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On the synthesis and structure of reactive halonium ions†

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Fluorinated diethyl and dipropyl halonium salts, $[Br(CH_2CF_3)_2][WCA]$ **1Br**, $[I(CH_2CHF_2)_2][WCA]$ **2I** and $[X(CH_2CH_2CF_3)_2][WCA]$ (X = Br **5Br**, I **5I**; WCA = $[Sb(OTeF_5)_6]^-$), were synthesized *via* fluoroalkylation or oxidation of bromofluoro and iodofluoro alkanes. The molecular structures of **1Br** and **2I**, as well as a second different solid-state structure of the previously reported chloronium salt **1Cl**, were determined by single-crystal X-ray diffraction. Additionally, the oxidation of 2-chloro-1,1,1-trifluoropropane $CHCl(CH_3)(CF_3)$ led to the formation of a highly reactive compound that activates isobutane to form the *tert*-butyl cation $[C_4H_9]^+$. Although the product could not be directly observed due to its thermal instability and low solubility, quantum-chemical calculations suggest the formation of an asymmetric chloronium ion with trifluoro *n*-propyl and isopropyl side chains.

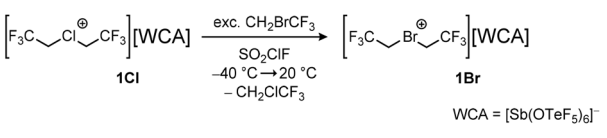
Introduction

Numerous stable diaryl and aryl-alkyl halonium ions have been reported in the literature. For example, iodonium salts derived from these compound classes are widely employed as efficient aryl or alkyl transfer reagents for electron-rich nucleophiles.[1] However, the chemistry of diaryl and aryl-alkyl bromonium salts remains largely underexplored, whereas recent studies by Miyamoto and Uchiyama have highlighted the use of diaryl chloronium salts as potent arylation agents.[2] A variety of stable diaryl halonium ions have been reported, but compounds containing dialkyl halonium ions are still rare. Since the early studies by Olah in this field,[3–6] only a few reports on the synthesis and application of these reactive ions can be found, with the noteworthy report on the first $[C–F–C]^+$ fluoronium ion in solution and the solid state.[7] This ion exhibits a sophisticated cage-like structure and is obtained by fluoride abstraction from the difluorinated double-norbornyl type precursor. The preparation of simpler dimethyl halonium ions $[X(CH_3)_2]^+$ (X = Cl, Br, I) can be achieved using multiple pathways such as methylation,[3–5,8] protonation,[6,9] halide abstraction[3–5] or halide oxidation[10,11] of the corresponding halomethane CH_3X. These dimethyl halonium ions are powerful electrophilic methylation reagents with increasing reactivity in the order $[I(CH_3)_2]^+ < [Br(CH_3)_2]^+ < [Cl(CH_3)_2]^+$.[6] Recently, our group reported on the synthesis of the fluorinated dialkyl halonium salts $[X(CH_2CF_3)_2][E(OTeF_5)_n]$ (X = Cl, I; E = Al, $n = 4$; E = Sb, $n = 6$).[10] While the iodonium salts are able to alkylate weak nucleophiles like 2,6-difluoropyridine, the chloronium salts showed exceptionally high reactivity, not only acting as fluoroalkyl transfer reagents but also in the activation of alkanes like *n*-pentane or *n*-butane, yielding branched carbocations.

To follow up on this chemistry, we were interested in the synthesis of more fluorinated dialkyl halonium salts with various alkyl substituents. The hitherto unknown fluorinated dialkyl bromonium salts are especially interesting, with an expected higher alkylation power than iodonium salts combined with a higher stability and more controlled reactivity than chloronium salts.

Results and discussion

The bromonium salt $[Br(CH_2CF_3)_2][Sb(OTeF_5)_6]$ **1Br** is obtained by the reaction of $[Cl(CH_2CF_3)_2][Sb(OTeF_5)_6]$ **1Cl** with CH_2BrCF_3 (Scheme 1). After an excess of CH_2BrCF_3 is condensed onto a solution of **1Cl** in SO_2ClF at −196 °C, the reaction mixture is warmed up to −40 °C and then slowly warmed up further to 20 °C over the time of one hour. Removing all volatiles under reduced pressure yields **1Br** as a colorless powder (78%). The bromonium salt is stable at room temperature for hours but decomposes overnight in an SO_2ClF solution.



