduced product **4** was formed, while for the other tertiary amines enamines were formed as well as **4** (Scheme VI).

Table II shows the yields of enamines **19**, **21**, and **23** formed in the reactions of iodide **1** with **18**, **20**, and **22**

(10) (a) Cantacuzene, D.; Wakselman, C.; Dorme, R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 1365. (b) Wakselman, C.; Cantacuzene, D. *Inf. Chim.* **1978**, *175*, 153.

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catalyzed by 5 mol % $Ni(PPh_3)_4$ at 20 °C.

The yields of the enamines **19**, **21**, and **23** derived from the tertiary amines **18**, **20**, and **22** are in the order $(RCH_2CH_2)_3N > (RCH_2CH_2)_2NCH_3 > RCH_2CH_2N(CH_3)_2$. These data show that two pathways (a and b) for abstraction of α-hydrogen of the aminium radical are possible (Scheme VII). If α-hydrogen abstraction is a random process, the yields of the three kinds of enamines **19**, **21**, and **23** should be 50%, 36%, and 20% (based on iodide) with complete consumption of the iodide, which are in agreement with our results.

Chemoselectivity of Reaction. In order to assess the chemoselectivity within a tertiary amine containing ethyl and propyl groups, we carried out the following reactions.

$$(CH_3CH_2CH_2)N(C_2H_5)_2 \xrightarrow[\text{yield 48\%}]{Cl(CF_2)_3CF_2I/Pd} \underset{\textbf{24}}{Cl(CF_2)_3CF_2CH{=}CHN(C_3H_7\text{-}n)} + \underset{\textbf{25}}{Cl(CF_2)_3CF_2C(CH_3){=}CHN(C_2H_5)_2}$$

24:25 = 2.5:1

$$(CH_3CH_2CH_2)_2NC_2H_5 \xrightarrow[\text{yield 50\%}]{Cl(CF_2)_3CF_2I/Pd} \underset{\textbf{26}}{Cl(CF_2)_3CF_2CH{=}CHN(C_3H_7\text{-}n)_2} + \underset{\textbf{27}}{Cl(CF_2)_3CF_2C(CH_3){=}CHN(C_2H_5)(C_3H_7\text{-}n)}$$

26:27 = 1:1.7

The results indicate that abstraction of hydrogen from an ethyl group is favored slightly over the *n*-propyl group, presumably due to steric effects.

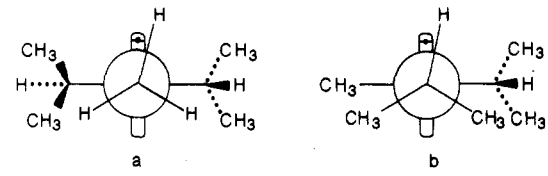
In order to evaluate the effect of double substitution at the α-carbon the reactions of R_FCF_2I with diisopropylmethylamine and isopropyldimethylamine were carried out. No (polyfluoroalkyl)enamine was obtained; only the reduced product was isolated. With isopropyldiethylamine and cyclohexyldiethylamine only **28** and **29** were obtained, indicating that only the ethyl group reacts.

$$Cl(CF_2)_3CF_2I + (CH_3)_2CHN(C_2H_5)_2 \xrightarrow{Ni} \underset{\textbf{28}\ (30\%)}{Cl(CF_2)_3CF_2CH{=}CHN(C_3H_7\text{-}i)}$$

$$Cl(CF_2)_3CF_2I + \text{(N(C}_2\text{H}_5\text{)}_2\text{ cyclohexyl)} \xrightarrow{Ni} \underset{\textbf{29}\ (34\%)}{Cl(CF_2)_3CF_2CH{=}CH\text{-(N cyclohexyl)}}$$

Many earlier reports[7d,8b,d,9a] and our observations indicate that the oxidation of tertiary amines occurs selectively at the α-carbon with the fewest substituents. The mechanism of deprotonation of the α-carbon of the aminium radical is somewhat like the mechanism of the E1 elimination,[8b] which requires at least partial overlap of the half-vacant p orbital of nitrogen with the developing carbon radical p orbital. Two conformations of the aminium radical required for the loss of the two types of protons in diisopropylmethylamine are shown in the Newman projections **a** and **b**. Clearly, the steric interactions are greater in **b** than in **a**. Therefore, the deprotonation at methyl is preferable to isopropyl.

