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Preparation of ylides containing the bis(perfluoroalkanesulphonyl)methylene functionality

Shi-Zheng Zhu* and Ai-Wen Li
Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu,
Shanghai, 200032 (China)

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Abstract

Various ylides containing the bis(perfluoroalkanesulphonyl)methylene functionality, $Y^{+}-{}^{-}C(SO_2R_f)_2$ ($Y = C_6H_5N$, Ph_3P, SMe_2) have been synthesized by the reaction of phenyliodonium bis(perfluoroalkanesulphonyl)methide with pyridine, triphenylphosphine and dimethyl sulphide in good yield.

During the study of the photoreaction of phenyliodonium bis(perfluoroalkanesulphonyl)methide, $PhI^{+}-{}^{-}C(SO_2R_f)_2$ (**1**), as a bis(perfluoroalkanesulphonyl) carbene precursor [1], it was interesting to find that the carbene intermediate $(R_fSO_2)_2C$: reacted readily with uncharged but polarizable nucleophiles. For example, irradiation of **1** with dimethyl sulphide gave dimethylsulphonium bis(perfluoroalkanesulphonyl)methide $Me_2S^{+}-{}^{-}C(SO_2R_f)_2$. We have reported the occurrence of an insertion reaction in the photolysis of **1** with benzene or toluene [1]; however, after treatment of **1** in pyridine, no insertion products could be detected but, instead, pyridinium ylide and iodobenzene were obtained. Recently, two similar results have been reported by Neiland [2] and Varvoglis and Hadjiarapoglou [3]:

$$PhI^{+}-{}^{-}CZ_2 + C_5H_5N \longrightarrow C_5H_5N^{+}-{}^{-}CZ_2 + PhI$$

($Z = PhCO$ and $PhSO_2$)

Varvoglis and Hadjiarapoglou [3] also obtained the sulphonium ylide, i.e. $Me_2(O)S^{+}-{}^{-}C(SO_2Ph)_2$. In our case, heating or irradiation of **1** in DMSO gave only a 1:1 adduct which could be considered as a donor–acceptor complex [4].

$$PhI^{+}-{}^{-}C(SO_2R_f)_2 \xrightarrow[h\nu \text{ or } \Delta]{\text{DMSO}} \text{DMSO}[PhI^{+}-{}^{-}C(SO_2R_f)_2]$$

Triphenylphosphine reacted easily with **1** to afford the corresponding triphenylphosphonium ylide containing the bis(perfluoroalkanesulphonyl)methide group:

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*Author to whom correspondence should be addressed.

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$$\mathrm{PhI^+{-}^-CX^1X^2} + \mathrm{Y:} \xrightarrow[67\text{–}88\ \%]{h\nu,\ 8\ h} \mathrm{Y^+{-}^-CX^1X^2} + \mathrm{PhI}$$

1(**a**-**c**) **2**(**a'**-**c'**) **3**(**aa'**-**cb'**)

1	X^1	X^2	**2**	Y:
a	CF_3SO_2	CF_3SO_2	**a'**	C_5H_5N
b	$C_4F_9SO_2$	$C_4F_9SO_2$	**b'**	SMe_2
c	$-SO_2(CF_2)_3SO_2-$		**c'**	PPh_3

The results obtained are summarized in Table 1.

All these new compounds are stable and could be stored at room temperature for several weeks without decomposition. Their structures are fully supported by spectral data and microanalyses.

In conclusion, some new ylides containing the bis(perfluroalkanesulphonyl)methylene functionality could be easily obtained by the transylidation reaction of phenyliodonium bis(perfluoroalkanesulphonyl)methides with triphenylphosphine, pyridine and dimethyl sulphide.

Experimental

Melting points were taken on a Thiele tube and are reported uncorrected. IR spectra were measured on a Shimadzu IR-440 spectrometer. NMR spectra were recorded on an EM-360 NMR spectrometer at 60 MHz. Chemical shifts were in ppm from external TMS for ^1H and from external TFA for ^{19}F, positive for upfield shifts. MS spectra were taken on an MS-4021 spectrometer.

The general procedure to prepare ylide **3** was as follows. A mixture of **1** (2.5 mmol) and **2** (50 mmol) in a 25 ml quartz flask equipped with reflux condenser, dry tube and magnetic stirring bar, was irradiated by UV at room

TABLE 1.