Scheme 1 Synthesis of the bromonium salt **1Br**.

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The ^{1}H and $^{13}C\{^{1}H,^{19}F\}$ NMR spectra of **1Br** ($\delta(^{1}H)$ = 5.65 ppm, $^{1}J_{C-H}$ = 164 Hz; $\delta(^{13}C\{^{1}H,^{19}F\})$ = 54.7 ppm, 120.1 ppm) show the expected low-field shift of the signals of the methylene group compared to the starting material CH_2BrCF_3 ($\delta(^{1}H)$ = 4.08 ppm; $\delta(^{13}C\{^{1}H\})$ = 25.2 ppm, 123.6 ppm). The ^{19}F NMR spectrum shows the triplet signal of the CF_3 group in the bromonium cation at −66.1 ppm and the signal of the collapsed AB_4 spin system of the $OTeF_5$ groups in the antimonate anion at −41.9 ppm. The complex signal of the antimonate anion has previously been discussed in detail in the literature.[12] Single crystals of **1Br** suitable for X-ray diffraction could be obtained by dissolving the compound in SO_2ClF and condensing isobutane at −196 °C onto the frozen solution. The layered sample was immediately stored in a −80 °C freezer. Compound **1Br** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 1). It marks the first obtained molecular structure of an acyclic dialkyl bromonium salt, with the only other reported dialkyl structure showing a three-membered cyclic bromonium moiety connected to 2,2′-biadamantane.[13] The anion in **1Br**, which has already been described in detail in literature,[12,14] consists of an antimony center octahedrally coordinated by six $OTeF_5$ moieties. The $[Br(CH_2CF_3)_2]^+$ cation forms a halogen bond with one of the two σ-holes on the bromine atom and a co-crystallized SO_2ClF molecule (d(Br1–O12) = 297.34(36) pm). A second Br1–O8 bond length below the sum of their van-der-Waals radii (337 pm) with 323.01(36) pm is observed, but does not appear in a specific direction. The CF_3 groups point in opposite directions with a torsion angle C1–C2–C3–C4 of 140.4(3)°. The C2–Br1–C3 bond angle is 101.82(16)° and the C–Br bond lengths are 195.8(4) pm and 195.7(3) pm and are in the range of C–Br distances in bromofluoro alkanes.[15] Our group has previously reported the molecular structure of the lighter homolog, the chloronium salt **1Cl**,[10] which crystallized in the same space group ($P\bar{1}$) but in a different unit cell than **1Br**. However, while further studying the chloronium salt, a coincidence led to the isolation of colorless crystals of **1Cl**. This newly recorded molecular structure of **1Cl** is isostructural to that of **1Br** (Fig. 1). Compared to the Cl–C bond lengths (182.1(5) pm and 181.9(5) pm) in the chloronium cation, the Br–C bond lengths are elongated by about 14 pm.

The halogen oxygen distances between the halonium cation and the SO_2ClF molecules (**1Cl**: 300.21(46) pm and 314.49(44) pm) are in a similar range. The co-crystalized molecules of SO_2ClF can be removed under reduced pressure. The absence of solvent is observed in the IR spectrum of the halonium salts (Fig. S24†). Due to their structural similarities, **1Cl**, **1Br** and the recently reported iodonium salt $[I(CH_2CF_3)_2][Sb(OTeF_5)_6]$ **1I**[10] show comparable signals in the IR spectra. Signals corresponding to the halonium cations experience a slight red-shift with increasing sizes of the central halogen atom (Fig. S25†).

