Reactions of Perfluoro-2-methyl-2-pentene with Carboxylic Acids, Alcohols, and Some Cyclic Amides. A New Fluorinating Reagent

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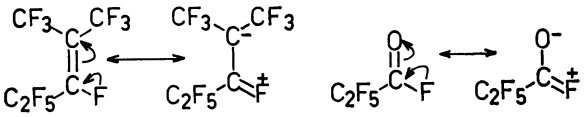
(Received July 1, 1980)

Perfluoro-2-methyl-2-pentene (PMP) reacts with carboxylic acids, alcohols, and 2-pyridone, giving Michael-type addition products, 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3-acyloxypentane, 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3-alkoxypentane, 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3(2-pyridyloxy)pentane, respectively, in good yields. In the presence of bases, carboxylic acids give acid fluorides, 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-pentanone, and 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-acyloxy-2-pentene (**4**), the yields changing with base, solvent, phase-transfer catalyst, and their combination. In the presence of triethylamine, fluorination occurs exclusively, producing acid fluorides in good yields. Alcohols and 2-pyridone are converted into alkyl fluorides and 2-fluoropyridine, respectively, with use of triethylamine as a base with an aprotic solvent. The reactions of PMP with 4-pyridone and 6-chloro-2-ethyl-5-methyl-4(3*H*)-pyrimidone were also examined. The fluorination reactions were rationalized by preferential replacement of the vinylic fluorine of PMP and a good leaving function of the perfluoro enol group of the intermediates such as **4**.

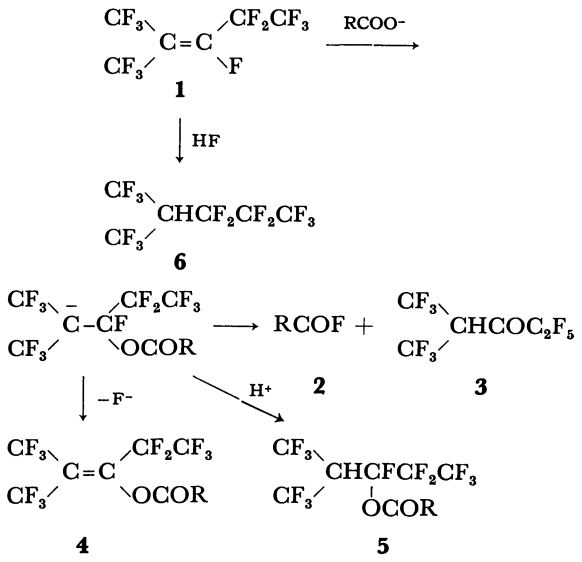
Since the discovery of oligomerization of tetrafluoroethylene and hexafuluoropropylene, studies on their oligomers have drawn much attentions.[1-5] Among the oligomers, perfuluoro-2-methyl-2-pentene (PMP) (**1**), a dimer of hexafluoropropene, is very susceptible to attack by nucleophiles. This high reactivity is attributable to the mesomeric assistance of the vinylic fluorine, the presence of two electrone-withdrawing trifluoromethyl groups which stabilize intermediate carbanion leading to polarization similar to that in the acid fluoride as shown below:[6]



PMP can be regarded as a homolog of perfluoropropionyl fluoride. On the other hand, perfluoro carboxylic acid esters are labile since perfluorocarboxylates are good leaving groups. Thus, the reaction products of PMP with hydroxyl compounds through replacement of the vinylic fluorine are also labile and undergo further reactions under appropriate reaction conditions. We have investigated the reactions of PMP with some carboxylic acids, alcohols, and cyclic amides and found that PMP acts as a fluorinating agent to replace the hydroxyl group with fluorine.

Results and Discussion

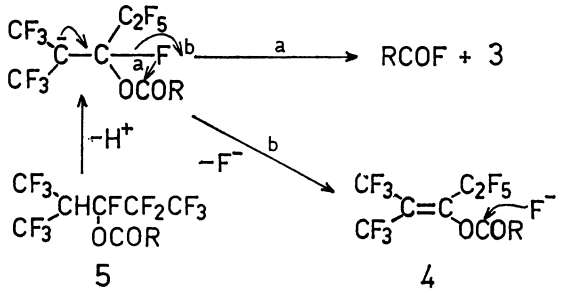
Reactions with Carboxylic Acids. Carboxylate anions react readily with PMP (**1**) either in a dipolar aprotic solvent (DMSO, DMF, acetone, or acetonitrile) or under nonaqueous phase-transfer catalysis conditions, giving acid fluorides (**2**) in good yields along with 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-pentanone (**3**), 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-acyloxy-2-pentene (**4**), 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3-acyloxypentane (**5**), and the HF addition product (**6**) (Scheme 1).[5] Further investigation has revealed that the reaction products are strongly dependent on the choice of base, solvent, phase-transfer catalysts and their combination.



Scheme 1.

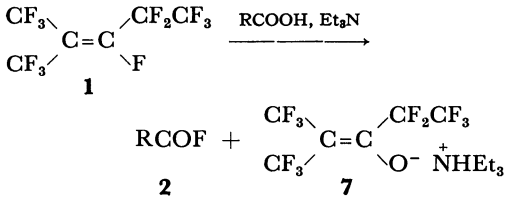
The results obtained by use of inorganic bases are summarized in Table 1. While the reaction of benzoic acid in acetone in the absence of base gave the Michael type addition product (**5**) (R=Ph) in moderate yield (run 1), K_2CO_3–acetone (run 2), K_2CO_3–acetonitrile–18-crown-6 (run 3), and K_2CO_3–benzene–octaglyme (run 6) reaction systems gave good yields of benzoyl fluoride. In the K_2CO_3–CH_2Cl_2–18-crown-6 (run 5) and K_2CO_3–CH_2Cl_2–quaternary ammonium salts (runs 9 and 10) reaction systems, the esters **4** and **5** (R=Ph) were formed concomitantly with benzoyl fluoride. The cases are typical for all reactions using Na_2CO_3 as a base. In spite of the strong interaction of Na^+ with 12-crown-4,[7] no significant difference was observed in the catalysis as compared with that of 18-crown-6 (runs 12 and 13). Use of $CaCO_3$ or CaO led to the exclusive formation of the saturated ester **5**, the reaction of calcium benzoate giving the unsaturated ester **4** selectively. The preferential formation of either the ester **4** or **5** in the presence of Na_2CO_3 or $CaCO_3$ is apparently due to the absence of an active fluoride anion in solution because of the low solubility of NaF and CaF_2.

The fluorination reactions were rationalized by assuming that the reaction goes through the esters **4** and **5**.[5] In fact, the reaction of the enol ester **4** (R=$PhCH_2$) with KF gave the benzoyl fluoride. The reaction, however, was slower than that of the saturated ester **5** (R=$PhCH_2$) with K_2CO_3, suggesting that intramolecular fluoride transfer is also possible (Path a, Scheme 2). The reaction mechanism is similar to that proposed in the fluorination reactions by 2-fluoropyridinium salts[8] and by picryl fluoride.[9]



Scheme 2.