In the comparison of the chemoselectivity between the cyclic and acyclic groups in N-substituted piperidines, it was found that the reactivity of *N*-methylpiperidine is somewhat like that of di-*n*-propylmethylamine. In the case of ethylpiperidine, the reactivity at the site of ring is almost



a b

the same as at the site of the ethyl group; while in the case of *n*-butylpiperidine, the reactivity at the site of ring is preferred over that of *n*-butyl group. These results are in agreement with the earlier observation that the reactivity of the ethyl group is greater than that of the *n*-propyl group.

$$Cl(CF_2)_3CF_2I + \text{(N cyclohexyl)} \longrightarrow \underset{\textbf{30}\ (33\%)}{\text{(N cyclohexyl)-CF}_2(CF_2)_3Cl}$$

$$Cl(CF_2)_3CF_2I + \text{(NC}_2\text{H}_5\text{ cyclohexyl)} \longrightarrow \underset{\textbf{31}\ (31\%)}{\text{(NC}_2\text{H}_5\text{ cyclohexyl)-CF}_2(CF_2)_3Cl} + \underset{\textbf{32}\ (15\%)}{\text{(N cyclohexyl)-CH=CHCF}_2(CF_2)_3Cl}$$

$$Cl(CF_2)_3CF_2I + \text{(N(Bu-}n\text{) cyclohexyl)} \longrightarrow \underset{\textbf{33}\ (30\%)}{\text{(N(Bu-}n\text{) cyclohexyl)-CF}_2(CF_2)_3Cl} + \underset{\textbf{34}\ (9\%)}{\text{(N cyclohexyl)-CH=CC}_2\text{H}_5\text{-CF}_2(CF_2)_3Cl}$$

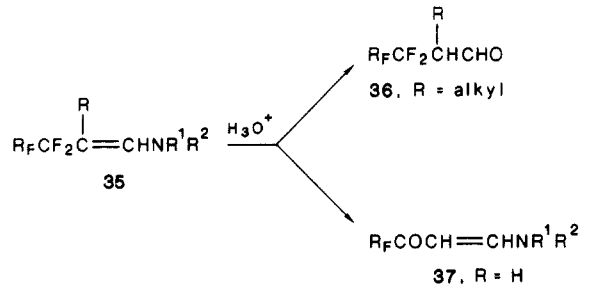
Hydrolysis of (Perfluoroalkyl)enamines. In our previous paper we reported that the behavior of the enamine can be ascribed to resonance by conjugation of the unshared pair of electrons of the nitrogen atom with the π-electrons of the double bond.

$$\underset{\textbf{A}}{R{-}C{=}C{-}\ddot{N}} \longleftrightarrow \underset{\textbf{B}}{R{-}\overset{-}{C}{-}C{=}\overset{+}{N}}$$

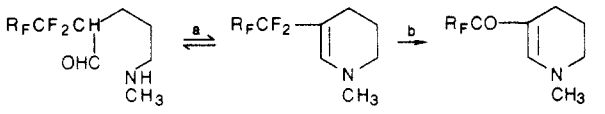
Hydrolysis of an enamine, in general, affords carbonyl compounds through iminium ion intermediates. However, when the R group in the above formula is R_FCF_2, form **B** predominates due to the stabilization of the anionic center, and the elimination of fluoride ion occurs, forming ultimately an enaminone.[2b,12] When both R_FCF_2 and alkyl group are present at the β-carbon of the enamine, the usual hydrolysis product, an aldehyde, is obtained. Thus, the hydrolysis of compound **35** forms aldehyde **36** or enaminone **37**, depending on the nature of the R group present. Table III shows the results of the hydrolysis of the various (fluoroalkyl)enamines.

The acid hydrolysis of *N*-alkyl-β-(polyfluoroalkyl)-$\Delta^{\alpha,\beta}$-piperidine **38**, however, afforded the enaminone **39** exclusively. This may be rationalized by the following

(12) (a) Nield, E.; Tatlow, J. C. *Tetrahedron* **1960**, *8*, 38. (b) Sweeney, R. F.; Veldhuis, B.; Gilbert, E. E.; Anello, L. G.; DuBois, R. J.; Cunningham, W. J. *J. Org. Chem.* **1966**, *31*, 3174. (c) Park, J. D.; Frank, W. C. *J. Org. Chem.* **1967**, *32*, 1336. (d) Park, J. D.; Cohen, S.; Lacher, J. R. *J. Am. Chem. Soc.* **1962**, *84*, 2919. (e) Blanc, M. Le.; Santini, G.; Riess, J. G. *Tetrahedron Lett.* **1975**, *47*, 4151.

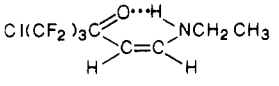


mechanism in which the aldehyde **40** is in equilibrium with **38** which proceeds irreversibly to **39**.



40 38 39

The configuration of the double bonds in all enaminones are trans as shown by the coupling constant of two olefinic hydrogens (11–13 Hz) except for **41**, the hydrolyzed product of enamine **14**, in which the coupling constant between the two olefinic hydrogens is 6.1 Hz. The cis configuration in **41** is undoubtedly favored by the existence of intramolecular hydrogen bonding as shown in **41**.



