Structural Dynamics of the First Alkylidenesulfur Difluoride Oxide, OFC − CH = SF₂ = O

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The pentafluorosulfanylacetic acid, $HOOC-CH_2-SF_5$, is dehydrated to the ketene $O=C=CH-SF_5$. Besides other more typical reactions this ketene isomerizes to the alkylidenesulfur tetrafluoride $OFC-CH=SF_4$ which is hydrolyzed to the title compound $OFC-CH=SF_2=O$. This first alkylidenesulfur difluoride oxide exists in three, possibly four different isomeric structures at low temperatures, as was determined by NMR techniques. This is a result of hindered rotation of the $C=S$ and $C-C$ bonds.

Strukturelle Dynamik des ersten Alkylidenschwefeldifluoridoxids

Pentafluorsulfanylessigsäure, $HOOC-CH_2-SF_5$, läßt sich zum Keten $O=C=CH-SF_5$ entwässern. Dieses zeigt typische Reaktionen, aber es isomerisiert auch zum Alkylidenschwefeltetrafluorid, $OFC-CH=SF_4$, welches vorsichtig zur Titelverbindung $OFC-CH=SF_2=O$ hydrolysiert werden kann. Dieses erste Alkylidenschwefeldifluoridoxid hat bei tiefen Temperaturen drei, vielleicht sogar vier verschiedene isomere Strukturen, wie mit der NMR-Spektroskopie gezeigt wird. Gehinderte Rotation der $C=S$- und $C-C$-Bindung wird für die Isomerie verantwortlich gemacht.

Sulfonium ylides, $R_2C^{\ominus} - {}^{\oplus}SR'_2$, are known since 1930[1], and there exists vast literature on their structure and reactivity[2,3,4]. The simplest member of the oxosulfonium ylides, $H_2C^{\ominus} - {}^{\oplus}S(O)(CH_3)_2$, was prepared in 1965 and was the starting point of yet another broad application in organic synthesis[5]. These well-established organic sulfonium ylides had as of then no S-fluorinated counterparts, $R_2C=SF_2$ and $R_2C=SF_2O$. But in recent years we succeeded in preparing S-fluorinated sulfonium ylides of the type $R_2C=SF_4$[6] and one example of $RC\equiv SF_3$[7], which were named alkylidenesulfur tetrafluorides and alkylidynesulfur trifluorides.

$$O=C=CH-SF_5 \quad \xrightarrow{80\,°C} \quad \begin{matrix} H \\ | \\ O=C-C-SF_5 \\ |\ \ | \\ O-C=CH-SF_5 \end{matrix} \qquad (1)$$

$$\xrightarrow{25\,°C,\ KF} \quad \text{Polymer} \qquad (2)$$

$$\xrightarrow{HX} \quad OXC-CH_2-SF_5 \qquad (3)$$

$$\xrightarrow[\text{glass}]{280\,°C} \quad OFC-CH=SF_4 \qquad (4)$$

The alkylidenesulfur tetrafluorides, $R_2C=SF_4$, are stereochemically rigid in spite of the pentacoordination of the sulfur atom[8,9]. This has been interpreted to be a result of the strong $C=S$ double bond, and this in turn is a function of the presence of fluorine atoms bonded to the sulfur atom. The alkylidynesulfur trifluoride, $F_3C-C\equiv SF_3$, exhibits non-linear geometry with very soft bending-force constants[10−12]. In this paper we present the preparation of the first alkylidenesulfur difluoride oxide, $OFC-CH=SF_2O$. It exhibits a particular case of nonrigidity, which will have to
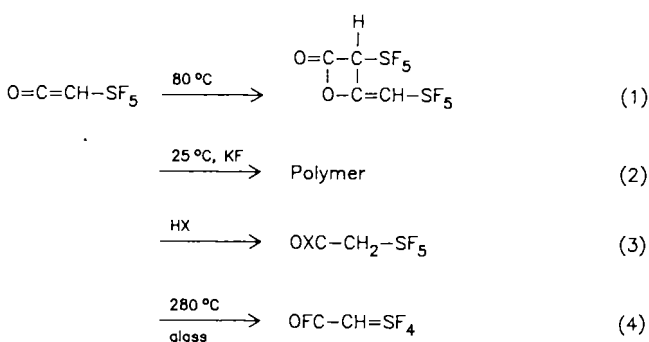
be compared with the dynamic behavior of its non-fluorinated counterparts. It may be noted here that among the vast number of phosphorus ylides only one has a fluorine atom bonded to the phosphorus atom[13]: $H_2C=PF-[N(CH_3)_2]_2$.

