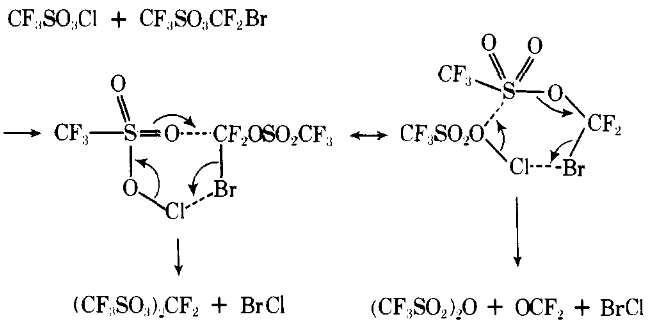
Scheme 1



lations in erythro and threo must be significantly different, as is apparently the case for $CF_3CO_2CFHCFHOSO_2CF_3$ and the related compounds of the type XCFHCFHY.

One additional point that can be made concerning the mechanism of these reactions relates to the low yields in the disubstitution reactions. The low yields of disubstituted products are not due to low thermal stability. $(CF_3SO_3)_2CF_2$ was recovered unchanged after heating at 150 °C in glass for 4 days. Therefore, the low yields and concurrent formation of trifluoromethanesulfonic acid anhydride and carbonyl compounds must be due to a side reaction during the displacement. Scheme I is proposed to explain this. This alternative transition state is very reasonable, and could account for the low percentage of disubstituted compounds. In addition, the failure to isolate tri- and tetrasubstituted esters can be explained in the same way; i.e., $C(OSO_2CF_3)_4$ is not necessarily kinetically unstable but is simply never formed.

In summary, the substitutive electrophilic dehalogenation reactions using CF_3SO_3Cl and CF_3SO_3Br offer considerable potential in synthesis. This work has greatly extended the number of perhalo esters of trifluoromethanesulfonic acid and extension to other organic and inorganic compounds should be possible. The apparent control of stereochemistry would appear to have some utility in synthesis, if wide extension of these reactions prove possible.

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Reaction of α-Arylvinyl Halides with Antimony Pentafluoride. A ^{1}H and ^{13}C NMR Spectroscopic Investigation

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Abstract: The α-arylvinyl halides **1–7** were reacted with SbF_5 in SO_2ClF and the solutions were investigated by ^{1}H and ^{13}C NMR spectroscopy. It is confirmed by the spectral data, especially by the observation of the J_{CF} and J_{CC} coupling constants, that vinyl cations were not generated under the described reaction conditions. SbF_5 reacts with the olefinic double bond of the α-arylvinyl halides **1–7** to form a σ complex to which we assign tentatively structure **11**.

Until 1969 vinyl cations in general were not considered to be very attractive intermediates, because they were thought to be highly unstable and therefore difficult to generate by bond heterolysis like a solvolysis reaction. From the extensive investigations carried out recently on the solvolysis of vinyl derivatives, especially of vinyl triflates and nonaflates,[1] it became clear that saturated and vinyl compounds show many qualitative similarities in their solvolytic reactivity. Now vinyl cations are generally accepted as reactive intermediates which are able to undergo, e.g., substitution, elimination, and rearrangement reactions.[1]

Recently we reported preliminary results on the attempts to generate vinyl cations in SO_2ClF by reaction of 1-*p*-anisyl-1-fluoro-2-methylpropene-1 (**1**) with SbF_5.[2] Though it has been published that, e.g., the phenylvinyl chloride (**7**) could be converted with SbF_5/SO_2ClF into the corresponding vinyl cation,[3] the present systematic investigation shows that arylvinyl cations are not formed under the conditions we have used.

Until now various spectroscopic investigations were carried out to demonstrate the existence of vinyl cations in solution.[1f,4] The first indication for the existence of vinyl cations was obtained using alkynyl cations, which may be regarded as vinyl cations in their mesomeric form.[4a-d,h] The alkynyl cations generated from the corresponding alkynyl alcohols by protonation under various conditions were investigated in detail

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Table I. ^{1}H NMR Parameters of **1**–**7** + SbF_5 in SO_2ClF and of **8a** and **8b**[a]

