Journal of Fluorine Chemistry 134 (2012) 56–62

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Dications in superacid HF/SbF_5: When superelectrophilic activation makes possible fluorination and/or C–H bond activation

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ARTICLE INFO

Article history:
Received 1 February 2011
Received in revised form 6 April 2011
Accepted 9 April 2011
Available online 25 May 2011

Keywords:
Superacid
Superelectrophile
Functionalization
Fluorination

ABSTRACT

The reactivity of aliphatic amides/ketones/imines and nitriles was studied in superacid HF/SbF_5 in the presence of CCl_4. After the identification of the reaction intermediates by *in situ* NMR experiments, we propose that the sp^3C–H bond functionalization (fluorination) by the superacid system is strongly dependant on the superelectrophilic character of the distonic dicationic intermediates.

1. Introduction

Selective functionalizations of non activated sp^3C–H bonds are among the most desired transformations in organic chemistry. Despite the recent advances made in this field [1], the development of methods for the direct conversion of carbon–hydrogen bonds into carbon–heteroatom bonds remains a critical challenge in organic chemistry. Direct C–H bond functionalization reactions are mainly limited by the inert nature of most carbon–hydrogen bonds and by the requirement to control selectivity. In addition, despite the abundance of literature describing CH activation of alkanes, examples of analogous reactions with functionalized alkanes are relatively scarce [2]. For example, selective direct fluorination of unactivated sp^3 hybridised carbon–hydrogen sites is largely limited to the work of Rozen [3–5] by using fluorine and to the Selectfluor® based electrophilic fluorination developed by Chambers and Sandford [6–8]. In due course of their extensive studies of natural product chemistry in superacids [9,10], Jacquesy et al. showed that aliphatic ketones, amides and imines can be functionalized (fluorinated) by using the HF/SbF_5/CCl_4 system [11,12], making this superacid based method an alternative to the existing ones. In this context, an accurate study of the superelectrophilic activated sp^3C–H bond functionalization in superacid [13] appeared to be important to further develop this chemistry.

In this paper, we report further advances made recently in this field, and we propose that after CH bond activation, the fluorination of the formed carbenium ion is strongly dependent on the nature of the distonic superelectrophile [14].

2. Results and discussion

During his earlier studies on polyprotonated species is superacid, Olah showed that trihalomethyl cations can be prepared and studied in superacidic media [15,16]. Following this work, the reactivity of halomethyl cations in superacid was studied by several groups [17,18]. In these studies, an increase reactivity of chloromethyl cations in hydride abstraction reactions with hydrocarbons in superacid HF/SbF_5 has been shown. To explain this behavior, protosolvation (or complexation by the Lewis acid) of the chlorine atoms in superacid was suggested [19] and confirmed by DFT calculations [20]. By further protonation or Lewis acid induced activation, CCl_3^+ is activated to a superelectrophile. In the presence of a CH bond, due to the σ-donor ability of a shared electron pair (of a σ-bond) *via* two electrons, a three-center bond formation after "$CCl_3^{+•}$" insertion probably occurs, leading to the formation of a carbonium ion. After $CHCl_3$ elimination, a carbenium ion is formed. To summarize the process, activated (by superelectrophilic activation) CCl_3^+ plays the role of hydride abstracting agent (Scheme 1).

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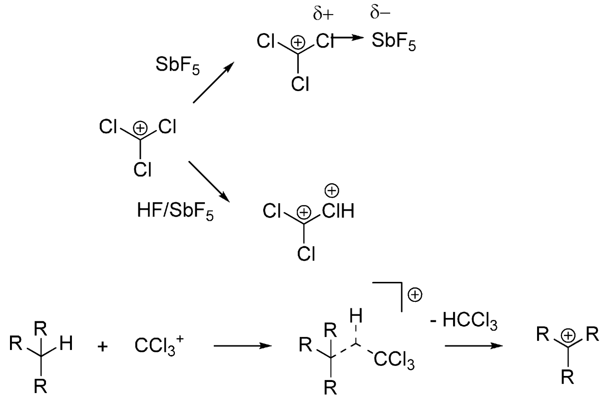
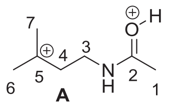
doi:10.1016/j.jfluchem.2011.04.022



Scheme 1. Hydride abstraction with activated CCl_3^+ in HF/SbF$_5$.

Table 1
^{13}C NMR spectral data (CD_3COCD_3 used as external standard) for the amide **1** in HF/SbF$_5$/CCl$_4$ conditions and the calculated ^{13}C NMR data (B3LYP/cc-pVTZ level).



Carbon number	Observed chemical shifts (ppm)	Multiplicity	Calculated chemical shifts (ppm)
1	17.6	CH_3	21.3
2	178.7	C	185.1
3	36.5	CH_2	40.2
4	55.0	CH_2	56.3
5	330.0	C	329.3
6,7	44.2	CH_3	51.9 and 46.6

Functionalized substrates being protonated in superacids, a similar reaction with the superelectrophile should occur on the richest electronic site, far from the protonated functional group. This hypothesis has been demonstrated by Jacquesy and his collaborators by performing selective functionalization of aliphatic amides in HF/SbF$_5$ in the presence of CCl$_4$ [11]. For example, after hydride abstraction and isomerization (or not), amide **1** was functionalized to give the corresponding alcohol **2**, fluorinated compound **3**, arylated product **4** or ester **5** by using various quenching methods (Scheme 2).

