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THE REACTION OF PERHALOGENOKETONES WITH ALLYLIC DERIVATIVES OF SILICON AND TIN

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Summary

For the purpose of this investigation a wide range of allylic derivatives of both silicon and tin were required, and we report the preparation of these in greatly improved yield by a low temperature modification of the hydrolysis stage of the Grignard procedure.

The non-catalysed reaction of β-alkenyltins with a number of perhalogenoacetones has been examined, and in all cases alkenyloxy derivatives have been isolated as exclusive products. The interaction of β-alkenylsilanes with perhalogenoacetones follows a different course in the absence of catalysts, yielding alcohols of the general type $R_3SiCH{=}CH(R')C(R_{hal})_2OH$. In the presence of aluminium chloride, however, significant yields of β-alkenyloxysilanes are formed.

An allylic rearrangement accompanies the β-alkenyltin insertion reaction, but in the case of the β-alkenylsilane formation, no such rearrangement takes place. From these observations possible mechanisms for the reactions are proposed.

Introduction

The reaction of perhalogenoketones and more particularly 1,1,1,3,3,3-hexafluoropropan-2-one (HFA) with organometallic reagents has in recent years been a source of considerable interest * and an extensive range of products have now been isolated in which ketone insertion has occurred into a metal—heteroatom bond. This work has been particularly fruitful in the fields of organosilicon and organotin chemistry where Si—H [2-5], Si—O [6], Si—N [7], Si—P [8], Si—S [9], Si—As [10], Sn—H [5], Sn—O [11, 12] and Sn—N [7] represent a few of the bonds with which perfluoroketones have been found to react. Ob-

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* For a review on the insertion reactions of organo-metals and -metalloids involving unsaturated substrates see ref. 1.

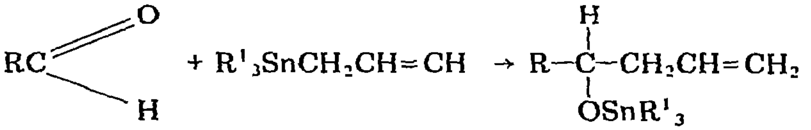
TABLE 1

YIELDS FROM GRIGNARD SYNTHESIS OF ALLYLIC DERIVATIVES OF SILICON AND TIN

Compound	This work (%)	Previously report yield (%)
$Me_3SiCH_2CH=CH_2$	89	51 [22]
$Me_3SiCH_2C(Me)=CH_2$	61	40 [25]
$Me_2Si(CH_2CH=CH_2)_2$	96	50 [26]
$MeSi(CH_2CH=CH_2)_3$	89	61 [26]
$Si(CH_2CH=CH_2)_4$	89	35 [27]
$Ph_3SiCH_2CH=CH_2$	96	90 [28]
$Me_3SnCH_2CH=CH_2$	85	48 [21]
$Sn(CH_2CH=CH_2)_4$	75	53 [27]
$Ph_3SnCH_2CH=CH_2$	94	88 [29]
$Me_3SnCH_2C(Me)=CH_2$	68	[a]
$Me_2Sn(CH_2CH=CH_2)_2$	53	[a]

[a] No yield reported previously.

servations of aldehyde insertion into a Si—C bond [13], stem from the experiments of Birkofer et al., who showed that reaction of trimethylsilylmethyl est or nitriles with aryl aldehydes in the presence of base afforded trimethylsilyl alkoxides. Subsequently, esters [14], and other aldehydes [14-19] have been shown to insert into activated Si—C and Sn—C bonds. Representative of these are the insertions of unsaturated molecules such as allyltrialkyltins [14, 15].



In contrast to these observations, there are to our knowledge no well authenticated examples of ketone insertion into either Sn—C or Si—C bonds. Koenig and Neumann [15] observed that acetophenone, *p*-bromoacetophenon and isobutenyl methyl ketone reacted incompletely with allyltriethyltin at 200°, although no products were identified; benzophenone was said to be unreactive. In the present paper we describe reactions of allylic derivatives of silicon and tin with perhalogenoketones to give products resulting either from metal—carbon or carbon—hydrogen insertion.

Although allylsilanes [20] and allyltins [21] have been known for many years, little attempt has been made to optimise their method of preparation vi the Grignard method, and reported yields are often indifferent (Table 1).

$$n\,CH_2{=}CHCH_2MgX + R_{4-n}MX_n \rightarrow R_{4-n}M(CH_2CH{=}CH_2)_n + n\,MgX_2$$

$(n = 1\text{-}4,\ M = Si \text{ or } Sn)$

It occurred to us that the reason for these indifferent yields could most reasonably be ascribed to the instability of allylsilanes [22] and allyltins [23] in the presence of acids and bases.

$$R_3SiCH_2CH{=}CH_2 \xrightarrow{H_3O^+} R_3SiOSiR_3 + CH_3CH{=}CH_2$$

This could become of major importance during the hydrolysis stage at the end of the reaction. In keeping with this proposal, we found that when the reaction products of trimethylchlorosilane and allylmagnesium bromide were hydrolyzed at −20°, an 89% yield of allyltrimethylsilane could be isolated. When hydrolysis was carried out at ambient temperatures the yields of allyltrimethylsilane from this preparation were drastically reduced to 30-40%, and the by-product was hexamethyldisiloxane, as expected from an allylic fission reaction in the polar medium. Using this preparative modification, we have been able to greatly improve upon previously reported yields for a large number of allylic derivatives of silicon and tin (Table 1). The only exceptions to this are the triphenylsilyl- and triphenyltin-derivatives, where reported yields were already high due to their much greater stability to hydrolytic fission [24].

Results and discussion

Allyltrimethyltin reacts vigorously with hexafluoroacetone (HFA) even at −20°, to give 4,4-bis(trifluoromethyl)-4-trimethylstannoxy-1-butene, the product resulting from a tin—allylic insertion reaction.

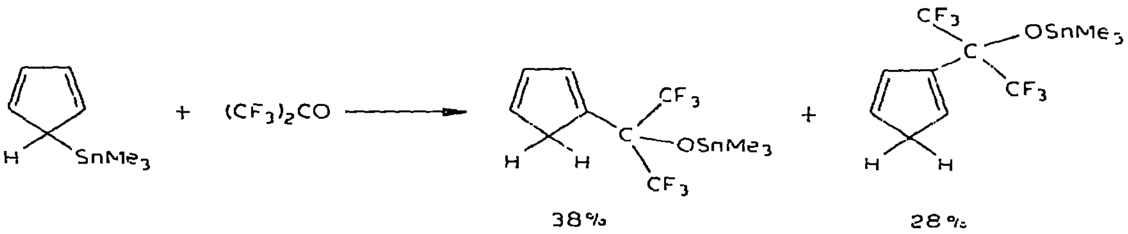
$$Me_3SnCH_2CH{=}CH_2 + (CF_3)_2CO \rightarrow Me_3SnOC(CF_3)_2CH_2CH{=}CH_2$$

The perhalogenoketones, 1-chloro-1,1,3,3,3-pentafluoro-2-propanone (MCPFA), 1,3-dichloro-1,1,3,3-tetrafluoro-2-propanone (DCTFA) and 1,1,3-trichloro-1,3,3-trifluoro-2-propanone (TCTFA) also react in a completely analogous fashion. The spectroscopic properties of these compounds (Tables 2 and 3) are entirely consistent with the proposed structures. The adducts are hydrolysed to give the expected alcohol and trimethyltin hydroxide.

$$Me_3SnOC(R_{hal})_2CH_2CH{=}CH_2 \xrightarrow{H_2O} CH_2{=}CHCH_2C(R_{hal})_2OH + Me_3SnOH$$

Dimethyldiallyltin reacts in a similar fashion to give both mono- and di-insertion products in good yield, dependant upon relative reagent ratios. An attempted reaction of tetrallyltin with HFA afforded only non-distillable polymeric material. The formation of polymeric materials has also been noted [30] in a similar reaction of tetrallyltin with sulphur dioxide.

It is interesting to note that this insertion reaction can also be extended to cyclic alkenes; thus indenyltrimethyltin and cyclopentadienyltrimethyltin react with HFA and MCPFA to give the expected Sn—C insertion products.

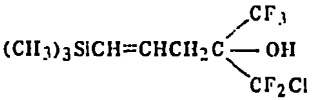
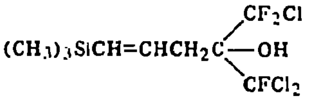
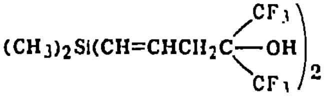
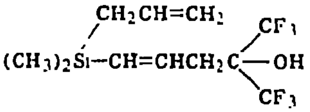
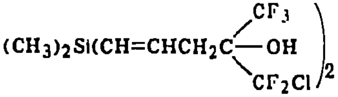


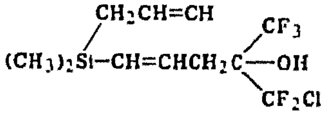
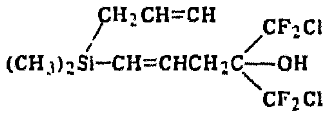
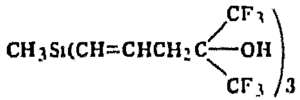
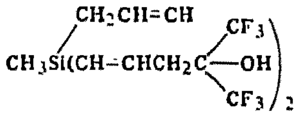
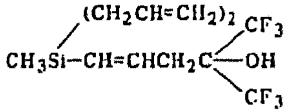
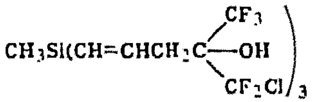
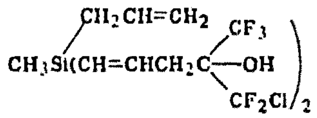
2-Butenyltrimethyltin upon reaction with HFA or MCPFA did not give the expected products from a simple Sn—C insertion reaction, but a complete rearrangement of the allylic fragment.

