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Lability of the trifluoromethyl group of trifluoromethoxybenzenes under HF/Lewis acid conditions

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ABSTRACT

The trifluoromethyl functionality of trifluoromethoxybenzenes (trifluoromethyl phenyl ethers) becomes labile under HF/Lewis acid conditions. Substrates with an unsubstituted para-position shed their $-CF_3$ groups while performing a Friedel–Crafts reaction upon another substrate molecule's trifluoromethoxy group to generate *p*-rosolic acids. Substrates that had blocking groups at the para-positions reacted ortho. The electron donating substituents methoxy and phenoxy interfered with the formation of rosolic acids.

1. Introduction

It was previously reported that 1,2-dichloro-1,1-difluoroethane (R-132b) is resistant to further fluorination to 2-chloro-1,1,1-trifluoroethane (R-133a) in a liquid HF reaction with Lewis acid catalysis [1]. That study was performed with Ta(V) halide catalysts as tantalum had been confirmed to be the most effective for the general conversion of trichloroethylene to R-133a [2]. The resistance of R-132b to reaction was overcome through the use of various benzotrifluorides as auxiliary solvents. During the initial survey of aromatic solvents, trifluoromethoxybenzene, **1**, was observed to undergo an unexpected side reaction to form a startling by-product. This publication reports the identity of the by-product and investigates the circumstances of its formation.

2. Results and discussion

2.1. Trifluoromethoxybenzene as an auxiliary solvent

The initial survey reactions were performed in the following manner. R-132b/auxiliary mix was charged to a pressure reactor containing pre-formed $TaClF_4$ in HF. The reactions were heated to 140 °C for 4 h and observed by pressure monitoring and gas chromatography for evidence of reaction. Benzotrifluorides (as reported) have an accelerating effect on the reaction.

With trifluoromethoxybenzene, **1**, as the auxiliary solvent, no acceleration was observed and, in fact, the small inherent reactivity of R-132b was suppressed. Examination of the reactor residue after venting R-132b, HF and unreacted trifluoromethoxybenzene presented a bit of a surprise. While it had been expected that all the components except $TaClF_4$ would distill from the hot reactor, the reactor was found to contain a large quantity of solid material (79% by mass vs. CF_3O–Ph). But, unlike light colored tantalum salts or black oligomers (tars), this solid was in the form of a remarkable emerald green crystal or glass! The unexpected appearance of this material warranted further investigation. The reactions were immediately repeated without R-132b and it was found not to be a required component for formation of the emerald green solid. It was therefore omitted from all further experiments. Also, no reaction occurred between refluxing trifluoromethoxybenzene and $TaCl_5$ or TaF_5, absent HF.

2.2. Identification of green (red) compound

Due to its dazzling color, it was hypothesized at first that the emerald green material might be a phenolic or aromatic complex of tantalum. Several of such species display color, though not the green that was observed [3] (the solid was assumed to be essentially one compound). At the very least, the tantalum catalyst would still be incorporated within the solid. For that reason and the fact that the solid exuded HF over time (as observed by the etching

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of sample vials) it was treated as hydroscopic and air sensitive, though it was not outwardly reactive with water. The material was insoluble in $CHCl_3$ or THF. It was somewhat soluble in acetone and methanol, but not water, however it dissolved in $NaOH_{(aq)}$, but not $HCl_{(aq)}$. It was sparingly soluble in anhydrous HF (at room temperature).

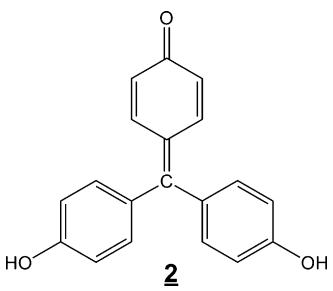
Several methods were employed to determine the nature and identify the trifluoromethoxybenzene reaction's green residue. The first method was an attempt at X-ray crystallography [4]. A preliminary analysis indicated that the material was not crystalline, but rather an amorphous glass and was therefore not subject to X-ray determination. During microscopic viewing of the material during mounting, it was observed that while the material appeared (reflected) green, it transmitted red when illuminated from behind. NMR analysis was stymied by poor or incomplete solubility in all the standard NMR solvents.