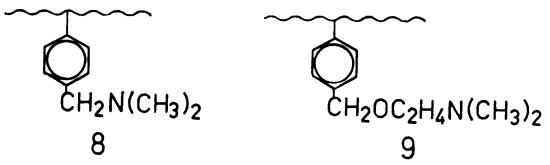
When triethylamine was used instead of inorganic bases, the reaction occurred within 1 h, giving acid fluorides with triethylammonium perfluoro-2-methyl-1-ethyl-1-propenolate (**7**) almost quantitatively. (Scheme 3 and Table 2).



Scheme 3.

Enolate **7** was stable to distillation and characterized by mass, IR, ^{19}F NMR, and ^1H NMR spectra. Martini and Schumann[10] reported its formation by the reaction of PMP with water.

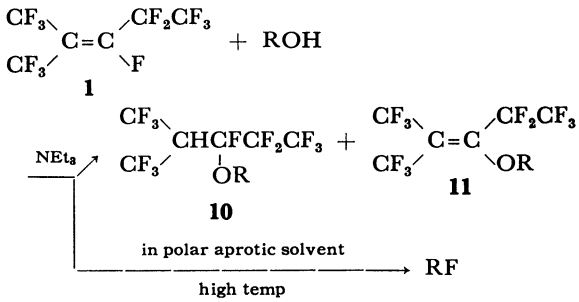
Employment of insoluble polystyrene-bound tertiary amines **8** (Amberlite IRA 68) and **9** gave acid fluorides in good yields (Table 2, runs 8—13). Even a catalytic



amount of the tertiary amine (run 13) gave acid fluorides in reasonable yield. The fluorination reactions using PMP and the insoluble resins (Table 1, run 10) are very simple, acid fluorides being readily obtained solely by filtration of the resins and the evaporation of solvent.

The reaction in the presence of triethylamine were extended to formic acid and perfluorooctanoic acid but were unsuccessful.

Reactions with Alcohols. Alcohols such as methanol, ethanol, and phenol react with PMP in the presence of triethylamine, yielding the following Michael-type addition products, 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3-alkoxypentane (**10**) and their HF elimination products, 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-alkoxy-2-pentene (**11**) (Scheme 4).[2c]



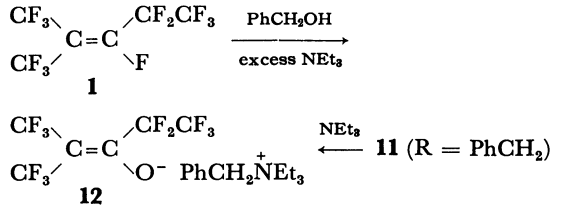
Scheme 4.

It has been found that PMP fluorinates alcohols in the presence of an equimolar amount of triethylamine in an aprotic polar solvent at high reaction temperatures, giving alkyl fluorides in fair to good yields (Scheme 4).

When a mixture of 1-dodecanol, PMP, and triethylamine in a 1 : 1 : 1 mole ratio was made to react in acetonitrile at 80 °C for 8 h, 1-fluorododecane was formed in 28% yield with the enol ether **11** (R=n-$C_{12}H_{25}$). The yield was almost unchanged even when the mole ratio was varied to 1 : 1 : 2, 1 : 2 : 1, and 1 : 2 : 2. Reaction of the mixture in 1 : 1 : 1 mole ratio was examined in various solvents (Table 3). Dipolar aprotic solvents such as DMF and sulfolane, when coupled with higher reaction temperatures, were favorable for the fluorination of alcohols. 2-Octanol was also fluorinated in one-step in moderate yield (runs 15 and 16).

The course of fluorination reaction can be monitored by ^{19}F NMR spectroscopy. In the reaction with 1-octanol, the perfluoro ethers **10** and **11** (R=n-C_8H_{17}) were formed initially in 26 and 56% yields, respectively, the prolonged reaction in sulfolane at 120 °C giving 1-fluorooctane in 74% yield. When the isolated ether **11** (R=n-$C_{12}H_{25}$) was reacted with triethylamine and PMP, 1-fluorododecane was formed in 45—58% yields. This indicates that the fluorination proceeds *via* the attack of fluoride ion on the perfluoro enol ethers **11**.

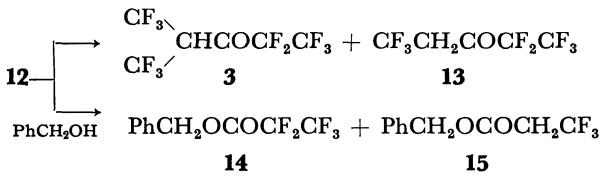
In the reactions with benzyl alcohol (runs 17 and 18), benzyl fluoride was formed in poor yields. Use of potassium carbonate as a base with 18-crown-6 in dichloromethane led to preferential formation of the perfluoroenol ether **11** (R=$PhCH_2$) (84% yield). Use of excess triethylamine gave rise to the formation of a viscous oily product without givin benzyl fluoride



Scheme 5.

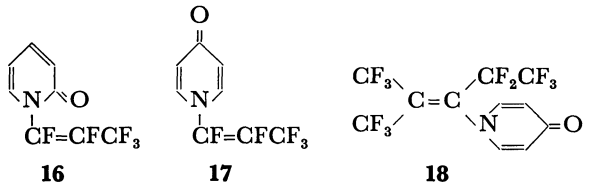
and the enol ether **11**. The oily product was identified with the product readily obtained by mixing the enol ether **11** (R=$PhCH_2$) with triethylamine, and identified as benzyltriethylammonium perfluoro-2-methyl-1-ethyl-1-propenolate (**12**) (Scheme 5).

^{19}F NMR analysis of the reaction of the enolate **12** with trifluoroacetic acid showed that the ketones **3** and **13** are formed in a 2 : 1 ratio (Scheme 6). The acid degradation of the triethylammonium enolate **7** also gave the two products.[7] Enolate **12** reacts slowly with benzyl alcohol, giving the two esters **14** and **15** (Scheme 6). These facts well explain the low yield of benzyl fluoride.

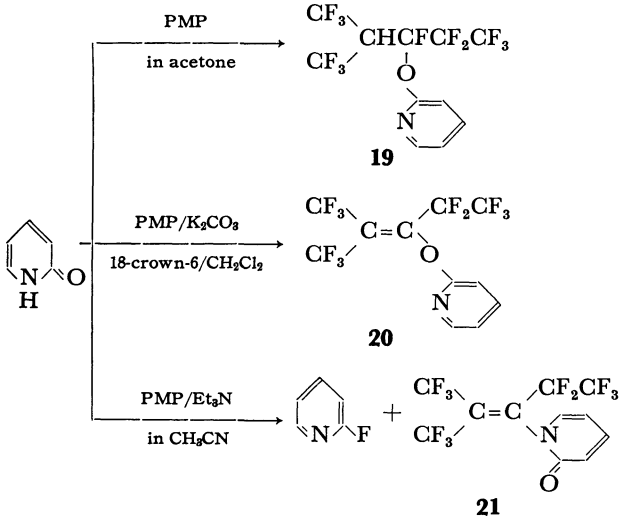


Scheme 6.

