Kurze Mitteilungen

Maximalumfang: 6 Schreibmaschinenseiten (alles inbegriffen). Bis zum 15. des Monats bei der Redaktion eingehende Manuskripte können günstigstenfalls am 15. des folgenden Monats veröffentlicht werden.

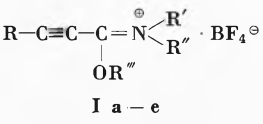
Iminium Substituted Acetylenes as Partners in Cycloaddition Reactions[1]*

Summary

The synthesis of acetylenic amidium salts, a new class of compounds, by the alkylation of acetylenic amides is described. In their Diels-Alder cycloaddition reaction with cyclopentadiene, acetylenic amidium salts were found to be more reactive dienophiles than ester-activated acetylenes.

Our interest in acetylenes activated by electron-withdrawing groups has led us to study the effect of iminium ethers as substituents on the acetylenic triple bond as compared with ester[2], cyano and in particular, nitro[3] substituents.

We have prepared acetylenic iminium ethers, **I**, as the first in the class of iminium substituted acetylenes.



I a – e

I are in fact amidium salts (Table **I**) being prepared from ready O-alkylation of propiolic amides with triethyloxonium fluoroborate. The acetylenic substituent R may be varied among *tert*-butyl, phenyl and hydrogen. Particularly characteristic for the activating effect of the iminium ether group is the qualitative comparison of reactivity towards cyclopentadiene at room temperature of **Ib**, *tert*-butyl-nitroacetylene and its ester and nitrile analogs[3]. From all of these only the nitro and iminium ether acetylenes react under these conditions, the addition of *tert*-butyl-nitroacetylene going to completion in 2 hr[3], **Ib** requiring 2 weeks.

Similarly **Ia** undergoes cycloaddition with cyclopentadiene at room temperature within 70 hr and compared to ester functionalized phenylacetylenes[4] is much faster reacting.

Unsubstituted propiolamidium compounds **Ic** to **e** react instantaneously with cyclopentadiene affording similar norbornadienyl amidium compounds, **II** (Table II) which themselves are useful compounds available for derivatization.

* Received June 2, 1975.

Table I. Acetylenic Amidium Compounds, **I**

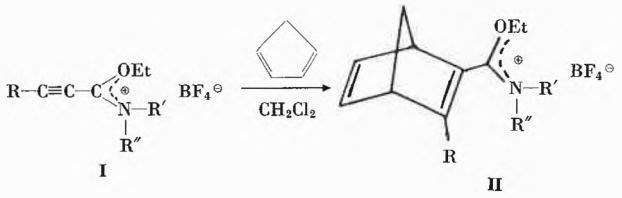
Compound	R	R′	R″	R‴	Yield %	mp °C	IR (CH_2Cl_2) cm^{-1} C≡C	amidium	other	^{1}H-NMR (δ) OCH_2CH_3	OCH_2CH_3	NR′	NR″	R
Ia	C_6H_5	CH_3	CH_3	CH_2CH_3	85	113–115	2205	1640	–	4.90 (q)	1.58 (t)	3.48 (s)	3.73 (s)	7.34–8.08 (m) [a]
Ib	$(CH_3)_3C$	CH_3	CH_3	CH_2CH_3	98	72–73	2220	1645	–	4.70 (q)	1.52 (t)	3.41 (s)	3.51 (s)	1.43 (s) [a]
Ic	H	CH_3	CH_3	CH_2CH_3	93	–	2120	1655	3270 (C≡C–H)	4.83 (q)	1.53 (t)	3.40 (s)	3.63 (s)	4.93 (s) [b]
Id	H	H	CH_3	CH_2CH_3	84	–	2130	1665	3270 (C≡C–H) 3220 (NH)	4.88 (q)	1.57 (t)	10.2 (bs)	3.22 (d)	4.70 (s) [b]
Ie[c]	H	H	H	CH_2CH_3	71	–	–	–	–	–				

a) $CDCl_3$; b) CD_2Cl_2; c) characterized by derivatization

Table II. Cycloadducts of **I** and Cyclopentadiene, **II**

R	R′	R″	Yield %	mp °C (decomp.)	^{1}H-NMR (δ) OCH_2CH_3	OCH_2CH_3	NR′	NR″	R	*H*-3,6	*H*-4,5	*H*-7
$(CH_3)_3C$	CH_3	CH_3	32	135–140	4.47 (q)	1.45 (t)	3.04, 3.33,	3.40, 3.43 [b] (4s)	1.08 (s)	3.95 (m)	6.94 (m)	2.08 (m) [a]
C_6H_5	CH_3	CH_3	85	122–123	3.90–4.20 (m)	1.31 (t)	3.13 (s)	3.41 (s)	6.96–7.60 (m) [c]	3.90–4.20 (m) [c]	6.96–7.60 (m) [c]	2.38 (m) [a]
H	CH_3	CH_3	87	–	4.30 (q)	1.42 (t)	3.25 (s)	3.33 (s)	7.66 (m)	4.00 (m)	7.00 (m)	2.22 (m) [c]
H	H	CH_3	87	–	4.50 (m) [d]	1.46 (t)	9.05 (bs)	3.10, [b] 3.26 (dd)	7.96 (m)	3.95 (m)	6.88 (m)	2.38 (m) [c]
H	H	H	71	120–123	4.60 (q)	1.50 (t)	8.74 (bs)	9.17 (bs)	8.40 (d)	4.02 (bd)	6.92 (dq)	2.25 (bs) [a]

a) $CDCl_3$; b) two sets of non equivalent methyl groups; c) masked; d) non-equivalent methylene; e) CD_2Cl_2



Other Diels-Alder and also 1,3-dipolar cycloaddition reactions of **I** will soon be reported[5].

Experimental

The following procedures should serve as examples for the synthesis of acetylenic amidium compounds and their cyclopentadiene cycloadducts.

N,N-Dimethyl-O-ethyl-tert-butylpropiolamidium tetrafluoroborate

tert-Butylpropiolamide[6] (0.95 g, 0.0062 mol) and triethyloxonium fluoroborate[7] (1.20 g, 0.0062 mol) were stirred at room temperature in anhydrous dichloromethane (20 ml) for 20 hr. The solvent was evaporated and the residue digested with anhydrous ether crystallizing a colorless solid which was recrystallized from ethanol/ether as colorless prisms.
Yield: 1.32 g (98%), mp 72 to 73°. Anal. calc. for $C_{11}H_{20}NOBF_4$: C 49.09; H 7.49; N 5.21. Found: C 48.87; H 7.64; N 5.37.

1-(N,N-Dimethyl-O-ethylcarboxamidium)-2-phenyl-3,6-endomethylene-1,4-cyclohexadiene

N,N-Dimethyl-O-ethyl-phenylpropiolamidium tetrafluoroborate (0.2 g, 0.0007 mol) in CH_2Cl_2 (15 ml) was stirred at room temperature with an excess (~2 ml) of freshly distilled cyclopentadiene. After 70 hr the triple bond absorption had completely disappeared. The excess diene and solvent were evaporated and anhydrous ether added to the residual oil. Crystallization was induced by scratching after adding a trace of ethyl acetate.
Yield: 0.21 g (85%), mp 122 to 123° (decomposition). Anal. calc. for $C_{18}H_{22}NOBF_4$: C 60.86; H 6.24; N 3.94. Found: C 61.19; H 5.96; N 3.94.