Surprisingly, a TLC survey showed the material to be chromatographable on silica. A strong red spot of Rf = 0.6 was achieved with 15 CH_2Cl_2/1 MeOH elution solvent. It was fully assumed that the complex was being stripped of tantalum and that only a ligand was being observed rising up the TLC plate (especially since the color changed). None-the-less, chromatography would allow for the isolation and identification of the 'ligand' and hopefully for back-tracking to the identity of the complex itself. The material was chromatographed and the isolated red fractions remained as red material upon evaporation of the solvent.

^1H NMR of the chromatographed material now exhibited a clean doublet of doublets of a clearly para-substituted aromatic system. ^{13}C NMR showed just 4 types of aromatic carbons and a few other small peaks. The ^{19}F NMR spectra, however, was peakless! Mass spectral analysis [5] in both positive and negative modes assigned a MW of 290 to the material. This indicated that the simple NMR spectra were reflecting equivalent signals of **3** 'aromatic' rings. IR showed both phenolic and carbonyl absorptions. Methylation with diazomethane generated a dimethyl ether. At this point, the identity of the red compound was assigned to be the bis-phenol quinone, *p*-rosolic acid, **2**. Comparison of the spectra with those of authentic *p*-rosolic acid (Fig. 1) verified the assignment (literature spectra are anomalous or incorrect [6,7]). Significant is the fact that this product is (Fig. 2) fluorine free and only one of the original three CF_3 carbons can be accounted for the product.

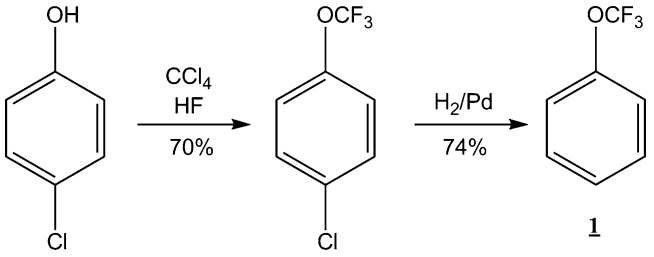
2.3. Precedent for p-rosolic acid (2) formation

CF_3 lability under HF/Lewis acid conditions was not anticipated while choosing CF_3O–Ph as an auxiliary solvent as CF_3O–Ph had been reported to be stable to Friedel–Crafts alkylation (in the presence of BF_3 as Lewis acid) [8–10] and was most certainly synthesized with HF and often, Lewis acid catalysts [11–16]! A closer look at the literature on the synthesis of trifluoromethoxybenzenes disclosed some interesting points. First, no mention is ever made of any green, red or otherwise noticeable solid reactor



2

Fig. 1. *p*-Rosolic acid.



1

Scheme 1. Literature synthesis of trifluoromethoxybenzene.

residues (though yields are not quantitative). Second, while yields of trifluoromethoxybenzenes are good to excellent for the reaction of substituted phenols with CCl_4 + HF, phenol itself gives low yields (note, these are non-L.A. catalyzed reactions). The preferred method of producing CF_3O–Ph is via the para-chlorophenol analog followed by reduction (Scheme 1) [10]! It now becomes suspect that the direct phenol + CCl_4 + HF reaction suffers from the side reactions of two Friedel–Crafts alkylations and a Fries rearrangement to generate *p*-rosolic acid.