Reactions with Some Cyclic Amides. It was claimed in a Japanese patent[11] that 2-pyridone and 4-pyridone react with hexafluoropropene in the presence of potassium carbonate, giving the *N*-substituted products **16** and **17**, respectively. When 4-pyridone was made to

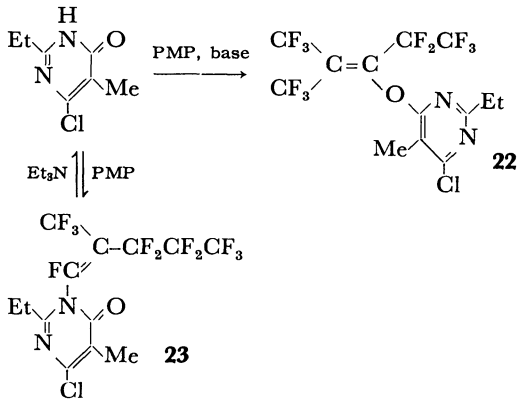


react with excess PMP in the absence of base in acetone at room temperature for 48 h, the *N*-substituted product **18** was formed quantitatively with the HF addition product **6**. However, a similar treatment of 2-pyridone in acetone gave *O*-substituted product, 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3-(2-pyridyloxy)pentane (**19**) (Michael-type addition product) in 84% yield. Another *O*-substituted product **20** was formed in 64% yield in dichloromethane in the presence of potassium carbonate and 18-crown-6. When triethylamine was employed as a base and the reaction was conducted in acetonitrile under reflux for 24 h, 2-fluoropyridine was formed in 73% yield with the *N*-substituted product **21** (25% yield) (Scheme 7). Use of DMF as a solvent also gave rise to the formation of 2-fluoropyridine (69% yield) after reaction at 120 °C for 2 h.



Scheme 7.

GLPC analysis of the course of the fluorination revealed that the *O*-substituted pyridine **20** and the *N*-substituted 2-pyridone **21** are initially formed, 2-fluoropyridine being gradually produced at the expence of **20**. Treatment of **20** with PMP and triethylamine in acetonitrile at 80 °C for 12 h gave 2-fluoropyridine in 90% yield (^{19}F NMR). No reaction took place in the absence of PMP. The reaction of **19** with triethylamine gave 2-fluoropyridine in 75% yield (^{19}F NMR). These facts clearly indicate that the fluorination occurs through the *O*-substituted pyridines **19** and **20**, and that active fluoride ion can also be formed by the degradation of PMP by triethylamine.



Scheme 8.

Fluorination by PMP in the presence of bases was extended to two pyrimidinones and cyanuric acid. 6-Hydroxy-2-methyl-4(3*H*)-pyrimidinone and cyanuric acid were recovered unchanged by the reaction in dichloromethane at room temperature for 48 h. By a similar treatment of 6-chloro-2-ethyl-5-methyl-4(3*H*)-pyrimidinone with excess PMP in the presence of base, the *O*-substituted product **22** was obtained in good yield (Scheme 8). No fluorination was observed even in the presence of triethylamine in dry sulfolane.

Close examination of the early stage of the reaction shows that the *N*-substituted products having larger retention volume are also formed as a mixture of at least three isomers, two of which were confirmed to be the unexpected *cis* and *trans* isomers **23** (Scheme 8). The attack of nucleophiles on the trifluoromethyl of PMP, *i.e.* the replacement of the allylic fluorine of PMP followed by rearrangement, was also observed in the cyclization reaction of PMP with *N,N*-dimethylhydrazine.[12] When a mixture of the *O*-substituted and *N*-substituted products was treated with triethylamine at room temperature, the *N*-substituted products gradually decomposed into the starting pyrimidinone, the *O*-substituted product **22** remaining unchanged.

Conclusion. The fluorination reactions of PMP

consist of two reactions, (a) replacement of the vinylic fluorine by carboxylates, alkoxides, or enolates leading to the perfluoropropenol esters or ethers, and (b) perfluoro enol oxygen-carbon fission followed by displacement by fluoride ion. The preferential fission of the enol oxygen-carbon was also observed in the isopropenyl derivatives.[13] Triethylammonium fluoride formed during the course of reactions in the presence of triethylamine might be the source of active fluoride ion causing an effective enol oxygen-carbon fission. The present fluorination reactions can be conducted in conventional glass vessels, the by-products being easily separable low-boiling substances and salts. Stable, storable, and low toxic PMP can be easily prepared from hexafluoropropene and is very easy to handle.[14] PMP appears to be advantageous as a small-scale fluorinating reagent as compared with *N,N*-diethyl-2-chloro-1,1,2-trifluoroethylamine,[15] SF_4–amine reagents,[16] HF–amine reagents,[17] and selenium tetrafluoride.[18] From the fact that most perfluoro enol derivatives with boiling points lower than expected are stable against distillation, PMP like trimethylsilyl chloride is promising as a protecting reagent of hydroxyl groups.

TABLE 1. REACTIONS OF BENZOIC ACID WITH PERFLUORO-2-METHYL-2-PENTENE (PMP) IN THE PRESENCE OF INORGANIC BASES WITH AND WITHOUT PHASE-TRANSFER CATALYSIS[a]

Run No.	Base	Solvent	Phase-transfer catalyst (mol %)	Reaction time/h (Rection temp)	Yield/% Reaction product		
					2	**4** and **5**	total
1	—	CH_3COCH_3	—	24 (room temp)	0	1(**4**) 35(**5**)	36
2	K_2CO_3	CH_3COCH_3	—	6(room temp)	74	—[b]	74
3	K_2CO_3	CH_3CN	18-crown-6(4%)	8(reflux)	68	trace	68
4	K_2CO_3	CH_2Cl_2	18-crown-6(38%)	24(reflux)	81	13	94
5	K_2CO_3	CH_2Cl_2	18-crown-6(4%)	8(reflux)	18	34	52
6	K_2CO_3	C_6H_6	octaglyme(10%)	8(reflux)	68	trace	68
7	K_2CO_3	CH_2Cl_2	octaglyme(14%)	8(reflux)	45	52	97
8	PhCOOK	CH_2Cl_2	octaglyme(14%)	8(reflux)	31	43	74
9	K_2CO_3	CH_2Cl_2	$(C_8H_{17})_3\overset{+}{N}CH_3Cl^-$	2(reflux)	39	48	87
10	K_2CO_3	CH_2Cl_2	Amberlite IRA-900(42%)	72(reflux)	47	21	68[c]
11	Na_2CO_3	CH_3COCH_3	—	3(reflux)	8	28(**4**) 28(**5**)	64
12	Na_2CO_3	CH_2Cl_2	12-crown-4(10%)	3(reflux)	5	53(**4**) 11(**5**)	69
13	Na_2CO_3	CH_2Cl_2	18-crown-6(10%)	2(reflux)	16	42(**4**) 13(**5**)	71
14	$CaCO_3$	CH_3COCH_3	—	12(reflux)	trace	3(**4**) 73(**5**)	76
15	CaO	CH_3COCH_3	—	18(reflux)	trace	3(**4**) 67(**5**)	70
16	$(PhCOO)_2Ca$	CH_2Cl_2	18-crown-6(10%)	4(room temp)	trace	58(**4**) 13(**5**)	71

a) PhCOOH (1.22 g, 10 mmol) and PMP (3 g, 10 mmol) were reacted in the presence of base (10 meq). b) Not determined. c) Benzoic acid anhydride was formed in 15% yield.