Bibliography

1 Iminium Salts, Part 14. Part 13: H.G.Viehe and P.George, *Chimia 29* (1975) 209.
2 J.Sauer, *Angew.Chem. (Internat.Ed.) 6* (1967) 16; S.Seltzer in *Advances in Alicyclic Chemistry*, Vol.2 (H.Hart and G.J.Karabatsos, Ed.), Academic Press, New York 1968, p.1–57; W.Carruthers, *Some Modern Methods of Organic Synthesis*, Cambridge University Press, London 1971, p.115–71.
3 V.Jäger and H.G.Viehe, *Angew.Chem. (Internat.Ed.) 8* (1969) 273.
4 R.S.Glass and D.L.Smith, *J.Org.Chem.39* (1974) 3712.
5 H.G.Viehe and J.S.Baum, to be submitted to the *Journal of Organic Chemistry*.
6 J.C.Motte, Dissertation, Université de Louvain, 1974.
7 H.Meerwein, *Org.Synthesis 46* (1966) 113.

Heinz G.Viehe and Jonathan S.Baum

Université de Louvain
Laboratoire de Chimie Organique
Place Louis-Pasteur, 1
B-1348 Louvain-la-Neuve, Belgium

Zur Bestimmung von Fließkonstanten in der Dünnschichtchromatographie*

Summary

Evaluating the parameters for continuous-flow-TLC-chambers it is necessary to determine the flow-parameters of the mobile phase. Based upon the classical theory of Cameron and Bell and Washburn two types of mathematical treatment for solvent-flow problems in TLC are discussed and verified experimentally. The so-called integral method computation gives a more precise result of the flow-constants, whereas the differential method shown as a graph immediately indicates changes in the solvent-flow.

Die Kenntnis von k-Werten für definierte Dünnschichten und Fließmittel ist u.a. nützlich für die Abschätzung der Fließgeschwindigkeit und damit der Trennzeit bei der Durchlauf-Dünnschichtchromatographie, wo das Fließmittel am Schichtende laufend verdampft wird.
Bei einer von uns konstruierten Trennkammer, die in einer späteren Mitteilung beschrieben werden soll, ist eine käufliche Dünnschichtfolie F waagrecht angeordnet (Abb.1). Ihr gebogenes Ende ragt in den Fließmitteltank T. Auf diese Art werden Störungen im Fließmittelnachschub, wie sie häufig bei Verwendung eines Steges aus Filterpapier auftreten, vermieden. Der Fließmittelspiegel kann im Tank auf konstanter Höhe gehalten werden.
Bei dieser Anordnung ist es schwierig, den Zeitpunkt $t = 0$ des Entwicklungsbeginnes und den Ort $z = 0$ der Eintauchlinie der Schicht in das Fließmittel genau zu bestimmen. Eine genaue Ortsbestimmung hingegen ist auf dem waagrechten Teil der Schicht möglich. Die experimentelle Bestimmung von k muß deshalb unter folgenden einschränkenden Bedingungen vorgenommen werden: ein beliebiger, genau fixierbarer Punkt P_0 im

Die Beziehung von Cameron und Bell[1]

$$z^2 = k \cdot t \qquad (1)$$

(z = Abstand Fließmittelauftragungsort–Fließmittelfront; k = Fließkonstante, abhängig von der Art der Dünnschicht und vom Fließmittel; t = Fließzeit seit Entwicklungsbeginn), welche eine vereinfachte Form einer Gleichung von Washburn[2] über das Fließen von Flüssigkeiten in kapillaren Körpern ist, ergibt nach einer Differenzierung folgenden Ausdruck für die Frontwanderungsgeschwindigkeit v:

$$v = \frac{dz}{dt} = \frac{1}{2}\sqrt{\frac{k}{t}} = \frac{k}{2z}. \qquad (2)$$

* Eingegangen am 12. Juni 1975.

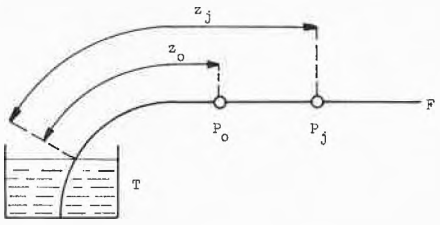


Abb. 1. Integrales Verfahren; T = Fließmitteltank, F = Dünnschichtfolie, die übrigen Symbole sind im Text erläutert

waagrechten Teil der Schicht sei um die Strecke z_0 von der Eintauchlinie entfernt. P_0 werde von der Fließmittelfront nach der Zeit t_0 erreicht. Die Werte von z_0 und t_0 seien nicht bekannt. Die Fließmittelfront erreicht nach den Zeiten t_j weitere, exakt vermeßbare Punkte P_j, die sich in den Abständen z_j von der Eintauchlinie befinden. Meßbare Größen sind die Strecken $(z_j - z_0)$ und die zu ihrem Durchlaufen benötigten Zeiten $(t_j - t_0)$.
Im folgenden werden zwei Verfahren erläutert, um die Fließkonstante unter den obenerwähnten einschränkenden Bedingungen zu bestimmen.

1. «Integrales» Verfahren

(1) wird auf die Punkte P_0 und P_j angewendet:

$$z_j^2 = k \cdot t_j,$$
$$z_0^2 = k \cdot t_0,$$

und die Differenz gebildet:

$$z_j^2 - z_0^2 = (z_j + z_0)(z_j - z_0) = k(t_j - t_0). \qquad (3)$$

Mit

$$z_j = z_0 + (z_j - z_0)$$

und den Definitionen

$$(z_j - z_0) = a_{j0}$$
$$(t_j - t_0) = t_{j0}$$

folgt aus (3)

$$(2\,z_0 + a_{j0})a_{j0} = kt_{j0}$$

oder

$$a_{j0}^2 + 2a_{j0}z_0 - kt_{j0} = 0. \qquad (4)$$

Da die Meßwerte a_{j0} und t_{j0} mit Meßfehlern behaftet sind, wird in (4) ein Korrekturglied, das Residuum r_j, eingeführt.
Werden die Meßdaten für n verschiedene Punkte P_1, P_2, P_3 ... aufgenommen, gelangt man zu einem System von n Gleichungen mit zwei zu bestimmenden und n residualen Unbekannten r_j:

$$\begin{aligned} a_{10}^2 + 2a_{10}z_0 - kt_{10} - r_1 &= 0,\\ a_{20}^2 + 2a_{20}z_0 - kt_{20} - r_2 &= 0,\\ &\vdots\\ a_{n0}^2 + 2a_{n0}z_0 - kt_{n0} - r_n &= 0. \end{aligned} \qquad (5)$$

Durch fünf Substitutionen

$$\gamma_j = a_{j0}^2;\ x_1 = z_0;\ \alpha_{1j} = 2a_{j0};\ x_2 = -k;\ \alpha_{2j} = t_{j0} \qquad (6)$$

gelangt man vom speziellen (5) zum allgemeinen Fall (7), der nach [3] gelöst werden kann:

$$\begin{aligned} \alpha_{11}x_1 + \alpha_{21}x_2 + \gamma_1 &= r_1,\\ \alpha_{12}x_1 + \alpha_{22}x_2 + \gamma_2 &= r_2,\\ &\vdots\\ \alpha_{1n}x_1 + \alpha_{2n}x_2 + \gamma_n &= r_n. \end{aligned} \qquad (7)$$