Entry[a]	Reactants	Products	M.p. (°C)	Yield[b] (%)
1	**1a**+**2a'**	**3aa'**	116–118	78
2	**1c**+**2a'**	**3ca'**	142–145	81
3	**1a**+**2b'**	**3ab'**	148	88
4	**1b**+**2b'**	**3bb'**	182	85
5	**1c**+**2b'**	**3cb'**	198	85
6[c]	**1a**+**2c'**	**3ac'**	247–249	67

[a] All reactions were conducted by irradiation via a 400 W low-pressure Hg lamp at room temperature in a quartz flask.

[b] Isolated yield based on reactant **1**.

[c] In this reaction, CH_2Cl_2 was used as a solvent.

temperature for 8 h. After removing the excess **2** or solvent, the residue was left standing overnight. The precipitate was filtered off, and the crude product was recrystallized from CH_3CN and $(CH_3)_2CO$ (1:1) to afford pure **3**.

Pyridinium bis(trifluoromethanesulphonyl)methide, $C_5H_5N^+-{}^-C(SO_2-CF_3)_2$ (**3aa**′): Analysis: Found: C, 27.20; H, 1.54; N, 4.14; F, 31.50%. Required for $C_8H_5F_6NO_4S_2$: C, 26.89; H, 1.40; N, 3.92; F, 31.93%. IR (KBr) (cm^{-1}): 3010 (vw); 1591 (w); 1440 (m); 1360 (s); 1328 (m); 1250 (m); 1200 (m); 1138 (vs); 987 (s); 918 (s); 879 (m); 738 (m); 698 (s); 600 (s); 550 (s). ^{1}H NMR $(CD_3)_2CO$ δ: 7.66–7.90 (m, 3H); 8.13–8.40 (m, 2H) ppm. ^{19}F NMR δ: 3.80 (s, $2\times CF_3$) ppm.

Dimethyl sulphonium bis(trifluoromethanesulphonyl)methide, $Me_2S^+-{}^-C(SO_2CF_3)_2$ (**3ab**′): Analysis: Found: C, 17.64; H, 1.54; F, 34.03%. Required for $C_5H_6F_6O_4S_3$: C, 17.64; H, 1.76; F, 33.53%. ^{1}H NMR $(CD_3)_2CO$ δ: 3.36 (s, $2CH_3$) ppm. ^{19}F NMR δ: 3.7 (s, $2\times CF_3$) ppm. IR (KBr) (cm^{-1}): 3000 (m); 2900 (w); 1422 (w); 1362 (vs); 1343 (s); 1320 (m); 1200 (vs); 1180 (vs); 1124 (s); 1105 (m); 1060 (m); 1020 (s); 983 (s); 950 (s); 680 (m); 648 (s); 602 (vs); 562 (m); 501 (m). MS *m/z* (% rel. abundance): 341 (M^+H, 31.72); 340 (M^+, 5.64); 331 (M^+-F, 1.57); 272 (M^+H-CF_3, 77.74); 255 (M^+-CF_3-O, 13.61); 239 (M^+-CF_3S, 7.27); 191 ($Me_2S{=}C^+SOCF_3$, 5.15); 163 ($M_2S^+CF_3$, 11.03); 145 ($CF_3SC^+{=}S$, 15.54); 117 (CF_3SO^+, 7.65); 69 ($CF_3{}^+$, 31.80); 63 ($^+SOCH_3$, 100); 62 (Me_2S^+, 29.19); 59 ($MeSC^+$, 45.23); 47 (MeS^+, 17.39).

Dimethyl sulphonium bis(perfluorobutanesulphonyl)methide, $Me_2S^+-{}^-C(SO_2C_4F_9)_2$ (**3bb**′): Analysis: Found: C, 20.61; H, 0.76; F, 53.21%. Required for $C_{11}H_6F_{18}O_4S_3$: C, 20.62; H, 0.93; F, 53.43%. ^{1}H NMR δ: 3.30 (s, $2CH_3$) ppm. ^{19}F NMR δ: 6.0 (s, $2CF_3$); 34.8 (m, $2CF_2$); 45.5 (m, $2CF_3$); 50.6 (m, $2\times SCF_3$) ppm. IR (KBr) (cm^{-1}): 3000 (w); 2980 (w); 1422 (w); 1380 (vs); 1350 (m); 1282 (m); 1261 (m); 1230 (s); 1200 (vs); 1150 (s); 1130 (s); 1110 (m); 1038 (s); 982 (m); 951 (m); 800 (m); 738 (m); 640 (m); 612 (m); 582 (s); 530 (m); 502 (m). MS (% rel. abundance): 641 (M^+H, 1.45); 640 (M^+, 1.85); 557 (M^+-SO_2-F, 1.55); 421 ($M^+-C_4F_9$, 100); 405 ($M^+-C_4F_9-O$, 18.72); 341 ($M^+-C_4F_9SO_2-O$, 1.07); 219 ($C_4F_9{}^+$, 10.36); 122 ($SOC^+{=}SMe_2$, 3.44); 69 ($CF_3{}^+$, 15.53); 62 (Me_2S^+, 99.90); 47 MeS^+, 5.87).

