Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 129 (2008) 131–136
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

A new method for the synthesis of trifluoromethylating agents—Diaryltrifluoromethylsulfonium salts

Lev M. Yagupolskii *, Andrej V. Matsnev, Raisa K. Orlova, Boris G. Deryabkin, Yurii L. Yagupolskii

Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Murmanska 5, 02094 Kyiv, Ukraine

Received 8 August 2007; received in revised form 5 October 2007; accepted 6 October 2007
Available online 13 October 2007

Abstract

A new synthetic method has been developed to prepare diaryltrifluoromethylsulfonium salts from diaryldifluorosulfuranes by the action of Me_3SiCF_3/F^-. This reaction is the transformation of nucleophilic trifluoro-methylating reagent into electrophilic one.

Keywords: Diaryltrifluoromethylsulphonium salts; Trifluoromethyl group; Diarylsulfides; Nucleophilic mechanism

1. Introduction

Organic compounds containing trifluoromethyl group have found wide application in the synthesis of medicines, pesticides, dyes, polymers, and a variety of other materials [1].

Initially, the synthesis of compounds containing trifluoromethyl group involved the replacement of the chlorine atoms in the CCl_3 group by fluorine atoms using HF or SbF_3, the reaction of carboxylic acids with SF_4, or the reaction of CF_3Cu with aromatic bromo and iodo derivatives [2]. Afterwards, radical trifluoromethylation reactions were used [1] which implied formation of the trifluoromethyl radical reacting unselectively with a substrate.

Prakash pioneered nucleophilic methods for the introduction of the trifluoromethyl group, with the application of Me_3SiCF_3/F^- system generating CF_3^- anion [3]; this strategy has been usefully employed in recent years.

An idea of electrophilic perfluoroalkylation in which a perfluoroalkyl group could be positively charged at first appeared to violate common sense. However, such reactions turned out to be quite possible provided the perfluoroalkyl group is bound to a positively charged heteroatom.

Among all the perfluoroalkyl moieties, the trifluoromethyl cation appears to be the most unfavorable one, as its positive charge is delocalized only over one carbon atom and three fluorine atoms. Therefore, the electrophilic perfluoroalkylation of various organics and inorganics using iodonium salts which we developed formerly (1978) [4] was restricted to introduction of perfluoroalkyl residues larger than the CF_3 group. At first, Cl^- was contained as an anion in these salts and then the BF_4^- anion was used to completely ionize the bond between the iodine atom and the perfluoroalkyl group. Later on (1982), Umemoto carried out his voluminous work on electrophilic perfluoroalkylation using compounds with the $CF_3SO_3^-$ anion (FITS reagents) [5] in which the $I–OSO_2CF_3$ bond was very polar but not completely ionic. As in our preceding experiments, Umemoto likewise failed to accomplish electrophilic trifluoromethylation with iodonium salts. Recently, cyclic compounds have been obtained which contain the iodine atom bound to the trifluoromethyl group and the oxygen atom. A lone electron pair on the oxygen atom significantly weakens the trifluoromethylating ability of such reagents [6].

One of the present authors succeeded to conduct electrophilic trifluoromethylation by means of diaryl(trifluoromethyl)-sulfonium salts $Ar_2S^+CF_3\ SbF_6^-$ in 1984 [7]. These trifluoromethylating reagents were obtained by the reaction of the salts $p\text{-}ClC_6H_4S^+(F)CF_3\ SbF_6^-$ with aromatic compounds. In the method that was developed, the electrophilic substitution only proceeds smoothly if electron-donor substituents are in the aromatic ring. On the other hand, such substituents partially neutralize a positive charge on the sulfur atom thus significantly reducing the trifluoromethylating

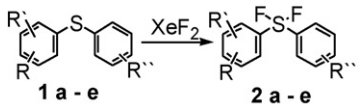
* Corresponding author.
E-mail address: matsnev@bpci.kiev.ua (A.V. Matsnev).

0022-1139/$ – see front matter
doi:10.1016/j.jfluchem.2007.10.001

reactivity of the salts obtained. Later on, Shreeve and co-workers [8] and Wakselman and co-workers [9] showed that reactions of this kind were also possible with benzene and its fluoro, chloro and trifluoromethoxy derivatives, i.e., with compounds usually entering into the Friedel–Krafts reaction and containing no strongly electron-withdrawing substituents.