Die Fehlerminimalisierungsbedingung nach dem Gauß-Algorithmus lautet:

$$\sum_{j=1}^{n} r_j^2 = \text{minimal}.$$

Quadrieren der einzelnen Zeilen von (7) und anschließende Summierung liefert

$$\sum_{j=1}^{n} r_j^2 = x_1^2 \sum_{j=1}^{n} \alpha_{1j}^2 + x_2^2 \sum_{j=1}^{n} \alpha_{2j}^2 + 2x_1x_2 \sum_{j=1}^{n} \alpha_{1j}\alpha_{2j}$$
$$+ 2x_1 \sum_{j=1}^{n} \alpha_{1j}\gamma_j + 2x_2 \sum_{j=1}^{n} \alpha_{2j}\gamma_j \qquad (8)$$

und kann unter Verwendung des skalaren Produkts für n-dimensionale Vektoren $\vec{e}$ und $\vec{f}$

$$(\vec{e}\cdot\vec{f}) = (\vec{f}\cdot\vec{e}) = \sum_{1}^{n} e_j \cdot f_j$$

mit $\vec{e} = (e_1, e_2 \ldots e_n)$ und $\vec{f} = (f_1, f_2 \ldots f_n)$

übersichtlich geschrieben werden als

$$(\vec{r}\cdot\vec{r}) = (\vec{\alpha_1}\cdot\vec{\alpha_1})x_1^2 + (\vec{\alpha_2}\cdot\vec{\alpha_2})x_2^2 + (\vec{\gamma}\cdot\vec{\gamma}) +$$
$$2(\vec{\alpha_1}\cdot\vec{\alpha_2})x_1x_2 + 2(\vec{\alpha_1}\cdot\vec{\gamma})x_1 + 2(\alpha_2\cdot\vec{\gamma})x_2 \qquad (9)$$

mit z. B.

$$\alpha_1 = (\alpha_{11}, \alpha_{12} \ldots \alpha_{1n}).$$

Alle skalaren Produkte auf der rechten Seite von (9) sind durch die Meßgrößen festgelegt, wie aus den Definitionen (6) ersichtlich ist. $(\vec{r}\cdot\vec{r})$ hängt also nur von x_1 und x_2 ab.
Die Minimalisierungsbedingungen

$$[\partial(\vec{r}\cdot\vec{r})/\partial x_1]_{x_2} = 0,$$
$$[\partial(\vec{r}\cdot\vec{r})/\partial x_2]_{x_2} = 0$$

führen zu den beiden Normalgleichungen

$$0 = \underbrace{(\vec{\alpha_1}\cdot\vec{\alpha_1})}_{E_{11}}x_1 + \underbrace{(\vec{\alpha_1}\cdot\vec{\alpha_2})}_{E_{12}}x_2 + \underbrace{(\vec{\alpha_1}\cdot\vec{\gamma})}_{E_{13}},$$
$$0 = \underbrace{(\vec{\alpha_2}\cdot\vec{\alpha_1})}_{E_{21}}x_1 + \underbrace{(\vec{\alpha_2}\cdot\vec{\alpha_2})}_{E_{22}}x_2 + \underbrace{(\vec{\alpha_2}\cdot\vec{\gamma})}_{E_{23}},$$

deren Auflösung

$$x_2 = (E_{13}E_{21} - E_{23}E_{11})/(E_{22}E_{11} - E_{12}E_{21}),$$
$$x_1 = -(E_{12}x_2 + E_{13})/E_{11} \qquad (10)$$

ergibt.

Als Kontrolle für die Güte der Ausgleichung kann das mittlere Residuum $\bar{\varrho}$ eingeführt werden. ϱ_1 sei das Residuum der j. Gleichung in (7) nach dem Einsetzen der durch obiges Verfahren ermittelten Werte x_1 und x_2. Dann gilt

$$\bar{\varrho} = \sqrt{(\vec{\varrho} \cdot \vec{\varrho})/n} \leqslant \varrho_{max}.$$

Je kleiner $\bar{\varrho}$, um so genauer sind die berechneten Werte.

2. «Differentielles» Verfahren

Im ebenen Teil der Schicht sind zwei Marken P_0 und P_z vorgegeben (Abb. 2), deren Distanzen von der Eintauchlinie z_0 bzw. z betragen. Zu den Zeiten t_0 bzw. t_z werden die Punkte von der Fließmittelfront erreicht. Meßbar seien ebenfalls nur Orts- und Zeitdifferenzen, also $(t_z - t_0)$ und $(z - z_0)$. Wandert die Front weiter, so erreicht sie nach der Zeit t_{z+x} die Marke P_{z+x}.

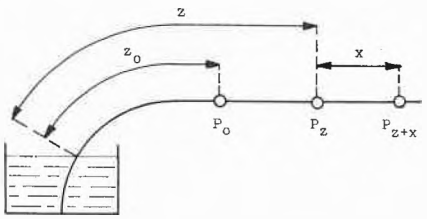


Abb. 2. Differentielles Verfahren; Erklärungen im Text

Mit den Definitionen

$$\Delta z = z - z_0,$$
$$\Delta t_z = t_z - t_0$$

läßt sich eine Gleichung analog (4) formulieren:

$$\Delta t_z = \frac{2z_0}{k} \Delta z + \frac{1}{k} (\Delta z)^2. \qquad (11)$$

Wird in (11) anstelle von Δz das Argument $(\Delta z + x)$ eingesetzt, d.h. das Zeitintervall berechnet, das das Fließmittel benötigt, um von P_0 nach P_{z+x} zu wandern,

$$\Delta t_{z+x} = \frac{2z_0}{k} (\Delta z + x) + \frac{1}{k} (\Delta z + x)^2,$$

so ergibt die Differenz zu (11)

$$t_{z+x} - t_z = \frac{2x}{k} \Delta z + \frac{2z_0 x}{k} + \frac{x^2}{k} \qquad (12)$$

die Zeit für die Wanderstrecke x wieder.
Sofern x = konstant, ist (12) eine lineare Gleichung:

$$t_{z+x} - t_z = b \cdot \Delta z + a \qquad (13)$$

mit

$$a = \frac{2z_0 x + x^2}{k},$$

$$b = \frac{2x}{k}. \qquad (14)$$

Eine Gerade vom Typ (14) wird experimentell erhalten, wenn n äquidistante Punkte vorgegeben werden und die Zeiten für die dazwischen liegenden Teilstrecken gemessen werden. Im rechtwinkligen Koordinatensystem werden auf der Abszisse die Δz-Werte, auf der Ordinate beim Ort des Intervallbeginns die zum Durchlaufen eines (oder mehrerer) Intervalls benötigten Zeiten eingezeichnet (Abb. 3). Für alle Punkte mit derselben Intervallzahl (also x = konstant!) müssen sich Geraden ergeben, aus denen durch lineare Regression die ausgeglichenen Größen $\bar{b}$ und $\bar{a}$ berechnet werden können. Daraus ergeben sich die Unbekannten als

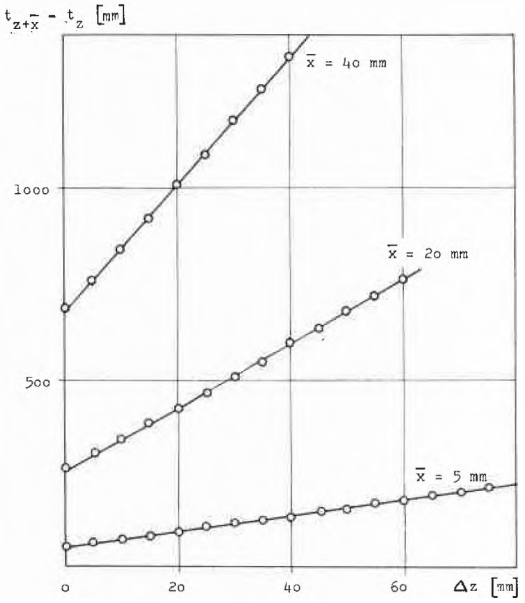


Abb. 3. Experimentelle Werte und Ausgleichsgeraden für verschiedene Intervalle $\bar{x}$ nach dem differentiellen Verfahren

$$\bar{k} = \frac{2\bar{x}}{\bar{b}}; \quad \bar{z}_0 = \frac{\bar{a} \cdot \bar{k}}{2\bar{x}} - \frac{\bar{x}}{2}; \quad \text{mit } x = \bar{x} \pm \Delta\bar{x}. \qquad (15)$$