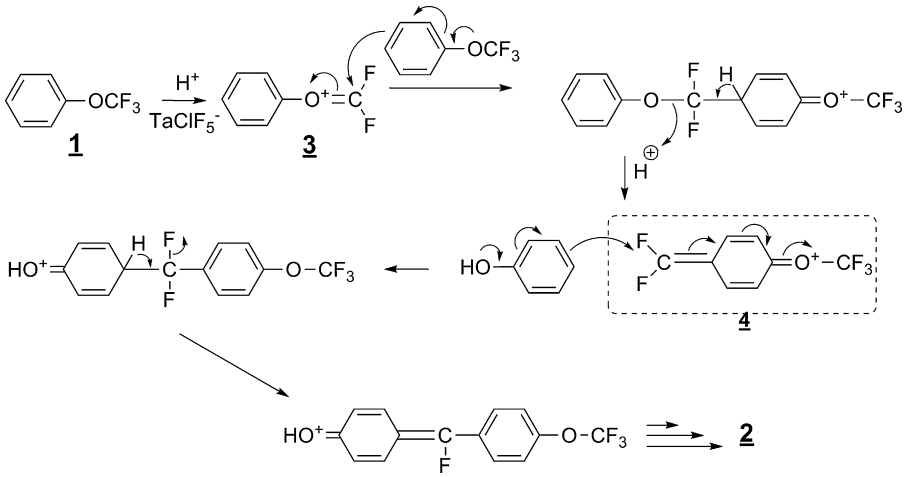
2.4. Mechanism of p-rosolic acid (2) formation

Clearly, under the reaction conditions, two CF_3O–Ph molecules were performing Friedel–Crafts reactions on the trifluoromethoxy group of another CF_3O–Ph. The CF_3O–Ph molecule that supplies the trifluoromethoxy group must at some stage perform a Fries rearrangement where the trifluoromethyl group acts in the place of a carboxylate, likely sooner than later. Gaussian calculations support a mechanism that begins with the formation of the anomerically stabilized difluoromethyl carbonium ion **3** (Scheme 2). A Friedel–Crafts reaction with a second CF_3O–Ph forms the first carbon–phenyl bond and allows for the elimination of phenol to generate **4**. The phenol can now reattach to **4** at its para-position, affecting the desired Fries rearrangement. This process continues, carbon-coupling a third phenol to the rearranged trifluoromethyl carbon. The full details of the mechanism as determined by Gaussian calculations are published under separate title [17].

2.5. Effect of substituents

It was decided to investigate the effects of ring substituents on the formation of rosolic acid. As the mechanistic intermediates are stabilized cations, it was thought that electron withdrawing ring substituents would destabilize the formation of these intermediates, while electron donating ring substituents would stabilize them. Concurrently, electron withdrawing ring substituents would make an attacking CF_3O–Ar less nucleophilic and electron donating substituents would make an attacking CF_3O–Ar more nucleophilic. The combined effects on nucleophile and nucleofuge might result in a draw, but only experimentation would tell.

Four substrates with electron withdrawing groups were chosen to determine whether electron-poor trifluoromethoxybenzenes would be more succeptable to nucleophilic attack. They are 1,2-(bis)-trifluoromethoxybenzene, **5**, 1,4-(bis)-trifluoromethoxybenzene, **6**, 2-chlorotrifluoromethoxybenzene, **7**, and 4-chlorotrifluoromethoxybenzene, **8**. The trifluoromethoxy groups on **5** and **6** would be expected to withdraw electron density from the ring to mutually suppress the formation of a **3** type oxonium intermediate. Similarly, the electron withdrawing chlorine groups in 2-chlorotrifluoromethoxybenzene, **7**, and 4-chlorotrifluoromethoxybenzene, **8** should suppress formation of an oxonium intermediate, but back-bonding could weaken that effect.



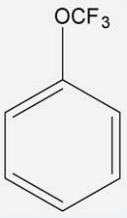
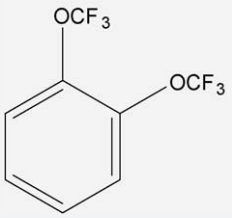
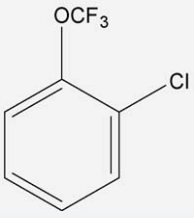
Scheme 2. Initial steps of *p*-rosolic acid formation from trifluoromethoxybenzene.