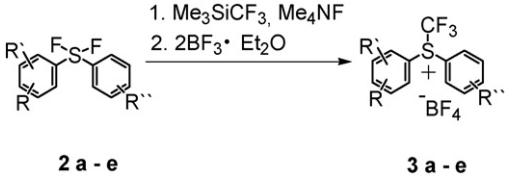
A much greater trifluoromethylating ability was exhibited by *S*-(trifluoromethyl)-dibenzothiophenium salts lacking electron-donor residues which were synthesized by Umemoto [10]. He succeeded in nitrating the salts obtained so that one or two nitro groups were introduced into the *meta* position to the trifluoromethylsulfonium moiety [10]. Subsequently, Shreeve also introduced a nitro group into the *meta* position to the sulfur atom by the nitration of diphenyl- and 4-fluorodiphenyl(trifluoromethyl)sulfonium salts [8]. The nitro compounds proved to be much more reactive than their non-nitrated analogues.

The present work is aimed at the development of a general synthetic method to prepare diaryl(trifluoromethyl)sulfonium salts, especially those containing strong electron-withdrawing substituents both at the *meta* and the *para* positions to the S^+-CF_3 group.



(**a**) R = R` = R`` = H;
(**b**) R = H, R` = R`` = 4-F;
(**c**) R = 3-CF_3, R` = 5-CF_3, R`` = H;
(**d**)R = R` = H; R`` = 4-NO_2;
(**e**)R = H, R` = R`` = 4-NO_2

Scheme 1.



Scheme 2.

2. Results and discussion

Appropriate diaryl sulfides chosen as starting compounds were reacted with xenon difluoride to afford diaryldifluorosulfuranes (Scheme 1).

Elemental fluorine can be used for fluorination as well [11]. However, we employed xenon difluoride as a reagent more conveniently handled in the laboratory.

The reaction strongly depends on the number of acceptor substituents in the aromatic rings. Thus, diphenyl sulfide reacts with xenon difluoride at 0 °C in petroleum ether to give solid diphenyldifluorosulfurane [12], whereas 4-nitrodiphenyl sulfide enters into the reaction only at 50–70 °C. Boron trifluoride etherate activating xenon difluoride can be used as a catalyst in this reaction; in this case, however, some side-reactions occur which significantly lower the yields of the desired products, diarylfluorosulfonium tetrafluoroborates. The compounds obtained entered into nucleophilic trifluoromethylation with the reagent Me_3SiCF_3/Me_4NF, i.e., with the trifluoromethyl anion, and yielded diaryltrifluoromethylsulfonium salts.

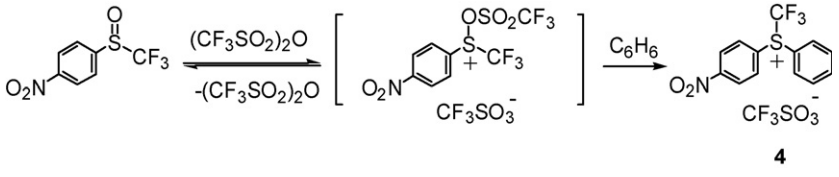
The method allows a conversion of the CF_3^- anion reacting with various substrates by a nucleophilic mechanism into an electrophilic reagent containing an electropositive $CF_3^{\delta+}$ group [13] (Scheme 2).

Salt **3d** bearing a triflate group as an anion was synthesized by the reaction of 4-nitrophenyltrifluoromethylsulfoxide [14] with benzene in the presence of excess trifluoromethanesulfonic anhydride. This reaction is probably an equilibrium one, especially if electron-withdrawing substituents are present in the benzene ring; therefore, a large excess of trifluoromethanesulfonic anhydride is needed (Scheme 3).

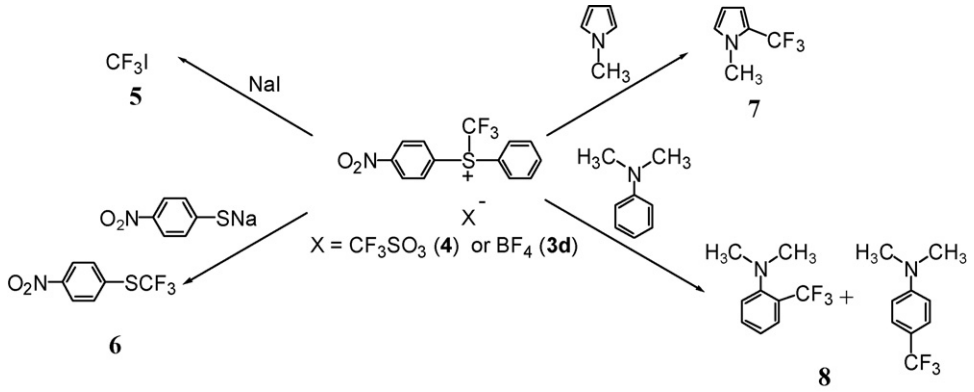
To study the reactivity of the diaryltrifluoromethylsulfonium salts obtained, they were subjected to reactions with different nucleophiles (Scheme 4). As expected, salts **3d** and **3e** appeared to be the most reactive. For instance, **3a** was found to react with sodium iodide only under heating, whereas the reaction with **3d** went to completion after 6 h at room temperature and **3e** provided CF_3I (**5**) after a 3-h reaction time at room temperature. 4-Nitrophenyl(phenyl)(trifluoromethyl)sulfonium tetrafluoroborate (**3d**) was reacted with sodium iodide and sodium *p*-nitrothiophenolate. Salt **4** reacted with *N*-methylpyrrole and *N*,*N*-dimethylaniline to furnish trifluoromethyl derivatives.