3. Beispiel

Alle Berechnungen wurden auf einem Computer Hewlett-Packard 2114 A ausgeführt. Die Meßwerte (Tabelle 1) wurden für ein Stück DC-Alurolle Kieselgel 60 F 254 Merck bei 20° mit wassergesättigtem Toluol als Fließmittel erhalten.
Das integrale Verfahren liefert folgende Werte:

$\bar{\varrho} = 14{,}93$; $z_0 = 20{,}8$ [mm]; $k = 4{,}83 \pm 0{,}05$ [mm$^2 \cdot$ sec^{-1}].

Mit dem differentiellen Verfahren wurden aus denselben Meßwerten für verschiedene Intervalle $\bar{x}$ die Werte in Tabelle 2 erhalten.
Der große Vorteil des auf der linearen Regression basierenden differentiellen Verfahrens liegt darin, daß ein sich

Tabelle 1. Meßwerte

a_{j0} [mm]	t [sec]	a_{j0} [mm]	t [sec]	a_{j0} [mm]	t [sec]	a_{j0} [mm]	t [sec]
0	0	20	258	40	677	60	1261
5	51	25	346	45	802	65	1431
10	113	30	446	50	946	70	1618
15	181	35	557	55	1097	75	1813
						80	2018

Tabelle 2. Mit dem differentiellen Verfahren erhaltene Werte

$\bar{x}$ [mm]	$\bar{a}$	$\bar{b}$	z_0 [mm]	k [mm² · sec⁻¹]
5,0 ± 0,3	48,0 ± 1,3	2,08 ± 0,03	20,6 ± 2,2	4,80 ± 0,30
20,0 ± 0,3	251,2 ± 1,9	8,38 ± 0,05	20,0 ± 0,8	4,77 ± 0,08
40,0 ± 0,3	669,2 ± 2,4	16,73 ± 0,10	20,0 ± 0,6	4,78 ± 0,05

während des Versuchs ändernder k-Wert graphisch sofort als trendhafte Abweichung von einer Geraden erkannt werden kann. Ein Nachteil ist, daß Längen- und Zeitmeßfehler für die relativ kleinen x-Intervalle stark ins Gewicht fallen. Dem kann zwar durch Verwendung größerer x-Werte begegnet werden; allerdings wird dann die Aussagekraft durch die sinkende Anzahl Meßwerte verringert. Beim integralen Verfahren läßt sich dagegen aus der graphischen Darstellung t_{j0} gegen a_{j0} kaum etwas herauslesen. Punkto Genauigkeit übertrifft jedoch dieses Verfahren das differentielle, weil sich Meßfehler bei den im Vergleich längeren Strecken und Zeiten weniger auswirken können.

Die vorliegende Arbeit wurde durch Mittel des Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung (Kredit Nr. 2526 71) ermöglicht.

Literatur

1 Cameron und Bell, *J. Physic. Chem. 10* (1906) 658.
2 E. W. Washburn, *Physic. Rev. 17* (1921) 273, 374.
3 E. Stiefel, *Numerische Mathematik*, B. G. Teubner, Stuttgart 1965.

M. Schweingruber, Y. Cramer, H. Arm*

Institut für organische Chemie der Universität Bern

* Adresse: Institut für organische Chemie, Erlachstraße 9a, 3000 Bern 9.

Complexes with macrocyclic ligands, VII[1]: Demetallation of Ni^{2+} macrocyclic complexes by cyanide ions*

Summary

The reaction of cyanide with Ni^{2+} macrocyclic complexes proceeds in two separated steps. In a first reaction one can observe the rapid formation of cyanide adducts with 1 : 1 and in some instances 1 : 2 stoichiometry, the spectra and stabilities of which are here reported. In the second step the cyanide adducts react with more CN^- to give $Ni(CN)_4^{2-}$ and the free ligand. Our results indicate striking differencies in rates as well as in mechanisms for the demetallation of the 12-, 13- and 14-membred macrocyclic Ni^{2+} complexes by cyanide ions.

Although the reaction of CN^- with Ni^{2+} macrocyclic complexes has often been used for preparative purposes to displace and isolate the ligand[2], no kinetic study of it has yet been presented. During our investigations on complexes with such macrocyclic tetraamines (Cyclam[3]) we have observed that the rates at which the demetallation (1) occurs, strongly depend on the size of the

$$Ni(Cyclam)^{2+} + 4CN^- \rightleftarrows Ni(Cyclam)(CN)_n^{(2-n)+} + (4-n)CN^- \rightarrow Ni(CN)_4^{2-} + Cyclam \quad (1)$$

* Received June 12, 1975

macrocyclic ring and on the presence or absence of substituents[4–6]. This preliminary communication reports similarities and dissimilarities found when CN^- reacts with the Ni^{2+} complexes of 1,4,7, 10-tetraazacyclododecane (Cyclam 12), 12,12-dimethyl-1,4,7,10-tetraazacyclotridecane (D Cyclam 13), 1,4,8,11-tetraazacyclotetradecane (Cyclam 14) and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (4 Me Cyclam 14). These compounds include on one side complexes with different ring sizes and thus different strains on the coordinated metal ion, on the other side complexes with different degrees of substitution at the coordinating nitrogen atoms. Both factors together are known to determine the structure and geometry at the metal ion. The yellow diamagnetic Ni^{2+} complexes of D Cyclam 13[7] and Cyclam 14[8] have been shown by X-ray structure analysis to be square planar, whereas the blue complex of Cyclam 12 with weak absorption bands at 356 nm (ε = 17.1 M^{-1} cm^{-1}) and 570 nm (ε = 9.6 cm^{-1}) contains octahedrally coordinated Ni^{2+}. 4 Me Cyclam 14 forms

two complexes with Ni^{2+} [6, 9, 10]. One obtained from the reaction of Ni^{2+} and the free ligand has a square pyramidal structure in the crystalline state $(Ni(4MeCyclam\ 14)(C_{4v}))$ [11], the other synthesized by alkylation of $Ni(Cyclam\ 14)^{2+}$ with methyliodide in DMSO/KOH is square planar $(Ni(4MeCyclam\ 14)(D_{4h}))$[12].

In spite of the differencies in their structures all complexes react with CN^- to give pink or mauve cyanide adducts, whose properties such as spectra and stabilities can be studied, whenever the second step of (1) is slow enough. The spectra of the adducts were measured on a Techtron 635 or on a Cary 118 spectrophotometer and are presented in Table 1. Spectrophotometric titrations and in some instances Job curves were used to study the complexation of CN^- with $Ni(Cyclam)^{2+}$. These results are also collected in Table 1.