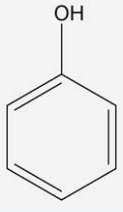
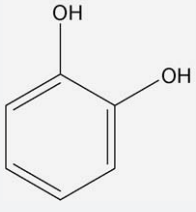
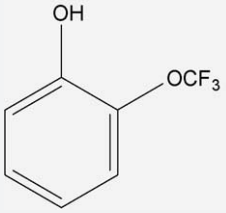
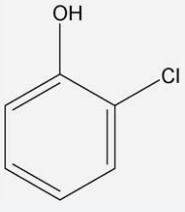
As one can see, testing of the four variously substituted trifluoromethoxybenzenes would also simultaneously determine whether ortho alkylation has a mechanistic contribution to the product distribution as there are two substrates with open para-positions and two substrates with blocked para-positions.

2.5.1. Electron withdrawing groups

Using the results of exposing trifluoromethoxybenzene, **1**, to HF and $TaCl_5$ based catalyst as the control, it appears qualitatively that the addition of the electron withdrawing $-OCF_3$ groups (**5**, **6**) has had only a slight enhancing effect. It appears that increasing the

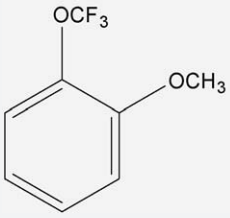
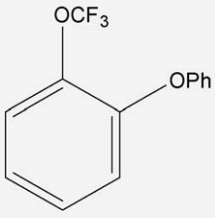
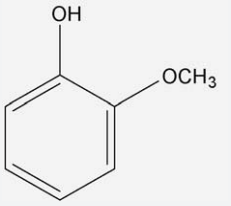
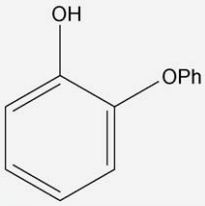
Table 1
Trifluormethoxybenzene substrates.

Reagents	1	5	6	7	8
HF and cat. $TaCl_5$					
Recovery[a] Ar–OCF_3	67%	71%	75%	69%	64%
Rosolic acids	25%	15%	20%	31%	20%[b]
Overall	92%	86%	95%	100%	84%

Reagents	9	10	11	12	13	14
CCl_4 and HF (no cat.)						
Yield[a] Ar–OCF_3	31%	0%	48%	100%	35%	55%
Rosolic acids	69%	0%[c]	45%	0%	47%	0%
Overall	100%	0%	93%	100%	82%	55%

[a] Distilled yields and recoveries in mole percent.
[b] Product retained CF_3 group.
[c] 100 wt.% recovery of rigid polyphenolic foam.

Table 2
Electron rich trifluoromethoxybenzenes.

Reagents	**15**	**16**	**17**
HF and cat. $TaCl_5$			
Recovery[a] Ar–OCF_3	0%	68%	–
By-products	45% HO–Ph–OCF_3 and HO–Ph–OCH_3 and 27% **21**	7% HO–Ph–OCF_3	–
Rosolic acids	Trace	0%	–
Overall	72%	75%	Not run
Reagents	**18**	**19**	**20**
CCl_4 and HF (no cat.)			
Yield[a] Ar–OCF_3	0%	6%	0%
By-products	–	–	10% **22**
Rosolic acids	Trace[b]	Trace[b]	7%[b]
Overall	0%	6%	17%

[a] Distilled yields and recoveries in mole percent.
[b] 100 wt.% recovery of rigid polyphenolic product.

"concentration" of $-OCF_3$ targets has resulted in a faster rate of reaction. The addition of an electron withdrawing chlorine substituent (**7**, **8**) had no appreciable effect on the reaction, that is, it did not suppress the lability of the $-CF_3$ group. In short, neither electron withdrawing substituent had any significant effect on the rate of $-CF_3$ lability.