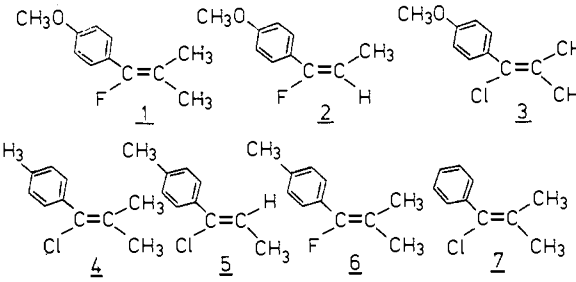
compd	*o*-H	*m*-H	*p*-R	β-CH_3	β-H	temp, °C
1	8.82	7.57				−70
	8.58	7.41	4.50	2.22		
	J_{om} = 9	$J_{o'm'}$ = 10				
2	8.4–8.8 br	7.53 br	4.63	2.18	5.5	−20
		J_{om} = 10		$^3J_{HH}$ = 7.0	$^3J_{HF}$ = 24.3	
3	8.65 br	7.47	4.56	2.22		−15
4	8.94	8.03				−30
	8.71	7.99	3.05	2.42		
	$J_{oo'}$ = 2.9;	$J_{mm'}$ = 1.1;				
	J_{om} = 9.0	$J_{om'}$ = 0.5				
5	8.93	8.01				−20
	8.50	7.98	3.05	2.32	6.02 br	
	$J_{oo'}$ = 2.3;			$^3J_{HH}$ = 6.7		
	J_{om} = 8.8					
6	8.82 br	8.03	3.07	2.36		−30
	J_{om} = 9.1		$^7J_{HF}$ = 2.6	$^4J_{HF}$ = 2.6		
7	9.26 br	8.03	8.76	2.42		−50
	J_{om} = 8.8	J_{mp} = 7.0	J_{op} = 1.2			
8a	8.7	7.6	4.43	1.59	4.4	−50
				$^3J_{HH}$ = 6.8		
8b	8.8	7.9	2.92	1.72	4.3	−50
			$^7J_{HF}$ = 2.0	$^3J_{HH}$ = 6.7	$^3J_{HF}$ = 32.9	

[a] Chemical shifts (ppm) relative to Me_4Si; coupling constants in hertz; br = broad; *o* = ortho, *m* = meta, *p* = para.

by ^{1}H and ^{13}C NMR spectroscopy. It was concluded that, depending upon the substitution pattern, the mesomeric vinyl cation structure is an important contributor to the structure of the alkynyl cations.[4a,d,h] Protonation of a series of alkynylferrocenes led to species which were assigned vinyl cation structures from their ^{1}H NMR spectra.[4f–h] An example for the generation of a species quite similar to the vinyl cation is that of the thiirenium ion, a long-lived bridged vinyl cation.[4j,k]

The chemistry of α-arylvinyl halides has been studied in solvolytic reactions[5] and the stabilizing effect of an α-aryl substituent with respect to a vinyl cation center is well documented. Therefore we have chosen this type of compound in our attempts to generate vinyl cations under stable ion conditions.

The α-arylvinyl halides **1**–**7** were reacted with SbF_5 in SO_2ClF and the solutions obtained were investigated systematically by ^{1}H and ^{13}C NMR spectroscopy. Compounds **1**–**7** are well suited for the NMR investigations for the following reasons. By comparison of the ^{1}H and ^{13}C NMR data with a number of known benzylic-type cations, it is possible to conclude whether cationic species are generated in the reaction of **1**–**7** with SbF_5. Variation of the para substituent in **3**, **4**, and **7** should show the mesomeric effect of the aryl ring. **2** and **5** have an olefinic proton serving as an NMR probe next to the positive center. **1**, **2**, and **6** containing F make it possible to use fluorine couplings as an additional sensitive probe. By comparison of **1** and **6** with **3** and **4** different reaction behavior of vinyl fluorides and vinyl chlorides should show up.



1 2 3

4 5 6 7

^{1}H NMR Spectroscopic Results

Table I summarizes the ^{1}H NMR spectroscopic results. A comparison with benzylic-type cations[6] shows remarkable similarities. The chemical shifts of the corresponding ortho, meta, and para protons are always in between those values of the secondary and tertiary benzyl cations. This can be regarded as a first indication of a benzylic-cation-type structure for the reaction products of **1**–**7** with SbF_5.

The resonance of the para substituent in phenylcarbenium ions is a reasonable measure of the extent of the positive charge on the aryl ring.[7] The value δ 8.76 ppm for the para proton of **7** + SbF_5 is in good agreement[8] with other phenylcarbenium ions.[6,7,9]

In addition to the considerable downfield shift of the aromatic protons compared to the precursors (Table III), the ortho protons and to a lesser extent the meta protons show interesting effects. Most of the *p*-CH_3 and *p*-OCH_3 substituted benzene derivatives show AA′BB′ spectra for reasons of symmetry. Arylcarbenium ions with different substituents at the C_α position show frequently nonequivalent ortho and less often also nonequivalent meta signals. This is due to the partial double bond character of the C_{aryl}–C^+ bond caused by delocalization of the positive charge into the aromatic ring. The extent of double-bond character depends on how much charge delocalization into the aryl ring is necessary to stabilize the cation. In some cases bond anisotropy and steric effects of the α substituents compensate each other as could be shown with α-halogen-styryl cations.[6c,9a,10]

1–**3** + SbF_5 show the deshielded aromatic pattern characteristic of benzylic cations and, in addition, the nonequivalence of the ortho (and to a lesser extent meta) protons characteristic for benzyl cations with two different α substituents. Below −25 °C the spectra show additional temperature-dependent broadening or splitting, respectively, due to the orientation of the O–CH_3 bond as the C_{aryl-O} bond rotation is "frozen out" (Figures 1 and 2). **4** and **5** + SbF_5 show also nonequivalence of the ortho protons and a small splitting of the meta protons (Figure 3). Upon warming the solutions from −100 to 0 °C these splittings do not become significantly smaller. This indicates a high barrier of rotation around the C_{aryl}–C_α bond which can be caused by high double-bond character or steric hindrance by bulky substituents at C_α. In contrast to **4** + SbF_5, **6** + SbF_5 shows only small line broadening of the ortho-proton signals (Figure 4). This might be due to accidental compen-