41

Conclusion

Since Stork and co-workers[13] reported the first example of alkylation of an enamine, enamine chemistry has progressed very rapidly and has become a very active area of organic chemistry.[14] Many methods have been developed for the synthesis of enamines. However, few methods for the synthesis of enamines directly from tertiary amines have appeared in the literature,[15] especially catalyzed by transition-metal complexes. Our reaction is an one-step reaction that directly produces a double bond in saturated tertiary amines followed by introduction of a fluoroalkyl group. The reaction conditions are very mild, the manipulations are simple, and the yields are good. Therefore, it provides a new, facile method for the synthesis of fluoroalkyl-substituted enamines and enaminones.

Experimental Section

Catalysts $Ni(PPh_3)_4$, $Pd(PPh_3)_4$, and $Pt(PPh_3)_4$ were prepared according to the literature.[16] Perfluoroalkyl and polyfluoroalkyl iodides was redistilled prior to use. Tertiary amines were purchased, the methyl group containing amines were prepared according to Eschweiler–Clarke's method, and all amines were treated with metallic sodium before use. All the experiments were carried out under N_2 atmosphere. NMR spectra were recorded on EM-360A, IR recorded on IR-440, and MS recorded on MS-4021 spectrometers.

Procedure. [2-(Perfluoro-*n*-butyl)vinyl]diethylamine (I) and [2-(Perfluoro-*n*-butyryl)vinyl]diethylamine (II). A mixture of 346 mg (1 mmol) of $CF_3(CF_2)_2CF_2I$, 200 mg (2 mmol) of NEt_3, and 57 mg (0.05 mmol) of $Pd(PPh_3)_4$ in 5 mL of hexane was stirred at 60 °C for 30 min (Pt catalyst 60 °C, 30 min; Ni catalyst room temperature, 1 h). ^{19}F NMR showed that the iodide has converted completely, and the yields of I and $CF_3(CF_2)_2CF_2H$ were 45% and 55% (based on iodide), respectively. After the solid, solvent, and excess amine were removed, I (yellow liquid) was obtained: IR 1652 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 6.48 (d, 1 H, J = 12 Hz), 3.95 (q, 1 H, J_{HH} = 12 Hz, J_{HF} = 11 Hz), 3.12 (q, 4 H, J = 7 Hz), 1.14 (t, 6 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 81.2 (t, 3 F, J = 10 Hz), 104.2 (q, 2 F, J_{HF} = 11 Hz, J_{FF} = 12 Hz), 123.9 (m, 2 F), 125.5 (m, 2 F).

I was treated with 5 mL of 2 M HCl at 40 °C for 1 h and then neutralized with dilute NaOH and extracted with ether. The extract was washed with H_2O and dried with Na_2SO_4. After removal of the solvent and chromatography on silica gel (eluted with 2:1 petroleum ether/ethyl acetate), 122 mg (92% based on I) of II was obtained. Recrystallization with methanol gave pure product: mp 30–32 °C; IR 1665 (C=O), 1580 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.82 (d, 1 H, J = 12 Hz), 5.18 (d, 1 H, J = 12 Hz, 3.36 (q, 2 H, J = 7 Hz), 3.22 (q, 2 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.15 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 79.3 (t, 3 F, J = 10 Hz), 119.8 (t, 2 F, J = 10 Hz), 125.9 (s, 2 F); MS, m/z 296, 295, 276, 169, 126 (100), 69. Anal. Calcd for $C_{10}H_{12}F_7NO$: C, 40.68; H, 4.07; F, 45.05; N, 4.75. Found: C, 40.63 H, 4.21; F, 44.55; N, 4.61.

[2-(Perfluoro-*n*-caproyl)vinyl]diethylamine: mp 45–47 °C; IR 1670 (C=O), 1582 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.71 (d, 1 H, J = 12 Hz), 5.16 (d, 1 H, J = 12 Hz), 3.30 (q, 2 H, J = 7 Hz), 3.27 (q, 2 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.16 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 79.6 (t, 3 F, J = 10 Hz), 118.3 (m, 2 F), 121.4 (m, 2 F), 125.1 (m, 2 F); MS, m/z 397, 396, 395, 376, 126 (100), 69. Anal. Calcd for $C_{12}H_{12}F_{11}NO$: C, 36.46; H, 3.04; F, 52.91; N, 3.54. Found: C, 36.60; H, 3.12; F, 52.64; N, 3.51.

[2-(Chlorodifluoroacetyl)vinyl]diethylamine: mp 20–21 °C; IR 1670 (C=O), 1581 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.71 (d, 1 H, J = 12 Hz), 5.12 (d, 1 H, J = 12 Hz), 3.40 (q, 2 H, J = 7 Hz), 3.27 (q, 2 H, J = 7 Hz), 1.28 (t, 3 H, J = 7 Hz), 1.21 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 63 (m, 2 F); MS, m/z 213, 212, 211, 126 (100), 85. Anal. Calcd for $C_8H_{12}ClF_2NO$: C, 45.80; H, 5.69; Cl, 16.59; N, 6.64. Found: C, 46.03; H, 5.67; Cl 16.66; N, 6.54.

