36. Secondary 2-Norbornyl Cation Intermediates Substituted at C(5) and C(7) by Electron-withdrawing Groups. Addition of Fluorosulfuric Acid to Unsaturated Norbornane Derivatives

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Summary

Low temperature ($-130°$ to $-110°$) addition of *exo*-norborn-5-en-2-ol (**7**) to excess HSO_3F in SO_2ClF yielded a mixture of *exo*-5-(fluorosulfonyloxy)-*exo*-2- and *endo*-2-norbornylhydroxonium ions (**9**+**10**) under kinetic control that was different from the mixture of **9**+**10** obtained by addition of *endo*-norborn-5-en-2-ol (**8**) to HSO_3F under kinetic control. These mixtures differed from the mixture of **9**+**10** observed at higher temperature ($-80°$ to $-60°$) (thermodynamic control). Addition of 3-nortricyclanol (**23**) or *exo*-2,3-epoxynorbornane (**24**) to HSO_3F at $-120° \pm 10°$ yielded a mixture containing the *exo*-2-(fluorosulfonyloxy)-*anti*-7- and *syn*-7-norbornylhydroxonium ions (**26**+**27**) as major adducts. Qualitative rates of the isomerization of **26**+**27** to the more stable ions **9**+**10** and of the isomerization **9**$\leftrightarrows$**10** were evaluated. The solvolysis of **9**+**10** in HSO_3F yielded the *exo*-2,*exo*-5- and *exo*-2,*endo*-5-norbornanediyl bis(fluorosulfates) (**21**+**22**). Norbornadiene and quadricyclane added 2 equivalents of HSO_3F and furnished kinetically a mixture of *exo*-2,*anti*-7- and *exo*-2,*syn*-7-norbornanediyl bis(fluorosulfates) (**36**+**37**) as major adducts. The latter **36**+**37** were isomerized into a kinetic mixture of the more stable isomers **21**+**22**. The rates of these isomerizations were compared. The use of DSO_3F and (*exo*-2-D)-norborn-5-en-2-ol (**15**) confirmed that heterolyses of the fluorosulfates were responsible for the observed isomerization; elimination-addition processes occurred but much more slowly. The results are interpreted in terms of substituted classical and σ-bridged secondary 2-norbornyl cation intermediates. It appears that the electron withdrawing substituents FSO_3 and H_2O^+ (HO) destabilize the σ-bridged 2-norbornyl cation more at C(5) than C(7). If the σ-bridged ions **5-Z** substituted at C(5) by Z=FSO_3 or H_2O^+ (HO) are transition states in the isomerization of the corresponding classical ions **3-Z**,**4-Z**, the free enthalpy difference between the 'non-classical' σ-bridged ion and the classical ions is not higher than the energy barrier to the quenching of the latter intermediates by FSO_3^- in HSO_3F/SO_2ClF.

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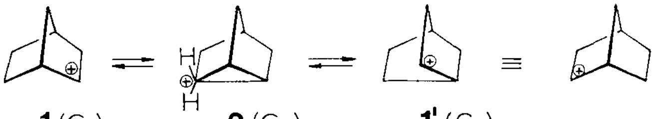
Introduction. - The nature of the secondary 2-norbornyl cation has stirred a controversy that is not yet settled [1]. A long-standing problem is whether this carbocation exists as a pair of 'rapidly equilibrating' enantiomorphic structures **1**⇄**1'** (double minimum energy hypersurface) or as a 'non-classical' σ-bridged carbonium ion **2** with C_s-symmetry in its ground state (single minimum energy hypersurface)[3]).

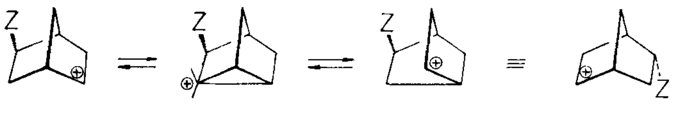


1 (C_1) **2** (C_s) **1'** (C_1)

In the gas phase, the 2-norbornyl cation is about 10 kcal/mol more stable than simpler acyclic or cyclic secondary carbenium ions [2]. Measurements related to the stability of the 2-norbornyl cation in solution have also shown this cation to be somewhat more stable than other simpler secondary alkyl cations in solution [1a, b, f] [3]. The ^{1}H- and ^{13}C-NMR. spectra of **1**⇄**2** in $SbF_5/SO_2ClF/SO_2F_2$ [1b] [4a-c] and its C(1s)-ESCA. spectrum [4a] did not allow its symmetry to be determined unequivocally [1d, e] [5]. These spectroscopic data [4] indicated, however, an important delocalization of the positive charge in the norbornane skeleton. The relatively high stability of the 2-norbornyl cation and its ability to delocalize the charge suggested the σ-bridged structure **2** for this ion in 'super-ionizing' media, **2** being one particular example of a substituted corner-protonated cyclopropane [6]. These carbonium ions are known to be transition states or intermediates in the rearrangements of most 'classical' carbenium ions [7]. *A priori* the C_s-symmetry is not necessary to explain the stability and charge delocalization in the secondary 2-norbornyl cation. An 'enhanced polarizability' (*i.e.* hyperconjugative interaction of the puckered cyclopentane ring C(1), C(7), C(4), C(5), C(6) with the empty *p* orbital at C(2) [8]) of the norbornane skeleton could also explain the 'special' thermodynamic and spectroscopic features of a pair of rapidly equilibrating classical ions **1**⇄**1'**.

The σ-bridged cation **2** is expected to delocalize the positive charge at the $H_2C(6)$ group more than the asymmetric ions **1**, **1'** because the C(6), C(2) distance must be shorter in **2** than in **1**, **1'** and because the overlap of the σ-C(6)-H(6*endo*) and σ-C(6), C(1) bonds with the empty *p* orbital at C(2) is better in **2** than in **1**, **1'**. These naïve considerations imply that an electron-withdrawing substituent Z at C(5) will destabilize the σ-bridged cation **2** more than the 'classical' ions **1**⇄**1'**. It is hoped that high level MO calculation will help to solve the problem of the nature of 2-norbornyl cation in the gas phase. For the moment, it is not unreasonable to say that recent calculations [5] suggest **1** and **2** to be of comparable stabilities. According to the above hypotheses, there should be a chance of detecting 2 equilibrating 'classical' 5-substituted secondary 2-norbornyl cations **3-Z** and **4-Z** and of estimating the energy barrier to their interconversion (expected to occur *via* the σ-bridged ion **5-Z** as transition state) for *strong* electron attracting groups Z. If the stability difference between **5-Z** and **3-Z** or **4-Z** were relatively small (*e.g.* smaller than the

3) We shall draw solid lines for bonds indicating apparently pentavalent carbocations even though, because of electron deficiency, some if not all the bonds must be partial [7a].

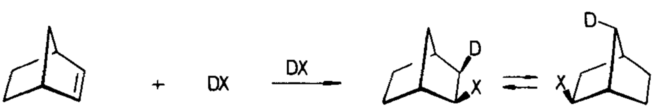


3-Z **5**-Z **4**-Z

energy barrier to the quenching of these ionic species by their counter-ions) with strongly destabilizing substituents Z, one would be tempted to conclude that the unsubstituted 2-norbornyl cation prefers the C_s-structure under the same conditions. These ideas have been the working hypotheses of the investigations we report here.

Stille [9] and *Brown* [1a,c] have attempted to prove the classical nature of the unsubstituted 2-norbornyl cation intermediate by trapping kinetic mixtures of adducts respectively of protic acids to 2,3-D_2-norbornene, and deuteriated acids to norbornene. It was assumed that all the products arose from quenching of cationic intermediates (ion-pairs, free ions, *etc.*) formed by base-acid exchange between the unsaturated hydrocarbon and the medium. Unless very strong acids are used, this assumption can be a fallacy [10]; acids as strong as HCl, HBr or CH_3SO_3H in acetic acid can add to (*E*)- and (*Z*)-2-butene *via* concerted Ad_E3-mechanisms [11], thus avoiding formation of cationic intermediates of the type generally involved in conditions of halide and ester heterolyses. Kinetic solvent isotope effects suggested, however, a rate-determining proton transfer in the addition of acetic acid to norbornene catalyzed by CF_3SO_3H [12]. A 'super-acid' such as HSO_3F [13] should be the best possible medium for generating carbocation intermediates in solution by proton transfer to unsaturated hydrocarbons. Under these conditions, the 2-norbornyl cations are highly stabilized by the strongly ionizing medium: the relative thermodynamic basicities of norbornenes or nortricyclanes being relatively high, their kinetic basicities are also expected to be relatively high, thus favouring proton transfers over processes that avoid generating cationic species on their pathway to the fluorosulfates.

Norbornene mixed with an excess (10–20×) of HSO_3F in SO_2ClF at $-130°$ yielded a solution of the *exo*-2-norbornyl fluorosulfate (**6**), the ^{1}H-NMR. and ^{13}C-NMR. spectra of which showed this ester to undergo a fast degenerate *Wagner-Meerwein* rearrangement at $-110°$ ($k \simeq 10\ s^{-1}$; $\Delta G^{\neq} \cong 8{,}6$ kcal/mol). This observation established that kinetic mixtures of the *exo*-3-D- and *syn*-7-D-2-norbornyl fluorosulfates (D-**6** and D-**6'**) in excess DSO_3F cannot be trapped and observed by the NMR. techniques available to us[4]). It is therefore necessary to destabilize the secondary 2-norbornyl cation intermediate in order to make possible the generation

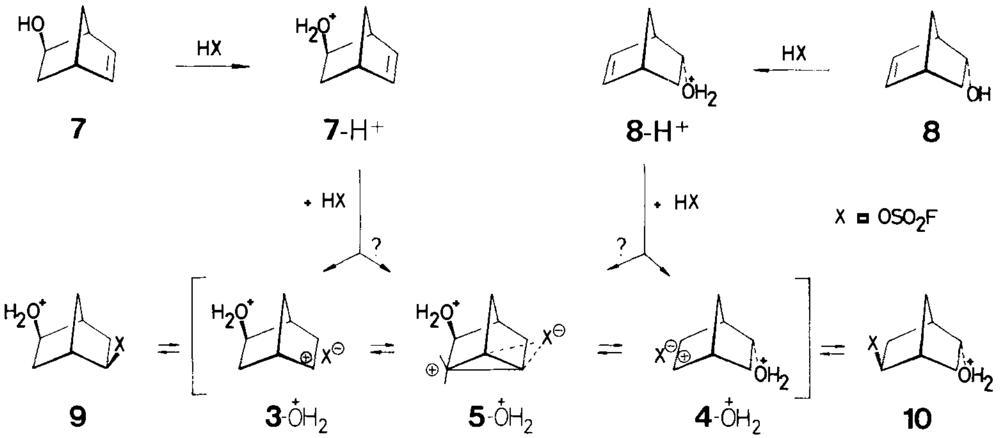


X = OSO_2F D-**6** D-**6'**

[4]) Polymerization of norbornene was observed at temperature above $-60°$ or when a small excess of HSO_3F was used.

and observation of kinetic mixtures of adducts arising from the HSO_3F (DSO_3F) additions to the corresponding norbornenes or nortricyclanes. This can be done by remote substitution at C(5) and C(7) with electron-withdrawing groups such as H_2O^+ (HO) and FSO_3. We now show that HSO_3F (DSO_3F) additions to *exo*- (**7**) and *endo*-norborn-5-en-2-ol (**8**) lead to kinetic mixtures of *exo*-5-(fluorosulfonyloxy)-*exo*-2 and *endo*-2-norbornylhydroxonium ions (**9**+**10**) at low temperature; these adducts could be equilibrated at higher temperature. Additions of HSO_3F to nortricyclan-3-ol (**23**) or *exo*-2,3-epoxynorbornane (**24**) furnished 2,7-disubstituted norbornanes (**26**+**27**) that could be isomerized into their more stable isomers **9**+**10**. The additions of HSO_3F to norbornadiene and to quadricyclane were also studied.

Scheme 1



Results and discussion. - *Addition of* HSO_3F *to* exo-*2- and* endo-*2-norborn-5-enols.* When *exo*-2 (**7**) or *endo*-2-norborn-5-enol (**8**) in CD_2Cl_2 or SO_2ClF were mixed at $-130°$ with a solution of HSO_3F in SO_2ClF in slight excess (2-3 equiv. of HSO_3F), the corresponding protonated alcohols **7**-H^+ and **8**-H^+ *(Scheme 1)* could be observed by ^1H- and ^{13}C-NMR. at $-110°$ (see *Table 4*). By increasing the excess of HSO_3F or by heating the mixture to *ca.* $-60°$, **7**-H^+ or **8**-H^+ added 1 mol of HSO_3F and gave different mixtures of *exo*-5-(fluorosulfonyloxy)-*exo*-2- and -*endo*-2-norbornylhydroxonium ions (**9**+**10**) (see *Fig. 1*) whose structures were deduced from their ^1H-, ^{13}C- and ^{19}F-NMR. characteristics (see *Tables 4, 5* and *7*) and by comparison with data obtained for other isomers to be discussed below. The ion **8**-H^+ reacted faster (3-4 times) than **7**-H^+. A similar reactivity difference has been noted with the acid-catalyzed hydration of **7** and **8** [14]. The difference is too small to justify assigning a specific role to the *endo*-OH group in **8** that would accelerate the proton transfer on the *endo* face of the *endo*-norborn-5-en-2-ol. It might be partly attributed to the stability difference between **7** and **8**, assuming **8** to be slightly less stable than its *exo*-isomer **7** [1a] [15] and assuming similar solvation for both protonated alcohols **7**-H^+ and **8**-H^+ [5]).

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[5]) *Cf.* protonated 2-dimethylaminonorbornanes and *N*-alkyl-2-azanorbornanes [16].