Diaryltrifluoromethylsulfonium salts were previously demonstrated to react with compounds bearing a negatively charged sulfur atom, e.g., with thiophenolates. It was of interest to ascertain whether compounds with an uncharged electron-rich sulfur atom could be trifluoromethylated. *N*,*N*,*N*′,*N*′-Tetraethylthiourea turned out to react with 4-nitrophenyl(phenyl)(trifluoromethyl)sulfonium salt to give sulfonium salt **9**.

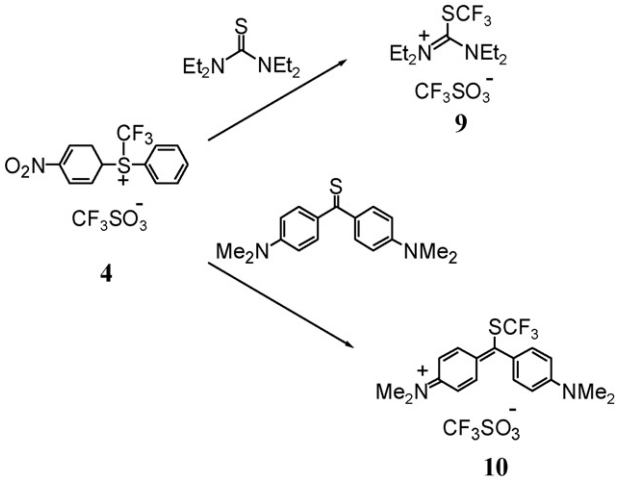
A thiocarbonyl group, if separated from electron-donor substituents by benzene rings, enters into the reaction as well. It was thus possible to obtain dye **10** by trifluoromethylation of Michler's thioketone. This dye was synthesized by one of us earlier using a hard-to-obtain reagent [15] (Scheme 5).



Scheme 3.



Scheme 4.



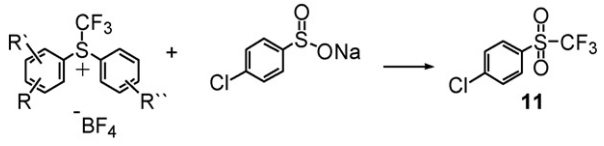
Scheme 5.

Not only thiophenolates but also the compounds of tetravalent sulfur, e.g., the salts of sulfinic acids, turned out to enter into electrophilic trifluoromethylations leading to the corresponding sulfones (Scheme 6).

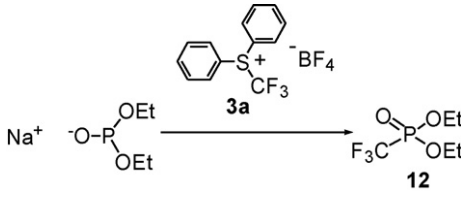
Using nucleophilic trifluoromethylation of arylsulfonyl fluorides, aryltrifluoromethylsulfones were previously obtained by one of the present authors together with collaborators [16].

The compounds of trivalent phosphorus also enter into the reactions of electrophilic trifluoromethylation. Diethoxytrifluoromethylphosphonate **12** was synthesized by the reaction of diethoxyphosphinate with diphenyl(trifluoromethyl)sulfonium salt (Scheme 7).