[2-(ω-Chlorohexafluoro-*n*-butyryl)vinyl]diethylamine: mp 42–43 °C; IR 1670 (C=O), 1580 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.78 (d, 1 H, J = 12.5 Hz), 5.16 (d, 1 H, J = 12.5 Hz), 3.36 (q, 2 H, J = 7 Hz), 3.19 (q, 2 H, J = 7 Hz), 1.20 (t, 3 H, J = 7 Hz), 1.15 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 65.6 (t, 2 F, J = 11 Hz), 118.4 (t, 2 F, J = 11 Hz), 119.9 (s, 2 F); MS, m/z 313, 312 311, 276, 126 (100), 85. Anal. Calcd for $C_{10}H_{12}ClF_6NO$: C, 38.46; H, 3.85; Cl, 11.22; F, 36.54; N, 4.48. Found: C, 38.03; H, 3.85; Cl, 10.97; F, 37.07; N, 4.40.

[2-(ω-Chlorohexafluoro-*n*-butyryl)vinyl]-*n*-propylethylamine: mp 44–45 °C IR 1660 (C=O), 1570 (C=C), 1080–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.86 (d, 1 H, J = 11.3 Hz), 5.21 (d, 1 H, J = 11.3 Hz), 3.66–3.01 (m, 4 H), 2.00–1.45 (m, 2 H), 1.26 (t, 3 H, J = 7 Hz), 0.95 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 65.7 (t, 2 F, J = 11.2 Hz), 117.7 (t, 2 F, J = 11.2 Hz), 119 (s, 2 F); MS, m/z 327, 326, 325, 306, 290, 140 (100), 56. Anal. Calcd for $C_{11}H_{14}ClF_6NO$: C, 40.55; H, 4.30; Cl, 10.91; F, 35.02; N, 4.30. Found: C, 40.75; H, 4.31; Cl, 10.93; F, 34.83; N, 4.29.

[2-(ω-Chlorohexafluoro-*n*-butyryl)vinyl]di-*n*-propylamine: mp 48–49 °C; IR 1655 (C=O), 1575 (C=C), 1060–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.90 (d, 1 H, J = 11.2 Hz), 5.22 (d, 1 H, J = 11.2 Hz), 3.50–2.92 (m, 4 H), 2.04–1.30 (m, 4 H), 0.97 (t, 6 H, J = 6.5 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 65.3 (t, 2 F, J = 12 Hz), 117.5 (t, 2 F, J = 12 Hz), 119 (s, 2 F); MS, m/z 341, 340, 339, 320, 304, 155, 154 (100), 70, 43. Anal. Calcd for $C_{12}H_{16}ClF_6NO$: C, 42.48; H, 4.72; Cl, 10.47; F, 33.63; N, 4.23. Found: C, 42.50; H, 4.84; Cl, 10.36; F, 33.53; N, 3.93.

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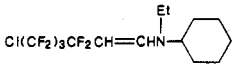
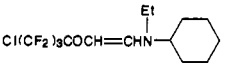
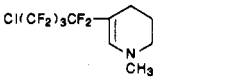
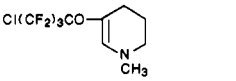
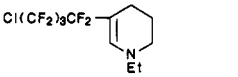
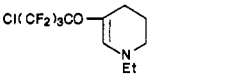
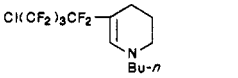
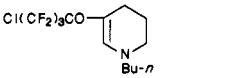
Table III. Hydrolysis of (Fluoroalkyl)vinylamines

enamine	product	yield,[a] %
$CF_3(CF_2)_2CF_2CH{=}CHNEt_2$	$CF_3(CF_2)_2COCH{=}CHNEt_2$	92
$CF_3(CF_2)_4CF_2CH{=}CHNEt_2$	$CF_3(CF_2)_4COCH{=}CHNEt_2$	86
$ClCF_2CF_2CH{=}CHNEt_2$	$ClCF_2COCH{=}CHNEt_2$	95
$Cl(CF_2)_3CF_2CH{=}CHNEt_2$	$Cl(CF_2)_3COCH{=}CHNEt_2$	83
$Cl(CF_2)_3CF_2CH{=}CH(Et)N(Pr\text{-}n)$	$Cl(CF_2)_3COCH{=}CH(Et)N(Pr\text{-}n)$	85
$Cl(CF_2)_3CF_2CH{=}CHN(Pr\text{-}n)_2$	$Cl(CF_2)_3COCH{=}CHN(Pr\text{-}n)_2$	94
		84
$Cl(CF_2)_5CF_2CH{=}CHNEt_2$	$Cl(CF_2)_5COCH{=}CHNEt_2$	95
$Cl(CF_2)_5CF_2CH{=}CHN(CH_3)Et$	$Cl(CF_2)_5COCH{=}CHN(CH_3)Et$	89
$Cl(CF_2)_5CF_2CH{=}CHN(CH_3)_2$	$Cl(CF_2)_5COCH{=}CHN(CH_3)_2$	96
$Cl(CF_2)_7CF_2CH{=}CHNEt_2$	$Cl(CF_2)_7COCH{=}CHNEt_2$	93
$Cl(CF_2)_5CF_2(CH_3)C{=}CHN(Pr\text{-}n)_2$	$Cl(CF_2)_5CF_2CH(CH_3)CHO$	69 (91)[b]
$Cl(CF_2)_5CF_2(CH_3)C{=}CH(CH_3)N(C_3H_7\text{-}n)$	$Cl(CF_2)_5CF_2CH(CH_3)CHO$	60 (87)
$Cl(CF_2)_5CF_2(CH_3)C{=}CHN(CH_3)_2$	$Cl(CF_2)_5CF_2CH(CH_3)CHO$	(83)
$Cl(CF_2)_5CF_2(Et)C{=}CHN(Bu\text{-}n)_2$	$Cl(CF_2)_5CF_2CH(Et)CHO$	46 (67)
$Cl(CF_2)_5CF_2(Et)C{=}CHN(CH_3)_2$	$Cl(CF_2)_5CF_2CH(Et)CHO$	52 (73)
$Cl(CF_2)_5CF_2(Et)C{=}CHN(CH_3)_2$	$Cl(CF_2)_5CF_2CH(Et)CHO$	(60)
		82
		90
		93

