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CF_3 Oxonium Salts, *O*-(Trifluoromethyl)dibenzofuranium Salts: In Situ Synthesis, Properties, and Application as a Real CF_3^+ Species Reagent§

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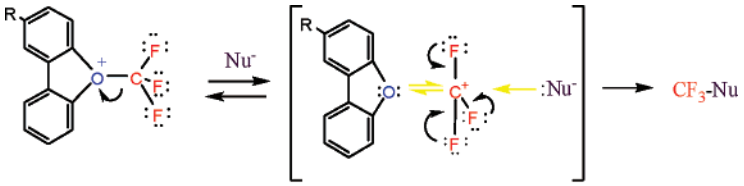
Received May 22, 2007



Nu⁻=Alcohols, phenols, amines, pyridines, sulfonates, $^-$OTf, BF_4^-, PF_6^-, SbF_6^-, $Sb_2F_{11}^-$

We report in situ synthesis of the first CF_3 oxonium salts, thermally unstable *O*-(trifluoromethyl)-dibenzofuranium salts, which furthermore have different counteranions (BF_4^-, PF_6^-, SbF_6^-, and $Sb_2F_{11}^-$) and ring substituents (*tert*-butyl, F, and OCH_3), by photochemical decomposition of the corresponding 2-(trifluoromethoxy)biphenylyl-2′-diazonium salts at −90 to −100 °C. The yields markedly increased in the order of $BF_4^- < PF_6^- < SbF_6^- < Sb_2F_{11}^-$. The CF_3 oxonium salts were fully assigned by means of ^1H and ^{19}F NMR spectroscopy at low temperature. The CF_3 salts decomposed to form CF_4 and dibenzofurans. The half-life times at −60 °C of the 2-*tert*-butyl salts having different counteranions were 29 min for BF_4^- salt **2d**, 36 min for PF_6^- salt **2c**, 270 min for SbF_6^- salt **2a**, and 415 min for $Sb_2F_{11}^-$ salt **2b**. Those at −60 °C of the $Sb_2F_{11}^-$ salts having different 2-substituents were 13 min for F salt **3b**, 63 min for H (unsubstituted) salt **1b**, and 415 min for *tert*-butyl salt **2b**. Thus, the stability of the CF_3 oxonium salts increased in the order of $BF_4^- < PF_6^- < SbF_6^- < Sb_2F_{11}^-$ and F < H < *tert*-butyl, which is in accord with the increasing orders of the non-nucleophilicity of counteranions and the electron-donating effect of ring subsitituents. 2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium hexafluoroantimonate (**2a**) was thus chosen and successfully applied as a real CF_3^+ species source to the direct *O*- and *N*-trifluoromethylations of alcohols, phenols, amines, anilines, and pyridines under very mild conditions. The thermal decomposition method with a mixture of diazonium salt **17a** and aryl- or alkylsulfonic acids, pyridine, or pyridines having an electron-withdrawing group also afforded CF_3O or CF_3N products. The trifluoromethylation mechanism is discussed and an S_N2 mechanism containing the transient formation of free CF_3^+ is proposed. Thus, the present study has demonstrated that the exceedingly reactive CF_3^+ species can be generated much easier than the CH_3^+ species, contrary to the common sense that CF_3^+ is extremely difficult to generate in solution.

Introduction

As half of the recently sold top ten drugs contain fluorine atoms and even more fluorinated drugs are predicted to be developed in the future, fluoroorganic compounds have gained tremendous attention in the field of chemistry and biochemistry.[1] One or a few fluorine atoms substituted at a specific site in an organic compound can dramatically alter its chemical and biological nature because of the fluorine atom's chemical extremism resulting from its highest electronegativity and small size closest to the hydrogen atom.[2] In particular, the trifluoromethyl (CF_3) group, three fluorine atoms collecting at one carbon, is useful because CF_3 brings in high stability and

§ A part of this work was described in U.S. patent 6,239,289 B1 (2001) and a review article: Umemoto, T. Recent Advances in Perfluoroalkylation Methodology. In *Fluorine-Containing Synthons*; Soloshonok, V. A., Ed.; ACS Symp. Ser. No. 911; American Chemical Society: Washington, D.C., 2005; Chapter 1, pp 2−15.

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(1) Fabulous Fluorine. *Chem. Eng. News* **2006**, *June 5*, 15−32.

10.1021/jo070896r CCC: $37.00
Published on Web 08/04/2007

lipophilicity in addition to the high electronegativity and the mimic effect by its small size.[2] However, introducing the CF_3 group into an organic molecule easily, selectively, and safely presents synthetic challenges. Therefore, extensive efforts have been made to develop useful methodologies for it.[1−4] In particular, nucleophilic trifluoromethylations have been studied extensively and applied to the preparation of trifluoromethylated compounds in this decade.[5] However, electrophilic trifluoromethylations have been developed slowly.[4] *O*-Trifluoromethyl oxonium salts have long been a target among chemists because the unique salts may be anticipated as a useful CF_3^+ source since *O*-methyl oxonium salts, well-known as Meerwein reagents, have been studied and widely used as a CH_3^+ source for methylation.[6] However, the *O*-trifluoromethyl salts have not been synthesized yet.

Trifluoromethylation via the standard S_N1 or S_N2 mechanisms comprising the transition state of CF_3^+ has been believed extremely hard to occur because it is so difficult to generate CF_3^+ due to the three, most electronegative fluorine atoms bonded to the strongly electron-deficient cationic carbon. Although CCl_3^+ and CBr_3^+ were generated in this manner, an attempt to generate and isolate the CF_3^+ species in solution failed.[7,8] Calculations have predicted that CF_3^+ is much less stable than CCl_3^+ and CBr_3^+ and that the electron-withdrawing effect of three fluorine atoms overwhelms their p-electron-donating effect to a carbocation.[7] The trifluoromethylation by the S_N1 or S_N2 CF_3^+ mechanisms has never been described except for only a harsh reaction of triflic acid and fluorosulfonic acid at high temperature, giving trifluoromethyl triflate (CF_3OTf) in 19% yield.[9] This reaction was suggested to proceed via the exceedingly reactive CF_3^+ ion in the superacid media. However, this trifluoromethylation is not applicable to the modern organic syntheses where complex and multifunctional compounds have been treated, because such strong reaction conditions hurt useful functional groups existing in the compounds. Accordingly, so far, there have been no reports of direct *N*-trifluoromethylation of amines, anilines, and pyridines, which may be expected to easily combine with the CF_3^+ species to give *N*-CF_3 compounds if the CF_3^+ species exist. Regarding direct *O*-trifluoromethylation, there have been some reports in addition to Olah's report[9] described above. Schreeve et al. reported that $CF_3S(OCF_3)_2CF_3$ reacted with phenol to give α,α,α-trifluoroanisole, but the nucleophlic attack of CF_3O oxygen at the ipso position was proposed as a reaction mechanism.[10] Feiring et al. reported that phenol was treated with CCl_4 in anhydrous HF at 100−150 °C in an autoclave to give α,α,α-trifluoroanisoles, but the attack of $^+CCl_nF_m$ on phenol, followed by the exchange reaction of Cl to F, was proposed as a reaction mechanism.[11] Kobayashi et al. reported that CF_3I reacted with AgOTf in benzene at 200 °C to give CF_3OTf in a high yield.[12] Makarov et al. reported that CF_3OCH_3 was obtained by a free radical reaction resulting from the reaction of CF_3NO with hydroxylamine in methanol.[13] However, these reported *O*-trifluoromethylations have had a limited scope for application.

We have developed *S*-, *Se*-, and *Te*-(trifluoromethyl)dibenzothio-, -seleno-, and -telluro-phenium salts as power-variable electrophilic[14] trifluoromethylating agents, whose reactivity varies depending on the electronegativity of the chalcogen atoms and ring substituents.[15] The nonheterocyclic electrophilic trifluoromethylating agents have also been developed.[16,17] Recently, a different type of trifluoromethyliodo(III) compound was reported.[18] The reagents react with nucleophiles according to the trifluoromethylation power to give *C*-, *P*-, or *S*-CF_3 products in good yields.[15,16,19−21] However, even the most powerful *S*-CF_3-dinitrodibenzothiophenium triflate cannot produce *O*- and *N*-CF_3 compounds except for its heating in a phenol solvent giving a *O*-CF_3 product, α,α,α-trifluoroanisole, in 13% yield. Their kinetic studies excluded the standard S_N2 mechanism for the trifluoromethylation and suggested a mechanism via a transition state that is sensitive to steric circumstances.[22] A

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(14) The term "*electrophilic* trifluoromethylating agents" used in fluorocarbon chemistry may simply mean the reagents that trifluoromethylate *nucleophilic* substrates. It does not mean that the reactive species in the trifluoromethylations are CF_3^+. This may be different from "*electrophilic* methylating agents" or "*electrophlic* methylations" used in hydrocarbon chemistry, in which it is implied that the reactive species are CH_3^+, accurately, $CH_3^{+\ \text{or}\ \delta+}$.

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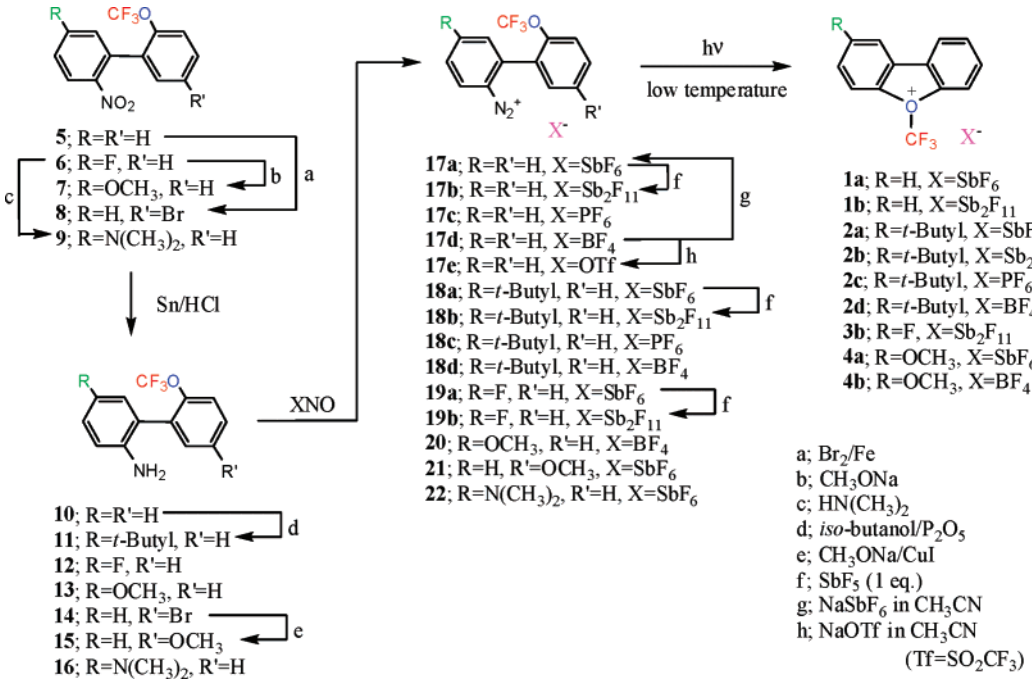
SCHEME 1



reaction mechanism via a *S*-*O* sulfurane intermediate followed by a kind of S_N2 type of trifluoromethylation was recently proposed for the reaction of *S*-CF_3-dibenzothiophenium triflate with carbanions of *β*-ketoesters.[21] However, it is not likely that these reactions proceed via a real S_N2 CF_3^+ trifluoromethylation mechanism because this type of trifluoromethylation was demonstrated to be well activated by UV irradiation.[20] Therefore the electrophilic trifluoromethylating agents reported so far may be considered as pseudo-CF_3^+ reagents. These results really attracted us to the yet unknown *O*-CF_3 onium salts because the oxygen atom has the highest electronegativity in the heteroatom salt series (Te < Se < S < O). In this paper, we describe the in situ synthesis and properties of the first CF_3 oxonium salts, *O*-(trifluoromethyl)dibenzofuranium salts, and their successful application as a real CF_3^+ species reagent to the direct *O*- and *N*-trifluoromethylations.