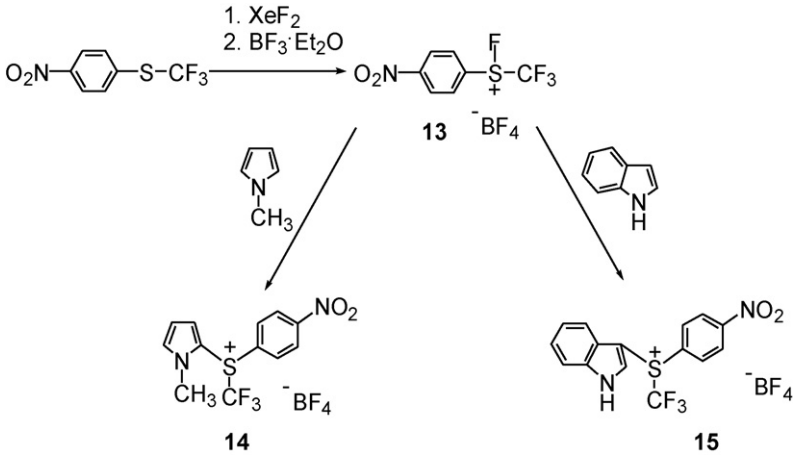
Trifluoromethylation with sulfonium salts is possible when the electrophilic attack is directed on a heteroatom not in its highest valence state as, for instance, nitrogen in sodium nitrite



Scheme 6.



Scheme 7.



Scheme 8.

[17], sulfur in the salts of thiols and sulfinic acids, or phosphorus in phosphinates.

The aryl(methyl)(trifluoromethyl)sulfonium salts synthesized earlier act as methylating rather than trifluoromethylating agents [7].

We obtained 4-nitrophenyl(trifluoromethyl)fluorosulfonium salt **13** to ascertain whether this reagent provides electrophilic trifluoromethylation or fluorination. For this purpose, salt **13** was reacted with electron-rich heterocycles, namely, *N*-methylpyrrole and indole. The reaction proved to involve substitution of the fluorine atom in salt **13** leading to hetaryl(4-nitrophenyl)(trifluoromethyl)sulfonium salts **14** and **15** (Scheme 8).

The compounds synthesized are the first representatives of the trifluoromethylsulfonium salts in which the $^{+}SCF_3$ group is bound to the heterocyclic moiety.

In conclusion, we have elaborated a new synthetic method to aryl- and hetaryl(trifluoromethyl)sulfonium salts and demonstrated a nontrivial transformation of the CF_3^- anion into the positively charged $CF_3^{\delta+}$ group attacking various substrates by an electrophilic mechanism.

3. Experimental

Moisture-sensitive reactions were carried out under dry argon using flame-dried glassware. All chemicals were of reagent grade or were purified by standard methods before use. Solvents were distilled from the appropriate drying agents immediately prior to use. Some reactions were monitored by thin-layer chromatography (TLC) on precoated silica gel Kieselgel 60 F/UV_{254} plates (Merck); spots were visualized with UV light. Purification of most products was performed by column chromatography (CC) on Silica gel, 70230 mesh 60A (Aldrich). ^1H and ^{19}F NMR spectra were recorded at 299.5 and 282.2 MHz, respectively with a Varian VXR-300 spectrometer, and chemical shifts are given in ppm relative to Me_4Si and CCl_3F, respectively, as internal standards. Coupling constants are given in Hz. Melting points were determined in open capillaries and are uncorrected.

*3.1. Sulfides **(1 a–e)** were synthesized by standard procedures [18]*

*3.1.1. Diphenyldifluorosulfurane **(2a)***

XeF_2 (0.22 g, 1.3 mmol) was added to a stirred solution of diphenylsulfide (0.23 g, 1.24 mmol) in pentane (5 mL) cooled to 0 °C. The reaction mixture was allowed to warm to rt and stirred till the end of effervesce of gas. The product precipitated as white crystals and was used without further purification after decantation of the solvent.

*3.1.2. 4,4′-Difluorodiphenyl(difluoro)sulfurane **(2b)***

XeF_2 (0.23 g 1.36 mmol) was added to 4,4′-difluorodiphenylsulfide (0.3 g, 1.35 mmol) which was cooled to 0 °C and stirred. The mixture was allowed to warm to rt and stirred till the end of effervesce of gas. The product was used without further purification.

*3.1.3. 3,5-Di(trifluoromethyl)diphenyldifluorosulfurane **(2c)***

XeF_2 (0.18 g, 1.07 mmol) was added to stirred 3,5-di(trifluoromethyl)phenylphenylsulfide (0.3 g, 0.93 mmol). The reaction mixture was heated to 50 °C and stirred at this temperature till the end of effervesce of gas; then reaction mixture became solid. The product was used without further purification.

*3.1.4. 4-Nitrophenylphenyldifluorosulfurane **(2d)***

XeF_2 (0.08 g, 0.47 mmol) was added to stirred 4-nitrophenylphenylsulfide (0.1 g, 0.43 mmol). The reaction mixture was heated to 50–70 °C and stirred at this temperature till the end of effervesce of gas. The product was used without further purification.