Careful addition of the alcohol **7** dissolved in SO_2ClF or dispersed in frozen CD_2Cl_2 to a large excess (10–20×) of HSO_3F in SO_2ClF at −130° to −110° afforded a kinetic mixture of the adducts **9**+**10** (see *Fig. 1A*). The kinetic product ratio **9/10** was practically insensitive (59/41–66/34) to the concentration of HSO_3F; it was measured by ^{13}C- and ^{19}F-NMR. between −100° and −85° (final concentration: **9**+**10**=0.2 to 0.7M; HSO_3F=2 to 4M). Under the same conditions, the *endo*-alcohol **8** yielded the same adducts but with a different kinetic product ratio **9/10** (43/57–45/55). When these mixtures were allowed to warm to −80° to −60°, equilibration of **9**⇄**10** was observed *(Scheme 1)*. The rates of the isomerization and the equilibrium constant K_e=[**9**]/[**10**] were dependent upon the concentration of HSO_3F (see *Table 1*): the larger the excess and concentration of HSO_3F, the faster was the isomerization **9**⇄**10**. The *exo*-5-(fluorosulfonyloxy)-*exo*-2-norbornylhydroxonium ion (**9**) was more stable than the *exo*-5-(fluorosulfonyloxy)-*endo*-2-norbornylhydroxonium ion (**10**) as expected by comparison with other 2-norbornyl derivatives [1a] [15] [16] thus reinforcing our hypotheses on the relative stabilities of **7**-H^+ and **8**-H^+ in HSO_3F/SO_2ClF.

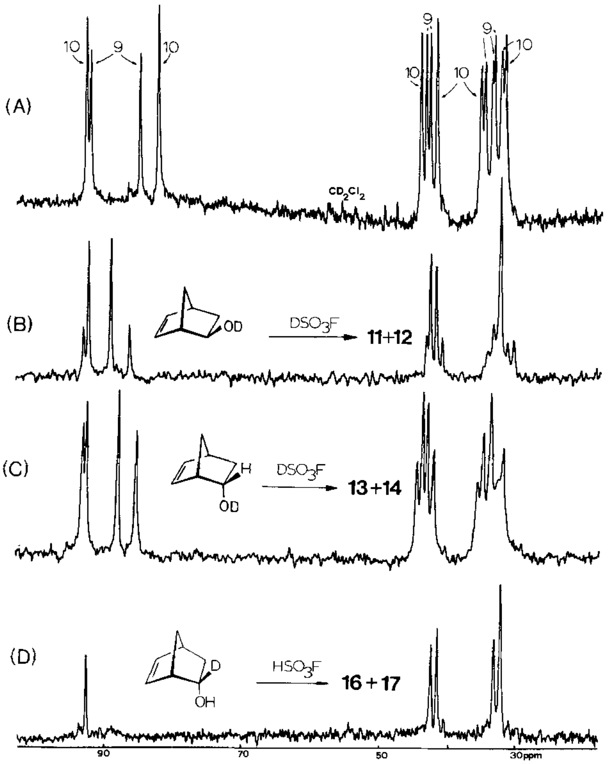


Fig. 1. ^{13}C-*NMR.* (15.08 MHz) *spectra in* $HSO_3F(DSO_3F)/SO_2ClF/CD_2Cl_2$ *of* (A): *a kinetic mixture of* **9**+**10** *obtained by addition of* HSO_3F (3-fold excess, −50°) *to* **8**; (B): *a kinetic mixture of* **11**+**12** *obtained by addition of* DSO_3F (10-fold excess, −75°) *to* **7**-*d*; (C): *a kinetic mixture of* **13**+**14** *obtained by addition of* DSO_3F (4-fold excess, −60°) *to* **8**-*d*; (D): *equilibrated mixture of* **16**+**17** *(1:11) obtained by addition of* HSO_3F (10-fold excess, −50°) *to* **15**.

Table 1. *Approximate first order rate constants of the isomerization* **10**→**9** (k_{10}) *as a function of the acid and substrate concentrations* (kinetic mixtures of **9**+**10** obtained by addition of HSO_3F/SO_2ClF to **7** or **8**

[HSO_3F][a])	[**9**+**10**][a])	T_m[°][b])	k_{10}[s^{-1}]	[**9**]/[**10**] at equilibrium at −50°
1.8	0.22	−60	$\sim 230 \cdot 10^{-5}$ [c])	7.3±0.5
2.3	0.2	−72	$\sim 87 \cdot 10^{-5}$ [c])	9.2±0.5
2.3	0.7	−70	$\sim 5.2 \cdot 10^{-5}$ [d])	12–15
4.0	0.2	−87	$\sim 8.5 \cdot 10^{-5}$ [d])	9.5±0.5
1.2	0.3	−52	$(55 \pm 6) \cdot 10^{-5}$ [e])	11.0±0.5

[a]) Approximate molar concentrations in SO_2ClF.
[b]) Temperature of the NMR. probe (±2°).
[c]) Kinetics measured by ^{19}F-NMR. (correlation coefficients: 0.99–0.994).
[d]) Kinetics measured by ^{13}C-NMR. (correlation coefficients: 0.986–0.98).
[e]) By measuring the kinetics of the isomerization of **26**+**27**→**9**⇄**10**, see text.

Addition of DSO_3F to exo-*2- and* endo-*2-norborn-5-enol.* When *O*(D)-*exo*-norborn-5-en-2-ol (**7**-d, previously equilibrated with an excess of D_2O) was reacted with an excess of DSO_3F in SO_2ClF at −120°, the deuteriated 2-norbornyl fluorosulfates **11**+**12** were obtained. Under the same conditions, *O*(D)-*endo*-norborn-5-en-2-ol (**8**-d) yielded the adducts **13**+**14** *(Scheme 2)*. The ^{1}H-NMR. of these solutions (−100° to −50°) compared with those of mixtures of **9**+**10** in HSO_3F/SO_2ClF showed a decreased intensity of the peaks attributed to the CH_2 hydrogen atoms corresponding to the substitution of one hydrogen atom by deuterium (see *Fig. 2*). The position of the deuterium in the adducts **11**, **12**, **13** and **14** was determined by FT{^{1}H}-^{13}C-NMR. The triplets expected for the carbon atoms bearing one D-atom were broadened (because of the quadrupolar relaxation of C–D and of the relatively high correlation time at < −50° and their intensity was decreased because of the smaller *Overhauser* effect (CDH *vs.* CH_2 [17]) (see *Fig. 1*). The ^{13}C-NMR. spectra of the solutions of **11**⇄**12** and **13**⇄**14** in DSO_3F/SO_2ClF remained unchanged below −50°; the ^{1}H-NMR. spectra did not show the formation of HSO_3F (no signal at

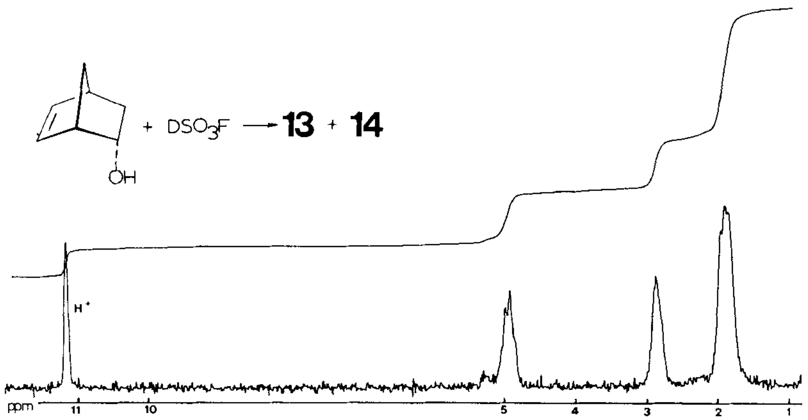
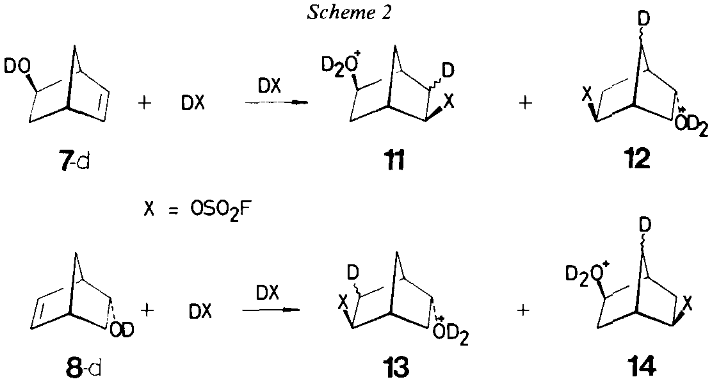
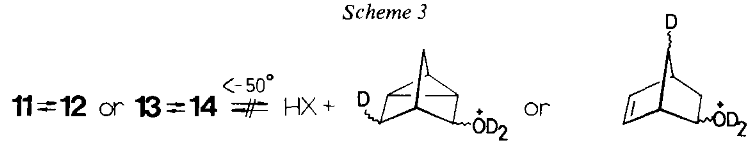


Fig. 2. *^{1}H-NMR.* (60 MHz) *of an equilibrated mixture of* **13**:**14** *(1:11) in DSO_3F(10 equiv.)+SO_2ClF + CD_2Cl_2* (−56°). The signal at 11.3 ppm is due to incomplete deuteriation of DSO_3F and **8**-d

Scheme 2



Scheme 3



$\delta_H = 11.3$ ppm for $HSO_3F + R\overset{+}{O}H_2 + R\overset{+}{O}DH$). The experiments established that elimination-addition processes of the type pictured in *Scheme 3* did not occur below $-50°$ after several hours.

Addition of HSO_3F to exo-*2*-D-endo-*norborn-5-en-2-ol* (**15**). When **15** in SO_2ClF was added slowly to an excess of HSO_3F in SO_2ClF at $-120°$ ($\pm 10°$), a mixture of the monodeuteriated adducts **16**+**17** was formed *(Scheme 4)*. ^{13}C-NMR. spectroscopy established that the deuterium substituted exclusively at C(2) (almost complete disappearance of the signal of the carbon atom bearing the H_2O^+ group was observed at $< -50°$; the C(2) was saturated by relatively fast proton noise decoupled pulses [18] (see *Fig. 1D*).The ^{1}H-NMR. spectrum confirmed the deuterium substitution at C(2). The ^{13}C-NMR. and the ^{1}H-NMR. spectra stayed unchanged below $-40°$, demonstrating that the OH-group migration *via* a protonated 7-oxatricyclo-[$2.2.1^{2,5}1$]octane intermediate **18** (yielding **19**⇌**20**) did not occur during the addition of **15** (and **8**) to HSO_3F nor during the isomerization **16**⇌**17** (and **9**⇌**10**). These results also confirmed the absence of elimination-addition processes *(Scheme 3)* below $-40°$.

If the adducts **9**+**10** can be considered to arise exclusively from proton transfer to the double bond of **7** and **8** (base-acid exchange reaction as a first step), the simplest way to rationalize our results is to assume the intermediacy of 2 equilibrating 'classical' 5-substituted 2-norbornyl cations (or ion-pairs) **3**-$\overset{+}{O}H_2$⇌**4**-$\overset{+}{O}H_2$ or **3**-OH⇌**4**-OH, **5**-$\overset{+}{O}H_2$ or **5**-OH being the transition state of their interconversion (hypothesis I). Equilibrating intermediate pairs **3**-$\overset{+}{O}H_2$⇌**5**-$\overset{+}{O}H_2$ (or **3**-OH⇌**5**-OH) or **5**-$\overset{+}{O}H_2$⇌**4**-$\overset{+}{O}H_2$ (or **5**-OH⇌**4**-OH) could also explain the facts (hypothesis II). Our results thus do not say whether the σ-bridged cation is a transition state or an intermediate which is more or less stable than one of the 'classical' ion **3**-Z or **4**-Z (Z = $\overset{+}{O}H_2$, OH). Because the kinetic product ratio [**9**]/[**10**] was close to 1 in the additions of HSO_3F to **7** and **8**, the free en-

Table 2. *Approximate first order rate constants of the isomerization of the* exo-*2-(fluorosulfonyloxy)-7-norbornyl-hydroxonium ions* **26**+**27** *to their 2,5-isomers* **9**+**10** ($k^I + k^{II}$, *see* Scheme 6) *and of the isomerization of the bisfluorosulfates* **36**+**37** *to their isomers* **21**+**22** ($k^{III} + k^{IV}$, *see* Scheme 7)

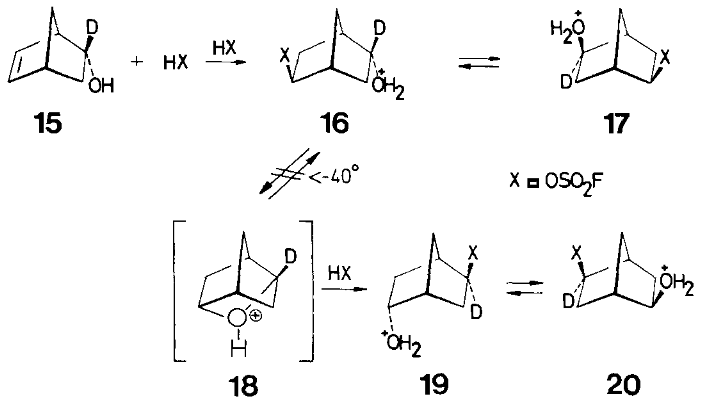
[HSO_3F] [a]	[**9**+**10**+**26**+**27**] [a]	T_m (°) [b]	$k^I + k^{II}$ [s^{-1}]	Variation of [**26**]/[**27**] at T_m [c]	Variation of [**9**]/[**10**] at T_m [c]
1.2	0.3	−52	$26 \cdot 10^{-5}$ [d]	1.1→1.2	1.8→11.0
4.0	0.4	−78	$23 \cdot 10^{-5}$ [d]	0.8→0.9	1.0→10.0
	[**21**+**22**+**36**+**37**]		$k^{III} + k^{IV}$ [s^{-1}]	Variation of [**36**]/[**37**] at T_m [c]	Variation of [**21**]/[**22**] at T_m [c]
3.0	0.3	−89	$10.5 \cdot 10^{-5}$ [e]	2.1→1.9	1.9→3.9
2.5	0.7	−89	$5.8 \cdot 10^{-5}$ [e]	2.1→2.0	1.8→2.8

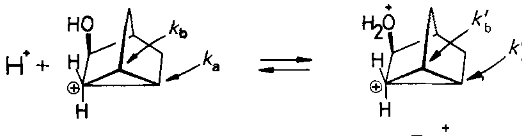
[a][b]) See *Table 1*.
[c]) During the kinetic run, until >4 half-lives.
[d]) By ^{19}F-NMR., by reporting ln[**26**+**27**]=f (time), correlation coefficient: 0.989-0.992.
[e]) By ^{13}C-NMR., by reporting ln[**36**+**37**]=f (time), correlation coefficient: 0.989-0.985.

thalpy barrier separating the intermediate pairs in hypotheses I or II must be about the same as the free enthalpy barrier of the quenching of this ionic species by FSO_3^- in HSO_3F/SO_2ClF. An other interpretation involves the equilibrating σ-bridged ions **5**-OH ⇄ **5**-$\overset{+}{O}H_2$ with the condition that they have different selectivities k_a/k_b and k'_a/k'_b toward FSO_3^- or HSO_3F to yield the adducts **9** and **10** (hypothesis III). Since the kinetic product ratio [**9**]/[**10**] was practically insensitive to the mode of addition of HSO_3F to **7** and **8** and to the excess and concentration of the acid, this hypothesis is not probable; furthermore, it is not clear why the ratio **5**-OH/**5**-$\overset{+}{O}H_2$ (or corresponding ion-pairs) should not be the same by protonation of **7** or **8** in HSO_3F.