[a] Isolated yield (based on enamine). [b] Figures in parentheses denote the yields determined by ^{19}F NMR.

[2-(ω-Chlorohexafluoro-*n*-butyryl)vinyl]ethylcyclohexylamine: mp 68–70 °C; IR 1650 (C=O), 1570 (C=C), 1040–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.83 (d, 1 H, J = 11.5 Hz), 5.25 (d, 1 H, J = 11.5 Hz), 3.31 (q, 2 H, J = 6.2 Hz), 3.62–2.97 (m, 1 H), 2.50–0.70 (m, 10 H), 1.25 (t, 3 H, J = 6.2 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 65.8 (t, 2 F, J = 11.2 Hz, 117.7 (t, 2 F, J = 11.2 Hz), 119 (s, 2 F); MS, m/z 367, 366, 365, 284, 181, 180, 98, 82, 56, 55 (100). Anal. Calcd for $C_{14}H_{18}ClF_6NO$: C, 46.03; H, 4.93; Cl, 9.73; F, 31.23; N, 3.84. Found: C, 45.89; H, 5.00; Cl, 9.63; F, 31.71; N, 3.68.

[2-(ω-Chlorododecafluoro-*n*-hexyl)vinyl]diethylamine: bp 60 °C (2 mmHg); IR 1650 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 6.49 (d, 1 H, J = 12.5 Hz), 3.90 (d, 1 H, J_{HH} = 12.5 Hz, J_{HH} = 11.8 Hz), 3.03 (q, 4 H, J = 7 Hz), 1.06 (t, 6 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 65.8 (t, 2 F, J = 12 Hz), 101.8 (q, 2 F, J_{HF} = 11.8 Hz, J_{FF} = 12 Hz), 118.7 (m, 2 F), 119.8 (m, 4 F), 121.4 (m, 2 F); MS, m/z 435, 434, 433, 414, 398, 148 (100), 98, 85. 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-(ω-Chlorodecafluoro-*n*-caproyl)vinyl]diethylamine: mp 50–52 °C; IR 1670 (C=O), 1580 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.92 (d, 1 H, J = 12.5 Hz), 5.28 (d, 1 H, J = 12.5 Hz), 3.48 (q, 2 H, J = 7 Hz), 3.32 (q, 2 H, J = 7 Hz), 1.28 (t, 3 H, J = 7 Hz), 1.23 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 66.1 (t, 2 F, J = 12 Hz), 118.9 (m, 6 F), 121.4 (m, 2 F); MS, m/z 413, 412, 411, 376, 126 (100), 85. Anal. Calcd for $C_{12}H_{12}ClF_{10}NO$: C, 35.00; H, 2.91; Cl, 8.4; F, 46.10; N, 3.39. Found: C, 35.16; H, 2.90; Cl, 7.94; F, 46.12; N, 3.28.

[2-(ω-Chlorodecafluoro-*n*-caproyl)vinyl]methylethylamine: mp 40–42 °C; IR 1672 (C=O), 1585 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.72 (d, 1 H, J = 12 Hz), 5.09 (d, 1 H, J = 12 Hz), 3.30 (q, 2 H, J = 7 Hz), 2.81 (s, 3 H), 1.20 (t, 3 H, J = 7 Hz); ^{19} F NMR ($CCl_4/CFCl_3$ ext) δ 66.2 (t, 2 F, J = 12.5 Hz), 118.7 (m, 6 F), 121.3 (m, 2 F); MS, m/z 399, 398, 397, 378, 362, 112 (100), 85. Anal. Calcd for $C_{11}H_{10}ClF_{10}NO$: C, 33.25; H, 2.52; Cl, 8.94; F, 47.86; N, 3.53. Found: C, 33.10; H, 2.63; Cl, 8.81; F, 48.28; N, 3.47.