*3.1.5. 4,4′-Dinitrodiphenyldifluorosulfurane **(2e)***

XeF_2 (0.14 g, 0.83 mmol) was added to stirred 4,4′-dinitrodiphenylphenylsulfide (0.2 g, 0.73 mmol). The reaction mixture was heated to temperature of beginning of gas effervesce and stirred at this temperature till the end of effervesce of gas.

*3.2. Typical procedure for synthesis of S-(trifluoromethyl)diarylsulfonium salts **(3a–e)***

A three-necked flask was charged with Me_4NF (0.12 g, 1.29 mmol) and glyme (5 mL). The mixture was cooled to ca. −60 °C, and Me_3SiCF_3 (0.36 g, 2.54 mmol) was added. The reaction mixture was stirred for ca. 1 h at −45 °C, then cooled to −65 °C, and diaryldifluorosulfurane (1.29 mmol) was added. The reaction mixture was stirred at this temperature for additional 40 min and then $BF_3{\cdot}Et_2O$ (0.37 g, 2.6 mmol) was added. The mixture was allowed to warm to rt, the solvent was evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2:CH_3CN = 4:1) to give the corresponding product.

*3.2.1. S-(Trifluoromethyl)diiphenylsulfonium tetrafluoroborate **(3a)***

Yield 75%, mp 99–101 °C; ^1H NMR ($CDCl_3$): δ 7.98–8.08 (m, 4H), 8.10–8.20 (m, 2H), 8.40–8.48 (m, 4H); ^{19}F NMR ($CDCl_3$): δ −50.3 (s, 3F), −150.1 (s, 4F). Anal. calcd for $C_{13}H_{10}BF_7S$: C, 45.61; H, 2.92. Found: C, 45.26; H, 3.19.

*3.2.2. S-(Trifluoromethyl)-4,4′-difluorodiphenylsulfonium tetrafluoroborate **(3b)***

Yield 61%, mp 113–114 °C; ^1H NMR ($CDCl_3$): δ 7.61 (d, 4H); 8.35 (d, 4H) ^{19}F NMR ($CDCl_3$): δ −50.19 (s, 3F); −95.86 (s, 2F); −150.9 (br s, 4F). Anal. calcd for $C_{13}H_8BF_9S$, C 41,26; H 2,12; S 8,48. Found: C, 40.97; H, 2.32; S, 8.90.

*3.2.3. S-(Trifluoromethyl)-3,5-di(trifluoromethyl)diphenylsulfonium tetrafluoroborate **(3c)***

Yield 42%, ^1H NMR ($CDCl_3$): δ 8.07 (t, 2H), 8.22 (t, 2H), 8.56 (d, 2H), 8.85 (s, 1H), 9.02 (s, 2H). ^{19}F NMR ($CDCl_3$): δ −47.79 (s, 3F), −62.32 (s, 6F), −149,57 (s, 4F). Anal. calcd for $C_{15}H_8BF_{13}S$: C, 37.66; H, 1.67. Found: C, 37.87; H, 1.96.

*3.2.4. S-(Trifluoromethyl)-4-nitrophenylphenylsulfonium tetrafluoroborate **(3d)***

Yield 40%, mp 135–137 °C (dec.); ^{1}H NMR ($CDCl_3$): δ 7.76–7.91 (m, 1H), 7.97–8.12 (m, 2H), 8.13–8.25 (m, 2H), 8.36–8.60 (m, 2H), 8.61–8.0 9 (m, 2H). ^{19}F NMR ($CDCl_3$): δ −48.6 (s, 3F), −149.8 (s, 4F). Anal. calcd for $C_{13}H_9BF_7NO_2S$: C, 40.31; H, 2.33; S, 8.27. Found: C, 40.13; H, 2.32; S, 8.23.

*3.2.5. S-(Trifluoromethyl)-4,4′-dinitrodiphenylsulfonium tetrafluoroborate **(3e)***

Yield 35%, mp 158–160 °C (dec.); ^{1}H NMR ($CDCl_3$): δ 8.76 (s). ^{19}F NMR ($CDCl_3$): δ −47.2 (s, 3F), −148.7 (s, 4F). Anal. calcd for $C_{13}H_8BF_7N_2O_4S$: S 7,40. Found: S 7,11.