Solvolysis of **9**+**10** in HSO_3F/SO_2ClF (approximate first order rate constant: ~5.6 10^{-5} s^{-1} at −21° and with [HSO_3F]≃2 M) afforded a ~3:1 mixture of the *exo*-2,*exo*-5 and *exo*-2,*endo*-5-norbornanediyl bisfluorosulfates **21**+**22** *(Scheme 5)*. This reaction was much slower than the isomerization **9** ⇄ **10** (see *Table 1*) under the same conditions. This is not surprising for heterolytic processes, since the FSO_3^- anion should be a much better leaving group than H_2O, H_2O being more basic than FSO_3^- [13].

Scheme 4



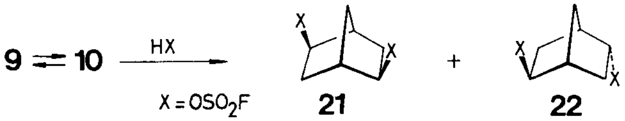


5-OH 5-$\overset{+}{O}H_2$

At RT., fast decomposition of **21** + **22** to intractable polymeric fluorosulfates and protonated norbornanone occurred, the latter being demonstrated by the ^{1}H-NMR. spectrum [19] and by quenching with water.

The mixtures of the deuteriated derivatives **11** + **12** and **13** + **14** also yielded mixtures of bisfluorosulfates **21** + **22** when allowed to warm up to $-20°$ (excess of HSO_3F). The ^{1}H-NMR. spectra of these solutions did not show any privileged position bearing a D-atom. Moreover, a signal at $\delta_H = 11.3$ ppm for $R\overset{+}{O}H_2 + HSO_3F$ appeared with a relative intensity of 2 H after 1 h at 0° (with $[HSO_3F] = 2$ to 3 M). Similarly, the mixture of **16** + **17** was solvolyzed to **21** + **22** whose ^{1}H-NMR. spectrum indicated scrambling of the D-atom in **21** + **22** and the medium. The same conclusion was reached by following the fluorosulfatolyses by ^{13}C-NMR. spectroscopy, indicating that elimination-addition processes *(e.g. Scheme 3)* did occur during the solvolyses **9** + **10** → **21** + **22** at $> -20°$. Analogous processes have been reported for the solvolyses of 3-nortricyclyl derivatives in $AcOD/D_2O$ at 25° which yielded norbornanone containing 30–50% D at all the positions [20][6]).

Scheme 5



Additions of HSO_3F to 3-nortricyclanol (**23**) *and* exo-*2,3-epoxynorbornane* (**24**). When **23** dissolved in SO_2ClF or dispersed in CD_2Cl_2 was mixed slowly with a solution of HSO_3F 2–3 equiv.) in SO_2ClF at $-130°$, the corresponding protonated alcohol **25** ($Z = H_2\overset{+}{O}$) was observed by ^{1}H- and ^{13}C-NMR. at $-110°$ (see *Table 4*). By increasing

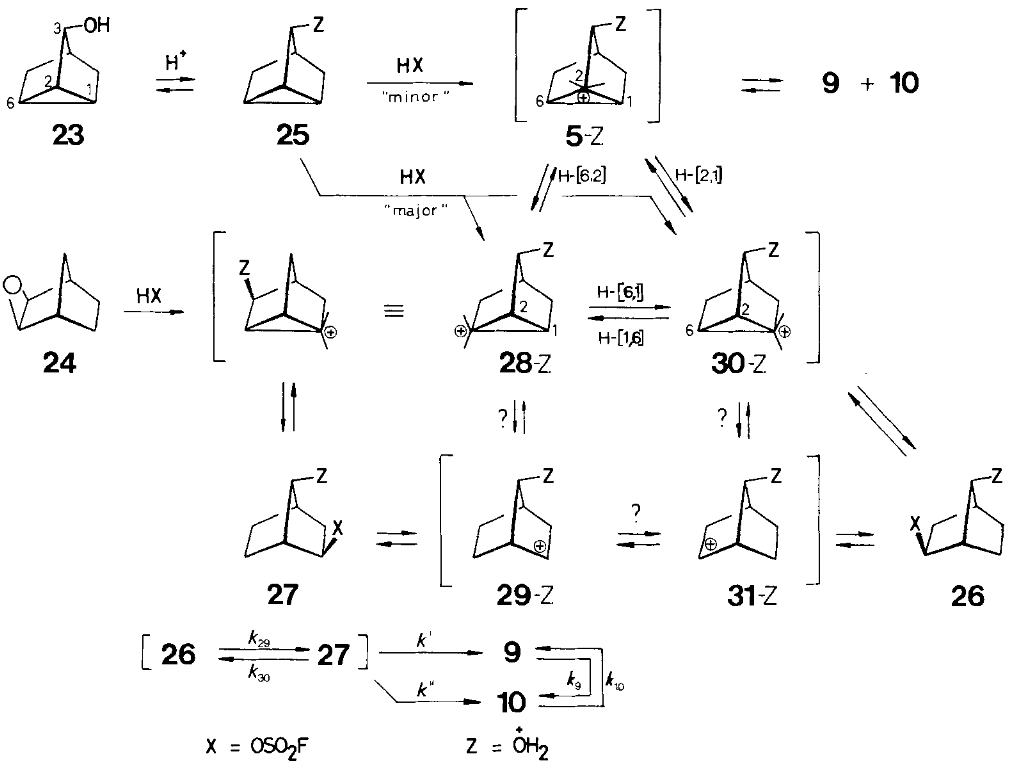
Table 3. *Kinetic mixtures* (%) *of 2,7- and 2,5-norbornanediyl bisfluorosulfates* **21**, **22**, **36**, **37** *formed by addition of $HSO_3F/SO_2ClF/CD_2Cl_2$ to norbornadiene* (**32**) *or quadricyclane* (**33**) *at $T < -110°$*

Precursor	$[HSO_3F]$ a)	[**21**+**22**+**36**+**37**] b)	T_m (°) c)	**36/37/21/22** d)
32	3.0	0.3	−100	46/18/17/18
32	1.4	0.75	−100	40/18/17/25
32	0.25	0.5	−100	74/15/4/7
33	3.5	0.7	−106	40/18/17/27
33	2.0	0.75	− 96	45/18/15/22
33	2.0	0.4	−100	36/12/30/21

a) Approximate molar conc. of the HSO_3F excess.
b) Approximate final conc. of the bis-adducts.
c) Temperature of the NMR. probe (±2°) of the first measurement.
d) ±5%, by integration of the ^{19}F- and ^{13}C-NMR. signals.

6) See also the perdeuteriation of norbornane derivatives [21].

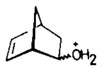
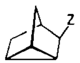
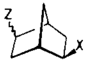
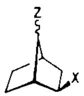
Scheme 6



the excess of HSO_3F or by allowing the mixture to warm to $-90°$, **25** added one equiv. of HSO_3F and yielded a clear solution containing traces of the ions **9** + **10** and the *exo*-2-(fluorosulfonyloxy)-*anti*-7- and -*syn*-7-norbornylhydroxonium ions (**26** + **27**) whose structures were established by ^{1}H-, ^{13}C- and ^{19}F-NMR. spectroscopy (see *Tables 4, 5* and *7*). The latter, **26** + **27** were isomerized into a *kinetic* mixture of **9** + **10** at higher temperature *(Scheme 6).*

The first order rate constants ($k' + k''$) of the isomerization of **26** + **27** → **9** + **10** depend on the concentration of HSO_3F *(cf. Table 2).* Less than 2% (^{19}F-NMR. detection limit) of **26** + **27** were present in the mixture at equilibrium ($-40°$). The kinetics of the rearrangements **26** + **27** → **9** ⇄ **10** *(Scheme 6)* were simulated by using a computer program employing the *Runge-Kutta* method for integrating the kinetic differential equations [22]. Several choices of rate constants were tried until a satisfactory fit with the experimental data was obtained. A serious simplification was possible because the concentration of **10** remained constant over about 3 half-lives after 1/3 of **26** + **27** had reacted, so evaluation of the first order rate constants $k' + k''$, k_9 and k_{10} was easy. With $[HSO_3F] = 1.2$ M and $[\mathbf{26}+\mathbf{27}+\mathbf{9}+\mathbf{10}] \cong 0.3$ M, we calculated $k_9 = (5 \pm 0.6) \cdot 10^{-5}\ s^{-1}$, $k_{10} = (55 \pm 6) \cdot 10^{-5} s^{-1}$ with $k' + k'' = (27 \pm 2) \cdot 10^{-5} s^{-1}$ and $k' = (0.7\text{-}1.0)k''$ at $-52°$ (by ^{19}F-NMR.). During the isomerization **26** + **27** → **9** + **10**, the product ratio [**26**]/[**27**] was practically constant (see *Table 2*), and slightly higher than the kinetic product ratio

Table 4. ${}^{13}C$-*NMR. characteristics of the dehydronorbornylhydroxonium ions* **7**-H^+, **8**-H^+, *of the 3-nortricyclyl derivatives* **25**, **34**, *the (fluorosulfonyloxy)norbornylhydroxonium ions* **9**, **10**, **26**, **27** *and the norbornanediyl bisfluorosulfates* **21**, **22**, **36**, **37** *in* HSO_3F/SO_2ClF (internal reference: $\delta_{CD_2Cl_2}$ = 53.6 ppm [47]); X = FSO_3

	RX	Temp. (°)	[RX]/[HX] in molar conc.	δ_C[a]) at C(1) [ppm]	C(2) [ppm]	C(3) [ppm]	C(4) [ppm]	C(5) [ppm]	C(6) [ppm]	C(7) [ppm]
	**7**-H^+	−90	0.7/2.0	47.1 (*d*)	85.2 (*d*)	33.0 (*t*)	41.1 (*d*)	143.1 (*d*)	130.5 (*d*)	45.4 (*t*)[b])
	8-H^+	−90	0.7/2.0	46.2 (*d*)	84.5 (*d*)	32.2 (*t*)	42.4 (*d*)	141.7 (*d*)	129.4 (*d*)	47.9 (*d*)[b])
	**25** (Z = H_2O^+)	−85	0.4/2.0	12.4 (*d*)	14.4 (*d*)	92.0 (*d*)	33.0 (*d*)	29.1 (*t*)	11.4 (*d*)	29.1 (*t*)[b])[c])
	34 (Z = FSO_3)	−50	0.4/0.05	13.7 (*d*)	14.0 (*d*)	96.0 (*d*)	33.8 (*d*)	30.0 (*t*)	11.7 (*d*)	29.5 (*t*)[b])[c])
	**9** (*exo*-Z = H_2O^+)	−60	0.4/2.0	40.4	83.2[c])	31.5	41.1	90.2	32.6	31.3
		−75	0.2/4.0	40.4	87.9	31.0	41.1	91.3	31.9	31.0
				(*d*, 151)	(*d*, 160)	(*t*, 137)	(*d*, 151)	(*d*, 160)	(*t*, 137)	(*t*, 137)
	10 (*endo*-Z = H_2O^+)	−60	0.3/2	39.6	80.6[c])	29.6	41.9	90.7	30.5	33.2
		−75	0.2/4.0	39.4	85.1	29.0	41.7	91.9	29.5	32.8
				(*d*, 151)	(*d*, 160)	(*t*, 137)	(*d*, 151)	(*d*, 160)	(*t*, 137)	(*t*, 137)
	21 (*exo*-Z = FSO_3)	−55	0.3/1.0	41.2	90.9	32.7	41.2	90.9	32.7	31.6
				(*d*, 155)	(*d*, 164)	(*t*, 135)	(*d*, 155)	(*d*, 164)	(*t*, 135)	(*t*, 133)
	22 (*endo*-Z = FSO_3)	−55	0.1/1.0	41.9	91.5	30.7	40.3	88.2	30.7	33.1
				(*d*, 153)	(*d*, 165)	(*t*, 135)	(*d*, 153)	(*d*, 165)	(*t*, 135)	(*t*, 135)
	**26** (*anti*-Z = H_2O^+)	−70	0.2/2.0	44.1	88.6[d])	34.7	37.3	23.2	19.3	85.8[d])
		−70	0.2/4.0	44.1 (*d*)	88.6 (*d*)	34.6 (*t*)	37.3 (*d*)	23.1 (*t*)	19.4 (*t*)	86.7 (*d*)[b])
	27 (*syn*-Z = H_2O^+)	−70	0.2/2.0	43.8	90.7[d])	34.9	38.3	23.2	19.3	87.5[d])
		−70	0.2/4.0	44.1 (*d*)	91.1 (*d*)	35.1 (*t*)	38.3 (*d*)	22.4 (*t*)	19.4 (*t*)	88.6 (*d*)[b])
	36 (*anti*-Z = FSO_3)	−55	0.2/1.0	44.9 (*d*)	88.5 (*d*)	35.3 (*t*)	38.1 (*d*)	24.2 (*t*)	20.5 (*t*)	91.0 (*d*)[b])
	37 (*syn*-Z = FSO_3)	−55	0.2/1.0	44.3 (*d*)	91.0 (*d*)	36.2 (*t*)	39.1 (*d*)	22.8 (*t*)	20.3 (*t*)	92.6 (*d*)[b])

a) Apparent multiplicity, ${}^1J$(CH) in Hz (±2 Hz), *s* = singlet, *d* = doublet, *t* = triplet.
b) Multiplicity determined from the proton single frequency 'off-resonance' decoupled ^{13}CFT-NMR. spectra [55].
c) These assignments are tentative; they are consistent with data reported for other 3-nortricyclyl derivatives [18] [56] [57].
d) δ_C the most affected by the variation of the conc. of HSO_3F.

(0.75-0.8) measured at lower temperature ($< -95°$). This indicated (but, because of the relatively large experimental errors, did not prove) that **26** and **27** were equilibrated before their isomerization to **9**+**10**.