[2-(ω-Chlorodecafluoro-*n*-caproyl)vinyl]dimethylamine: mp 45–47 °C; IR 1670 (C=O), 1585 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.82 (d, 1 H, J = 12 Hz), 5.15 (d, 1 H, J = 12 Hz), 3.20 (s, 3 H), 2.89 (s, 3 H); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 66.3 (t, 2 F, J = 12.5 Hz), 118.7 (m, 6 F), 121.3 (m, 2 F); MS, m/z 385, 384, 383, 364, 348, 98 (100), 85. Anal. Calcd for $C_{10}H_8ClF_{10}NO$: C, 31.23; H, 2.17; Cl, 9.27; F, 49.61; N, 3.66. Found: C, 31.47; H, 2.26; Cl, 9.25; F, 49.30; N, 3.59.

[2-(ω-Chlorotetradecafluoro-*n*-capryloyl)vinyl]diethylamine: mp 53–54 °C; IR 1665 (C=O), 1580 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 7.78 (d, 1 H, J = 12 Hz), 5.17 (d, 1 H, J = 12 Hz), 3.40 (q, 2 H, J = 7 Hz), 3.25 (q, 2 H, J = 7 Hz), 1.22 (t, 3 H, J = 7 Hz), 1.16 (t, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 66.4 (t, 2 F, J = 12.5 Hz), 118.8 (m, 4 F), 120.2 (m, 6 F), 121.1 (m, 2 F); MS, m/z 513, 512, 511, 492, 476, 126 (100), 98, 85. Anal. Calcd for $C_{14}H_{12}ClF_{14}NO$: C, 32.88; H, 2.35; Cl, 6.85; F, 52.05; N, 2.74. Found: C, 33.22; H, 2.37; Cl, 6.78; F, 51.64; N, 2.70.

[2-Methyl-2-(ω-chlorododecafluoro-*n*-hexyl)vinyl]di-*n*-propylamine: bp 75 °C (2 mmHg); IR 1650 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 6.35 (s, 1 H), 3.17 (t, 4 H, J = 7 Hz), 1.93 (s, 3 H), 1.60 (m, 4 H), 1.01 (t, 6 H); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 66.5 (t, 2 F, J = 12.5 Hz), 107.1 (t, 2 F, J = 12.5 Hz), 119.2 (m, 2 F), 120.2 (m, 6 F); MS, m/z 477, 476, 475, 456, 440, 190, 85, 43 (100). Anal. Calcd for $C_{15}H_{18}ClF_{12}N$: C, 37.89; H, 3.79 Cl, 7.37; F, 48.00; N, 2.95. Found: C, 37.73; H, 3.89; Cl, 7.08; F, 47.63; N, 3.07.

2-Methyl-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-8-chlorooctanal: bp 70–72 °C (15 mmHg); IR 1742 (C=O), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 9.55 (s, 1 H), 3.70–2.50 (m, 1 H), 1.24 (d, 3 H, J = 7 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 67 (t, 2 F, J = 12 Hz), 114 (m, 2 F), 119.3 (m, 2 F), 120.1 (m, 6 F); MS, m/z 393, 392, 391 (100). Anal. Calcd for $C_9H_5ClF_{12}O$: C, 27.55; H, 1.28; Cl, 8.90; F, 58.16; N, 3.58. Found: C, 27.80; H, 1.32; Cl, 9.15; F, 58.05; N, 3.45.

[2-Methyl-2-(ω-chlorododecafluoro-*n*-hexyl)vinyl]-*n*-propylmethylamine: bp 80 °C (5 mmHg); IR 1660 (C=C), 1100–1300 (C—F) cm^{-1}; ^1H NMR (CCl_4) δ 6.26 (s, 1 H), 2.96 (s, 3 H), 2.37 (t, 2 H, J = 6 Hz), 1.88 (s, 3 H), 1.80–1.25 (m, 2 H), 0.90 (t, 3 H, J = 6 Hz); ^{19}F NMR ($CCl_4/CFCl_3$ ext) δ 67.0 (t, 2 F, J = 12 Hz), 107.5 (t, 2 F, J = 12 Hz), 119.6 (m, 2 F), 120.6 (m, 6 F); MS, m/z 449, 448, 447, 412, 85, 42 (100). Anal. Calcd for $C_{13}H_{14}ClF_{12}N$: C, 34.90; H, 3.13; Cl, 7.83; F, 51.01; N, 3.13. Found: C, 35.35; H, 2.97; Cl, 7.77; F, 50.67; N, 3.05.