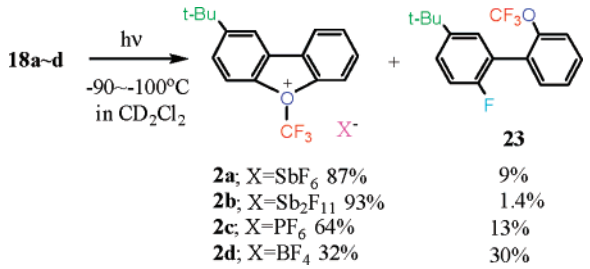
Results and Discussions

Synthesis of 2-(Trifluoromethoxy)biphenylyl-2′-diazonium Salts. 2-(Trifluoromethyl)biphenylyl-2′-diazonium salts **17**−**22** were synthesized as precursors of *O*-(trifluoromethyl)dibenzofuranium salts **1**−**4**. 1-Iodo-2-(trifluoromethoxy)benzene was heated with 1-bromo-2-nitrobenzene at 190 °C for 4 h in the presence of copper to give 2-nitro-2′-(trifluoromethoxy)biphenyl (**5**) in 57% yield. The same treatment with 2-bromo-4-fluoro-1-nitrobenzene gave **6** in 60% yield. Treatment of **6** with CH_3-ONa produced 5-methoxy-2-nitro-2′-(trifluoromethoxy)biphenyl (**7**) in 93% yield. Bromination of **5** with Br_2/Fe produced 5-bromo-2′-nitro-2-(trifluoromethoxy)biphenyl (**8**) in 89% yield. **9** was obtained in 95% yield by treatment of **6** with dimethylamine. Reduction of **5**, **6**, **7**, **8**, and **9** with tin gave amino derivatives **10**, **12**, **13**, **14**, and **16**, respectively, in high yields. 5-*tert*-Butyl derivative **11** was prepared in 60−73% yield by treatment of **10** with isobutanol/P_2O_5. **11** was also prepared in 87% yield by coupling 2-(trifluoromethoxy)phenylboric acid with 2-bromo-4-*tert*-butylaniline in the presence of $Pd(PPh_3)_4$ as a catalyst. **15** was prepared in 68% yield by treatment of **14** with CH_3ONa/CuI/collidine. **10** was treated with $NOSbF_6$, $NOPF_6$, and $NOBF_4$ in dichloromethane to give diazonium SbF_6^- salt **17a**, PF_6^- salt **17c**, and BF_4^- salt **17d** in 70%, 78%, and 86% yields, respectively. Similarly, salts **18a**, **18c**, and **18d** were synthesized from **11** in 58%, 88%, and 59% yields, respectively, and salts **19a**, **20**, **21**, and **22** were synthesized from **12**, **13**, **15**, and **16** in 56%, 89%, 42%, and 86% yields, respectively. $Sb_2F_{11}^-$ salts **17b**, **18b**, and **19b** were in situ prepared by adding an equimolar amount of SbF_5 to **17a**, **18a**, and **19a** in dichloromethane. Triflate **17e** was synthesized in 90% yield by the counteranion exchange reaction of **17d** with sodium triflate. Salt **17a** was also synthesized in 71% yield from **17d** by the exchange reaction with $NaSbF_6$.

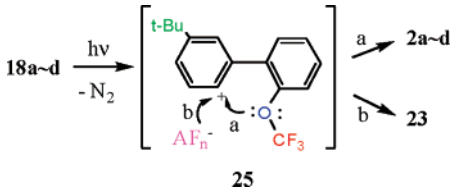
Photochemical Decomposition of Diazonium Salts: In Situ Synthesis of *O*-(Trifluoromethyl)dibenzofuranium Salts 1a,b, 2a−d, 3b, and 4a,b. We have found that photochemical decomposition of diazonium salts **17a,b**, **18a**−**d**, **19b**, **20**, and **21** in dichloromethane with a high-pressure Hg lamp at low temperature (−90 to −100 °C) produces *O*-(trifluoromethyl)-dibenzofuranium salts **1a**,**b** and their *tert*-butyl **2a**−**d**, fluoro **3b**, and methoxy **4a**,**b** derivatives. The photoreaction of **19a** was not carried out because **19a** is insoluble in dichloromethane. The diazonium $Sb_2F_{11}^-$ salts and the *tert*-butyl-substituted diazonium salts are particularly suitable for the photochemical reaction because of high solubility in dichloromethane even at very low temperature. Diazonium salt **22** having $N(CH_3)_2$ produced no CF_3 oxonium salt under the same photoreaction.

As shown in Scheme 2 and Figure 1, *tert*-butyl diazonium salts **18a**−**d** were irradiated to give the CF_3 oxonium salts **2a**−**d** and byproduct **23**, yields of which greatly varied depending on the counteranions. As other byproducts, tetrafluoromethane and a small amount (3%) of 5-*tert*-butyl-2-chloro-2′-(trifluoromethoxy)biphenyl (**24**) were observed. The former (CF_4) was identified by an authentic sample and the latter was tentatively assigned by GC-Mass and ^{19}F NMR analysis. The chlorine atom of the latter **24** probably came from the solvent. The yields of **2a**−**d** increased and the byproduct **23** decreased with the

SCHEME 2



SCHEME 3

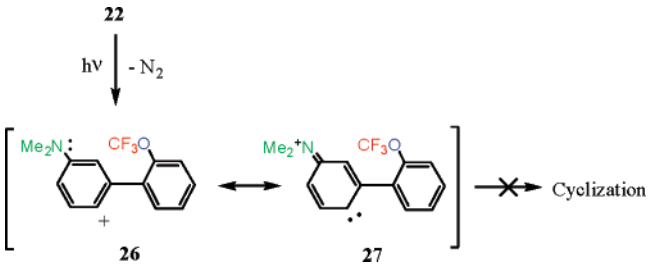


increase of non-nucleophilicity of the counteranions in the order of BF_4^- < PF_6^- < SbF_6^- < $Sb_2F_{11}^-$. The least nucleophilic $Sb_2F_{11}^-$ salt **2b** in this series gave the highest yield (93%) of the CF_3 oxonium salt **2b** and the lowest yield (1.4%) of byproduct **23**. SbF_6^- salt **2a** was obtained in 87% yield together with 9% of **23**.

The highest yield of **2b** with the least nucleophilic $Sb_2F_{11}^-$ anion is clearly explained as shown in Scheme 3. There may be two competitive reactions, routes a and b, of the intermediate biphenyl cation **25** with the oxygen atom of the CF_3O group and with the fluorine atoms of the counteranions. Route a becomes more predominant with the decrease of nucleophilicity of the counteranion AF_n^-.

No formation of the CF_3 oxonium salt from diazonium salt **22** having $N(CH_3)_2$ can be explained by great deactivation of the intermediate biphenyl cation **26** by the strongly electron-donating group causing **27**, which may make it impossible to cyclize to the CF_3 oxonium salt.

SCHEME 4



The dichloromethane-d_2 solutions of the diazonium salts were irradiated and their NMR spectra were measured at low temperature. The ^1H NMR spectra of unsubstituted $Sb_2F_{11}^-$ salt **1b** and 2-*tert*-butyl-substituted SbF_6^- salt **2a** were fully assigned by COSY spectrum at −70 °C. $H_{1,8}$, $H_{2,7}$, $H_{3,6}$, and $H_{4,5}$ in **1b** appear at 8.13, 7.94, 8.04, and 8.31 ppm. Figure 2 shows the COSY spectrum of **2a**. H_8 (8.09 ppm), H_7 (7.92), H_6 (8.03), and H_5 (8.30) each in **2a** appear at the same position as the corresponding proton in **1b**, while H_1 (8.21), H_3 (7.89), and H_4 (7.99) in **2a** appear in a different position. In particular, H_4 in **2a** appears quite upfield. Since the H_4 is not influenced by the steric effect of the *tert*-butyl substituent, it is evident that the electron-donating *tert*-butyl substituent at the 2-position remarkably increases the electron density around the H_4 proton in **2a**.

Singlet CF_3 peaks were observed in the range of −51 to −54 ppm in the ^{19}F NMR spectra. The electronic effect of the substituents reflects the ^{19}F chemical shifts of CF_3 groups at −70 °C: −51.88 ppm for F salt **3b** ($Sb_2F_{11}^-$), −52.38 and −51.99 ppm for H (unsubstituted) salts **1a** (SbF_6^-) and **1b** ($Sb_2F_{11}^-$), −52.65 and −52.64 ppm for *tert*-butyl salts **2a** (SbF_6^-) and **2b** ($Sb_2F_{11}^-$), and −53.22 ppm for CH_3O salt **4a** (SbF_6^-). Thus, the chemical shifts appear upfield in the order of F < H < *tert*-butyl < CH_3O, which agrees with the increasing order of the electron-donating effect of the substituents.

Thermal Change and Half-Life Times of CF_3 Oxonium Salts. Figure 3 shows a consecutive change in the ^1H and ^{19}F

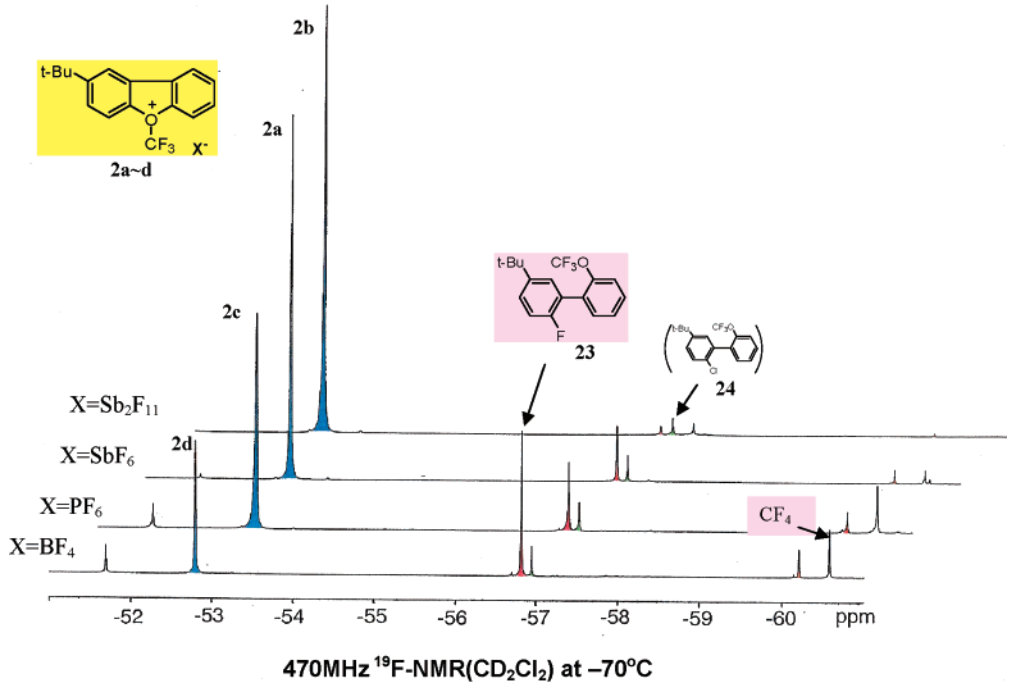


FIGURE 1. ^{19}F NMR after photoreaction of 5-*tert*-butyl-2′-(trifluoromethoxy)biphenylyl-2-diazonium salts **18a**−**d**.

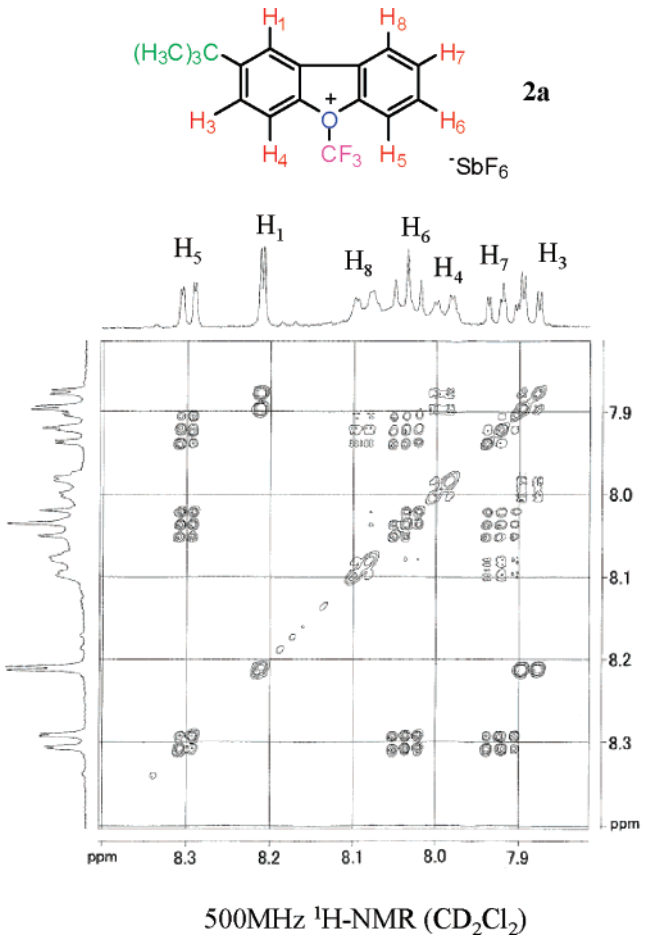
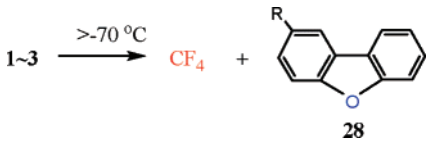


FIGURE 2. COSY spectrum of CF_3 oxonium salt **2a** at −70 °C.