Acid additions to *exo*-2,3-epoxynorbornanes afford *exo*-2,*syn*-7-disubstituted norbornane derivatives [23]; the 2,3-disubstituted isomers are not normally observed [24] because the *exo*-3-hydroxy-2-norbornyl cation intermediates isomerize rapidly by a *Wagner-Meerwein* rearrangement into the *syn*-7-hydroxy-2-norbornyl cation intermediates or form the corresponding σ-bridged carbonium ions (**28**-OH in *Scheme 6*) that are attacked by the nucleophile selectively at the carbon atom (C(1) of norbornene oxide) away from the electron-withdrawing substituent. When *exo*-2,3-epoxynorbornane **24** diluted in SO_2ClF or dispersed in CD_2Cl_2 was added slowly to a 4-20-fold excess of HSO_3F in SO_2ClF at $-110°$ a mixture of the adducts **26**+**27** (>94%) and **9**+**10** (<6%) was formed as in the case of the addition of HSO_3F to 3-nortricyclanol (**23**) *(Scheme 6)*. The kinetic product ratio [**26**]/[**27**] was dependent upon the HSO_3F excess and varied between 0.67 to 0.9 for mixtures prepared at $-110°$ and measured by ^{19}F-NMR. at $-95°$ [7]).

These results are most simply interpreted by invoking the formation of the cationic intermediate **28**-Z or **29**-Z (Z=$\overset{+}{O}H_2$ or OH) that allows the H-[6,1]-shift to occur, yielding a mixture of the adducts **26**+**27**. An energy barrier of 6-7 kcal/mol has been measured for the H-[6,2]-shift in 2-norbornyl cations in SbF_5/SO_2ClF [1a] [26]. It must be higher than the energy barrier of the quenching of **28**-Z⇄**30**-Z (or **29**-Z⇄**31**-Z)[8]) with FSO_3^- or HSO_3F (~3 kcal/mol for ion-pairs, if diffusion limited [27]). This implies that the adducts **26** and **27** are equilibrated *via* these intermediates during their formation at about $-110°$. The H-[6,2]-shift **28**-Z→**5**-Z or/and H-[1,2]-shift **30**-Z→**5**-Z are not favoured since the more stable adducts **9**+**10** are formed in minor amounts only by addition of HSO_3F to **23** or **24**. This suggests a higher energy barrier for the H-[6,2]- and/or H-[1,2]-migrations than for the H-[6,1]- and H-[1,6]-migrations, which could be due to the lower stability of the 5-substituted σ-bridged cation **5**-Z compared with that of the 7-substituted 2-norbornyl cations **28**-Z,**30**-Z (Z=$\overset{+}{O}H_2$, OH). The relatively high stereoselectivity of the addition of HSO_3F to 3-nortricyclanol (**23**) favouring the less stable adducts **26**+**27** over the more stable isomers **9**+**10** could also be explained by a higher stability of **28**-Z,**30**-Z (or **29**-Z,**31**-Z) over that of **5**-Z (or **3**-Z,**4**-Z) or the corresponding ion-pairs (Z=$\overset{+}{O}H_2$, OH).

A lower limit of 1.7 kcal/mol is obtained (less than 2% of **26**+**27** being observed in equilibrium with **9**+**10** at $-50°$) for the free enthalpy difference between **26** and **9** ([**9**]/[**10**]=7.3-12, see *Table 1*). This difference should not be higher than 2-3 kcal/mol as suggested by the comparison of the heats of formation ($\Delta\Delta H \simeq \Delta\Delta G$?) of model compounds [15] and by assuming that there is no special differential solva-

7) Regardless of the nature (σ-bridged or classical) of the 2-norbornyl cation intermediates, the kinetic product ratio of the addition of HSO_3F to **23** or **24** may not be the same because of the relatively high energy barriers to the H-[1,6]- and H-[6,1]-migrations that equilibrate the ionic intermediates **28**-Z⇄**30**-Z or **29**-Z⇄**31**-Z; *cf.* [25].

8) Because the 3-Z-2-norbornyl cations are expected to be much less stable than the 7-Z-2-norbornyl cations, it is highly probable that the pair **28**-Z, **29**-Z corresponds to the same intermediate (single energy minimum); the same can be said about the pair **30**-Z, **31**-Z.

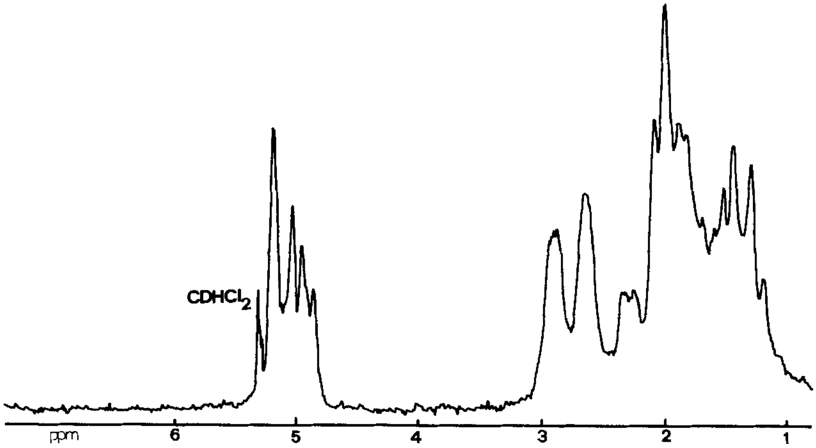


Fig. 3. *^{1}H-NMR.* (60 MHz) *spectrum of a kinetic mixture of* **21**+**22**(traces) *and* **36** *(major)*+**37** ($-90°$, [HSO_3F]$\simeq$0.4M)

tion effect on the pairs **26**+**27** and **9**+**10**. The kinetics of the rearrangements of **26**+**27**→**9**+**10** and **9**⇄**10** showed these reactions to have comparable activation free enthalpies ($\Delta G_1^{\ddagger} \simeq \Delta G_2^{\ddagger}$, see *Fig. 5*). If one considers an energy barrier of 6-7 kcal/mol for the H-[6,2]- and H-[1,2]-shifts [1a] [26] corresponding to the rearrangements **28**-Z→**5**-Z and **30**-Z→**5**-Z respectively, a free enthalpy diagram can be constructed in which the σ-bridged ions **28**-Z, **30**-Z are more stable than the σ-bridged ion **5**-Z *(Fig. 5)*. This conclusion is in complete agreement with the deductions made from product analysis of the additions of HSO_3F (in excess, at $< -100°$) to 3-nortricyclanol (**23**) and *exo*-2,3-epoxynorbornane (**24**).

Our interpretations of these results might become relevant to the nature of the secondary 2-norbornyl cation if the observed substituent effects on the stability of this cation could be reproduced with electron-withdrawing substituents other than Z=$\overset{+}{O}H_2$, OH. Deprotonation ($\overset{+}{O}H_2 \rightleftarrows OH + H^+$) of the (fluorosulfonyloxy)norbornylhydroxonium ions **9**, **10**, **26** and **27** could occur before the ionization of the fluorosulfates and therefore cloud the simple pictures presented. We show now that very similar substituent effects can be observed for secondary 2-norbornyl cation intermediates substituted at C(5) or C(7) by Z=FSO_3.

Additions of HSO_3F to norbornadiene (**32**) *and quadricyclane* (**33**)[9]. Norbornadiene and quadricylane derivatives add protic acids [12a] [29] and electrophiles [30] to give 3-nortricyclyl and norborn-5-en-3-yl derivatives, probably *via* 3-nortricyclic cationic intermediates [31]. When norbornadiene dissolved in SO_2ClF or dispersed in CD_2Cl_2 was mixed slowly with a solution of 1.2 equiv. of HSO_3F in SO_2ClF at $-120°$, a clear, slightly yellow solution was formed. Its ^{1}H-, ^{13}C- and ^{19}F-NMR. spectra taken at $-100°$ confirmed that a mixture of 3-nortricyclyl fluorosulfate (**34**) and *exo*-norborn-5-en-2-yl fluorosulfate (**35**) was obtained under these carefully controlled conditions. The product ratio [**34**]/[**35**] was 6/1 to 6/2 when 1.1 to 1.3 equiv. of HSO_3F were employed. Using a larger excess of HSO_3F solutions of the *exo*-2,

[9]) Preliminary report, see [28].

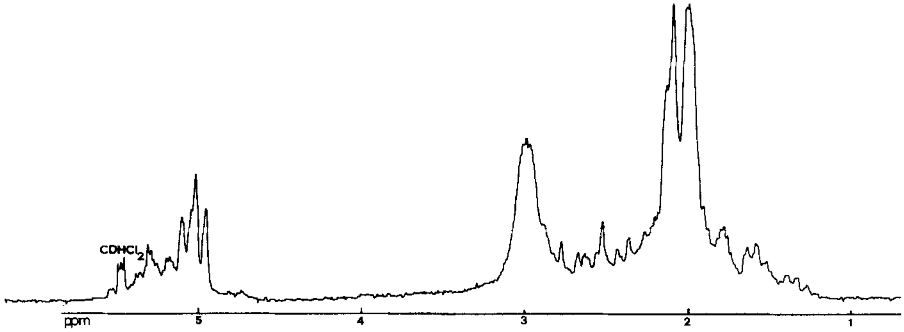


Fig. 4. *¹H-NMR.* (60 MHz) *spectrum of a thermodynamic mixture of* **21**:**22** *(2.5:1)+1 equiv. of HSO_3F* (−10°)

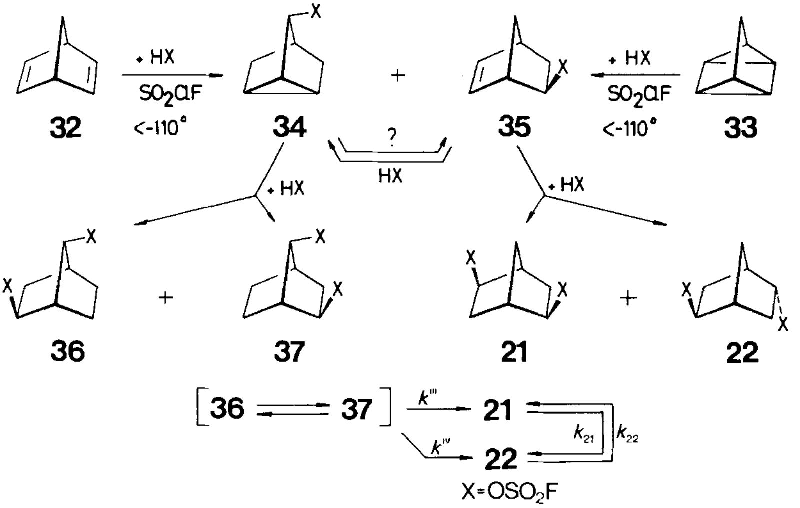
anti-7- and *exo*-2,*syn*-7-norbornanediyl bisfluorosulfates (**36**+**37**) and of a kinetic mixture of the *exo*-2,5-norbornanediyl bisfluorosulfates **21**+**22** were observed at < −100° (see *Table 3*). Mixtures of **34**+**35**+0.1 equiv. of HSO_3F polymerized rapidly at −60° (**35** disappeared slightly faster than **34**).

The same monoadducts **34**+**35** and bis-adducts **36**+**37**+**21**+**22** were obtained by adding HSO_3F/SO_2ClF to quadricyclane (**33**) under the same conditions (see *Table 3, Scheme 7*).

By analogy with the additions of HSO_3F to 3-nortricyclanol (**23**) and norbornenols **7**, **8**, **34** is assumed to yield preferentially **36**+**37** whereas **35** is assumed to yield **21**+**22** by addition of HSO_3F. We cannot exclude a possible isomerization **34**⇄**35** under our conditions. Various mixtures of **36**+**37**+**21**+**22** were obtained as a function of the acid excess and the unsaturated precursors **32** and **33** (see *Table 3*); proof of these structures is given below.

In presence of a 5-10-fold excess of HSO_3F in SO_2ClF (with or without CD_2Cl_2), the 2,7-adducts **36**+**37** were isomerized to their more stable 2,5-isomers **21**+**22** at

Scheme 7



$> -90°$ (see *Table 2*). At equilibrium, less than 2% of **36**+**37** were detected (by ^{19}F-NMR., $-80°$). The product ratio [**36**]/[**37**] did not vary within the limits of experimental error ($\pm 10\%$) during the isomerization **36**+**37**→**21**+**22**. A kinetic mixture of **21**+**22** was formed; **21** and **22** were equilibrated competitively with their formation from **36**+**37**. These observations were completely analogous to the isomerizations of the *exo*-2-(fluorosulfonyloxy)-*anti*-7- and -*syn*-7-norbornylhydroxonium ions **26**+**27** to the more stable *exo*-5-(fluorosulfonyloxy)-*exo*-2- and -*endo*-2-norbornylhydroxonium ions **9**+**10** *(Scheme 6)*.

The isomerization **36**+**37**→**21**+**22** and **22**⇆**21** were somewhat faster than the corresponding isomerizations **26**+**27**→**9**+**10** and **10**⇄**9** under similar conditions. By assuming a kinetic stationary state between **36** and **37**, the simulated kinetics of the isomerizations **37**+**36**→**21**+**22** and **22**⇄**21** fitted our experimental data for $k''' + k'^{v} = (10.5 \pm 1) \cdot 10^{-5}\ s^{-1}$ (see *Table 2*), $k_{22} = (35 \pm 3) \cdot 10^{-5}\ s^{-1}$ ($\Delta G_2^{\ddagger} = 13.3$–$13.7$ kcal/mol) and $k_{21} = (9 \pm 1) \cdot 10^{-5}\ s^{-1}$ when [**36**+**37**+**21**+**22**]=0.3 M and HSO_3F= 3.0 M at $-89 \pm 2°$ (*Scheme 7;* see *Fig. 5*, Z=X=FSO_3).

