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FLUORINATION OF POLYHALOGENATED UNSATURATED COMPOUNDS WITH VANADIUM PENTAFLUORIDE

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SUMMARY

Vanadium pentafluoride reacts with polyfluorinated and polychlorinated olefins, alkadienes, cycloalkenes and cyclodienes in $CFCl_3$ or without a solvent at -25° to 100°C, forming products of addition of two fluorine atoms across the C=C bond.

INTRODUCTION

Earlier we have reported fluorination of hexafluorobenzene, decafluorodiphenyl, octafluoronaphthalene [1], pentafluoropyridine, 3-chlorotetrafluoropyridine, perfluoroanthracene [2] and pentafluorobenzene derivatives C_6F_5X (X = H, D, Alk, OAlk, OH, CN, NO_2) [1-4] by vanadium pentafluoride. This paper presents the results of our studies on the reactions of vanadium pentafluoride with polyhalogenated olefins, dienes, cycloalkenes and cyclohexadienes.

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RESULTS AND DISCUSSION

Polyhalogenated alkenes and cycloalkenes

Fluorination of terminal fluoroolefins by vanadium pentafluoride proceeds readily at -30 to -20°C in $CFCl_3$ solution. The only reaction products are the respective polyfluoroalkanes (Table 1) formed in high yields.

$$\begin{array}{ccccc} CF_2{=}CXR_F & + & VF_5 & \xrightarrow[-\,VF_4]{CFCl_3} & CF_3{-}CFXR_F \\ \text{"1", "3"} & & & & \text{"2", "4"} \end{array}$$

$X = Cl$, $R_F = C_2F_5$ ("1","2")
$X = F$, $R_F = (CF_2)_4CFClCF_2Cl$ ("3","4")

The reactivity of tetrachloroethylene "5" towards VF_5 does not differ from that of terminal fluoroolefins. It reacts with VF_5 at -20°C to give 1,2-difluorotetrachloroethane "6". No chlorine exchange for fluorine is observed.

Perfluoromethylvinyl ether "7" is more stable against vanadium pentafluoride than alkenes "1", "3" and "5". Its transformation to perfluoroethylmethyl ether "8" takes place only at 40°C, but even at that temperature the reaction rate is low.

$$\begin{array}{ccccc} CF_2{=}CF{-}OCF_3 & + & VF_5 & \longrightarrow & CF_3CF_2OCF_3 \\ \text{"7"} & & & & \text{"8"} \end{array}$$

This is in agreement with the data on the electrophilic fluoromercuration of perfluoropropylene and ether "7" by mercury difluoride in HF. The addition of HgF_2 to perfluoropropylene proceeds at 75°C (24 h) [5], whereas with compound "7" HgF_2 reacts only at 150°C (20 h) [6]. At the same time, the radical fluorination of polyhaloolefins by fluorine is known to give rise to a large amount of fluorodimerization products [7]. In the fluorinations of unsaturated compounds by vanadium pentafluoride, however, not a single product of this type has been found.

Internal fluoroolefins react with vanadium pentafluoride at higher temperatures than the terminal ones. The reactivity