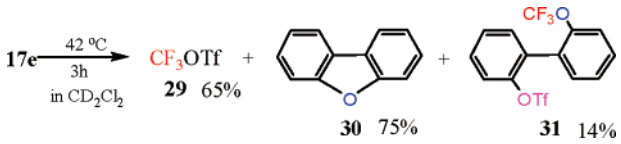
NMR spectra of **2a** with the increase of the temperature from −80 to −30 °C. The CF_3 signal gradually decreased at more than −70 °C and completely disappeared at −30 °C, while the signal of CF_4 increased, but small byproducts **23** and **24** were not changed. The ^{1}H NMR changed in accord with the change in the ^{19}F NMR. Other CF_3 oxonium salts showed similar behavior. This indicates that the CF_3 oxonium salts are thermally unstable and decompose to give CF_4 and dibenzofuran **28** (Scheme 5).

By means of the ^{19}F NMR technique, the half-life times of CF_3 oxonium salts **1b**, **2a**−**d**, and **3b** were measured. Salts **4a**,**b** were excluded because they have a CH_3O group whose oxygen atom may make a complex with SbF_5 added or may react with the CF_3^+ of its own molecule or another molecule. Figure 4 (left) shows the half-life times of the *tert*-butyl CF_3 oxonium salts having different counteranions. The half-life times are 29 min for BF_4^- salt **2d**, 36 min for PF_6^- salt **2c**, 270 min for SbF_6^- salt **2a**, and 415 min for $Sb_2F_{11}^-$ salt **2b** at −60 °C. This increasing order is in accordance with the increasing order of non-nucleophilicity of the counteranions ($BF_4^- < PF_6^- < SbF_6^- < Sb_2F_{11}^-$). Figure 4 (right) shows the half-life times of the CF_3 oxonium $Sb_2F_{11}^-$ salts having different substituents at the 2-position. The half-life times are 13 min for F salt **3b**, 63 min for H salt **1b**, and 415 min for *tert*-butyl salt **2b** at −60 °C. These are 4 min for **3b**, 24 min for **1b**, and 46 min for **2b** at −50 °C. This increasing order is in accordance with the increasing order of the electron-donating effect of the substituents (F < H < *tert*-butyl). These results definitely demonstrate

SCHEME 5



SCHEME 6



that less nucleophilicity of the counteranion and more electron-donating effect of the substituent make the CF_3 oxonium salts stabilized. The stabilizing effect by the substituents reflects the ^{19}F chemical shifts of CF_3 groups as discussed above.

Thermal Decomposition of 2-(Trifluoromethoxy)biphenylyl-2′-diazonium Salts. Triflate **17e** was heated in dichloromethane-d_2 at 42 °C for 3 h. The decomposition products were CF_3OTf (**29**), dibenzofuran (**30**), and 2-(trifluoromethanesulfonyloxy)-2′-(trifluoromethoxy)biphenyl (**31**) (Scheme 6). Their yields were 65%, 75%, and 14%, respectively. The formation of products **29** and **30** can be explained by the immediate decomposition of thermally unstable *O*-(trifluoromethyl)dibenzofuranium triflate (**33**), which was formed through biphenyl cation **32** (Scheme 7).

Product **31** may be formed by the reaction of the reactive biphenyl cation **32** with the counteranion $^-$OTf. As expected from the thermal instability of the CF_3 oxonium salts, NMR trace experiment of the thermal decomposition at 42 °C did not show any intermediates other than the starting diazonium triflate and the decomposition products.

The thermal decomposition of the diazonium salts **17a**,**c**−**e** in phenol was carried out (Scheme 8). The yields of **30** remained almost unchanged (74−78%). This means that the cyclization to the thermally unstable CF_3 oxonium salts in the thermal reactions occurred in almost the same yields regardless of the counteranions. However, a great difference was observed in the yields of **34** among the counteranions. Salt **17a** having the least nucleophilic SbF_6^- in the series gave the highest yield (73%) of **34**, indicating that the intermediate CF_3 oxonium SbF_6^- salt reacted almost exclusively with phenol, not with its own counteranion SbF_6^-. The possibility that CF_3OTf (**29**) resulting from the decomposition of **33** reacted with phenol to give **34** in the case of triflate **17e** was excluded because **29** has been known not to act as a source of CF_3^+.[23]

Synthetic Application of Photochemically Prepared 2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium Hexafluoroantimonate (2a) as a Real CF_3^+ Species Reagent. As mentioned above, **2a** can be synthesized in high yields and is more stable due to the electron-donating *tert*-butyl subsitituent and less nucleophilic SbF_6^- anion. In addition, **2a** and its starting diazonium salt **18a** are soluble in dichloromethane even at very low temperature. Therefore, **2a** was chosen and its reactivity was examined. Reagent **2a** was in situ prepared by the photoreaction of **18a** at −90 to −100 °C and allowed to react with alcohols, phenols, amines, anilines, and pyridines at −90 to −10 °C for 3 h. The results are shown in Table 1. Alcohols

(23) Kobayashi, Y.; Yoshida, T.; Kumadaki, I. *Tetrahedron Lett.* **1979**, 3865−3866.

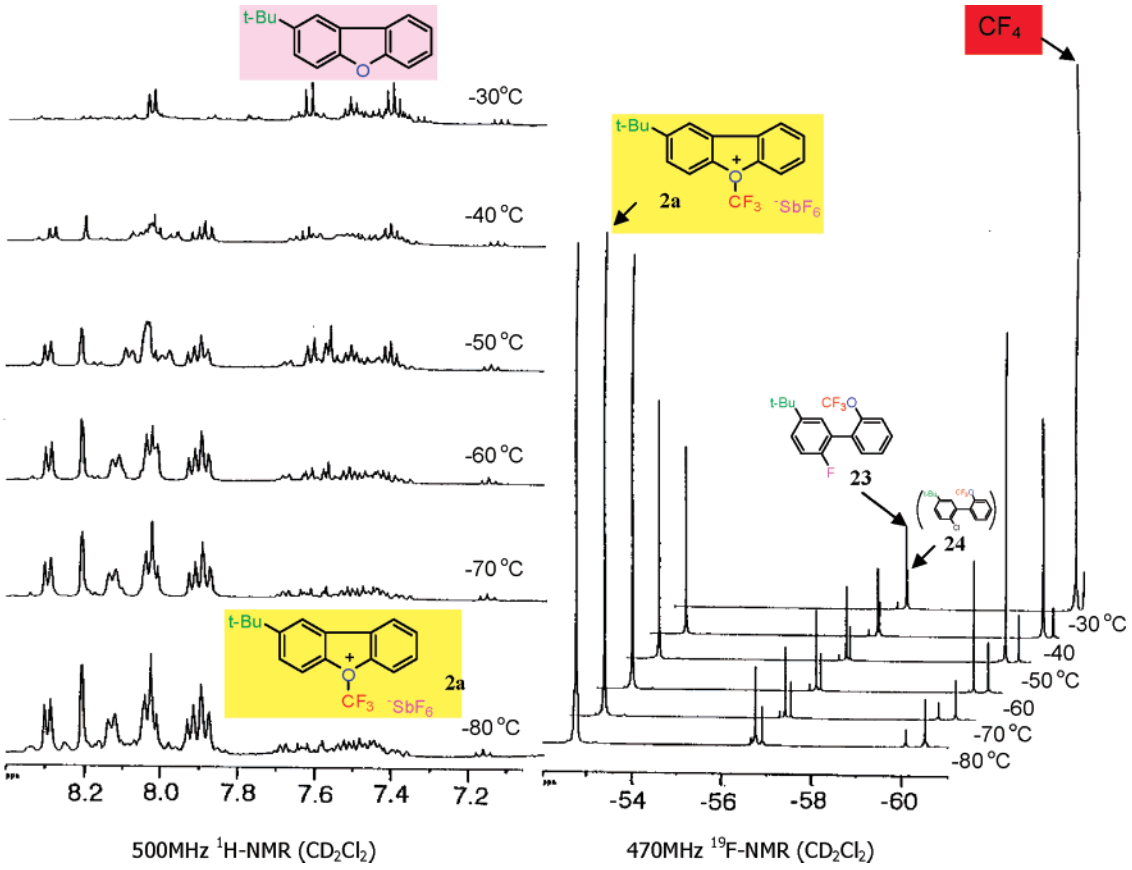


FIGURE 3. Thermal change of ^{1}H and ^{19}F NMR of **2a** at −80 to −30 °C.

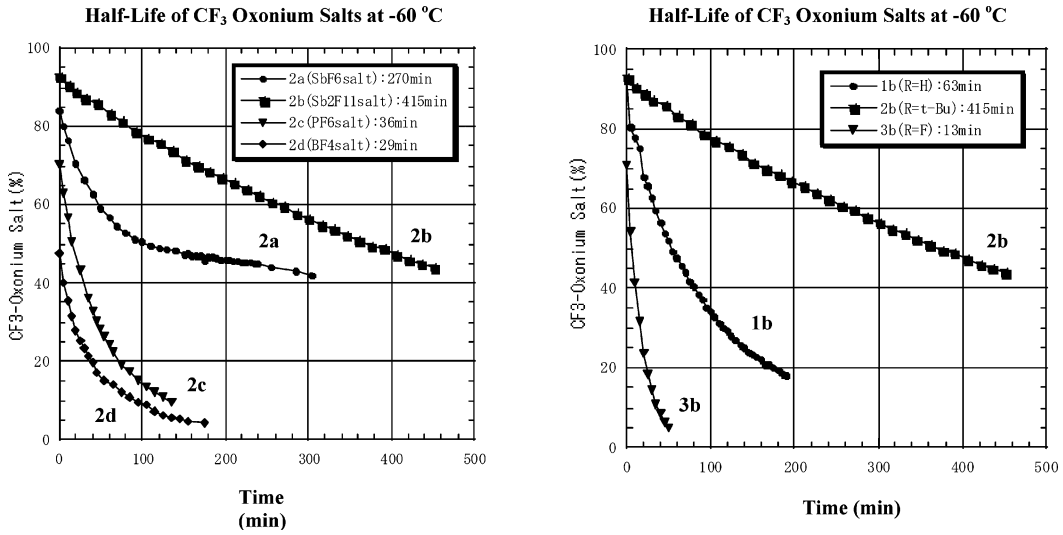


FIGURE 4. Half-life times with different anions (left) and different substituents (right).

and phenols were smoothly trifluoromethylated with **2a** at low temperature in the presence of 2-choloropyridine or di(isopropyl)ethylamine as an acid ($HSbF_6$) trap to give *O*-CF_3 products in high yields. Primary and secondary amines and anilines gave *N*-CF_3 products in high or good yields. For some cases, two equivalent amounts of amines and anilines were used, where an equivalent amount of them was consumed as an acid trap. As an acid trap, bulky di(isopropyl)ethylamine was better than 2-chloropyridine, because some of the 2-chloropyridine could be trifluoromethylated. Tertiary amines and pyridines gave trifluoromethyl quaternary ammonium and pyridinium salts in fair to good yields. Pyridines with electron-withdrawing and -donating substituents gave similar yields of the *N*-trifluoromethylpyridinium salts.

