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2-Trifluoromethyl-1,3-dithianylium triflate: a convenient 'masked' electrophilic pentafluoroethylation reagent☆

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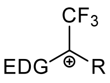
Abstract—With 2-trifluoromethyl-1,3-dithianylium triflate for the first time the synthesis, isolation and full structural characterization of an α-perfluoroalkylcarbenium salt was achieved. The title compound can be easily obtained on a preparative scale. The thermally stable dithianylium salt in combination with fluorodesulfurization chemistry is a promising novel reagent for the electrophilic polyfluoroalkylation of organic substrates, demonstrated by the pentafluoroethylation of *O*-nucleophiles.

α-Trifluoromethylcarbenium ions are a structurally remarkable species, since they are inductively destabilized by the trifluoromethyl group as a strong electron-withdrawing substituent ($\sigma_m = 0.43$, $\sigma_p = 0.54$[1]), e.g. the comparison of reaction enthalpies for $CF_3CH_3 \rightarrow CF_3CH_2^+ + H^-$ and $CH_3CH_3 \rightarrow CH_3CH_2^+ + H^-$ shows, that the formation of the trifluoroethyl cation is by 53 kcal mol^{-1} less favorable than the ethyl cation.[2]

In numerous studies α-polyfluoroalkyl carbenium ions have been postulated as intermediates,[3] or generated in situ under special conditions and then characterized.[4] In these cases the cationic center was additionally stabilized by electron-donating substituents (aryl or heteroatom, type **1**). Stabilizing by charge delocalization in this case is effective enough to allow the study of the cation in solution or in the gas phase by spectroscopic methods.

Nevertheless, such cases are rare, and the synthesis of carbenium salts in isolated form is rather difficult. To the best of our knowledge only few compounds of such type have been isolated, namely the cluster complexes **2**, where the α-trifluoromethylcarbenium center is stabilized by a direct metal···C$^+$ interaction.[5]



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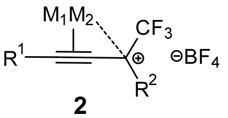
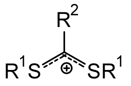


2



3

EDG = electron-donating group; M_1, M_2 = Co_2L_6 or $L_3CoMoL'_3$
(L, L' = CO, Cp, PPh_3, $Ph_3PCH_2PPh_3$).

It is also known[6] that a single arylthio moiety is not sufficient to stabilize the cation **1** (EDG = ArS, R = H). However, non-fluorinated carbenium ions containing two alkylthio substituents (type **3**) are stable, and the corresponding salts can be easily obtained on a preparative scale.[7] Such compounds have great synthetic potential; e.g. by the addition of phenols or acidic alcohols followed by oxidative fluorodesulfurization[8] new α,α-difluoroalkylethers, liquid crystalline molecules were synthesized,[7d,e] so far not available using other methods.

In the framework of our search for novel reagents for selective polyfluoroalkylation of organic molecules under mild conditions,[9] we wish to report here the synthesis, X-ray molecular structure (as the first example of structurally defined α-CF_3 carbenium ion) and demonstrate the perspectives of synthetic application of 2-trifluoromethyl-1,3-dithianylium triflate $\mathbf{4^+} \cdot CF_3SO_3^-$ as a new convenient reagent for 'electrophilic' pentafluoroethylation.

Keywords: carbenium ions; fluorine and compounds; desulfurization; X-ray crystal structures; thioethers.