With the successful isolation of the halonium ions ($[X(CH_2CF_3)_2]^+$ X = Cl, Br, I), we were interested in the synthesis of differently substituted fluoroethyl halonium salts. To achieve that, we reacted the chloronium salt **1Cl** with an excess of CH_2ICHF_2 in SO_2ClF. The reaction does not yield the asymmetric iodonium cation $[I(CH_2CF_3)(CH_2CHF_2)]^+$ but the symmetric $[I(CH_2CHF_2)_2]^+$ cation (Scheme 2a). Most likely, the asymmetric cation is formed *in situ* but is able to selectively transfer the less fluorinated alkyl chain CH_2CHF_2 to another molecule of CH_2ICHF_2, yielding the symmetric cation in **2I** (91%). This result stands in contrast to the work of Minkwitz on fluorinated dialkyl iodonium salts, who was able to isolate the asymmetric salt $[I(CF_3)(CH_3)][MF_6]$ (M = As, Sb) (Scheme 2b).[16] The product is obtained by methylation of CF_3I, which is used in excess, by the strong methylation system CH_3F/SbF_5 in SO_2. In this case, the CF_3 group cannot be transferred from the asymmetric iodonium cation, as the resulting CH_3I is more nucleophilic than CF_3I, preventing the formation of a symmetric cation.

The ^{1}H and $^{13}C\{^{1}H,^{19}F\}$ NMR spectra of **2I** show the signals of the methylene group at $\delta(^{1}H)$ = 5.16 ppm and $\delta(^{13}C\{^{1}H\})$ = 37.4 ppm and the signals of the CHF_2 group at $\delta(^{1}H)$ = 6.42 ppm and $\delta(^{13}C\{^{1}H\})$ = 109.9 ppm. The ^{19}F NMR spectrum shows the doublet of triplet signal of the CHF_2 group at −109.8 ppm with coupling constants of $^{2}J_{F-H}$ = 16.7 Hz and $^{3}J_{F-H}$ = 1.8 Hz and the signal of the collapsed AB_4 spin system of the $OTeF_5$ groups in the antimonate anion at −41.9 ppm.

Single crystals of **2I** suitable for X-ray diffraction could be obtained by dissolving the compound in SO_2ClF, layering the

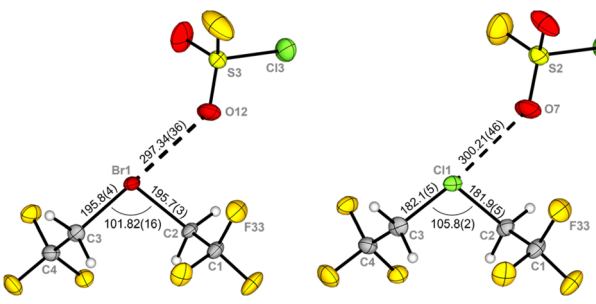
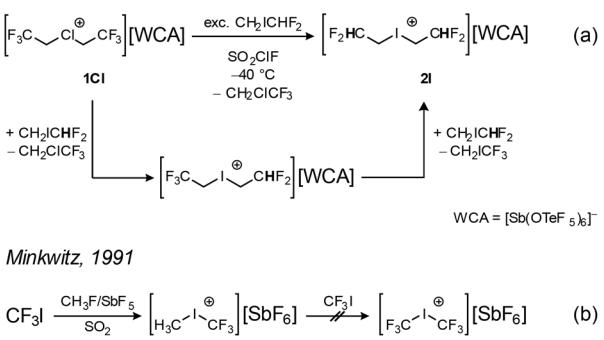


Fig. 1 Molecular structure of the bromonium cation in **1Br** (left) and the isostructural chloronium cation in **1Cl** in the solid state. Two of the three co-crystalized solvent molecules SO_2ClF and the anion $[Sb(OTeF_5)_6]^-$ are omitted for clarity. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: **1Br** C1–C2 151.4(5), C3–C4 151.4(5), C1–C2–C3–C4 140.4(3); **1Cl** C1–C2 1.507(7), C3–C4 1.517(7), C1–C2–C3–C4 141.0(4). For crystallographic details see ESI.†



Scheme 2 Synthesis of the iodonium salt **2I** (a) and the asymmetric iodonium salt $[I(CH_3)(CF_3)][SbF_6]$ (b).