2.5.2. Ortho substitution

It was expected that substituting the para-positions of various trifluoromethoxybenzenes might stop the formation of rosolic acids. The para-substituted trifluoromethoxybenzenes **6** and **8** produced rosolic acids despite the blocking groups, apparently by ortho-attack. Total yields are extremely high, indicating that free phenols are not generated in excess (see below). Thus, the generation of rosolic acids from **6** and **8** indicates the electrophilic strength that an anomerically stabilized Ph–O=CF_2^+ cation can exert.

2.6. Revisiting of Ar–OH + CCl_4 + HF → Ar–OCF_3

The need to synthetically prepare the substrates **5**–**8** for the above tantalum catalyzed reactions afforded the opportunity to repeat several of the literature experiments for preparing trifluoromethoxybenzenes and to observe for the generation of rosolic acids. The bottom row of Table 1 shows the results of those observations. Clearly, the loss in yield suffered in the literature examples is the result of the generation of *p*-rosolic acids for those substrates capable of reaction at the para-position. Phenolic substrates with blocked para-positions did not form rosolic acids, even though they did form trifluoromethyl ethers (the reaction of compound **14** was incomplete within the standard 8 h timeframe of these reactions). It is remarkable that in all the above listed references for producing trifluoromethoxybenzenes none have reported such a visibly evident by-product. Even if subject to base neutralization, aqueous solutions of rosolic acids are bright red to maroon and each readily accounts for the less than quantitative yields of all reactions save catechol, **10**.

2.7. Electron donating groups (Table 2)

Both ortho- and para-methoxy substituted trifluoromethoxybenzenes, **15** and **16** were prepared in order to examine the effect of electron donating substituents on the formation of rosolic acids. Unfortunately, in the ortho substituted case **15**, the methyl group proved to be just as labile as the trifluoromethyl group. Loss of both groups individually was observed in the recovery of 2-hydroxyanisole and 2-trifluoromethoxyphenol. Interestingly, an appreciable amount (27%) of rearrangement product **21** was isolated. Only a trace of rosolic acid was isolated. The para-substituted case was equally ineffective in producing rosolic acids, but was, for the most part, recovered unchanged.

A hopefully less labile electron donating substituent (phenyl) was incorporated into this study with the preparation of 2-

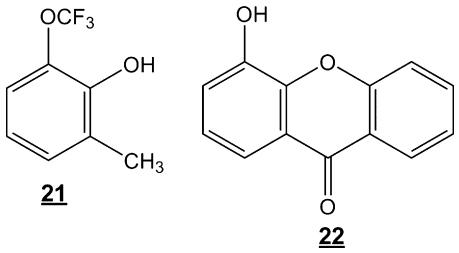


Fig. 2. Reaction side products.

hydroxydiphenyl ether **20**. Upon treatment of **20** with CCl_4/HF some rosolic acid was formed, but the predominant product was 4-hydroxyxanthone **22**. Scheme 3 shows that for this by-product a difluoromethyl oxonium intermediate like **3** is formed, but is, this time, intercepted by an intramolecular Friedel–Crafts reaction before the intermolecular formation of rosolic acid can begin. In light of this predominant side reaction, the Lewis acid reaction of **17** was not attempted.

The spate of side reactions for all the electron rich examples was frustrating, but does certainly indicate that for these systems, rosolic acid formation is a much less favorable event than the alternative reactions.

2.8. Lewis acid effectiveness

A series of pentavalent Lewis acid (halide) catalysts were surveyed for their effectiveness in catalyzing the CF_3 removal/*p*-rosolic acid generation. Table 3 shows the results listed in increasing order of effectiveness as measured by the mole % of *p*-rosolic acid formed vs. CF_3O–Ph.

It can be concluded that $SbCl_5$ would be the best general choice for performing Lewis acid catalyzed reactions on trifluoromethyl phenyl ethers, no matter the relative catalyst activity, as $SbCl_5$ is least likely to generate rosolic acids as a side reaction.

Table 3
Yield of *p*-rosolic acid from Ph–OCF_3 with various Lewis acid catalysts.