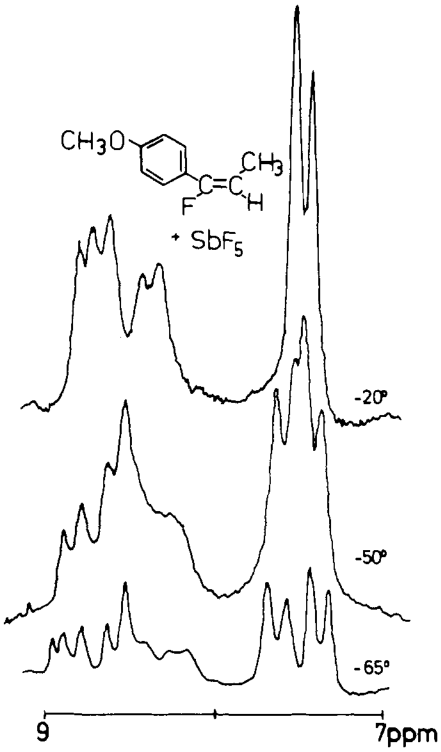


Figure 1. ^{1}H NMR of **2** + SbF_5 in SO_2ClF: temperature dependence of aromatic region.

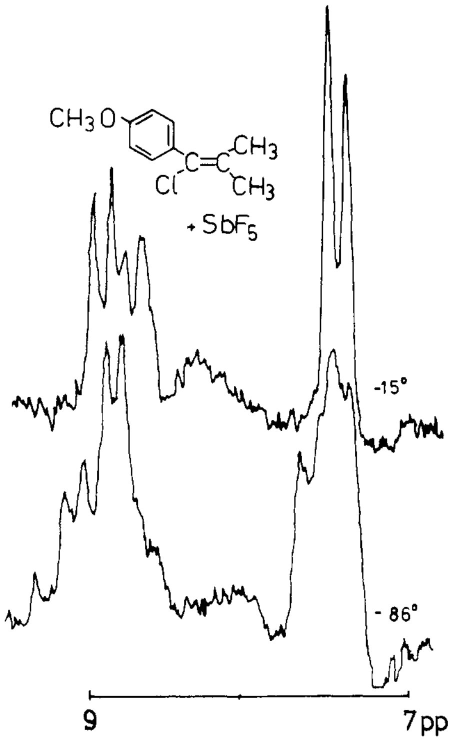


Figure 2. ^{1}H NMR of **3** + SbF_5 in SO_2ClF: temperature dependence of aromatic region.

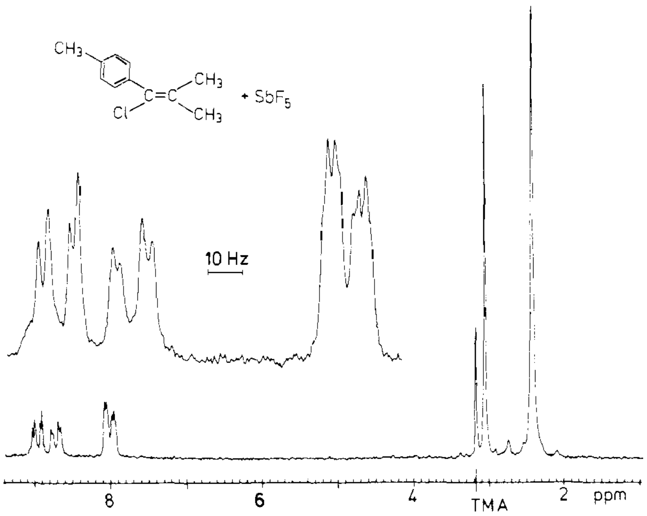
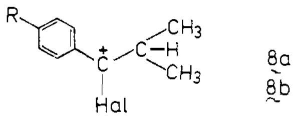


Figure 3. ^{1}H NMR of **4** + SbF_5 in SO_2ClF at -30 °C; TMA 3.17 ppm. Inset: aromatic region expanded.

sation of the different effects leading to nonequivalence of the chemical shift. The ortho protons of **7** + SbF_5 are broadened at low temperatures (Figure 5). A doublet results upon warming to -20 °C. The electron-donating capability of the phenyl ring in **7** + SbF_5 is smaller than in **1**–**6** + SbF_5, thus leading to less double-bond character of the C_{aryl}–C_α bond. In this case steric hindrance of rotation by bulky substituents at C_α is probably the main reason for broadening of the ortho-proton signals at low temperatures.