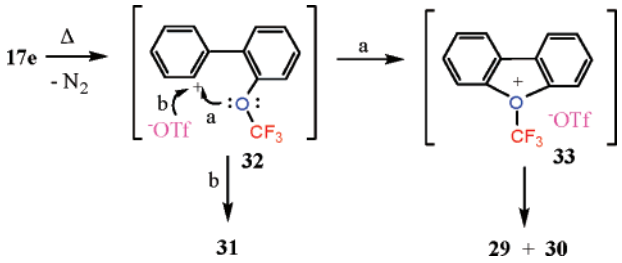
It is worthy to note that the reactive **2a** did not react with aromatics such as toluene and naphthalene. Reagent **2a** was in situ prepared photochemically and was treated with 2 equiv of toluene and naphthalene in dichloromethane at low temperature to room temperature. But we did not detect any (trifluoromethyl)toluene and -naphthalene. Although we did not search for

TABLE 1. ***O*- and *N*-Trifluoromethylations with 2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium Hexafluoroantimonate (2a)**

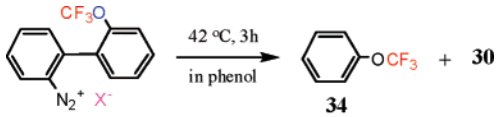
run	substrate[a]	base[b]	product	yield (%)[c]	^{19}F NMR (CD_3CN)
1	2-phenylethanol	α-chloropyridine	$PhCH_2CH_2OCF_3$	80	−59.8 (s)
2	*n*-$C_{10}H_{21}OH$	$(i\text{-Pr})_2NEt$	*n*-$C_{10}H_{21}OCF_3$[d]	82	−59.6 (s)
3	phenol	$(i\text{-Pr})_2NEt$	$PhOCF_3$	75	−57.5 (s)
4	*p*-cresol	$(i\text{-Pr})_2NEt$	*p*-$TolylOCF_3$	78	−57.6 (s)
5	*p*-methoxyphenol	$(i\text{-Pr})_2NEt$	*p*-$CH_3OC_6H_4OCF_3$	83	−58.0 (s)
6	*p*-bromophenol	$(i\text{-Pr})_2NEt$	*p*-$BrC_6H_4OCF_3$	74	−57.3 (s)
7	*p*-acetylphenol	$(i\text{-Pr})_2NEt$	*p*-$CH_3COC_6H_4OCF_3$	83	−57.3 (s)
8	*p*-cyanophenol	$(i\text{-Pr})_2NEt$	*p*-$NCC_6H_4OCF_3$	85	−57.4 (s)
9	*p*-nitrophenol	$(i\text{-Pr})_2NEt$	*p*-$O_2NC_6H_4OCF_3$	81	−57.4 (s)
10	aniline	aniline	$PhNHCF_3$[e]	93	−55.1 (d, J = 5.6 Hz)
11	*N*-methylaniline	*N*-methylaniline	$PhN(CH_3)CF_3$[f]	71	−59.6 (s)
12	*N*,*N*-dimethylaniline		$PhN^+(CH_3)_2CF_3SbF_6^-$[g]	49	−73.5 (s)
13	benzylamine	benzylamine	$PhCH_2NHCF_3$[h]	74	−57.2 (d, J = 7.4 Hz)
14	*tert*-butylamine	*tert*-butylamine	*t*-$BuNHCF_3$[i]	38	−49.1 (d, J = 7.7 Hz)
15	diethylamine	diethylamine	Et_2NCF_3[j]	49	−59.4 (s)
16	indoline	$(i\text{-Pr})_2NEt$	*N*-CF_3-indoline[k]	68	−60.6 (s)
17	dibenzylamine	$(i\text{-Pr})_2NEt$	$(PhCH_2)_2NCF_3$[l]	46	−59.1 (s)
18	pyridine		*N*-CF_3-pyridinium SbF_6	70	−60.2 (s)
19	3-chloropyridine		*N*-CF_3-3-Cl-pyridinium SbF_6	64	−59.7 (s)
20	4-cyanopyridine		*N*-CF_3-4-CN-pyridinium SbF_6	66	−59.9 (s)
21	methyl isonicotinate		*N*-CF_3-4-CH_3OCO-pyridinium SbF_6	82	−59.8 (s)
22	4-methylpyridine		*N*-CF_3-4-CH_3-pyridinium SbF_6	64	−60.5 (s)

[a] An equimolar amount of a substrate to **18a** was used. [b] An equimolar amount of a base to **18a** was used except for runs 12 and 18−22 where a base was not used. [c] Yields were determined by ^{19}F NMR with $C_6H_5CF_3$ as a standard and calculated based on **2a**, which was in situ prepared in 87−89% yield. [d] Kuroboshi, M.; Suzuki, K.; Hiyama, T. *Tetrahedron Lett.*, **1992,** *33,* 4173−4176. [e] Ruppert, I. *Tetrahedron Lett.*, **1980,** *21,* 4893−4896. [f] High MS; M^+ 175.06116 (calcd for $C_8H_8F_3N$ 175.06088). [g] High MS; M^+ 190.08480 (calcd for $C_9H_{11}F_3N$ 190.08436). [h] High MS; M^+ 175.06045 (calcd for $C_8H_8F_3N$ 175.06088). [i] See footnote *e*. [j] Pawelke, G. *J. Fluorine Chem.* **1991,** *52,* 229−234. [k] Hiyama, T.; Kuroboshi, M.; Wakakuri, S. Jpn Kokai Tokkyo Koho JP05 78,286. [l] Kuroboshi, M.; Hiyama, T. *Tetrahedron Lett.* **1992,** *33,* 4177−4178.

SCHEME 7



SCHEME 8



17; X^-	34	30
17a; SbF_6^-	73%	78%
17c; PF_6^-	70%	74%
17d; BF_4^-	34%	76%
17e; ^-OTf	33%	74%

the formation of CF_4 at that time, it may be thought that **2a** as a hard acid reacted with a hard base, the fluoride anion of SbF_6^-, to give CF_4, which is an extremely stable compound, but **2a** could not react with such a soft base as toluene and naphthalene.

Synthetic Application of Thermally Prepared *O*-(Trifluoromethyl)dibenzofuranium Hexafluoroantimonate (1a) as a Real CF_3^+ Species Reagent. A synthetic application of thermally prepared **1a** was also carried out as shown in Table 2. An equimolar mixture of its precursor **17a**, 2-phenylethanol, and 2-chloropyridine in dichloromethane was heated under reflux for 3 h to give trifluoromethyl 2-phenylethyl ether in a low yield (run 1). When 2 equiv of 2-phenylethanol were used, the product was obtained in 52% yield. An equimolar mixture of **17a**, *p*-toluenesulfonic acid, and pyridine in dichloromethane was heated under reflux for 4 h to give trifluoromethyl *p*-toluenesulfonate in a high yield (run 3). Similarly, trifluoromethyl *p*-octylbenzenesulfonate, trifluoromethyl 2-naphthalenesulfonate, and trifluoromethyl 3-bromocamphor-8-sulfonate were obtained in 52%, 61%, and 56% yields, respectively. An equimolar mixture of **17a** and pyridine, 3-chloro-, 4-cyano-, or 4-(methoxycarbonyl)pyridine gave the corresponding *N*-CF_3-pyridinium salts in 50%, 53%, 46%, and 33% yields, respectively, but 4-methylpyridine gave only 4% of *N*-CF_3-4-methylpyridinium salt (run 11). The low yield of the latter case is probably due to more nucleophilicity of 4-methylpyridine, which may interfere with cyclization of the intermediate biphenyl cation to the CF_3-oxonim salt **1a**, because analogous **2a**, which was in situ prepared photochemically at low temperature, reacted with 4-methylpyridine to give the *N*-CF_3-4-methylpyridinium salt in 64% yield (Table 1, run 22).

Trifluoromethylation Mechanism. The decomposition reaction of the CF_3 oxonium salts giving CF_4 can be considered as a trifluoromethylation reaction of a CF_3 oxonium cation with its counteranion that is a nucleophile. Since the life time of the CF_3 oxonium salt depends on the nucleophilicity of the counteranion, it is evident that the trifluoromethylation reaction is rate-determined by the nucleophilicity of nucleophile. From a reaction mechanism standpoint, this trifluoromethylation is a bimolecular nucleophilic substitution, that is, the S_N2 mechanism. The *N*- and *O*-trifluoromethylations occur with alcohols, amines, etc. that are nucleophiles.

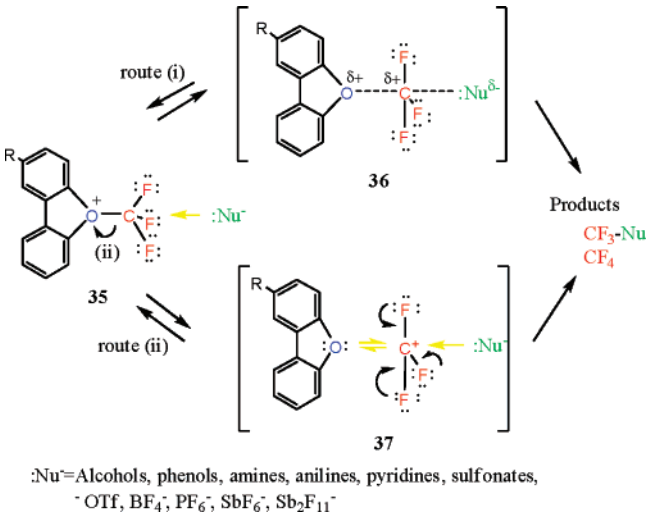
As shown in Scheme 9, routes i and ii may be considered for the CF_3^+ trifluoromethylation. Route i is a mechanism via five-coordinated carbon transition state **36** where a cationic charge is neutralized as much as possible by a nucleophile, and has often been thought as being a standard S_N2 methylation mechanism in hydrocarbon chemistry. Route ii is a mechanism of the formation of a definite and transient CF_3^+ ion in equilibrium with **35**, as shown in **37**, which then abstracts a

TABLE 2. ***O*- and *N*-Trifluoromethylations by Means of Thermal Decomposition of 2-(Trifluoromethoxy)biphenylyl-2′-diazonium Hexafluoroantimonate (17a)**

run	substrate[a]	base[b]	products	yield (%)[c]
1	2-phenylethanol	2-chloropyridine	$PhCH_2CH_2OCF_3$	36
2	(2-naphthyl)methanol	2-chloropyridine	(2-naphthyl)-CH_2OCF_3	11[e]
3	*p*-toluenesulfonic acid[d]	pyridine	*p*-tolyl-SO_2OCF_3	79
4	sodium *p*-(*n*-octyl)benzenesulfonate		*p*-(*n*-octyl)benzene-SO_2OCF_3	52
5	2-naphthalenesulfonic acid	pyridine	(2-naphthyl)-SO_2OCF_3	61
6	ammonium 3-bromocamphor-8-sulfonate[f]		3-bromocamphor-8-SO_2OCF_3	56
7	pyridine		*N*-CF_3-pyridinium SbF_6	50
8	3-chloropyridine		*N*-CF_3-3-Cl-pyridinium SbF_6	53
9	4-cyanopyridine		*N*-CF_3-4-CN-pyridinium SbF_6	46
10	methyl isonicotinate		*N*-CF_3-4-CH_3OCO-pyridinium SbF_6	33
11	4-methylpyridine		*N*-CF_3-4-CH_3-pyridinium SbF_6	4

[a] An equimolar amount of a substrate to **17a** was used. [b] An equimolar amount of a base to **17a** was used except for runs 4 and 6−11 where a base was not used. [c] Yields were determined by ^{19}F NMR with $C_6H_5CF_3$ as a standard. [d] Monohydrate was used. [e] When 5 and 10 equiv of (2-naphthyl)methanol to **17a** were used, 40% and 48% yields were obtained, respectively. [f] Ammonium (1*R*)-(*endo*,*anti*)-(+)-3-bromocamphor-8-sulfonate was used as a substrate.

SCHEME 9



fluoride anion from the counteranions or couples with alcohols, amines, etc. at their *O*- and *N*-sites. The CF_3^+ ion is on and off the lone-paired electrons of the oxygen atom of the dibenzofuran. Route ii may be likely to occur, because it is unthinkable that $Sb_2F_{11}^-$ attacks the CF_3 carbon according to route i since $Sb_2F_{11}^-$ is known to be a really non-nucleophilic anion.[24] Christe's calculation has evaluated the fluoride anion affinity (pF^- 12.7) of Sb_2F_{10} to be extremely high, which is larger than pF^- 11.3 of SbF_5.[24] Furthermore, CF_3^+ may be strongly stabilized by the conjugation of the lone-paired p-electrons of the three fluorine atoms (Figure 5). This is quite different from the case of methylation in hydrocarbon, in which such stabilization is not expected in the CH_3^+ ion because of no p-electrons on a hydrogen atom. It has been calculated that CF_3^+ is more stable by about 20 kcal/mol than CH_3^+.[25] By this great difference, it is understandable that the CF_3 oxonium salts are thermally unstable, in other words, the CF_3^+ species is easily generated, while *O*-methyldibenzofuranium-tetrafluoroborate and -2,4,6-trinitrobenzenesulfonate are stable solids to at least 80 °C since they were synthesized by heating the corresponding biphenylyldiazonium salts under reflux in a benzene solvent.[6c]

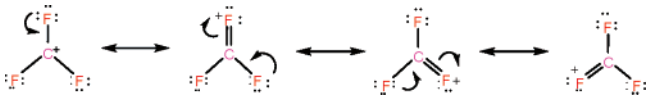


FIGURE 5. Conjugation of lone-paired p-electrons of three fluorine atoms.

To our knowledge, the decomposition reaction of the CF_3 oxonium $Sb_2F_{11}^-$ salts giving CF_4 is the first example of the fact that the so-called non-nucleophilic $Sb_2F_{11}^-$ anions become a source of fluoride anions, that is, a nucleophile.[26] The formation of biphenyl fluoride **23** by the photodecomposition of **18b** may be another example. It has been known that BF_4^- is a source of a fluoride anion as seen in the Schieman reaction, a decomposition reaction of aryldiazonium BF_4^- salts in which aryl cations attack BF_4^- to give aryl fluorides.[27] The driving force of the reaction of CF_3^+ with PF_6^-, SbF_6^-, and $Sb_2F_{11}^-$ ions giving CF_4 may be the great formation energy of a very stable CF_4 molecule. Contrary to the exceeding reactivity of CF_3^+, it was surprising to us that the CF_3 oxonium salt **2a** could not react with aromatics such as toluene and naphthalene as mentioned above. Thus, it may be supposed that CF_3^+ has no potential to react with such aromatics since this reaction does not generate enough formation energy to take place.