$SbCl_5$	$MoCl_5$	$TaCl_5$	WCl_6	$NbCl_5$
10%	15%	25%	25%	39%

2.9. Final identity of the green solid

It must be remembered that *p*-rosolic acid, **2**, is the material isolated from silica gel chromatography, not that isolated straight from the reactor. Understanding that the red of *p*-rosolic acid is due to the conjugated quinone methide system, one would expect that the material in its green form would be different from that chromophore, for example a carbocation fluoride salt such as **23**. To support this contention, authentic *p*-rosolic acid, **2**, was treated with HF at 140 °C for 1 h. Upon vaporization of the HF at 100 °C, followed by aspiration, a quantitative yield of emerald green solid was recovered. As might be expected, ^{1}H NMR showed no significant difference from *p*-rosolic acid. ^{13}C NMR showed shifts of the carbon signals assigned to the quinone ring C-1, C-3 and the methylene carbon. Solid state ^{13}C showed similar changes but was not sufficiently resolved for any conclusions to be made [18]. No F–C coupling was observed. However, ^{19}F NMR exhibited a strong peak at −147 ppm, attributable to $Ar_3C^+F^-$. No free HF was observed (−167 ppm). The IR spectra for this material showed the continued existence of a carbonyl peak at 1590 cm^{-1}. Interestingly, the *p*-rosolic acid + HF compound became red upon grinding with KBr, but regained its green reflectance upon compression in the pellet die. The *p*-rosolic acid–KBr pellet was red to both transmitted and reflected observation.

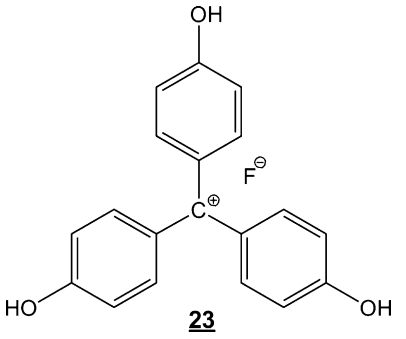
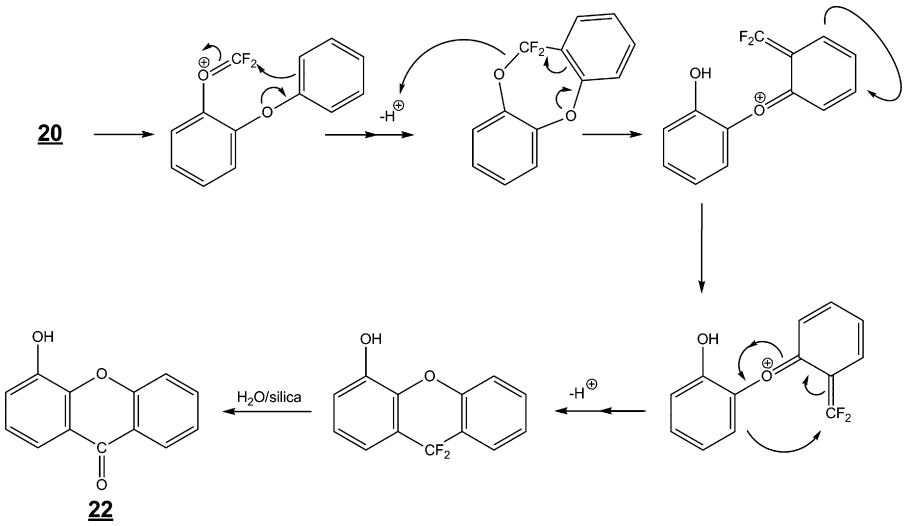


Fig. 3. (Tris)-*p*-hydroxyphenylcarbonium fluoride.



Scheme 3. Mechanism of 4-hydroxyxanthone by-product.

3. Conclusion

Trifluoromethoxyaryls (trifluoromethyl aryl ethers) are susceptible to cleavage of the $-CF_3$ group from the phenolic oxygen in HF/Lewis acid conditions via the formation of a difluoromethyl oxonium cation. The cleavage is accomplished by Friedel–Crafts attack on the difluoromethyl oxonium cation by additional trifluoromethoxyaryls to form rosolic acids as highly colored solid residues. Electron withdrawing substituents and para-blocking groups on the aromatic ring have little effect on the rate of cleavage, though the rosolic acid isomer changes accordingly. Electron donating groups accelerate alternative reactions.