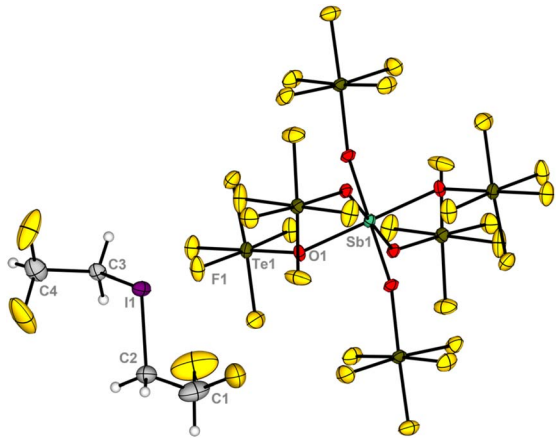


Fig. 2 Molecular structure of the iodonium salt **2I** in the solid state. Displacement ellipsoids set at 50% probability. For crystallographic details see ESI.†

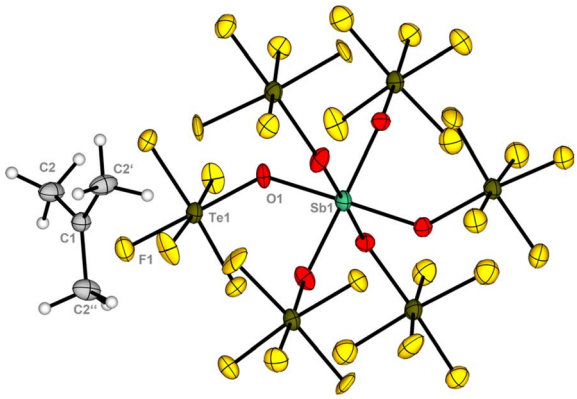


Fig. 3 Molecular structure of the *tert*-butyl salt **3** in the solid state. Displacement ellipsoids set at 50% probability. For crystallographic details see ESI.†

solution with *n*-pentane and storing the sample at −80 °C. Compound **2I** crystallizes in the triclinic space group $P\bar{1}$ (Fig. 2). The cation is disordered in the structure, preventing an accurate analysis of the bond length and angles.

In addition to the partially fluorinated diethyl halonium salts, we were interested in the synthesis of dipropyl derivatives. Our first attempts focused on the oxidation of 2-chloro-1,1,1,3,3,3-hexafluoropropane $CHCl(CF_3)_2$ to obtain a highly fluorinated diisopropyl chloronium salt. Unfortunately, $CHCl(CF_3)_2$ shows a high resistance towards strong oxidizers. While the xenonium salt $[XeOTeF_5][Sb(OTeF_5)_6]$ is able to oxidize the chlorine atom of CH_2ClCF_3, it does not in the case of $CHCl(CF_3)_2$ to yield the desired chloronium salt. Similar limitations have been observed by Schrobilgen, who showed that $[XeOTeF_5][Sb(OTeF_5)_6]$ is able to oxidize $CFCl_3$ and CF_2Cl_2, yielding chlorofluoro carbocations, but is unreactive towards the higher fluorinated CF_3Cl.[17] Therefore, we replaced one electron-withdrawing CF_3 group in $CHCl(CF_3)_2$ with a CH_3 group. With this adjustment, the xenonium salt $[XeOTeF_5][Sb(OTeF_5)_6]$ oxidizes the Cl atom in 2-chloro-1,1,1-trifluoropropane $CHCl(CH_3)(CF_3)$, to yield a highly reactive, temperature-sensitive colorless solid. Upon condensing $CHCl(CH_3)(CF_3)$ onto the characteristically yellow xenonium salt solution in SO_2ClF and warming the mixture up to −60 °C, discoloration and the precipitation of the product is observed. The low solubility in SO_2ClF at low temperatures prevented the direct observation of the product *via* low temperature NMR spectroscopy. The high reactivity of the product led us to believe that a novel chloronium salt was obtained in this reaction.

The crystallization of the product presented significant challenges, as no suitable crystals for X-ray diffraction could be obtained from a solution of SO_2ClF. The previously reported method for crystallizing fluorinated alkyl chloronium salts was unsuccessful in this instance.[10] However, when an SO_2ClF solution of the product was layered with isobutane, colorless crystals were isolated, which were identified as the *tert*-butyl salt $[C_4H_9][Sb(OTeF_5)_6]$ **3**. The compound crystalizes in the trigonal space group *R*3 (Fig. 3). The *tert*-butyl cation shows a trigonal planar structure with C–C bond lengths of 1.445(9) pm and C–C–C bond angles of 119.99(3)°. The obtained values are in good agreement with previously reported structures of the *tert*-butyl cation.[18–20]

The activation of alkanes confirms the exceptionally high reactivity previously reported for fluorinated dialkyl chloronium salts or highly fluorinated carbocations like the perfluoro trityl cation.[21] For example, the chloronium salt **1Cl** has been used to activate *n*-pentane, *n*-butane and cyclohexane to yield tertiary carbocations stabilized by the weakly coordinating $[Sb(OTeF_5)_6]^-$ anion.[10] Interestingly, isobutane showed no reactivity towards **1Cl**, indicating a higher reactivity of the newly obtained chloronium salt.

