Synthesis and Reactions of 1-Aryl-2,2-bis(perfluoroalkanesulfonyl)ethylenes

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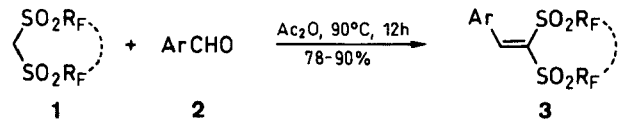
The title compounds **3** were prepared by condensation of bis(perfluoroalkanesulfonyl)methanes **1** with aromatic aldehydes in high yields. Reactions of **3** with pyridine and dimethyl phosphite were studied.

Perfluoroalkanesulfonyl groups (R_FSO_2) are known as very strong electron-attracting substituents.[1-2] This property is often used in the activation of C–C multiple and α-C–H bonds. The synthesis and reactions of perfluoroalkanesulfonyl substituted alkenes and alkynes are of great interest in synthetic organic chemistry.[3-6]

Recently, Hanack et al[7] reported the preparation of 2-aryl-1-(perfluoroalkanesulfonyl)acrylonitriles, $R_FSO_2C(CN)=CHAr$. Under the reaction conditions employed by these authors,[7] no 1-aryl-2,2-bis(perfluoroalkanesulfonyl)ethylenes **3** could be detected as the reaction product from **1** and aromatic aldehydes **2**. The reason for the failure of this reaction was attributed to the high stability of the easily formed anion from **1** due to the inductive effect of two R_FSO_2 groups, that the nucleophilicity is reduced to a minimum to react with a positively polarized carbon atom.

In connection with our systematic investigation on **1**,[8,9] this paper describes a successful synthesis of the ethylene derivatives **3** which have a bis(perfluoroalkanesulfonyl) moiety. A series of 1-aryl-2,2-bis(perfluorosulfonyl)ethylenes **3** were obtained in good yields by condensation of **1** with aromatic aldehydes in acetic anhydride (Scheme 1) (Table).



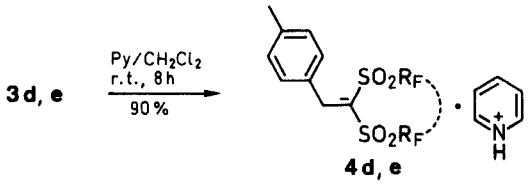
1 **2** **3**

Scheme 1

In this reaction, the first step might involve the protonation of the carbonyl oxygen atom by **1** which is a stronger acid than trifluoroacetic acid.[9] The cation formed was captured by $(R_FSO_2)_2CH^-$ giving an adduct. It was then dehydrated to afford the product **3**. Their structure were fully supported by analytical and spectral data. The products **3** are yellow solids and are sensitive to moisture. When exposed to air they are decomposed to starting aldehyde and **1**.

This reaction showed that the carbon–carbon double bond in **3** is very polar due to the two strong electron-withdrawing groups.[2] The very low field chemical shifts of the ethylene proton and the carbon which the proton bonded (for example in **3e**, $\delta_H = 8.90$, $\delta_C = 165.2$) confirmed this point. Extension of this reaction to aliphatic aldehydes and trichloroacetaldehyde failed.

Compounds **3** readily reacted with anhydrous pyridine forming the corresponding stable pyridinium salt (Scheme 2).

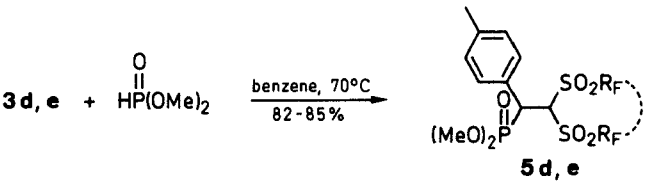


4d, e

Scheme 2

These dipolar complexes are white solids, thermally stable and not hydroscopic. They are easily separated and purified by recrystallization.

The very polar carbon–carbon double bond of the compounds **3** was also subjected to addition reaction with dialkyl phosphite, e.g. the adduct 1-[bis(perfluoroalkanesulfonyl)methyl]benzyl dimethyl phosphite **5** was obtained by treatment of **3** with dimethyl phosphite in benzene (Scheme 3).



