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**Title:** Revisiting the perfluorinated trityl cation

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# Revisiting the perfluorinated trityl cation

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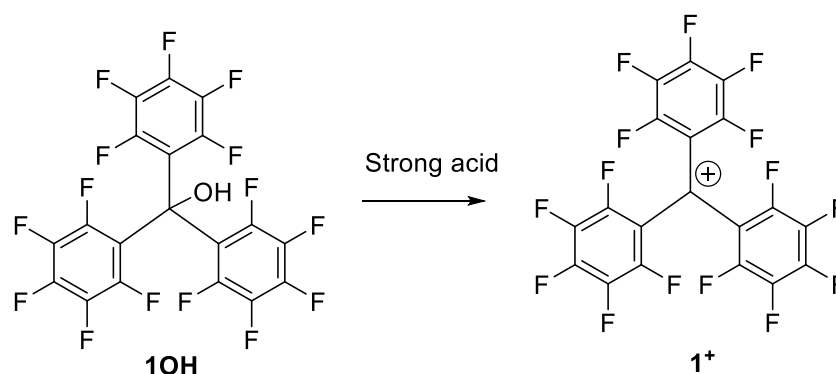
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## ABSTRACT

While ultimately not isolable for X-ray structural characterization, the free perfluorinated trityl cation is shown to be observable in neat triflic acid, which represents milder conditions than previous reports of this cation in “magic acid” or oleum. A triflate-bound species can be generated in organic solvents using stoichiometric amounts of triflic acid and is shown to be synthetically viable for hydride abstraction from Et<sub>3</sub>SiH. It is demonstrated that the *para* position on the –C<sub>6</sub>F<sub>5</sub> rings is the primary point of attack for decomposition of the cation.

## INTRODUCTION

The perfluorinated analogue of the trityl cation ( $1^+$ ) was first observed in superacidic media<sup>1</sup> independently by Filler<sup>2</sup> and by Olah<sup>3</sup> in the 1960s, generated by protonation of an alcohol precursor ( $1\text{OH}$ , Scheme 1). The stability of  $1^+$  was limited in oleum, with a half life of 2 minutes at room temperature.<sup>2</sup> In “magic acid” ( $\text{HSO}_3\text{F}-\text{SbF}_5$ ),  $^{19}\text{F}$  NMR spectra could be obtained at  $-60^\circ\text{C}$ ,<sup>3</sup> but there was no details on attempts at isolation. Filler was able to demonstrate that the cation can be used as a one-electron oxidant in 100%  $\text{H}_2\text{SO}_4$  and that the corresponding neutral radical is relatively stable.<sup>4</sup>



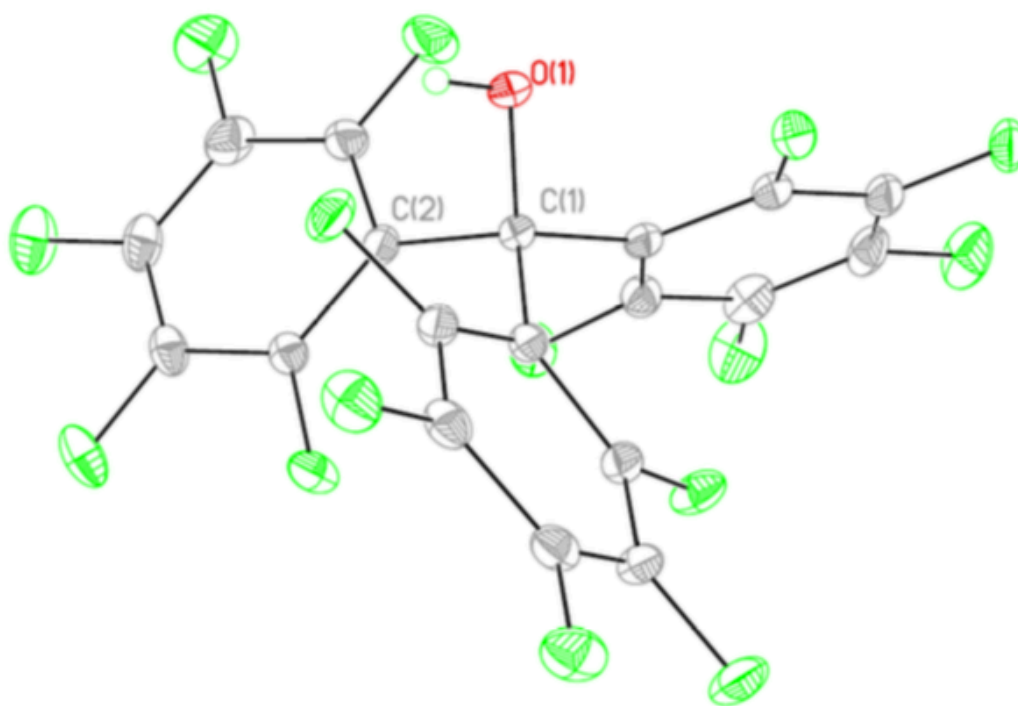
**Scheme 1.** Generation of trityl cation  $1^+$  under superacidic conditions.