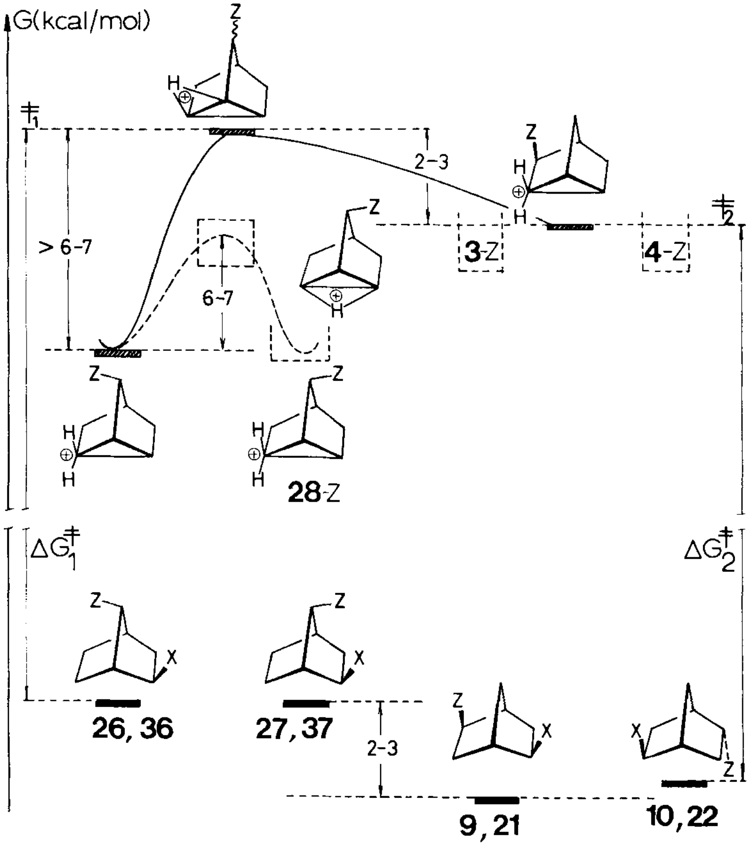


Fig. 5. *Free enthalpy diagram for the rearrangements of 7-substituted* exo-*2-norbornyl fluorosulfates* (X=FSO_3, Z=H_2O^+, FSO_3) *to the 5-substituted* exo-*2-norbornyl fluorosulfates* ($\Delta G_1^{\ddagger}$) *and the isomerization of* exo-*5-substituted* exo-*2-norbornyl fluorosulfate* ⇄ endo-*5-substituted* exo-*2-norbornyl fluorosulfate* ($\Delta G_2^{\ddagger} \simeq \Delta G_1^{\ddagger}$; $-100°$ to $-50°$ in HSO_3F/SO_2ClF)

The isomerizations **36**+**37**→**21**+**22** and **21**⇄**22** are competitive ($\Delta G_1^{\neq} \simeq \Delta G_2^{\neq}$, see *Fig. 5*); a free enthalpy difference ΔG(**36**, **37**−**21**)≃2-3 kcal/mol is assumed as in the case of ΔG(**26**, **27**−**9**). If the isomerization **36** and/or **37**→**21**, **22** imply 6,2- and/or H-[1,2]-migrations (**36**→**30-Z**→**5-Z**→**21**+**22** and/or **37**→**28-Z**→**5-Z**→**21**+**22**, Z=OSO_2F, see *Scheme 6*) with a transition state 6-7 kcal/mol above the classical or σ-bridged 7-(fluorosulfonyloxy)-2-norbornyl cations [1a] [26], one can conclude that the FSO_3 group destabilizes the σ-bridged secondary 2-norbornyl cation intermediates in HSO_3F/SO_2ClF more when substituting C(5) than C(7). Parallel results have been reported for the activation parameters of the solvolyses of substituted secondary 2-norbornyl esters [1a]. In particular, the transition states of

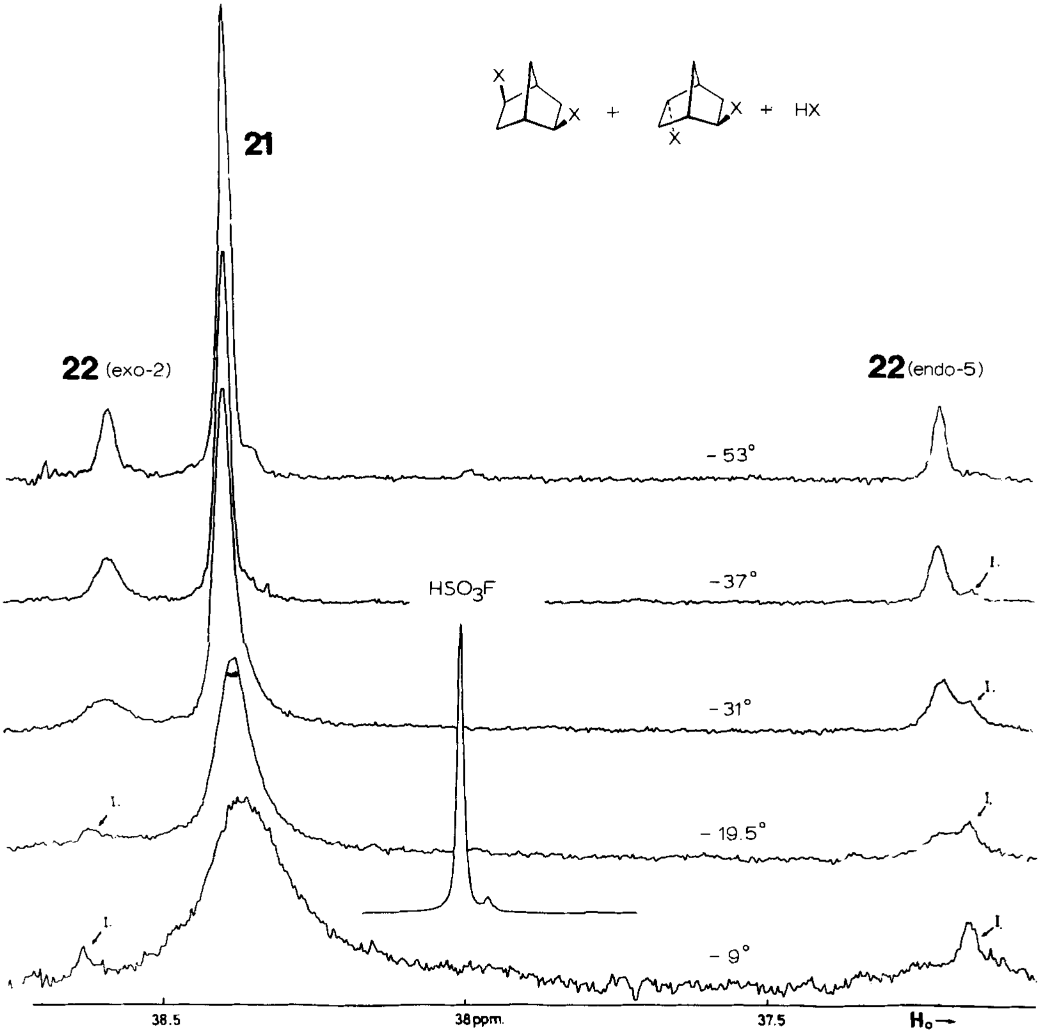
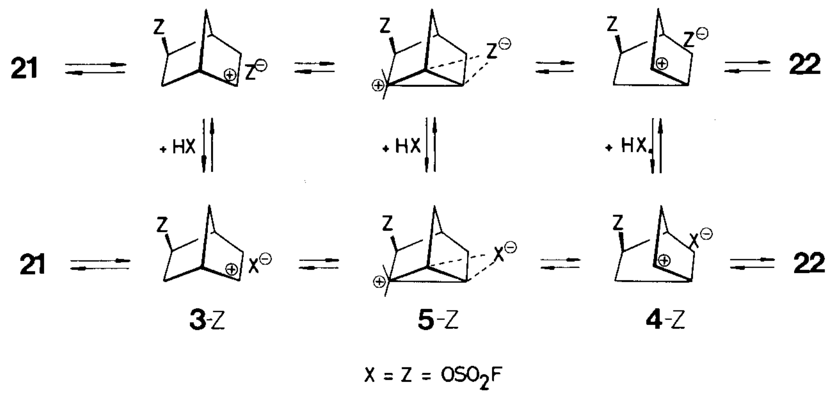


Fig. 6. ^{19}*F-NMR. spectrum of a mixture of* **21**+**22** *(3:1)+20 equiv. of HSO_3F in SO_2ClF+CD_2Cl_2 as a function of temperature.* The line-width of the HSO_3F peak stayed practically constant between −60° to −20°. I= impureties

the buffered acetolyses of *exo*- and *endo*-2-norbornyl tosylates are more destabilized by the *exo*-5-methoxy than by the *anti*-7-methoxy group [32a] (see also the effect of 7-oxo [32b] and 5-oxo [32c] groups and of other polar substituents [32d] on the solvolysis rates of 2-norbornyl esters; the transition states of these reactions may differ *a priori* from the transition states of the rearrangements studied here).

The ^{19}F-NMR. spectrum (as well as the ^{1}H- and ^{13}C-NMR. spectra) of the mixture of the bisfluorosulfates **21**+**22** in a large excess (20×) of HSO_3F/SO_2ClF (1/1 to 3/1, *v/v*) is temperature dependent. Above −40°, line broadening is observed (see *Fig. 6*). ^{19}F-NMR. line shape analysis as a function of the temperature should enable us to evaluate the relative activation parameters of the isomerization **21**⇄**22** and of the FSO_3 group exchanges between HSO_3F and **21**, **22** and to establish the mechanism limits for the processes (distinction between the intermediacy of a σ-bridged cation **5**-Z or of fast equilibrating classical ions or ion-pairs **3**-Z⇄**4**-Z (Z=OSO_2F)). Unfortunately this was not possible because **21** and **22** were already decomposing slowly at −30° (forming impurities whose ^{19}F-NMR. signals perturbed the broadened lines under investigation). Complete coalescence of HSO_3F+**21**+**22** ^{19}F-signals must occur above +10° and could not be observed because of too rapid decomposition at this temperature. The following observations could, nevertheless, be made: a) The line-broadening of the peak attributed to the *exo*-2-FSO_3 group in **22** was 2.1–2.7 times as large as that of the *endo*-5-FSO_3 group in **22** (between −40° and −28°, after deduction of the natural line-width and line-broadening due to long-range H,F couplings); b) The line-broadening of the FSO_3 signal of **21** was 0.5–0.7 time as large as that of the *endo*-5-FSO_3 peak of **22** (between −40° and −28°; [**21**]/[**22**]=3.0 at −30°). The *endo*-5-FSO_3 group in **22** exchanged with the *exo*-2,5-FSO_3 groups of **21**, but not directly with HSO_3F because it must be less reactive than the *exo*-2-FSO_3 group in a S_N1 displacement [1a] [33] by HSO_3F. A $\Delta G^{\ddagger}_{2}$ (**22**→**21**)=13.5–13.8 kcal/mol at −31° was evaluated from the line-broadening of the *endo*-5-FSO_3 of **22** (k=2–3 s^{-1}). A $\Delta G^{\ddagger}_{2}$ (**22**→**21**)=13.3–13.7 kcal/mol at −89°±2° was obtained from the slow kinetics **21**→**22** of the same solution; this allowed estimation of $\Delta S^{\ddagger}$=−8 to −3 e.u. for the isomerization of **22**→**21**, in agreement with expectations [1a] [33].

Scheme 8



Our observations therefore suggest that *external return intervenes competitively with the ionization and isomerization* of **21** and **22** *(Scheme 8)*[10]). We conclude that if the σ-bridged cation **5-Z** is a transition state rather than an intermediate in the isomerization **21**$\rightleftarrows$**22**, its free enthalpy is not higher than that of the classical ions **3-Z**, **4-Z** plus the free enthalpy barrier to their quenching by FSO_3^- in HSO_3F (< 3 kcal/mol, if diffusion limited: $k_D > 10^{10}\ s^{-1}$ at $-30°$ [27]).

Structural determination and spectral assignments of the adducts **9**, **10**, **21**, **22**, **26**, **27**, **34**, **35**, **36** *and* **37**. The fluorosulfates discussed in this work cannot be isolated pure; their structures were deduced from their ^{1}H-, ^{13}C- and ^{19}F-NMR. spectra and were consistent with their mode of formation, their expected reactivity in an ionizing medium and their expected relative stabilities.

The ^{13}C-NMR. spectra of **9**, **10**, **21**, **22**, **26**, **27**, **36** and **37** (see *Table 4*) confirmed the bis-substitution of the norbornane skeleton. There was no quaternary carbon atom, thus excluding substituted bridgehead centres and geminal bis-substitution of a methylene group. Only **21** displayed ^{13}C- and ^{19}F-NMR. signals consistent with C_2-symmetry. The other bisfluorosulfates cannot have C_s-symmetry. The ^{1}H-NMR. spectra of mixtures of **21** (major) + **22** (minor) (see *Fig. 4*) showed signals attributed to **21** that were comparable to those reported for *exo*-2,*exo*-5-difluoronorbornane [34] and *exo*-2,*exo*-5-norbornanediol [35]. In particular, the shape of the multiplet at $\delta_H \simeq 5$ ppm attributed to H–C(2) and H–C(5) (see *Fig. 4*) was consistent with *exo*-substitution (^3J(H–C(1),H–C(2) (*endo*)) $\simeq$ 0 Hz, ^3J(H–C(1),H–C(2) (*exo*)) $\simeq$ 3–4 Hz [36]) and not with *endo*-substitution as in **38** *(Table 6)*. **21** was more stable than **22** in agreement with *exo*-2 substituted norbornanes being more stable than their *endo*-2 isomers [1a] [15].

The ^{1}H- and ^{13}C-NMR. of **9** and **10** were very similar to those of **21** and **22**. The *exo*-substitution of the FSO_3 group agreed with the well known *exo*-selectivity of the acid additions to norbornene derivatives [1a] [9] [37]. The spectral assignments of **9** and **10** could be made without ambiguity by comparing their spectra with those of the deuteriated derivatives **11**$\rightleftarrows$**12**, **13**$\rightleftarrows$**14** *(Scheme 2)* and **16**$\rightleftarrows$**17** *(Scheme 4)*. The carbon atoms bearing the H_2O^+ substituent showed a δ_C strongly dependent upon the concentration of HSO_3F, probably because of the equilibrium: ROH + $HSO_3F \rightleftarrows R\overset{+}{O}H_2 + FSO_3^-$ (see *Table 4, Fig. 1*).