As the direct characterisation of the product resulting from the oxidation of $CHCl(CH_3)(CF_3)$ was unsuccessful, we added an electrophile scavenger to the obtained suspension to explore its alkylation ability. Pentafluoropyridine was chosen in this case as it was shown before that it reacts with the dimethyl chloronium salt $[Cl(CH_3)_2][Al(OTeF_5)_4]$ and **1Cl** to form room temperature stable pyridinium salts.[10,22] Upon addition of a few drops of the pyridine to the cold suspension, a color change to dark red, indicating the formation of a pyridinium ion, was observed. The reaction mixture was warmed up to room temperature and all volatiles were removed under reduced pressure.

To our surprise, the NMR analysis of the reaction product shows the formation of the pyridinium salt $[F_5C_5N(CH_2CH_2CF_3)][Sb(OTeF_5)_6]$ **4** (97%), which does not contain a trifluoro isopropyl but rather a trifluoro *n*-propyl ($CH_2CH_2CF_3$) motive (Fig. 4). The two H_A atoms of the CH_2 group connected to the nitrogen atom show the characteristic low field shift of alkylated pentafluoropyridine.[10,22] The splitting pattern of the signal is due to a coupling of H_A to H_B and the *ortho*-fluorine atoms F_o on the pyridine ring, leading to a triplet of triplets ($^3J_{H-H} = 5.95$ Hz, $^4J_{H-F} = 2.8$ Hz). Furthermore, a coupling of the CF_3 group to H_B ($^3J_{H-F} = 9.55$ Hz) and a long-range coupling to F_o ($^6J_{F-F} = 3.8$ Hz) and F_m ($^7J_{F-F} = 0.75$ Hz) is observed.

The obtained data lead us to believe that the reaction product of $[XeOTeF_5][Sb(OTeF_5)_6]$ and $CHCl(CH_3)(CF_3)$ is not

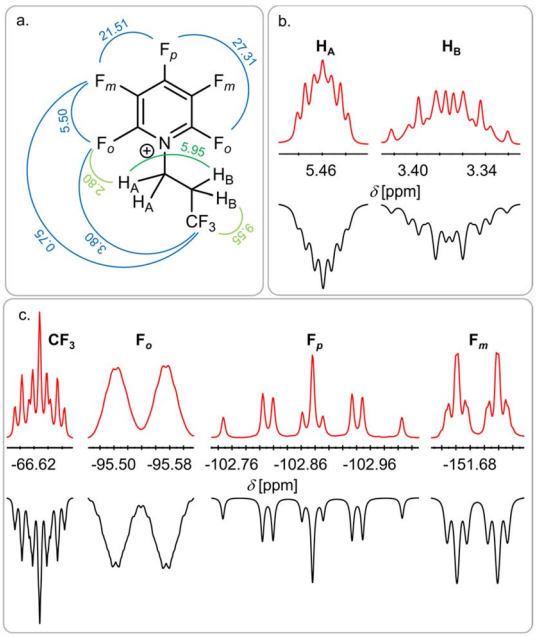


Fig. 4 Structure of the obtained pyridinium ion with the observed coupling constants in Hz (a) and the corresponding signals in the ^{1}H NMR spectrum (b) and the ^{19}F NMR spectrum (c). Red: experimental spectrum, black: simulated spectrum. The full spectrum can be found in the ESI (Fig. S13).†

the symmetric isopropyl but rather an *n*-propyl substituted chloronium salt. Quantum-chemical calculations have been performed to explain the formation of this elusive chloronium ion.