The electrophilicities of partially fluorinated trityl cations have been studied recently by Mayr and co-workers,<sup>5,6</sup> but the fully fluorinated analogue was not included. Given the explosion in utility observed for the boron counterpart, trispentafluorophenyl borane,<sup>7,8</sup> and the availability of new counterions for reactive cations<sup>9,10</sup> we proposed in a theoretical paper in 2014 that it was time to revisit the fully fluorinated analogue of the trityl cation.<sup>11</sup> We predicted that its fluoride and hydride affinities would be very high, much higher than those of trityl cation and trispentafluorophenyl borane. Stephan and co-workers also theoretically considered the perfluorinated trityl cation as an extreme Lewis acid showing good correlation between predicted Global Electrophilicity Indexes and Lewis acidity.<sup>12</sup>

Herein we report on our efforts to observe and isolate cation  $1^+$  as a triflate or carborane salt in non-superacidic media along with an initial exploration of its chemistry as a potential hydride acceptor.

## RESULTS AND DISCUSSION

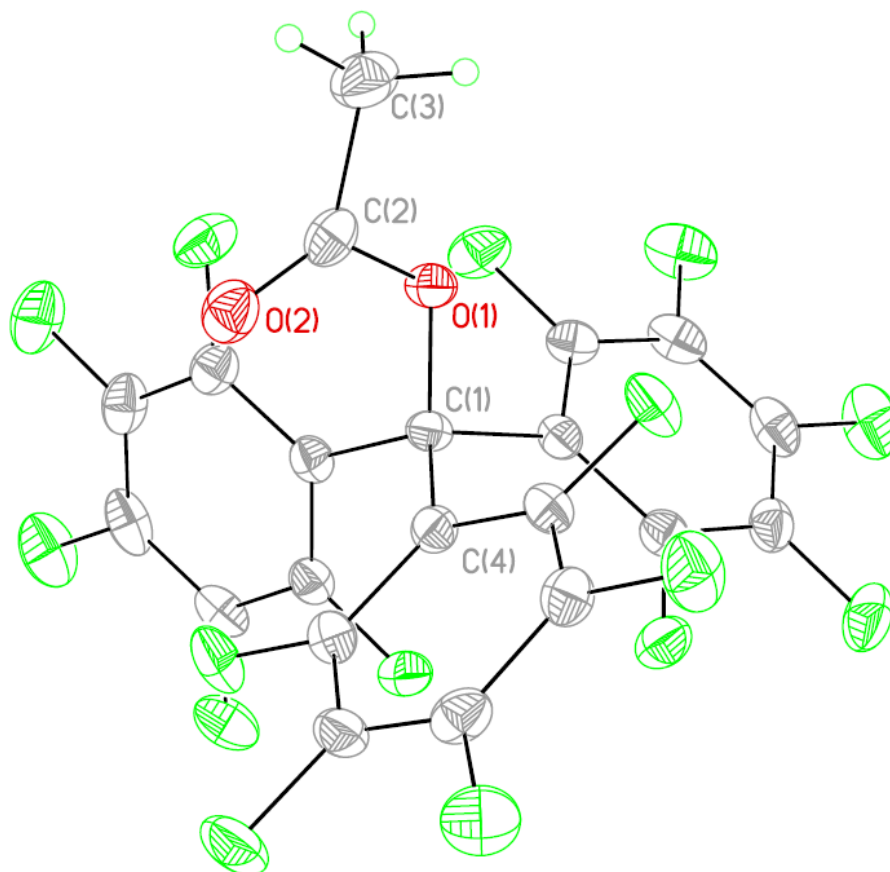
Our initial goal was to prepare a halo derivative of **1OH** for use in halide abstraction routes to form **1<sup>+</sup>**. The starting alcohol **1OH** was initially synthesized by Filler *et al.* by reacting  $\text{LiC}_6\text{F}_5$  with decafluorobenzophenone.<sup>2</sup> They reported being unable to synthesize a halogenated derivative. We repeated their synthesis of **1OH** and further verified its structure by X-ray (Figure 1). *Caution: in the course of a routine 2 g synthesis, we experienced an explosion from  $\text{LiC}_6\text{F}_5$ , despite the mixture being held in a dry-ice/ $\text{EtOH}$  bath.* We subsequently found that replacing the lithium reagent with the Grignard reagent  $\text{BrMg-C}_6\text{F}_5$ , generated from Mg metal and  $\text{Br-C}_6\text{F}_5$ , provides a suitable alternative route to **1OH**, albeit with a somewhat lower yield.