5d, e

Scheme 3

Table 1. Compounds **3** Prepared

	Substrate **1**		Substrate **2**		Product	Distillation Temp (°C/Torr)	Yield[a] (%)	mp (°C)
	R_F	R_F						
1a	SO_2CF_3	SO_2CF_3	**2a**	Ph	**3a**	118–120/1	90	95–97
1b	$SO_2C_4F_9$	$SO_2C_4F_9$	**2b**	Ph	**3b**	146–150/1	86	127–129
1c	]—$SO_2(CF_2)_3SO_2$—[		**2c**	Ph	**3c**	121–123/1	90	120–123
1d	SO_2CF_3	SO_2CF_3	**2d**	4-MeC_6H_4	**3d**	112–114/1	85	94
1e	]—$SO_2(CF_2)_3SO_2$—[		**2e**	4-MeC_6H_4	**3e**	123–126/1	84	125–126
1f	]—$SO_2(CF_2)_3SO_2$—[		**2f**	4-$NO_2C_6H_4$	**3f**	151–154/1	78	134–136

[a] Isolated yield based on **1**.

The proton chemical shifts of the two methoxy groups in the products were found to be different, e. g. in compound **5e**, they occur at δ = 3.85 and 3.70 as doublets ($^3J_{HP}$ = 10 Hz). It is reasonable to consider that in compounds **5** the two methoxy groups on the phosphorous atom are diastereotopic with respect to the asymmetric carbon atom attached to the phosphorous atom.

In summary, we have synthesized a new class of ethylene derivatives bringing two strong electron-attracting groups R_FSO_2; the very polar carbon–carbon double bond allows the addition reaction to take place. Further studies on the chemistry of these alkenes are in progress.

Melting points were taken in a Thiele apparatus and are uncorrected. All reactions were conducted under dry conditions. Solvent was purified freshly prior to the reaction. The following instruments were used. IR: Shimadzu IR-440, MS: Finnigan GC-MS 4021 (70 eV). ^{1}H NMR and ^{19}F NMR: Varian-360L Instrument with TMS and TFA as an internal and external standard, respectively. ^{13}C NMR and ^{31}P NMR: JEOL-90 QX Instrument with TMS and H_3PO_4 as internal and external standard, respectively. $(CD_3)_2CO$ was used as solvent throughout. Elemental analyses were performed by the analysis department of this institute. Compounds **1** were prepared according to the literature method.[10] For new compounds satisfactory microanalyses were obtained: C ± 0.41, H ± 0.45, F ± 0.42.

1-Aryl-2,2-bis(perfluoroalkanesulfonyl)ethylenes 3a–3f; General Procedure:

A solution of aromatic aldehyde (5 mmol), **1** (5 mmol) and anhydrous Ac_2O (5 mL) was heated for 12 h at 90 °C. After removing the excess of Ac_2O and formed AcOH, the residue was distilled under vacuum to give **3** (Table).

1-Phenyl-2,2-bis(trifluoromethanesulfonyl)ethylene (**3a**):

IR (KBr): ν = 3050 (=CH), 1602 (C=C), 1545, 1500, 1452, 1380 (SO_2), 1320, 1220–1110 cm^{-1} (CF).

^{1}H NMR: δ = 8.87 (s, 1 H, =CH), 7.80–7.50 (m, 5 H_{arom}).

^{19}F NMR: δ = 1.03 (s, CF_3).

^{13}C NMR: δ = 120.3 [=C($SO_2CF_3)_2$], 128.3, 129.9, 139.9, 148.6 (C_6H_5), 166.3 (=CH).

MS: *m/z* (%) = 369 (M^+H), 2.79), 368 (M^+, 11.62), 299 ($M^+ - CF_3$, 16.82), 235 ($M^+ - CF_3SO_2$, 50.16), 234 ($M^+ - H - CF_3SO_2$, 51.43), 166 ($M^+ - CF_3SO_2 - CF_3$, 13.93), 165 ($M^+ - H - CF_3SO_2 - CF_3$, 55.20), 133 ($CF_3SO_2^+$, 4.32), 102 ($M^+ - 2CF_3SO_2$, 100), 77 ($C_6H_5^+$, 52.43), 69 ($CF_3^+$, 82.30).

1-Phenyl-2,2-bis(perfluorobutanesulfonyl)ethylene (**3b**):

IR (KBr): ν = 3043 (=CH), 1595 (C=C), 1500, 1453, 1380 (SO_2), 1320, 1230–1110 cm^{-1} (CF).