(continued on p. 221)

TABLE 2

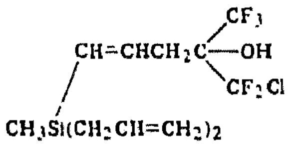
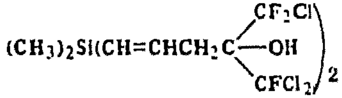
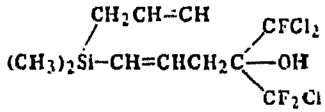
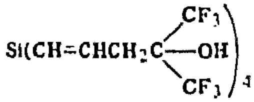
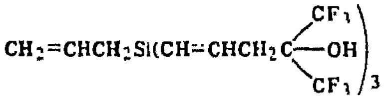
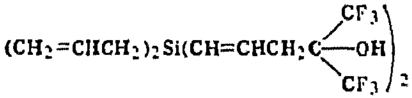
PERHALOGENOKETONE INSERTION REACTIONS WITH ORGANOSILICON AND ORGANOTIN DERIVATIVES

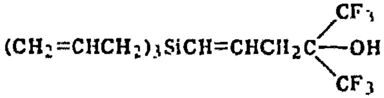
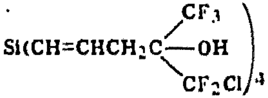
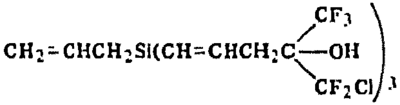
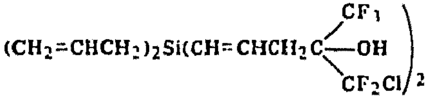
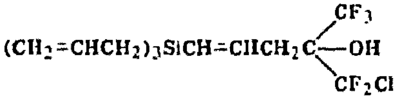
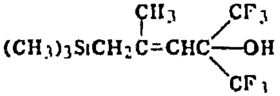
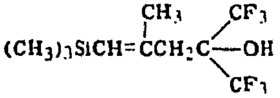
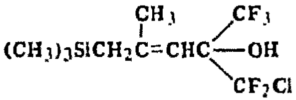
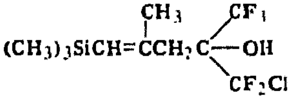
Reactants (reagent ratio)	Product	B.p. (°C/mm) [M.p.](°C)	Yield (%)	Reaction conditions[a]	Selected IR absorptions (cm^{-1})	
					ν(OH)	ν(C=C)
$(CH_3)_3SiCH_2CH=CH_2$ + CF_3COCF_3 (1/1.1)	$(CH_3)_3SiCH=CHCH_2C(CF_3)_2OH$	59/14	86	100°/48h	3595, 3515	1602
$(CH_3)_3SiCH_2CH=CH_2$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SiCH=CHCH_2C(CF_3)(CF_2Cl)OH$	79/15	89	100°/24h	3580, 3515	1605
$(CH_3)_3SiCH_2CH=CH_2$ + $CF_2ClCOCF_2Cl$ (1/1.1)	$(CH_3)_3SiCH=CHCH_2C(CF_2Cl)_2OH$	56/0.7	83	100°/24h	3560, 3505	1603
$(CH_3)_3SiCH_2CH=CH_2$ + $CF_2ClCOCFCl_2$ (1/1.1)	 $(CH_3)_3SiCH=CHCH_2C(CF_2Cl)(CFCl_2)OH$	63/0.015	59	100°/24h	3560, 3500	1606
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + CF_3COCF_3 (1/2.2)	 $(CH_3)_2Si(CH=CHCH_2C(CF_3)_2OH)_2$	79/0.01	79	100°/24h	3595, 3495	1607
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + CF_3COCF_3 (1/1)	 $(CH_3)_2Si(CH_2CH=CH_2)-CH=CHCH_2C(CF_3)_2OH$	43/0.65	53	100°/24h	3590, 3500	1631, 1609
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + CF_3COCF_2Cl (1/2.2)	 $(CH_3)_2Si(CH=CHCH_2C(CF_3)(CF_2Cl)OH)_2$	98/0.005	78	100°/24h	3580, 3500	1607

$(CH_3)_2Si(CH_2CH=CH_2)_2$ + CF_3COCF_2Cl (1/1)		58/0.35	35	100°/24h	3575, 3500	1631, 1609
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + $CF_2ClCOCF_2Cl$ (1/2.2)		128/0.02	65	100°/48h	3580, 3500	1607
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + $CF_2ClCOCF_2Cl$ (1/1)		74/0.4	57	100°/24h	3560, 3495	1631, 1608
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_3 (1/3.5)		124/0.03	74	100°/48h	3490, 3595	1607
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_3 (1/2)		98/0.05	65	100°/24h	3595, 3500	1632, 1608
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_3 (1/1)		66/0.8	60	100°/24h	3595, 3500	1632, 1610
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_2Cl (1/3.3)		156/0.04	72	100°/48h	3580, 3495	1606
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_2Cl (1/2)		115/0.015	40	100°/24h	3575, 3495	1631, 1608

(continued)

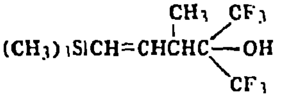
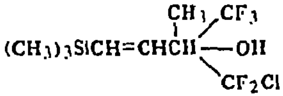
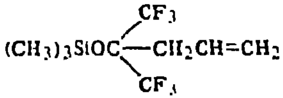
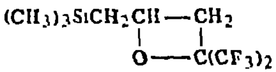
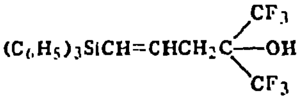
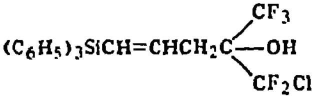
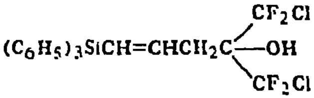
TABLE 2 (continued)

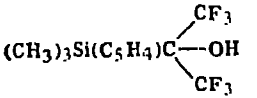
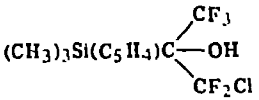
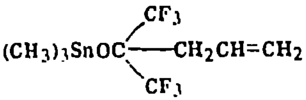
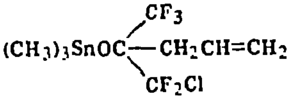
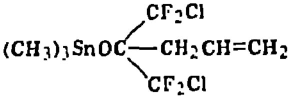
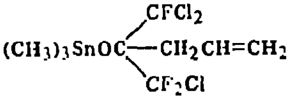
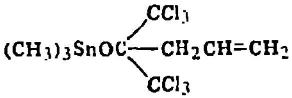
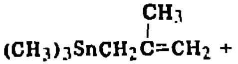
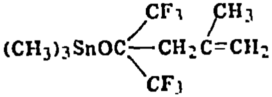
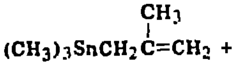
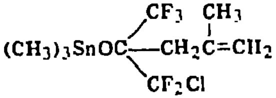
Reactants (reagent ratio)	Product	B.p. (°C/mm) [M.p.] (°C)	Yield (%)	Reaction conditions^a	Selected IR absorptions (cm^{-1})	
					ν(OH)	ν(C=C)
$CH_3Si(CH_2CH=CH_2)_3$ + CF_3COCF_2Cl (1/1)	 $CH_3Si(CH_2CH=CH_2)_2CH=CHCH_2C(CF_3)(CF_2Cl)OH$	73/0.03	30	100°/24h	3580, 3500	1631, 1609
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + $CF_2ClCOCFCl_2$ (1/2.1)	 $(CH_3)_2Si(CH=CHCH_2C(CF_2Cl)(CFCl_2)OH)_2$	150/0.015	40	100°/48h	3560, 3500	1606
$(CH_3)_2Si(CH_2CH=CH_2)_2$ + $CF_2ClCOCFCl_2$ (1/1)	 $(CH_3)_2Si(CH_2CH=CH)-CH=CHCH_2C(CFCl_2)(CF_2Cl)OH$	107/0.35	30	100°/24h	3560, 3500	1631, 1607
$Si(CH_2CH=CH_2)_4$ + CF_3COCF_3 (1/4.4)	 $Si(CH=CHCH_2C(CF_3)_2OH)_4$	146-148/0.03	45	105°/48h	3580, 3500	1604
$Si(CH_2CH=CH_2)_4$ + CF_3COCF_3 (1/2.5)	 $CH_2=CHCH_2Si(CH=CHCH_2C(CF_3)_2OH)_3$	127-129/0.01	42	100°/48h	3595, 3495	1634, 1607
$Si(CH_2CH=CH_2)_4$ + CF_3COCF_3 (1/2)	 $(CH_2=CHCH_2)_2Si(CH=CHCH_2C(CF_3)_2OH)_2$	109/0.03	41	100°/48h	3595, 3495	1634, 1610

$Si(CH_2CH{=}CH_2)_4$ + CF_3COCF_3 (1/1)	 $(CH_2{=}CHCH_2)_3SiCH{=}CHCH_2C(CF_3)_2OH$	82/0.07	48	100°/24h	3595, 3500	1634, 1611
$Si(CH_2CH{=}CH_2)_4$ + CF_3COCF_2Cl (1/4.4)	 $Si(CH{=}CHCH_2C(CF_3)(CF_2Cl)OH)_4$	178-180/0.03	46	105°/120h	3580, 3500	1603
$Si(CH_2CH{=}CH_2)_4$ + CF_3COCF_2Cl (1/3)	 $CH_2{=}CHCH_2Si(CH{=}CHCH_2C(CF_3)(CF_2Cl)OH)_3$	162-4/0.06	32	105°/120h	3580, 3500	1632, 1607
$Si(CH_2CH{=}CH_2)_4$ + CF_3COCF_2Cl (1/2)	 $(CH_2{=}CHCH_2)_2Si(CH{=}CHCH_2C(CF_3)(CF_2Cl)OH)_2$	130/0.03	35	105°/100h	3580, 3500	1633, 1608
$Si(CH_2CH{=}CH_2)_4$ + CF_3COCF_2Cl (1/1)	 $(CH_2{=}CHCH_2)_3SiCH{=}CHCH_2C(CF_3)(CF_2Cl)OH$	84/0.01	45	105°/100h	3580, 3495	1631, 1609
 $(CH_3)_3SiCH_2C(CH_3){=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SiCH_2C(CH_3){=}CHC(CF_3)_2OH$	70/14	40	60°/28h	3590, 3480	1628
 $(CH_3)_3SiCH_2C(CH_3){=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SiCH{=}C(CH_3)CH_2C(CF_3)_2OH$	70/14	15	60°/28h	3590, 3480	1604
 $(CH_3)_3SiCH_2C(CH_3){=}CH_2$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SiCH_2C(CH_3){=}CHC(CF_3)(CF_2Cl)OH$	85.5/12	26	60°/28h	3580, 3480	1629
 $(CH_3)_3SiCH_2C(CH_3){=}CH_2$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SiCH{=}C(CH_3)CH_2C(CF_3)(CF_2Cl)OH$	85.5/12	25	60°/28h	3580, 3480	1605

(continued)

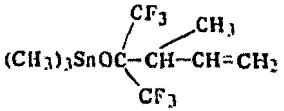
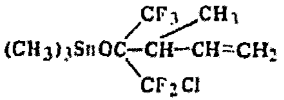
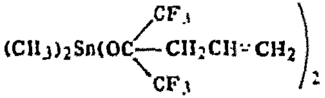
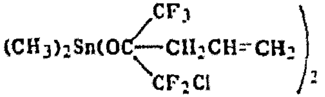
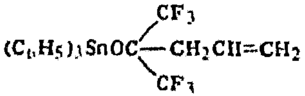
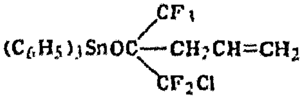
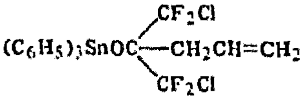
TABLE 2 (continued)