**Figure 1.** Solid-state structure of **1OH**. Thermal ellipsoids are depicted at the 50% probability level.

In an attempt to form the bromo derivative, **1OH** was reacted with neat acetyl bromide, following the reported procedure for the formation of trityl bromide from trityl alcohol.<sup>13</sup> Fluorine-19 NMR of

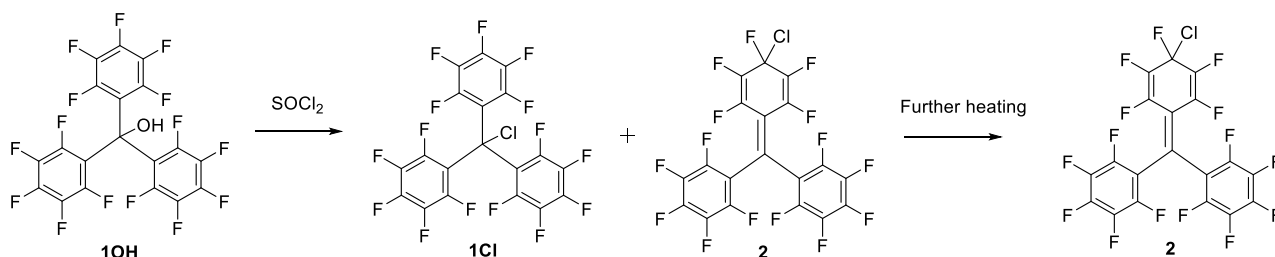
the reaction mixture and isolated material gave the expected three resonances, shifted from those in **1OH**. However, X-ray studies revealed the presence of the acetate derivative, **1OAc**, rather than the targeted bromide (Figure 2). The  $^1\text{H}$  NMR spectrum of the isolated powder contained a singlet, confirming identity of the bulk material with the single crystal.



**Figure 2.** Solid-state structure of **1OAc**. Thermal ellipsoids are depicted at the 50% probability level.

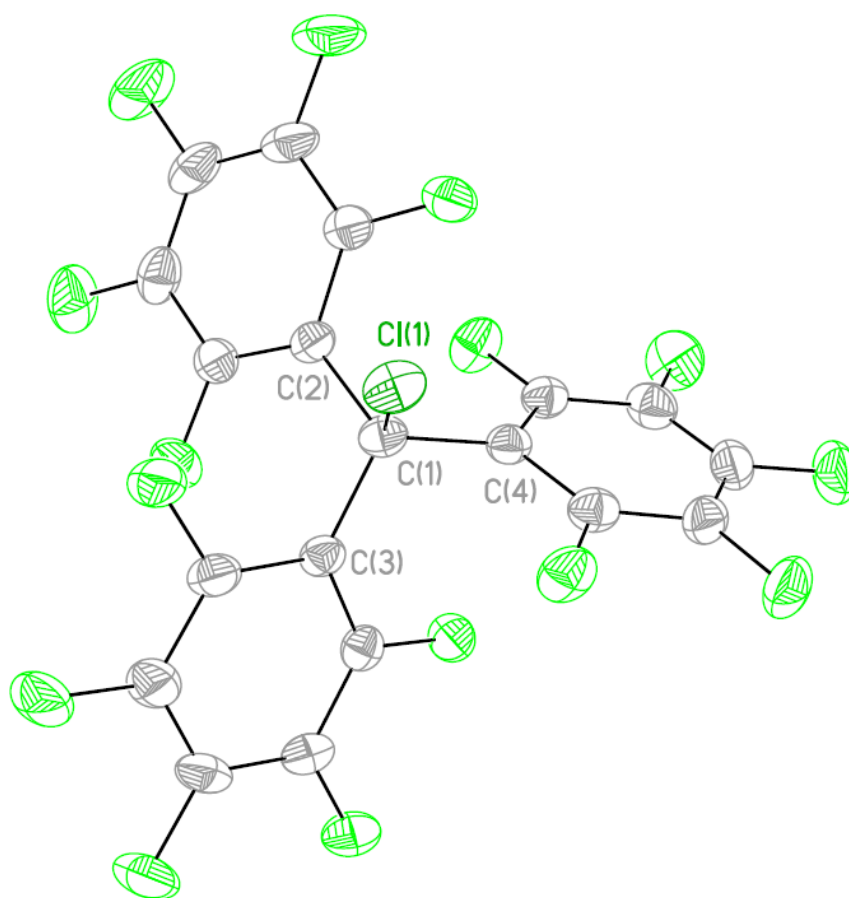
We next used  $\text{SOCl}_2$  to form the chloro derivative (Scheme 2). Reaction in *p*-xylene at 142 °C consistently resulted in a crude product showing nine  $^{19}\text{F}$  NMR signals. The mixture could be chromatographically separated into two compounds, one showing six signals, the other showing the

expected three signals from symmetric  $-\text{C}_6\text{F}_5$  groups. X-ray diffraction revealed the latter structure to be the targeted tris(perfluorophenyl) chloride **1Cl** (Figure 3). The former compound, with six  $^{19}\text{F}$  signals, was revealed to be chlorinated at the *para*-position forming an  $\text{sp}^3$  hybridized carbon, **2** (Figure 4). Heating **1Cl** to high temperatures results in transformation to **2**, presumably by attack from chlorine onto the *para*-position, which is known to be a reactive site on  $-\text{C}_6\text{F}_5$  rings with respect to nucleophilic attack.<sup>14</sup> Efforts to minimize formation of this *para*-substituted isomer through various synthetic modifications (lower reaction temperatures, Vilsmeier-Haack chemistry or alternative chlorinating agents) failed to give better yields of the desired **1Cl**. Indeed, **2** often became the sole product. Nevertheless, under milder reaction temperatures ( $\leq 80^\circ\text{C}$  approx.) **2** shows significantly reduced solubility relative to the desired tris(perfluorophenyl) chloride, allowing isolation of **1Cl** in reasonable purity.