The solutions of the α-fluorostyrenes **1**, **2**, and **6** in SbF_5/SO_2ClF show fluorine couplings, thus indicating that the halogen stays in the molecule on reaction with the Lewis acid. In **2** + SbF_5 the fluorine coupling to the proton in the β position (5.5 ppm) is 24 Hz. This is a typical value for a $^3J_{HF}$ coupling in carbenium ions. The $^3J_{HF}$ coupling in the phenylmethylfluorocarbenium ion is 22.8 Hz.[9a] The increasing value of the coupling constant in going from the precursor **2** ($^3J_{HF} = 21.3$ Hz) to **2** + SbF_5 is typical for fluorocarbenium ions. **6** + SbF_5 shows a long-range coupling ($^7J_{HF} = 2.6$ Hz) to the p-methyl group. There is no such coupling observable in the precursor. Again this is typical for carbenium ions, where the coupling is transmitted through p–π interaction via the positive center. A comparable coupling ($^7J_{HF} = 2.7$ Hz) is found in the p-fluorostyryl cation.[9a]

The ^{1}H NMR data of the alkyl part of **1**–**7** + SbF_5 furnished the following results. The β-dimethyl substituted compounds **1**, **3**, **4**, **6**, and **7** show after reaction with SbF_5 equivalent β-methyl groups. Considering two different substituents at C_α, it follows that free rotation around the C_α–C_β bond is possible. At very low temperatures (<-100 °C) the β substituents give rise to distinctly broader lines than those observed for the p-CH_3 and p-OCH_3 signals. This indicates either slowing down of C_α–C_β bond rotation leading to nonequivalence or unresolved fluorine coupling to the β-SbF_4 substituent. Owing to the limited temperature range and additional broadening due to viscosity at lower temperatures this effect could not be studied in detail. The methyl protons, three bonds apart from the positive center, show a downfield shift of 0.4–0.6 ppm,[11] whereas the β protons in **2** and **5** + SbF_5, which are only separated by two bonds from the positive charge, show no significant downfield shift. The obvious explanation is that there are no longer olefinic protons or allylic methyl groups in the reaction species but strongly deshielded protons or methyl groups bound to an sp^3 carbon.



8a: R = OCH_3 ; Hal = F
8b: R = CH_3 ; Hal = Cl

A comparison of the spectral characteristics of **1**–**7** + SbF_5 with α-halogen-benzyl cations of structure **8** generated by protonation of the olefinic precursors with magic acid shows their different nature compared to the SbF_5 reaction products (Table I). **8a**, for example, shows a typical isopropyl coupling pattern ($^3J_{HH} = 6.7$ Hz), whereas **1**, **3**, **4**, **6**, and **7** + SbF_5 do not show such a splitting. This excludes protonation of **1**–**7** on

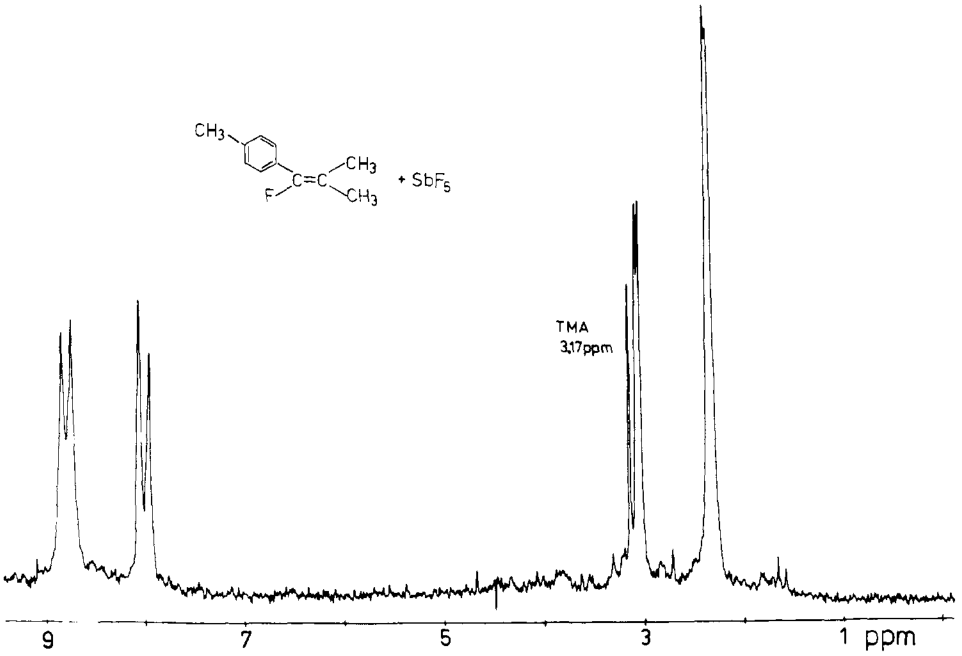


Figure 4. ^{1}H NMR of **6** + SbF_5 in SO_2ClF at −30 °C; TMA 3.17 ppm.