TABLE 1

Fluorination of polyhaloalkenes and -cycloalkenes

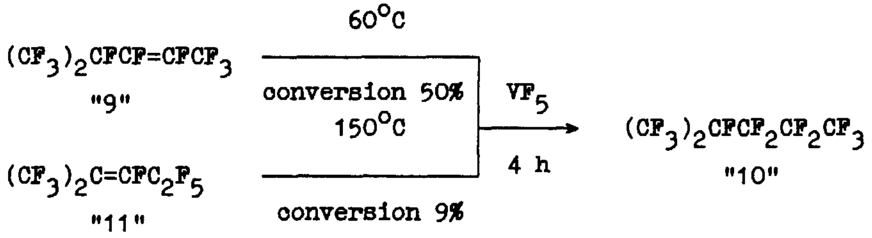
Compound mmol	VF_5 mmol	$CFCl_3$ ml	Temperature °C	Time min	Method	Alkene conversion %	Products yield %
"1" 23	49	17	-20	30	A	90	"2" 81
"3" 23	82	20	-20	30	A	100	"4" 83
"5" 8.4	22.0	2	-20	30	A	48	"6" 72
"7" 7	27	2	40	180	C	50	"8" 40
"9" 5.7	17.0	-	60	240	C	50	"10"94
"11"7.7	28.0	-	150	240	C	9	"10"86
"12"6.5	27.0	-	100	300	C	100	"2" 46
"13"6.9	13.0	4	-20	15	A	42	"14"66
"15"9.3	20.5	-	25	60	C	56	"16"32
"15"6.2	25.0	-	60	180	C	74	"16"59
"17"2.2	13.7	-	60	120	B	68	"18"62
"19"1.4	4.8	-	25	120	B	81	"20"60
"19"2.5	8.2	-	60	120	B	90	"20"74
"21"13.9	42.5	-	25	120	B	87	cis-"23"16 trans-"23"56
"22"6.8	19.0	-	25	120	B	64	"24"89
"22"10.1	48.0	-	60	180	B	94	"24"95
"25"5.6	18.0	-	150	240	B	0	
"25"1.5	6.8	-	250	180	B	65	"27"91
"26"2.6	8.3	-	250	420	B	0	
"28"0.8	1.6	0.6	25	30	B	29	"29"62 "30"35
"31"6.9	6.9	10	-20	20	A	20	"33"96
"31"34	171	40	-20	20	A	85	"33"36 "34"32 "35"19
"32"6.8	6.8	10	-20	20	A	22	"33"93 "34" 2.2 "35" 0.8

(continued)

TABLE 1 (cont.)

"32"10	40	10	-20	20	A	98	"33"66 "34"20 "35"11
"36"0.65	2.0	2	-20	15	A	100	"38"85
"39"2.2	9.6	-	25	60	B	69	"40"35 "41"55

of fluoroolefins with two perfluoroalkyl groups at the C=C bond is higher than that of fluoroolefins with three or four perfluoroalkyl groups. Thus at 60°C, alkene "9" undergoes 50% conversion to perfluoro-2-methylpentane "10" during 4 h whereas the conversion of its isomer "11" even at 150°C during the same time does not exceed 9%.



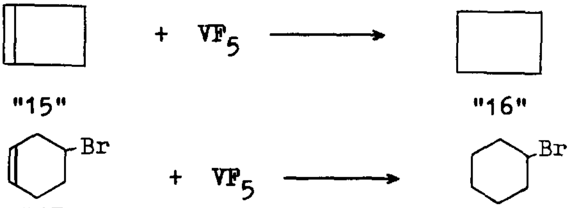
To complete fluorination of alkene "9", the reaction should be conducted at 150-170°C.

Substitution of vinyl fluorines by chlorine raises the fluorination rate of polyhaloalkenes. This is readily evident in the case of the reaction of "12" and "13" with VF_5. The former is fluorinated at 100°C while the latter reacts quickly at a temperature as low -20°C.

$$\underset{\text{"12"}}{CF_3CCl{=}CFCF_3} + VF_5 \xrightarrow[100^\circ C,\ 5\ h]{} \underset{\text{"2"}}{CF_3CFClCF_2CF_3}$$

$$\underset{\text{"13"}}{CF_3CCl{=}CClCF_3} + VF_5 \xrightarrow[-20^\circ C,\ 0.5\ h]{} \underset{\text{"14"}}{CF_3CFClCFClCF_3}$$

The reactivity of polyfluorinated cycloalkenes is similar to that of internal olefins and seems to be slightly dependent on cycle size. Perfluorocyclobutene "15" reacts with VF_5 at 20-22°C, though after 1 h conversion of this cycloalkene is 50%. At 50-60°C the fluorination is more efficient. At the same time, 4-bromononafluorocyclohexene "17" does not react with VF_5 at 25°C, but is fluorinated at 50-60°C, giving bromoundecafluorocyclohexane in 62% yield.