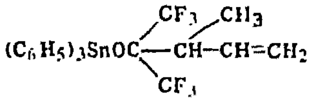
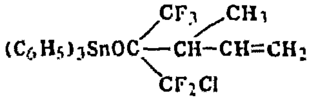
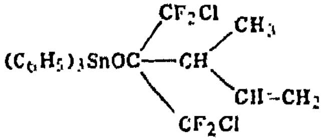
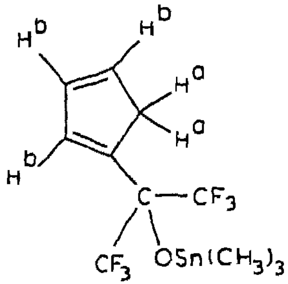
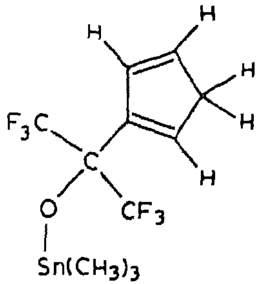
Reactants (reagent ratio)	Product	B.p. (°C/mm) [M.p.] (°C)	Yield (%)	Reaction conditions[a]	Selected IR absorptions (cm^{-1})	
					ν(OH)	ν(C=C)
$(CH_3)_3SiCH_2CH{=}CHCH_3$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SiCH{=}CHCH(CH_3)C(CF_3)_2OH$	38/1	60	100°/100h	3580, 3510	1602
$(CH_3)_3SiCH_2CH{=}CHCH_3$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SiCH{=}CHCH(CH_3)(CF_3)(CF_2Cl)OH$	37/0.09	56	105°/260h	3575, 3500	1604
$(CH_3)_3SiCH_2CH{=}CH_2$ + CF_3COCF_3 (1/1.1/0.01 $AlCl_3$)	 $(CH_3)_3SiOC(CF_3)_2CH_2CH{=}CH_2$	38/15	51	25°/24h		1642
$(CH_3)_3SiCH_2CH{=}CH_2$ + CF_3COCF_3 (1/1.1)		58/14	41	−20°/24h		
$(C_6H_5)_3SiCH_2CH{=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(C_6H_5)_3SiCH{=}CHCH_2C(CF_3)_2OH$	[55-57]	65	60°/28h	3595, 3520	1607
$(C_6H_5)_3SiCH_2CH{=}CH_2$ + CF_3COCF_2Cl (1/1.3)	 $(C_6H_5)_3SiCH{=}CHCH_2C(CF_3)(CF_2Cl)OH$	[69-71]	53	80°/24h	3570, 3520	1606
$(C_6H_5)_3SiCH_2CH{=}CH_2$ + $CF_2ClCOCF_2Cl$ (1/2)	 $(C_6H_5)_3SiCH{=}CHCH_2C(CF_2Cl)_2OH$	[52-54]	49	100°/24h	3575, 3520	1606

$(CH_3)_3SiC_5H_5$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3Si(C_5H_4)C(CF_3)_2OH$	55/0.3	55	80°/48h	3595, 3495	
$(CH_3)_3SiC_5H_5$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3Si(C_5H_4)C(CF_3)(CF_2Cl)OH$	63/0.04	35	100°/48h	3580, 3500	
$(CH_3)_3SnCH_2CH{=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SnOC(CF_3)_2CH_2CH{=}CH_2$	69/13	72	25°/24h		1639
$(CH_3)_3SnCH_2CH{=}CH_2$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SnOC(CF_3)(CF_2Cl)CH_2CH{=}CH_2$	46/1	81	80°/3h		1641
$(CH_3)_3SnCH_2CH{=}CH_2$ + $CF_2ClCOCF_2Cl$ (1/1.25)	 $(CH_3)_3SnOC(CF_2Cl)_2CH_2CH{=}CH_2$	50/0.005	85	25°/24h		1641
$(CH_3)_3SnCH_2CH{=}CH$ + $CF_2ClCOCFCl_2$ (1/1.5)	 $(CH_3)_3SnOC(CFCl_2)(CF_2Cl)CH_2CH{=}CH_2$		86[b]	25°/24h		1641
$(CH_3)_3SnCH_2CH{=}CH_2$ + CCl_3COCCl_3(1/2)	 $(CH_3)_3SnOC(CCl_3)_2CH_2CH{=}CH_2$		45[b]	50°/24h		1641
 $(CH_3)_3SnCH_2\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SnOC(CF_3)_2CH_2\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$	45/1	57	25°/12h		1645
 $(CH_3)_3SnCH_2\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SnOC(CF_3)(CF_2Cl)CH_2\overset{CH_3}{\overset{\vert}{C}}{=}CH_2$	59/0.9	58	25°/12h		1646

(continued)

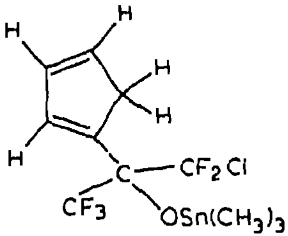
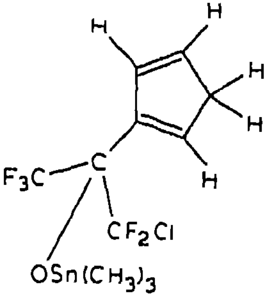
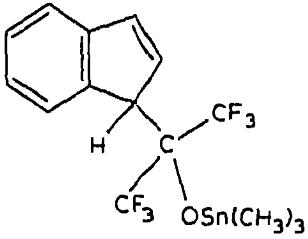
TABLE 2 (continued)

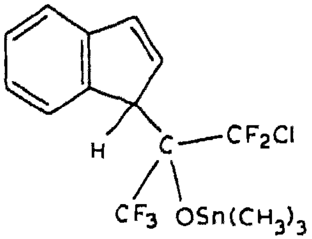
Reactants (reagent ratio)	Product	B.p. (°C/mm) [M.p.] (°C)	Yield (%)	Reaction conditions[a]	Selected IR absorptions (cm^{-1})	
					ν(OH)	ν(C=C)
$(CH_3)_3SnCH_2CH{=}CHCH_3$ + CF_3COCF_3 (1/1.1)	 $(CH_3)_3SnO\underset{CF_3}{\overset{CF_3}{C}}-\overset{CH_3}{CH}-CH{=}CH_2$	38/1	69	25°/10h		1641
$(CH_3)_3SnCH_2CH{=}CHCH_3$ + CF_3COCF_2Cl (1/1.1)	 $(CH_3)_3SnO\underset{CF_2Cl}{\overset{CF_3}{C}}-\overset{CH_3}{CH}-CH{=}CH_2$	54/0.8	65	25°/24h		1640
$(CH_3)_2Sn(CH_2CH{=}CH_2)_2$ + CF_3COCF_3 (1/2.2)	 $(CH_3)_2Sn\left(O\underset{CF_3}{\overset{CF_3}{C}}-CH_2CH{=}CH_2\right)_2$	62-64/0.06	70	25°/24h		1644
$(CH_3)_2Sn(CH_2CH{=}CH_2)_2$ + CF_3COCF_2Cl (1/2.5)	 $(CH_3)_2Sn\left(O\underset{CF_2Cl}{\overset{CF_3}{C}}-CH_2CH{=}CH_2\right)_2$	84/0.01	63	50°/24h		1645
$(C_6H_5)_3SnCH_2CH{=}CH_2$ + CF_3COCF_3 (1/1.1)	 $(C_6H_5)_3SnO\underset{CF_3}{\overset{CF_3}{C}}-CH_2CH{=}CH_2$	Oil	90	40°/24h		1642
$(C_6H_5)_3SnCH_2CH{=}CH_2$ + CF_3COCF_2Cl (1/1.2)	 $(C_6H_5)_3SnO\underset{CF_2Cl}{\overset{CF_3}{C}}-CH_2CH{=}CH_2$	Oil	90	80°/6h		1642
$(C_6H_5)_3SnCH_2CH{=}CH_2$ + $CF_2ClCOCF_2Cl$ (1/1.5)	 $(C_6H_5)_3SnO\underset{CF_2Cl}{\overset{CF_2Cl}{C}}-CH_2CH{=}CH_2$	Oil	85	100°/12h		1643

$(C_6H_5)_3SnCH_2CH{=}CHCH_3$ + CF_3COCF_3 (1/1.1)	 $(C_6H_5)_3SnOC(CF_3)_2CH(CH_3)CH{=}CH_2$	Oil	80	25°/12h	1640
$(C_6H_5)_3SnCH_2CH{=}CHCH_3$ + CF_3COCF_2Cl (1/1.1)	 $(C_6H_5)_3SnOC(CF_3)(CF_2Cl)CH(CH_3)CH{=}CH_2$	Oil	78	25°/15h	1640
$(C_6H_5)_3SnCH_2CH{=}CHCH_3$ + $CF_2ClCOCF_2Cl$ (1/2)	 $(C_6H_5)_3SnOC(CF_2Cl)_2CH(CH_3)CH{=}CH_2$	Oil	75	90°/24h	1641
$(CH_3)_3SnC_5H_5$ + CF_3COCF_3 (1/1.1)		59/0.1	38	25°/24h	
$(CH_3)_3SnC_5H_5$ + CF_3COCF_3 (1/1.1)		59/0.1	28	25°/24h	

(continued)

TABLE 2 (continued)

Reactants (reagent ratio)	Product	B.p. (°C/mm) [M.p.] (°C)	Yield (%)	Reaction conditions[a]	Selected IR absorptions (cm^{-1})	
					ν(OH)	ν(C=C)
$(CH_3)_3SnC_5H_5$ + CF_3COCF_2Cl (1/1.1)		61/0.005	34	25°/24h		
$(CH_3)_3SnC_5H_5$ + CF_3COCF_2Cl (1/1.1)		61/0.005	33	25°/24h		
$(CH_3)_3SnC_9H_7$ + CF_3COCF_3 (1/1.1)		83/0.01	85	25°/24h		

$(CH_3)_3SnC_9H_7$ + CF_3COCF_2Cl (1/1.1)		92/0.005	79	25°/24h

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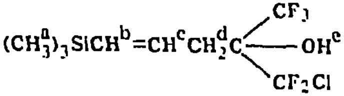
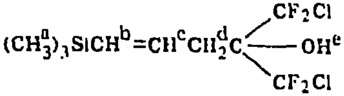
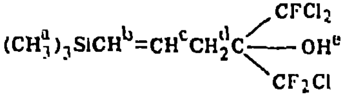
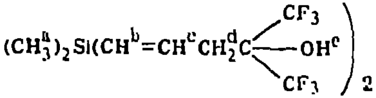
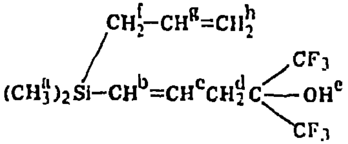
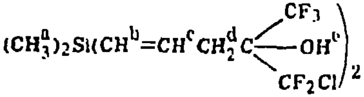
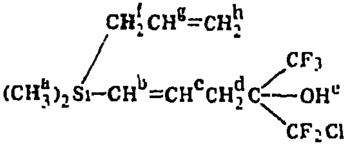
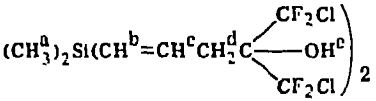
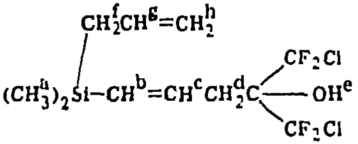
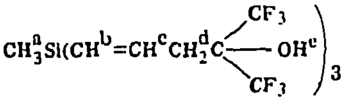
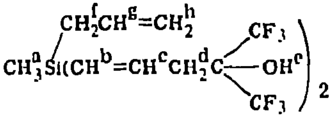
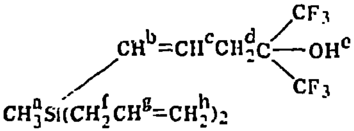
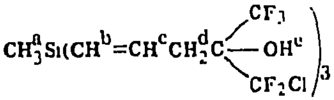
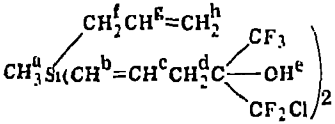
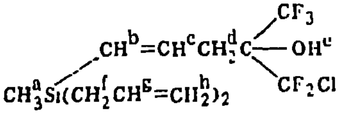
[a] Reaction conditions are tabulated as temperature/reaction time. [b] These products were unstable to distillation, and figures represent yields after the removal of volatile materials under vacuum.