☆ The colour picture presented in the graphical abstract was performed using program MOLEKEL 4.2: Flükinger, P.; Lüthi, H. P.; Portmann, S.; Weber, J. Swiss Center for Scientific Computing, Manno, Schweiz, 2002

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The dithianylium salt $4^{+}\cdot CF_3SO_3^{-}$, a colorless crystalline solid, was obtained in 66% yield reacting propane-1,3-dithiol (**5**) with trifluoroacetic anhydride, followed by treatment with trifluoromethanesulfonic acid (Scheme 1).[10]

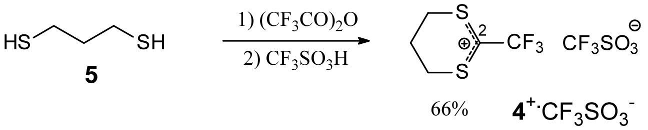
The ^{1}H, ^{13}C and ^{19}F NMR data confirm the proposed structure. The ^{13}C resonance at $\delta = 208.3$ is due to the carbenium character of the C(2) carbon.[7d]

The X-ray structure analysis of **4**[11] exhibit a half-chair conformation for the 1,3-dithiane ring (Fig. 1). The atoms C(7), C(2), S(2) and S(3) are co-planar (average deviation 0.3 pm), C(4), C(5) and C(6) are above or below this plane by −6.7, 61.6 and −9.8 pm, respectively.

The C(2)–C(7) bond length in $\mathbf{4}^{+}$ is 154.3(3) pm, i.e. by ca. 5 pm longer than the corresponding bond length in the non-fluorinated cation $\mathbf{6}^{+}$ (Table 1). The S–C(2) bonds are almost of the same length. Comparative DFT calculations[12] for the cation $\mathbf{4}^{+}$ and its methyl analogue $\mathbf{7}^{+}$, for which a solid state molecular structure is not known yet, exhibit a bond lengthening of the same order (Table 1).

Compound $4^{+}\cdot CF_3SO_3^{-}$ is unexpectedly stable. Protected from air, it can be stored at −30°C for months without any change, at ambient temperature it shows a slow greyish discoloration. $4^{+}\cdot CF_3SO_3^{-}$ can even be handled under air for a short time without decomposition.

One of the most challenging problems in preparative fluoroorganic chemistry is a satisfying method for electrophilic perfluoroalkylation. The reactivity of almost all known 'electrophilic' reagents for perfluoroalkylation[13] is based on an electron transfer, preceding the transfer of the perfluoroalkyl radical. The reactivity of these reagents is limited, e.g. for primary alcohols only *one* example of *O*-polyfluoroalkylation using *O*-CF_3-dibenzofuranium salt was reported.[13d] Direct *O*-polyfluoroalkylation of secondary alcohols is unknown to the best of our knowledge.



Scheme 1. Synthesis of the dithianylium salt $4^{+}\cdot CF_3SO_3^{-}$.

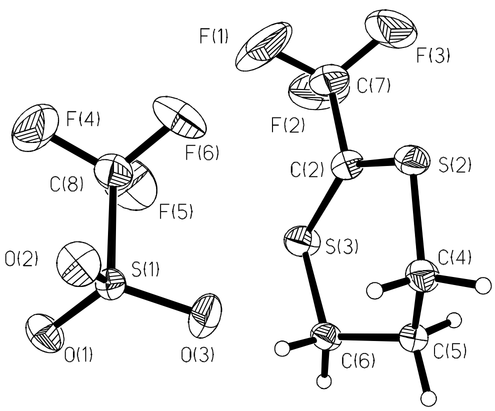
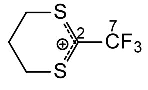
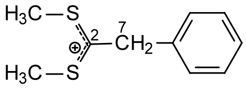
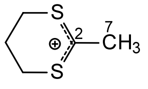


Figure 1. Molecular structure of $4^{+}\cdot CF_3SO_3^{-}$ (thermal ellipsoids with 50% probability).

Table 1. Selected bond lengths (pm) for cations $\mathbf{4}^{+}$, $\mathbf{6}^{+}$ and $\mathbf{7}^{+}$


$\mathbf{4}^{+}$


$\mathbf{6}^{+}$


$\mathbf{7}^{+}$

Bond	4^{+a}	6^{+b}	4^{+c}	7^{+c}
C(2)–C(7)	154.3(3)	150(2)	155.8	150.8
S–C(2)[d]	166.5(1)	167.5(14)	168.4	169.3

[a] X-Ray structure analysis, this paper.