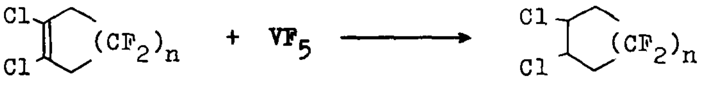


"15" "16"

"17" "18"

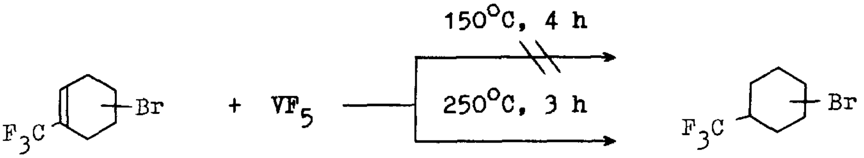
All unmarked bonds to fluorine.

Substitution of vinyl fluorines by chlorine increases the fluorination rate of C=C bonds in cycloalkenes. For example, in contrast to cycloalkene "17", chlorononafluorocyclohexene "19" is easily fluorinated at 25°C, forming chloroundecafluorocyclohexane "20". Agitating vanadium pentafluoride with 1,2-dichlorooctafluorocyclohexene "22" or 1,2-dichlorohexafluorocyclopentene "21" at 25°C leads to the formation of 1,2-dichloroperfluorocycloalkanes. At 50-60°C the conversion of cyclohexenes "19" and "22" is 90-94%, whereas for cyclohexene "17" it is only 68%. The reaction mixtures contained no products of chlorine substitution by fluorine or bromine substitution by fluorine.

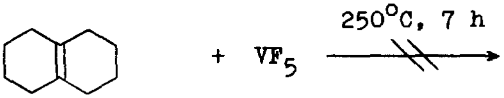


n = 1 "21" "23" (cis:trans=1:3.5)
n = 2 "22" "24"

Substitution of vinyl fluorines by perfluoroalkyl groups sharply slows down fluorination of the double bond. This tendency clearly shows itself on passing from bromocyclohexene "17" to 4(5)-bromoperfluoro-1-methylcyclohexene "25" and to perfluoro[4,4,0]bicyclodecene "26". Cyclohexene "25" is fluorinated at 250°C, whereas compound "26" is stable to VF_5 at this temperature.

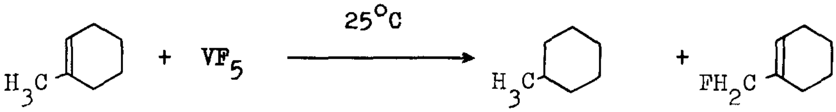


"25" "27"



"26"

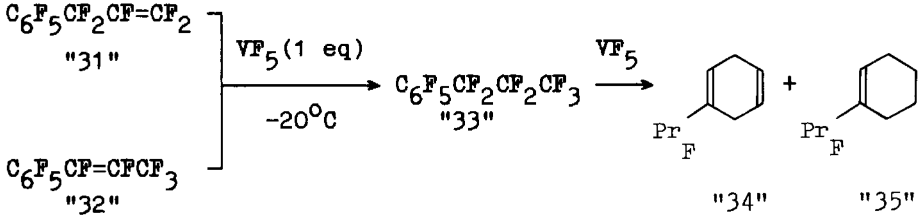
The reaction of vanadium pentafluoride with 1-methylnonafluorocyclohexene "28" proceeds in a more complex way, *via* fluorination of the double bond and substitution of one hydrogen by fluorine.



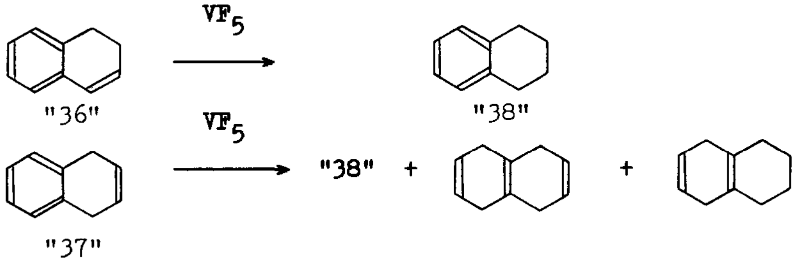
"28" "29" "30"

It is worthwhile to note here that the reaction of 2,3,4,5,6-pentafluorotoluene with vanadium pentafluoride also leads to the formation of pentafluorobenzyl fluoride, along with the products of fluorination of their aromatic ring [4].