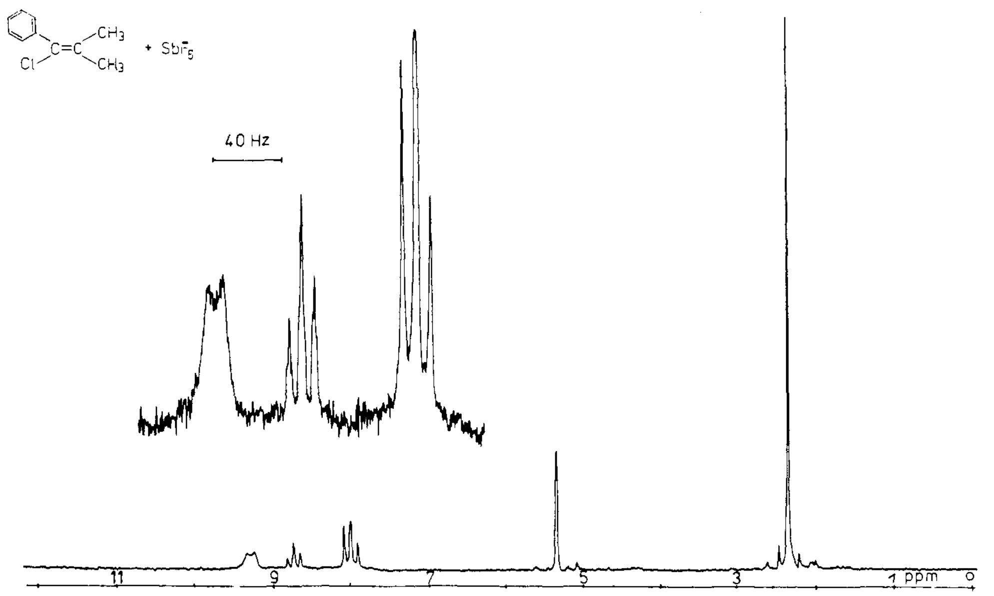


Figure 5. ^{1}H NMR of **7** + SbF_5 in SO_2ClF at −50 °C; $CHDCl_2$ 5.21 ppm. Inset: aromatic region expanded.

reaction with SbF_5, which might be possible due to protic impurities often present in SbF_5. The stronger downfield shift of the β protons (Δδ 1–1.6 ppm) and β-methyl groups (Δδ 0.5–0.6 ppm) in **1–7** + SbF_5 compared to **8**-type cations indicates either a strong electron-withdrawing substituent in the β position or participation of the alkyl part in delocalizing the positive charge in **1–7** + SbF_5. A comparison of **7** + SbF_5 with the phenylmethylchlorocarbenium ion[9a] shows stronger downfield shift of the aromatic protons for **7** + SbF_5 (Δδ ortho 0.36 ppm, Δδ meta 0.16 ppm, Δδ para 0.19 ppm). This can be explained by less stabilization of the positive charge in **7** + SbF_5 due to less effective back-donation of the halogen, leading to more delocalization of the positive charge into the aromatic π system.

The ^{1}H NMR data led to quite detailed information about the aryl part of the structure, whereas conclusions about the exact structure of the alkyl part require more data, especially concerning the nature of the C_α–C_β bond. Therefore the ^{13}C NMR spectra were investigated.

^{13}C NMR Spectroscopic Results

Owing to the highly nucleophilic character of styrenes, which cause easy polymerization,[12] it is difficult to generate sufficiently concentrated solutions for ^{13}C NMR. For example, the ^{13}C NMR spectra of a solution of **1** in SbF_5/SO_2ClF at 6 vol % showed complex product formation.[2] Thus interpretation and structure assignment were difficult. Additionally the ^{13}C spectra of *p*-methoxybenzyl-type cations become complex at low temperatures because of formation of rotational isomers caused by frozen rotation of the CH_3O group which shows up as separate signals or line broadening only.[12] ^{13}C spectra of **4** + SbF_5 also show byproduct formation at concentrations of 6 vol %.[14] To obtain ^{13}C spectra of less concentrated solutions within reasonable time ^{13}C-enriched compounds were used; **1** and **4** were prepared with 10 and 90% ^{13}C enrichment, respectively, at the α position and **4**, **6**, and **7** were prepared with 90% ^{13}C enrichment in the α and β positions.[15] The samples were reacted with SbF_5 in SO_2ClF at low concentrations (~1

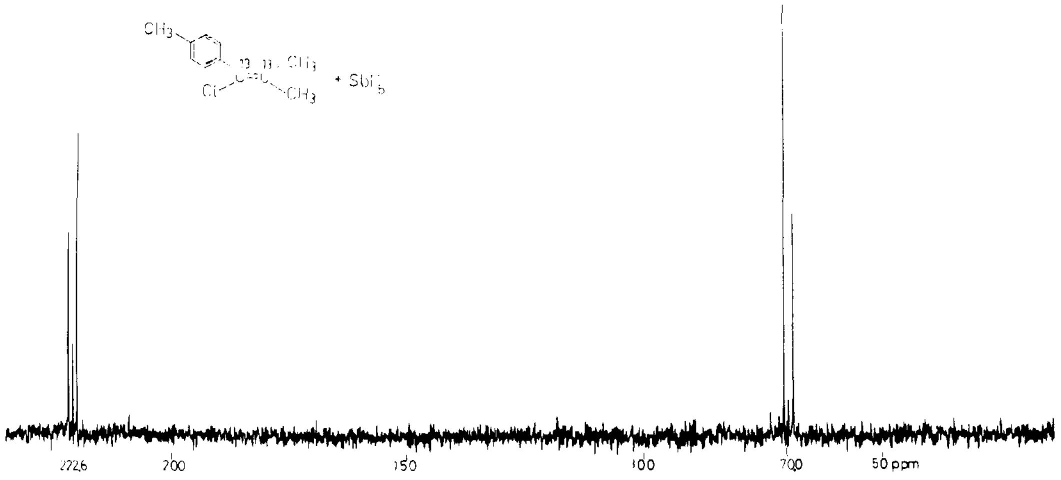


Figure 6. ^{13}C NMR of $^{13}C_\alpha$-$^{13}C_\beta$-**4** + SbF$_5$ in SO$_2$ClF at −90°C.