*3.3. S-(Trifluoromethyl)-4-nitrophenylphenylsulfonium triflate **(4)***

A three-necked flask was charged with 4-nitrophenyltrifluoromethylsulfoxide (0.2 g, 0.89 mmol) and 4 mL of benzene. The solution was cooled to 2–3 °C, and trifluorometanesulphonic anhydride (1.18 g, 4.2 mmol) was added. The reaction mixture was stirred for 24 h at rt. The excesses of benzene and anhydride were evaporated in vacuum (20 Torr). Then CH_2Cl_2 (5 mL) was added. The solution obtained was washed with cold water (3 mL × 7 mL), dried over $MgSO_4$ and concentrated in vacuum. The residue was purified by silica gel chromatography (CH_2Cl_2:CH_3CN = 4:1) to give 0.16 g of **4** (42.5%). ^{1}H NMR ($CDCl_3$): δ 7.86–7.89 (d, 2H); 8.36–8.39 (d, 2H); 8.65–8.75 (m, 5H). ^{19}F NMR ($CDCl_3$): δ −48.95 (s, 3F). −78.7 (s, 3F). Anal. calcd for $C_{14}H_9F_6NO_5S_2$: C 37.42; H 2.00; S 14.25. Found: 37.22; H 2.29; S 13.65.

*3.4. Trifluoroiodomethane **(5)***

To a suspension of NaI (0.1 g, 0.67 mmol) in CH_3CN (3 mL) salt **3a** (0.2 g, 0.59 mmol) was added. The reaction mixture was refluxed for 15 min. The product was distilled into a receiver cooled with liquid nitrogen. The yield of **5** was quantitative. ^{19}F NMR ($CDCl_3$): δ −15.5 (s). GLC data: holding time, 4 min. ^{19}F NMR ($CDCl_3$): δ −15.5 (s).

*3.5. 4-Nitrophenyltrifluoromethylsulfide **(6)** was prepared from **3d** according to literature procedure [7]*

*3.5.1. 7. 2-Trifluoromethyl-N-methylpyrrole **(7)***

A two-necked flask was charged with a solution of salt **4** (0.2 g, 0.45 mmol) in water-free THF (1 mL) and *N*-methylpyrrole (0.9 g, 11.1 mmol). The mixture was refluxed for 7 h. Then water (5 mL) was added. The product was extracted with pentane, dried over $MgSO_4$ and concentrated in vacuum. The residue was purified by silica gel chromatography (pentane) and yielded 0.06 g of **7** (90%). ^{1}H NMR ($CDCl_3$): δ 4.55 (s, 3H); 6.8 (t, 1H); 7.25 (d, 1H); 7.48 (d, 1H). ^{19}F NMR ($CDCl_3$): δ −59.08 (s, 3F). Anal. calcd for $C_6H_6F_3N$: C, 48.32; H, 4.03; N, 9.39. Found: C, 48.29; H, 3.97; N, 9.20.

*3.6. Mixture of o- and p-trifluoromethyl-N, N-dimethylanilines **(8)***

A two-necked flask was charged with a solution of salt **4** or **3d** (0.5 g, 1.1 mmol) in water-free CH_3CN (5 mL) and *N*,*N*-dimethylaniline (0.3 g, 2.5 mmol). The mixture was refluxed for 6 h. The reaction was monitored by TLC. After the reaction completed, the solvent was evaporated. The residue was purified by silica gel chromatography (pentane). Evaporation of the solvent yielded 0.17 g of ca. 3:1 mixture of *o*- and *p*-trifluoromethyl-*N*,*N*-dimethylanilines (82%). ^{1}H NMR ($CDCl_3$): δ 2.83 (s, 6H, *p*-$N(CH_3)_2$); 2.85 (s, 6H, *o*-$N(CH_3)_2$); 6.57 (m, 1H); 6.70 (d, 2H, HC–(C–$N(CH_3)_2$)–CH); 7.06 (m, 1H,); 7.25 (m, 1H); 7.27 (d, 2H, HC–CCF_3–CH), 7.55 (m, 1H). ^{19}F NMR ($CDCl_3$): δ −59.46 (s, 3F, *p*-CF_3);−60.12 (s, 3F, *o*-CF_3). Anal. calcd for $C_9H_{10}F_3N$: C 54.20; H 5.05; N 7.90. Found: C 54.18; H 5.02; N 7.75.

*3.7. Tetraethylamino(trifluoromethylthio)carbenium triflate **(9)***

A two-necked flask was charged with a solution of salt **4** (0.1 g, 0.22 mmol) in water-free CH_3CN (5 mL) and tetraethylthiourea (0.05 g, 0.27 mmol). The mixture was heated to 80 °C in the heating bath and stirred at this temperature for 16 h. The reaction was monitored by TLC. After the reaction completed, the solvent was evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2:CH_3CN = 8:1). Evaporation of the solvent yielded 0.06 g of **9** (79%). ^{1}H NMR ($CDCl_3$): δ 1.38 (*t*, 3H); 3.8 (q, 2H). ^{19}F NMR ($CDCl_3$): δ −38.5 (s, 3F), −78.3 (c, 3F); FAB-HRMS: *m*/*z* 257 ([M-$CF_3SO_3^-$], $C_{11}H_{20}F_6N_2O_3S_2$ calcd 257).