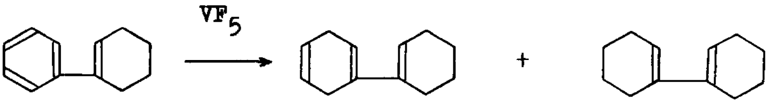
It is interesting to compare the reactivity of the perfluorinated C=C bond and the aromatic ring. For that purpose we studied the reaction of VF_5 with perfluoro-3-propenylbenzene "31" and perfluoro-1-propenylbenzene "32". With a deficiency of VF_5, both fluorinations proceed with a high regioselectivity, almost the only product being perfluoropropylbenzene "33". In an excess of VF_5, the products of further fluorination "34" and "35" are formed.



As shown above, the internal perfluoroalkenes are fluorinated by VF_5 at a higher temperature than the terminal ones. Hence, easy fluorination of C=C bond of compound "32" seems to be due to conjugation of the olefinic fragment with the aromatic ring. This is in agreement with the results of fluorinations of isomeric perfluoro-1,2- and 1,4-dihydronaphthalenes "36" and "37". The former is transformed exclusively to perfluorotetralin "38", whereas fluorine addition to the olefinic fragment of the latter proceeds concurrently with fluorination of the aromatic ring [1].



At the same time, the reaction of VF_5 with perfluoro-1-phenylcyclohexene "39" occurs only at the aromatic ring. This is explained by the absence of conjugation of the C=C bond of the cyclohexenyl fragment with the C_6F_5 group because of their non-coplanarity. The negative inductive effect of the pentafluorophenyl group also leads to increased deactivation of the olefinic fragment in compound "39" as compared with that in compounds "32", "36" and "37" (cf. the relative reactivity of cyclohexenes "17" and "25").



"39" "40" "41"

Polyhalogenated aliphatic dienes and cyclohexadienes

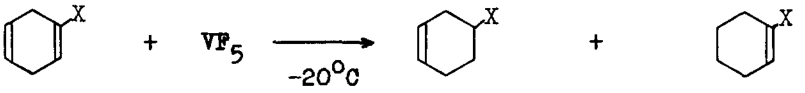
In view of our results on the reactions of VF$_5$ with polyhalogenated alkenes and cycloalkenes, it seems reasonable to suggest that the fluorination rate of the C=C bond in nonconjugated aliphatic or cyclic dienes is chiefly governed by the nature and number of substituents at the sp^2-hybrid carbon atoms and does not depend on mutual disposition of olefinic fragments. To confirm this supposition, we have studied fluorination of polyfluorinated cyclohexadienes by vanadium pentafluoride.

Treatment of the CFCl$_3$ solution of perfluoro-1,4-cyclohexadiene "42" with 4 equivalents of VF$_5$ at -25°C leads to the formation of perfluorocyclohexene "43" (Table 2).
Increase of temperature from -25 to 25°C raises conversion of diene "42" from 26 to 100%, but the only product of fluorination remains cyclohexene "43". Substitution of one of vinyl fluorines in compound "42" by hydrogen or chlorine leads to increased fluorination rate of this olefinic fragment as compared with the CF=CF fragment. 1-H-Heptafluoro-1,4-cyclohexadiene "44" is fluorinated at -25°C to form predominantly 4-H-nonafluorocyclohexene "45". Fluorination of 1-chloroheptafluoro-1,4-cyclohexadiene "46" proceeds in a similar way. With vinyl fluorine in diene "42" substituted by the trifluoromethyl group, fluorination occurs only at 20-25°C to give exclusively perfluoro-1-methylcyclohexene "50".