The ^{1}H-NMR. spectra of mixtures of **36** (major) + **37** (minor) (see *Fig. 3*) were comparable with those reported for *exo*-2,*anti*-7-difluoronorbornane [38] and *exo*-2,*anti*-7-norbornanediol [35] (br. *s* at δ_H = 5.15 ppm and br. *t* at δ_H = 4.9 ppm). Little information was given by the ^{1}H-NMR. spectra about the substitution pattern of **10**, **22**, **26**, **27** and **37**. The ^{13}C-NMR. spectra were more helpful. By making use of the FSO_3 and H_2O^+ substituent effects on δ_C of norbornane derivatives *(Table 5)*, the calculated ^{13}C-NMR. spectra *(Table 6)* of disubstituted norbornanes were compared with the experimental data and confirmed the proposed structures.

Polar substituent effects on δ_C of norbornane derivatives. Owing to the rigidity of the norbornane skeleton, the assignment of the C-signals based on the substituent

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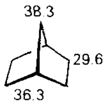
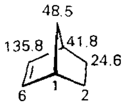
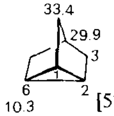
[10]) Our results could also be explained by a scheme in which the cation **3-Z** or **4-Z** (or the corresponding ion-pairs) is never attained as an intermediate in these cases **5-Z** can be an intermediate (Z = FSO_3).

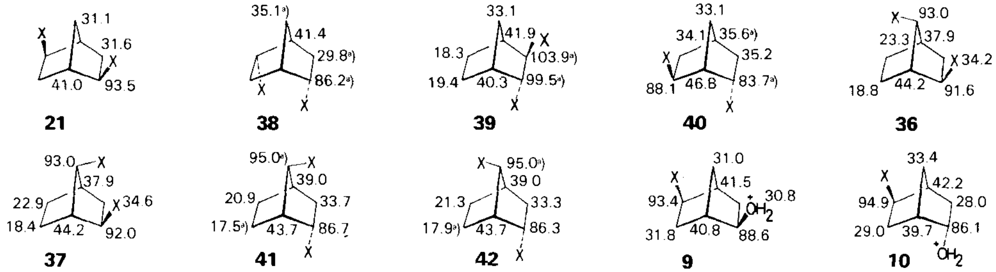
Table 5. *Polar substituent effects on δ_C of 2- and 7-substituted norbornanes, norbornenes and nortricyclane* (ppm)

Skeleton	Substituent	Substituent effect on δ_C of						
		C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)
	*exo*-2-OH [39d]	7.9	45.1	12.6	−0.9	−1.5	−5.2	−3.9
	-OAc [39d]	5.3	47.9	10.1	−0.8	−1.3	−5.2	−3.0
	-OSO_2CH_3	6.2	56.0	8.9	−0.8	−1.7	−5.7	−3.2[a])
	-OSO_2F	5.6	66.3	8.9	−0.9	−2.4	−6.9	−3.6[b])
[39d]	-$\overset{+}{O}H_2$	5.4	61.4	8.1	−0.4	−2.5	−6.7	−3.7[c])
	endo-2-OH [39d]	6.2	43.3	9.8	0.9	0.3	−9.6	−0.7
	-OAc [39d]	4.0	46.1	7.5	0.4	−0.1	−8.6	−1.3
	-OSO_2F	4.9	61.0	8.0	0.2	−4.4	−7.8	−1.6[d])
	-$\overset{+}{O}H_2$	4.3	58.9	5.3	0.3	−1.0	−9.5	−1.3[e])
	syn-7-OH [39]	4.1	−2.5	−2.5	4.1	−2.5	−2.5	40.7
	-$\overset{+}{O}H_2$	2.5	−3.9	−3.9	2.5	−4.3	−4.3	53.8[f])
	*exo*-2-OH [39d]	8.3	47.7	12.3	−1.1	5.0	−1.7	−2.9
	-OAc	4.8	49.7	9.3	−1.9	5.2	−3.2	−3.0[g])
	-$\overset{+}{O}H_2$	5.3	60.6	8.4	−0.7	7.9	−4.7	−3.1[h])
[39d]	*endo*-2-OH [39d]	6.3	47.7	13.0	1.1	4.8	−4.1	−0.3
	-OAc	3.5	49.9	9.5	0.0	2.8	−4.1	−1.3[g])
	-$\overset{+}{O}H_2$	4.4	59.9	7.6	0.6	6.5	−5.8	−0.6[h])
	3-OH [57]	2.9	5.6	43.6	5.7	−4.0	0.4	−2.8
	-OAc	2.4	3.0	46.5	3.4	−3.2	0.9	−3.1[i])
	-$\overset{+}{O}H_2$	2.1	4.0	58.6	3.1	−4.3	1.1	−4.3[h])
[57]	-OSO_2F	3.4	3.7	62.6	3.9	−3.4	−1.4	−3.9[h])

a) 1.0M in CD_2Cl_2 containing 1 equiv. of CH_3SO_3H; by increasing the conc. of CH_3SO_3H, $\delta_C(2)$ is shifted to lower field (α-effect = 57.6 ppm in CH_3SO_3H 9M).
b) 1.0M in CD_2Cl_2/SO_2ClF (1/2), with 1.1 equiv. of HSO_3F, at −100°.
c) 1.0M in CD_2Cl_2/SO_2ClF (1/2), with 1.5 equiv. of HSO_3F, at −60°; in the presence of 0.85 equiv. of HSO_3F an α-effect of 59.4 ppm is measured for $\delta C(2)$.
d) Calculated by comparison of the δ_C of **22** and **6** *(Table 4)*.
e) 0.35M in CD_2Cl_2/SO_2ClF (1/2) with 1.5 equiv. of HSO_3F at −60°.
f) 0.3M in CD_2Cl_2/SO_2ClF (1/2) with 1.4 equiv. of HSO_3F at −60°; the distinction between $\delta C(2,3)$ and $\delta C(5,6)$ was made by measuring the spectrum of (*exo*-2,3-D_2)-*anti*-7-norbornanol in $HSO_3F/SO_2ClF/CD_2Cl_2$. This alcohol was prepared by deuteration (D_2/Pd/C in CH_3OD at 25°) of *anti*-7-norborn-2-enol. The upfield substituent effect of the D atoms on $\delta C(2,3)$ (−0.4 ppm) was taken into account.
g) 2.0M in $CDCl_3$, δ_{CDCl_3} = 76.9 ppm.
h) See *Table 4*.
i) 0.5M in $CDCl_3$; the assignments for $\delta C(5,7)$ are not definitive [18].

effects on δ_C [39] is normally easy. Increments for the FSO_3 and H_2O^+ substituent effects have not been reported. We have determined them by recording the spectra of *exo*-2-norbornyl fluorosulfate (**6**), of *exo*-2 and *endo*-2-norbornylhydroxonium ions and of (*exo*-2,*exo*-3-D_2)-*anti*-7-norbornylhydroxonium ion (see *Table 5*). The α-effect of the FSO_3 group was larger than that of the H_2O^+, CH_3SO_3 and CH_3COO substituents, in agreement with the empirical rule correlating α-effects with the electron-withdrawing ability of the substituent [40]. The β-effect on $\delta C(1)$ and on

Table 6. *Calculated δ_C for norbornanediyl bisfluorosulfates and (fluorosulfonyloxy)norbornylhydroxonium ions* by assuming additivity of the increments associated with the substituent effects reported in the *Table 5* (X = FSO_3)

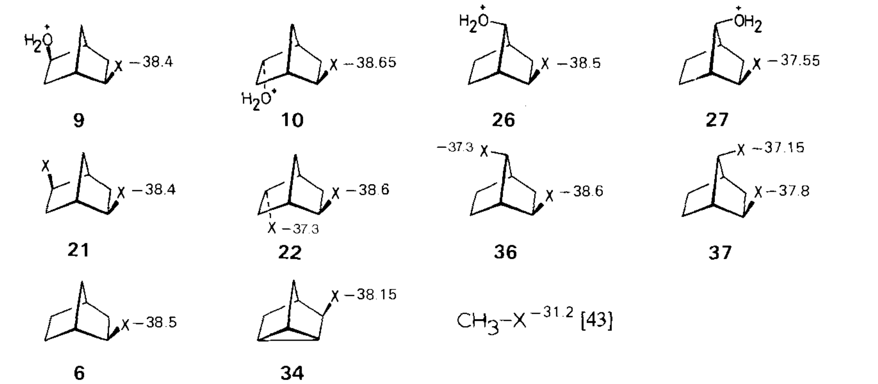


a) δ_C deviating most from experimental data and which exclude the hypothetical structures **38**–**42**.

δ C(3) decreased with the electron-withdrawing ability of the substituent at the *exo*-2 or *endo*-2 positions. The other substituent effects were about the same for H_2O^+ and FSO_3 at C(2). One typical feature of the δ_C of norbornanes is the upfield γ-effects of the 2- and 7-substituents [39] [41] (see *Table 5*). These effects are responsible for the relatively low δ C(5,6) in 2,7-disubstituted norbornanes (compare **21**, **22** with **36**, **37** or **9**, **10** with **26**, **27**).

The calculated δ_C of the bisfluorosulfates **38**–**42** (with an *endo*-2 FSO_3 group) deviate strongly from the observed spectra of **36**, **37** *(Table 6)*. Since **36** and **37** are equilibrating it would be unexpected if the *endo*-2 fluorosulfates were more stable than their *exo*-2 isomers [1a] [15]. The distinction between **36** and **37** cannot be made unambigously by ^{13}C-NMR. spectroscopy but ^{19}F-NMR. spectra can help in solving this problem.

Table 7. *^{19}F-NMR. chemical shifts* (δ_F, ppm) *of the monofluorosulfates* **6**, **34**, **9**, **10**, **26** *and* **27** *and of the bisfluorosulfates* **21**, **22**, **36** *and* **37** *in $HSO_3F/SO_2ClF/CD_2Cl_2$* (internal reference: $\delta_{SO_2ClF} = -99.1$ ppm [48]); X = FSO_3 a))



a) The δ_F are slighty dependent upon the conc. of HSO_3F and the temperature ($\Delta\delta_F \cong 0.1$ ppm for [HSO_3F] = 0.3 to 4.0M and −80° to −30°).

Because of the similarities between the H_2O^+ and FSO_3 substituent effects on δ_C, the structures **26** and **27** could be deduced from **36** and **37**.

^{19}F-NMR. characteristics of the fluorosulfates. The δ_F of *exo*-2-norbornyl, 3-nortricyclyl fluorosulfates and of the HSO_3F adducts to norbornenols (**9**, **10**), to nortricyclanol (**26**, **27**) and to norbornadiene (**21**, **22**, **36**, **37**) are reported in *Table 7.* Below $-50°$, the half-height line-width of the FSO_3 signals varied between 1.5 and 2 Hz (with a line-width of 0.5 Hz for the SO_2ClF singlet). These line-broadenings were due to long-range H,F couplings [42]. ^4J(H,F)=0.4 Hz and ^5J(H,F)=0.9 Hz have been reported [43] for CH_3OSO_2F and $CH_3CH_2OSO_2F$ respectively. The δ_F of the *exo*-2-(fluorosulfonyloxy) substituent in **9**, **21**, **26**, **27**, **37** and in *exo*-2-norbornyl fluorosulfate are about the same (-38.4 to -38.6 ppm). When the *exo*-2-FSO_3 group is perturbed by the bulk of another substituent such as H_2O^+ or FSO_3 (**27** and **37**) a shielding effect of about 1 ppm is observed. The *endo*-2-FSO_3 group in **22**, the *syn*-7 and the *anti*-7-FSO_3 groups are also shielded relative to the *exo*-2-FSO_3 substituents. A feature of the spectrum of **37** is the apparent doublets observed for the FSO_3 signals. This can be attributed to a through-space F,F coupling (J(F,F)$\simeq$2 Hz, see *Fig. 7*) between the *syn*-7 and *exo*-2-FSO_3 groups. Such couplings have been reported for difluorohydrocarbons [44]. This observation can be proposed as a criterium for differentiating the assignments of the spectra characteristics between **36** and **37**; in particular, it confirms the *exo*-2 substitution in **37**.

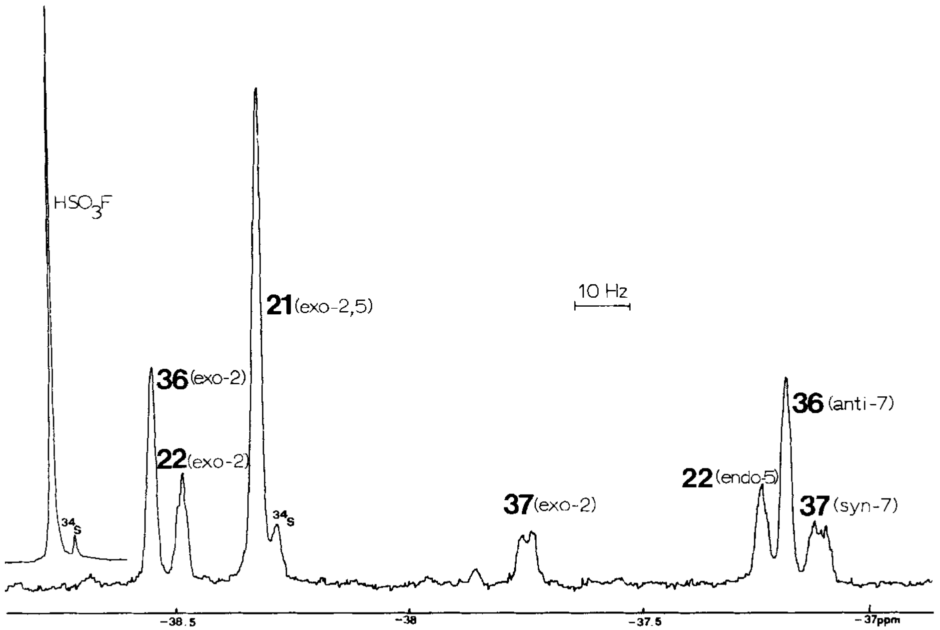


Fig. 7. *^{19}F-NMR.* (84.67 MHz) *spectrum of a mixture of the bisfluorosulfates* **21**+**22**+**36**+**37**+ *~1 equiv. of HSO_3F* ($SO_2ClF+CD_2Cl_2$; $-50°$; $\delta_{HSO_3F}=-41.8$ ppm). Upfield satellites of F $^{34}SO_3$ [58] are visible for the intense peaks (HSO_3F; **21**)

Conclusion. - 1) The secondary 2-norbornyl cation intermediate formed in HSO_3F/SO_2ClF is destabilized when substituted at C(5) by an electron-withdrawing groups such as FSO_3 or H_2O^+ (HO). A destabilization of about 5 kcal/mol is estimated for the 5-FSO_3 substituent by comparing the rate constants of the *Wagner-Meerwein* rearrangements of *exo*-2-norbornylfluorosulfates ($\Delta G^{\neq}$ (**6**→**6'**) ≃ 8.6 kcal/mol at −110°) and of 2,5-norbornanediyl bisfluorosulfates ($\Delta G_2^{\neq}$ (**22**→**21**) ≃ 13.5 kcal/mol at −89°; $\Delta S^{\neq} \simeq -5$ e.u.) in HSO_3F (3.0 M) + SO_2ClF.