TABLE 3

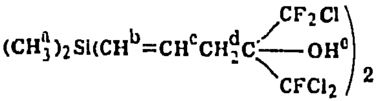
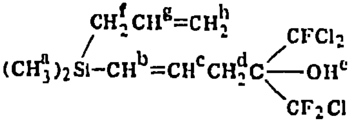
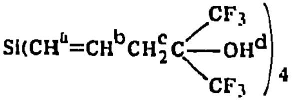
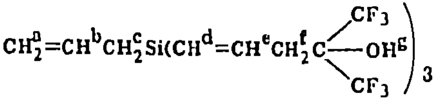
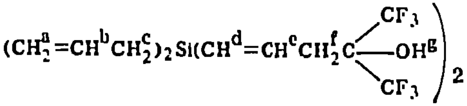
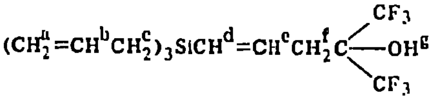
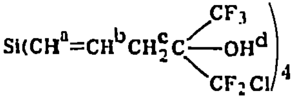
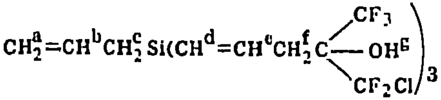
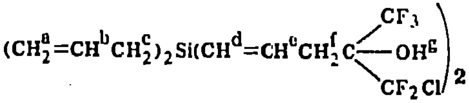
NMR SPECTRA OF INSERTION PRODUCTS

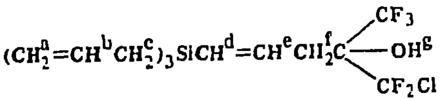
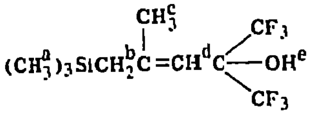
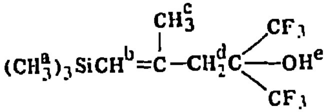
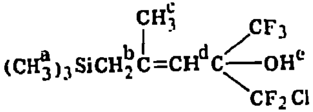
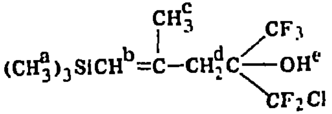
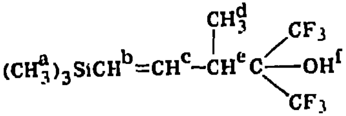
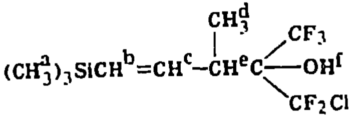
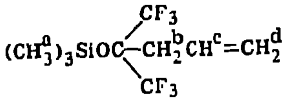
Compound	^{1}H Resonances (τ values) [a]	^{19}F Resonances (ppm upfield from $CFCl_3$)
$(CH_3^a)_3SiCH^b{=}CH^cCH_2^dC(CF_3)_2OH^e$	(a) 9.82, s; (b, c) 3.80, m; (d) 7.17, d, J 7Hz; (e) 6.92, s	CF_3 76.3, s
 $(CH_3^a)_3SiCH^b{=}CH^cCH_2^dC(CF_3)(CF_2Cl)OH^e$	(a) 9.84, s, (b, c) 3.83, m; (d) 7.11, d, J 7Hz; (e) 6.85, s	CF_3 73.8, t, ^4J 15Hz CF_2 61.4, q, ^4J 15Hz
 $(CH_3^a)_3SiCH^b{=}CH^cCH_2^dC(CF_2Cl)_2OH^e$	(a) 9.84, s; (b, c) 3.82, m; (d) 7.05, d, J 7Hz; (e) 6.76, s	CF_2 58.8, s.
 $(CH_3^a)_3SiCH^b{=}CH^cCH_2^dC(CFCl_2)(CF_2Cl)OH^e$	(a) 9.78, s; (b, c) 3.77, m; (d) 6.90, d, J 7Hz; (c) 6.61, s	CF_2 56.2, d ^3J 15.5Hz CF 60.0, t ^3J 15.5Hz
 $(CH_3^a)_2Si(CH^b{=}CH^cCH_2^dC(CF_3)_2OH^e)_2$	(a) 9.70, s; (b, c) 3.72, m; (d) 7.18, d, J 7Hz; (e) 6.69, s	CF_3 76.2, s.
 $(CH_3^a)_2Si(CH_2^fCH^g{=}CH_2^h)CH^b{=}CH^cCH_2^dC(CF_3)_2OH^e$	(a) 9.82, s; (b, c, g) 3.95, m; (d) 7.19, d, J 7Hz; (e) 6.87, s; (f) 8.40, d, J 8Hz; (h) 5.16, m	CF_3 76.4, s
 $(CH_3^a)_2Si(CH^b{=}CH^cCH_2^dC(CF_3)(CF_2Cl)OH^e)_2$	(a) 9.72, s; (b, c) 3.82, m; (d) 7.15, d, J 7Hz; (e) 6.73, s	CF_3 73.9, dt, ^4J 12Hz CF_2 61.6, dq, ^4J 12Hz
 $(CH_3^a)_2Si(CH_2^fCH^g{=}CH_2^h)CH^b{=}CH^cCH_2^dC(CF_3)(CF_2Cl)OH^e$	(a) 9.80, s; (b, c, g) 3.95, m; (d) 7.15, d, J 7Hz; (e) 6.82, s; (f) 8.41, d, J 7.5Hz; (h) 5.18, m	CF_3 73.9, t, ^4J 12 Hz CF_2 61.5, q, ^4J 12Hz

	(a) 9.70, s; (b, c) 3.83, m; (d) 7.00, d, J 7Hz; (e) 6.60, s	CF_2 59.3, s
	(a) 9.81, s; (b, c, g) 3.83, m; (d) 7.02, d, J 7Hz; (e) 6.65, s; (f) 8.37, d, J 7.5Hz; (h) 5.15, m	CF_2 58.7, s
	(a) 9.51, s; (b, c) 3.65, m; (d) 7.12, d, J 6Hz, (e) 6.55, s	CF_3 76.4, s
	(a) 9.73, s; (b, c, g) 3.82, m; (d) 7.35, d, J 6.5Hz; (e) 6.67, s; (f) 8.23, d, J 7.5Hz; (h) 5.12, m	CF_3 76.2, s
	(a) 9.79, s; (b, c, g) 3.90, m; (d) 7.19, d, J 6.5Hz; (e) 6.83, s, (f) 8.33, d, J 7.5Hz; (h) 5.08, m	CF_3 76.3, s
	(a) 9.51, s; (b, c) 3.70, m; (d) 7.12, d, J 6.5Hz; (e) 6.77, s	CF_3 74.0, tt, ^4J 12Hz CF_2 61.7, tq, ^4J 12Hz
	(a) 9.66, s; (b, c, g) 3.90, m; (d) 7.15, d, J 6.5Hz; (e) 6.70, s; (f) 8.33, d, J 7.5Hz, (h) 5.15, m	CF_3 74.4, dt, ^4J 12Hz CF_2 61.7, dq, ^4J 12Hz
	(a) 9.79, s; (b, c, g) 3.90, m; (d) 6.92, d, J 7Hz; (e) 6.67, s; (f) 8.36, d, J 8Hz; (h) 5.11, m	CF_3 73.9, t, ^4J 12Hz CF_2 61.5, q, ^4J 12Hz

(continued)

TABLE 3 (continued)

Compound	^1H Resonances (τ values) ^{a}	^{19}F Resonances (ppm upfield from $CFCl_3$)
 $(CH^a_3)_2Si(CH^b{=}CH^cCH^d_2C(CF_2Cl)(CFCl_2)OH^e)_2$	(a) 9.69, s; (b, c) 3.84, m; (d) 6.97, d, J 6.5Hz; (e) 6.53, s	CF_2 55.7, dd, ^4J 15Hz CF 59.9, dt, ^4J 15Hz
 $(CH^a_3)_2Si(CH^f_2CH^g{=}CH^h_2)-CH^b{=}CH^cCH^d_2C(CFCl_2)(CF_2Cl)OH^e$	(a) 9.82, s; (b, c, g) 3.66, m, (d) 7.09, d, J 7Hz; (e) 6.70, s; (f) 8.40, d, J 8Hz; (h) 5.16, m	CF_2 55.9, d, ^4J 15Hz CF 59.9, t, ^4J 15Hz
 $Si(CH^a{=}CH^bCH^c_2C(CF_3)_2OH^d)_4$	(a,b) 3.63, m; (c) 7.20, d, J 5Hz; (d) 6.73, s	CF_3 76.1, s
 $CH^a_2{=}CH^bCH^c_2Si(CH^d{=}CH^eCH^f_2C(CF_3)_2OH^g)_3$	(a) 5.13, m; (b, d, e) 3.81, m; (c) 8.18, d, J 7Hz, (f) 7.12, d, J 6Hz, (g) 6.60, s	CF_3 76.3, s
 $(CH^a_2{=}CH^bCH^c_2)_2Si(CH^d{=}CH^eCH^f_2C(CF_3)_2OH^g)_2$	(a) 5.08, m; (b, d, e) 3.87, m; (c) 8.21, d, J 7Hz; (f) 7.19, d, J 6.5 Hz; (g) 6.61, s	CF_3 76.2, s
 $(CH^a_2{=}CH^bCH^c_2)_3SiCH^d{=}CH^eCH^f_2C(CF_3)_2OH^g$	(a) 5.17, m; (b, d, e) 3.94, m; (c) 8.29, d, J 7Hz; (f) 7.17, d, J 7Hz; (g) 6.74, s	CF_3 76.6, s
 $Si(CH^a{=}CH^bCH^c_2C(CF_3)(CF_2Cl)OH^d)_4$	(a,b) 3.66, m; (c) 7.10, d, J 6Hz; (d) 6.98, s	CF_3 73.9, m CF_2 61.8, m
 $CH^a_2{=}CH^bCH^c_2Si(CH^d{=}CH^eCH^f_2C(CF_3)(CF_2Cl)OH^g)_3$	(a) 5.12, m; (b, d, e) 3.79, m; (c) 8.18, d, J 7Hz; (f) 7.10, d, J 6Hz; (g) 6.62, s	CF_3 74.0, tt, ^4J 12Hz CF_2 61.9, tq, ^4J 12Hz
 $(CH^a_2{=}CH^bCH^c_2)_2Si(CH^d{=}CH^eCH^f_2C(CF_3)(CF_2Cl)OH^g)_2$	(a) 5.17, m; (b, d, e) 3.83, m; (c) 8.21, d, J 7Hz; (f) 7.15, d, J 6Hz; (g) 6.71, s	CF_3 74.0, dt, ^4J 12Hz CF_2 61.5, dq, ^4J 12Hz