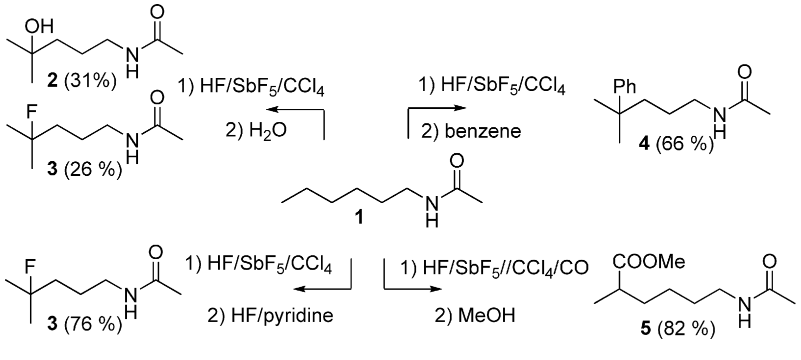
In previous studies [21], we showed that ammonium–carbenium gitonic superelectrophiles (1,3 dications) can be fluorinated in superacid HF/SbF$_5$, despite the very low nucleophilic character of the solvated fluorine in the polymeric anionic form $Sb_nF_{5n+1}^-$ of the superacidic medium [22]. Interestingly the formation of the fluorinated amide **3** after reaction of substrate **1**, seems to indicate that even a distonic carboxonium–carbenium dication, obtained after protonation of the amide function, hydride abstraction and isomerisation, can be fluorinated in this media. To confirm the involvement of this dication in the formation of the fluorinated amide **3**, and the dramatic role of the protonation of the function on the activation of the carbenium electrophilic site toward fluorination, *in situ* NMR experiments were performed. Amide **1** was dissolved in HF/SbF$_5$ (21.6 mol% SbF$_5$) in the presence of CCl$_4$ (1.2 equiv.) and studied by ^{13}C NMR and DEPT experiments at -20 °C. To compare experimental NMR chemical shifts with those from theory, model calculations were also performed on the postulated intermediate [23] (Table 1).

When compound **1** is dissolved in superacid in the presence of CCl$_4$, the dicationic carboxonium–carbenium structure **A** is observed in the ^{13}C NMR spectrum. The observed signals at 330.0 ppm and 178.7 ppm confirmed respectively the presence of the carbenium ion and the protonation of the amide function [29]. This is also confirmed by the observed signals at 55.0 ppm (CH_2) and 44.2 ppm (CH_3) strongly deshielded by the effect of the proximal carbenium ion. These observed chemical shifts in good agreement with the calculated data, strongly support the hypothesis of the involvement of the distonic superelectrophilic carboxonium–carbenium dication **A** in the functionalization (fluorination) of amide **1**. In this case, the electronic withdrawing effect of the protonated amide seems to be sufficient to activate the carbenium ion toward the fluorination process.

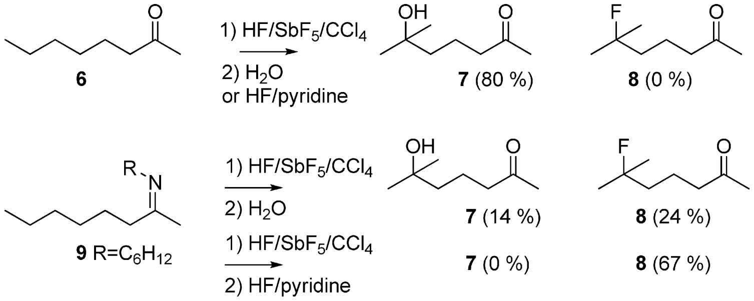
Amide behavior in these conditions prompted us to examine carefully the reactivity of corresponding ketones and imines. Ketone **6** led only to the hydroxylated product **7** after reaction in HF/SbF$_5$ in the presence of CCl$_4$ and hydrolysis, regardless the quenching conditions used (even after quenching with the fluorinating agent HF/pyridine) (Scheme 3) [12]. On the other hand, imine **9** led to a mixture of alcohol **7** and fluorinated product **8**. After treatment of the reaction mixture with HF/pyridine and hydrolysis, the fluorinated product **8** could be selectively synthesized.

The difference in behavior of ketone and imine was attributed to the intermediacy of a six-membered ring carboxonium ion, preventing the substrate from fluorination when ketones react in superacid (Scheme 4).