^{1}H NMR: δ = 8.88 (s, 1 H, =CH), 7.83–7.50 (m, 5 H_{arom}).

^{19}F NMR: δ = 5.3 (s, CF_3), 37.3 (s, CF_2S), 45.3 (m, CF_2), 50.5 (m, CF_2).

MS: *m/z* (%) = 669 (M^+H, 1.68), 668 (M^+, 3.94), 385 ($M^+ - C_4F_9SO_2$, 50.66), 283 ($C_4F_9SO_2^+$, 2.18), 267 ($C_4F_9SO^+$, 1.32), 166 ($C_6H_4CH{=}SO_2^+$, 12.67), 77 ($C_6H_5^+$, 83.64), 69 (CF_3^+, 100).

1-Phenyl-2,2-(1,1,3,3-tetraoxodithiohexafluorocyclohexylene)-ethylene (**3c**):

IR (KBr): ν = 3040 (=CH), 1600 (C=C), 1510, 1450, 1385 (SO_2), 1320, 1270–1120 cm^{-1} (CF).

^{1}H NMR: δ = 8.78 (s, 1 H, =CH), 7.85–7.53 (m, 5 H_{arom}).

^{19}F NMR: δ = 42.0 (m, 4 F), 47.7 (m, 2 F).

MS: *m/z* (%) = 380 (M^+, 2.58), 364 ($M^+ - SO_2$, 3.97), 252 ($M^+ - 2SO_2$, 7.36), 251 ($M^+ - 2SO_2 - H$, 8.86), 166 ($M^+ - C_3F_6SO_2$, 17.51), 150 ($C_3F_6^+$, 8.01), 100 ($C_2F_4^+$, 68.30), 77 ($C_6H_5^+$, 100), 64 (SO_2^+, 82.56).

1-Tolyl-2,2-bis(trifluoromethanesulfonyl)ethylene (**3d**):

IR (KBr): ν = 3030 (=CH), 2980 (w, CH_3), 1604 (C=C), 1582, 1523, 1420, 1381 (SO_2), 1230–1180 cm^{-1} (CF).

^{1}H NMR: δ = 8.92 (s, 1 H, =CH), 7.82–7.52 (A'ABB', 4 H_{arom}), 2.40 (s, 3 H, CH_3).

^{19}F NMR: δ = 1.30 (s, CF_3).

^{13}C NMR δ = 22.2 (CH_3), 121.3 [=C($SO_2CF_3)_2$], 126.7, 129.9, 135.6, 149.5 (C_6H_5), 165.4 (=CH).

MS: *m/z* (%) = 383 (M^+ H, 1.73), 382 (M^+, 12.57), 313 ($M^+ - CF_3$, 5.43), 248 ($M^+ - CF_3SO_2 - H$, 32.40), 180 ($M^+ - CF_3SO_2 - CF_3$, 8.84), 179 ($M^+ - CF_3SO_2 - H - CF_3$, 24.01), 133 ($CF_3SO_2^+$, 4.18), 116 ($M^+ - 2CF_2SO_2$, 37.85), 115 ($M^+ - 2CF_3SO_2 - H$, 44.51), 91 ($CH_3C_6H_4^+$, 11.58), 69 ($CF_3^+$, 100).

1-Tolyl-2,2-(1,1,3,3-tetraoxodithiohexafluorocyclohexylene)-ethylene (**3e**):

IR (KBr): ν = 3030 (=CH), 2998 (CH_3), 1610 (C=C), 1550, 1390, 1380 (SO_2), 1210–1140 cm^{-1} (CF).

^{1}H NMR: δ = 8.80 (s, 1 H, =CH), 7.83–7.50 (AA'BB', 4 H_{arom}), 2.44 (s, 3 H, CH_3).

^{19}F NMR: δ = 42.6 (m, 4 F), 48.0 (M, 2 F).

^{13}C NMR: δ = 22.3 (CH_3), 122.6 (HC=C), 126.2, 129.8, 135.4, 149.4 (C_6H_5), 165.2 (=CHAr).

MS: *m/z* (%) = 394 (M^+, 6.09), 330 ($M^+ - SO_2$, 1.43), 265 ($M^+ - 2SO_2 - H$, 2.04), 251 ($M^+ - 2SO_2 - CH_3$, 2.32), 228 [$(CF_2SO_2)_2^+$, 2.95], 150 ($C_3F_6^+$, 6.54), 131 ($C_3F_5^+$, 16.69), 116 ($M^+ - C_3F_6S_2O_3$, 17.30), 100 ($C_2F_4^+$, 64.94), 91 ($MeC_6H_4^+$, 100).