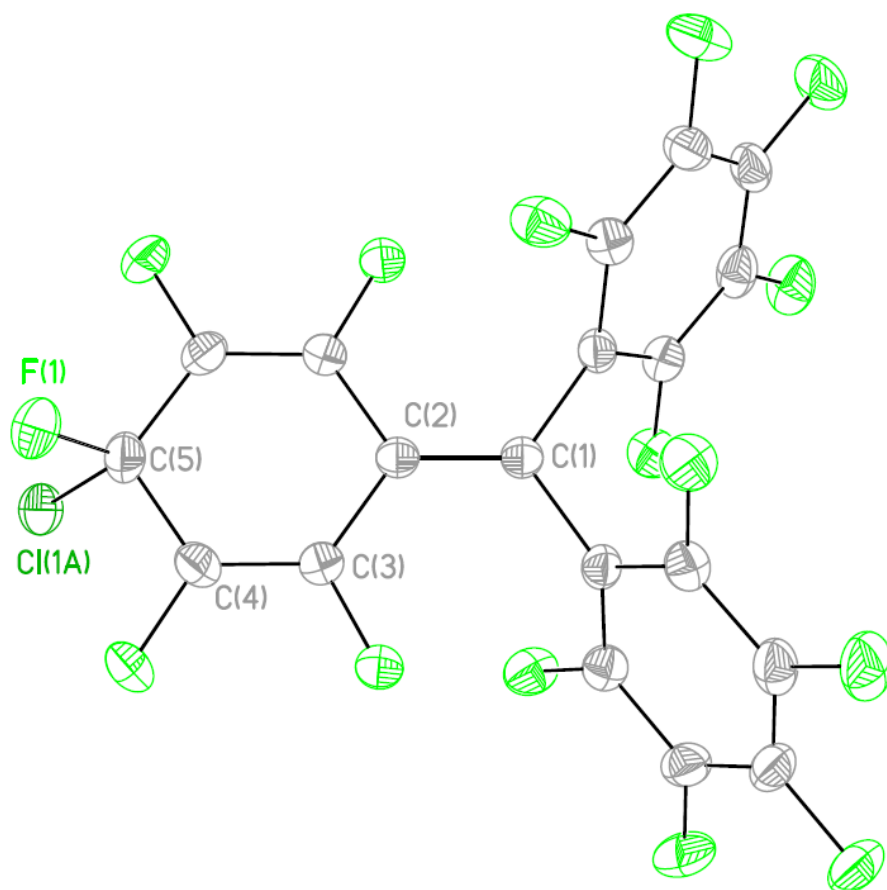
**Scheme 2.** Generation of chloro-derivatives **1Cl** and **2**.

Examination of the solid-state contacts in **1Cl** shows that the intermolecular contact for the chloride atom and the *para*-carbon position of an adjacent molecule is  $3.35\text{ \AA}$ , less than the sum of their Van der Waals radii of  $\sim 3.5\text{ \AA}$ . These are the closest contacts for these atoms, indicative of the Lewis basic nature of the terminal chloride and more importantly, the Lewis acidic nature of the *para*-carbon atom.



**Figure 3.** Solid-state structure of **1Cl**. Thermal ellipsoids are depicted at the 50% probability level.

Selected bond distances (Å): C(1)-Cl(1) 1.845(2), C(1)-C(4) 1.538(3).



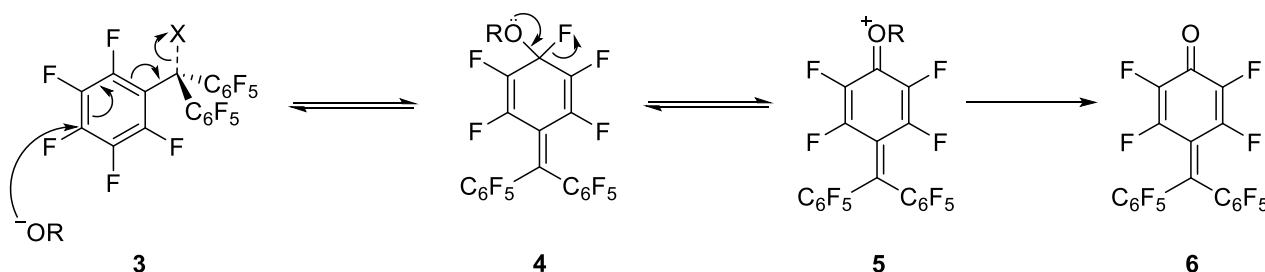
**Figure 4.** Solid-state structure of **2**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-Cl(1A) 1.727(3), C(5)-F(1) 1.415(5), C(4)-C(5) 1.484(2), C(3)-C(4) 1.327(2), C(2)-C(3) 1.466(2), C(1)-C(2) 1.355(3).