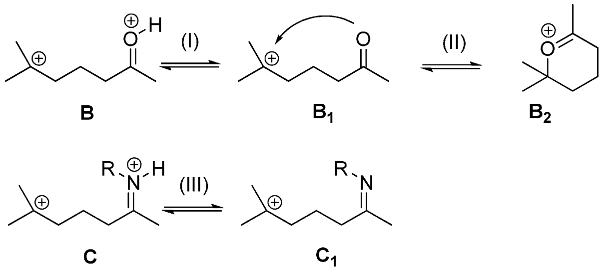
After reaction of ketone **6** in superacid in the presence of CCl$_4$, the dication **B** could be formed. Taking into account a slow exchange rate between the protonated form and the neutral form of the ketone function in superacid [30], the equilibrium (I) was postulated. A stabilization of the carbenium ion $\mathbf{B_1}$ through the formation of a six-membered ring carboxonium ion $\mathbf{B_2}$ could account to explain the absence of fluorination in this case. Then, it appeared that the imino group could be used as a “protecting group” for the ketone function. The obtained protonated imine, less prone to deprotonation, prevented substrate from any undesired



Scheme 2. Functionalization of aliphatic amide in HF/SbF$_5$/CCl$_4$.



Scheme 3. Reactivity of aliphatic ketone and imine in $HF/SbF_5/CCl_4$.

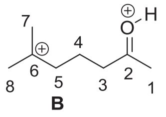


Scheme 4. Postulated intermediates in the reaction of ketone **6** and imine **9** in HF/SbF_5 in the presence of CCl_4.

stabilization by intramolecular cyclisation. As a consequence, dication **C** showed a superelectophilic character, allowing the fluorination process. To characterize the postulated intermediate generated from the sp^3C–H bond activation of the aliphatic substrate, compound **6** was dissolved in HF/SbF_5 (13.6 mol% SbF_5, conditions identical to reaction conditions) in the presence of CCl_4

Table 2

^{13}C NMR spectral data (CD_3COCD_3 used as external standard) for the ketone **6** in $HF/SbF_5/CCl_4$ conditions and the calculated ^{13}C NMR data (B3LYP/cc-pVTZ level).



Carbon number	Observed chemical shifts (ppm)	Multiplicity	Calculated chemical shifts (ppm)
1	27.8	CH_3	32.4
2	245.2	C	250.1
3	40.0	CH_2	43.9
4	16.2	CH_2	19.0
5	57.2	CH_2	57.0
6	333.0	C	331.9
7,8	43.6	CH_3	50.7 and 45.6

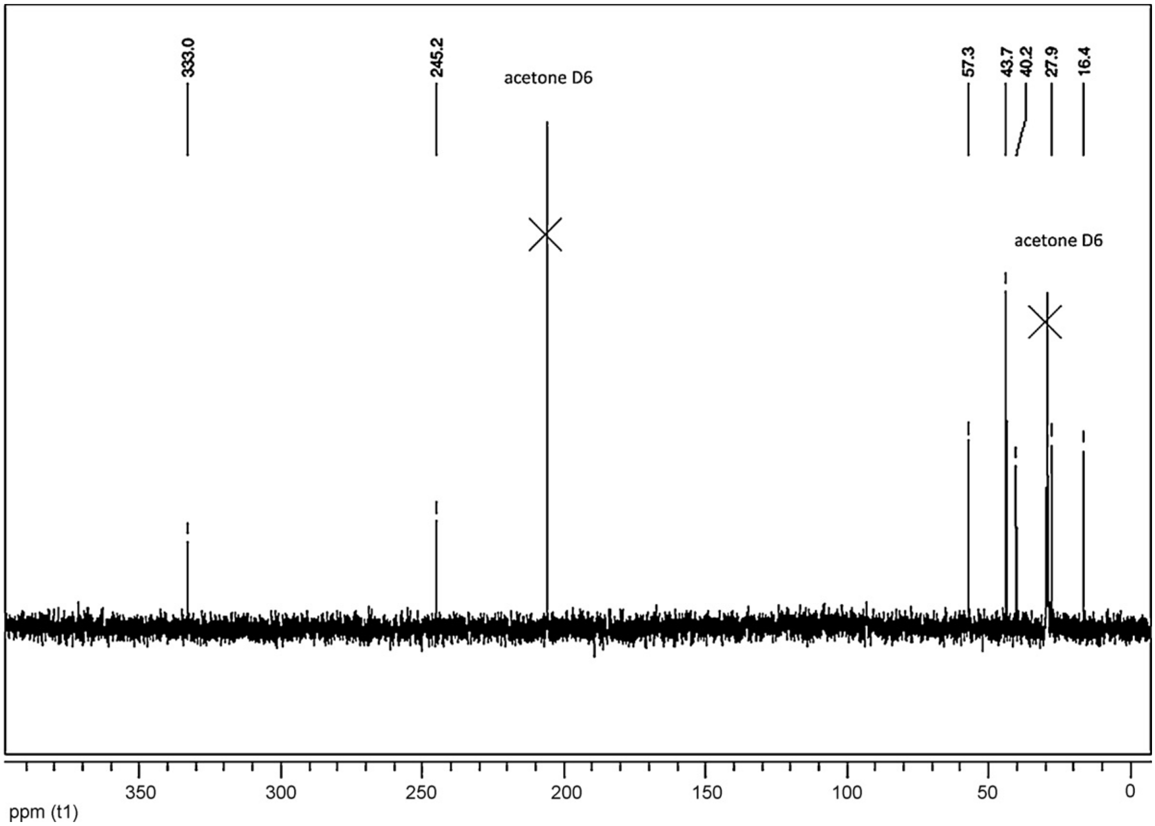
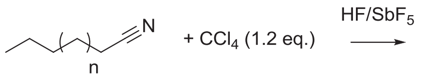
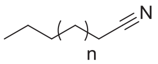
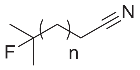
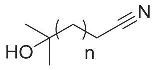


Fig. 1. ^{13}C NMR spectrum of the dication **B** from the reaction of ketone **6** in HF/SbF_5, in the presence of CCl_4 at −20 °C (CD_3COCD_3 is used as external standard).