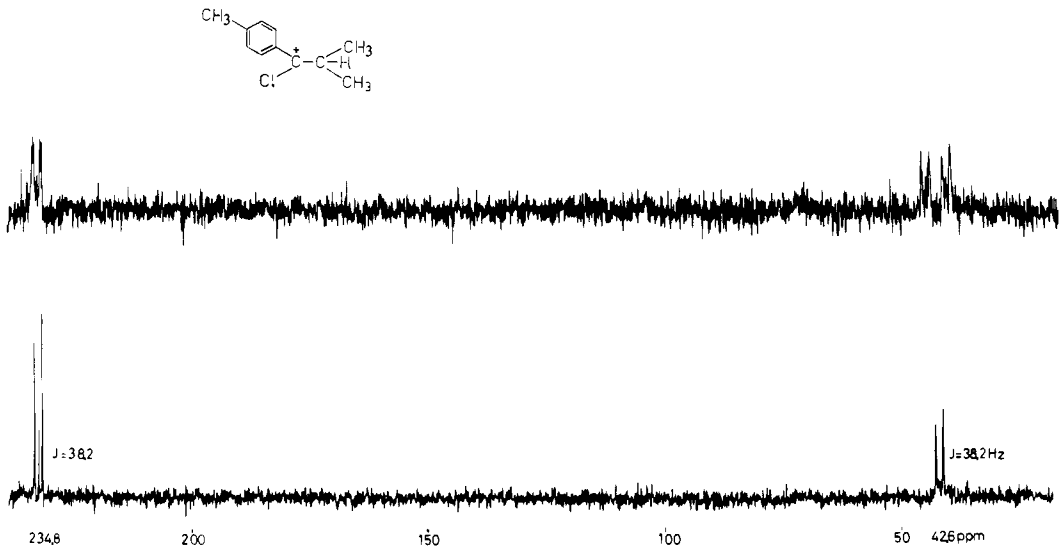


Figure 7. ^{13}C NMR of $^{13}C_\alpha$-$^{13}C_\beta$-**8b** in HSO$_3$F/SbF$_5$/SO$_2$ClF at −90°C. Upper trace: off-resonance spectra.

vol %) and investigated by ^{13}C NMR. A 1% solution of **4** labeled with 90% ^{13}C in the α position in SbF$_5$/SO$_2$ClF shows only one peak at 222 ppm which is typical for *p*-methylbenzyl cations.[10a,16] The α,β 90% double labeled **4** (J_{CC} = 85.3 Hz) was also reacted with SbF$_5$. The ^{13}C NMR spectrum shows two doublets both with a small middle peak due to monolabeled compound at 222.6 and 70.0 ppm (J_{CC} = 42.6 Hz) (Figure 6). Off-resonance decoupling confirms that both carbons bear no protons. Protonation of the double-labeled **4** yields the *p*-tolyl-α-chloroisopropylcarbenium ion (**8b** type) with C_α at 238.4 ppm and C_β at 42.6 ppm (J_{CC} = 8.2 Hz). Off-resonance decoupling leads to further doublet splitting of the doublet at 42.6 ppm, confirming a proton at C_β (Figure 7).

Measurements of CC coupling constants were performed with double-labeled samples and gave the following results. **4** shows a quite high value ($J_{C_\alpha C_\beta}$ = 85.3 Hz) for an sp^2-sp^2 coupling constant compared with unsubstituted styrene ($J_{C_\alpha C_\beta}$ = 70 Hz).[17] This can be explained by the effect of electronegative substituents and alkyl substitution in **4**.[18] The α-fluorostyrene **6** has an even higher magnitude of the CC coupling constant (91.6 Hz). A *p*-methyl substitution has no significant effect, which can be seen by comparing **4** with **7** ($J_{C_\alpha C_\beta}$ = 85.1 Hz). On reaction of **4** with magic acid to give **8b**, which is sp^2-sp^3 hybridized, the s character decreases and so does J_{CC} from 85.3 Hz in **4** to 38.7 Hz in **8b**. The value for **8b** is in reasonable agreement with similar sp^2-sp^3 hybridized compounds (e.g., acetophenone, $J_{C_\alpha C_\beta}$ = 43.3 Hz).[17] The species generated from the reaction of **4** with SbF$_5$ shows $J_{C_\alpha C_\beta}$ = 42.6 Hz. For a vinyl cation with sp-sp^2 hybridization[19] one would expect an increase of the coupling constant. Almost twice as large coupling constants are reported for other types of sp-sp^2 hybridized carbenium ions (e.g., benzoyl cation, $J_{C_{ipso}C_\alpha}$ = 81.2 Hz).[20] The similarity of the coupling constants of **8b** and **4** + SbF$_5$ led us to conclude that **4** + SbF$_5$ is sp^2-sp^3 hybridized. The same should be valid for **6** + SbF$_5$ ($J_{C_\alpha C_\beta}$ = 46.8 Hz) and **7** + SbF$_5$ ($J_{C_\alpha C_\beta}$ = 41.2 Hz) (Table II).