4. Experimental

4.1. General

Anhydrous hydrogen fluoride was Mexichem Fluor S.A. Authentic *p*-rosolic acid was from Sigma. Chlorophenols, hydroquinone and pyrocatechol were from Aldrich. Dibenzodioxin was prepared by the method of Rayne et al. [19]. Trifluoromethoxybenzenes **5**–**8** were prepared by the method of Feiring [2,10]. 2-Phenoxyphenol (**20**) was prepared via the Ullman coupling of **16** [20]. 97% R-132b and trifluoromethoxybenzenes, **3** and **11**, were from Synquest Labs. Tantalum (V) chloride was NOAH Technologies 99.99%. Reactions were performed in a Parr 300 mL hastelloy mini-reactor. ^1H and ^{13}C NMR was performed on a Bruker AV-400. ^{19}F MNR was performed on a Bruker DPX-250. MS was performed on an Agilent 6210 Time-of-Flight spectrometer.

Cautionary note: anhydrous HF causes instantaneous severe burns to the skin and mucous membranes. HF should be handled with full PPE protection. An ample supply of HF antidote gel should be kept on hand before handling HF. See reference for burn treatment procedures [21].

4.2. Example 1 generation of p-rosolic acid, 2, from trifluoromethoxybenzene, 1

720 mg (0.002 mol) $TaCl_5$ was charged to the reactor. The reactor was evacuated and cooled with ice. 50 g (2.5 mol) anh. hydrogen fluoride was charged. The solution was heated with stirring to 140 °C for 1 h. The reactor was again cooled with ice. 10.0 g (0.06 mol) trifluoromethoxybenzene was injected and the reactor was heated to 140 °C for 4 h. The reactor was vented hot into ice wherein 6.7 g unreacted trifluoromethoxybenzene was recovered. The reactor was put under vacuum and cooled. The reactor residue consisted of 1.5 g of a green solid. The solid was chromatographed on silica gel with 15 CH_2Cl_2/1 MeOH as eluent to yield *p*-rosolic acid, **2**, as a red solid.

IR (KBr); ν 3180, 1590, 1449, 1349, 1290, 1161; EIMS Calc'd for C_3HClF_2: 290.0943. Found: 291.1038 (M+1).

^1H NMR (d_6-DMSO, 400 MHz): δ 6.93 (6H, d, J = 8.6 Hz), 6.93 (6H, d, J = 8.6 Hz); ^{13}C NMR (d_6-DMSO, 100 MHz): δ 79.8, 114.0, 118.2, 127.2, 128.9, 139.3, 140.8, 155.7, 169.1; ^{19}F NMR ($CDCl_3$, 235 MHz): no peaks.

4.3. Example 2 spectra of authentic p-rosolic acid

IR (KBr); ν 3180, 1590, 1449, 1349, 1290, 1161, 1020; ^1H NMR (d6-DMSO, 400 MHz): δ 6.93 (6H, d, J = 8.6 Hz), 6.93 (6H, d, J = 8.6 Hz); ^{13}C NMR (d6-DMSO, 100 MHz): δ 79.8, 114.0, 118.2, 127.2, 128.9, 139.3, 140.8, 155.7, 169.1; ^{19}F NMR ($CDCl_3$, 235 MHz): no peaks.

4.4. Example 3 generation of (tris)-p-hydroxyphenylcarbonium fluoride (Fig. 3), 23

1.0 g *p*-rosolic acid was charged to the reactor. The reactor was evacuated and cooled with ice. 40 g (2.0 mol) anh. hydrogen fluoride was charged. The solution was heated with stirring to 100 °C for 1 h. The reactor was vented warm into ice, then put under vacuum and cooled. The reactor residue consisted of 1.03 g (tris)-*p*-hydroxyphenylcarbonium fluoride, **23**, as a green solid.