[b] X-Ray structure analysis with $SbCl_6^{-}$ as counter ion.[7c]

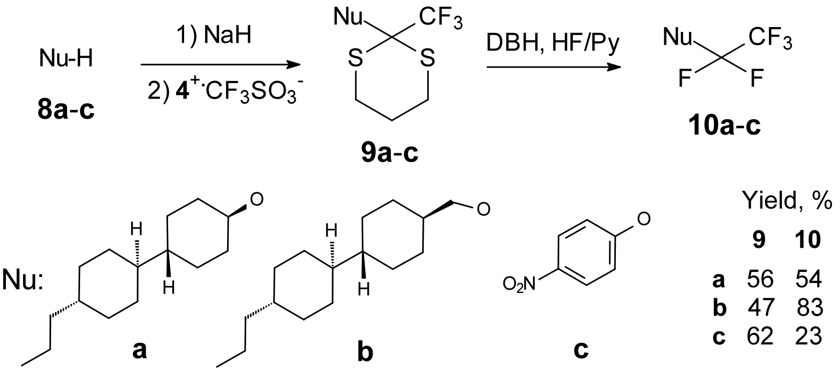
[c] DFT calculation (B3LYP/6-31G*).[12]

[d] Average value.

Our preliminary results show, that $4^{+}\cdot CF_3SO_3^{-}$ can be used as a reagent for the electrophilic introduction of polyfluoroalkyl substituents in organic substrates. This application of $4^{+}\cdot CF_3SO_3^{-}$ opens up new synthetic perspectives, clearly demonstrated by the successful pentafluoroethylation of oxygen nucleophiles **8**, especially in the case of secondary alcohol **8a**. Treatment of deprotonated **8** with $4^{+}\cdot CF_3SO_3^{-}$ gave the dithioorthoesters **9**, which in their turn were oxidatively fluorodesulfurized using 1,3-dibromo-5,5-dimethylhydantoin (DBH) in 70% HF/pyridine solution, forming the pentafluoroethyl substituted compounds **10** (Scheme 2).[14] It should be pointed out, that C_2F_5O derivatives **10**, being important for liquid crystal applications, are hardly accessible otherwise.

The polyfluoroalkylation of other *O*, *C*, *N* and *P*-nucleophiles via $4^{+}\cdot CF_3SO_3^{-}$ together with study of other aspects of its reactivity, as well as the synthesis of similar stable α-perfluoroalkyl carbenium salts are in progress[15] and will be published elsewhere.

In conclusion, we report a convenient synthesis of the α-trifluoromethyl carbenium salt $4^{+}\cdot CF_3SO_3^{-}$. Two electron-donating alkylthio substituents are sufficient for stabilizing the carbenium center, in spite of the electron-withdrawing CF_3 group, allowing us to isolate and fully characterize the title compound. The X-ray investigation (the *first* example for an α-trifluoromethyl carbenium species) showed, that the $^{+}C–CF_3$ bond is by 5 pm longer than the respective $^{+}C–CH_3$ bond in the analogous compound. Compound $4^{+}\cdot CF_3SO_3^{-}$, easy to synthesize on preparative scale, is a new and inexpensive reagent for 'electrophilic' introduction of pentafluoroethyl moiety into organic substrates.



Scheme 2. Synthesis of the pentafluoroethylether **10**.