	(a) 5.15, m; (b, d, e) 3.94, m; (c) 8.28, d, J 7Hz; (f) 7.17, d, J 6.5 Hz; (g) 6.74, s	CF$_3$ 74.0, t, ^4J 12Hz CF$_2$ 61.7, q, ^4J 12Hz
	(a) 9.84, s; (b) 8.25, s; (c) 8.00, s; (d) 4.30, s; (e) 6.66, s;	CF$_3$ 76.2, s
	(a) 9.90, s; (b) 7.33, s; (c) 7.16, s; (d) 5.07, s; (e) 6.46, s	CF$_3$ 76.6, s
	(a) 9.90, s; (b) 8.26, s; (c) 8.00, s; (d) 4.41, s (e) 6.61, s	CF$_3$ 73.3, t, ^4J 12Hz CF$_2$ 62.6, q, ^4J 12Hz
	(a) 9.96, s; (b) 5.10, 5.20, s; (c) 7.13, s; (d) 7.30, s (e) 6.41, s	CF$_3$ 74.3, t, ^4J 12Hz CF$_2$ 63.1, q, ^4J 12Hz
	(a) 9.76, s; (b, c) 3.90, m (d) 8.66, d, J 7Hz; (e) 6.97, m; (f) 6.98, s	CF$_3$ 74.0, m 72.1, m
	(a) 9.80, s; (b, c) 4.00, m; (d) 8.72, d, J 7Hz; (e) 6.96, m; (f) 7.00, s	CF$_3$ 70.3, m CF$_2$ 57.2, m
	(a) 9.76, s; (b) 7.38, d, J 6Hz; (c) 4.07, m; (d) 4.77, m	CF$_3$ 75.4, s

(continued)

TABLE 3 (continued)

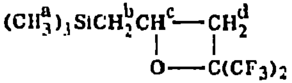
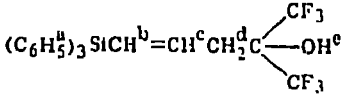
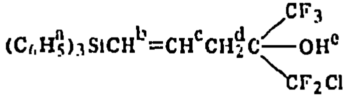
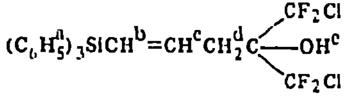
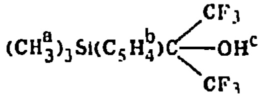
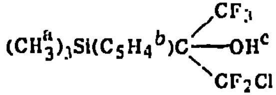
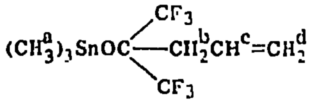
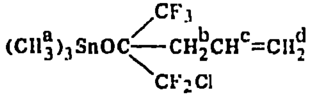
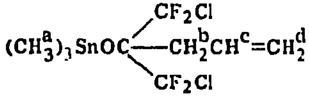
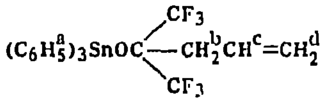
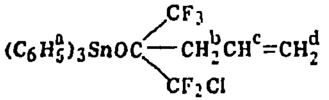
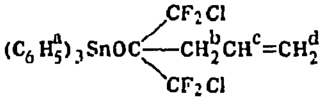
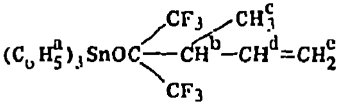
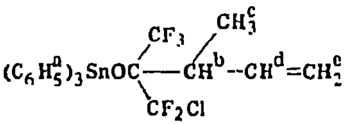
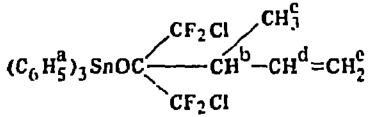
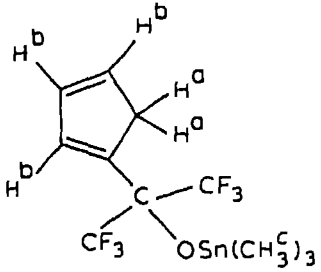
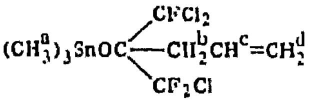
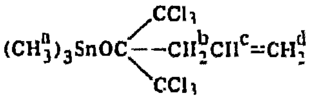
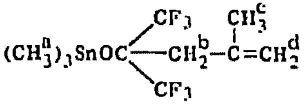
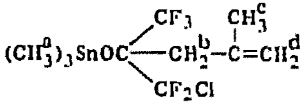
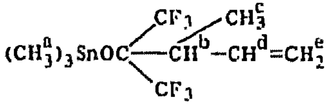
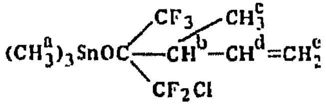
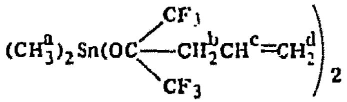
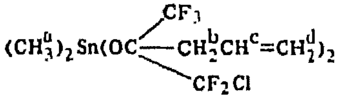
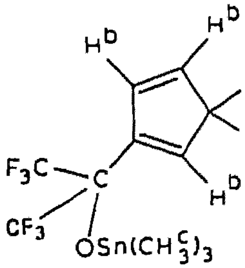
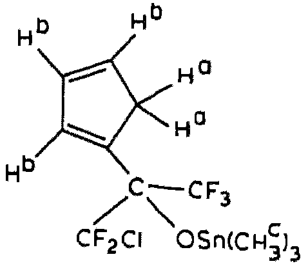
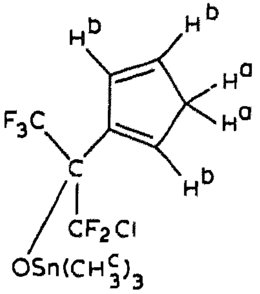
Compound	^{1}H Resonances (τ values)^{a}	^{19}F Resonances (ppm upfield from CFCl$_3$)
	(a) 9.96, s; (b) 8.81, m; (c) 5.01, m; (d) 7.25, m	CF$_3$ 79.5, m
	(a) 2.60, m; (b, c) 3.50, m; (d) 7.44, d, J 6Hz; (e) 7.73, s	CF$_3$ 75.9, s
	(a) 2.65, m, (b, c) 3.53, m; (d) 7.39, d, J 6Hz; (e) 7.63, s	CF$_3$ 73.2, t, ^{4}J 12Hz CF$_2$ 61.7, q, ^{4}J 12Hz
	(a) 2.54, m; (b, c) 3.55, m; (d) 7.41 d, J 7Hz; (e) 7.35, s	CF$_2$ 58.8, s
	(a) 9.97, s; 9.79, s; (b) 3.30, m; 6.55, m; (c) 6.66, s	CF$_3$ 76.0, s
	(a) 9.98, s; 9.81, s; (b) 3.34, m; 6.63, m; (c) 6.71, s	CF$_3$ 74.0, t, $J_{AB-X(av)}$13Hz CF$_2$ 61.9, m
	(a) 9.54, s, ^{a}J 56Hz; (b) 7.44, d, J 7Hz; (c) 4.11, m, (d) 4.91, m	CF$_3$ 76.3, s
	(a) 9.51, s, ^{a}J 56Hz; (b) 7.37, d, J 7Hz; (c) 4.11, m; (d) 4.90, m	CF$_3$ 72.4, t, ^{4}J 12Hz CF$_2$ 60.0, q, ^{4}J 12Hz
	(a) 9.50, s, ^{a}J 55Hz; (b) 7.33, d, J 7Hz; (c) 4.18, m; (d) 4.96, m	CF$_2$ 57.9, s

TABLE 3 (continued)

Compound	^1H Resonances (τ values)[a]	^{19}F Resonances (ppm upfield from $CFCl_3$)
 $(C_6H_5^a)_3SnOC(CF_3)_2CH_2^bCH^c{=}CH_2^d$	(a) 2.56, m; (b) 7.42, d, J 7Hz; (c) 4.05, m; (d) 5.04, m	CF_3 75.0, s
 $(C_6H_5^a)_3SnOC(CF_3)(CF_2Cl)CH_2^bCH^c{=}CH_2^d$	(a) 2.61, m; (b) 7.36, d, J 7Hz; (c) 4.15, m; (d) 5.12, m	CF_3 72.2, t, ^4J 12Hz CF_2 59.6, q, ^4J 12Hz
 $(C_6H_5^a)_3SnOC(CF_2Cl)_2CH_2^bCH^c{=}CH_2^d$	(a) 2.53, m; (b) 7.27, d, J 7Hz (c) 4.12, m; (d) 5.04, m	CF_2 56.8, s
 $(C_6H_5^a)_3SnOC(CF_3)_2CH^b(CH_3^c)CH^d{=}CH_2^e$	(a) 2.67, m; (b) 7.26, m; (c) 8.81, d, J 7Hz; (d) 4.18, m, (e) 5.16, m	CF_3 71.5, q, ^4J 8Hz 71.3, q, ^4J 8Hz
 $(C_6H_5^a)_3SnOC(CF_3)(CF_2Cl)CH^b(CH_3^c)CH^d{=}CH_2^e$	(a) 2.67, m; (b) 7.12, m; (c) 8.78, d, J 7Hz; (d) 4.08, m; (e) 5.16, m	CF_3 68.9, m CF_2 56.0, m
 $(C_6H_5^a)_3SnOC(CF_2Cl)_2CH^b(CH_3^c)CH^d{=}CH_2^e$	(a) 2.66, m; (b) 7.02, m; (c) 8.71, d, J 7Hz; (d) 4.16, m; (e) 5.13, m	
	(a) 6.88, s (br); (b) 3.41, m, (c) 9.59, s, ^2J 55Hz	CF_3 75.1, s