Table 3
Reaction of nitriles with HF/SbF$_5$/CCl$_4$.[a]



Entry	*n*	Substrate	Products (yield)[b]	
				
1	1	**10**	No reaction	
2	2	**11**	**16** (26)	**17** (29)
3	3	**12**	**18** (17)	**19** (54)
4	4	**13**	**20** (12)	**21** (50)
5	5	**14**	**22** (15)	**23** (33)
6	6	**15**	Complex mixture	

[a] Reaction conditions: HF/SbF5 (mol% SbF$_5$ = 13.6)/CCl$_4$ (1.2 equiv.)/−30 °C/5 min.

[b] Yields obtained after purification by flash-chromatography.

(1.2 equiv.) and studied by ^{13}C NMR and DEPT experiments (Table 2 and Fig. 1). When ketone **6** is ionized in superacid, in the presence of CCl$_4$ at −20 °C, an unambiguous ^{13} C NMR spectrum is observed. All the signals are consistent with the formation of the reactive dicationic electrophile **B**, and are in reasonably good agreement with the calculated chemical shifts. It also should be noted that no signals consistent with the cyclic carboxonium ion **B$_2$** are observed. These data are in good agreement with the observation of similar long-lived carboxonium–carbenium dication in HF/SbF$_5$ (mol% SbF$_5$ = 21.6) reported previously by Brouwer and Kiffen [31].

These data clearly suggest that the superlectrophile **B** is in much greater concentration than **B$_2$** in the media and that the ketone **6** and the more basic imine **8** [32] respectively react through the formation of intermediates **B** and **C**. When the distance between the charge centers are identical, the carboxonium–carbenium dication **B** cannot be fluorinated whereas the iminium–carbenium dication **C** leads to fluorinated product. These data support the hypothesis that superelectrophilic activation of a carbenium ion by a proximal charge is not only dependant on the distance between charges but also depends on the nature of the protonated function and its deactivating effect.

To confirm this hypothesis, a series of various nitriles was submitted to similar reaction conditions (Table 3).

Except for nitrile **10** which is too deactivated to react (Table 3, entry 1), nitriles **11**–**14** showed similar behavior leading to a mixture of fluorinated and hydroxylated products (Table 3, entries 2–5). The limit of the reaction was found with the formation of a complex mixture of compounds after reaction of substrate **15** in superacid (Table 3, entry 6). To improve the yield in fluoro derivative, HF/pyridine (excess) was added at the end of the reaction. However, no significant improvement was observed and alcohols were still present in the crude mixtures. The behavior of the nitriles confirms that the nature of the protonated function, in addition to the repulsion of charges, is also primordial in the distonic superelectrophilic activation. To validate this hypothesis, the identification of the reaction intermediate was crucial. Dicationic intermediates involving protonated nitriles can be directly observed. For example, the dicationic intermediate **D**, coming from the reaction of nitrile **12** in HF/SbF$_5$ (mol% SbF$_5$ = 13.6) in the presence of CCl$_4$ (1.2 equiv.) at −20 °C was observed as a cleanly formed specie (Fig. 2).

In the ^{13}C NMR spectrum, the carbenium resonance is observed at 334.6 ppm and the nitrilium ion one at 96.7 ppm [33]. In addition, the CH$_2$ signal at 60.4 ppm and the CH$_3$ signal at 45.1 ppm confirm the presence of methylene and methyl groups strongly