With the requisite tris(perfluorophenyl) chloride in hand, we set about investigating its reaction with various halide abstraction agents.  $^{19}\text{F}$  NMR analysis of a 1:1 mixture of **1Cl** and silver triflate (AgOTf) after stirring at ambient temperature for 20 hours in acetonitrile indicated formation of a new species having similar characteristics to **1OH**. However, concentration of the colourless reaction mixture resulted in isolation of a new red solid whose  $^{19}\text{F}$  NMR showed five new resonances. X-ray analysis revealed this compound to be the trienone **6** (Scheme 3, Figure 5), previously reported from quenching reactions between **1OH** and  $\text{H}_2\text{SO}_4$  with water.<sup>15</sup> Although employing stringent anhydrous conditions, we initially surmised that trace amounts of water lead to

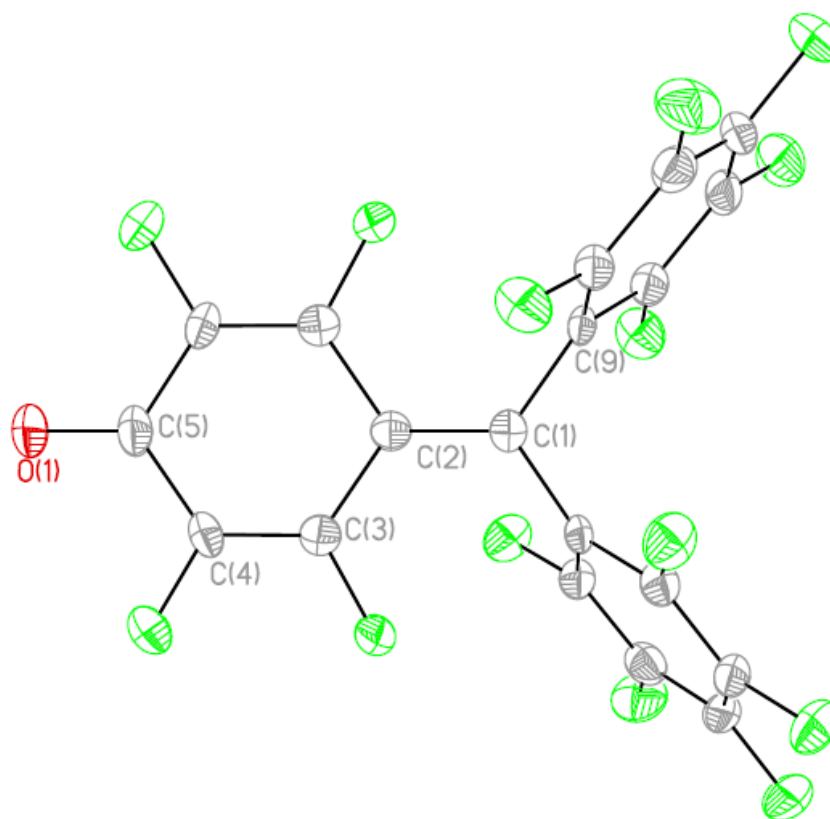


its formation. However, despite all reasonable efforts to exclude water from the system, we continued to isolate **6** as the sole reaction product, suggesting water does not represent the source of the new ketonic oxygen atom. The same outcome was observed when employing a stoichiometric amount of trimethylsilyl triflate (TMSOTf) instead of AgOTf. Attempts at using  $\text{Ag}_2[\text{B}_{12}\text{Cl}_{12}]$  as a halide abstraction agent introducing the weakly coordinating  $[\text{B}_{12}\text{Cl}_{12}]^{2-}$  anion<sup>16</sup> resulted in no reaction.

A plausible reaction pathway to rationalize this reproducible formation of **6** is proposed in Scheme 3. Attack of an oxygen-containing nucleophile at the *para* position of one perfluorinated aryl ring results in formation of triene **4** through loss of leaving group X. Subsequent elimination of F yields the more stable conjugated trienone **6** via **5**.



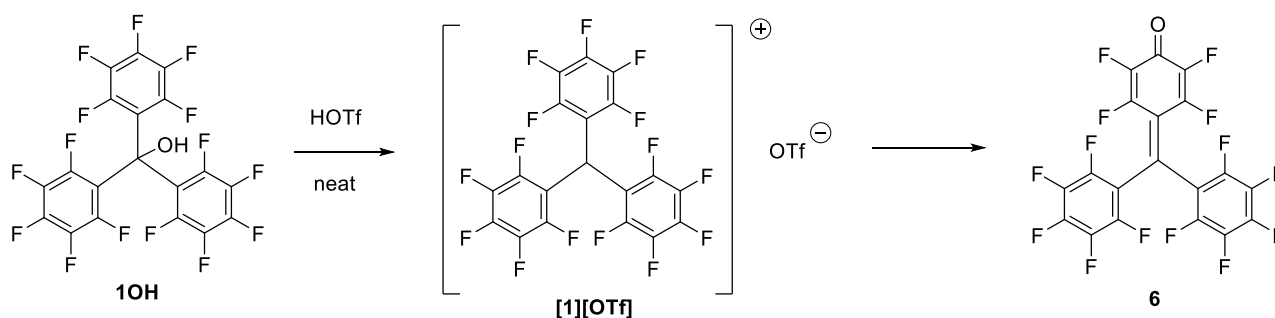
**Scheme 3.** Proposed mechanism for the generation of ketone **6**.



**Figure 5.** Solid-state structure of **6**. Thermal ellipsoids are depicted at the 50% probability level. Selected bond distances (Å): C(5)-O(1) 1.214(3), C(4)-C(5) 1.460(2), C(3)-C(4) 1.329(2), C(2)-C(3) 1.462(2), C(1)-C(2) 1.357(3), C(1)-C(9) 1.494(2).