Table 1. Absorption spectra and stability constants of the cyanide adducts of $Ni(Cyclam)^{2+}$ at 25° and $I = 0.2$

Compound	λ,nm (ε, $M^{-1}cm^{-1}$)	log K
$Ni(Cyclam\ 12)CN^+$	510 (10), 780 (7)	> 3 a) b)
$Ni(DCyclam\ 13)CN^+$	a)	2.18 c)
$Ni(Cyclam\ 14)CN^+$	342 (45.9), 490 (19.7)	4.29 d)
$Ni(Cyclam\ 14)(CN)_2$	480 (10.6), 730 (7.5)	~2.4
$Ni(4MeCyclam\ 14)(D_{4h})CN^+$	368 (98), 558 (54)	7.11
$Ni(4MeCyclam\ 14)(D_{4h})(CN)_2$	e)	3.76
$Ni(4MeCyclam\ 14)(C_{4v})CN^+$	390 (108), 610 (55)	> 3 a) b)

a) Following step too fast to obtain accurate values; b) Job curves indicate 1 : 1 stoichiometry; c) determined kinetically; d) log K = 4.26 at 25° and I = 0.1, F.P.Hinz & D.Margerum, *Inorg. Chem. 13* (1974) 2941; e) solubility too low.

The 1 : 1 compounds of $Ni(Cyclam\ 14)^{2+}$, $Ni(4MeCyclam\ 14)(D_{4h})^{2+}$ and $Ni(4MeCyclam\ 14)(C_{4v})^{2+}$ exhibit two bands in the visible part of their spectra with molar absorptivities between 20 and 108 $M^{-1}\ cm^{-1}$, which could indicate pentacoordination of the metalion. The 1 : 2 adducts of $Ni(Cyclam\ 14)^{2+}$ and $Ni(4MeCyclam\ 14)(D_{4h})^{2+}$ having low intensity bands ($\varepsilon \leqslant 10\ M^{-1}\ cm^{-1}$) are probably octahedral. Both types of geometry have previously been observed for the cyanide adducts of other macrocyclic complexes[13].

The second step of (1) is slower than the formation of the adducts and can be followed spectrophotometrically either by classical means or stopped flow techniques, monitoring the optical density at 268 nm where $Ni(CN)_4^{2-}$ strongly absorbs. Most of our measurements were done under pseudo-first order conditions, using a large excess of cyanide. Some typical values for k_{obs} are given in Table 2 for three different $[CN^-]$.

For $Ni(Cyclam\ 12)^{2+}$, $Ni(DCyclam\ 13)^{2+}$ and $Ni(4MeCyclam\ 14)(C_{4v})^{2+}$ the pseudo-first order rate constants increase with $[CN^-]$ increasing from 10^{-3} to 10^{-1}M. Plots of log k_{obs} as a function of log $[CN^-]$ show that the slope changes from up to three at low $[CN^-]$ to lower values reaching unity slope in some instances at high $[CN^-]$. From the *p*H-dependence of k_{obs} it is clear that HCN is also a reactive species. These observations closely resemble those made on similar reactions between CN^- and other Ni^{2+} complexes and can be explained by similar mechanisms[14]. $Ni(Cyclam\ 14)^{2+}$ and $Ni(4MeCyclam\ 14)(D_{4h})^{2+}$, however, significantly differ in their reactivity toward CN^- when compared to the macrocyclic complexes just described and the other Ni^{2+} complexes studied so far. In the case of $Ni(Cyclam\ 14)^{2+}$ k_{obs} increases linearly from 5.10^{-4}M to about 10^{-2}M to reach a broad maximum. At higher $[CN^-]$ we then find an inhibition by CN^-, which follows the rate law (2). The *p*H-dependence of k_{obs} for the inhibited

$$d[Ni(CN)_4^{2-}]/dt = k_{obs}[Ni(Cyclam\ 14)^{2+}]/[CN^-] \quad (2)$$

reaction additionally indicates that between *p*H 10.5 and 12.5 k_{obs} consists of a *p*H indipendent term and one proportional to $[OH^-]$. The role of OH^- could be explained either by assuming a reactive hydroxide complex or by postulating a conjugate base formed by deprotonation of one of the coordinated amino groups. This would in some way correspond to the reverse of the mechanism postulated for the formation of macrocyclic complexes, for which the conjugate base is needed to reach the square planar geometry[5]. An other indication that the conjugate base of the dicyanide adduct of $Ni(Cyclam\ 14)^{2+}$ could play an important role is the fact that $Ni(4MeCyclam\ 14)(D_{4h})^{2+}$ although forming stable 1 : 1 and 1 : 2 cyanide complexes does not react with further CN^- to the products at a measurable rate.

Table 2. Pseudo-first order rate constants k_{obs} for the demetallation of $Ni(Cyclam)^{2+}$ at 25°, I = 0.2 and *p*H = 10.5

Compound	$-\log k_{obs}(s^{-1})$ at $[CN^-] = 10^{-3}M$	$[CN^-] = 10^{-2}M$	$[CN^-] = 10^{-1}M$
$Ni(Cyclam\ 12)^{2+}$	3.42	2.0	0.95
$Ni(DCyclam\ 13)^{2+}$	1.2	–.3	
$Ni(Cyclam\ 14)^{2+}$	5.0	4.45	5.35
$Ni(4MeCyclam\ 14)(C_{4v})$		3.25	2.25
$Ni(4MeCyclam\ 14)(D_{4h})$		> 7	

The large differencies observed in the kinetics and the rates of the demetallation of the macrocyclic complexes studied are striking in view of the formation of very similar intermediates and products.

References

1 Part VI is the last ref. in 4.
2 D.H. Busch, *Helv. Chim. Acta*, Fasciculus extraordinarius Alfred Werner (1967) 174; N. Curtis, *Coord. Chem. Rev. 3* (1968) 3; L.F. Lindoy and D.H. Busch in *Preparative Inorganic Chemistry* (Ed. W.L. Jolly), Vol. 6, New York 1971, p. 1.
3 Cyclam is here used as abbreviation for all cyclic amines.
4 Th. Kaden, *Helv. Chim. Acta 53* (1970) 617; *54* (1971) 2307; R. Buxtorf and Th. A. Kaden, *Helv. Chim. Acta 57* (1974) 1035; L. Hertli and Th. A. Kaden, *Helv. Chim. Acta 57* (1974) 1897; W. Steinmann and Th. A. Kaden, *Helv. Chim. Acta*, in press.
5 Th. A. Kaden, *Proc. XVI ICCC, Dublin 1974*, p. 3.46.
6 R. Buxtorf, W. Steinmann and Th. A. Kaden, *Chimia 28* (1974) 15.
7 J. Whaters and K. Whittle, *J. Inorg. Nucl. Chem. 34* (1972) 155.
8 B. Bosnich, R. Mason, P. Pauling, G. B. Robinson and M. L. Tobe, *Chem. Commun. 1965*, 97.
9 E. K. Barefield and F. Wagner, *Inorg. Chem. 12* (1973) 2435.
10 F. Wagner, M. Mocella, M. D'Aniello, A. Wang and E. K. Barefield, *J. Amer. Chem. Soc. 96* (1974) 2625.
11 M. D'Aniello, M. Mocella, F. Wagner, E. K. Barefield and J. Paul, *J. Amer. Chem. Soc. 97* (1975) 192.
12 E. K. Barefield, F. Wagner, M. T. Mocella and M. J. D'Aniello, *Proc. XVI ICCC, Dublin 1974*, p. 4.39.
13 Y. M. Curtis and N. F. Curtis, *Austr. J. Chem. 18* (1965) 1933.
14 R. G. Pearson and D. A. Sweigart, *Inorg. Chem. 9* (1970) 1167; G. B. Kolski and D. W. Margerum, *Inorg. Chem. 8* (1969) 1125; G. K. Pagenkopf, *J. Coord. Chem. 2* (1972) 129; G. K. Pagenkopf, *Inorg. Chem. 13* (1974) *1591*; E. J. Billo, *Inorg. Chem. 12* (1973) 2783.