As has been described recently in a short communication[14], the novel ketene $O=C=CH-SF_5$ undergoes some typical ketene reactions such as dimerization (eq. 1), polymerization (eq. 2), and addition across the $C=C$ bond (eq. 3). The [1, 3] fluorine shift at high temperatures (eq. 4) was unexpected, but has been verified by means of conventional physical methods including a low-temperature X-ray crystal-structure analysis of the product $OFC-CH=SF_4$[14]. This reaction is certainly intermolecular, since a glass surface is necessary. There is only one similar reaction known to us. The ketene $(F_3C)_2C=C=O$ rearranges to $F_3C-C-(CFO)=CF_2$ on prolonged heating at $350\,°C$[15].
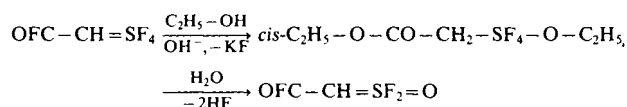
The driving force of the [1,3] fluorine shift (eq. 4) is certainly the formation of a conjugated double-bond system from a cumulated one, in spite of the fact that a $C=S$ bond is formed in place of a $C=C$ bond.

The molecular structure of $OFC-CH=SF_4$ is basically trigonal bipyramidal with two axial and two equatorial fluorine atoms, and the carbon atom also occupies an equatorial position. The $C=S$ bond length is that of a short double bond (1.602 Å) and the carbon substituents are fixed in the axial plane of the molecule[14]. There is no indication of a torsional nonrigidity of the $C=S$ bond at any temperature between $-100\,°C$ and $+100\,°C$. This geometry and the torsional rigidity seem to be general for $R_2C=SF_4$ compounds[8,9,16,17].

Generally, the $>C=SF_4$ compounds show two typical reactions: Cleavage of SF_4 with formation of a carbene, and polar addition across the $C=S$ bond[18].

$$OFC-CH=SF_4 \xrightarrow[OH^-,-KF]{C_2H_5-OH} cis\text{-}C_2H_5-O-CO-CH_2-SF_4-O-C_2H_5,$$

$$\xrightarrow[-2HF]{H_2O} OFC-CH=SF_2=O$$

The addition of ethanol across the $C=S$ bond is a special example of such an addition reaction.

So far we have observed that water totally decomposes alkylidenesulfur tetrafluorides. Here, however, we succeeded in obtaining fluorocarbonylmethylidenesulfur difluoride oxide as the first hydrolysis product and the first material containing the $\rangle C=SF_2=O$ group.

The overall structure of this novel material can be derived from the simple ^{19}F- and ^{1}H-NMR spectra obtained at slightly elevated temperatures, see Fig. 1 and Table. The vibrational spectra (IR and Raman) show the typical vibrations v_{CH} (3131 cm^{-1}), v_{CO} (1822), v_{SO} (1407), and v_{SF} (947, 841). One of the three bands at 1328, 1186, or 1099 will be v_{CS}.
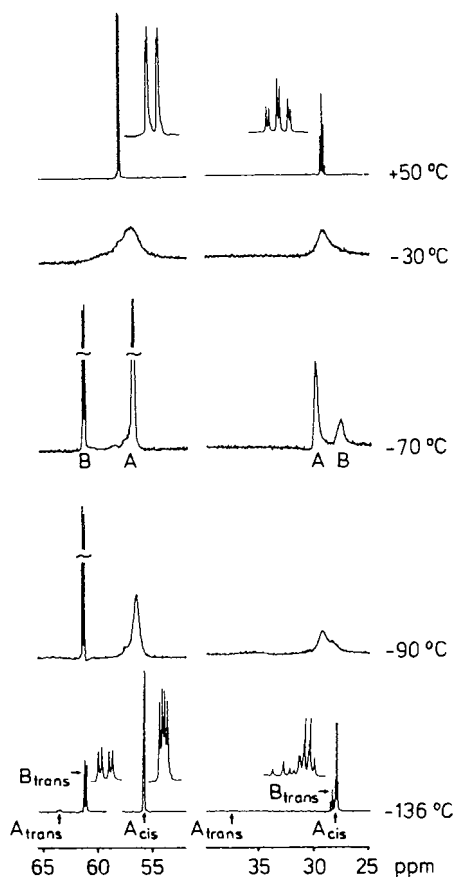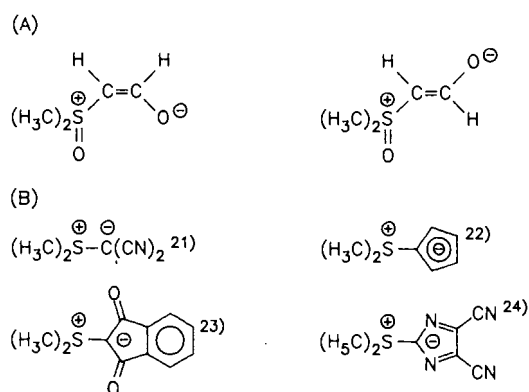

Fig. 1. Temperature-dependent ^{19}F-NMR spectra of OFC$-$CH$=$SF$_2$$=$O; the inserts are expanded 1:10

The structure of OFC$-$CH$=$SF$_2$$=$O, however, is not as simple as the formula suggests. On cooling to $-70\,^\circ$C two isomers are detectable, on cooling to $-136\,^\circ$C three isomers are observed in the ^{19}F-NMR spectra, see Fig. 1 and Table. Band overlap and line broadening at low temperature in the ^{1}H-NMR spectra allow separation of the two multiplets only at $-70\,^\circ$C.