Dimethyl sulphonium 1,1,3,3-tetraoxo-1,3-dithioperfluorocyclohexyl ylide, $Me_2S^+-{}^-\overline{CSO_2(CF_2)_3S}O_2$ (**3cb**′): Analysis: Found: C, 20.70; H, 1.21; F, 32.45%. Required for $C_6H_6F_6O_4S_3$: C, 20.46; H, 1.70; F, 32.28%. ^{1}H NMR δ: 3.35 (s, $2CH_3$) ppm. ^{19}F NMR δ: 42.5 (m, $2CF_2$); 50.0 (m, CF_2) ppm. IR (KBr) (cm^{-1}): 3000 (w); 2982 (w); 1428 (m); 1378 (vs); 1358 (m); 1340 (m); 1280 (m); 1260 (m); 1218 (s); 1160 (vs); 1060 (m); 1023 (s); 978 (s); 957 (s); 900 (m); 705 (s); 653 (m); 620 (m); 565 (m); 550 (s).

Pyridinium 1,1,3,3-tetraoxo-1,3-dithioperfluorocyclohexyl ylide, $C_5H_5N^+-{}^-\overline{CSO_2(CF_2)_3S}O_2$ (**3ca**′): Analysis: Found: C, 29.70; H, 1.32; F, 31.50%. Required for $C_9H_5F_6NO_4S_2$: C, 29.27; H, 1.36; F, 30.90%. ^{1}H NMR δ: 7.63–7.90 (m, 3H); 8.10–8.33 (m, 2H) ppm. ^{19}F NMR δ: 42.3 (m, $2SCF_2$); 49.8 (m, CF_2) ppm. IR (KBr) (cm^{-1}): 3002 (vw); 1592(w); 1442 (m); 1358 (s); 1330 (m); 1271 (m); 1242 (m); 1199 (m); 1140 (vs); 980 (s); 920 (s); 898 (m); 740 (m); 700 (m); 679 (s); 642 (m); 600 (s); 560 (s); 538 (s). MS *m/z* (% rel. abundance): 370 (M^+H, 1.71); 369 (M^+, 5.94); 353 (M^+-O, 0.38); 337 (M^+-2O, 0.51); 253 ($M^+-C_2F_4-O$, 4.75); 240 ($M^+-CF_2-C_5H_5N$, 1.08); 205 ($M^+-C_2F_4-SO_2$, 45.76); 204 ($M^+H-C_3F_6-O$, 51.99); 156 ($M^+H-C_3F_6-SO_2$, 23.97); 100 ($C_2F_4^+$, 18.09); 80 (SO_3^+ or $C_5H_5NH^+$, 78.96; 79 ($C_5H_5N^+$, 57.13); 64 (SO_2^+, 15.41); 52 ($C_3H_2N^+$, 100).

Triphenylphosphonium bis(trifluoromethylsulphonyl)methide, $Ph_3P^+-C(SO_2CF_3)_2$ (**3ac**): Analysis: Found: C, 46.81; H, 2.93%. Required for $C_{21}H_{15}F_6PO_4S_2$: C, 46.67; H, 2.78%. ^1H NMR δ: 7.63–8.10 (m, $3C_6H_5$) ppm. ^{19}F NMR δ: (s, $2CF_3$) ppm. IR (KBr) (cm^{-1}): 3040 (m); 1590 (m); 1481 (m); 1440 (m); 1340 (s); 1220 (m); 1180 (m); 1162 (s); 1118 (s); 1098 (s); 1000 (m); 962 (s); 742 (m); 721 (s); 698 (s); 600 (s); 540 (s); 500 (m). MS *m/z* (% rel. abundance): 541 (M^+H, 1.95); 477 (M^+-SO_2, 2.96); 463 ($M^+-C_6H_5$, 3.33); 355 ($M^+-P(C_6H_5)_2$, 26.34); 279 (M^+H-PPh_3, 100); 262 ($^+PPh_3$, 14.10); 199 ($CF_3SO_2{}^+POF$, 21.16); 185 (Ph_2P^+, 14.10); 183 ($CF_3SO_2{}^+PF$, 33.11); 133 ($CF_3SO_2{}^+$, 7.01); 108 (PhP^+, 7.99); 77 ($C_6H_5{}^+$, 35.15).

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