2-Ethyl-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-8-chlorooctanal: bp 68–70 °C (8 mmHg); IR 1738 (C=O), 1100–1300 (C—F) cm^{-1};

^{1}H NMR (CCl_4) δ 9.62 (s, 1 H), 3.46-2.50 (m, 1 H), 2.28-1.70 (m, 2 H), 1.04 (t, 3 H, J = 7 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 67.2 (t, 2 F, J = 12.5 Hz), 113.7 (m, 2 F), 120.2 (m, 2 F), 120.8 (m, 6 F); MS, m/z 409, 407 (100), 405, 387. Anal. Calcd for $C_{10}H_7ClF_{12}O$: C, 29.56; H, 1.72; Cl, 9.74; F, 56.16. Found: C, 29.66; H, 1.91; Cl, 9.65; F, 55.57.

***N*-Methyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 92-94 °C (2 mmHg); IR 1580 (O=C-C=C), 1100-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.43 (s, 1 H), 3.17 (t, 2 H, J = 5.7 Hz), 3.10 (s, 3 H), 2.27 (t, 2 H, J = 5.6 Hz), 2.07-1.60 (m, 2 H); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.4 (t, 2 F, J = 11.4 Hz), 108.3 (t, 2 F, J = 11.5 Hz), 118.1 (s, 2 F); MS, m/z 311, 310, 309, 290, 274, 125, 124 (100). Anal. Calcd for $C_{10}H_{10}ClF_6NO$: C, 38.83; H, 3.24; Cl, 11.49; F, 36.89; N, 4.53. Found: C, 38.46; H, 3.39; Cl, 11.01; F, 36.80; N, 4.50.

***N*-Ethyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 76-78 °C (0.2 mmHg); IR 1580 (O=C-C=C), 1060-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.50 (s, 1 H), 3.33 (q, 2 H, J = 6.5 Hz), 3.27 (t, 2 H, J = 6 Hz), 2.28 (t, 2 H, J = 5.5 Hz), 2.10-1.60 (m, 2 H), 1.24 (t, 3 H, J = 6.5 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.5 (t, 2 F, J = 11.2 Hz), 108.5 (m, 2 F), 118.4 (m, 2 F); MS, m/z 325, 324, 323, 288, 139, 138 (100). Anal. Calcd for $C_{11}H_{12}ClF_6NO$: C, 40.87; H, 3.72; Cl, 10.99; F, 35.29; N, 4.33. Found: C, 40.70; H, 3.74; Cl, 10.93; F, 34.82; N, 4.22.

***N*-*n*-Butyl-$\Delta^{\alpha,\beta}$-2-(ω-chlorohexafluoro-*n*-butyryl)piperidine**: bp 75-78 °C (0.1 mmHg); IR 1575 (O=C-C=C), 1060-1300 (C-F) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.46 (s, 1 H), 3.52-2.97 (m, 4 He, 2.30 (t, 2 H, J = 5.7 Hz), 2.10-1.15 (m, 6 H), 0.95 (t, 3 H, J = 5.4 Hz); ^{19}F NMR (CCl_4/$CFCl_3$ ext) δ 65.4 (t, 2 F, J = 11.3 Hz), 108.1 (m, 2 F), 118.2 (s, 2 F); MS, m/z 353, 352, 351, 332, 316, 166 (100). Anal. Calcd for $C_{13}H_{16}ClF_6NO$: C, 44.44; H, 4.56; Cl, 10.11; F, 32.48. Found: C, 44.41; H, 4.82; Cl, 9.96; F, 31.97.