Table II. ^{13}C NMR Data of ^{13}C-Labeled **1**, **4**, **6**, and **7** in SbF$_5$/SO$_2$ClF and of **8a** and **8b**

precursor	C_α, ppm	C_β, ppm	$^1J_{CC}$, Hz	$^1J_{CF}$, Hz	$^2J_{CF}$, Hz
1	181[a]			329	
6	205	66.8	46.8	342	24.5
4	222	69.7	42.6		
7	236.5	72.6	41.1		
8a	208	33.0		344	16
8b	234	42.6	38.2		

[a] Reference 2.

Table II summarizes the ^{13}C NMR spectroscopic results. The shift of C_α of **1**, **4**, **6**, and **7** + SbF$_5$ is dependent on the electron-donating capability of the para substituent, decreasing from *p*-hydrogen to *p*-methyl to *p*-methoxy. The large stabilizing effect of the *p*-methoxy group is reflected in the upfield

Table III. ^{1}H NMR Parameters of **1–7**^{a}

compd	*o*	*m*	*p*-R	*E*-subst	*Z*-subst
1	7.24 J_{om} = 8.3	6.78	3.74	1.73 J_{HF} = 3.4	1.80 J_{HF} = 2.9
2	7.33 J_{om} = 8.9	6.82	3.77	1.74 J_{HF} = 2.3	5.27 J_{HF} = 21.3 J_{HH} = 7.4
3	7.15 J_{om} = 9.1	6.76	3.76	1.72 $J_{CH_3CH_3}$ = 0.3	1.96
4		7.13	2.35	1.74	1.99
5	7.34 J_{om} = 8.2	7.04	2.32	6.07	1.92 J_{HH} = 6.7
6	7.21 J_{om} = 8.3	7.09	2.34	1.81 J_{HF} = 3.5	1.75 J_{HF} = 2.8
7		7.24		1.73	1.99

^{a} Chemical shifts (ppm) in CCl_4/CCl_3F relative to Me_4Si; coupling constants in hertz.

Table IV. ^{13}C NMR Parameters of **1–7**^{a,b}

compd	C_1	$C_{2,6}$	$C_{3,5}$	C_4	*p*-R	C_α	C_β	*E*-CH$_3$	*Z*-CH$_3$
1	125.96 (30.9)	129.73 (4.4)	113.55	159.63 (1.5)	55.28	152.09 (236.8)	109.71 (20.6)	16.67 (9.6)	18.82 (4.4)
2	125.08 (30.9)	129.29 (5.1)	113.8	160.3	55.40	157.49 (237.5)	101.40 (28.7)	11.53 (8.8)	
3	126.03	130.44	113.29	159.24	54.72	132.01	129.15	21.90	22.03
4	125.86	128.82^c	129.24^c	137.46	21.12	136.65	129.89	21.86	22.03
5	124.92	126.22	128.76	137.53	20.99	134.0	120.63		14.88
6	130.51 (30.8)	128.23 (4.4)	128.82	138.09	21.22	152.32 (236.2)	110.26 (20.5)	16.70 (8.8)	18.78 (4.4)
7	130.40	129.56^c	128.39^c	128.06^c		139.63	126.12	22.19	21.45

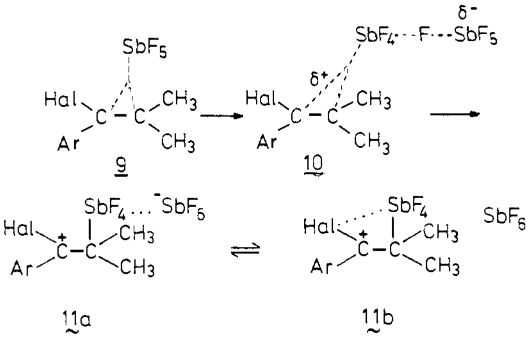
^{a} Chemical shifts (ppm) relative to Me_4Si. ^{b} J_{CF} (Hz) in parentheses. ^{c} Assignment not ascertained.

position for C_α in **1** + SbF_5 (181 ppm). The shift difference in **4** + SbF_5 (C_α 222 ppm) and **6** + SbF_5 (C_α 205 ppm) can be explained as a combination of a substituent effect and the different capability of the halogens to stabilize a positive charge by back-donation (F > Cl).[21] The C_β shift of **4**, **6**, and **7** + SbF_5 is in the region of strongly deshielded sp^3 carbons, being more deshielded than C_β in **8b**. The increase of $^1J_{CF}$ from **1** + SbF_5 (329 Hz) to **6** + SbF_5 (342 Hz) can be explained by the lesser stabilization of the positive charge by the aryl group and consequently increased interaction of the fluorine in **6** + SbF_5. The spectra did not change with increasing temperature until decomposition became rapid above −30 °C.