IR (KBr); ν 3162, 1589, 1448, 1354, 1293, 1161; ^1H NMR (d6-DMSO, 400 MHz): δ 6.93 (6H, d, J = 7.4 Hz), 6.93 (6H, d, J = 7.4 Hz); ^{13}C NMR (d6-DMSO, 100 MHz): δ 79.8, 114.0, 116.9, 131.3, 139.3, 140.8, 155.7, 164.7; ^{19}F NMR ($CDCl_3$, 235 MHz): δ −147.7.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jfluchem.2010.08.003.

References

[1] R.K. Belter, N.K. Bhamare, J. Fluorine Chem. 127 (2006) 1606.
[2] A. Feiring, US Patent 4,258,225 (1981).
[3] K.C. Malhotra, U.K. Banerjee, S.C. Chaudhry, Transition Met. Chem. 7 (1982) 14.
[4] F. Franczak, Louisiana State University Dept. of Chemistry, Baton Rouge, LA 70803.
[5] D. Pu, Louisiana State University Dept. of Chemistry, Baton Rouge, LA 70803.
[6] Scifinder and SBDS database no. 12337HSP-48-202. These publications offer the same reference spectra. In d6-DMSO, supposedly the quinone and phenol signals are differentiated. This phenomenon was not seen with our samples. It is understood that any trace moisture or DMSO itself may set the *p*-rosolic acid quinone and phenols into proton exchange equilibria and coalesce the signals. The literature does not indicate whether low temperature or strict anhydrous conditions were applied. A 'differentiated quinone' signal was obtained with the use of d6-acetone. However, the integration values changed over time to become a single pair of doublets, indicating deuterium exchange of the phenolic–OH groups to be in effect rather than differentiation of the quinone signal.
[7] B. Mehta, H.S. Sharma, S. Bhardwaj, Int. J. Chem. Sci. 5 (2007) 960, This publication assigns 15 H's to the 14 H "Compound-[2]", *p*-rosolic acid. It also assigns integration values of 3H and 6H to what should be 4H and 4H phenolic signals.
[8] G.A. Olah, T. Yamato, T. Hashimoto, J.G. Shih, N. Trivedi, B.P. Singh, M. Piteau, J.A. Olah, J. Am. Chem. Soc. 109 (1987) 3708.
[9] M. Desbois, Bull. Soc. Chim. Fr. 6 (1986) 885 (BF_3).
[10] B. Langlois, M. Desbois, Ann. Chim. Fr. 9 (1984) 729.
[11] A.E. Feiring, J. Org. Chem. 44 (1979) 2907 (BF_3, SbF_3).
[12] J. Salome, C. Mauger, S. Brunet, V. Schanen, J. Fluorine Chem. 125 (2004) 1947 ($NbCl_5$, $TaCl_5$).
[13] K.R. Benson, J. Hickey, W.S. Derwin, M.J. Fifolt, S. Mandal, US Patent 6,118,028 (2000) ($SbCl_5$, $MoCl_5$).
[14] A. Feiring, US Patent 4,157,344 (1979) (BF_3).
[15] N.N. Yarovenko, A.S. Vasileva, Zh. Obshch. Khim. 28 (1958) 2502 (SbF_3/$SbCl_5$).
[16] B. Langlois, G. Soula, Bull. Soc. Chim. Fr. 6 (1986) 925 (no cat.).
[17] R.K. Belter, C.A. McFerrin, J. Fluorine Chem. 131 (2010), xxxx.
[18] W. Treleaven, Louisiana State University Dept. of Chemistry, Baton Rouge, LA 70803.
[19] S. Rayne, R. Sasaki, P. Wan, Photochem. Photobiol. Sci. 4 (2005) 876.
[20] A. Alphasi, H. Firouzabadi, A. Khalafi-nejad, Synth. Commun. 13 (1983) 335.
[21] D. Peters, R. Methchen, J. Fluorine Chem. 79 (1996) 161.