Comparison of CF_3 Oxonium Salts with CF_3 Sulfonium and Selenium Salts. The reactivity of the CF_3 oxonium (*O*-CF_3) salts was compared with that of *S*- and *Se*-(trifluoromethyl)dibenzothio- and -seleno-phenium triflates, which are stable solids.[15a,b] It showed a completely different reaction manner. With phenol in the presence of a base, the *O*-CF_3 salt produced an *O*-trifluoromethylated product, α,α,α-trifluoroanisole, while 3,7-dinitro-*S*-CF_3-dibenzothiophenium triflate gave *C*-trifluoromethylated products, *p*- and *o*-CF_3-phenol. *S*-CF_3-dibenzothiophenium triflate remained unreacted when heated in a phenol solvent without a base at 90 °C for 22 h, but the more reactive 3,7-dinitro-*S*-CF_3-dibenzothiophenium triflate produced α,α,α-trifluoroanisole in 13% yield when heated at 80 °C for 1.5 h. The *S*-CF_3 thiophenium triflate was heated at 200 °C to give CF_3OTf (**29**) and the 3,7-dinitro-*S*-CF_3 thiophenium triflate at 140 °C produced **29**. The reactivity of the 3,7-dinitro *S*-CF_3 salt activated by two strong electron-withdrawing nitro groups

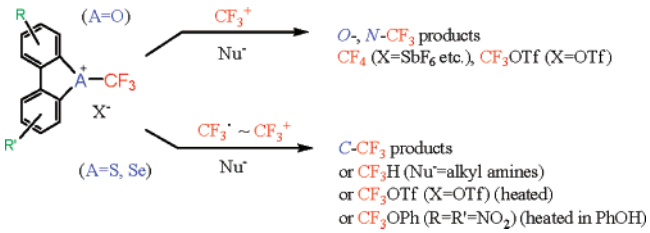
(24) (a) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151−153. (b) Dagani, R. *Chem. Eng. News* March 3, 2003, p 44−47.

(25) Reynolds, C. H. *J. Chem. Soc., Chem. Commun.* **1991**, 975−976.

(26) Lectka et al. have shown that aryl cations can abstract fluoride anions from CF_3 substituents of aromatic rings: Ferraris, D.; Cox, C.; Anand, R.; Lectka, T. *J. Am. Chem. Soc.* **1997**, *119*, 4319−4320.

(27) Roe, A. *Org. React.* **1968**, *4*, 193−228.

SCHEME 10



comes closer to that of the *O*-CF_3 salts which exclusively undertake *O*-trifluoromethylation. With aniline, the *O*-CF_3 salt **2a** produced *N*-CF_3 aniline, while *S*- and *Se*-CF_3 salts gave *C*-CF_3 products, a mixture of *o*- and *p*-CF_3 anilines. With an alkyl amine, the *O*-CF_3 salt **2a** produced the *N*-CF_3 amine, while *S*-CF_3-dibenzothiophenium triflate decomposed to give CF_3H. This decomposition of the *S*-CF_3 salt may be explained to occur via a one-electron-transfer mechanism from an easily oxidizable amine to the electron-deficient *S*-CF_3 salt, forming a free radical $CF_3^{\bullet}$ species that abstracts a hydrogen atom from the amine or solvent to give CF_3H.

These remarkable differences should be due to the difference in the reaction mechanism. The *O*-CF_3 salts may exclusively undertake the S_N2 mechanism including the real CF_3^+ as discussed above, while the *S*- and *Se*-CF_3 salts may undertake a different reaction mechanism varying from $CF_3^{\bullet}$ to CF_3^+ depending on the reactivity of nucleophiles, the trifluoromethylating power of the *S*- and *Se*-CF_3 salts, and reaction conditions. The difference between *O*-CF_3 and *S*- and *Se*-CF_3 salts should be due to that of the electron-withdrawing effect of the hetero atoms bonding to the CF_3 carbon. The oxygen atom of the CF_3-O^+ salt would have a strong electron-withdrawing effect enough to generate the real CF_3^+, but the effect of the sulfur and selenium atoms of the CF_3-S^+ and -Se^+ salts would be insignificant enough to generate the CF_3^+ and thus the reaction mechanism varies.

Conclusions

The first CF_3 oxonium salts, thermally unstable *O*-(trifluoromethyl)dibenzofuranium salts having different counteranions and ring substituents, have been in situ synthesized and characterized. The non-nucleophilicity of the counteranions is important for the synthesis, and both significant effects of the counteranions and the ring substituents on the stability and reactivity of the CF_3 oxonium salts have been disclosed from the measurement of their half-life times. The CF_3 oxonium salts generate CF_3^+ species at low temperature, which is exceedingly reactive since it abstracts a fluoride anion from the extremely non-nucleophilic $Sb_2F_{11}^-$ at low temperature to give CF_4. 2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium hexafluoroantimonate (**2a**) was chosen as a real CF_3^+ species reagent and successfully applied to the direct *O*- and *N*-trifluoromethylations of a variety of organic compounds, which were difficult to do by conventional methods. Thus, these results have eliminated the common sense that the CF_3^+ species is extremely difficult to generate in a solution.

Experimental Section

2-Nitro-2′-(trifluoromethoxy)biphenyl (5). A mixture of 36.0 g (125 mmol) of 2-(trifluoromethoxy)iodobenzene, 20.2 g (100 mmol) of 2-bromonitrobenzene, and 20 g (0.314 g-atom) of Cu powder (copper bronze from Aldrich) was heated with stirring on an oil bath at 190 °C for 3 h. After cooling, the reaction mixture was combined with Et_2O and filtered through celite to remove Cu powder. The filtrate was concentrated and column chromatographed on silica gel with ethyl acetate (EtOAc)−hexane (1/5) as an eluent to give 17.8 g (63%) of **5**: mp 47−48 °C; ^{1}H NMR δ 7.33 (1H, dt, J = 8, 1 Hz), 7.36−7.40 (2H, m), 7.40 (1H, dm, J = 8 Hz), 7.45 (1H, ddd, J = 8, 7, 2 Hz), 7.56 (1H, td, J = 8, 1 Hz), 7.68 (1H, td, J = 8, 1 Hz), 8.07 (1H, dd, J = 8, 1 Hz); ^{19}F NMR δ −58.0 (3F, s); IR (KBr) 1530 (NO_2) 1359 (NO_2) cm^{-1}; MS *m*/*z* 283 (M^+), 198 ($M^+ - OCF_3$). Anal. Calcd for $C_{13}H_8FNO_3$: C, 55.13; H, 2.85; N, 4.95. Found: C, 55.17; H, 2.79; N, 4.81.

5-Fluoro-2-nitro-2′-(trifluoromethoxy)biphenyl (6). Similarly to **5**, 90 g (0.31 mol) of 2-(trifluoromethoxy)iodobenzene, 55 g (0.25 mol) of 2-bromo-4-fluoronitrobenzene, and 80 g (1.26 g-atom) of Cu powder were reacted and posttreated to give 43.9 g (61%) of **6**: mp 67.1−67.6 °C; ^{1}H NMR δ 7.10 (1H, dd, J = 8, 3 Hz), 7.24 (1H, ddd, J = 9, 7, 3 Hz), 7.32−7.37 (2H, m), 7.41 (1H, td, J = 8, 1 Hz), 7.48 (1H, td, J = 8, 2 Hz), 8.14 (1H, dd, J = 9, 5 Hz); ^{19}F NMR −58.0 (3F, s, CF_3), 104.1 (1F, ddd, J = 5, 7, 8 Hz, F); IR (KBr) 1531 (NO_2) 1358 (NO_2) cm^{-1}; MS *m*/*z* 216 ($M^+ - OCF_3$). Anal. Calcd for $C_{13}H_7FNO_3$: C, 51.84; H, 2.34; N, 4.65. Found: C, 51.83; H, 2.20; N, 4.61.

5-Methoxy-2-nitro-2′-(trifluoromethoxy)biphenyl (7). Under an Ar atmosphere, a solution of 4.51 g (15 mmol) of **6** in 30 mL of MeOH was added into a solution of 2.85 g (53 mmol) of NaOMe in 60 mL of methanol. The mixture was heated under reflux for 6 h. After cooling, the reaction mixture was poured into H_2O and extracted with Et_2O. The organic layer was separated, washed with saturated brine, dried with $MgSO_4$, and filtered. The filtrate was evaporated under reduced pressure to give crude **7**, which was column chromatographed on silica gel with EtOAc−hexane (1:10) as an eluent to give 4.37 g (93%) of pure **7**: mp 70−71 °C (EtOAc−hexane): ^{1}H NMR δ 3.91 (3H, s), 6.82 (1H, d, J = 3 Hz), 7.00 (1H, dd, J = 3, 9 Hz), 7.28−7.52 (4H, m), 8.16 (1H, d, J = 9 Hz); ^{19}F NMR δ −57.9 (s); IR (KBr) 1575, 1514, 1346, 1308 cm^{-1}; MS *m*/*z* 313 (M^+). Anal. Calcd for $C_{14}H_{10}F_3NO_4$: C, 53.68; H, 3.22; N, 4.47. Found: C, 53.68; H, 3.08; N, 4.43.

5-Bromo-2′-nitro-2-(trifluoromethoxy)biphenyl (8). Under an Ar atmosphere, 15.0 g (53 mmol) of **5** and 0.5 g of Fe powder were put into a flask with a condenser cooled with dry ice−acetone and the reaction mixture was heated to 140 °C. Into the mixture, 12.7 g (80 mmol) of Br_2 was added in one portion. The reaction mixture was heated at 140 °C for 20 min, cooled, and extracted with Et_2O. The extract was washed with 6 N aq HCl solution, water, 10% aq $Na_2S_2O_3$ solution, and saturated brine, dried with $MgSO_4$, and filtered. The filtrate was evaporated to dryness to give 17.1 g (89%) of crude **8**, which was purified by column chromatography on silica gel with EtOAc−hexane (1:10) as an eluent. **8**: mp 63−64 °C (EtOAc−hexane); ^{1}H NMR δ7.20 (1H, dd, J = 9, 1 Hz), 7.39 (1H, dd, J = 8, 1 Hz), 7.48−7.65 (3H, m), 7.71 (1H, td, J = 8, 1 Hz), 8.12 (1H, dd, J = 8, 1 Hz); ^{19}F NMR δ −58.4 (d, J = 1.5 Hz); IR (KBr) 1524 (NO_2), 1354 (NO_2) cm^{-1}; MS *m*/*z* 363, 361 (M^+), 278, 276 ($M^+ - OCF_3$). Anal. Calcd for $C_{13}H_7BrF_3NO_3$: C, 43.12; H 1.95; N, 3.87. Found: C, 43.23; H, 1.83; N, 3.81.

5-Dimethylamino-2-nitro-2′-(trifluoromethoxy)biphenyl (9). Into a solution of 0.60 g (2 mmol) of **6** in 4 mL of EtOH was added 0.63 mL (6 mmol) of 50% aq Et_2NH solution. The mixture was stirred for 24 h at room temperature, poured into H_2O, and extracted with CH_2Cl_2. The extract was washed with H_2O and saturated brine, and dried with $MgSO_4$, and filtered. The filtrate was evaporated to dryness to give a residue, which was column chromatographed on silica gel with EtOAc−hexane (1:5) as an eluent to give 0.62 g (95%) of **9**: mp 136−138 °C; ^{1}H NMR δ 3.09 (6H, s), 6.41 (1H, d, J = 3 Hz), 6.65 (1H, dd, J = 3, 9 Hz), 7.25−7.48 (4H, m), 8.16 (1H, d J = 9 Hz); ^{19}F NMR δ −57.6 (d, J = 1 Hz); IR (KBr) 1599 (NO_2), 1490 (NO_2) cm^{-1}; MS *m*/*z*

326 (M^+), 325, 241 ($M^+ - OCF_3$), 240. Anal. Calcd for $C_{15}H_{13}F_3N_2O_3$: C, 55.22; H, 4.02; N, 8.59. Found: C, 55.12; H, 3.95; N, 8.53.

Reduction of 2-Nitro-2′-(trifluoromethoxy)biphenyl (5): A Typical Procedure. Into a solution of 7.1 g (25 mmol) of **5** in 125 mL of EtOH was added 50 mL of concd HCl solution and 6.3 g of tin powder. The solution was heated under reflux for 2 h. After cooling, the reaction mixture was poured into ice water. After being neutralized with 10% aq NaOH solution, it was extracted with Et_2O several times and the combined ethereal solution was washed with H_2O and then with saturated brine and dried on $MgSO_4$. After filtration, the filtrate was evaporated to dryness to give 5.94 g (94%) of **10**. Compounds **12**, **13**, **14**, and **16** were prepared in a similar manner as **10**.