TABLE 2. FLUORINATION OF CARBOXYLIC ACIDS WITH PMP IN THE PRESENCE OF TERTIARY AMINES[a]

Run No.	Carboxylic acid	Tertiary amine	Solvent	Reaction time/h (Reaction temp)	Yield/%[b] RCOF
1	C_6H_5COOH	$N(Et)_3$	CH_3COCH_3	3(room temp)	86
2	*p*-$NO_2C_6H_4COOH$	$N(Et)_3$	CH_3COCH_3	3(reflux)	73
3	C_2H_5COOH	$N(Et)_3$	$CH_3C_6H_5$	3(room temp)	60
4	C_2H_5COOH	$N(Et)_3$	CH_2Cl_2	1(room temp)	96[c]
5	$CH_3(CH_2)_4COOH$	$N(Et)_3$	CH_2Cl_2	0.5(room temp)	64
6	$CH_3(CH_2)_4COOH$	$N(Et)_3$	CH_2Cl_2	1(room temp)	94[c]
7	$CH_3(CH_2)_6COOH$	$N(Et)_3$	CH_2Cl_2	1(room temp)	88[d]
8	C_6H_5COOH	resin **8**[e]	CH_3COCH_3	48(room temp)	68
9	C_6H_5COOH	resin **9**[f]	CH_3COCH_3	96(room temp)	42[g,h]
10	$CH_3(CH_2)_6COOH$	resin **8**[e]	CH_3COCH_3	48(room temp)	81
11	$CH_3(CH_2)_6COOH$	resin **9**[f]	CH_3COCH_3	96(room temp)	50[g,i]
12	$CH_3(CH_2)_6COOH$	resin **9**[f]	C_6H_6	120(room temp)	52[e,j]
13	$CH_3(CH_2)_6COOH$	resin **9**[k]	C_6H_6	48(room temp)	90[e,l]

a) Carboxylic acid(10 mmol) and PMP (10 mmol) were reacted in the presence of triethylamine (10 mmol). b) Isolated yield. c) NMR yields combined with GLPC analysis. d) After distillation three times. e) Amberlite IRA-68 (1 g) used (amino unit, 56 mol%). f) 0.25 g used (*ca.* 5 mol%). g) GLPC yield. h) The esters (**4** the main ester) were formed in 12% yield, the unreacted acid (41%) being recovered. i) The ester **5** was formed in 3% yield, the unreacted acid (44%) being recovered. j) The esters (**5** the main ester) were formed in 22% yield, the unreacted acid (26%) being recovered. k) 0.5 g used (10 mol%). l) The ester **5** was formed in 10% yield.

Table 3. Fluorination of alcohols by PMP and triethylamine[a)]

Run No.	Alcohol	Reaction conditions			Yield/%[b)] R–F
		Solvent	Temp/°C	Time/h	
1	$CH_3(CH_2)_{11}OH$	CH_3COCH_3	reflux	8	23
2	$CH_3(CH_2)_{11}OH$	CH_3CN	reflux	8	40
3	$CH_3(CH_2)_{11}OH$	$CH_3C_6H_5$	reflux	8	41
4	$CH_3(CH_2)_{11}OH$	xylene	reflux	8	40
5	$CH_3(CH_2)_{11}OH$	dioxane	reflux	8	48
6	$CH_3(CH_2)_{11}OH$	DMF	120	2	62
7	$CH_3(CH_2)_{11}OH$	DMF	120	8	58
8	$CH_3(CH_2)_{11}OH$	DMF	130	2	63
9	$CH_3(CH_2)_{11}OH$	DMF	140	2	64
10	$CH_3(CH_2)_{11}OH$	DMF	150	2	64
11	$CH_3(CH_2)_{11}OH$	sulfolane	120	2	56
12	$CH_3(CH_2)_{11}OH$	sulfolane	130	2	68(67)[c)]
13	$CH_3(CH_2)_{11}OH$	sulfolane	140	2	73
14	$CH_3(CH_2)_7OH$	sulfolane	130	2	75
15	2-octanol	sulfolane	130	2	39
16	2-octanol	CH_3COCH_3	reflux	8	36
17	$C_6H_5CH_2OH$	CH_3COCH_3	reflux	24	12
18	$C_6H_5CH_2OH$	DMF	120	2	15

a) See Experimental. b) ^1H NMR yield using triphenylmethane as internal references. c) Isolated yield.

Experimental

^1H NMR and ^{19}F NMR spectra were recorded with a JEOL LMN-PS-100 spectrometer, ^{19}F NMR spectra being obtained in the presence of 1,1,2-trichlorotrifluoroethane as an internal standard and peak center positions being given in ppm upfield from trichlorofluoromethane. Mass spectra were determined with a Hitachi RMU-6E mass spectrometer, GC–Mass spectra with a Hitachi RMU-6MG spectrometer at 20 eV connected with a Hitachi M-5201 apparatus using 3 m × 3 mm column of 5% Silicone OV-1 on Uniport KS, and IR spectra with a JEOL IR-E spectrophotometer. GLPC analysis and preparative scale GLPC were carried out on a Yanagimoto G-8 model instrument equipped with a thermal conductivity detector. The columns were Silicone SE-30 on a Diasolid L (60—80 mesh) (1.5 m × 4 mm) and Silicone OV-1 on a Uniport KS (60—80 mesh) (3 m × 4 mm).

Materials. Perfluoro-2-methyl-2-pentene (PMP) (supplied from Neos Co. Kobe) was used after distillation. All inorganic bases were used after being ground to powder and dried in a vacuum oven at 100 °C for 24 h. 6-Chloro-2-ethyl-5-methyl-4(3*H*)-pyrimidinone was prepared from propionitrile, phosgene and hydrogen chloride.[16] Amberlite IRA-900 (ammonium chloride type) and IRA-68 (tertiary amine type) (resin **8**) were used after washing and drying. Other commercial chemicals were used after purification.