1-(4-Nitrophenyl)-2,2-(1,1,3,3-tetraoxohexanefluorocyclohexylene)ethylene (**3f**):

IR (KBr): ν = 3045 (=CH), 1608 (C=C), 1554, 1490, 1380 (SO_2), 1220–1110 cm^{-1} (CF).

^{1}H NMR: δ = 8.40 (s, 1 H, =CH), 8.23–7.65 (AA'BB', 4 H_{arom}).

^{19}F NMR: δ = 43.0 ((m, 4 F), 48.5 (m, 2 F).

MS: *m/z* (%) = 426 (M^+ H, 1.27), 425 (M^+, 3.32), 409 (M^+ – O, 1.18), 361 ($M^+ - SO_2$, 8.83), 297 ($M^+ - 2SO_2$, 2.63), 211 ($M^+ - C_3F_6SO_2$, 18.30), 150 ($C_3F_6^+$, 16.34), 131 ($C_3F_5^+$, 21.50), 122 ($NO_2C_6H_4^+$, 3.67), 100 ($C_2F_4^+$, 69.30), 64 (SO_2^+, 100).

Reaction of 3d with Pyridine; Typical Procedure:

A mixture of **3 d** (1.91 g, 5 mmol), CH_2Cl_2 (10 mL) and anhydr. pyridine (2 mL) was stirred at r. t. for 8 h. After removing the CH_2Cl_2 and unreacted pyridine the residue was recrystallized from MeCN/CH_2Cl_2 to give **4d**; yield: 2.0 g (90 %); mp 162–164 °C.

IR (KBr): ν = 3050 (CH_{arom}), 2995, 2990 (CH_3), 1620, 1490 ($C{=}C_{arom}$), 1440 (CH_3), 1355 (SO_2), 1193, 1162 cm^{-1} (CF).

^{1}H NMR: δ = 9.02–8.20 (m, 5 $H_{pyridine}$), 7.80–7.40 (m, 4 H_{arom}), 4.60 (s, 1 H, CHAr), 2.36 (s, 3 H, CH_3).

^{19}F NMR: δ = 2.50 (s, 2 × CF_3).

MS: *m/z* (%) = 392 ($M^+ - CF_3$, 1.28), 383 (M^+ H–C_5H_5N, 7.82),313 ($M^+ - CF_3 - C_5H_5N$, 4.27), 248 ($M^+ - CF_3 - C_5H_5N - H - SO_2$, 19.36), 195 ($M^+ - 2CF_3SO_2$, 2.50), 194 ($M^+ - 2CF_3SO_2 - H$, 11.25), 179 ($M^+ - 2CF_3SO_2 - H - CH_3$, 22.21), 116 ($M^+ - C_5H_5N - 2CF_3SO_2$), 47.15), 80 ($C_5H_5N^+H$, 100), 79 ($C_5H_5N^+$, 27.56), 91 ($CH_3C_6H_4$, 3.66), 69 ($CF_3^+$, 18.32).

4e; yield: 81 %; mp 186–189 °C.

IR (KBr): ν = 3048 (CH_{arom}), 2995, 2990, 2980 (CH_3), 1610, 1498 ($C{=}C_{arom}$), 1443 (CH_3), 1360, 1330 (SO_2), 1200, 1120 cm^{-1} (CF).

^{1}H NMR: δ = 9.03–8.20 (m, 5 $H_{pyridine}$) 7.83–7.40 (AA'BB', 4 H_{arom}), 4.63 (s, CH_{arom}), 2.35 (s, CH_3).

^{19}F NMR: δ = 43.5 (m, 4 F), 49.0 (m, 2 F).

MS: *m/z* (%) = 457 (M^+ –O), 2.63), 394 ($M^+ - C_5H_5N$, 37.63), 330 ($M^+ - C_5H_5N - SO_2$, 7.11), 259 ($M^+ - C_3F_6SO_2$, 3.86), 258 ($M^+ - C_3F_6SO_2 - H$, 4.75), 116 ($M^+ - C_3F_6SO_2 - SO_2 - C_5H_5N$, 13.69), 100 ($C_2F_4^+$, 62.1), 91 ($CH_3C_6H_4^+$, 91.60), 80 ($C_5H_5N^+H$, 100), 79 ($C_5H_5N^+$, 28.44).