2) If the σ-bridged cations **5**-Z (Z = H_2O^+ (HO) and FSO_3) are transition states rather than intermediates in the additions of HSO_3F to *exo*-2- and *endo*-2-norborn-5-enols (**7**, **8**) and *exo*-2-norborn-5-enyl fluorosulfate (**35**) and in the reversible isomerizations of the adducts **9** ⇄ **10** and **21** ⇄ **22**, then their free enthalpies are not higher than those of the classical intermediates **3**-Z, **4**-Z plus the free enthalpy barrier to their quenching by FSO_3^- in HSO_3F/SO_2ClF.

3) The stability difference between the 5-substituted σ-bridged ions **5**-Z and the classical ions **3**-Z, **4**-Z being relatively small, it will be even smaller in the case of the unsubstituted 2-norbornyl cation; at the limit the σ-bridged ion **2** might be more stable than the classical ions **1**, **1'** in HSO_3F/SO_2ClF. This conclusion implies an electron-attracting substituent at C(5) to destabilize more the σ-bridged than the classical ion because the positive charge-delocalization at C(6) should be greater in the former than in the latter ion. This hypothesis is not inconsistent with what follows.

4) The kinetic stereoselectivity of the additions of HSO_3F to 3-nortricyclanol (**23**) and 3-nortricyclyl fluorosulfate (**34**), as well as the comparison of the rate constants of the isomerizations of the 2,7-norbornanediyl adducts to their more stable 2,5-isomers (**26** + **27** → **9** + **10** and **36** + **37** → **21** + **22**) and the reversible isomerizations of the 2,5-norbornanediyl adducts (**9** ⇄ **10** and, respectively, **21** ⇄ **22**) suggest that an electron-withdrawing group at C(5) destabilizes the σ-bridged 2-norbornyl cation more than at C(7)[11]. This fact can be rationalized by assuming a larger positive charge delocalization at C(6,5) than at C(1,7) or by invoking a 'special polarisability' of the 2-norbornyl cation skeleton that would render the effects of a substituent such as FSO_3 or H_2O^+ (HO) more sensitive at C(5) than at C(7) (hyperconjugative effects outweighing the expected field and inductive effects [45]; the n(0) electrons of the groups FSO_3, H_2O^+ (HO) could also perturb a simple picture derived from the pure electrostatic effects of these substituents [46]).

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[11]) MINDO/3 calculations on 2-norbornyl cations substituted by an HO or H_2O^+ group agreed with this conclusion. MINDO/3 calculations showed also that classical *exo*-5- and *endo*-5-hydroxy-2-norbornyl cations are energy minima, the corresponding σ-bridged ion **5**-OH being a transition state about 2,5 kcal/mol above the classical ion **3**-OH; with the protonated alcohols, the σ-bridged ion **5**-$\overset{+}{O}H_2$ was found about 6 kcal/mol above the classical ions **3**-$\overset{+}{O}H_2$ and **4**-$\overset{+}{O}H_2$ [46].

Experimental Part

^1H-NMR. spectra were recorded on a *Bruker* WP-60 (60 MHz) or a *Bruker* HX-90 (90 MHz) spectrometer in the FT mode. The signal of $CDHCl_2$ was used as internal reference ($\delta = 5.3$ ppm, $\delta_{TMS} = 0.0$ ppm). The ^{13}C-NMR. spectra were measured on a *Bruker* WP-60 (15.08 MHz, spectrum width: 3750 Hz, 4096 points) or a *Bruker* HX-90 (22.63 MHz, spectrum width: 6000 Hz, 4096 points) in the FT mode. The δ_C are reported relative to external TMS; CD_2Cl_2 was used as internal reference (53.6 ppm [47]). ^{19}F-NMR. spectra were measured on a *Bruker* HX-90 spectrometer in the FT mode (84.67 MHz), δ_F being relative to $CFCl_3$ (0.0 ppm, [48]); negative δ_F corresponds to deshielded F-atoms. The D-signal of CD_2Cl_2 was used as lock signal. Temperature stabilization of the NMR. probes were made by using a *Bruker* BST 100-700 regulator. Temperatures were measured directly in a rotating reference tube containing CH_2Cl_2 before and after the recording of spectra of superacid samples (Pt resistance of 100 Ohms/ice-water). Product ratios and kinetics were measured by integration of the ^{19}F- or ^{13}C-NMR. peaks or by the 'Xeroxing-cutting-weighing' technique.

HSO_3F *(Fluka)* was distilled twice under reduced pressure and stored under N_2 in a desiccator, and redistilled *in vacuo* before use. DSO_3F, SO_2ClF *(Aldrich)* and CD_2Cl_2 *(Radium Chemie AG)* were distilled *in vacuo* before use. *Exo*-Norborn-5-en-2-ol (**7**) [49], *endo*-norborn-5-en-2-ol (**8**) [50], 3-nortricyclanol (**23**) [51], *exo*-2,3-epoxynorbornane (**24**) [52] and quadricyclane (**33**) [53] were prepared by known procedures. (*Exo*-2-D)-*endo*-norborn-5-en-2-ol (**15**) was prepared according to [50] by reducing dehydronorcamphor with $LiAl(OCH_3)_3D$ in tetrahydrofuran; yield: 80%, D > 99% (MS.); m.p. 107-108° (sublimation at 90°/15 Torr), [54] 110°.

General procedure for the preparation of unstable fluorosulfates by addition of HSO_3F to unsaturated precursors RX. These reactions must be carried out with exclusion of air and moisture. Polymerization can be avoided if the precursor RX dissolved in SO_2ClF (with or without CD_2Cl_2) is dispersed rapidly in a large excess of HSO_3F/SO_2ClF at low temperature, by using a vacuum line with the apparatus in *Figure 8* and the following procedure.

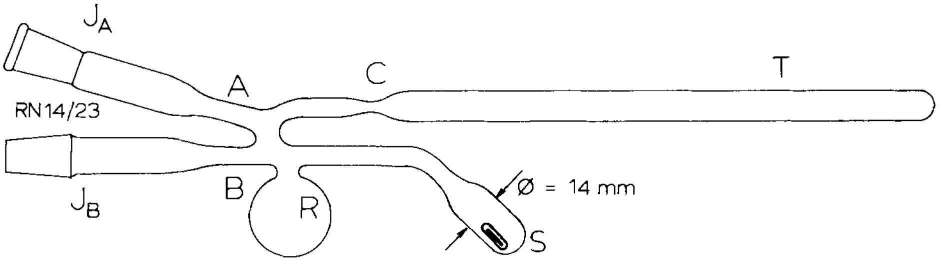

Fig. 8. *Apparatus for mixing HSO_3F with RX in SO_2ClF*

A stopper is placed at J_A (ground joint), the apparatus is connected to a vacuum line *via* J_B (vertically) and evacuated. Dry N_2 is introduced *via* J_B and is allowed to flush the apparatus when J_A is opened. A weighed amount (0.2 to 3 g) of HSO_3F is introduced with a pipette into the NMR. tube T which is then cooled in liquid N_2. A stopper is placed again at J_A and the apparatus is evacuated completely. A known amount of SO_2ClF (1 to 2 ml) is transferred on the vacuum line into T. Dry N_2 is introduced into the apparatus. The tube T is removed from the liquid N_2 bath until the SO_2ClF has dissolved the HSO_3F completely; then T is again frozen in liquid N_2. Under N_2 and trough J_B, a weighed amount of the precursor RX is place into the side-arm S containing a Pyrex coated magnetic bar. The stopper is replaced at J_A and the apparatus is evacuated *via* J_B. A known amount of SO_2ClF (+possibly CD_2Cl_2) is condensed at B and is allowed to flow slowly to S under N_2; the side-arm S is withdrawn from the liquid N_2 bath until complete solution of RX in SO_2ClF (+CD_2Cl_2); then this solution is frozen at once with liquid N_2 (crystallization of the precursor RX must be avoided). The apparatus is evacuated on the vacuum line; joints J_A and J_B are sealed successively under vacuum. The complete apparatus is then immersed into a bath of EtOH/MeOH/liquid N_2 at −130° to −110°. When the solution of HSO_3F/SO_2ClF in T has melted, it is poured into the 'reactor' R. The solution of RX + SO_2ClF (+CD_2Cl_2) in the side-arm S is poured portionwise with vigorous shaking, into the reactor R. After mixing, the adduct mixture is poured into the NMR. tube T, keeping the apparatus immersed in the $-130°$ bath. More than one NMR. tubes can be connected at C; this allows various analyses of the same solution of fluorosulfates to be made. The NMR. tubes are immersed in liquid N_2 and sealed. Depending upon the precursor RX and the concentration of HSO_3F, CD_2Cl_2 can lead to the formation of two phases at low temperature.

REFERENCES

[1] a) *H.C. Brown & P.v.R. Schleyer,* 'The Nonclassical Ion Problem', Plenum Press, New York, N.Y. 1977; b) *G.A. Olah,* Accounts chem. Res. *9,* 41 (1976); c) *H.C. Brown,* Tetrahedron *32,* 179 (1976); d) *J.M. Kramer,* Adv. phys. org. Chemistry *11,* 177 (1975); e) *F.K. Fong,* J. Amer. chem. Soc. *96,* 7638 (1974); Accounts chem. Res. *9,* 433 (1976); f) *G.D. Sargent,* 'Carbonium Ions', G.A. Olah & P.v.R. Schleyer, Ed., Wiley-Interscience, New York, N.Y. Vol. 3, p. 1099 (1972); g) *H.C. Brown & M. Ravindranathan,* J. Amer. chem. Soc. *100,* 1865 (1978).

[2] *F. Kaplan, P. Cross & R. Prinstein,* J. Amer. chem. Soc. *92,* 1445 (1970); *J.J. Solomon & F.H. Field,* ibid. *98,* 1567 (1976); *R.H. Staley, R.D. Wieting & J.L. Beauchamp,* ibid. *99,* 5964 (1977); *M. Meot-Ner & F.H. Field,* ibid. *100,* 1356 (1978).

[3] *D.M. Brouwer & H. Hogeveen,* Progr. phys. org. Chemistry *9,* 179 (1972); *H. Hogeveen,* Adv. phys. org. Chemistry *10,* 29 (1973); *E.M. Arnett & C. Petro,* J. Amer. chem. Soc. *100,* 5408 (1978); *R. Haseltine, N. Wong, T.S. Sorensen & A.J. Jones,* Canad. J. Chemistry *53,* 1891 (1975).

[4] a) *G.A. Olah, G. Liang, G.D. Mateescu & J.L. Riemenschneider,* J. Amer. chem. Soc. *95,* 8698 (1973); b) *G.A. Olah & G. Liang,* ibid. *96,* 195 (1974); c) *G.A. Olah, A.M. White, J.R. DeMember, A. Commeyras & C.Y. Lui,* ibid. *92,* 4627 (1970); d) *D.G. Farnum, R.E. Botto, W.T. Chambers & B. Lam,* ibid. *100,* 3847 (1978).

[5] a) *D.T. Clark, B.J. Cromarty & L. Colling,* J. Amer. chem. Soc. *99,* 8120 (1977); b) *D.W. Goetz, H.B. Schlegel & L.C. Allen,* ibid. *99,* 8118 (1977); c) *M.J.S. Dewar, R.C. Haddon, A. Komornicki & H. Rzepa,* ibid. *99,* 377 (1977).

[6] *P.C. Hariharan, L. Radom, J.A. Pople & P.v.R. Schleyer,* J. Amer. chem. Soc. *96,* 599 (1974); *P.K. Bischof & M.J.S. Dewar,* ibid. *97,* 2278 (1975); *S.-L. Chong & J.L. Franklin,* ibid. *94,* 6347 (1972); *D.J. McAdoo, F.W. McLafferty & P.F. Bente,* ibid. *94,* 2027 (1972); *P.P. Dymerski, R.M. Prinstein, P.F. Bente & F.W. McLafferty,* ibid. *98,* 6834 (1976); *T. Pakkanen & J.L. Whitten,* ibid. *97,* 6337 (1975).

[7] a) *M. Saunders, P. Vogel, E.L. Hagen & J. Rosenfeld,* Accounts chem. Res. *6,* 53 (1973); b) *C.H. DePuy, A.H. Andrist & P.C. Fünfschilling,* J. Amer. chem. Soc. *96,* 948 (1974); *C.C. Lee, A.J. Cessna, E.C.F. Ko & S. Vassie,* ibid. *95,* 5688 (1973); *C.C. Lee & R. Reichle,* J. org. Chemistry *42,* 2058 (1977); *W. Kirmse, H.-J. Ratajczak & G. Rauleder,* Chem. Ber. *110,* 2290 (1977).

[8] *M. Hardy, P.-A. Carrupt & P. Vogel,* Helv. *59,* 1685 (1976); *P. Vogel,* Chimia *31,* 53 (1977); *A. Streitwieser, Jr. & S. Alexandratos,* J. Amer. chem. Soc. *100,* 1979 (1978) and ref. therein.

[9] *J.K. Stille & R.D. Hughes,* J. org. Chemistry *36,* 340 (1971); see also *K.-T. Liu,* Tetrahedron Letters *1978,* 1129.

[10] *K.B. Becker & C.A. Grob,* Synthesis *1973,* 789; *D.J. Pasto, G.R. Meyer & B. Lepeska,* J. Amer. chem. Soc. *96,* 1858 (1974); *R.C. Fahey, C.A. McPherson & R.A. Smith,* ibid. *96,* 4534 (1974); *R.M.G. Roberts,* J. chem. Soc. Perkin II *1976,* 1374; *P. Naab & H.A. Staab,* Chem. Ber. *111,* 2982 (1978).

[11] *D.J. Pasto & J.F. Gadberry,* J. Amer. chem. Soc. *100,* 1469 (1978).