Liselotte Hertli and Thomas A. Kaden

Institut für Anorganische Chemie der Universität, CH-4056 Basel, Switzerland

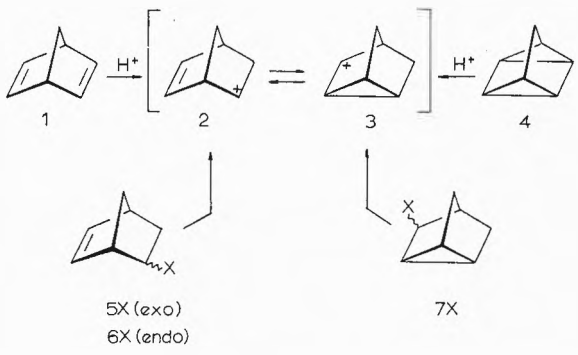
Double Addition of Fluorosulfuric Acid to Norbornadiene and Quadricyclane*

Summary

The same mixture of exo-2-exo-5- (**11**) and endo-2-exo-5-norbornanediyl (**12**) bisfluorosulfates is formed when norbornadiene or quadricyclane is treated with an excess of HSO_3F in SO_2ClF at $-100°$. This observation is rationalized by a mechanism that does not involve the 5-norbornen-2-yl ⇄ nortricyclyl cation rearrangement. Classical 5-substituted 2-norbornyl cations are possible intermediates.

Introduction

The 5-norbornen-2-yl cation intermediate (**2**) has been postulated to intervene in solvolysis of 5-norbornen-2-yl and nortricyclyl derivatives (**5X**, **6X**, **7X**)[1] and in acid additions to norbornadiene (**1**) and quadricyclane (**4**)[2].



Product analysis as well as label scrambling experiments indicate that the cationic intermediate **2**, if formed, equilibrates partially or completely with the nortricyclyl cation intermediate **3**. This latter cation is expected to be much more stable than **2** since **7X** derivatives are more stable than **5X** and **6X** derivatives (by about 1 Kcal/mol[3]) and because the secondary cation **3** benefits from the strong stabilization (about 20 Kcal/mol) of the favorably oriented cyclopropane ring[4]. If the homoconjugative stabilization in **2** is not larger than in 3-cyclopenten-1-yl[5] or 3-cyclohexen-1-yl cations[6], one predicts cation **3** to be at least 10 Kcal/mol more stable than the 5-norbornen-2-yl cation **2**[7]. This energy gap implies that solvent and nucleophile effects (ion pairing phenomena) on the solvolysis of **5X**, **6X**, and **7X** derivatives and acid additions to norbornadiene and quadricyclane must play a dominant role in the formation of the norbornenyl products **5X** if **2** is formed. An other alternative could be that **2** being too high in energy, is never formed as a true intermediate together with **3** in usual, non-photochemical[9] conditions; the **5X** products would then arise from **3** directly or from cationic intermediates different from **2** or **3**, or from non-ionized intermediates. Possible intermediates could be substituted norbornyl cations formed by protonation of the double bond of **5X** and **6X** derivatives. All the numerous experiments reported thus far do not exclude such an hypothesis. An experiment where the 5-norbornen-2-yl cation **2** is generated as a long lived species or, at least, as a true intermediate should be extremely instructive. With this goal in mind we have studied the protonation of norbornadiene and quadricyclane in super-acids and wish to report our preliminary results.

* Received June 13, 1975.

Table 1. NMR spectra of solutions of **11** and **12** in $HSO_3F/SO_2ClF/CD_2Cl_2$ (Bruker HX 90, FT mode, deuterium lock: CD_2Cl_2)

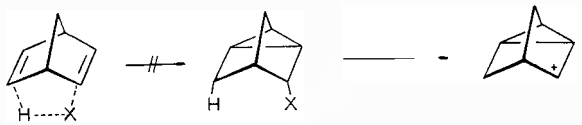
	Compound	δ in ppm (relative intensity; multiplicity; coupling constant in Hz)
^{1}H-NMR (− 70°) ref.: δ_{CDHCl_2} = 5,3 ppm δ_{TMS} = 0,0 ppm	**11** (major)	5,0 (2H; bt); 2,85 (2H; bs); 1,95 and 1,8 (5–6H; m)
	12 (minor)	5,3 (bm); 3,0 to 1,2 (bm)
^{13}C-NMR (− 70°) ref.: $\delta_{CD_2Cl_2}$ = 53,6 ppm δ_{TMS} = 0,0 ppm	**11** (73 ± 3%)	92,7 (2C; d; 164 ± 2); 41,1 (2C; d; 155 ± 3); 32,4 (2C; t; 135 ± 3); 31,6 (1C; t; 130 ± 3)
	12 (27 ± 3%)	93,5 (1C; d; 165 ± 5); 89,7 (1C; d; 165 ± 5); 41,8 (1C; d; 155 ± 5); 40,2 (1C; d; 155 ± 5); 33,1 (1C; t; 130 ± 10); 30,4 (2C; t; 130 ± 10)
^{19}F-NMR (− 56°) ref.: δ_{SO_2ClF} = − 99,1 ppm [26] δ_{CFCl_3} = 0,0 ppm	**11** (74 ± 3%)	− 38,5 (s)
	12 (26 ± 3%)	− 38,7 (s); − 37,3 (s) − 41,8 (HSO_3F)

s = singlet; d = doublet; t = triplet; m = multiplet; b = broad.

Results and Discussion

Recently, Olah and coworkers have prepared the nortricyclyl cation **3** as a stable, directly observable species by dissolving the nortricyclanol (**7-OH**) in "magic-acid" (SbF_5/HSO_3F)[10]. When the quadricyclane **4** is treated in similar conditions, we obtained a black mixture containing only traces of nortricyclyl cation **3** together with polymerized material. Using the same mixture of $SbF_5/HSO_3F/SO_2ClF$ to protonate norbornadiene or 5-norbornen-2-ols (**5-OH**, **6-OH**) yellow solutions were obtained whose ^{1}H-NMR spectra were quite similar to that reported in figure 1, and displayed signals at $\delta < 5{,}3$ ppm (see table 1). This observation is not consistent with a classical cation of type **2**. Moreover, no trace of the known nortricyclyl cation **3** could be detected in the mixtures obtained[11].

The electrophilic addition of protic acids (HX) to olefins has long been considered to involve intermediates with carbocation character[12]. Protonation of one double bond of norbornadiene is expected to yield a cationic intermediate[13] of type **2** that can formally isomerize into **3**. The fact that no trace of **3** could be observed in the solution obtained by protonation of norbornadiene with magic-acid suggests that (a) the direct formation of **3** does not occur and (b) if the homoallyl cation **2** is formed, its isomerization into the corresponding cyclopropylcarbinyl cation **3** is not competitive with other processes yielding the observed mixture.