*3.8. Bis[4-(N,N-dimethylamino)phenyl](trifluoromethylthio)carbenium triflate **(10)***

A two-necked flask was charged with a solution of salt **4** (0.1 g, 0.22 mmol) in water-free CH_3CN (5 mL) and Michler's thioketone (0.13 g, 0.46 mmol). The mixture was heated to 80 °C and stirred at this temperature for 16 h. The reaction was monitored by TLC. After the reaction completed, the solvent was evaporated. The residue was purified by silica gel chromatography (CH_2Cl_2:CH_3CN, 8:1). Evaporation of the solvent yielded 0.07 g of **10** (72%). ^{1}H NMR ($CDCl_3$): δ 3.39 (s, 6H), 7.01 (d, 4H), 7.73 (d, 4H). ^{19}F NMR ($CDCl_3$): δ −38.5 (s, 3F), −78.3 (s, 3F); FAB–HRMS: *m*/*z* 341 ([M-$CF_3SO_3^-$], $C_{18}H_{20}F_6N_2O_3S_2$ calcd 341).

*3.9. Reaction of sodium salt of 4-chlorobenzenesulfinic acids and diphenyl(S-trifluoromethyl)sulfonium tetrafluoroborate **(3a)***

A solution of sodium salt of 4-chlorobenzenesulfinic acid (0.06 g, 0.3 mmol) and salt **2a** (0.1 g, 0.29 mmol) in water-free DMSO (5 mL) was stirred at 100 °C for 3 h. The reaction mixture was then poured onto water. The product was extracted with ether

(3 mL × 5 mL), dried over $MgSO_4$ and concentrated in vacuum. The residue was purified by silica gel chromatography (pentane). Evaporation of the solvent yielded 0.06 g of **11** (81%). Mp = 55–56 °C (pentane) [20]. ^{19}F NMR ($CDCl_3$): δ −76.9.

3.10. Reaction of sodium diethoxyphosphinate and diphenyl(S-trifluoromethyl)sulfonium tetrafluoroborate

To a solution of diethoxyphosphineoxide (0.4 g, 2.9 mmol) in water-free glyme (2 mL) sodium hydride (0.17 g, 3.56 mmol) was added. The reaction mixture was stirred for 1 h, and then the solution became transparent. A solution of salt **3a** (0.61 g, 1.78 mmol) in glyme (1 mL) was added to the reaction mixture. The reaction mixture was stirred for additional 3 h at rt and then poured onto water. The product was extracted with diethyl ether and dried over $MgSO_4$. Evaporation of the solvent resulted in 0.25 g of **12** (70%). Bp = 55–57 °C (7 Torr) [19]. ^{19}F NMR ($CDCl_3$): δ −73.22 (d, 3F, J = 121 Hz).

3.11. 4-Nitrophenyl(fluoro)trifluoromethylsulfonium tetrafluoroborate **(13)**

XeF_2 (0.14 g, 0.83 mmol) and $BF_3{\cdot}Et_2O$ (0.1 g, 0.71 mmol) were added to a stirred solution of 4-nitrophenyltrifluoromethylsulfide (0.15 g, 0.67 mmol) in dichloromethane (5 mL) at −60 °C. The reaction mixture was stirred at rt till the end of effervesce of gas. The product was used without further purification.

3.12. Typical procedure for synthesis of S-(trifluoromethyl) arylhetarylsulfonium salts **(14, 15)**

An appropriate heterocycle (2.7 mmol) was added dropwise to a solution of salt **13** (0.43 g, 1.32 mmol) in dichloromethane (5 mL) at −60 °C. The reaction mixture was allowed to warm to rt and stirred for 24 h at rt. Then the solvent was evaporated, and the residue was purified by silica gel chromatography (CH_2Cl_2:CH_3CN, 8:1). Evaporation of solvent resulted in salts **14** and **15**:

- **(14)**: *N*-Metylpyrrole was used as starting heterocycle; mixture α:β = 1:1, mp = 110–112 °C; ^1H NMR ($CDCl_3$): δ 3.88 (s, 3H), 4.12 (s, 3H), 6.62–7.61 (m, 6H), 8.21–8.63 (m, 8H). ^{19}F NMR ($CDCl_3$): −54,0 (s, 3F), −54.1 (s, 3F), −150.1 (s, 8F). Anal. calcd for $C_{12}H_{10}BF_7N_2O_2S$: C, 36.92; H, 2.56; N 7.18. Found: C, 37.18; H, 2.57; N, 7.20.
- **(15)**: Indole was used as starting heterocycle; mp = 164–166 °C; ^1H NMR ($CDCl_3$): δ 7.50 (*t*, 1H), 7.61 (*t*, 1H), 7.73 (d, 1H), 7.97 (d, 1H), 8.54 (d, 2H), 8.71 (d, 2H), 9.14 (s, 1H), 12.68 (br s, 1H). ^{19}F NMR ($CDCl_3$): δ −53.4 (s, 3F), −149.2 (s, 4F). Anal. calcd for $C_{15}H_{10}BF_7N_2O_2S$: C, 42.25; H, 2.35. Found: C, 41.75; H 2.02.