Acknowledgements

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10. Preparation of $\mathbf{4}^{+}\cdot CF_3SO_3^-$: trifluoroacetic anhydride (22.3 g, 106 mmol) was added dropwise, under stirring to propane-1,3-dithiol (10.6 g, 98 mmol), while cooling to 0°C. Then, trifluoromethanesulfonic acid (23.3 g, 155 mmol) was added dropwise within 30 min at −10°C. After the mixture had been stirred for 2 h at 0°C, acetic anhydride (41.3 g, 405 mmol) was added dropwise within 20 min at 0°C. The mixture was diluted with diethyl ether (150 mL) and stirred for 5 min, the precipitated solid was filtered off and washed with diethyl ether (3×40 mL) to afford product $\mathbf{4}^{+}\cdot CF_3SO_3^-$ (21.7 g, 66%) as a colorless solid, mp 146–149°C. To be protected against air and moisture, the compound is stable for months, but decomposes slowly through the contact with acetonitrile at room temperature. ^1H NMR (200.1 MHz, $CDCl_3$:CH_3CN (3:2), TMS): δ 2.28–2.39 (2H, m, C^5H_2), 3.80 (4H, t, ^3J (H,H) = 5.4 Hz, 2×SCH_2) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$:CD_3CN (3:2), TMS): δ 14.8 (s, C^5), 33.0 (s, C^4, C^6), 118.4 (q, ^1J (C,F) = 283.0 Hz, C^7F_3), 119.4 (q, ^1J (C,F) = 319.0 Hz, C^8F_3), 208.3 (q, ^2J (C,F) = 36.2 Hz, C^2) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$:CH_3CN (3:2), $CFCl_3$): δ −79.94 (3F, s, C^8F_3), −64.26 (3F, s, C^7F_3) ppm. MS (FAB, 4-nitrobenzylalcohol): positive, *m*/*z* (%) 187 (100) [M^+ ($C_5H_6F_3S_2$)]; negative, *m*/*z* (%) 149 (100) [$CF_3SO_3^-$], 299 (43) [2×$CF_3SO_3^-$+H^+]. HRMS for cation ($C_5H_6F_3S_2$): found

186.9863; calcd 186.9863, ±10 ppm, Pr_4NBr (186.2222) as standard.

11. Colorless plates of $\mathbf{4}^{+}\cdot CF_3SO_3^{-}$ suitable for X-ray investigation were obtained from $CH_3CN{:}Et_2O$ (1:1) at −35°C. Crystal data for $\mathbf{4}^{+}\cdot CF_3SO_3^{-}$: $C_6H_6F_6S_3O_3$, $M_r = 336.29$, crystal size $0.15\times0.50\times0.50$ mm^3, monoclinic, space group $P2_1/c$, $a = 1360.40(10)$, $b = 784.80(10)$, $c = 1154.80(10)$ pm, $\beta = 102.890(10)°$, $V = 1.2018(2)$ nm^3, $Z = 4$, $\rho_{\mathrm{ber}} = 1.859$ Mg/m^3, $\mu = 0.691$ mm^{-1}. From 6350 reflections measured 2742 were independent ($R_{\mathrm{int}} = 0.0282$). $R = 0.0334$ (I> 2(I)), $R_w = 0.0918$ (F^2, all data), 165 parameters, largest difference peak and hole 0.782/−0.531 e Å^{-3}, $\theta_{\max} = 27.5°$, Mo-Kα radiation ($\lambda = 71.073$ pm), $T = -100°C$. The structure was solved by direct methods and refined using the SHELX program system (Sheldrick, G. M. SHELX-97, University of Göttingen, 1997). All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated as a riding model. Crystallographic data (excluding structure factors) have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. 186353. Copies of the data can be obtained, free of charge, via the Internet http://www.ccdc.cam.ac.uk, or on application to the director; CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Tel.: (+44)1223-336-408; fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.
12. DFT calculation: B3LYP/6-31G*; the optimized structures have only positive eigen frequencies. *Gaussian 98*, Revision A.6: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, USA, 1998.
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14. Preparation of **10a**: to a suspension of **8a** (1.3 g, 6 mmol) in THF (40 mL) NaH (0.26 g of 60% suspension in mineral oil, 6.5 mmol NaH) was added at room temperature. The mixture was heated to reflux for 12 h, the solvent removed in vacuo to afford the sodium salt of **8a** (1.5 g) as a yellowish solid. A suspension of $\mathbf{4}^{+}\cdot CF_3SO_3^{-}$ (2.0 g, 6 mmol) in THF (25 mL) was prepared at −70°C. Then, the sodium salt of **8a** (1.5 g, 6 mmol) was added in portions, under stirring at −60°C. The mixture was allowed to warm up to ca. 0°C, poured into water (300 mL) and extracted with diethyl ether (4×40 mL). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness. The residue is a yellowish solid (2.3 g), corresponding ^1H NMR data—mixture of **9a** and **8a** (60:40 mol). **9a**: ^1H NMR (200.1 MHz, $CDCl_3$, TMS): δ 0.65–1.38 (20H, m), 1.63–1.73 (6H, m), 1.88–2.05 (2H, m), 2.88, 3.12 (two m, each 2H, 2 SCH_2), 4.08 (1H, m, OCH) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, $CFCl_3$): δ −78.10 (s) ppm.