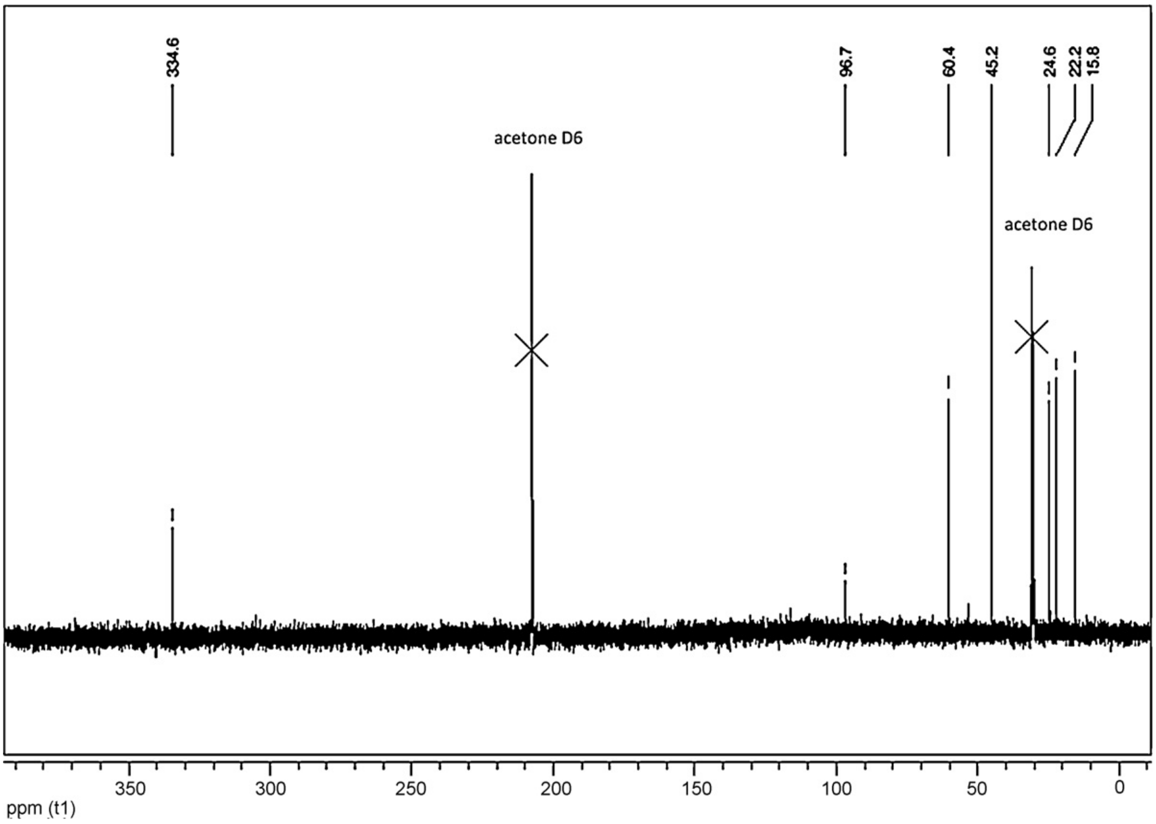
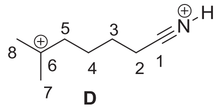


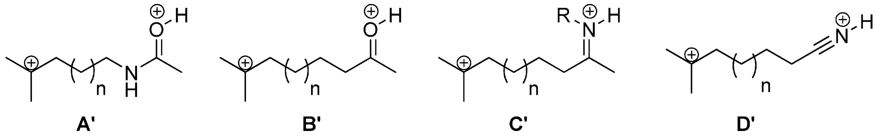
Fig. 2. ^{13}C NMR spectrum of the dication **D** from the reaction of nitrile **12** in HF/SbF$_5$, in the presence of CCl$_4$ at −20 °C (CD$_3$COCD$_3$ is used as external standard).

Table 4

^{13}C NMR spectral data (CD_3COCD_3 used as external standard) for the nitrile **12** in $HF/SbF_5/CCl_4$ conditions and the calculated ^{13}C NMR data (B3LYP/cc-pVTZ level).



Carbon number	Observed chemical shifts (ppm)	Multiplicity	Calculated chemical shifts (ppm)
1	96.7	C	110.0
2	15.7	CH_2	15.2
3 or 4	22.2	CH_2	25.3
4 or 3	24.6	CH_2	26.6
5	60.4	CH_2	59.5
6	334.6	C	332.2
7,8	45.1	CH_3	50.1 and 45.1



Scheme 5. Dicationic intermediates involved in the reaction of aliphatic amides, ketones, imines, and nitriles in HF/SbF_5 in the presence of CCl_4.

deshielded by the effect of the proximal carbenium ion. In addition to these direct observations, the experimental values are in reasonably good agreement with the calculated data (Table 4).

All these data indicate that the dications of general structures **A′**, **B′**, **C′** and **D′** are respectively involved in the functionalization process of the amides, ketones, imines and nitriles in the $HF/SbF_5/CCl_4$ system (Scheme 5).

These results strongly support the following hypothesis: for the studied distonic superelectrophiles, the relative activation of the carbenium ion reacting site is also influenced by the nature of the protonated function in addition to charge repulsion.

3. Conclusion

In conclusion, this study allowed us to confirm that the fluorination of dicationic superelectrophiles in superacid HF/SbF_5 is strongly dependant on the nature of the dication. When the distance between the charges remains an important parameter, by identifying the reaction intermediates involved in the C–H functionalization process, we showed that the nature of the protonated function in the distonic superelectrophile has a strong effect on its superelectrophilic character. This work opens future innovative development for this particular chemistry.

4. Experimental

4.1. General methods

The authors draw the reader's attention to the dangerous features of superacidic chemistry. Handling of hydrogen fluoride and antimony pentafluoride must be done by experienced chemists with all the necessary safety arrangements in place.

Reactions performed in superacid were carried out in a sealed Teflon® flask with a magnetic stirring. No further precautions have to be taken to prevent mixture from moisture (test reaction worked out in anhydrous conditions leads as expected to the same results).

Yields refer to isolated pure products. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded on a 300 MHz (and 400 MHz) Bruker spectrometer.

Mass spectra were measured in the electron impact mode (EI). High resolution mass spectra were performed on a Micromass ZABSpec TOF by the Centre Régional de Mesures Physiques de l'Ouest, Université Rennes (France) when compounds were sufficiently stable.