When optimizing the structure of the secondary carbocation $[CH(CH_3)(CF_3)]^+$ that should result from the initial oxidation of $CHCl(CH_3)(CF_3)$, we observe a migration of one hydrogen atom of the CH_3 group towards the secondary carbon atom **cat1** (Fig. 5). We assume the CF_3 group destabilizes the positive charge at the secondary carbon atom. As a result, the C1–C2 bond shows an increased double bond character (C1–C2 bond length 137.6 pm, NBO bond order 1.43). The hydrogen atom is positioned above the C1–C2 bond, resulting in comparable C1–H and C2–H bonds lengths and NBO bond orders. The C1 and C2 atoms possess slightly negative Mulliken charges, allowing to describe

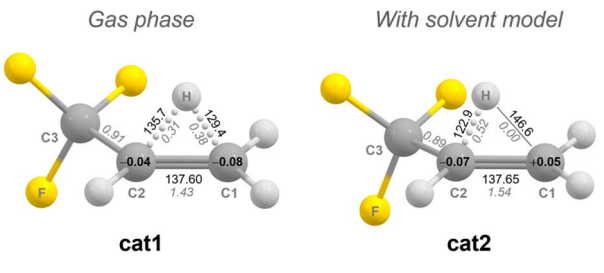


Fig. 5 Calculated structures with selected bond lengths, bond orders (italics) and atomic Mulliken charges of the carbocationic intermediate **cat1** in the gas phase and **cat2** with a solvent model applied formed by the oxidative halide abstraction of $CHCl(CH_3)(CF_3)$ with $[XeOTeF_5][Sb(OTeF_5)_6]$ (B3LYP-D3(BJ)/cc-pVTZ). Bond lengths are given in pm.

cat1 as a trifluoropropene molecule, with a proton coordinated to the C1–C2 bond.

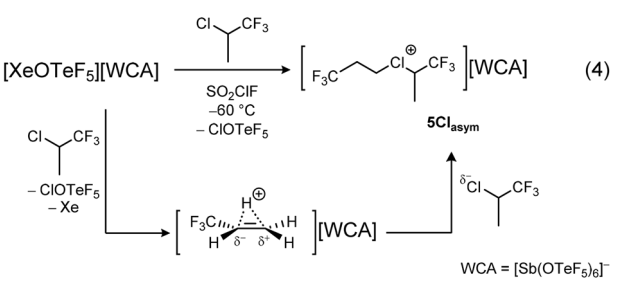
When a solvent model is applied ($\varepsilon = 100$), the hydrogen atom shifts further towards the secondary carbon atom **cat2**. Therefore, the C1–C2 double bond character is increased (NBO bond order C1–C2: 1.54), whereas the C1–H NBO bond order drops to zero. The terminal atom (C1) is now slightly positively charged. Further computational details and the results of a QTAIM analysis for **cat1** and **cat2** can be found in the ESI.†

In general, aliphatic carbocations can act as strong Brønsted acids and eliminate a proton through double bond formation in the presence of a nucleophile.[23] However, nonfluorinated aliphatic carbocations can be stabilized in the gas phase or the condensed phase in weakly nucleophilic solvents and with weakly coordinating anions (WCAs).[10,18–20,24]

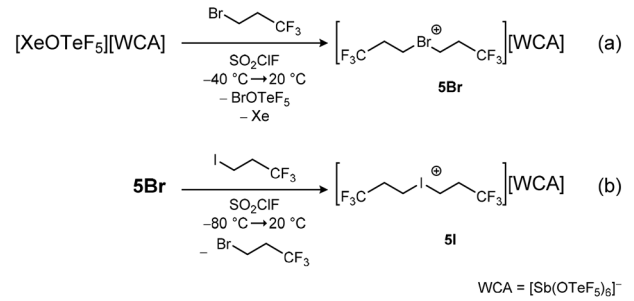
In the present case, the CF_3 group increases the Brønsted acidity of the initial secondary carbocation to the point that deprotonation of the CH_3 group occurs even without a nucleophilic partner, followed by the subsequent coordination of the proton to the newly formed double bond.