References

[1] (a) P. Kirsch, In Modern Fluoroorganic Chemistry, Wiley-VCH, Weinheim, 2004;
(b) K. Uneyama, In Organofluorine Chemistry, Blackwell, Oxford, 2006;
(c) J.-A. Ma, D. Cahard, J. Fluorine Chem. 128 (2007) 975–996.

[2] (a) L.M. Yagupolskii, Kiev (1988);
(b) M.A. McClinton, D.A. McClinton, Tetrahedron 48 (1992) 6555–6666.

[3] G.K.S. Prakash, A.K. Yudin, Chem. Rev. 97 (1997) 757–786.

[4] L.M. Yagupolskii, I.I. Maletina, N.V. Kondratenko, V.V. Orda, Synthesis (1978) 835–837.

[5] T. Umemoto, Y. Kuriu, H. Shuyama, O. Miyano, S.-I. Nakayama, J. Fluorine Chem. 20 (1982) 695–698.

[6] (a) P. Eisenberger, S. Gischig, A. Togni, Chem. Eur. J. 12 (2006) 2579–2586;
(b) I. Kieltsch, P. Eisenberge, A. Togni, Angew. Chem. Int. Ed. 46 (2007) 754–757.

[7] L.M. Yagupolskii, N.V. Kondratenko, O.N. Timofeeva, Zh. Org. Khim. 20 (1984) 115–118, Chem. Abstr., 100 (1984) 191494e.

[8] J.-J. Yang, R.L. Kirchmeier, J.M. Shreeve, J. Org. Chem. 63 (1998) 2656–2660.

[9] E. Magnier, J.C. Blazejewski, M. Tordeux, C. Wakselman, Angew. Chem. Int. Ed. 45 (2006) 1279–1282.

[10] (a) T. Umemoto, S. Ishihara, Tetrahedron Lett. 31 (1990) 3579–3582;
(b) T. Umemoto, S. Ishihara, J. Am. Chem. Soc. 115 (1993) 2156–2164;
(c) T. Umemoto, Chem. Rev. 96 (1996) 1757–1777.

[11] I. Ruppert, J. Fluorine Chem. 14 (1979) 81–84.

[12] M. Janzen, Can. J. Chem. 55 (1977) 3031–3034.

[13] L.M. Yagupolskii, A.V. Matsnev, R.K. Orlova, Y.L. Yagupolskii, Abstract of Papers, 18th International Symposium on Fluorine Chemistry, Bremen, Germany, July 30–August 4, 2006, PM-Grafik-Design, Herstellung, Wachtersbach, 2006, 150.

[14] N.V. Kondratenko, V.N. Movchun, L.M. Yagupolskii, J. Org. Chem. USSR (Engl. Transl.) 25 (1989) 1005–1006.

[15] A. Haas, A. Waterfeld, C. Klare, G. Moller, N. Kondratenko, L. Yagupolskii, Chem. Ber. 128 (1995) 435–436.

[16] V. Movchun, A. Kolomeitsev, Y.L. Yagupolskii, J. Fluorine Chem. 70 (1995) 255–257.

[17] K. Muralidharan, R. Chakraborty, J.M. Shreeve, J. Fluorine Chem. 125 (2004) 1967–1968.

[18] (a) J. Jilek, J. Pomykacek, J. Holubek, E. Svatek, M. Ryska, Collect. Czech. Chem. Commun. 49 (1984) 603–620;
(b) S. Montanari, C. Paradisi, G. Scorrano, J. Org. Chem. 56 (1991) 4274–4279;
(c) H. Price, L. Stacy, J. Am. Chem. Soc. 68 (1946) 498–500.

[19] I.G. Maslennikov, A.N. Lavrent'ev, M.V. Lyubimova, Yu.I. Shvedova, V.B. Lebedev, Zh. Obshch. Khim. 53 (1983) 2417.

[20] N.V. Kondratenko, O.A. Radchenko, L.M. Yagupolskii, J. Org. Chem. USSR 20 (1984) 2051–2052 (Engl. Transl.).