Discussion

The ^{1}H and ^{13}C NMR data (Tables I and II) show that the carbon-halogen bond is not cleaved on reaction of the α-arylvinyl halides **1–7** with SbF_5. This is evident from the fluorine couplings in the reaction products when starting from the fluorine-containing precursors **1**, **2**, and **6**. Thus no stable vinyl cations are generated under these conditions. The values of J_{CC} and the chemical shift of C_β show that the double bond is absent in the reaction products. The shift data and the magnitude of the fluorine coupling constants rule out a donor-acceptor complex with only limited charge separation.[22] Protonation of the double bond can be excluded by comparison with carbenium ions of type **8**.

The sp^2 hybridization of the vinyl carbon in **1–7** strengthens the bond to the halogen, thus leading to a lower inherent reactivity toward cleavage of the bond than in benzyl halides. Conjugation of the double bond with the α-aryl group reduces the ground-state energy in the substituted styrenes **1–7**. This also leads to a lower reactivity, whereas π ground state conjugation between the halogen and the double bond is not very important.[5] The double bond in vinyl halides is a potential reaction center by itself; thus it seems reasonable to consider a reaction of the Lewis acid with the double bond.[23] The first step could be an addition of SbF_5 to the double bond forming a π complex **9**. Cleavage can be accomplished by polarization through participation of excess SbF_5 as depicted in **10**. A carbenium ion center is developed in the benzylic position leading to **11**, which can be stabilized in the same way as an α-halogen benzyl cation. The negative charge need not necessarily be located at the antimony directly attached to the σ complex but anions of the Sb_xF_{5x+1} type may be present in solution.[24]



The lack of fluorine coupling of the SbF_4 substituent to C_β is most likely due to rapid exchange above −100 °C of these fluorines with those of the SbF_6^- gegenions. Coordination of the β-SbF_4 substituent with the α halogen as in **11b** is indicated by line broadening of the β-methyl protons below −100 °C. Additional unresolved fluorine coupling to the SbF_4 substituent may also contribute. The decreased α-carbon-fluorine coupling in the σ complexes **11** as compared to **8**-type cations also indicates complexation of α halogen. The equilibrium representation **11a** ⇆ **11b** is mechanistically plausible and in accord with the spectroscopic data. Quantitative data for the dynamic equilibrium **11a** ⇆ **11b** have not been obtained so far, mainly because of the limited stability of the solutions and the inherent complexity of these systems, which exhibit several internal restricted rotations and various modes of interaction with the gegenions or excess SbF_5.

Other σ complexes between substituted cyclobutadienes and $AlCl_3$ were recently investigated by Hogeveen.[25] Comparison of the C_β-^{13}C shift of **11** with the corresponding shift in these complexes would be quite informative. Unfortunately these signals were absent in the ^{13}C spectra of the $AlCl_3$ σ complexes of cyclobutadienes.

The results of quenching the solutions of **1–7** in SbF_5/SO_2ClF at −78 °C with K_2CO_3/CH_3OH or $NaOCH_3/CH_3OH$, respectively, are in agreement with the proposed structure **11**. The corresponding aryl isopropyl ketones and methyl vinyl ethers were found in moderate yields. A small amount of starting vinyl halides could be detected in some cases. The products arise from nucleophilic attack at the carbenium ion center and subsequent elimination of SbF_4X.

Conclusion

The reaction of SbF_5 with the α-halogen styrenes **1–7** in SO_2ClF takes place at the olefinic double bond and does not lead to a ionic cleavage of the carbon–halogen bond. This does not mean that stable vinyl cations cannot be generated due to any inherent instability, but other reactions, i.e., additions to the double bond, can compete with ionic cleavage, which might be slow. Thus using other concepts and precursors and different methods to generate vinyl cations will show whether an unequivocal spectroscopic proof of vinyl cations is possible.

Experimental Section

Compounds **3**, **4**, **5**, and **7** were prepared using slightly modified literature procedures.[26] The preparation of the vinyl fluorides **1**, **2**, and **6** has been described elsewhere.[27]

The ^{13}C-enriched compounds **1**, **4**, **6**, and **7** were prepared following known procedures[15,28] up to the substituted styrenes, which were converted into vinyl fluorides and vinyl chlorides as described in the literature.[29,30]

SbF_5 (Aldrich) was refluxed for several hours and distilled twice in an all-glass apparatus. SO_2ClF (Cationics) was distilled from SbF_5. Solutions of SbF_5 in SO_2ClF were prepared under dry nitrogen and sealed in ampules. A freshly opened ampule was used for each run.

Reactions of Vinyl Halides with Antimony Pentafluoride. Approximately 0.1 mmol of the vinyl halide in 2 mL of SO_2ClF was very slowly added from a cold dropping device to 2 mL of SbF_5/SO_2ClF (ca. 80 mg SbF_5/mL) at ca. −120 °C in a special apparatus[31] with vigorous mechanical stirring. The resulting slightly colored solutions were transferred immediately into precooled NMR tubes. The carbenium ions **8** were generated similarly using an excess of FSO_3H/SbF_5 (1:1).

NMR Spectroscopy. ^1H and ^{13}C NMR spectra were obtained using a Bruker HX 90 NMR spectrometer in the FT mode, equipped with a fluorine lock, a 16K data memory, and a temperature unit B-ST 100/700. External referencing (Me_4Si) was used in ^{13}C NMR. Tetramethylammonium bromide (TMA) (δ 3.17 ppm) was used as a reference in ^1H NMR.

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