The addition of neat triflic acid to solid **1OH** at -30 °C resulted in immediate generation of a deep maroon solution (Scheme 4).  $^{19}\text{F}$  NMR spectroscopy of the solution with the NMR probe set at -30 °C revealed three signals at -115, -128, and -157 ppm. The strongly downfield shift of the *para* and *ortho* fluorine atoms is consistent with the observations of Olah and co-workers for ionized **1**<sup>+</sup> in strongly acidic media.<sup>3</sup> The  $^{13}\text{C}$  NMR spectrum of the mixture shows a peak at 171 ppm that can be assigned to the central carbon. This is well downfield from there the signal for the central carbon appears in **1OH**, consistent with the change from  $\text{sp}^2$  to  $\text{sp}^3$  hybridization in the cation. The chemical shift for the parent trityl cation in chlorosulfonic acid solution is ~ 200 ppm.<sup>17</sup> The upfield shift for the perfluorinated derivative can be rationalized on the basis of increased  $\pi$  donation to the central carbon by the fluorine atoms. This is consistent with theoretical calculations of the two cations, with

the predicted  $^{13}\text{C}$  NMR shift of the trityl cation at 213 ppm and the predicted shift for  $1^+$  at 175 ppm. While this cation is stable for at least two hours at  $-30\text{ }^\circ\text{C}$ , warming to room temperature results in decomposition, with ketone **6** being the main product after a sample was held overnight. This is an improvement over previous methods, as oleum cannot be used at low temperature, and “magic acid” is far less convenient/accessible than triflic acid, and triflic acid allows the cation to be observed at warmer temperatures than magic acid.

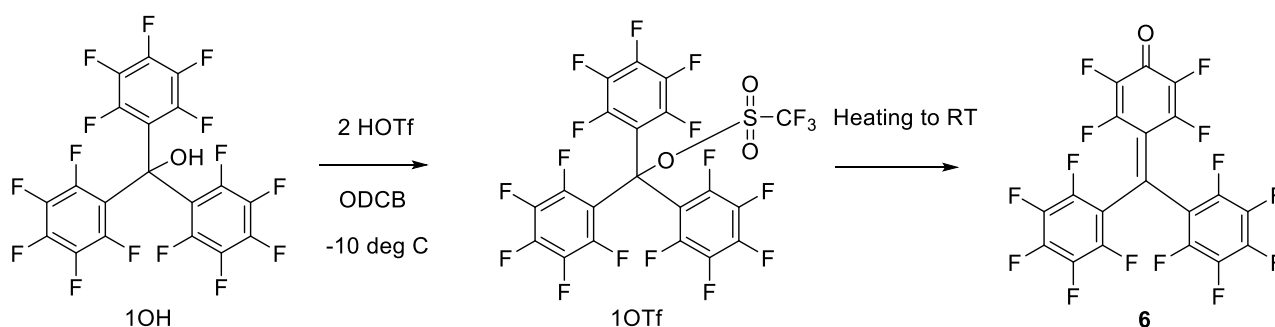


**Scheme 4.** Generation of  $1^+$  as a triflate salt in neat HOTf and decomposition to **6** upon warming.

Neat triflic acid though remains a harsh medium and likely precludes the synthetic use of  $1^+$ . We therefore explored its formation in organic solvents. Reacting two equivalents of HOTf (one to protonate the alcohol, and the second to sequester the resulting equivalent of  $\text{H}_2\text{O}$ ) with **1OH** in *ortho*-dichlorobenzene (ODCB) resulted in the immediate formation of a dark red colored solution (Scheme 5). The  $^{19}\text{F}$  NMR spectrum of the reaction mixture at  $-10\text{ }^\circ\text{C}$  was relatively clean, with three  $^{19}\text{F}$  signals at -142.5, -153.6, and -162.8 ppm. These signals are distinctly different from those of **1OH** in the same solvent, but far upfield to what is consistent with a free cation, as observed with neat triflic acid. Warming to room temperature resulted in decomposition of the mixture to signals consistent with **6** as the main product after 48 hours. The data is consistent with the formation of **1OTf** with the triflate fragment remaining bound to the carbon centre. The  $^{13}\text{C}$  NMR chemical shift provides support for this notion, the shift of the central carbon is 71 ppm, consistent with an  $\text{sp}^3$  hybridized centre. This can be compared to a shift of 57 ppm in **1Cl**. Theoretical calculations of the  $^{13}\text{C}$  NMR spectrum are again consistent with the observed results, with a shift of 90 ppm predicted for the central carbon in the triflate bound species **1OTf**, far upfield of what is predicted and observed for the free cation in strong acid above. The parent trityl cation remains ionized in ODCB solution, with an observed  $^{13}\text{C}$  NMR shift of 209 ppm. If the triflate remained bound to the central