TABLE 2

Fluorination of polyhalo-1,3-butadienes and polyfluorocyclohexadienes

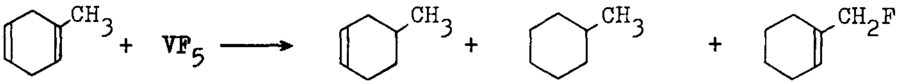
Compound mmol	VF_5, mmol ($CFCl_3$,ml)	Temperature, °C (Time, min)	Method (Alkane conversion,%)	Products, yield, %
"42" 3.0	12.1 (5)	-25 (15)	A (26)	"43" 87
"42" 4.8	19.2 (6)	25 (25)	B (100)	"43" 91
"44 1.0	2.1 (5)	-25 (20)	A (39)	"45"75,"47" 4
"46" 1.7	6.2 (5)	-25 (15)	A (45)	"19"27,"48"59
"46" 3.8	15.2 (6)	25 (20)	B (100)	"20"38,"48"57
"49" 1.5	6.8 (6)	25 (20)	B (70)	"50" 92
"51" 1.6	5.5 (6)	25 (20)	B (100)	"52"53,"29"11 "30"29
"53" 1.3	5.5 (5)	-25 (15)	A (29)	"43" 83
"54" 21	62 (7)	-20 (20)	A (81)	cis-"12" 20 trans-"12"36,"2" 8
"55" 20	96 (30)	-20 (20)	A (97)	"56"34,"57"30
"55" 40	205 (50)	-20(180)	A (100)	"56"37,"57"31



X		Yield, %	
X = F	"42"	"43" 87	-
H	"44"	"45" 75	"47" 4
Cl	"46"	"48" 59	"19" 27
CF_3	"49"	-	"50" 92

At 25°C the products of fluorination of diene "46" in excess VF_5 are cyclohexene "48" and chloroundecafluorocyclohexane "20" which is formed in these conditions from 1-chlorononafluorocyclohexene (see above).

1-Methylheptafluoro-1,4-cyclohexadiene "51" does not react with VF_5 at -25°C, and at 20-25°C it is transformed to a mixture of 4-methylnonafluorocyclohexene, methylundecafluorocyclohexane and 1-fluoromethylnonafluorocyclohexene.



"51" "52" "29" "30"

The two latter compounds are the products of fluorination of 1-methylnonafluorocyclohexene "28".

Thus the relative rate of fluorination of the formally independent non-equivalent olefinic fragments of 1,4-cyclohexadiene derivatives actually depends on the donating or accepting ability of a substituent at the C=C bond. However it should be borne in mind that 1-X-heptafluoro-1,4-cyclohexadienes react with VF_5 at a lower temperature than the respective 1-X-nonafluorocyclohexenes. For example, fluorination of the CF=CCl bond in cyclohexadiene "46" occurs at -25°C, and in cyclohexene "19" at +25°C. Simultaneously the CF=CF bond is fluorinated, though to a less extent, whereas fluorine addition to this fragment in polyfluorocyclohexenes is observed only at 50-60°C.

Fluorination of perfluoro-1,3-cyclohexadiene "53" at -25°C leads to perfluorocyclohexene. Other polyfluorinated 1,3-cyclohexadiene derivatives are currently not readily available, and their reactions with VF_5 have not been studied.

The terminal polyhalo-1,3-alkadienes react with vanadium pentafluoride in the same conditions as terminal alkenes. The reaction of VF_5 with 2-chloropentafluoro-1,3-butadiene "54" proceeds chiefly by fluorine 1,4-addition (formation of alkene "12"). As polyfluoroalkane "2" is formed from "12" under more drastic conditions (see above), it seems to be here the product of sequential 1,2-addition of fluorine.

$$CF_2{=}CCl{-}CF{=}CF_2 \;+\; VF_5 \longrightarrow CF_3CCl{=}CFCF_3 \;+\; CF_3CClFCF_2CF_3$$

"54" "12" "2"

Treatment of perchloro-1,3-butadiene "55" with VF_5 at $-25^{\circ}C$ leads to the formation of 1,2,3,4-tetrafluorohexachlorobutane "56" and 1,1,2,4-tetrafluorohexachlorobutane "57" in about equal yields. A special experiment has shown that there is no mutual conversion of compounds "56", "57" under the reaction conditions. This indicates the parallel routes of their formation though the mechanism of their formation is still unclear.