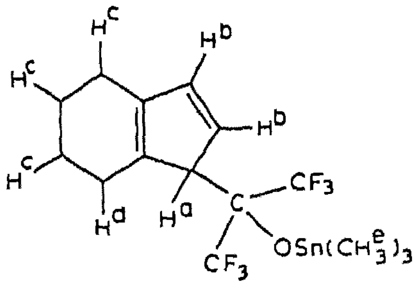
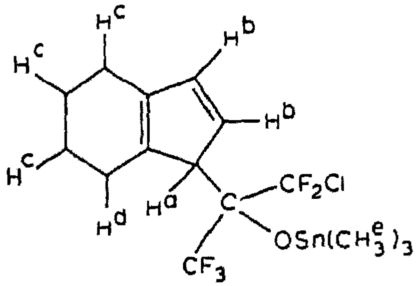
 $(CH^a_3)_3SnOC(CFCl_2)(CF_2Cl)CH^b_2CH^c{=}CH^d_2$	(a) 9.48, s, ^{a}J 56Hz; (b) 7.31, d, J 7Hz; (c) 4.10, m; (d) 4.93, m	
 $(CH^a_3)_3SnOC(CCl_3)(CCl_3)CH^b_2CH^c{=}CH^d_2$	(a) 9.39, s, ^{a}J 55Hz; (b) 6.85, d, J 7Hz; (c) 4.05, m; (d) 4.90, m	
 $(CH^a_3)_3SnOC(CF_3)(CF_3)CH^b_2{-}C(CH^c_3){=}CH^d_2$	(a) 9.54, s, ^{a}J 56Hz; (b) 7.54, s (br); (c) 8.18, s; (d) 5.21, s (br)	CF_3 75.3, s
 $(CH^a_3)_3SnOC(CF_3)(CF_2Cl)CH^b_2{-}C(CH^c_3){=}CH^d_2$	(a) 9.53, s, ^{a}J 56Hz; (b) 7.50, s (br); (c) 8.23, s; (d) 5.20, s (br)	CF_3 74.0, t, ^{4}J 12Hz CF_2 62.4, q, ^{4}J 12Hz
 $(CH^a_3)_3SnOC(CF_3)(CF_3)CH^b(CH^c_3){-}CH^d{=}CH^e_2$	(a) 9.52, s, ^{a}J 56Hz; (b) 7.31, m; (c) 8.80, d, J 7.5Hz; (d) 4.04, m; (e) 4.95, m	CF_3 72.2, m
 $(CH^a_3)_3SnOC(CF_3)(CF_2Cl)CH^b(CH^c_3){-}CH^d{=}CH^e_2$	(a) 9.52, s, ^{a}J 56Hz; (b) 7.22, m; (c) 8.82, d, J 7.5Hz; (d) 4.09, m; (e) 5.00, m	CF_3 69 3, m CF_2 56.6, m
 $(CH^a_3)_2Sn(OC(CF_3)(CF_3)CH^b_2CH^c{=}CH^d_2)_2$	(a) 9 14, s, ^{a}J 69Hz; (b) 7.31, d, J 6.5 Hz; (c) 4.10, m; (d) 4.91, m	CF_3 75 4, s
 $(CH^a_3)_2Sn(OC(CF_3)(CF_2Cl)CH^b_2CH^c{=}CH^d_2)_2$	(a) 9.10, s, ^{a}J 69Hz; (b) 7.25, d, J 7Hz; (c) 4.09, m; (d) 4.85, m	CF_3 73 3, t, ^{4}J 12Hz CF_2 60 8, q, ^{4}J 12Hz

(continued)

	(a) 7.03, s(br); (b) 3.41, m; (c) 0.59, s, ${}^{2}J$ 55Hz	CF_3 75.3, s
	(a) 6.87, s(br); (b) 3.41, m; (c) 9.57, s, ${}^{2}J$ 55Hz	CF_3 72.9, t, ${}^{4}J$ 12Hz CF_2 60.6, m
	(a) 7.03, s(br); (b) 3.41, m, (c) 9.57, s, ${}^{2}J$ 55Hz	CF_3 73.2, t, ${}^{4}J$ 12Hz CF_2 60.6, m

(continued)

TABLE 3 (continued)

Compound	^{1}H Resonance (τ values)^a	^{19}F Resonances (ppm upfield from $CFCl_3$)
	(a) 6.13, s(br); (b) 3.51, m; (c) 2.92, m; (d) 2.32, m; (e) 9.65, s, ^aJ 52Hz	CF_3 74.5, q, ^4J 9Hz 71.7, q, ^4J 9Hz
	(a) 6.04, s(br); (b) 3.45, m; (c) 2.87, m; (d) 2.17, m; (e) 9.56, s, ^aJ 52Hz	CF_3 72.8, t, ^4J 12Hz 70.2, t, ^4J 12Hz CF_2 59.0, m 55.8, m

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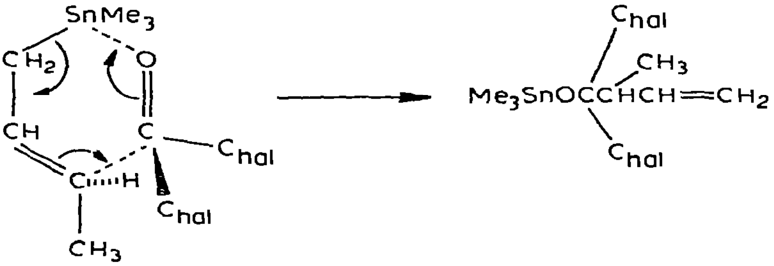
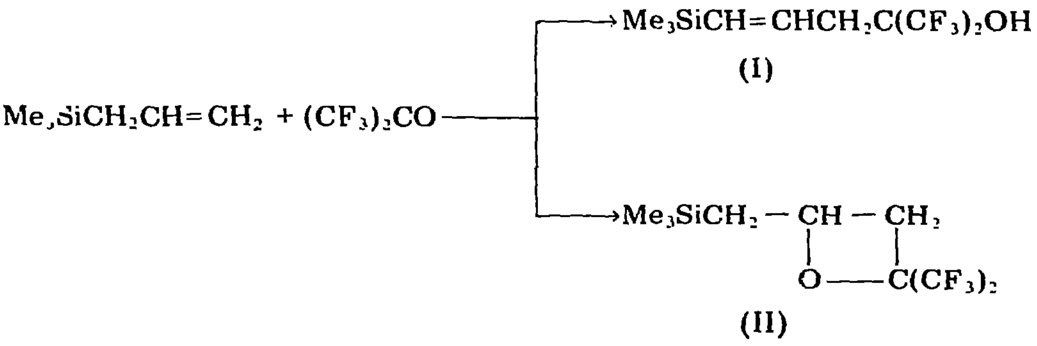
^{a} Protons are indicated by subscripts: ^aJ is the unresolved $^{119/117}Sn{-}CH_3$ coupling constant in the appropriate insertion product.

$$Me_3SnCH_2{-}CH{=}CHMe + (CF_3)_2CO \rightarrow Me_3SnO{-}C(CF_3)_2CH(Me)CH{=}CH_2$$

Similar reactions with 2-butenyltriphenyltin also result in complete skeletal rearrangement. Rearrangements of this type have been observed previously in the reaction of aldehydes [14, 31] and sulphur dioxide [32] with β-alkenyltins, and they have been rationalised in terms of a cyclic transition state. This mechanism would seem to be equally plausible for the perhalogenoketone insertions, where reaction would be promoted by the electron deficient and weakly polarised carbonyl group of the substrate. The observation that other labile groups attached to tin, such as benzyl, fail to react with HFA in this way is additional evidence favouring this mechanism, since these other substituents are unable to rearrange in an allylic fashion.



In complete contrast, when allyltrimethylsilane is allowed to react with HFA in the absence of catalyst three products may be isolated in varying yield dependent upon conditions. When the two reactants are heated at 140° for 48 h, the alcohol I is the exclusive volatile reaction product (85% yield). The heating of I with a three-fold excess of HFA at 120° for 40 days failed to induce any further reaction. Allyltrimethylsilane and allyltriphenylsilane react at 100° in a similar fashion with the perhalogenoketones HFA, MCPFA and DCTFA to give the analogous alcohols as products (Tables 2 and 3). Similarly diallyldimethylsilane, triallylmethylsilane and tetraallylsilane react with HFA and MCPFA with suitable variation of reagent ratios to produce good yields of analogous alcohols which result from partial and complete ketone insertion (Tables 2 and 3).

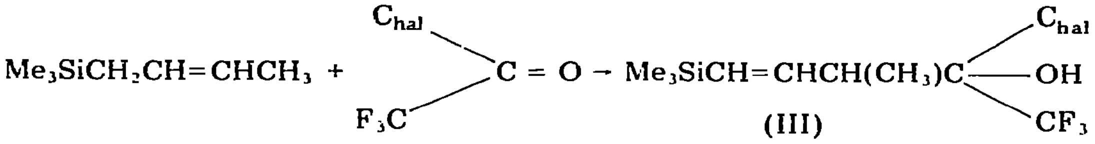


$$Me_3SiCH_2CH{=}CH_2 + (CF_3)_2CO \rightarrow Me_3SiCH{=}CHCH_2C(CF_3)_2OH \quad \text{(I)}$$

$$Me_3SiCH_2CH{=}CH_2 + (CF_3)_2CO \rightarrow Me_3SiCH_2{-}\underset{\displaystyle O\text{———}C(CF_3)_2}{CH{-}CH_2} \quad \text{(II)}$$

When the reaction between allyltrimethylsilane and HFA is allowed to proceed at 50°, a second product, the oxetane II is obtained (15% yield) in addition to I; and the yield of oxetane may be raised to 40% when the reaction is carried out at −20°.

The reaction of 2-butenyltrimethylsilane with HFA afforded the alcohol III in which no skeletal rearrangement had occurred. This observation is in sharp contrast to that with 2-butenyltrimethyltin:

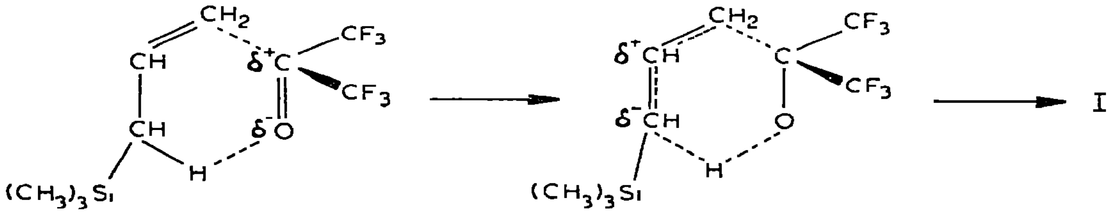


$$Me_3SiCH_2CH{=}CHCH_3 + (C_{hal})(F_3C)C{=}O \rightarrow Me_3SiCH{=}CHCH(CH_3)C(C_{hal})(OH)(CF_3) \quad \text{(III)}$$

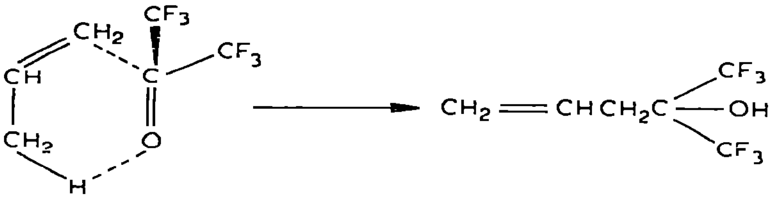
$C_{hal} = CF_3$ or CF_2Cl

The incursion of steric strain in the transition state is evidenced by the slower rate of reaction of 2-butenyltrimethylsilane relative to the unsubstituted precursor, and the fact that 2-butenyltriphenylsilane fails to react with HFA at 140°.