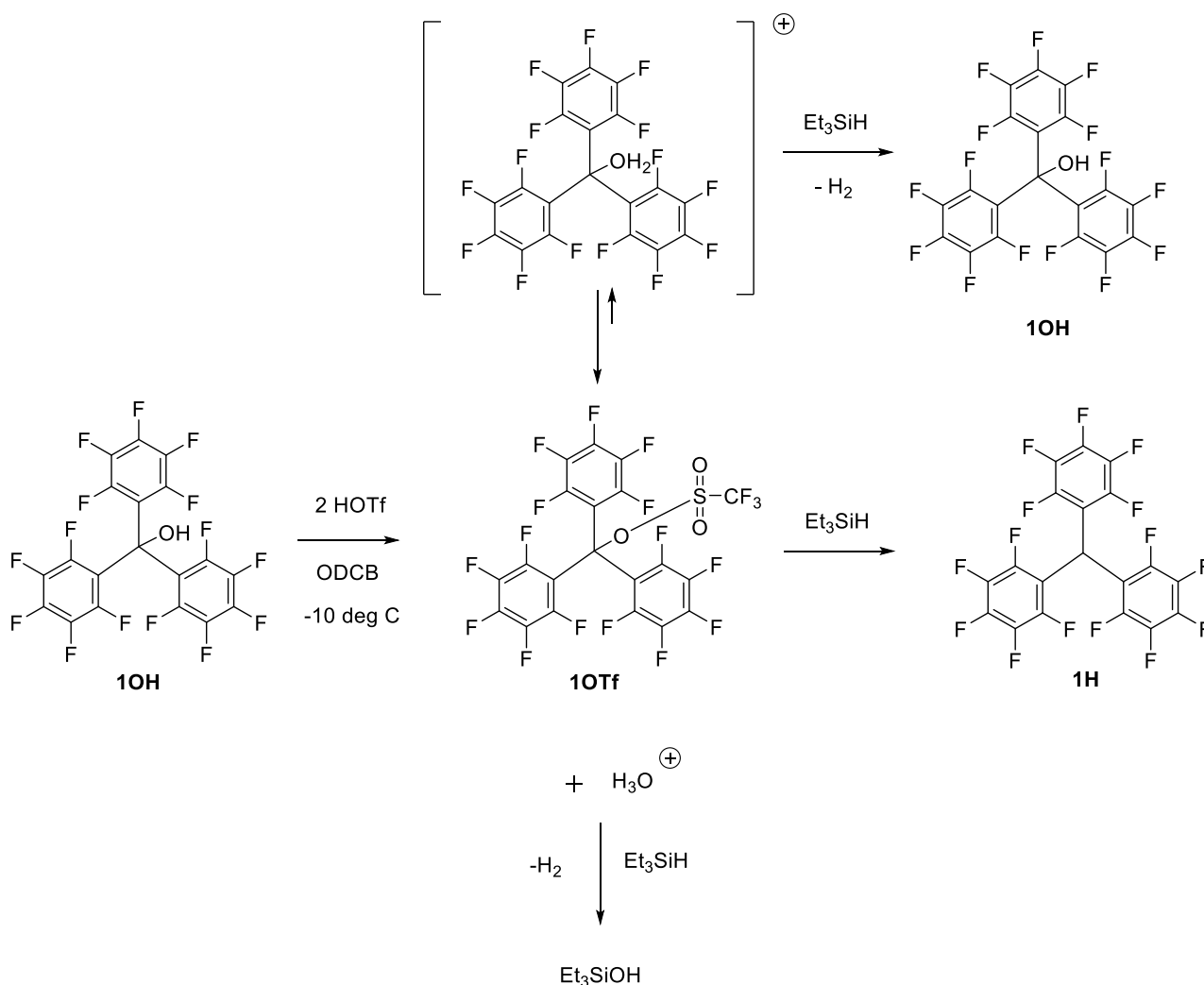
carbon for the parent trityl cation a  $^{13}\text{C}$  NMR shift of 110 ppm is predicted. The difference can be rationalized with the greater Lewis acidity of the perfluorinated analogue.

To confirm our previous hypothesis that the presence of trace water in the reaction mixture does not result in formation of trienone **6** (see Scheme 3), we further reacted two equivalents of HOTf with **1OH** in ODCB. Subsequent addition of five equivalents of  $\text{H}_2\text{O}$  results only in regeneration of **1OH** via  $^{19}\text{F}$  NMR analysis of the crude reaction mixture.



**Scheme 5.** Generation of **1OTf** and decomposition to **6** upon warming.

To lend support to the proposed formation of **1OTf** and determine its potential synthetic utility, we explored its ability to act as a hydride acceptor, which would be expected behavior if **1OTf** had indeed been generated. Addition of  $\text{Et}_3\text{SiH}$  as a hydride donor to a solution of **1OTf** prepared from **1OH** and two equivalents of HOTf at -10 °C in ODCB (Scheme 6), resulted in an NMR spectrum consistent with the presence of two species, one the regenerated alcohol **1OH**, and the other as tris(pentafluorophenyl)methane **1H**.<sup>18</sup> Performing the reaction in toluene at low temperature allowed for simpler isolation of **1H** in a pure form, because toluene is more easily removed under vacuum. We hypothesize that the competing reactions shown in Scheme 6 account for this distribution of products. Nevertheless, the generation of **1H** is supportive of the generation of **1OTf** with the  $^{19}\text{F}$  NMR suggesting the triflate anion remains bound as it is too strongly coordinating to allow ionization to  $1^+$  in low dielectric media.