2-Amino-2′-(trifluoromethoxy)biphenyl (10): oil; ^{1}H NMR δ 3.2−3.8 (2H, br s), 6.73−6.87 (2H, m), 7.06 (1H, dd, J = 8, 1 Hz), 7.19 (1H, dd, J = 8, 1 Hz), 7.32−7.47 (4H, m); IR (neat) 3473 (NH_2), 3385 (NH_2) cm^{-1}; MS *m*/*e* 253 (M^+). Anal. Calcd for $C_{13}H_{10}F_3NO$: C, 61.66; H, 3.98; N, 5.53. Found: C, 61.79; H, 3.98; N, 5.34.

2-Amino-5-fluoro-2′-(trifluoromethoxy)biphenyl (12): yield 94%; oil; ^{1}H NMR δ 6.71 (1H, dd, J = 9, 5 Hz), 6.81 (1H, dd, J = 9, 3 Hz), 6.92 (1H, td, J = 9, 3 Hz), 7.34−7.46 (4H, m); ^{19}F NMR δ −57.7 (3F, s, CF_3), 127.3 (1F, td, J = 9, 5 Hz, F); IR (neat) 3472 (NH_2) 3385 (NH_2) cm^{-1}; MS *m*/*e* 271 (M^+). Anal. Calcd for $C_{13}H_9F_4NO$: C, 57.57; H, 3.34; N, 5.16. Found: C, 57.40; H, 3.18; N, 5.07.

2-Amino-5-methoxy-2′-(trifluoromethoxy)biphenyl (13): yield 91%; oil; ^{1}H NMR δ 3.18 (2H, br s), 3.75 (3H, s), 6.67 (1H, d, J = 3 Hz), 6.76 (1H, dd, J = 9, 1 Hz), 6.81 (1H, dd, J = 9, 3 Hz), 7.30−7.50 (4H, m); ^{19}F NMR δ −57.6 (s); IR (neat) 3448 (NH_2), 3372 (NH_2) cm^{-1}; MS *m*/*z* 283 (M^+). Anal. Calcd for $C_{14}H_{12}F_3NO_2$: C 59.37; H; 4.27; N, 4.95. Found: C, 59.12; H, 4.15; N, 4.94.

2-Amino-5′-bromo-2′-(trifluoromethoxy)biphenyl (14): yield 80%; oil; ^{1}H NMR δ 6.76 (1H, dd, J = 8, 1 Hz), 6.81 (1H, td, J = 8, 1 Hz), 7.03 (1H, dd, J = 8, 2 Hz), 7.20 (1H, td, J = 8, 2 Hz), 7.25 (1H, dq, J = 9, 1 Hz), 7.52 (1H, dd, J = 9, 3 Hz), 7.57 (1H, d, J = 3 Hz); ^{19}F NMR δ −57.9 (d, J = 1 Hz); IR (neat) 3474 (NH_2), 3385 (NH_2) cm^{-1}; MS *m*/*z* 333, 331 (M^+). Anal. Calcd for $C_{13}H_9BrF_3NO$: C, 47.01; H, 2.73; N, 4.22. Found: C, 46.91; H, 2.60; N, 4.29.

2-Amino-5-dimethylamino-2′-(trifluoromethoxy)biphenyl (16): yield 85%; mp 48−49 °C (EtOAc−hexane); ^{1}H NMR δ 2.84 (6H, br s), 3.22 (2H, br s), 6.57 (1H, br s), 6.74 (2H, br s), 7.32−7.45 (4H, m); ^{19}F NMR δ −57.5 (s); IR (KBr) 3389 (NH_2), 3201 (NH_2) cm^{-1}; MS *m*/*z* 296 (M^+). Anal. Calcd for $C_{15}H_{15}F_3N_2O$: C, 60.81; H, 5.10; N, 9.45. Found: C, 60.35; H, 5.16; N, 9.53.

2-Amino-5-*tert*-butyl-2′-(trifluoromethoxy)biphenyl (11). Method A: A mixture of 6.36 g (25 mmol) of **10**, 3.9 g (27.5 mmol) of P_2O_5, and 3.71 g (50 mmol) of isobutanol under N_2 atmosphere was heated in an autoclave at 220 °C for 12 h. After cooling, 80 mL of H_2O was added to the reaction and the mixture was extracted with EtOAc. The organic layer was separated and washed with aq alkaline solution and then with saturated brine and dried on $MgSO_4$. After filtration, the filtrate was concentrated and the residue was column chromatographed on silica gel with hexane and then a mixture of hexane and EtOAc (20/1 → 3/1) as an eluent to give 4.89 g (63%) of **11**: oil; ^{1}H NMR δ 7.45 (1H, dd, J = 7.1, 1.8 Hz), 7.40−7.34 (3H, m), 7.22 (1H, dd, J = 8.4, 2.3 Hz), 7.10 (1H, d, J = 2.3 Hz), 6.77 (1H, d, J = 8.4 Hz), 1.29 (9H, s, 3 × CH_3); ^{19}F NMR δ −57.6 (s); IR (KBr) 2964, 1621, 1508, 1257, 1220, 1168 cm^{-1}; MS *m*/*z* 309 (M^+), 294 ($M^+ - CH_3$), 279 ($M^+ - 2CH_3$).

Method B: A mixture of 7.0 g (31 mmol) of 2-bromo-4-*tert*-butylaniline, 12.7 g (61 mmol) of 2-(trifluoromethoxy)phenylboric acid, 5.16 g (61 mmol) of $NaHCO_3$, 3.55 g (3 mmol) of tetra(triphenylphosphine)palladium, and 330 mL of dimethoxyethane/H_2O (10/1 v/v) was purged with argon and heated under reflux for 64 h. After cooling, the reaction mixture was poured into aq $NaHCO_3$ solution. The solution was extracted with Et_2O and the ether layer was separated and dried with $MgSO_4$. After filtration, the filtrate was concentrated and the residue was column chromatographed on silica gel with hexane−EtOAc (20/1 → 7/1) to give 8.3 g (87%) of **11**.

2-Amino-5′-methoxy-2′-(trifluoromethoxy)biphenyl (15). Into 30 mL of dry MeOH were added 2.1 g (90 mmol) of Na and then 30 mL of collidine and 5.8 g (30 mmol) of dry CuI. A solution of 10.0 g (30 mmol) of **14** in 50 mL of collidine was added into the mixture under stirring. The reaction mixture was heated under reflux on an oil bath at 140 °C for 21 h. After the solution was cooled, EtOAc was added to the reaction mixture and the mixture was filtered through celite. The filtrate was evaporated and the residue was column chromatographed on silica gel with EtOAc−hexane (1:5) to give 5.8 g (68%) of **15**: mp 83−89 °C; ^{1}H NMR δ 3.60 (2H, br s), 3.82 (3H, s), 6.77 (1H, dd, J = 8, 1 Hz), 6.81 (1H, td, J = 8, 1 Hz), 6.90 (1H, d, J = 3 Hz), 6.91 (1H, dd, J = 8, 3 Hz), 7.07 (1H, dd, J = 8, 1 Hz), 7.19 (1H, td, J = 8, 1 Hz), 7.28 (1H, dm, J = 8 Hz); ^{19}F NMR δ −58.3 (s); IR (KBr) 3432 (NH_2), 3381 (NH_2) cm^{-1}; MS *m*/*z* 283 (M^+). Anal. Calcd for $C_{14}H_{12}F_3NO_2$: C, 59.37; H, 4.27; N, 4.95. Found: C, 59.59; H, 4.06; N, 4.81.

Preparation of Diazonium Salts 17a, 17c, 17d, 18a, 18c, 18d, 19a, 20, 21, and 22: A Typical Procedure. Into a stirred solution of 1.27 g (5 mmol) of **10** in 10 mL of CH_2Cl_2 cooled at −78 °C was added 1.46 g (5.5 mmol) of $NOSbF_6$. The mixture was gradually warmed to 0 °C for a period of 3 h. Et_2O was added to the reaction mixture and the resulting precipitate was collected by filtration. The precipitates were recrystallized from CH_3CN/Et_2O to give 1.75 g (70%) of diazonium salt **17a**. Similarily, **17c** and **17d** were prepared by the reaction of **10** with $NOPF_6$ and $NOBF_4$ in 78% and 86% yields, respectively. **18a**, **18c**, and **18d** were prepared by the reaction of **11** with $NOSbF_6$, $NOPF_6$, and $NOBF_4$ in 58%, 88%, and 59% yields, respectively. **19a** and **20** were prepared by the reaction of **12** and **13** with $NOSbF_6$ and $NOBF_4$ in 56% and 89% yields, respectively. **21** and **22** were prepared by the reaction of **15** and **16** with $NOSbF_6$ in 42% and 86% yields, respectively.

2-(Trifluoromethoxy)biphenylyl-2′-diazonium hexafluoroantimonate (17a): mp 80−81.5 °C dec (CH_3CN-Et_2O); ^{1}H NMR (CD_3CN) δ 7.58−7.73 (3H, m), 7.73 −7.86 (1H, m), 7.92−8.10 (2H, m), 8.37 (1H, td, J = 8, 1 Hz), 8.62 (1H, dd, J = 8, 1 Hz); ^{19}F NMR (CD_3CN) δ −57.3 (3F, d, J = 1.5 Hz, CF_3), −102 to −143 (6F, m, SbF_6); IR (KBr) 2265 (N_2^+) cm^{-1}; MS (FAB) *m*/*e* 265 ($M^+ - SbF_6$), 237 (265 − N_2); high mass $M^+ - SbF_6$ ($C_{13}H_8F_3N_2O$) 265.05825 (calcd 265.05887).

2-(Trifluoromethoxy)biphenylyl-2′-diazonium hexafluorophosphate (17c): mp 91−96 °C dec (CH_3CN-Et_2O); ^{1}H NMR (CD_3CN) δ 7.58−7.73 (3H, m), 7.73 −7.86 (1H, m), 7.92−8.10 (2H, m), 8.37 (1H, td, J = 8, 1 Hz), 8.62 (1H, dd, J = 8, 1 Hz); ^{19}F NMR (CD_3CN) δ −57.2 (3F, d, J = 1.5 Hz, CF_3), −71.6 (6F, d, J = 706 Hz, PF_6); IR (KBr) 2276 (N_2^+) cm^{-1}; MS (FAB) *m*/*z* 265 ($M^+ - PF_6$), 237 (265 − N_2); high mass $M^+ - PF_6$ ($C_{13}H_8F_3N_2O$) 265.05810 (calcd 265.05887).

2-(Trifluoromethoxy)biphenylyl-2′-diazonium tetafluoroborate (17d): mp 90−93 °C dec (CH_3CN-Et_2O); ^{1}H NMR (CD_3CN) δ 7.58−7.73 (3H, m), 7.73 −7.87 (1H, m), 7.92−8.10 (2H, m), 8.37 (1H, td, J = 8, 1 Hz), 8.64 (1H, dd, J = 8, 1 Hz); ^{19}F NMR (CD_3CN) δ −57.2 (3F, d, J = 1.5 Hz, CF_3), −150.4 (4F, s, BF_4); IR (KBr) 2282 (N_2^+) cm^{-1}; MS (FAB) *m*/*z* 265 ($M^+ - BF_4$), 237 (265 − N_2); high MS $M^+ - BF_4$ ($C_{13}H_8F_3N_2O$) 265.05833 (calcd 265.05887).

5-*tert*-Butyl-2′-(trifluoromethoxy)biphenylyl-2-diazonium hexafluoroantimonate (18a): mp 84.7−85.8 °C dec; ^{1}H NMR δ 8.67 (1H, d, J = 8.9 Hz), 7.96 (1H, dd, J = 8.9, 1.9 Hz), 7.77 (1H, d, J = 1.9 Hz), 7.74−7.69 (2H, m), 7.63 (1H, dt, J = 1.0, 7.7 Hz), 7.54 (1H, d, J = 8.3 Hz), 1.44 (9H, s, *t*-C_4H_9); ^{19}F NMR δ −58.4 (3F, s, CF_3), −96 to −149 (6F, m, SbF_6); IR (KBr) 2974, 2262

(N_2^+), 1589, 1560, 1248, 1220, 1196, 1071 cm^{-1}; MS (FAB) *m/z* 321 ($M^+ - SbF_6$); high MS $M^+ - SbF_6$ ($C_{17}H_{16}F_3N_2O$) 321.12033 (calcd 321.12147).