Reaction of 3d with Dimethyl Phosphite; Typical Procedure:
A mixture of **3d** (1.9 g, 5 mmol), $HP(O)(OMe)_2$ (0.6 g, 5 mmol), and benzene (5 mL) was heated for 12 h at 70 °C. After removal of the solvent, the residue was crystallized from MeCN giving **5d**; yield: 2 g (81 %); mp 108–110 °C.

IR (KBr): ν = 3035 (CH_{arom}), 2993, 2910, 2858 (CH_3, CH), 1603, 1500, 1463, 1410, 1388 (SO_2), 1348, 1270, 1235 (P=O), 1030 (P–O–C).

^1H NMR: δ = 7.46–700 (AA'BB', $4H_{arom}$), 5.93 [s, 1 H, $CH(SO_2CF_3)_2$], 4.70 [d, 1 H, CHP (O)], $^2J_{P,H}$ = 24 Hz), 3.83 (d, 3 H, $POCH_3$, $^3J_{P,H} \approx 10$ Hz), 3.66 (d, 2 H, $POCH_3$), 2.3 (s, 3 H, CH_3).

^{19}F NMR: δ = 2.30 (s, $2 \times CF_3$).

MS: *m/z* (%) = 493 (M^+ H, 26.31), 492 (M^+, 11.87), 491 (M^+ –H, 21.36), 476 (M^+ –O, 2.51), 423 (M^+ – CF_3, 2.47), 383 [M^+ – $PO(OMe)_2$, 100].

5e; yield: 88 %; mp 138 °C.

IR (KBr): 3030 (CH_{arom}), 2990, 2905, 2850 (CH_3, CH), 1608, 1510, 1450, 1400, 1390 (SO_2), 1350, 1270, 1240 (P=O), 1035, 910 cm^{-1} (P–O–C).

^1H NMR: δ = 7.53–7.03 (AA'BB', $4H_{arom}$), 5.97 [s, 1 H, $CH(SO_2CF_3)_2$], 4.72 [d, 1 H, CHP(O), $^2J_{P,H}$ = 24 Hz), 3.85 (d, 3 H, $POCH_3$, $^3J_{P,H} \approx 10$ Hz), 3.70 (d, 3 H, $POCH_3$), $^3J_{P,H}$ = 10 Hz), 2.30 (s, 3 H, CH_3).

^{19}F NMR δ = 34.2 (AB, CF_2C, axial, $^2J_{FF}$ = 270 Hz), 42.5 (AB, CF_2S, axial, $^2J_{F,F}$ = 207 Hz), 46.7 (AB, CF_2S, equatorial), 56.7 (AB, CF_2C, equatorial).

^{13}C NMR: δ = 20.0 (CH_3), 41.8 (CHAr), 53.7 (OCH_3), 65.3 ($CHSO_2$), 128.5, 129.4, 141.5, 147.0 (C_6H_4).

^{31}P NMR: δ = 30.40 (s).

MS: *m/z* (%) = 505 (M^+ H, 100), 503 (M^+ –H, 22.51), 307 (M^+ H –C_3F_6SO, 21.04), 91 ($CH_3C_6H_4^+$, 21.65), 78 [$P(O)OCH_3$, 5.59].

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(1) Gramstad, T.; Haszeldine, R. N. *J. Chem. Soc.* **1957**, 4069.
(2) Stang, P. J.; Hanack, M.; Subramanian L. R. *Synthesis* **1982**, 85.
(3) Laping, K.; Hanack, M. *Tetrahedron Lett.* **1979**, 1309.
(4) Hanack, M. Wilhelm, B.; Subramanian, L. R. *Synthesis* **1988**, 592.
(5) Zhu, S. Z., unpublished work.
(6) Massa, F.; Hanack, M.; Subramanian, L. R. *J. Fluor. Chem.* **1982**, *19*, 601.
(7) Hanack, M.; Bailer, G.; Hackenberg, J.; Subramanian, L. R. *Synthesis* **1991**, 1205.
(8) Zhu, S. Z.; Chen, Q. Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1459.
(9) Zhu, S. Z.; Chen, Q. Y.; Wu, G. *J. Fluor. Chem.* **1993**, *60*, 283.
(10) Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358.