As a result of studies on the reactions of vanadium pentafluoride with polyhalogenated compounds, we can build the following series of C=C bond reactivity variation depending on substituents :

$$CF_2{=}CFR_F > R_FCF{=}CFR_F > (R_F)_2C{=}CFR_F > (R_F)_2C{=}C(R_F)_2$$

$$>C{=}C<_X \quad : \quad X = H \geqslant Cl > CH_3 > F > R_F \geqslant OR_F$$

It is readily evident that the relative reactivity of polyhalogenated unsaturated compounds with VF_5 clearly indicates the electrophilic nature of this fluoride. However it seems untimely to judge about the fluorination mechanism.

EXPERIMENTAL

The NMR spectra were recorded on a Varian A56/60A (^1H at 60 MHz, ^{19}F at 56.4 MHz) and WP 200 SY instruments (^{19}F at 188,31 MHz). The internal standard is TMS (^1H) and C_6F_6 (F^{19}). The IR spectra were recorded on a Specord IR 75 instrument in CCl_4 solutions; mass-spectra, on a Finnigan MAT-2800 instrument.

Vanadium pentafluoride was synthesized by treatment of vanadium with fluorine in a flow system in a nickel reactor. Before use VF_5 was distilled [ref.].

TABLE 3

NMR spectral data

Compound	^{19}F chemical shifts (ppm)	Coupling constants (Hz)
"2"	85.0(3F^{1}),83.4(1F^{4}),42.2(2F^{3}), 24.3(1F^{2})	J(2,3)= 10
"4"(n.c.)	99.5(2F^{1}),82.0(3F^{8}),48.5(2F^{7}), 44.2(CF$_{3}$),41.0(2CF$_{2}$),36.6(2F^{3}), 31.8(1F^{2})	
"29" [8][a]	43.5(2F^{2A,6A}),39.1(2F^{3A,5A}), 38.3(1F^{4A}),26.3(2F^{2B,6B}), 23.6(2F^{3B,5B}),21.0(1F^{4B})	J(AB) ~ 280
"30"(n.c.)[b]	51.1(2F^{6}),42.1(2F^{3}),39.9(1F^{2}), 28.9(4F^{4,5}),-60.1(1F$^{\alpha}$)	J(H-F,gem)= 47
"34"(n.c.)	83.8(3F$^{\gamma}$),60.8(2F^{6}),53.1(2F$^{\alpha}$,1F^{2}), 49.6(2F^{3}),36.9(2F$^{\beta}$),11.2(1F^{5}),4.4(1F^{4})	
"35"(n.c.)	81.6(3F$^{\gamma}$),56.0(1F^{2}),53.8(2F$^{\alpha}$,2F^{6}), 41.8(2F^{3}),36.6(2F$^{\beta}$),27.8(2F^{4},2F^{5})	
"52"(n.c.)[c]	57.8(1F^{3A}),54.6(1F^{5A}),43.1(1F^{6A}), 35,8(1F^{5B}),25.8(1F^{6B}),9.7(1F^{2}), 7.6(1F^{1}),-8.4(1F^{4})	J(AB) ~ 275-285
"56"(L,D or meso)[d]	102.4(1F^{1},1F^{4}),53.5(1F^{2},1F^{3})	J(2,3)=-10, J(1,2)=(3,4)=-17.6 J(1,4)=-19.0
"56"(meso or L,D)[d]	103.5(1F^{1},1F^{4}),52.5(1F^{2},1F^{3})	J(1,2)=(3,4)=-15.2 J(1,3)=(2,4)=12.8 J(1,4)=-21.2 J(2,3)=-10.7
"57"(n.c.)[d]	110.4(1F^{1A}),106.2(1F^{1B}), 103.2(1F^{4}),58.7(1F^{2})	J(AB)=160, J(1B,2)=-13 J(1A,4)=-28, J(1B,4)=-25, J(2,4)=16 J(1A,2)=-10

[a] δ(H) 1.61, [b] δ(H) 5.24, [c] δ(H) 1.98, [d] The ^{19}F NMR spectrum has been interpreted by M.V.Galakhov.