5-*tert*-Butyl-2′-(trifluoromethoxy)biphenylyl-2-diazonium hexafluorophosphate (18c): mp 95.0−95.7 °C (CH_3CN-Et_2O); ^1H NMR δ 8.76 (1H, d, J = 8.9 Hz), 7.94 (1H, dd, J = 8.9, 1.9 Hz), 7.74 (1H, d, J = 1.9 Hz), 7.72−7.68 (2H, m), 7.61 (1H, dt, J = 1.1, 7.6 Hz), 7.53 (1H, m), 1.42 (9H s); ^{19}F NMR δ −58.32 (3F, s), −72.81 (6F, d, J = 712 Hz); IR (KBr) 2970, 2267, 1590, 1562, 1245, 1220, 1183, 1073 cm^{-1}; low mass (FAB) *m/z* 321 ($M^+ - PF_6$); high MS $M^+ - PF_6$ ($C_{17}H_{16}F_3N_2O$) 321.12116 (calcd 321.12147).

5-*tert*-Butyl-2′-(trifluoromethoxy)biphenylyl-2-diazonium tetrafluoroborate (18d): oily and sticky product; ^1H NMR δ 8.91 (1H, d, J = 8.9 Hz), 7.93 (1H, dd, J = 8.9, 1.9 Hz), 7.79 (1H, dd, J = 7.7, 1.7 Hz), 7.73 (1H, d, J = 1.9 Hz), 7.69 (1H, dt, J = 1.7, 7.7 Hz), 7.61 (1H, dt, J = 1.1, 7.7 Hz), 7.52 (1H, dd, J = 1.1, 7.7 Hz), 1.42 (9H, s); ^{19}F NMR δ −58.22 (3F, s), −151.60 (4F, s); IR (KBr) 2971, 2268, 1589, 1562, 1260, 1220, 1178, 1072 cm^{-1}; MS (FAB) *m/z* 321 ($M^+ - BF_4$); high MS $M^+ - BF_4$ ($C_{17}H_{16}F_3N_2O$) 321.12209 (calcd 321.12147).

5-Fluoro-2′-(trifluoromethoxy)biphenylyl-2-diazonium hexafluoroantimonate (19a): mp 130−131 °C dec; ^1H NMR (CD_3CN) δ 7.58−7.89 (6H, m), 8.71 (1H, dd, J = 9, 5 Hz); ^{19}F NMR (CD_3CN) δ −57.2 (3F, s, CF_3), −82.2 (1F, td, J = 8, 5 Hz, F), −102 to −144 (6F, m, SbF_6); IR (KBr) 2272 (N_2^+) cm^{-1}; MS (FAB) *m/z* 283 ($M^+ - SbF_6$); high MS $M^+ - SbF_6$ ($C_{13}H_7F_4N_2O$) 283.04965 (calcd 283.04945).

5-Methoxy-2′-(trifluoromethoxy)biphenylyl-2-diazonium tetrafluoroborate (20): mp 65−67 °C; ^1H NMR (CD_3CN) δ 4.11 (3H, s), 7.32−7.50 (2H, m), 7.55 −7.85 (4H, m), 8.55 (1H, d, J = 9 Hz); ^{19}F NMR (CD_3CN) δ −57.2 (3F, s, CF_3), −150.4 (4F, s, BF_4); IR (KBr) 2228 (N_2^+) cm^{-1}; MS (FAB) *m/z* 295 ($M^+ - BF_4$); high MS $M^+ - BF_4$ ($C_{14}H_{10}F_3N_2O_2$) 295.07023 (calcd 295.06944).

5-Methoxy-2-(trifluoromethoxy)biphenylyl-2′-diazonium hexafluoroantimonate (21): mp 78−80 °C dec ($CH_2Cl_2-CH_3CN-Et_2O$); ^1H NMR (CD_3CN) δ 3.89 (3H, s), 7.18 (1H, d, J = 3 Hz), 7.29 (1H, dd, J = 9, 3 Hz), 7.56 (1H, dm, J = 9 Hz), 7.98 (1H, dd, J = 8, 1 Hz), 8.01 (1H, td, J = 8, 1 Hz), 8.37 (1H, td, J = 8, 1 Hz), 8.61 (1H, dd, J = 8, 1 Hz); ^{19}F NMR (CD_3CN) δ −57.7 (3F, s, CF_3), −96 to −149 (6F, m, SbF_6); IR (KBr) 2284 (N_2^+) cm^{-1}; MS (FAB) *m/z* 295 ($M^+ - SbF_6$); high MS $M^+ - SbF_6$ ($C_{14}H_{10}F_3N_2O_2$) 295.06848 (calcd 295.06944).

5-Dimethylamino-2′-(trifluoromethoxy)biphenylyl-2-diazonium hexafluoroantimonate (22): mp 136−139 °C (CH_3CN-Et_2O); ^1H NMR (CD_3CN) δ 8.10 (1H, d, J = 9.7 Hz), 7.72−7.51 (4H, m), 7.01 (1H, dd, J = 9.7, 2.5 Hz), 6.82 (1H, d, J = 2.5 Hz), 3.40 (3H, s), 3.35 (3H, s); ^{19}F NMR (CD_3CN) δ −57.92 (3F, s).

Counteranion Exchange Reaction of Diazonium Salt 17d—Preparation of Diazonium Salts 17a and 17e: A Typical Procedure. Into a stirred solution of 997 mg (5.7 mmol) of NaOTf cooled at −20 °C was added 2.0 g (5.7 mmol) of **17d**. The mixture was gradually warmed to room temperature for a period of 2 h. Some CH_2Cl_2 was added to the mixture and the insoluble solid was removed by filtration. The filtrate was evaporated to dryness under reduced pressure without heating. The residue was washed with Et_2O and recrystallized from CH_2Cl_2/Et_2O to give 2.13 g (90%) of **17e**. Similarly, **17a** was prepared in 71% yield from **17d** with $NaSbF_6$ instead of NaOTf and agreed with the product (**17a**) from the reaction of **10** and $NOSbF_6$.

2-(Trifluoromethoxy)biphenylyl-2′-diazonium triflate (17e): mp 76−78 °C dec (CH_3CN-Et_2O); ^1H NMR (CD_3CN) δ 7.63−7.69 (3H, m), 7.80 (1H, ddd, J = 8, 7, 3 Hz), 7.97 (1H, dd, J = 8, 1 Hz), 8.01 (1H, td, J = 8, 1 Hz), 8.37 (1H, td, J = 8, 1 Hz), 8.63 (1H, d, J = 8 Hz); ^{19}F NMR (CD_3CN) δ −57.1 (3F, s, OCF_3), −77.9 (3F, s, SCF_3); IR (KBr) 2286 (N_2^+) cm^{-1}; MS (FAB) *m/e* 265 ($M^+ - OSO_2CF_3$). Anal. Calcd for $C_{14}H_8F_6N_2O_4S$: C, 40.59; H, 1.95; N, 6.76. Found: C, 40.61; H, 1.85; N, 6.89.

Photochemical Decomposition of 2-(Trifluoromethoxy)biphenylyl-2′-diazonium Salts—In Situ Synthesis of *O*-(Trifluoromethyl)dibenzofuranium Salts 1a,b, 2a−d, 3b, and 4a,b: A Typical Procedure. A solution of 6.5 mg (12 μmol) of **18a** and 1.1 mg (7.5 μmol) of benzotrifluoride (as an internal standard for ^{19}F NMR analysis) in 0.6 mL of CD_2Cl_2 was placed into a Pyrex glass NMR tube, then the tube was sealed after being purged with N_2. The tube was immersed in an EtOH−liquid N_2 bath (a Pyrex glass container) cooled to −106 °C, and irradiated for 45 min from about 3.5 cm away with a high-pressure mercury lamp (400 W; main light wavelength, 253.7 nm) positioned outside of the bath. A bath temperature of −90 to −100 °C was maintained during the irradiation. After the irradiation, the ^{19}F NMR was measured at −80 °C. The reaction solution in the NMR tube at the low temperature of −90 to −106 °C was homogeneous both before and after irradiation. The analysis of the NMR spectrum showed **2a** was produced in 87% yield and **23** and **24** were produced in 9% and 3% yield, respectively.

2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium hexafluoroantimonate (2a): ^1H NMR (CD_2Cl_2 at −70 °C) δ 8.30 (1H, dd, J = 7.6, 1.5 Hz, 5-H), 8.21 (1H, d, J = 2.3 Hz, 1-H), 8.09 (1H, dm, J = 9.1 Hz, 8-H), 8.03 (1H, t, J = 7.6 Hz, 6-H), 7.99 (1H, dq, J = 9.5, 2.3 Hz, 4-H), 7.92 (1H, ddd, J = 9.1, 7.6, 1.5 Hz, 7-H), 7.89 (1H, dd, J = 9.5, 2.3 Hz, 3-H), 1.44 (9H, s, 2-*t*-C_4H_9); ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −52.65 (s, CF_3). **5-*tert*-Butyl-2-fluoro-2′-(trifluoromethoxy)biphenyl (23):** ^1H NMR δ 7.44−7.41 (2H, m), 7.39−7.35 (3H, m), 7.33 (1H, dd, J = 2.5, 7.1 Hz), 7.07 (1H, t, J = 9.1 Hz), 1.33 (9H, s, *t*-Bu); ^{19}F NMR δ −57.66 (3F, s, CF_3), −21.22 (1F, s, 2-F); IR (neat) 3065, 2967, 1509, 1486, 1258, 1219, 1169, 823, 761 cm^{-1}; GC-MS *m/z* 312 (M^+), 297 ($M^+ - CH_3$), 269 ($M^+ - C_3H_7$). ***O*-(Trifluoromethyl)dibenzofuranium hexafluoroantimonate (1a):** ^1H NMR (CD_2Cl_2 at −70 °C) δ 8.26 (2H, br d, J = 8 Hz, 4,5-H), 8.09 (2H, br d, J = 8 Hz, 1,8-H), 8.00 (2H, br t, J = 8 Hz, 3,6-H), 7.91 (2H, br t, J = 8 Hz, 2,7-H); ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −52.38 (s, CF_3). ***O*-(Trifluoromethyl)-dibenzofuranium undecafluorodiantimonate (1b):** ^1H NMR (CD_2Cl_2 at −70 °C) δ 8.31 (2H, dd, J = 1.4, 7.6 Hz, 4,5-H), 8.13 (2H, dd, J = 2.3, 8.9 Hz, 1,8-H), 8.04 (2H, t, J = 7.6 Hz, 3,6-H), 7.94 (2H, ddd, J = 8.9, 7.6, 1.4 Hz, 2,7-H); ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −51.99 (s, CF_3). **2-*tert*-Butyl-*O*-(trifluoromethyl)-dibenzofuranium undecafluorodiantimonate (2b):** ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −52.64 (s, CF_3). **2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium hexafluorophosphate (2c):** ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −52.96 (s, CF_3). **2-*tert*-Butyl-*O*-(trifluoromethyl)dibenzofuranium tetrafluoroborate (2d):** ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −52.79 (s, CF_3). **2-Fluoro-*O*-(trifluoromethyl)dibenzofuranium undecafluorodiantimonate (3b):** ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −51.88 (s, CF_3). **2-Methoxy-*O*-(trifluoromethyl)dibenzofuranium hexafluoroantimonate (4a):** ^1H NMR (CD_2Cl_2 at −70 °C) δ 8.26 (1H, d, J = 7 Hz, 5-H), 8.11 (1H, d, J = 8 Hz, 4-H), 8.05−7.98 (2H, m, 6,8-H), 7.93 (1H, t, J = 8 Hz, 7-H), 7.65 (1H, s, 1-H), 7.33 (1H, m, 3-H), 4.04 (3H, s, CH_3); ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −53.22 (s, CF_3). **2-Methoxy-*O*-(trifluoromethyl)dibenzofuranium tetrafluoroborate (4b):** ^{19}F NMR (CD_2Cl_2 at −70 °C) δ −53.20 (s, CF_3).

Measurement of Half-Life Time of *O*-(Trifluoromethyl)-dibenzofuranium Salts. Into a NMR tube were placed the diazonium salt (0.025 mmol), benzotrifluoride (1.5−2 μL) and CD_2Cl_2 (0.6 mL) containing a trace amount of $CFCl_3$ as a standard for ^{19}F NMR, then the NMR tube was sealed. The NMR tube was irradiated with a high-pressure Hg lump in a bath of −90 to −100 °C for 45 min. After the irradiation, the reaction mixture was solidified by immersing the NMR tube into liquid nitrogen. The NMR tube was set at −70 °C in the NMR instrument and its NMR spectrum was measured to identify the *O*-(trifluoromethyl)-dibenzofuranium salts. After that, the ^{19}F NMR spectra were measured at the designated temperature (−60 or −50 °C) successively with a time interval. A half-life time was determined as the time when the amount of the *O*-CF_3-dibenzofuranium salt was reduced to half. The results are described in the text.