[12] a) *R.M.G. Roberts,* J. chem. Soc. Perkin II *1976,* 1183; b) *W.K. Chwang, V.J. Nowlan & T.T. Tidwell,* J. Amer. chem. Soc. *99,* 7233 (1977); see also *M. Lajunen & T. Sura,* Tetrahedron *34,* 189 (1978).

[13] *L.P. Hammett & A.J. Deyrup,* J. Amer. chem. Soc. *54,* 2721 (1932); *R.J. Gillespie & T.E. Peel,* ibid. *95,* 5173 (1973); *J.B. Senior,* Pure appl. Chemistry *41,* 373 (1975); *J. Sommer, P. Rimmelin & T. Drakenberg,* J. Amer. chem. Soc. *98,* 2671 (1976).

[14] a) *V.J. Nowlan & T.T. Tidwell,* Accounts chem. Res. *10,* 252 (1977); b) *M. Lajunen & P. Hirvanen,* Finn. chem. Letters *1978,* 38.

[15] *Y. Brunel & A. Rassat,* Tetrahedron *34,* 1343 (1978); *E.M. Engler, J.D. Andose & P.v.R. Schleyer,* J. Amer. chem. Soc. *95,* 8005 (1973).

[16] *F.M. Menger, M. Perinis, J.M. Jerkunica & L.E. Glass,* J. Amer. chem. Soc. *100,* 1503 (1978).
[17] *J.B. Stothers,* 'Topics in Carbon-13 NMR Spectroscopy', G.C. Levy, Ed., Wiley-Interscience, New York, *1,* 229 (1974).
[18] *P. Vogel, R. Delseth & D. Quarroz,* Helv. *58,* 508 (1975).
[19] *D.G. Farnum & G. Mehta,* J. Amer. chem. Soc. *91,* 3256 (1969).
[20] *N.H. Werstiuk & T. Kadai,* Canad. J. Chemistry *50,* 3350 (1972).
[21] *N.H. Werstiuk & T. Kadai,* Canad. J. Chemistry *54,* 2213 (1974) and ref. therein.
[22] *H. Margenau & G.M. Murphy,* 'The Mathematics of Physics and Chemistry', Van Nostrand, Ed., New York 1956, 486.
[23] *P.D. Bartlett & W.P. Giddings,* J. Amer. chem. Soc. *82,* 1240 (1960); *S. Winstein & E.T. Stafford,* ibid. *79,* 505 (1957); *H.M. Walborsky & D.F. Loncrini,* J. org. Chemistry *22,* 1117 (1957); *J.K. Crandall,* ibid. *29,* 2830 (1964); *R.N. McDonald & T.E. Tabor,* ibid. *33,* 2934 (1968); *A.P. Gray & D.E. Heitmeier,* ibid. *34,* 3253 (1969); *R. Baker, D.E. Halliday & T.J. Mason,* Tetrahedron Letters *1970,* 591; *A. Chollet & P. Vogel,* Helv. *61,* 732 (1978).
[24] *A. Chollet, J.-P. Hagenbuch & P. Vogel,* Helv. submitted for publication.
[25] *H. Christol, J. Coste, F. Prietrasanta, F. Plénat & G. Renard,* J. chem. Res. (S) *1978,* 62.
[26] *R. Haseltine, N. Wong, T.S. Sorensen & A. Jones,* Canad. J. Chemistry *53,* 1891 (1975); *R. Haseltine, K. Ranganayakulu, N. Wong & T.S. Sorensen,* ibid. *53,* 1901 (1975).
[27] *D.N. Hague,* 'Fast Reactions', Wiley-Interscience, New York, *1971,* p. 12.
[28] *D. Quarroz, J.-M. Sonney & P. Vogel,* Chimia *29,* 306 (1975).
[29] *A. Gregorčič & M. Zupan,* Tetrahedron *33,* 3243 (1977); *I. Tabushi, K. Yamamura & A. Togashi,* J. org. Chemistry *41,* 2169 (1976); *E.F. Magoon & L.H. Slaugh,* J. organomet. Chemistry *55,* 409 (1973); *T.C. Morrill & B.E. Greenwald,* J. org. Chemistry *38,* 2769 (1971) and ref. therein.
[30] *J. Kagan,* Helv. *55,* 2356 (1972); *A. Heumann & B. Waegell,* Nouv. J. Chimie *1,* 277 (1977); *A. Gregorčič & M. Zupan,* J. chem. Soc. Perkin I *1977,* 1446; *G.F. Koser & J.N. Faircloth,* J. org. Chemistry *41,* 583 (1976); *T.C. Morrill, S. Malasanta, K.M. Warren & B.E. Greenwald,* ibid. *40,* 3032 (1975); *T. Kobayashi, M. Kodama & S. Itô,* Tetrahedron Letters *1975,* 655.
[31] *J.-M. Sonney, P. Vogel & U. Burger,* Tetrahedron Letters *1978,* 824 and ref. therein.
[32] a) *P.v.R. Schleyer, P.T. Stang & D.J. Raber,* J. Amer. chem. Soc. *92,* 4275 (1970); b) *J.C. Greever & D.E. Gwynn,* Tetrahedron Letters *1969,* 813; c) *P.G. Gassman & J.L. Marshall,* J. Amer. chem. Soc. *88,* 2822 (1966); d) *D. Lenoir, W. Röll, E. Weiss & G. Wenke,* Tetrahedron Letters *1976,* 1991 and ref. therein.
[33] *T.W. Bentley & C.T. Bowen,* J. chem. Soc. Perkin II *1978,* 557 and ref. therein; *J.M. Harris, D.L. Mount & D.J. Raber,* J. Amer. chem. Soc. *100,* 3139 (1978); *H.C. Brown, M. Ravindranathan, F.J. Chloupek & I. Rothberg,* ibid. *100,* 3143 (1978).
[34] *S.A. Shackelford,* Tetrahedron Letters *1977,* 4265.
[35] *J. Paasivirta & P. Äyräs,* Suomen Kemistilehti *B41,* see also: *P. Äyräs & J. Paasivirta,* ibid. *B42,* 61 (1969); *W.C. Baird, Jr. & M. Buza,* J. org. Chemistry *33,* 4105 (1968); *A.J. Baggaley, R. Brettle & J.R. Sutton,* J. chem. Soc. Perkin I *1975,* 1055.
[36] *H. Joela,* Org. magn. Reson. *9,* 338 (1977) and ref. therein; *R. Gassend, Y. Limousin & J.C. Maire,* ibid. *6,* 259 (1974); *R. Sanchez-Obregon, M. Salmon & F. Walls,* ibid. *4,* 885 (1972); *E.I. Snyder & B. Franzus,* J. Amer. chem. Soc. *86,* 1166 (1964); *J. Meinwald & Y.C. Meinwald,* ibid. *85,* 2514 (1963); *K. Tori, K. Kitahonoki, Y. Takono, H. Tanida & T. Tsuji,* Tetrahedron Letters *1964,* 559; *S.E. Masar & H. Krieger,* Suomen Kemistilehti *B42,* 1 (1969); *J. Paasivirta,* ibid. *B44,* 131 (1971); *R.V. Moen & H.S. Makowski,* Analyt. Chemistry *43,* 1629 (1971); *A. Chollet, C. Mahaim, C. Foetisch, M. Hardy & P. Vogel,* Helv. *60,* 59 (1977).
[37] *H.A. Bruson & T.N. Riener,* J. Amer. chem. Soc. *67,* 723 (1945); *L. Schmerling,* ibid. *68,* 195 (1946); *L. Schmerling, J.P. Luvisi & R.W. Welch,* ibid. *78,* 2819 (1956); *T.G. Traylor & A.W. Baker,* Tetrahedron Letters *19,* 14 (1959); *J. Paasivirta,* Acta chem. Scand. *27,* 374 (1973); *H.C. Brown & K.-T. Liu,* J. Amer. chem. Soc. *97,* 600, 2469 (1975); *S. Inagaki, H. Fujimoto & K. Fukui,* ibid. *98,* 4054 (1976).
[38] *M. Zupan, A. Gregorčič & A. Pollak,* J. org. Chemistry *42,* 1562 (1977); *D.D. Tanner & P. Van Bostelen,* J. Amer. chem. Soc. *94,* 3187 (1972); see also: *D.D. Tanner & G.C. Gidley,* J. org. Chemistry *33,* 38 (1968); *M.L. Poutsma,* J. Amer. chem. Soc. *87,* 4293 (1965); *D.R. Marshall, P. Reynolds-Warnhoff, E.W. Warnhoff & J.R. Robinson,* Canad. J. Chemistry *49,* 885 (1971); *F.H. Dean, D.R. Marshall, E.W. Warnhoff & F.L.M. Pattison,* ibid. *45,* 2279 (1967).

[39] a) *J.B. Grutzner, M. Jautelat, J.B. Dence, R.A. Smith & J.D. Roberts,* J. Amer. chem. Soc. *92,* 7107 (1970); b) *E. Lippmaa, T. Pehk, J. Paasivirta, N. Belikova & A. Plati,* Org. magn. Reson. *2,* 581 (1970); *E. Lippmaa, T. Pehk, N. Belikova, A.A. Bobyleva, A.N. Kalinichenko, M.D. Ordubadi & A.F. Platé* ibid. *8,* 74 (1976); c) *N.H. Werstiuk, R. Taillefer, R.A. Bell & B.G. Sayer,* Canad. J. Chemistry *50,* 2146 (1972); d) *J.B. Stothers, C.T. Tan & K.C. Teo,* ibid. *54,* 1211 (1976); e) *G.S. Poindexter & P.J. Kropp,* J. org. Chemistry *41,* 1215 (1976); *W. Kitching, M. Marriott, W. Adcock & D. Doddrell,* ibid. *41,* 1671 (1976).

[40] *J.B. Stothers,* '^{13}C-NMR. Spectroscopy', Academic Press, New York 1972; *G.E. Maciel,* 'Topics in Carbon-13 NMR. Spectroscopy', G.C. Levy, Ed., Wiley-Interscience, New York, *1,* 53 (1974); *J.B. Lambert, D.A. Netzel, H.-N. Song & K.K. Liliamstrom,* J. Amer. chem. Soc. *98,* 3778 (1976); *Y. Terui, K. Tori & N. Tsuji,* Tetrahedron Letters *1976,* 621.

[41] *D. Quarroz, J.-M. Sonney, A. Chollet, A. Florey & P. Vogel,* Org. magn. Reson. *9,* 611 (1977); see also *R. Bicker, H. Kessler & G. Zimmermann,* Chem. Ber. *111,* 3200 (1978); *R. Bicker, H. Kessler, A. Steigel & G. Zimmermann,* ibid. *111,* 3215 (1978).

[42] *L. Covalli,* 'Annual Reports NMR. Spectroscopy', E.F. Mooney, Ed., Academic Press, New York, *6B,* 43 (1976); *R. Fields,* ibid. *7,* 1 (1977); *5A,* 99 (1972); *W.J.E. Parr, T. Schaefer & K. Marat,* Canad. J. Chemistry *55,* 3243 (1977); *T. Schaefer & W.J.E. Parr,* ibid. *55,* 2835 (1977); *56,* 1717 (1978); *R.E. Wasylishen & M. Barfield,* J. Amer. chem. Soc. *97,* 4545 (1975).

[43] *M.G. Ahmed, R.W. Alder, G.H. James, M.L. Sinnott & M.C. Whiting,* J. chem. Soc. Chem. Commun. *1968,* 1533; see also: *G.A. Olah & R.J. Spear,* J. Amer. chem. Soc. *97,* 1845 (1975).

[44] *F.B. Mallory, C.W. Mallory & M.-C. Fedarko,* J. Amer. chem. Soc. *96,* 3536 (1974); *F.B. Mallory,* ibid. *95,* 7747 (1973); *F.B. Mallory, C.W. Mallory & W.M. Ricker,* ibid. *97,* 4770 (1975); *A.D. Buckingham & J.E. Cordle,* J. chem. Soc. Faraday Transaction II *1974,* 994.

[45] *C.A. Grob,* Angew. Chem. *88,* 621 (1976); *W. Fischer & C.A. Grob,* Helv. *61,* 1588 (1978); *L.M. Stock,* J. chem. Education *49,* 400 (1972).

[46] *P.-A. Carrupt & P. Vogel,* in preparation.

[47] *G.C. Levy & J.D. Cargioli,* J. magn. Reson. *6,* 143 (1972).

[48] *P.A.W. Dean & R.J. Gillespie,* J. Amer. chem. Soc. *91,* 7260 (1969).

[49] *S.J. Cristol, T.C. Morrill & R.A. Sanchez,* J. Amer. chem. Soc. *88,* 3087 (1966).

[50] *H.C. Brown & H.R. Deck,* J. Amer. chem. Soc. *87,* 5620 (1965).

[51] *J. Meinwald & J.K. Crandall,* J. Amer. chem. Soc. *88,* 1292 (1966).

[52] *H.M. Walborsky & D.F. Loncrini,* J. Amer. chem. Soc. *76,* 5396 (1954).

[53] *I. Tabushi, K. Yamamura & Z.-I. Yoshida,* J. Amer. chem. Soc. *94,* 787 (1972); *G.S. Hammond, P. Wyatt, C.D. DeBoer & N.J. Turro,* ibid. *86,* 2532 (1964); *G.S. Hammond, N.J. Turro & A. Fischer,* ibid. *83,* 4674 (1961); *W.G. Dauben & R.L. Cargill,* Tetrahedron *15,* 197 (1961).

[54] *J.D. Roberts, E.R. Trumbull, Jr., W. Bennett & R. Armstrong,* J. Amer. chem. Soc. *72,* 3116 (1950).

[55] *K.G.R. Pachler,* J. magn. Reson. *7,* 442 (1972); *G. Jikeli, W. Herrig & H. Günther,* J. Amer. chem. Soc. *96,* 323 (1974); *E.W. Hagaman,* Org. magn. Reson. *8,* 389 (1976).

[56] *D.P. Kelly & H.C. Brown,* J. Amer. chem. Soc. *97,* 3897 (1975); *A.W. McCulloch, A.G. McInnes, D.G. Smith & J.A. Walter,* Canad. J. Chemistry *54,* 2013 (1976).

[57] *E. Lippmaa, T. Pehk & J. Paasivirta,* Org. magn. Reson. *5,* 277 (1973).

[58] *R.A. Stewart & S. Fujiwara,* J. chem. Physics *49,* 965 (1968); *S.A. Linde & H.J. Jakobsen,* J. magn. Reson. *17,* 411 (1975).