TABLE 4

IR spectral data

Compound	ν (cm^{-1})
"29" [8]	3021, 2959 (C-H), 1454, 1393, 1368, 1321, 1300, 1249, 1197, 1159, 1094, 1043, 996, 927, 917
"30"(n.c.)	2961, 2909 (C-H), 1706 (CF=CCH$_2$F), 1535, 1514, 1501, 1388, 1350, 1330, 1301, 1232, 1176, 1136, 1120, 1087, 1052, 1039, 985, 956, 932
"34"(n.c.)	1771 (CF=CF), 1702 (CF=CC$_3$F$_7$), 1495, 1393, 1360, 1345, 1281, 1257, 1242, 1211, 1194, 1167, 1149, 1125, 1110, 1091, 1079, 1058, 1033, 982, 932
"35"(n.c.)	1695 (CF=CC$_3$F$_7$), 1551, 1535, 1530, 1513, 1503, 1367, 1333, 1301, 1279, 1247, 1233, 1187, 1150, 1134, 1121, 1093, 1077, 1037, 977, 935
"48"(n.c.)	1742 (FC=CF), 1357, 1285, 1246, 1229, 1220, 1179, 1145, 1104, 1070, 1037, 1017, 955, 855
"52"(n.c.)	3019, 2954 (C-H), 1747 (FC=CF), 1367, 1311, 1298, 1243, 1193, 1164, 1140, 1115, 1086, 1060, 1038, 1007, 948, 923, 910
"57"(n.c.)	1540, 1160, 1125, 1110, 1084, 1032, 1005, 964, 918, 873, 695, 641

TABLE 5

Analytical data

Compound	Found/Calculated				Formula	M^+ [a]
	C	H	Cl	F		
"4"(n.c.)[b]	20.1		15.8	64.2	$C_8Cl_2F_{16}$	
	20.4		15.1	64.5		
"29" [8]	28.3	1.1		70.5	$C_7H_3F_{11}$	
	28.3	1.0		70.6		
"30"(n.c.)					$C_7H_2F_{10}$	275.9964
						275.9997
"34"(n.c.)					C_9F_{14}	373.9754
						373.9776
"35"(n.c.)					C_9F_{15}[c]	392.9815[c]
						392.9760
"48"(n.c.)					C_6ClF_9 (^{35}Cl)	277.9542
						277.9545
"52"(n.c.)	32.5	1.3		66.1	$C_7H_3F_9$	
	32.6	1.2		66.3		
"57"(n.c.)[d]	15.0		64.0	21.1	$C_4Cl_6F_4$	
	14.2		63.2	22.5		

NOTE : [a] From high-resolution mass-spectrum, [b] B.p. 140-141°C, [c] (M^+-19), [d] B.p. 192-194°C.

Fluorination with Vanadium Pentafluoride

Method A. An unsaturated compound and $CFCl_3$ were placed into a polychlorotrifluoroethylene reactor provided with a Teflon stirrer and Teflon-coated thermocouple, and the mixture was cooled to -25 to -20°C. Then a solution of VF_5 in an equal amount of $CFCl_3$ was added portionwise, during stirring, at such a rate as to keep the temperature down at -20°C. The mixture was then agitated and poured onto ice. The organic layer was separated, washed with cold water, dried over $MgSO_4$ or $CaCl_2$, and the solvent was distilled off. Known compounds were identified by using NMR and GLC analysis with addition of authentic samples: in all cases, identical values were recorded. New compounds were isolated by preparative GLC.

Method B. Into a 10 ml nickel tube, vanadium pentafluoride was placed, cooled to -20 to - 10°C, and a fluorinated unsaturated compound (or its $CFCl_3$ solution) was added. The tube was hermetically closed and shaken at the above temperature. The tube was cooled to -20 to -10°C and the reaction mixture poured onto ice. Then the mixture was treated as described above.

Method C. The reaction was carried out as described under Method B (without a solvent), but after having been kept for some time, the reaction products were distilled off from the tube to the trap (-78°C). Then they were treated with water, dried and analysed.

Tables 3, 4 and 5 show the IR and NMR spectra and the analytical data of new compounds.

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