All separations were done under flash-chromatography conditions on silica gel (15–40 μm). Compounds **2**–**5** and **7**, **8** have been previously reported [11,12].

4.2. Reaction of nitriles in superacidic media

General procedure: To a mixture of SbF_5 (30 g, 0.134 mol) and HF (20 g, 1 mol) maintained at −30 °C in a Teflon® flask, was successively added the substrate (1 g, × mmol) and the carbon tetrachloride (CCl_4, 1.2 equiv.). The reaction mixture was magnetically stirred at the same temperature for 10 min. The reaction mixture was then neutralized with water/ice (100 mL) and sodium carbonate (25 g) and then extracted with dichloromethane (X 3). The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. The products were isolated by column chromatography over silica gel.

4.2.1. Reaction of nitrile 11

After reaction of substrate **11**, following the general procedure, 5-fluoro-5-methylhexanenitrile **16** (298 mg, 26%) and 5-hydroxy-5-methylhexanenitrile **17** (328 mg, 29%) were successively eluted with the mixture dichloromethane/methanol (99/1).

Compound **16**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.35 (6H, d, J = 21.2 Hz, H-6), 1.75 (4H, m, H-3 and H-4), 2.47 (2H, t, J = 6.9 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 17.4 (CH_2, C-3), 19.9 (CH_2, C-2), 23.6 ($2CH_3$, d, J = 25 Hz, C-6), 39.7 (CH_2, d, J = 25 Hz, C-4), 94.5 (C, d, J = 155 Hz, C-5), 119.8 (C, C_1). $^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$, ppm): −138.1 MS (EI, 70 eV): m/z (relative intensity %) 129 (7), 109 (8), 41 (100). HRMS (ESI): Calc for C_6H_9NF: 114.07190, found 114.0721.

Compound **17**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.18 (6H, s, H-6), 1.60 (2H, m, H-3), 1.74 (2H, m, H-4), 2.43 (2H, t, J = 7.2 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 17.2 (CH_2, C-2), 20.3 (CH_2, C-3), 29.0 ($2CH_3$, C-6), 42.1 (CH_2, C-4), 70.0 (C, C-5), 119.7 (C, C-1). MS (EI, 70 eV): m/z (relative intensity %) 128 (3), 59 (100).

4.2.2. Reaction of nitrile **12**

After reaction of substrate **12**, following the general procedure, 6-fluoro-6-methylheptanenitrile **18** (205 mg, 17%) and 6-hydroxy-6-methylheptanenitrile **19** (615 mg, 54%) were successively eluted with the mixture ethylacetate/petroleum ether (30/70).

Compound **18**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.36 (6H, d, *J* = 22.0 Hz, H-7), 1.64 (6H, m, H-3 and H-4 and H-5), 2.40 (2H, t, *J* = 7.1 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 17.0 (CH_2, C-2), 23.0 (CH_2, C-4), 26.0 (CH_2, C-3), 26.9 (2CH_3, d, *J* = 25 Hz, C-7), 40.7 (CH_2, d, *J* = 23 Hz, C-4), 95.3 (C, d, *J* = 164 Hz, C-6), 122.2 (C, C-1). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, ppm): −138.4 MS (EI, 70 eV): *m/z* (relative intensity %) 143 (2), 112 (13), 59 (100).

Compound **19**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.25 (6H, s, H-7), 1.56 (6H, m, H-3 and H-4 and H-5), 2.39 (2H, t, *J* = 7.0 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 17.2 (CH_2, C-2), 23.5 (CH_2, C-4), 25.8 (CH_2, C-3), 29.2 (2CH_3, C-7), 42.8 (CH_2, C-5), 70.7 (C, C-6), 125.9 (C, C-1). MS (EI, 70 eV): *m/z* (relative intensity %) 142 (3), 59 (100). HRMS (ESI): Calc for $C_8H_{14}NO$: 140.10754, found 140.1072.

4.2.3. Reaction of nitrile **13**

After reaction of substrate **13**, following the general procedure, 7-fluoro-7-methyloctanenitrile **20** (143 mg, 12%) and 7-hydroxy-7-methyloctanenitrile **21** (557 mg, 50%) were successively eluted with the mixture dichloromethane/methanol (99/1).

Compound **20**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.31 (6H, d, *J* = 21.2 Hz, H-8), 1.41–1.72 (8H, m, H-3 and H-4 and H-5 and H-6), 2.46 (2H, t, *J* = 7.1 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 23.3 (CH_2, C-5), 25.5 (CH_2, C-3), 26.6 (2CH_3, d, *J* = 25 Hz, C-8), 29.1 (CH_2, C-4), 41.2 (CH_2, d, *J* = 22 Hz, C-6), 94.5 (C, *J* = 164 Hz, C-7), 121.0 (C, C-1). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, ppm): −137.9. HRMS (ESI): Calc for C_8H_8NF: 137.06411, found 137.0627.