The existence of OFC$-$CH$=$SF$_2$O in three different isomers poses a severe structural problem.

In sulfonium ylides[19] such as $(H_3C)_2S^\oplus - {}^\ominus CH - C(O)OCH_3 \leftrightarrow (H_3C)_2S^\oplus - CH = C(O^\ominus)OCH_3$ two isomers have been observed at low temperatures. These are considered cis and trans isomers of the (partial) $C=C$ bond adjacent to the sulfur atom. OHC$-{}^\ominus$CH$-$S$^\oplus$(CH$_3$)$_2$$=$O[20] is certainly the closest non-fluorinated relative of OFC$-$CH$=$SF$_2$$=$O that is known. Again structures with $C=C$ bonds have been assigned to its two isomers [Scheme, (A)]. No isomerism due to the "$C=S$ bond" is known in sulfur ylides.

Scheme

(A)

(B)

Crystal structures exist of a few sulfonium ylides [Scheme, (B)]. The ylidic S$-$C bond lengths are 1.719, 1.712, 1.707, and 1.745 Å, respectively, while in H$_2$C$=$SF$_4$ and OFC$-$CH$=$SF$_4$ these bond lengths are 1.554[8,9] and 1.602 Å[14]. These differences certainly justify the formulation of zwitterionic single bonds in the nonfluorinated species. But it should be noted that in these four ylides the (almost perfect) plane around the ylidic carbon atom is almost the same as the mirror plane of the $(H_3C)_2S^\oplus$ part of the molecules (see Fig. 2, also Fig. 27 in ref.[2]). If this staggered configuration is not a result of crystal forces in these four very different molecules, it could be that the S$-$C bond prefers this specific orientation, thus indicating a small double-bond character here, too.

Unfortunately, detailed structural information on oxosulfonium ylides is not available.

As already indicated by the short $C=S$ distances in H$_2$C$=$SF$_4$ and OFC$-$CH$=$SF$_4$, we also expect a much stronger $C=S$ bond in OFC$-$CH$=$SF$_2$$=$O than in organic sulfonium ylides or oxosulfonium ylides as a result of the electronegativity of the fluorine and oxygen atoms. But precise structural data are not yet available. Since we observe
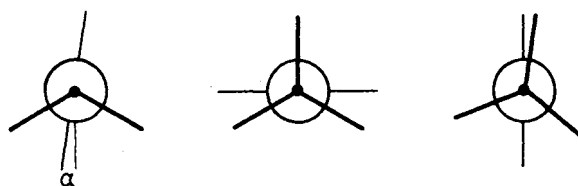
Fig. 2. Torsion angle about C$-$S and C$-$P ylide bonds. Left: View along the C$-$S bond in the four known sulfur ylide crystal structures; the deviation α from the perfectly staggered orientation is 7.7°[21], 3.1°[22], 9.8°[23], and 4.7°[24]. Middle: View along the C$-$P bond in $(H_5C_6)_3P^\oplus - {}^\ominus CH_2$.[29] Right: View along the C$-$P bond in $(H_5C_6)_3P^\oplus - {}^\ominus cp$[30] and $(H_5C_6)_3P^\oplus - {}^\ominus C[CF_2]_3$[31]

two coalescence points and up to three isomers on cooling to $-136\,^\circ$C and since all isomers have equivalent fluorine atoms bonded to sulfur, we have to conclude that the rotations of the C=S bond *and* of the C–C bond are frozen out. We believe the C=S bond rotation to be frozen out first on cooling, resulting in the isomers **A** and **B** (Fig. 1 and 3). The NMR assignments of the two isomers **A** and **B** is tentative. It is based on trends of chemical shifts and coupling constants, and on some intuition. Since there exist no such values for comparison, we are aware that the assignments could be interchanged.
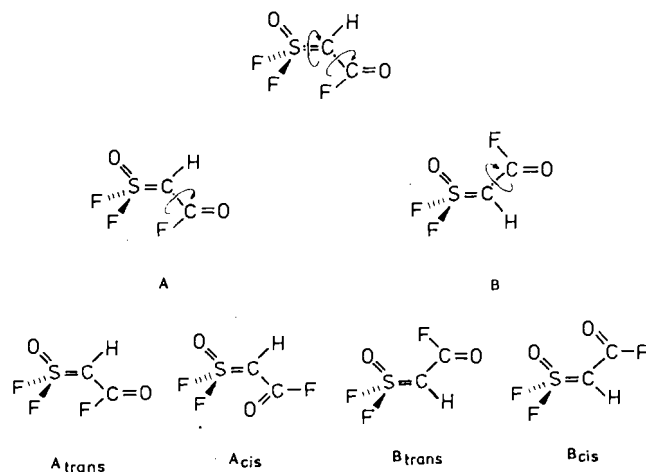
Fig. 3. Subsequent freezing of the C=S and C–C bond in OFC–CH=SF$_2$=O. Top: Free rotation above room temperature. Middle: Free rotation of the OFC group at $-70\,^\circ$C. Bottom: The four possible isomers at $-136\,^\circ$C