Preparation of the 2-(Dimethylamino)ethoxy Resin **9**. 2-(Dimethylamino)ethanol (5.5 g, 61.8 mmol) and 40 ml of toluene were placed in a 100 ml three-necked flask equipped with a magnetic stirrer, reflux condenser, thermometer, and an inlet tube for nitrogen gas. Into this was added sodium hydride (2.0 g, *ca.* 42 mmol) under nitrogen. After the solution had been stirred at room temperature until the evolution of hydrogen gas ceased, 3.0 g of chloromethylated poly (styrene) (6.48 mmol) (2% DVB) (100—200 mesh) (Nakarai Chemical Co.) was added. The flask was then placed in an oil bath maintained at 85 °C and the mixture was stirred for 48 h under nitrogen. The resulting resin (**9**) was collected by filtration, washed successively with 350 ml of 4 : 1 THF : H_2O and 500 ml of THF, and washed continuously with THF using a Soxhlet apparatus for 48 h and then dried *in vacuo* at 100 °C. The resin (3.13 g) was obtained. Found: C, 86.09; H, 8.00; N, 2.35; Cl, 0.29%. Calcd for: C, 85.79; H, 8.33; N, 2.61; Cl, 0.29%. Calulation is based on chloromethyl unit mole of the starting resin, the degree of cross-linking by 2% DVB, and the unreacted chlorine content of the resin. Dimethylamino unit: 1.87 mmol/g-resin (dry).

Reactions. The technique used in each reaction was almost the same. Hydroxyl compounds (10 mmol), base (equivalent), and solvent (10 ml) were placed in a 30 ml-flask equipped with a magnetic stirrer and a reflux condenser. When necessary, phase transfer catalysts (4—56 mol%) were added. Stirring was started and the slurry was cooled down to 0 °C with an ice–water bath. PMP (10 mmol or more) was added dropwise and the reaction mixture was then warmed to room temperature or higher. After an appropriate reaction time the solid products and/or solid catalysts were filtered off and the filtrate was concentrated, distilled and analyzed by GLPC, ^1H NMR, and ^{19}F NMR spectroscopy. In case of the reaction mixture containing high-boiling solvent and/or ammonium salts, the products were extracted continuously with pentane using a liquid-liquid extraction apparatus. Most products were known compounds, giving ^1H NMR, ^{19}F NMR, IR, and mass spectra in line with their structures. The following are representative examples (Tables 1, 2, and 3.)

Reaction of Benzoic Acid with PMP in the Presence of K_2CO_3 and Octaglyme (Table 1 and run 7). Benzoic acid (1.22 g, 10 mmol), PMP (3 g, 10 mmol), K_2CO_3 (0.7 g, 5 mmol) and octaglyme (1 g) were made to react in CH_2Cl_2 (10 ml) under reflux for 8 h. After removal of solvent, the concentrate was distilled under reduced pressure, giving two fractions (Fr-1 2.49 g, Fr-2 0.16 g). GLPC analysis showed that each fraction consists of the benzoyl fluoride (**2**, R=Ph) and the ester **4** (R=Ph). Thus the fractions were quantitatively analyzed by GLPC (Silicone SE-30, toluene as an internal reference. *cf.* Table 1). In another reaction under similar conditions, a very small amount of the ester **5** (R=Ph) with a larger retention volume than that of **4** (R=Ph), was also observed with a trace of an unidentified product having the

largest retention volume.

Reaction of Benzoic Acid with PMP in the Presence of $CaCO_3$ (run 14). Benzoic acid (1.22 g) was treated with $CaCO_3$ (0.5 g) and PMP (3 g) in acetone (10 ml) under reflux for 12 h. The reaction mixture was concentrated and distilled under reduced pressure, giving a distillate (3.2 g). GLPC analysis indicated that it consists of the ester **5** (R=Ph), a small amount of the ester **4** (R=Ph), and traces of benzoyl fluoride and an unidentified product.

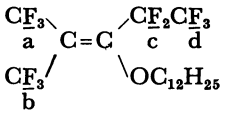
Reaction of Benzoic Acid with PMP in the Presence of Triethylamine (Table 2 and run 1). Benzoic acid (1.22 g) was treated with triethylamine (1.0 g) and PMP (3 g) in acetone (30 ml) at room temparature for 3 h. After removal of solvent, the concentrate was distilled under reduced pressure, yielding benzoyl fluoride (1.2 g, 86%) and triethylammonium perfluoro-2-methyl-1-ethyl-1-propenolate (**7**) (1.2 g, 30%). The latter product gave IR, ^{19}F NMR, and mass spectra in line with those of the product obtained by the reaction of PMP with triethylamine and water in acetonitrile. (bp 40—55 °C/0.1—0.2 Torr, lit,[8] 44.5 °C/0.2 Torr). (1 Torr=133.322 Pa).

Reaction of Octanoic Acid with PMP in the Presence of the Amberlite-IRA-68 (resin 8) (Table 2 and run 10). Octanoic acid (1.44 g, 10 mmol), PMP (3.0 g, 10 mmol), and Amberlite IRA-68 (1 g, 5.6 mmol of the amino unit) was made to react in 10 ml of acetone at room temperature for 48 h. The reaction mixture was filtered, concentrated, and distilled under reduced pressure, giving octanoic acid fluoride (1.31 g, 81%).

Reaction of Octanoic Acid with PMP in the Presence of the Resin 9 (Table 2 and run 13). Octanoic acid (0.144 g), PMP (0.3 g), and the resin **9** (0.05 g, 0.1 mmol) were allowed to react in benzene (1 ml) at room temparature for 48 h. The reaction mixture was filtered, concentrated, and analyzed by GLPC and ^1H NMR. GLPC analysis showed the disappearance of the starting octanoic acid and the absence of the ester **4** ($R=C_8H_{17}$). On the basis of ^1H NMR analysis, 90% yield of octanoic acid and 10% yield of the ester **5** ($R=C_8H_{17}$) were confirmed.

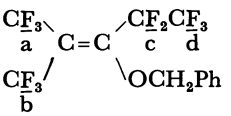
Reaction of 1-Dodecanol with PMP in the Presence of Triethylamine (Table 3 and run 2). A mixture of 1-dodecanol (1.86 g, 10 mmol), triethylamine (1.0 g, 10 mmol), and PMP (3.0 g, 10 mmol) was treated in acetonitrile (10 ml) under reflux for 8 h. After removal of the solvent, the product was extracted with pentane using a liquid-liquid extraction apparatus (8 h). The extract was concentrated to *ca.* 20% solution and analyzed by ^1H NMR spectroscopy. 40% yield of dodecyl fluoride was confirmed. By vacuum distillation, a mixture (2.03 g) of dodecyl fluoride and 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-dodecyl-2-pentene (**11**) was obtained. The latter product (*ca.* 29% yield), confirmed on the basis of ^1H NMR and GLPC analysis, was isolated by preparative GLPC: IR (neat) 2940 (CH_2), 1640 (C=C), 1100—1400 (C–F) cm^{-1}; MS (70 eV), *m/e* (rel intensity, fragmentation), 466 (<1, M^+), 423 (<1, $M^+-C_3H_7$), 409 (<1, $M^+-C_4H_9$), 395 (<1, $M^+-C_5H_{11}$), 381 (<1, $M^+-C_6H_{13}$), 281 (<1, C_6F_{11}), 259 (<1, C_6F_9O), 181 (<1, C_4F_7), 179 (<1, C_4F_6HO), 169 (<1, $C_{12}H_{25}$), 168 (<1, $C_{12}H_{24}$), 159 (2, C_4F_5O), 140 (1, $C_{10}H_{20}$), 128 (4, C_9H_{20}), 119 (1, C_2F_5), 113 (9, C_8H_{17}), 112 (1, C_8H_{16}), 111 (2, C_8H_{15}), 99 (14, C_7H_{15}), 98 (3, C_7H_{14}), 97 (6, C_7H_{13}), 86 (4, C_6H_{14}), 85 (31, C_6H_{13}), 84 (4, C_6H_{12}), 83 (9, C_6H_{11}), 82 (2, C_6H_{10}), 72 (3, C_5H_{12}), 71 (79, C_5H_{11}), 70 (8, C_5H_{10}), 69 (15, CF_3), 68 (3), 67 (3), 58 (5), 57 (100), 56 (9), 55 (27), 54 (3), 53 (2), 44 (3), 43 (78), 42 (10), 41 (35), 39 (15): ^{19}F NMR ($CDCl_3$) $\delta_a=56.9$, $\delta_b=60.0$, $\delta_c=114.5$, $\delta_d=81.2$, $J_{a-b}=9.8$, $J_{a-c}=20.2$, $J_{a-d}=3.3$ Hz.