Thermal Decomposition of 17e in CD_2Cl_2. In a NMR tube were placed 21 mg (0.05 mmol) of **17e**, 0.7 mL of CD_2Cl_2, 6.1 μL (0.05 mmol) of benzotrifluoride as a standard for ^{19}F NMR analysis, and a trace amount of $CFCl_3$. The NMR tube was sealed and heated in an oil bath at 42 °C for 3 h. After cooling, the reaction mixture was analyzed by NMR measurement and the yields of products **29** and **31** were determined. After that, the NMR tube was opened. The reaction solution was added with 5.4 mg of hexadecane as a GC standard and the yield of **30** was determined by GC. The yields of **29**, **30**, and **31** were 65%, 75%, and 14%, respectively. A new compound **31** was isolated and identified.

2-Trifluoromethanesulfonyloxy-2′-(trifluoromethoxy)biphenyl (31): oil; ^1H NMR δ 7.33−7.56 (m); ^{19}F NMR δ −57.7 (3F, s, OCF_3), −74.7 (3F, d, SCF_3); IR (neat) 1478, 1424, 1248, 1214, 1174, 1139, 889, 767 cm^{-1}; GC-MS *m*/*z* 386 (M^+). Anal. Calcd for $C_{14}H_8F_6O_4S$: C, 43.53; H, 2.09. Found: C, 43.79; H, 2.00.

Thermal Decomposition of 2-(Trifluoromethoxy)biphenylyl-2′-diazonium Salts 17a,c−e in Phenol. A mixture of 0.30 mmol of the diazonium salt and 1 mL of phenol in a sealed glass tube was stirred for 3 h on a bath at 42 °C. The reaction mixture was analyzed by GC with hexacosane as a standard and by ^{19}F NMR with benzotrifluoride as a standard. The results are shown in Scheme 8.

***O*- and *N*-Trifluoromethylation of Alcohols, Phenols, Primary and Secondary Amines, and Anilines with 2a: A Typical Procedure.** A solution of 0.05 mmol of **18a** and 0.025 mmol of benzotrifluoride (as an internal standard for ^{19}F NMR) in 0.4 mL of CH_2Cl_2 was placed into a Pyrex glass tube, which was then immersed in a Pyrex glass vessel filled with an EtOH−liquid N_2 bath at −90 to −100 °C and irradiated for 70 min with a high-pressure Hg lamp (400 W) positioned outside of the vessel at about 3.5 cm from the tube of the solution. The ^{19}F NMR measured at −90 °C after the irradiation showed that **2a** was prepared in the solution in 87−89% yield. And then a solution of 0.05 mmol of a substrate and 0.05 mmol of an acid-trap (shown in Table 1) in 50 μL of CH_2Cl_2 were added into the solution kept at −90 °C and the reaction mixture was gradually warmed to −10 °C over a period of 3 h. After that, a portion of the reaction mixture was diluted with CD_3CN and analyzed by ^{19}F NMR. The yield of the product was calculated from the amount of the standard (benzotrifluoride). The results are shown in Table 1. The products were identified by the NMR and GC-mass or high mass analysis or by comparing with authentic samples. Some of the products were isolated for identification. Data for the new compound are as follows.

2-Phenylethyl trifluoromethyl ether: ^1H NMR δ 3.00 (2H, t, J = 7 Hz), 4.15 (2H, t, J = 7 Hz), 7.21 (2H, d, J = 7 Hz), 7.25 (1H, t, J = 7 Hz), 7.32 (2H, d, J = 7 Hz); ^{19}F NMR δ −61.2 (s); GC-MS *m*/*z* 190 (M^+); high MS calcd for $C_9H_9F_3O$ 190.06055, found 190.06069.

***N*-Trifluoromethylation of Tertiary Amines and Pyridines with 2a.** These reactions were carried out in the same manner as for *O*- and *N*-trifluoromethylation of an alcohol etc. mentioned above except for a tertiary amine or a pyridine instead of a nucleophile and an acid-trap. The results are shown in Table 1. Spectral data and elemental analysis of the new compounds are as follows.

***N*-(Trifluoromethyl)pyridinium hexafluoroantimonate:** mp 138−141 °C (CH_3CN−Et_2O); ^1H NMR (CD_3CN) δ 8.36 (2H, t, J = 7 Hz), 8.96 (1H, tt, J = 7, 1 Hz), 9.21 (2H, dm, J = 7 Hz); ^{19}F NMR (CD_3CN) δ −60.2 (3F, s, CF_3), −96 to −149 (6F, m, SbF_6); IR (KBr) 3150, 3104, 2343, 1634, 1491, 1276, 1252, 1235, 1209, 1110, 1084, 1048, 787, 657 cm^{-1}; MS (FAB) *m*/*z* 148 ($M^+ - SbF_6$). Anal. Calcd for $C_6H_5F_9NSb$: C, 18.77; H, 1.31; N, 3.65. Found: C, 18.99; H,1.18; N, 3.79.

3-Chloro-*N*-(trifluoromethyl)pyridinium hexafluoroantimonate: mp 162.5−165.5 °C (CH_3CN−CH_2Cl_2−Et_2O); ^1H NMR (CD_3CN) δ 8.35 (1H, t, J = 8.6, 6.2 Hz), 8.95 (1H, d, J = 8.6 Hz), 9.18 (1H, d, J = 6.2 Hz), 9.42 (1H, s); ^{19}F NMR (CD_3CN) δ −59.9 (3F, s, CF_3), −103 to −143 (6F, m, SbF_6); IR (KBr) 3138, 3086, 1627, 1490, 1453, 1262, 1222, 1195, 1089, 1025, 817, 742, 658 cm^{-1}; MS (FAB) *m*/*z* 184, 182 ($M^+ - SbF_6$). Anal. Calcd for $C_6H_4ClF_9NSb$: C, 17.23; H, 0.96; N, 3.35. Found: C, 17.29; H, 0.79; N, 3.42.

4-Cyano-*N*-(trifluoromethyl)pyridinium hexafluoroantimonate: mp 139−145 °C (EtOAc); ^1H NMR (CD_3CN) δ 8.70 (2H, d, J = 7 Hz), 9.45 (2H, dm, J = 7 Hz); ^{19}F NMR (CD_3CN) δ −59.9 (3F, s, CF_3), −96 to −150 (6F, m, SbF_6); IR (KBr) 3140, 3086, 1646, 1562, 1462, 1314, 1263, 1223, 1181, 1084, 1042, 863, 757, 662, 638 cm^{-1}; MS (FAB) *m*/*z* 173 ($M^+ - SbF_6$). Anal. Calcd for $C_7H_4F_9N_2Sb$: C, 20.56; H, 0.99; N, 6.85. Found: C, 20.96; H, 0.98; N, 7.00.

4-Methoxycarbonyl-*N*-(trifluoromethyl)pyridinium hexafluoroantimonate: mp 160−164 °C (CH_3CN−CH_2Cl_2−Et_2O); ^1H NMR (CD_3CN) δ 4.06 (3H, s, CH_3), 8.72 (2H, d, J = 7 Hz), 9.39 (2H, d, J = 7 Hz); ^{19}F NMR (CD_3CN) δ −60.0 (3F, s, CF_3), −102 to −144 (6F, m, SbF_6); IR (KBr) 3154, 3074, 1741, 1646, 1576, 1465, 1439, 1338, 1318, 1273, 1245, 1229, 1209, 1130, 1082, 1041, 796, 665 cm^{-1}; MS (FAB) *m*/*z* 206 ($M^+ - SbF_6$). Anal. Calcd for $C_8H_7F_9NO_2Sb$: C, 21.75; H, 1.60; N, 3.17. Found: C, 21.82; H, 1.44; N, 3.17.

4-Methyl-*N*-(trifluoromethyl)pyridinium hexafluoroantimonate: mp 148.6−149.5 °C (CH_3CN−Et_2O); ^1H NMR (CD_3CN) δ 8.99 (2H, dm, J = 7 Hz), 8.14 (2H, d, J = 7 Hz), 2.80 (3H, s); ^{19}F NMR (CD_3CN) δ −60.41 (3F, s, CF_3), −96 to −149 (6F, m, SbF_6); IR (KBr) 3148, 3092, 1642, 1485, 1256, 1198, 1084, 1043, 828, 662 cm^{-1}; MS (FAB) *m*/*z* 162 ($M^+ - SbF_6$); high MS $M^+ - SbF_6$ ($C_7H_7NF_3$) 162.05275 (calcd 162.05306).

***O*- and *N*-Trifluoromethylation of Alcohols, Sulfonic Acids, and Pyridines by Thermal Decomposition of 17a: A Typical Procedure.** Under an Ar atmosphere, a stirred solution of 1 mmol of a substrate, 1 mmol of a base, and 1 mmol of **17a** in 4 mL of CH_2Cl_2 was heated under reflux for 3 h. The base was not used in the case that the substrate is a salt of sulfonic acid and a pyridine. After cooling, 0.5 mmol of benzotrifluoride as a ^{19}F NMR reference was added into the reaction mixture and the yield of the product was determined by ^{19}F NMR analysis. The results are shown in Table 2. Data for the new compounds are as follows.

(2-Naphthyl)methyl trifluoromethyl ether: mp 55.5−56.5 °C; ^1H NMR δ 5.15 (2H, s), 7.46 (1H, dd, J = 9, 2 Hz), 7.51 (2H, td, J = 9, 3 Hz), 7.83 (1H, s), 7.83−7.88 (2H, m), 7.88 (1H, d, J = 9 Hz); ^{19}F NMR δ −60.7 (s); IR (KBr) 1408, 1303, 1205, 1123, 857, 824, 755, 474 cm^{-1}; GC-MS *m*/*z* 226 (M^+), 141 ($M^+ - OCF_3$), 69 (CF_3^+). Anal. Calcd for $C_{12}H_9F_3O$: C, 63.72; H, 4.01. Found: C,63.37; H, 3.89.

Trifluoromethyl *p*-toluenesulfonate: oil; ^1H NMR δ 2.50 (3H, s), 7.43 (2H, d, J = 8 Hz), 7.90 (2H, d, J = 8 Hz); ^{19}F NMR δ −54.4 (s); IR (neat) 1598, 1411, 1226, 1160, 1087, 945, 814, 749, 664, 572, 548 cm^{-1}; GC-MS *m*/*z* 240 (M^+). Anal. Calcd for $C_8H_7F_3O_3S$: C, 40.00; H, 2.94. Found: C, 40.14; H, 2.81.

Trifluoromethyl 2-naphthalenesulfonate: mp 47−47.5 °C; ^1H NMR δ 7.70 (1H, td, J = 8, 2 Hz), 7.76 (1H, td, J = 8, 2 Hz), 7.94 (1H, dd, J = 8, 2 Hz), 7.98 (1H, d, J = 8 Hz), 8.05 (1H, d, J = 8 Hz), 8.07 (1H, d, J = 8 Hz), 8.62 (1H, d, J = 2 Hz); ^{19}F NMR δ −54.2 (s); IR (KBr) 1412, 1249, 1218, 1197, 1163, 1072, 951, 816, 756, 664, 636, 568, 548 cm^{-1}; GC-MS *m*/*z* 276 (M^+). Anal. Calcd for $C_{11}H_7F_3O_3S$: C, 47.83; H, 2.55. Found: C, 47.89; H, 2.51.

Trifluoromethyl *p*-octylbenzenesulfonate: oil; ^1H NMR δ 0.88 (3H, t, J = 6 Hz), 1.15−1.45 (10H, m), 1.66 (2H, m), 2.73 (2H, t, J = 8 Hz), 7.42 (2H, dd, J = 8, 2 Hz), 7.92 (2H, dd, J = 8, 2 Hz); ^{19}F NMR δ −54.29 (s); IR (neat) 2930, 2858, 1414, 1226, 1160, 1088, 946, 750, 576 cm^{-1}; GC-MS *m*/*z* 338 (M^+). Anal. Calcd for $C_{15}H_{21}F_3O_3S$: C, 53.24; H, 6.26. Found: C, 53.22; H, 6.38.

Trifluoromethyl 3-bromocamphor-8-sulfonate: oil; ^1H NMR; δ 1.05 (3H, s), 1.30 (3H, s), 1.57−1.71 (2H, m), 1.92−2.12 (1H,

m), 2.26−2.43 (1H, m), 3.05 (1H, t, J = 4 Hz), 3.39 (1H, d, J =14 Hz), 3.73 (1H, d, J = 14 Hz), 4.63 (1H, dd, J = 5, 2 Hz); ^{19}F NMR δ −53.69 (s); IR (neat) 2974, 1759, 1408, 1230, 1144, 944, 769, 638, 567 cm^{-1}; GC-MS m/z 380 and 378 (M^+). Anal. Calcd for $C_{11}H_{14}BrF_3O_4S$: C, 34.84; H, 3.72. Found: C, 34.90; H, 3.61.

Supporting Information Available: Copies of ^{1}H and ^{19}F NMR spectra of new compounds and H−H COSY spectrum of **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO070896R