    A suspension of 1,3-dibromo-5,5-dimethylhydantoin (2.3 g, 8 mmol) in CH_2Cl_2 (10 mL) was cooled to −78°C. Then, 70% HF/pyridine solution (3.1 g, 108 mmol HF) was added dropwise, followed by solution of 60% **9a** (1.9 g, 2.7 mmol) in CH_2Cl_2 (10 mL) over a time span of 10 min. The well stirred mixture was allowed to warm up to ca. 20°C and poured into ice-cold water (ca. 150 g) and treated with 1N NaOH. The organic phase was separated, and the aqueous phase extracted using CH_2Cl_2 (4×25 mL). The combined organic phases were dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (2 mL) and filtrated over a short silica gel column (eluent pentane). A further purification was achieved by two recrystallizations from ethanol to yield **10a** (0.5 g, yield 54%) as colorless crystals, mesophase sequence C 43 S_B (43) I. **10a**: ^1H NMR (200.1 MHz, $CDCl_3$, TMS): δ 0.85 (3H, t, CH_3, ^3J (H-H) = 6.8 Hz), 0.68–1.89 (21H, m), 1.97–2.16 (2H, m), 4.24 (1H, tt, $^*CH$, ^3J (H-H) = 11.1, ^3J (H-H) = 4.6 Hz) ppm. ^{13}C NMR (90.6 MHz, $CDCl_3$, TMS): δ 14.4 (s, CH_3), 20.0, 27.9, 30.1, 33.1, 33.4, 39.7 (s, CH_2), 37.5, 41.8, 42.6 (s, CH), 77.3 (t, O-CH, ^3J (C-F) = 3.7 Hz), 115.4 (tq, CF_2, ^1J (C-F) = 269.0, ^2J (C-F) = 41.2 Hz), 116.8 (qt, $CF3$, ^1J (C-F) = 284.5, ^2J (C-F) = 46.1 Hz) ppm [the assignment of CH, CH_2, and CH_3 signals was based on DEPT 135 experiment]. ^{19}F NMR (188.3 MHz, $CDCl_3$, $CFCl_3$): δ −88.08 (2F, s, CF_2), −86.83 (3F, s, CF_3) ppm. MS (EI, 70 eV, 25°C): m/z (%) 342 (2) [M^+ ($C_{17}H_{27}F_5O$)], 206 (100) [$M^+{-}C_2F_5OH$], 125 (50) [$M^+{-}C_6H_{10}OC_2F_5$], 69 (100) [CF_3^+], 41 (35) [$CH_2{=}CH\text{-}CH_2^+$], 29 (10) [$C_2H_5^+$]. HRMS for M^+: found 342.1968; calcd 342.1982, 4.1 (10.0) ppm, 1.4 (10.0) mmu.
15. The C_4F_9 analogue of $\mathbf{4}^{+}\cdot CF_3SO_3^{-}$ and $[(R_2N)_2CR^F]^+\cdot CF_3SO_3^-$ ($R^F = CF_3$, C_2F_5) were also obtained: Sevenard, D. V.; Kolomeitsev, A. A.; Kalinovich, N.; Königsmann, M. H.; Kirsch, P.; Röschenthaler, G.-V., unpublished results.