Fluorination of 1-Dodecanol with PMP (Table 3 and run 12). 1-Dodecanol (1.86 g, 10 mmol) was treated with triethylamine (1.0 g, 10 mmol) and PMP (3.0 g, 10 mmol) in 5 ml of sulfolane at room temperature until the reaction mixture became homogeneous. The mixture was further reacted at 130 °C for 2 h. After removal of the low-boiling products, the residue was extracted with pentane using a liquid-liquid extraction apparatus (6 h). The extarct was distilled to give 1.26 g of pure dodecyl fluoride (67% yield).



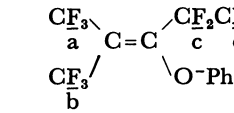
11 (P = $C_{12}H_{25}$)

Reaction of Benzyl Alcohol with PMP in the presence of K_2CO_3 and 18-Crown-6. To a slurry of benzyl alcohol (0.54 g, 5 mmol), K_2CO_3 (0.35 g, 2.5 mmol), and CH_2Cl_2 (10 ml) were added PMP (1.5 g, 5 mmol) and 18-crown-6 (0.13 g, 0.5 mmol). The mixture was refluxed for 4 h. The solid products were filtered and the filtrate was concentrated and distilled under reduced pressure, giving 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3-benzyloxy-2-pentene (**11**) (1.63 g, 84% yield): bp 56 °C/4 Torr; IR (neat) 1640 ($(CF_3)_2C$=C), 1100—1400 (C–F); MS (70 eV), *m/e* (relintensity, fragmentation), 388 (<1, M^+), 181 (2, C_4F_7), 179 (2, C_4F_5HO), 159 (2, C_4F_5O), 119 (2, C_2F_5), 107 (5, $PhCH_2O$), 91 (100, $PhCH_2$); ^{19}F NMR ($CDCl_3$) $\delta_a=56.6$, $\delta_b=59.6$, $\delta_c=114.3$, $\delta_d=81.3$, $J_{a-b}=9.5$, $J_{a-c}=20$, $J_{a-d}=3.3$, $J_{b-d}\simeq 1$, $J_{c-d}\simeq <1$ Hz.



11 (R = $PhCH_2$)

Isolation of Benzyltriethylammonium Perfluoro-2-methyl-1-ethyl-1-propenolate (12). Benzyl alcohol (1.08 g, 10 mmol) was treated with PMP (3.0 g, 10 mmol) and triethylamine (1.01 g, 10 mmol) in dichloromethane (10 ml) at room temperature for 24 h. The reaction mixture was concentrated and distilled under reduced pressure. The distillate (0.723 g) consists of the enol ether **11** (R=$PhCH_2$) and the ammonium enolate **7** as a minor component. The residue is identical with benzyltriethylammonium perfluoro-2-methyl-1-ethyl-1-propenolate (**12**), which was obtained quantitatively by the 1 : 1 reaction of the enol ether **11** and triethylamine in CH_2Cl_2: IR (neat) 1600 ($(CF_3)_2C$=C), 1100—1400 (C–F) cm^{-1}; MS (70 eV, DI), *m/e* (rel intensity, fragmentation), 163 (13, $PhCH_2NEt_2$), 148 (48, $PhCH_2NEtCH_2$), 91 (100, $PhCH_2$); ^1H NMR ($CDCl_3$) δ=1.4 (9H, t), 3.2 (6H, q), 4.4 (2H, s), 7.7 (5H, s); ^{19}F NMR ($CDCl_3$) $\delta_a=49.8$, $\delta_b=55.3$, $\delta_c=117.3$, $\delta_d=81.6$, $J_{a-b}=10.7$, $J_{a-c}=19.6$, $J_{a-d}=1.4$, $J_{b-c}=2.0$, $J_{b-d}<1$, $J_{c-d}<1$, Hz.



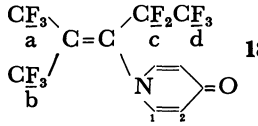
12

The chemical shift at 166.9 ppm observed can be assigned to the fluoride ion of triethylammonium fluoride formed during the course of reaction.

Reaction of the Benzyltriethylammonium Enolate 12 with Benzyl Alcohol. The ammonium enolate **12** (0.389 g, 0.08 mmol) was reacted with benzyl alcohol (0.11 g, 0.1 mmol) in 1 ml of CH_2Cl_2 at room temperature for 3 d. GC mass analysis showed that benzyl perfluoropropionate (**14**) and benzyl 3,3,3-trifluoropionate (**15**) are formed with a small amount of benzyl fluoride. Products **14** and **15** were isolated by preparative GLPC and analyzed. Benzyl perfluoropropionate (**14**): IR (neat) 1780 (C=O), 1215, 1155 (C–F), 1025 (C–O ester) cm^{-1}; MS (70 eV), *m/e* (relintensity, fragmentation), 254 (57, M^+), 204 (1, $M^+-C_2F_5$), 119 (10, C_2F_5), 107

(11, $PhCH_2O$), 91 (100, $PhCH_2$), 90 (93, PhCH); ^1H NMR ($CDCl_3$) δ=5.32 (2H, s), 7.34 (5H, s); ^{19}F NMR ($CDCl_3$) δ=84 (3F, t), 122.6 (2F, q), J=1.8 Hz. Benzyl 3.3.3-trifluoropropionate (**15**): IR (neat) 1755 (C=O) cm^{-1}; MS (70 eV) *m/e* (rel intensity, fragmentation), 218 (42, M^+), 198 (4, M^+-HF), 111 (6, CF_3CH_2CO), 108 (100, $PhCH_2OH$ or $C_3F_2H_2O_2$), 107 (20, $PhCH_2O$), 91 (70, $PhCH_2$ or C_3F_2OH), 90 (84, PhCH, or C_3F_2O); ^1H NMR ($CDCl_3$) δ=3.16 (2H, q, J_{H-F}=10 Hz), 5.16 (2H, s), 7.34 (5H, s); ^{19}F NMR ($CDCl_3$) δ=64.3 (t, J_{F-H}=10).