Upon formation, **cat2** can readily react with the negative polarized chlorine atom in $CHCl(CH_3)(CF_3)$, with a reaction enthalpy of −106 kJ mol^{-1}, leading to the formation of the asymmetric chloronium salt $[Cl(CH_2CH_2CF_3)(CH(CH_3)(CF_3))][Sb(OTeF_5)_6]$ $\mathbf{5Cl_{asym}}$ (Scheme 3). The asymmetric ion in $\mathbf{5Cl_{asym}}$ is energetically favoured by 5 kJ mol^{-1} (with solvent model 21 kJ mol^{-1}) compared to the symmetric diisopropyl $[Cl(CH(CH_3)(CF_3))_2]^+$ ion. The earlier described reaction of $\mathbf{5Cl_{asym}}$ with NC_5F_5, yielding exclusively the *n*-propyl substituted pyridinium salt **4** (Fig. 4), can then be explained by the energetically favoured transfer of the *n*-propyl group (−122 kJ mol^{-1}) compared to the transfer of the isopropyl group (−97 kJ mol^{-1}).

While the fluorinated asymmetric dipropyl chloronium salt $\mathbf{5Cl_{asym}}$ could not be isolated due to its high reactivity and low stability, we were interested in the synthesis of more stable fluorinated symmetric dipropyl bromonium and iodonium salts. The reaction of the xenonium salt $[XeOTeF_5][Sb(OTeF_5)_6]$ and 1-bromo-3,3,3-trifluoropropane $CH_2BrCH_2CF_3$ in SO_2ClF yields a dark red solution, indicating the formation of the side product $BrOTeF_5$, which is described in literature as a ruby red liquid (Scheme 4a).[25] Removing all volatiles under reduced pressure and washing the product with *n*-pentane yields the bromonium salt $[Br(CH_2CH_2CF_3)_2][Sb(OTeF_5)_6]$ **5Br** as an off-white powder in good yields (89%). The compound is stable at



Scheme 3 Synthesis of the asymmetric chloronium salt $\mathbf{5Cl_{asym}}$.



Scheme 4 Synthesis of the bromonium salt **5Br** (a) and the iodonium salt **5I** (b).

room temperature for hours but decomposes overnight. The ^{1}H and $^{13}C\{^{1}H,^{19}F\}$ NMR spectra show the characteristic low-field shift of the signals corresponding to the CH_2 group connected to the bromine atom upon halonium ion formation ($\delta(^{1}H) = 5.46$ ppm and $\delta(^{13}C\{^{1}H,^{19}F\}) = 34.0$ ppm, 59.0 ppm, 123.0 ppm). A shift of $\Delta\delta$ 1.56 ppm in the ^{1}H and 38.8 ppm in the $^{13}C\{^{1}H,^{19}F\}$ NMR spectra of the obtained product compared to the starting material indicates the successful halonium salt formation, with similar shifts being observed in the $[Br(CH_2CF_3)_2]^+$ ion.

The iodonium salt $[I(CH_2CH_2CF_3)_2][Sb(OTeF_5)_6]$ **5I** is obtained by the reaction of **5Br** with 1,1,1-trifluoro-3-iodopropane in SO_2ClF (Scheme 4b). Compound **5I** is obtained as a dark red, room temperature stable solid in good yields (88%). The reaction of **5Br** with an iodofluoroalkane shows its ability to act as a strong alkylating agent, transferring the trifluoropropyl group to weakly basic substrates.

Conclusions

In conclusion, we report on the synthesis and characterization of the fluorinated diethyl and dipropyl halonium salts **1Br**, **2I**, **5Br** and **5I**. We obtained the molecular structures of **1Br**, **2I**, and the previously reported **1Cl** in the solid state. Notably, **1Br** is of particular interest as it represents the first structure of an acyclic dialkyl bromonium salt. Furthermore, we obtained a highly reactive product from the reaction of 2-chloro-1,1,1-trifluoropropane with $[Xe(OTeF_5)][Sb(OTeF_5)_6]$. Due to the compound's thermal instability and low solubility, direct characterization was not possible. However, its reactivity towards isobutane and NC_5F_5, along with quantum-chemical calculations, suggests the formation of the asymmetric fluorinated dialkyl chloronium ion $\mathbf{5Cl_{asym}}$.

Data availability

Additional details regarding experimental methods and experimental data are given in the ESI.†

Author contributions

L. F. designed and performed the experiments, analyzed the data and prepared the manuscript. M. H. L. performed experiments. A. W. measured and refined the crystal structures and revised the manuscript. C. M. performed quantum-chemical calculations on the reactivity and structure of the asymmetric chloronium ion. S. R. supervised the project and revised the manuscript.

Conflicts of interest

There are no conflicts to declare.

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