Compound **21**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.14 (6H, s, H_8), 1.20 (2H, t, ^{3}J = 7.1 Hz, H_6), 1.41 (4H, m, H_4 and H_5), 1.63 (2H, ^{5}q, ^{3}J = 7.0 Hz, H_3), 2.41 (2H, t, ^{3}J = 7.0 Hz, H_2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 17.0 (CH_2, C_2), 23.0 (CH_2, C_5), 25.8 (CH_2, C_3), 29.0 (CH_2, C_4), 29.1 (2CH_3, C_8), 43.3 (CH_2, C_6), 70.6 (C, C_7), 126.2 (C, C_1). HRMS (ESI): Calc for $C_9H_{16}NO$: 154.12319, found 154.1225.

4.2.4. Reaction of nitrile **14**

After reaction of substrate **14**, following the general procedure, 8-fluoro-8-methylnonanenitrile **22** (163 mg, 15%) and 8-hydroxy-8-methylnonanenitrile **23** (363 mg, 33%) were successively eluted with the mixture dichloromethane/methanol (99/1).

Compound **22**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.30 (6H, d, *J* = 21.1 Hz, H-9), 1.35–1.69 (10H, m, H-3 and H-4 and H-5 and H-6 and H-7), 2.46 (2H, t, ^{3}J = 7.1 Hz, H_2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 16.8 (CH_2, C-2), 23.3 (CH_2, C-6), 25.2 (CH_2, C-3), 26.5 (2CH_3, d, *J* = 25 Hz, C-9), 28.4 (CH_2, C-4), 28.9 (CH_2, C-5), 41.0 (CH_2, d, *J* = 23 Hz, C-7), 95.2 (C, d, *J* = 138 Hz, C-8), 125.0 (C, C-1). ^{19}F{^{1}H} NMR (282 MHz, $CDCl_3$, ppm): −137.6. HRMS (ESI): Calc for $C_{10}H_{18}N$: 152.14392, found 152.1439.

Compound **23**: ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.20 (6H, s, H-9), 1.43–1.65 (10 H, m, H-3 and H-4 and H-5 and H-6 and H-7), 2.36 (2H, t, *J* = 7.0 Hz, H-2). ^{13}C NMR (75 MHz, $CDCl_3$, ppm): 16.9 (CH_2, C-2), 22.7 (CH_2, C-6), 23.7 (CH_2, C-3), 28.3 (CH_2, C-5), 28.9 (2CH_3, C-9), 29.0 (CH_2, C-4), 43.4 (CH_2, C-7), 70.2 (C, C-8), 123.6 (C, C-1). MS (EI, 70 eV): *m/z* (relative intensity %) 168 (28), 59 (100). HRMS (ESI): Calc for $C_8H_{14}NO$: 140.10754, found 140.1072.

Acknowledgements

We thank the region Poitou-Charentes (grant to F.L. and G. C.), the CNRS and the University of Poitiers for financial support.

References

[1] R.H. Crabtree (Ed.), Chem. Rev. 110 (2010), 575–1211, special issue "selective functionalization of CH bonds".

[2] A.J. Vetter, R.D. Rieth, W.W. Brennessel, W.D. Jones, J. Am. Chem. Soc. 131 (2009), 10742–10752, and references cited therein.

[3] S. Rozen, G. Ben-Scushan, J. Org. Chem. 51 (1986) 3522–3527.

[4] S. Rozen, C. Gal, J. Org. Chem. 52 (1987) 2769–2779.

[5] S. Rozen, C. Gal, J. Org. Chem. 52 (1987) 4928–4933.

[6] R.D. Chambers, M. Parsons, G. Sandford, R. Bowden, Chem. Commun. (2000) 959–960.

[7] R.D. Chambers, M. Parsons, G. Sandford, J.S. Moilliet, J. Chem. Soc., Perkin Trans. 1 (2002) 2190–2197.

[8] R.D. Chambers, T. Nakano, M. Parsons, G. Sandford, A.S. Batsanov, J.A.K. Howard, J. Fluorine Chem. 129 (2008) 811–816.

[9] J.C. Jacquesy, in: G.K.S. Prakash, P.R. Schleyer (Eds.), Stable Carbocation Chemistry, John Wiley and Sons, Inc., New York, 1997, pp. 549–574.

[10] J.C. Jacquesy, in: G.A. Olah (Ed.), Carbocation Chemistry, John Wiley and Sons, Inc., New York, 2004, pp. 359–376.

[11] (a) A. Martin, M.-P. Jouannetaud, J.-C. Jacquesy, Tetrahedron Lett. 37 (1996) 2967–2970;
(b) J.-C. Jacquesy, M.-P. Jouannetaud, A. Martin, Bull. Soc. Chim. Fr. 134 (1997) 425–438.

[12] S. Thibaudeau, A. Martin-Mingot, M.-P. Jouannetaud, J.-C. Jacquesy, Tetrahedron 58 (2002) 6643–6649.

[13] G.A. Olah, G.K.S. Prakash, A. Molnar, J. Sommer, Superacid Chemistry, 2nd ed., John Wiley and Sons, Inc., New York, 2009.

[14] G.A. Olah, D. Klumpp, Superelectrophiles and Their Chemistry, John Wiley and Sons, Inc., New York, 2009.

[15] G.A. Olah, L. Heiliger, G.K.S. Prakash, J. Am. Chem. Soc. 111 (1989) 8020–8021.