Reaction of 4-Pyridone with PMP. 4-Pyridone having one mole of water of crystalization (0.452 g, 4 mmol) was treated with PMP (3 g, 10 mmol) in acetone (10 ml) at room temperature for 6 h. GLPC analysis indicated the formation of a single product. After the reaction mixture was evaporated to dryness, the solid product was purified by sublimation under reduced pressure (1 Torr, 120—140 °C), giving 1-(perfluoro-2-methyl-1-ethyl-1-propenyl)-4-pyridone (**18**) (0.82 g, 55% yield): mp 90—93 °C; IR (KBr disk) 1660 (shoulder) ($(CF_3)_2$-C=C), 1635 (C=O) cm^{-1}; MS (70 eV), *m/e* (rel intensity, fragmentation), 375 (10, M^+), 356 (1, M^+-F), 347 (7, M^+-CO), 337 (5, M^+-F_2), 328 (2, M^+-CFO), 318 (1, M^+-3F), 309 (3, M^+-CF_2O), 124 (100, C_6H_3FNO), 105 (48, C_6H_3NO), 96 (59, C_5H_3FN), 77 (37, C_5H_3N), 69 (13, CF_3), 51 (22, C_4H_3), 50 (19, CF_2), 44 (100, CH_2NO); ^1H NMR (acetone-d_6) δ_1=7.87 (d), δ_2=6.26 (d), J_{12}=*ca.* 9 Hz; ^{19}F NMR (acetone-d_6) δ_a=58.1, δ_b=60.5, δ_c=112.7, δ_d=80.5, J_{a-b}=10.8, J_{a-d}=9.7, $J_{b-d}<1$, $J_{b-c}<1$, J_{c-d}=2.0 Hz. The same reaction (4-pyridone, 22.6 mg (0.2 mmol) and PMP, 300 mg (1 mmol) in acetone-d_6 (1 ml))was monitored by ^1H NMR and GLPC analysis. Quantitative formation of **6** and **18** was confirmed, suggesting that PMP acts as a scavenger of HF.



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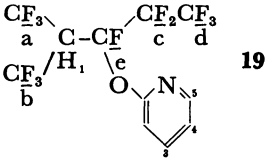
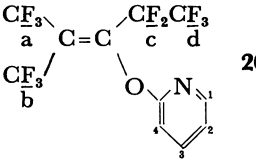
Reaction of 2-Pyridone with PMP in the absence of Base. 2-Pyridone (0.95 g, 10 mmol) was treated with PMP (6 g, 20 mmol) in acetone (15 ml) at room temparature for 3 h. After removal of the solvent, the unreacted 2-pyridone was filtered and the residue distilled unde reduced pressure, giving 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-3(2-pyridyloxy)-pentane (**19**) (3.31 g, 84% yield): bp 66—66.5 °C/5 Torr; IR (neat) 1600 (ring), 1170—1300 (C–F) cm^{-1}; MS (70 eV), *m/e* (rel intensity, fragmentation), 395 (1, M^+), 376 (1, M^+-F), 356 (1, M^+-HF_2), 306 (8, M^+-CHF_4), 300 (3, C_6F_{12}), 281 (27, C_6F_{11}), 231 (35, C_5F_9), 212 (5, C_5H_8), 193 (4, C_5F_7), 181 (100, C_4F_7), 162 (2, C_4F_6), 159 (3, C_4F_5O), 143 (9, C_4F_5), 97 (16, C_5H_4FN), 95 (47, C_5H_5NO), 78 (90, C_5H_4N), 69 (90, CF_3), 51 (13, CF_2H); ^1H NMR ($CDCl_3$) δ_1=6.20 (heptulet), δ_2=6.90 (d), δ_3=7.76 (mc), δ_4=7.17 (mc), δ_5=8.21 (dd), $J_{1a}=J_{1b}$=8.6, J_{1-e}=8.6, J_{23}=*ca.* 8, J_{34}=*ca.* 8, J_{45}=*ca.* 5; ^{19}F NMR ($CDCl_3$) δ_a,δ_b=60.1 (mc), δ_e=122.1 (m), δ_d=79.5 (d), δ_e=115.3 (m), $J_{a-c}=J_{b-c}$=*ca.* 26, J_{d-e}=12 Hz.



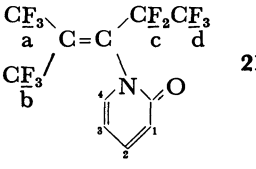
19

Reaction of 2-Pyridone with PMP in the presence of K_2CO_3 and 18-Crown-6. 2-Pyridone (0.476 g, 5 mmol) was treated with PMP (3.0 g, 10 mmol) in CH_2Cl_2 (10 ml) in the presence of K_2CO_3 (0.7 g, 5 mmol) and 18-crown-6 (0.15 g, 0.56 mmol) at room temparature for 24 h. The reaction mixture was worked up as described above, giving 1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethyl-3(2-pyridyloxy)-2-pentene (**20**) (1.21 g, 64% yield): bp 57 °C/10 Torr; IR (neat) 1665 ($(CF_3)_2$-C–C), 1600, 1580 (ring), 1100—1300 (C–F) cm^{-1}. MS (70 eV), *m/e* (rel intensity, fragmentation), 375 (<1, M^+), 356 (8, M^+-F), 337 (<1, M^+-F_2), 318 (1, M^+-F_3), 306 (68, M^+-CF_3), 287 (1, M^+-CF_4), 268 (7, M^+-CF_5), 237 (16, $M^+-C_2F_6$), 218 (2, $M^+-C_2F_7$), 206 (1, $M^+-C_3F_7$), 181 (<1, C_4F_7); 159 (1, C_4F_5O), 119 (1, C_2F_5), 97 (4, C_5H_4FN), 78 (100, C_5H_4N), 69 (10, CF_3), 51 (26, C_4H_3); ^1H NMR ($CDCl_3$) δ_1=8.14 (mc), δ_2=7.14 (mc), δ_3=7.74 (mc), δ_4=6.96 (d), J_{12}=*ca.* 4.5, J_{23}=*ca.* 7, J_{34}=*ca.* 9 Hz; ^{19}F NMR ($CDCl_3$) δ_a=57.7, δ_b=61.1, δ_c=113.4, δ=81.4, J_{a-b}=9.9, J_{a-c}=20.1, J_{a-d}=6.2, J_{b-c}=1.9, J_{c-d}=1.5 Hz.