**Scheme 6.** Reaction pathways of **1OTf** with hydride donor Et<sub>3</sub>SiH.

Carborane anions are much less coordinating than triflate and often allow isolation of extremely reactive cations.<sup>9</sup> To determine if the *closo*-carborane anion [HCB<sub>10</sub>Cl<sub>11</sub>]<sup>-</sup> might allow isolation of “free” **1**<sup>+</sup> in non-super acidic media, solid alcohol **1OH** was mixed with two equivalents of solid [C<sub>6</sub>H<sub>7</sub>][HCB<sub>10</sub>Cl<sub>11</sub>], the protonated benzene salt of the carborane. IR spectroscopy indicated that mixing the two solids did not result in any reaction but the addition of a drop of benzene resulted in the immediate generation of a maroon slurry, which was followed by immediate evaporation. IR spectroscopy of the resulting solid indicated loss of **1OH**. The vibrations associated with stretching of C<sub>central</sub>-C<sub>ipso</sub> bonds are shifted to lower frequencies (1604-1611 cm<sup>-1</sup>) compared to **1OH** (1653 cm<sup>-1</sup>). For comparison, calculated vibration frequencies using B3LYP-D3(BJ)/def2-TZVPP give 1671-1678 cm<sup>-1</sup> for **1OH** and 1667 cm<sup>-1</sup> for **1**<sup>+</sup>. For comparison, the IR spectrum for the trityl salt of the same carborane anion shows stretches associated with the central-ipso C-C bonds at 1577 cm<sup>-1</sup> while the computationally predicted vibration for the trityl cation is found at 1630 cm<sup>-1</sup>. The differences in

the experimental/computationally predicted vibrations for the central-*isopropyl* C-C bonds in **1OH**, the targeted **1**<sup>+</sup> and trityl cation are in good agreement. The blue shift for the perfluorinated compound is likely a result of a stronger C-C bond induced by the  $\pi$  donor ability of the fluorine atoms, consistent with the differences in the <sup>13</sup>C NMR chemical shifts discussed above.

Despite this evidence for the existence of **1**<sup>+</sup> in the solid state, it does not appear that the cation is stable in low polarity solvents. Addition of 2 equivalents of [C<sub>6</sub>H<sub>7</sub>][CHB<sub>10</sub>Cl<sub>11</sub>] to a solution of **1OH** in a variety of arene solvents (toluene, benzene, ODCB) did result in the immediate formation of red solutions, they underwent decolorization within minutes and we were unable to identify any <sup>19</sup>F NMR signals consistent with formation of **1**. Attempted dissolution of the solid resulting from the slurry in the IR experiment in arene solvents also resulted in rapid decolorization of the solution.

## CONCLUSIONS

We have demonstrated that the perfluorinated trityl cation is relatively stable in neat triflic acid. In less polar organic solvents the triflate is bound but nevertheless shows reactivity as a hydride acceptor with silanes. The free cation appears to exist in the solid state when the counterion is switched to an ultra-inert carborane but intrinsic decomposition prevents its full characterization. It is apparent that the para-carbon position of the -C<sub>6</sub>F<sub>5</sub> ring is the Achilles heel of this reactive species.

## ASSOCIATED CONTENT

**Supporting Information.** Experimental details with associated <sup>1</sup>H, <sup>19</sup>F, IR spectra of synthesized compounds and reaction mixtures. Computational details and Cartesian coordinates for calculated species. X-ray crystallographic details in .cif format.

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## ACKNOWLEDGMENT

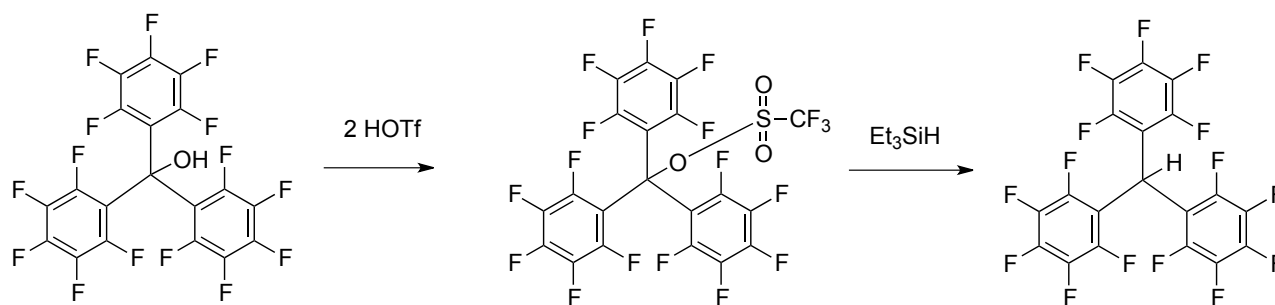
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TOC Graphic and Abstract



Accessible synthon for the perfluorinated trityl cation

Blast from the past. A triflate bound derivative of the perfluorinated trityl cation can be generated from triflic acid in organic solvent at -20°C and used as a hydride acceptor. The free cation can also be observed in neat triflic acid. Attack on the –para carbon by nucleophiles is the primary mode of decomposition of the cation.