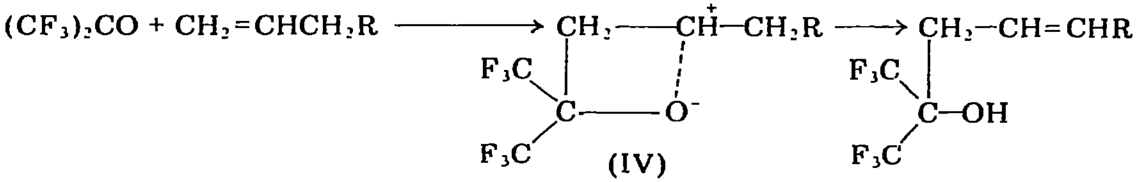
In our view, these observations are most reasonably accomodated within a mechanism involving a six-centre process in which there is a significant polar contribution to the transition state.



As an explanation for double bond migration in olefin/HFA reactions, a concerted mechanism has previously been proposed [33-36] involving a six-membered cyclic transition state and this is illustrated below for propylene.



Adelman [37] has criticised this mechanism and proposed instead a four-membered cyclic dipolar intermediate IV, on the basis of product studies with a sensitive difunctional trapping agent, allyl glycidyl ether.



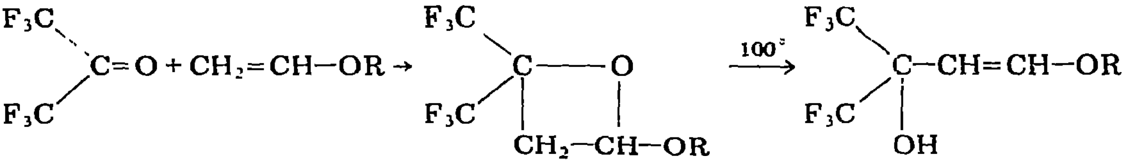
$$(CF_3)_2CO + CH_2{=}CHCH_2R \longrightarrow \underset{\text{(IV)}}{CH_2{-}\overset{+}{C}H{-}CH_2R \,/\, (F_3C)_2C{-}O^-} \longrightarrow CH_2{-}CH{=}CHR \,/\, (F_3C)_2C{-}OH$$

An appreciable solvent effect was observed in the reaction of DCTFA with 2,4,4-trimethyl-1-pentene, and large differences in rates of adduct formation were observed for olefins containing electron withdrawing and donating substituents.

It is also pointed out that the high rate of reaction of olefins with HFA has not been observed previously in non-catalysed 1,5-hydrogen shift reactions believed to proceed in a concerted fashion [38-40]. The observation that there was no rearrangement in the reaction of β-pinene with HFA (rearrangement in β-pinene reactions has previously been taken as good evidence for carbonium ion intermediates), was related to geometrical limitations to orbital interpenetration rather than the absence of carbonium ion intermediates. However, evidence [33, 36] that reactions of HFA with terminal olefins lead exclusively to 1,1-bis(trifluoromethyl)-3-alken-1-ols seems difficult to rationalise in terms of carbonium ion formation. Likewise, the formation of β-silyl carbonium ions in the reaction of allylic silanes with perhalogenoketones would seem unreasonable because of the known instability of these intermediates [22, 41].

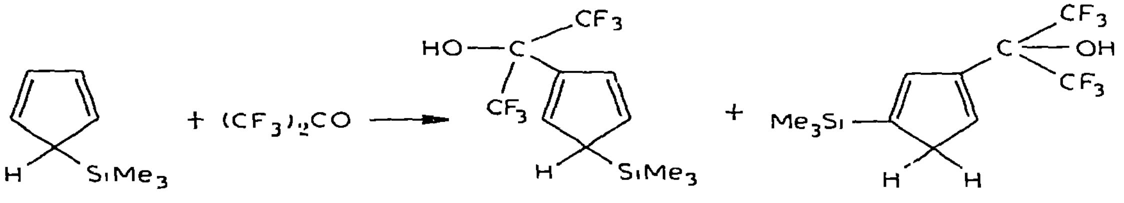
In the mechanism we propose, a significant increase in rate would be expected, relative to concerted 1,5-hydrogen shift reactions, but free carbonium ions need never be produced and rearrangement would not be expected.

Whilst oxetanes prepared previously [42] by photoinitiated addition of fluoroketones to fluoroolefins were suggested to arise via diradical species, the oxetane II more probably forms via a four-centre process which again has polar characteristics. Oxetanes derived from vinyl ethers have been shown to isomerise thermally to give substituted alkenes.



However, this is discounted as a significant route to the formation of I since the oxetane II fails to isomerise to I at measurable rates below 180°.

The product from reaction of cyclopentadienyltrimethylsilane and HFA shows a strong IR absorption at 3500 cm^{-1} again suggesting alcohol formation. The proton NMR spectrum is interpreted in terms of a mixture consisting predominantly of V and VI although other isomers may be present in smaller quantities.

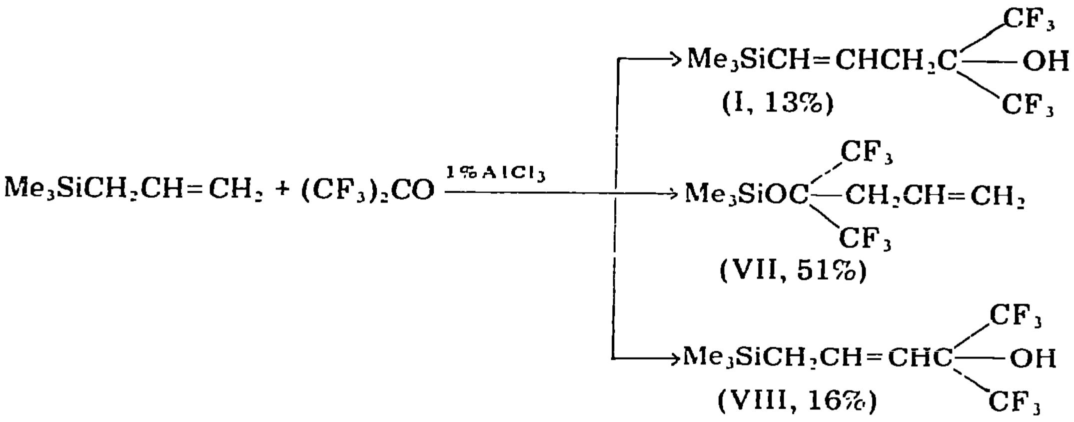


(V) (VI)

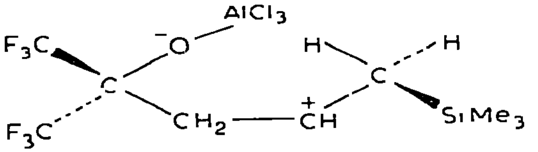
(V, VI produced in ratio 10/1)

Cyclopentadienyltrimethylsilane and MCPFA react in a similar manner to give the expected alcohol which again exists as a mixture of isomers.

When allyltrimethylsilane is allowed to react with HFA in the presence of 1% aluminium chloride, I (13%) is formed together with two other products VII (51%) and VIII (16%).



It has been suggested [40] that the aluminium chloride-catalysed reaction of olefins with HFA proceeds through a Friedel—Crafts type of reaction involvin a free carbonium ion (or equivalent associated species). Reaction then proceeds via an initial electrophilic attack of the HFA/AlCl$_3$ complex at the unsaturated centre. This intermediate can then rearrange by proton elimination or by tri-



methylsilyl migration to give the observed products. This product distribution is also consistent with the absence of carbonium ion intermediates in the non-catalysed reaction. The non-catalysed and aluminium chloride catalysed reaction of allyltrimethyltin and HFA afford 4,4-bis(trifluoromethyl)-4-trimethyl-stannoxy-1-butene in each case. However, in the latter reaction, considerable quantities of trimethyltin chloride (30%) are also formed, suggestive of polar transition state intermediates leading to trialkyltin fission.

Spectroscopy

The reactions of perhalogenoketones with β-alkenyl derivatives of tin lead in all cases to products resulting from an insertion reaction into the allyl—tin bond. The structures of the products are established unambiguously by means of their ^{1}H NMR and IR spectra. Typically, NMR spectra show terminal allylic patterns and methylene shifts consistent with direct attachment to $-C(C_{hal})_2-$ rather than to oxygen. The IR spectra show a strong C=C stretch in the 1639-1646 cm^{-1} region consistent with a terminal alkenyl-linkage well removed from the tin atom.

The product from reaction of crotyltrimethyltin and HFA has a ^{1}H NMR spectrum which shows a typical three proton, terminal allylic pattern, fully in accordance with a complete rearrangement of the allylic fragment. The downfield shift of the methine proton τ 7.31 also supports the proposed structure.

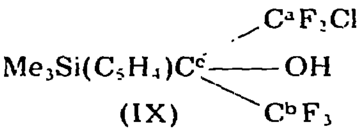
The non-catalysed reaction of allyltrimethylsilane with HFA affords the alcohol I as the major product. The proton NMR spectrum of I shows the pattern of an isopropenyl linkage centred at τ 3.80 and the large downfield methylene shift to τ 7.17 is consistent with the close proximity of the hydroxyl and trifluoromethyl substituents. The absorption at τ 6.92 disappears upon exchange with deuterium oxide and is assigned to the hydroxyl proton. The IR absorptions at 3595, 3515 (OH stretch) and 1602 cm^{-1} (vinylic C=C stretch) also support this structure.

The silyl ether VIII predominates in the reaction product mixture when the interaction of allyltrimethylsilane with HFA is catalysed by aluminium chloride. The ^{1}H NMR spectrum of VIII bears strong resemblances to the allyl—tin insertion product spectra and the absence of an IR OH absorption and the shift of the C=C stretching frequency to 1641 cm^{-1} are also in agreement with this structure.

By examining the ^{1}H NMR spectrum of the product from interaction of crotyltrimethylsilane and HFA it is immediately apparent that no rearrangement has taken place; of particular note in this spectrum, is the two-proton olefinic absorption centred at τ 4.00 and the large downfield shift of the methine proton to τ 6.96, indicating direct attachment to the —C(CF$_3$)$_2$OH substituent.