20

Reaction of 2-Pyridone with PMP in the Presence of Triethylamine. 2-Pyridone (0.95 g, 10 mmol), triethylamine (1.0 g, 10 mmol) and PMP (3.0 g, 10 mmol) were treated in 15 ml of acetonitrile under reflux for 24 h. Quantitative analysis by ^{19}F NMR using trifluoromethylbenzene as an internal standard revealed the formation of 2-fluoropyridine (73%) and 1-(perfluoro-2-methyl-1-ethyl-1-propenyl)-2-pyridone (**21**) (25%). The reaction mixture was concentrated under reduced pressure, each product being isolated by preparative GLPC (Silicone SE-30) and analyzed. 2-Fluoropyridine was identified by IR comparison. 1-(perfluoro-2-methyl-1-ethyl-1-propenyl)-2-pyridone (**21**): mp 61—65 °C; IR (KBr disk) 1695 ($(CF_3)_2C$=C), 1610 (ring), 1100—1300 (C–F); MS (70 eV), *m/e* (rel intensity, fragmentation), 375 (2, M^+), 356 (4, M^+-F), 318 (19, M^+-F_3), 306 (33, M^+-CF_3), 268 (100, M^+-CF_3), 243 (8, $M^+-C_3F_5H$), 237 (6, $M^+-C_2F_6$), 78 (86, C_5H_4N), 69 (25, CF_3), 51 (22, C_4H_3); ^1H NMR ($CDCl_3$) δ_1=6.54 (d), δ_2=7.38 (m), δ_3=6.24 (t), δ_4=7.0 (d), J_{12}=*ca.* 10, J_{23}=*ca.* 7, J_{34}=*ca.* 7, J_{24}=*ca.* 2 Hz; ^{19}F NMR ($CDCl_3$) δ_a=58.5, δ_b=61.4, δ_c=110.7, δ_d=80.2, J_{a-b}=10.9, J_{a-c}=20.7, J_{a-d}=9.8 Hz.



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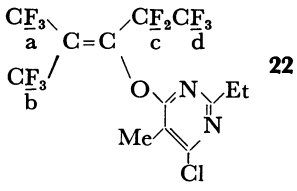
Reaction of 6-Chloro-2-ethyl-5-methyl-4(3H)-pyrimidinone with PMP in the presence of Triethylamine. The pyrimidinone (0.518 g, 3 mmol), triethylamine (1.0 g, 10 mmol) and PMP (3.0 g, 10 mmol) were reacted in CH_2Cl_2 (10 ml) at room temparature for 48 h. The reaction mixture was subjected to the usual work-up. Pure 6-chloro-2-ethyl-5-methyl-4-(perfluoro-1-ethyl-2-methyl-1-propenoxy)pyrimidine (**22**) was obtained by vacuum distillation (1.27 g, 94% yield): bp 59 °C/1 Torr; IR (neat) 1675 ($(CF_3)_2C$=C), 1610, 1535 (ring) cm^{-1}; MS (70 eV), *m/e* (rel intensity, fragmentation), 452 (19, M^+), 433 (7, M^+-F), 383 (100, M^+-CF_3), 345 (31, M^+-CF_5), 334 (17, $M^+-C_2H_3F_3Cl$), 171 (6, $M^+-C_6F_{11}$), 155 (40, $M^+-C_6F_{11}O$), 69 (17, CF_3); ^1H NMR ($CDCl_3$) δ=1.25 (3H, t), 2.28 (3H, s), 2.84 (2H, q), J=8 Hz; ^{19}F NMR ($CDCl_3$) δ_a=57.9, δ_b=61.3, δ_c=113.5, δ_d=81.7, J_{a-b}=10, J_{a-c}=20.5, J_{a-d}=6.2, J_{b-d}=—1, J_{b-c}=1.3, J_{c-d}=1.5 Hz.



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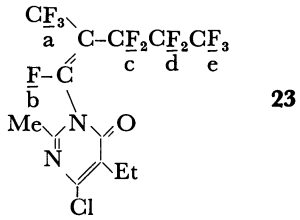
Reaction of 6-Chloro-2-ethyl-5-methyl-(3H)-pyrimidinone with PMP in the presence of K_2CO_3 and 18-crown-6. The pyrimidinone (0.518 g, 3 mmol) was reacted with PMP (3.0 g, 10 mmol) in CH_2Cl_2 (10 ml) in the presence of K_2CO_3 (0.7 g, 5 mmol) and 18-crown-6 (0.08 g, 0.3 mmol) at room temparature for 8 h. The reaction mixture was worked up in the usual manner, 0.86 g of the oil products being obtained by vaccum distillation. GLPC analysis (Silicone OV-1, 120 °C, 60 ml (H_2)/min) showed the formation of one major product (retention volume 64 ml) with three minor components (retention volume: peak a, 90 ml, peak b, 110 ml, peak c, 130 ml, peak area ratio a : b : c=1 : 4 : 6). Each component was isolated by preparative GLPC. The major product was identified as **22** and the components b and c as isomers of 6-chloro-5-ethyl-2-methyl-3-(perfluoro-2-methyl-1-pentenyl)-4(3H)-pyrimidinone (**23**). component b: IR (neat) 1710 (RfC=CF and C=O), 1605 and 1530 (ring) cm^{-1}. MS (70 eV), *m/e* (rel intensity, fragmentation), 452 (13, M^+), 433 (<1, M^+-F), 383 (1, M^+-CF_3), 333 (1, C_2F_5), 283 (17, $M^+-C_3F_7$), 181 (<1, C_4F_7), 171 (1, $M^+-C_6F_{11}$), 155 (100, $M^+-C_6F_{11}O$), 69 (6, CF_3); ^1H NMR ($CDCl_3$) δ=1.30 (3H, t), 2.86 (2H, q), 2.27 (3H, s), J=8 Hz; ^{19}F NMR ($CDCl_3$) δ_a=57.5, δ_b=51.9, δ_c=109.2, δ_d=126.5, δ_e=81.3, J_{a-b}=25.4, J_{a-c}=12.2, J_{a-d}=6.6, J_{b-c}=10.3, J_{c-e}=10.3 Hz. Component c: IR (neat) 1710 (RfC=CF), 1610, 1535 (ring)



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cm^{-1}; MS (70 eV), *m/e* (rel intensity, fragmentation), 452 283 (16, $M^+-C_3F_7$), 181 (<1, C_4H_7), 155 (100, $M^+-C_6F_{11}O$), 69 (5, CF_3); ^1H NMR ($CDCl_3$) δ=1.28 (3H, t), 2.30 (3H,s), 2.85 (2H, q), J=8 Hz; ^{19}F NMR ($CDCl_3$) δ_a=58.0, δ_b=53.3, δ_c=109.5, δ_d=127.4, δ_e=81.2. The spectrum was less amenable to analysis due to the combined effects of many unresolved couplings; component a was only analyzed by GC-mass spectrum: MS (20 eV) *m/e* (rel intensity, fragmentation), 452 (100, M^+), 433 (8, M^+-F), 383 (23, M^+-CF_3), 333 (17, $M^+-C_2F_5$), 281 (22, C_6F_{11}), 171 (46, $M^+-C_6F_{11}$), 155 (18, $M^+-C_6F_{11}O$), 69 (4, CF_3).

The authors wish to express their thanks to Prof. Daniel Swern, Temple University, for his encouragement and helpful suggestion. They are also grateful to the Neos Co. Ltd. for the supply of the fluorocompounds. The present work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

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