Registry No. **1**, 16486-97-8; **3** (R = H, n = 1)), 108836-15-3; **3** (R = H, n = 2), 108836-16-4; **3** (R = CH_3, n = 0), 107728-86-9; **3** (R = CH_3, n = 2), 108836-17-5; **3** (R = Et, n = 0), 107728-87-0; **4**, 307-22-2; **5**, 108836-18-6; **7**, 108836-19-7; **8**, 108836-20-0; **18**, 121-44-8; **19**, 98968-85-5; **20**, 3405-42-3; **21**, 108836-08-4; **22**, 927-62-8; **23**, 108836-21-1; **24**, 108836-12-0; **25**, 108836-22-2; **26**, 108836-13-1; **27**, 108836-23-3; **28**, 108868-11-7; **29**, 108836-14-2; **30**, 108836-24-4; **31**, 108836-25-5; **32**, 108868-12-8; **33**, 108836-26-6; **34**, 108836-27-7; **39** (R_F = $ClCCF_2)_3$), 108836-09-5; (n-Pr)$_3$N, 102-69-2; $(CH_3CH_2)_2NCH_3$, 616-39-7; (n-Pr)N$(CH_3)_2$, 926-63-0; $[(CH_3)_2CHCH_2]_2NCH_3$, 10471-20-2; (n-Pr)N$(C_2H_5)_2$, 4458-31-5; (n-Pr)$_2$NC_2H_5, 20634-92-8; $(CH_3)_2CHN(C_2H_5)_2$, 6006-15-1; (i-Pr)$_2$NCH_3, 10342-97-9; Ni$(PPh_3)_4$, 15133-82-1; Pd$(PPh_3)_4$, 14221-01-3; Pt$(PPh_3)_4$, 14221-02-4; $Cl(CF_2)_6PdI(PPh_3)_2$, 108894-59-3; $Cl(CF_2)_3CF_2I$, 5848-38-4; $CF_3(CF_2)_2CF_2CH$=CHNEt$_2$, 98968-83-3; $CF_3(CF_2)_4CF_2CH$=CHNEt$_2$, 107728-83-6; $ClCF_2CF_2CH$=CHNEt$_2$, 107728-84-7; $Cl(CF_2)_3CF_2CH$=CHNEt$_2$, 98968-84-4; $Cl(CF_2)_7CF_2CH$=CHNEt$_2$, 107728-85-8; CF_3-$(CF_2)_2COCH$=CHNEt$_2$, 22769-73-9; $CF_3(CF_2)_4COCH$=CHNEt$_2$, 107728-88-1; $ClCF_2COCH$=CHNEt$_2$, 107728-89-2; Cl-$(CF_2)_3COCH$=CHNEt$_2$, 98968-86-6; $Cl(CF_2)_3COCH$=CHN-(Et)Pr-n, 108836-03-9; $Cl(CF_2)_3COCH$=CHN(Pr-n)$_2$, 108836-04-0; $Cl(CF_2)_3COCH$=CHN(Et)C_5H_{11}, 108836-05-1; $Cl(CF_2)_5COCH$=CHNEt$_2$, 98968-87-7; $Cl(CF_2)_5COCH$=CHN(CH_3)Et, 108836-06-2; $Cl(CF_2)_5COCH$=CHN$(CH_3)_2$, 108836-07-3; $Cl(CF_2)_7COCH$=CHNEt$_2$, 107728-90-5; $Cl(CF_2)_5CF_2CH(CH_3)CHO$, 107728-91-6; $Cl(CF_2)_5CF_2CH(Et)CHO$, 107728-92-7; *N*-(1-butenyl)pyrrolidine, 13937-89-8; *N*,*N*-diethylcyclohexylamine, 91-65-6; *N*-methylpiperidine, 626-67-5; *N*-etylpiperidine, 766-09-6; *N*-*n*-butylpiperidine, 4945-48-6; *N*-ethyl-$\Delta^{\alpha,\beta}$-β-(ω-chlorohexafluoro-*n*-butyryl)piperidine, 108836-10-8; *N*-*n*-butyl-$\Delta^{\alpha,\beta}$-β-(ω-chlorohexafluoro-*n*-butyryl)piperidine, 108836-11-9.

Highly Stereoselective Synthesis of *Z*,*E* Conjugated Diene Type Sex Pheromones†

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Insect sex pheromones **1**-**4** which contain a *Z*,*E* conjugated diene were synthesized by using a new formyl-olefination method, followed by a Wittig reaction. Thus, the aldehydes **6a**-**c** reacted with (formylmethyl)triphenylarsonium bromide (**5**) in THF-ether (trace H_2O) in the presence of K_2CO_3 at room temperature to give *E*-α,β-unsaturated aldehydes **7a**-**c**. These reacted with alkylidene phosphorane generated with *n*-BuLi in THF-HMPA to afford (*Z*,*E*)-diene derivatives **1**-**4** in good overall yield and high stereoselectivity.

Conjugated diene compounds are an important class of sex attractants for insects. Among the four geometrical isomers, a great number of dienes with *Z*,*E* configuration have already been identified as the components of sex pheromones; for example, (3*Z*,5*E*)-3,5-tetradecadien-1-ol acetate (**1**) for the Carpenterworm moth (*Prionoxystus robiniae*),[1] (5*Z*,7*E*)-5,7-dodecadien-1-ol (**2**) for *Dendrolimus spectabilis*,[2] (5*Z*,7*E*)-5,7-dodecadien-1-ol acetate (**3**) for *Dendrolimus punctatus*,[3] and (5*E*,7*Z*)-5,7-dodecadienal (**4**) for *Malacosoma californicum*.[4] Compounds **1**, **2**, and **4** have been synthesized[1,5,6] by nonstereoselective Wittig reactions. Recently, compound **3** was obtained with 85% stereoselectivity and in 31% overall yield.[7] In our previous

Scheme I[a]

$[Ph_3AsCH_2CHO]^+Br^- + RCHO \xrightarrow{i} RCH$=CHCHO (*E* isomer, >98%)

5	**6a**	**7a**, R = $CH_3(CH_2)_7$
	b	**b**, R = $CH_3(CH_2)_3$
	c	**c**, R = $THPO(CH_2)_4$

yields: 75-90%

[a] (i) Et_2O-THF (7:3), trace H_2O/K_2CO_3, 20 °C, 18-24 h.

† This is paper 54 in the series on the application of organic compounds substituted with elements of groups 15 and 16 in organic synthesis.[11]

(1) Doolittle, R. E.; Roelofs, W. L.; Solomon, J. D.; Carde, R. T.; Beroza, M. *J. Chem. Ecol.* **1976**, *2*, 399.

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