When CD_2Cl_2 solutions of norbornadiene or quadricyclane were extracted with a 5 to 10-fold excess of HSO_3F in SO_2ClF at − 100° (under vacuum), we obtained clean, slightly yellow solutions whose ^{1}H-, ^{13}C- and ^{19}F-NMR spectra were respectively identical (see table 1). The ^{1}H-NMR spectrum stays unchanged in the range of − 110° to + 10°. At 20° fast decomposition is observed. This spectrum (see figure 1) indicates the presence of a mixture of compounds whose main contributor must have a symmetrical structure or at least, must be equilibrated rapidly on the NMR time scale. Signal integration shows 2 : 2 : 5–6 ratios for the three broad peaks at δ = 5,0; 2,85 and 1,9 ppm respectively. This suggests an eventual bisprotonation. The ^{13}C-NMR spectrum (see table 1) confirms the presence of one main product of symmetrical structure and of a minor product of unsymmetrical structure. The non-proton decoupled ^{13}C-NMR spectrum proves that two protons have been added to the norbornadiene or to the quadricyclane by protonation with an excess of HSO_3F. The δ (^{13}C) values correlate the δ (^{1}H) values and are inconsistent with classical dicationic species. Non-classical, highly stabilized dications could not be excluded before measuring the ^{19}F-NMR spectra of those solutions. Those spectra (see table 1) display the expected signals for SO_2ClF and HSO_3F plus three singlets that can be attributed to a symmetrical bis-fluorosulfate (major) and to a un-

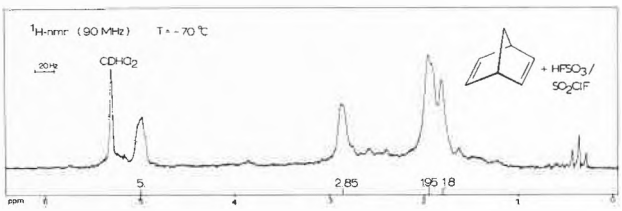


Figure 1. ^{1}H-NMR spectrum of the mixture of **11** and **12** in $HSO_3F/SO_2ClF/CD_2Cl_2$ (the triplet at δ = 0,3 ppm is an impurity [grease]).

symmetrical bis-fluorosulfate (minor)[16]. Thus, the ^{19}F-NMR spectra strongly indicate that covalent products are formed by treatment of norbornadiene and quadricyclane with an excess of super acid such as HSO_3F.

The structures **11** and **12** for the bis-fluorosulfates are deduced by comparison of the ^{1}H-NMR spectra (see fig. 1) with those published for the corresponding diols[18]. **11** and **12** are consistent with the exocis addition of protic acids (HX) to the double bond of norbornadiene and with the reported data on acid additions to 5-norbornen-2-yl derivatives[19]. The absence of stable, bishomoaromatic 2-norbornen-7-yl cation[20] in the solution obtained when using an excess of $SbF_5/HSO_3F/SO_2ClF$ seems to exclude the formation of 2,7-disubstituted norbornane derivatives. Nevertheless, those derivatives can be formed in less acidic media[18].

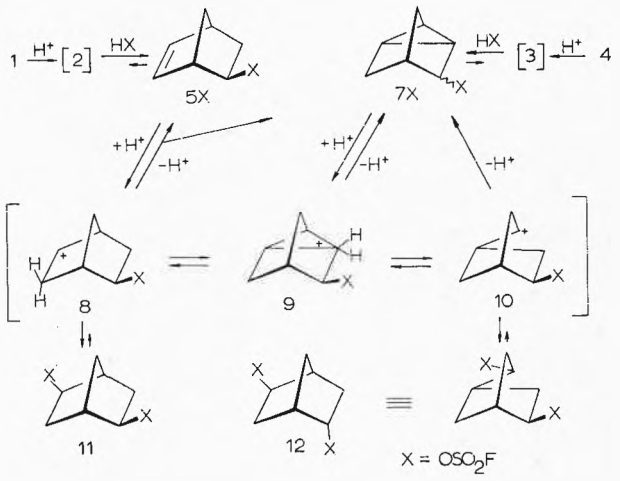
Quenching experiments with H_2O yielded very low yield of the corresponding diols. Attemps to isolate the bis-fluorosulfates **11** and **12** have failed thus far[21].

The mechanism outlined in scheme 1 is proposed to rationalize the formation of **11** and **12**. It is supported by the following experimental results. When one mole of HSO_3F is used to protonate one mole of norbornadiene or one mole of quadricyclane, different mixtures of **5**-OSO_2F and **7**-OSO_2F are formed. By increasing the amount of HSO_3F, **5**-OSO_2F reacts rapidly and yields the 3 : 1 mixture of **11** and **12**, thus confirming the existence of equilibrating intermediates **8** and **10**. **7**-OSO_2F adds one mole of HSO_3F much slower than **5**-OSO_2F, and in presence of a large excess of acid, yields the same mixture of **11** and **12** (by ^{1}H-NMR and ^{19}F-NMR). Due to the inductive effect of the substituent in C(2), the centre C(6) is the most probable site of proton attack on **5X** and **6X**. It appears therefore, that the centre C(2) of **7**-OSO_2F is protonated to yield the bridged cation **9** that leads to the observed products **11** and **12**. One cannot tell whether the non-classical ion **9** is a true intermediate or not. It may well relaxe into the classical 5-substituted norbornyl cations **8** and **10**. According to Brown[14, 24], a non-classical bridged cation should yield a **11** : **12** ratio close to 1 : 1 (a ratio of 3 : 1 is found). The hypothesis of classical cation intermediates seems to be supported by the following observations. The treatment of exo-2-deuterio-endo-5-norbornen-2-ol with an excess of HSO_3F in SO_2ClF furnished a solution whose ^{1}H-NMR spectrum was quite similar to the one reported in figure 1, except for the signal integration that gave 1 : 2 : 5–6 ratios for the three main peaks. By heating this solution up to 20°, no change could be detected in these ratios. This stricking observation does not exclude an equilibration of **11** and **12**; nevertheless it indicates that dissociation of **11** and **12** into cationic species undergoing hydrogen or carbon scrambling is a very slow process in HSO_3F/SO_2ClF. At 10°, no line broadening could be detected in the ^{1}H-NMR spectrum of a mixture of **11** and **12**, thus indicating a minimum energy barrier of 14 to 15 Kcal/mol for a process equilibrating the bis-fluorosulfates.

Temperature dependence studies of the ^{19}F-NMR spectra of the mixture of **11** and **12** in an excess of HSO_3F/SO_2ClF showed a larger line broadening for the signal assigned to the exo-fluorosulfate of **12** ($\delta = -38{,}7$ ppm) than for the other fluorosulfate signals ($\delta = -38{,}5$ and $-37{,}3$ ppm) when increasing the temperature (−20° to 10°). This result indicates that the exo-fluorosulfate of **12** exchanges faster with HSO_3F than the exo-fluorosulfates of **11** and the endo-fluorosulfate group of **12**. This observation also shows that the rearrangement **10** ⇄ **9** ⇄ **8** is slower than the exchange of the exo-fluorosulfate of **12** with the medium, thus indicating that the classical norbornyl cation **10** is slightly more stable than the non-classical norbornyl cation **9**.

According to the mechanism outlined in scheme 1 the norbornenyl-nortricyclyl rearrangement (**2** ⇄ **3**) is not necessary to rationalize the isomerization of **5X** and **7X** products. This process could be acid catalyzed and proceed *via* 5-substituted norbornyl cation intermediates of type **8** and **10**. 1,2-eliminations and 1,3-eliminations[25] would compete to yield the **5X** and **7X** products respectively, as observed in buffered solvolysis of **5X**, **6X** and **7X** derivatives[1]. Our mechanism could also rationalize the label scrambling observed during solvolysis of **5X** and **6X** derivatives, if the 5-substituted norbornyl cation intermediates **8** and **10** equilibrate with the nortricyclyl cation intermediate **3**. In particular, the occurance of equilibrating **8** ⇄ **10** could be responsible of the partial tritium scrambling between C(3,7) and C(6) in the 5-norbornen-2-yl acetate obtained in buffered acetolysis of 3-exo-t-5-norbornen-2-yl brosylate[1b]. Norbornadiene and quadricyclane react with HCl and DCl and are found to furnish the same mixture of **5**-Cl and **7**-Cl. This observation[2b] is also rationalized by our mechanism, although it does not exclude the other mechanisms proposed.