[16] G.A. Olah, Y.K. Mo, in: G.K.S. Prakash, P.R. Schleyer (Eds.), Carbonium Ions. vol. 5, John Wiley and Sons, Inc., New York, 1976, pp. 2135–2162.

[17] H. Vancik, K. Percac, D.E. Sunko, J. Am. Chem. Soc. 112 (1990) 7418–7419.

[18] J. Sommer, J. Bukala, Acc. Chem. Res. 26 (1993) 370–376.

[19] G.A. Olah, Angew. Chem. Int. Ed. Engl. 32 (1993) 767–922.

[20] G.A. Olah, G. Rasul, A.K. Yudin, A. Burrichter, G.K.S. Prakash, A.L. Christyakov, I.V. Stankevich, I.S. Akhrem, N.P. Gambaryan, M.E. Vol'pin, J. Am. Chem. Soc. 118 (1996) 1446–1451.

[21] (a) S. Thibaudeau, A. Martin-Mingot, M.-P. Jouannetaud, O. Karam, F. Zunino, Chem. Commun. (2007) 3198–3200;
(b) E. Vardelle, D. Gamba-Sanchez, A. Martin-Mingot, M.-P. Jouannetaud, S. Thibaudeau, J. Marrot, Chem. Commun. (2008) 1473–1475;
(c) F. Zunino, F. Liu, C. Berrier, A. Martin-Mingot, S. Thibaudeau, M.-P. Jouannetaud, J.-C. Jacquesy, C. Bachmann, J. Fluorine Chem. 129 (2008) 775–780;
(d) E. Vardelle, A. Martin-Mingot, M.-P. Jouannetaud, C. Bachmann, J. Marrot, S. Thibaudeau, J. Org. Chem. 74 (2009) 6025–6034;
(e) F. Liu, A. Martin-Mingot, M.-P. Jouannetaud, O. Karam, S. Thibaudeau, Org. Biomol. Chem. 7 (2009) 4789–4797.

[22] (a) B. Bonnet, G. Mascherpa, Inorg. Chem. 19 (1980) 785–788;
(b) D. Mootz, K. Bartmann, Angew Chem. Int. Ed. Engl. 27 (1988) 391–392;
(c) J.-C. Culmann, J. Sommer, J. Am. Chem. Soc. 112 (1990) 4057–4058;
(d) J.-C. Culmann, M. Fauconet, R. Jost, J. Sommer, New J. Chem. 23 (1999) 863–867;
(e) J. Sommer, P. Canivet, S. Schwartz, P. Rimmelin, New J. Chem. 5 (1981) 45–53.

[23] All structures were studied using the B3LYP method [24] of the density functionnal theory. The structures were fully optimized using the correlation-consistent double zêta + polarization basis sets of Dunning [25] (B3LYP/cc-pVDZ). Chemical shifts were calculated using the GIAO method [26] (Gauge Including Atomic Orbital) with the correlation-consistent triple zêta + polarization basis sets of Dunning [2] (B3LYP/cc-pVTZ). All calculations were performed with the Gaussian 03 package [27]. The chemical shifts are referred to TMS. Chemical shifts of carbon atoms are scaled according to: $\delta_{corr} = 0.9706\delta_{calc} - 0.89$. This equation was deduced from a comparative study between theoretical values obtained with the method described above and known experimental values for carbocationic structures [28].

[24] (a) Becke's three parameters hybrid method using the LYP correlation functionnal of Lee et al;
(b) A.D. Becke, J. Phys. Chem. 98 (1993) 5648–5652;
(c) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785–789.

[25] T.H. Dunning, J. Chem. Phys. 90 (1989) 1007–1023.

[26] (a) R. Ditchfield, Mol. Phys. 27 (1974) 789–807;
(b) K. Wolinski, J.F. Hinton, P. Pulay, J. Am. Chem. Soc. 112 (1990) 8251–8260.

[27] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford, CT, 2004 .

[28] V. Vrcek, O. Kronja, H.-U. Siehl, J. Chem. Soc. Perkin Trans. 2 (90) (1999) 1317–1321.
[29] D.A. Klumpp, R. Rendy, Y. Zhang, A. Gomez, A. McElrea, Org. Lett. 6 (2004) 1789–1792, and references cited therein.
[30] G.A. Olah, M. Calin, D.H. O'Brien, J. Am. Chem. Soc. 89 (1967) 3586–3590.
[31] D.M. Brouwer, A.A. Kiffen, Recl. Trav. Chim. Pays-Bas 92 (1973) 906–914.
[32] G.A. Olah, P. Kreienbühl, J. Am. Chem. Soc. 89 (1967) 4756–4759.
[33] The observed upfield shift of the resonance of the nitrilium carbon is in accordance with previously reported 13C NMR data for nitrilium ions, please see:
(a) S. Saito, Y. Sato, T. Ohwada, K. Shudo, J. Am. Chem. Soc. 116 (1994) 2312–2317;
(b) Y. Sato, M. Yato, T. Ohwada, S. Saito, K. Shudo, J. Am. Chem. Soc. 117 (1995) 3037–3043;
(c) S. Nakamura, H. Sugimoto, T. Ohwada, J. Org. Chem. 73 (2008) 4219–4224.