The product from reaction of cyclopentadienyltrimethylsilane and HFA shows a strong IR absorption at 3500 cm^{-1}, again suggesting alcohol formation. The proton NMR spectrum is interpreted in terms of a mixture consisting primarily of V and VI although other isomers may be present in smaller proportions. The isomer V shows a sharp singlet at τ 9.97, a singlet at τ 6.66 which exchanges with deuterium oxide, and broad absorptions at τ 6.50 and 3.15. Absorptions at τ 9.79, 6.66 and 3.40 are assigned to V. Previous studies on cyclopentadienyltrimethylsilane [44] have shown that at room temperature the 1 isomer predominates with small quantities of the 2 and 5 isomers interconverting by prototropic and metallotropic shifts. The downfield shift of the trimethylsilyl protons to τ 9.79 is characteristic of this group changing its point of attachment from an sp^3 to an sp^2 carbon atom [45].

The insertion products of MCPFA have previously shown [46, 47] interesting features in their ^{19}F NMR spectra due to the asymmetry developed in the adduct and they have been analysed in terms of ABX$_3$ systems. The ^{19}F NMR spectrum of IX shows this typical pattern; C^c is the centre of asymmetry in the molecule and this renders the two fluorine atoms on C^a non-equivalent. Coupling within the AB system (C^{a}F$_2$) gives two doublets which are further split into four interpenetrating quartets by coupling with X$_3$ (C^{b}F$_3$). The C^{b}F$_3$ signal itself appears as a triplet by virtual coupling with the C^{a}F$_2$ group. This feature is not generally observed in the other alkene insertion products with MCPFA and in these cases it is likely that AB is too small for splitting to be observed.



$$\mathrm{Me_3Si(C_5H_4)C^c(C^aF_2Cl)(OH)(C^bF_3)}$$

(IX)

Experimental

All melting points and boiling points are uncorrected. IR spectra were obtained with a Perkin—Elmer 257 grating spectrometer and NMR spectra were determined using a Perkin—Elmer R10 spectrometer operating at 60MHz for protons and 56.44 MHz for ^{19}F nuclei, and with a Jeol JNM-MH-100 100MHz spectrometer, either as neat liquids or solutions in carbon tetrachloride.

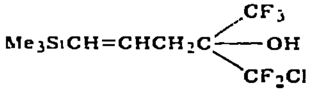
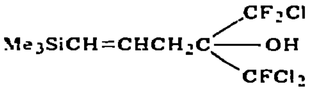
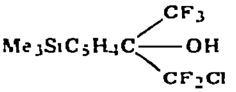
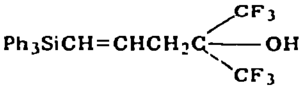
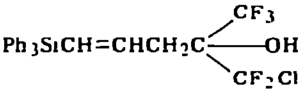
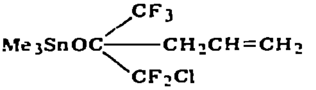
The analytical data for a representative cross-section of insertion products are given in Table 4.

All reactions and subsequent manipulations, as a matter of course, were conducted under an atmosphere of dry nitrogen and solvents were dried prior to use.

The following were prepared using previously reported methods; 2-butenyltrimethylsilane [48], cyclopentadienyltrimethylsilane [33], (trimethylstannyl)-cyclopentadiene [49] and benzyltriphenyltin [50].

TABLE 4

ELEMENTAL ANALYSES OF REPRESENTATIVE COMPOUNDS

Compound	Analysis found (calcd.) (%)	
	C	H
$\mathrm{Me_3SiCH{=}CHCH_2C(CF_3)_2OH}$	38.7 (38.6)	4.6 (5.0)
 $\mathrm{Me_3SiCH{=}CHCH_2C(CF_3)(OH)(CF_2Cl)}$	36.5 (36.4)	4.7 (4.7)
$\mathrm{Me_3SiCH{=}CHCH_2C(CF_2Cl)_2OH}$	34.4 (34.5)	4.3 (4.4)
 $\mathrm{Me_3SiCH{=}CHCH_2C(CF_2Cl)(OH)(CFCl_2)}$	32.4 (32.3)	4.1 (4.2)
$\mathrm{Me_3SiC_5H_4C(CF_3)_2OH}$	43.7 (43.4)	4.7 (4.6)
 $\mathrm{Me_3SiC_5H_4C(CF_3)(OH)(CF_2Cl)}$	41.2 (41.1)	4.6 (4.4)
 $\mathrm{Ph_3SiCH{=}CHCH_2C(CF_3)(OH)(CF_3)}$	61.4 (61.8)	4.4 (4.3)
 $\mathrm{Ph_3SiCH{=}CHCH_2C(CF_3)(OH)(CF_2Cl)}$	59.8 (59.7)	4.3 (4.2)
$\mathrm{Ph_3SiCH{=}CHCH_2C(CF_2Cl)_2OH}$	57.8 (57.7)	4.0 (4.0)
$\mathrm{Me_3SnOC(CF_3)_2CH_2CH{=}CH_2}$	29.4 (29.2)	3.7 (3.8)
 $\mathrm{Me_3SnOC(CF_3)(CH_2CH{=}CH_2)(CF_2Cl)}$	27.9 (27.9)	3.5 (3.6)

The synthesis of allylic precursors via the reaction of β-alkenyl Grignard reagents with the appropriate chlorosilane or chlorostannane is illustrated by the reaction of allylmagnesium bromide with silicon tetrachloride. The yields of other materials using this modification are shown in Table 1.

Silicon tetrachloride with allylmagnesium bromide

30 g (0.176 mol) of silicon tetrachloride was added to a solution of 0.9 mol of allylmagnesium bromide in 600 ml of diethyl ether at a rate sufficient to maintain gentle reflux. After addition the slurry was refluxed for 2 h. The mixture was then cooled to $-20°$ and a 10% solution of ammonium chloride ($\approx$ 200 ml) was slowly added dropwise with efficient stirring over a period of 2 h. After this time two clear layers had developed and the organic phase was separated. The aqueous phase was extracted with 3 × 100 ml of diethyl ether and the combined organic phases were dried ($MgSO_4$) and fractionated. The yield of tetraallylsilane was 70.8g (88%); b.p. 86.5°/10 mm [lit. [27] b.p. 87°/10 mm]. NMR: τ 4.26 (m, 4H, C=CHC), 5.13 (m, 8H, CH_2=C) and 8.42 (d, 8H, J 8Hz, CCH_2Si).

The above procedure was followed in the preparation of the following; allyltrimethylsilane, b.p. 84-85.5° [lit. [22] b.p. 84.9°]; (2-methylallyl)trimethylsilane, b.p. 109°/747 mm [lit. [25] b.p. 110.5-112°]; dimethyldiallylsilane, b.p. 134-136° [lit. [26] b.p. 136.8°/759 mm]; methyltriallylsilane, b.p. 67°/50 mm [lit. [26] b.p. 68°/50 mm]; allyltriphenylsilane, m.p. 88-89° [lit. [28] m.p. 88-89°]; allyltrimethyltin, b.p. 50°/35 mm [lit. [51] b.p. 128-129°/ 767 mm]; tetraallyltin, b.p. 52°/0.2 mm [lit. [27] b.p. 52°/0.2 mm]; allyltriphenyltin, m.p. 72-74° [lit. [29] m.p. 73.5-74.5°]; (2-methylallyl)trimethyltin, b.p. 46°/18 mm and dimethyldiallyltin, b.p. 67°/16 mm.

2-Butenyltriphenylsilane

A solution of 3.17 g (0.035 mol) of 1-chloro-2-butene in 10 ml of tetrahydrofuran was added dropwise to a solution of 0.032 mol of triphenylsilyllithium in 60 ml of tetrahydrofuran cooled in ice. After addition the mixture was hydrolysed with 30 ml of water and the organic phase was separated, dried ($MgSO_4$) and concentrated. Recrystallisation of the residue from light petroleum (b.p. 60-80°) gave 6.4 g (60%) of product m.p. 69-71° NMR: τ 2.67 (m, 15H, Ph_3Si), 4.65 (m, 2H, CH=CH), 7.78 (d, 2H, J 5 Hz, $SiCH_2C$) and 8.46 (d, 3H, J 4.5 Hz, CH_3C).

2-Butenyltriphenyltin

Using a similar procedure, 2-butenyltriphenyltin was prepared from 1-chloro-2-butene and triphenyltinlithium in 73% yield (as a mixture of *cis* and *trans* isomers); m.p. 56-58° [lit. [48] m.p. 57-59°] NMR: τ 2.74 (m, 15H, Ph_3Sn), 4.55 (m, 2H, CH=CH), 7.68 (d, 2H, J 6 Hz, J ($^{119/117}Sn-CH_2$) 66 Hz not resolved) and 8.44 (d, 3H, J 5 Hz, CH_3C).

2-Butenyltrimethyltin

A solution of 0.09 mol of trimethyltinlithium was prepared from 19.9 g (0.1 mol) of trimethyltin chloride and 1.74 g (0.25 mol) of lithium wire in 80 ml of 1,2-dimethoxyethane. The solution was filtered from excess lithium, cooled in ice and 9 g (0.1 mol) of 1-chloro-2-butene was added with stirring. Work up in the usual fashion afforded 14.2 g (65%) of product (as a mixture of cis and trans isomers), b.p. 53-55°/6 mm [lit. [48] b.p. 148-154°] NMR τ 4.72 (m, 2H, CH=CH), 8.44 (m, 5H, CH_3C, CH_2Sn) and 9.94 (s, 9H, $J(^{119}Sn—CH_3)$ 52.5 Hz, $J(^{117}Sn—CH_3)$ 49 Hz, Me_3Sn).

(Trimethylstannyl)indene

Dimethylaminotrimethyltin [49] 5.0 g (0.024 mol) was added dropwise to 11.6 g (0.1 mol) of redistilled indene. The mixture was then fractionated to give 5.25 g (82%) of product, b.p. 84°/0.07 mm [lit. [52] b.p. 64°/0.015 mm] NMR τ 2.74 (m, 4H, C_6H_4), 3.42 (m, 2H, CH=CH), 6.42 (m, 1H, CHSn) and 10.15 (s, 9H, $J(^{119}Sn—CH_3)$54 Hz, $J(^{117}Sn—CH_3)$ 50 Hz).

The reactions of perhalogenoketones with β-alkenylsilanes and stannanes were carried out using degassed mixtures of the appropriate reactants, sealed in Carius tubes and heated to the required temperature. Interactions with solid reactants were carried out in benzene as 20% solutions. 1,1,1,3,3,3-hexafluoro-2-propanone and 1-chloro-1,1,3,3,3-pentafluoro-2-propanone were handled using conventional vacuum transfer techniques. The physical and spectroscopic properties of the products are reported in Tables 2 and 3.

2,2-Bis(trifluoromethyl)-4-(trimethylsilylmethyl)oxetane(II)

A mixture of 0.01 mol of allyltrimethylsilane and 0.011 mol of 1,1,1,3,3,3-hexafluoro-2-propanone were allowed to react at −20° for 24 h. Distillation afforded a mixture of II and 1,1-bis(trifluoromethyl)-5-trimethylsilyl-4-pentene-1-ol (I). This mixture was chromatographed on alumina and elution with light petroleum/benzene (20/1) gave the product in 30% yield (a crude yield of 40% was estimated from NMR analysis of the initial distillate).

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