Scheme 1



Conclusion

The 5-norbornen-2-yl cation (**2**) could not be prepared as a stable species by protonation of norbornadiene in super acids such as HSO_3F or HSO_3F/SbF_5 in SO_2ClF. A mixture of covalent 2,5-norbornanediyl bis-fluorosulfates **11** and **12** is formed instead. If the first cationic intermediate formed is **2**, it is an unstable species that does not isomerize into the stable nortricyclyl cation **3**, but reacts further with the medium. Our results conform with theoretical expectations on the stabilization of **2** (an asymmetrical bis-homocyclopropenyl cation) by homoconjugation. This homoconjugative stabilization appears to be small in contrast to the one observed in the isomeric 2-nornornen-7-yl cation (a symmetrical bis-homocyclopropenyl cation).

Because the same mixture of **11** and **12** is obtained by double addition of HSO_3F to norbornadiene and quadricyclane or by HSO_3F addition to the monofluorosulfates **5**-OSO_2F and **7**-OSO_2F, it is proposed that the same equilibrating 5-substituted norbornyl cations **8** and **10** are common intermediates. It is suggested that those intermediates (or their corresponding ion-pairs) can intervene in the product equilibration and label scrambling processes observed when solvolyzing 5-norbornen-2-yl derivatives or when adding acids of type HX to norbornadiene or quadricyclane.

Acknowledgements

The authors wish to thank Professor Dr. H. Dahn (FN 2.772.72) and the "Fonds national suisse de la recherche scientifique" (FN 2.0440.73) for financial support. We are also grateful to Professor Dr. J.-P. Kintzinger and Mr. C. Delseth for help in recording some NMR spectra.

1 a) P. Vogel, R. Delseth and D. Quarroz, *Helv. Chim. Acta 58* (1975) 508 and references cited therein;
b) C. C. Lee and E. C. F. Ko, *J. Amer. Chem. Soc. 96* (1974) 8032;
c) H. C. Brown, M. Ravindranathan and E. N. Peters, *ibid. 96* (1974) 7351.

2 a) T. C. Morrill and B. E. Greenwald, *J. Org. Chem. 36* (1971) 2769 and references cited therein;
b) E. F. Magoon and L. H. Slaugh, *J. Organomet. Chem. 55* (1973) 409.

3 P. v. R. Schleyer, *J. Amer. Chem. Soc. 80* (1958) 1700; S. Winstein and E. M. Kosower, *ibid. 81* (1959) 4399.

4 W. J. Hehre and P. C. Hiberty, *ibid. 96* (1974) 302; D. S. Kabakoff and E. Namanworth, *ibid. 92* (1970) 3234; V. Buss, P. v. R. Schleyer and L. C. Allen, *Top. Stereochem. 7* (1973) 253; R. D. Bach, J. H. Siefert, M. T. Tribble, R. A. Greengard and N. A. LeBel, *J. Amer. Chem. Soc. 95* (1973) 8182.

5 M. Saunders and R. Berger, *ibid. 94* (1972) 4049.

6 G. Seybold, P. Vogel, M. Saunders and K. B. Wiberg, *ibid. 95* (1973) 2045.

7 Unless there is a special stabilizing effect such as homoaromaticity, a secondary homoallyl cation is estimated to be at least 10 Kcal/mol less stable than the corresponding allyl cation[5, 6]. From the values of the rotation barriers found in secondary cyclopropylcarbinyl[4] and allyl cations[8], the stabilization of a secondary carbenium ion by a bissected cyclopropyl group or by a vinyl group can be estimated to about 20 Kcal/mol.

8 N. L. Allinger and J. H. Siefert, *J. Amer. Chem. Soc. 97* (1975) 752; P. v. R. Schleyer, T. M. Su, M. Saunders and J. C. Rosenfeld, *ibid. 91* (1969) 5174.

9 W. Kirmse and R. Siegfried, *Chem. Ber. 105* (1972) 2754.

10 G. A. Olah and G. Liang, *J. Amer. Chem. Soc. 95* (1973) 3792; G. A. Olah, G. Liand, K. A. Babiak and R. K. Murray, jr., *ibid. 96* (1974) 6794; G. A. Olah and G. Liang, *ibid. 97* (1975) 1920.

11 Several investigators have made analogous observations: P. Ahlberg, private communication; J. D. Nichols, Ph. D. Thesis, The Pennsylvania State University, 1971.

12 P. B. D. de la Mare and R. Bolton, *Electrophilic Additions to Unsaturated Systems*, Elsevier, New York, N. Y., 1966.

13 One-step 1,2-dipolar cycloadditions of hydrogen chloride and trifluoroacetic acid to norbornene derivatives have been excluded as a possible mechanism that avoids the formation of a true norbornyl cation intermediate[14]. Molecular orbital symmetry rules also are unfavorable for a one-step molecular addition of protic acid to olefins[15].

14 H. C. Brown and K-T. Liu, *J. Amer. Chem. Soc. 97* (1975) 600, 2469.

15 R. G. Pearson, *Acc. Chem. Res. 4* (1971) 152.

16 The ^{19}F-NMR spectrum of the stable 2-hydroxy-5-norbornen-2-yl cation[17] obtained by protonation of 5-norbornen-2-one in HSO_3F does not display those extra peaks.

17 H. G. Richey, jr. and R. K. Lustgarten, *J. Amer. Chem. Soc. 88* (1966) 3136.

18 P. Ayras and J. Paasivirta, *Suomen Kemistilehti B 42* (1969) 61; J. Paasivirta, *Acta Chem. Scand. 22* (1968) 2200; J. W. H. Faber, *Chem. Abstr. 68* (1968) 21600q.

19 J. Meinwald, J. K. Crandall and P. G. Gassman, *Tetrahedron 18* (1962) 815; E. Kantolahti, *Acta Chem. Scand. 27* (1973) 2667.

20 M. Brookhart, A. Diaz and S. Winstein, *J. Amer. Chem. Soc. 88* (1966) 3135.

21 Solvolysis of 5-norbornen-2-yl brosylates in non-buffered CF_3COOH or CF_3CH_2OH furnished also 2,5-norbornanediyl derivatives[22]. Addition of acids different from HSO_3F to norbornadiene and **5X**, **6X** derivatives is well documented. Depending upon the acidity and the experimental conditions various mixtures of disubstituted norbornanes can be formed together with the usual **5X** and **7X** derivatives[2, 18, 19, 23].

22 P. Vogel and J.-M. Sonney, unpublished results.

23 N. H. Werstiuk and T. Kadai, *J. Chem. Soc. Chem. Commun. 1970*, 1613.

24 H. C. Brown, B. G. Gnedin, Ken'ichi Takeuchi and E. N. Peters, *J. Amer. Chem. Soc. 97* (1975) 610; H. C. Brown, *Acc. Chem. Research 6* (1973) 377.

25 N. H. Werstiuk, *Canad. J. Chem. 53* (1975) 26.

26 P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc. 91* (1969) 7260.

Daniel Quarroz, Jean-Marie Sonney and Pierre Vogel

Institut de chimie organique de l'Université
2, rue de la Barre
CH-1005 Lausanne (Switzerland)