The difference in free energy of these two isomers is calculated to be 1.4 ($\pm$0.4) kJ mol^{-1} from their relative abundance of approximately 2:1. The free energy of activation for the C=S rotation is then calculated according to ref.[25] and is found to be 49.0 ($\pm$2.5) kJ mol^{-1} for **A** and 47.6 ($\pm$2.1) kJ mol^{-1} for **B**. If **A** and **B** were regarded as ylides with polar C–S bonds, this barrier would be considered high. However, the rotational barrier of H$_2$C=SF$_4$ is estimated to be at least 118 kJ mol^{-1}. This number is derived from the fact that even at $+100\,^\circ$C no change in the A$_2$BB'XX' pattern of the NMR spectrum can be seen (rotation about the C=S bond would lead to an A$_4$X$_2$ pattern). Also, the bond energy of the double bond in CH$_2$=SF$_4$ is 372 kJ mol^{-1} (by mass spectrometric measurements[26]), and 377 kJ mol^{-1} in F$_3$C–CH=SF$_4$ (by thermochemical calculation from the equilibrium F$_2$C=CH–SF$_4 \rightleftharpoons$ F$_3$C–CH=SF$_4$[27]). This is about 120 kJ mol^{-1} more than a C–S single bond, in surprisingly good agreement with the 118 kJ mol^{-1} value mentioned above.

Therefore, we need an explanation as to why the rotational barrier of the C–S bond in OFC–CH=SF$_2$=O is so low. Since it is not obvious why the $>$C=SF$_2$=O molecular fragment should have so much more ylidic (zwitterionic) bond character than $>$C=SF$_4$, the difference may be a result of different geometries. Let us first consider the rotational bar-

rier in H$_2$C=CH$_2$: Except for the good π overlap the barrier is so high (268 kJ mol^{-1}) also because only at the torsional angles of 90° and 270° the maximum energy is reached, the minima being at 0° and 180°. CH$_2$=SF$_4$, however, already reaches the next minimum at a torsional angle of 90° of the methylene group, since axial and equatorial fluorine atoms are able to interchange positions like in a Berry mechanism if the molecule is 120 kJ mol^{-1} higher in energy. Four minima and maxima within 360° must result in a lower rotational barrier than two if comparable torsional force constants are assumed.

Because of its lower symmetry the rotation about the C=S bond in OFC–CH=SF$_2$=O certainly has a more complicated energy profile. Two slightly different minima (1.4 kJ mol^{-1} difference) with a coplanar OFC–CH–S–O framework are separated by four configurations with a planar OFC–CH–S–F framework. These may be small minima on the profile lowering the total rotational barrier to the small value of 49 kJ mol^{-1}.

OFC–CH=SF$_2$=O is isoelectronic with the phosphorus ylides, and the same structural discussion could also be adressed to this class of compounds. But here again little is known about the orientation of the plane formed by the substituents of the ylidic carbon versus the trigonal geometry around the phosphorus atom. In the electron diffraction work on (H$_3$C)$_3$P$^\oplus$ – $^\ominus$CH$_2$, the plane of the methylene group was fixed during the calculation[28]. An eclipsed position was found for (H$_5$C$_6$)$_3$P$^\oplus$ – $^\ominus$CH$_2$ in the solid state[29]. (H$_5$C$_6$)$_3$P$^\oplus$ – $^\ominus$cp[30] and (H$_5$C$_6$)$_3$P$^\oplus$ – $^\ominus$C[CF$_2$]$_3$[31], however, have orientations where the ring planes are staggered, see Fig. 1. Altogether the C–P bond rotation of phosphorus ylides has not drawn very much attention. But this may change because there is one very recent report on a torsional barrier of 60.3 kJ mol^{-1} in the compound H$_9$C$_4$[(H$_5$C$_2$)$_2$N]$_2$P=CH–C$_6$H$_5$. Here, two isomers are observed on cooling[32].

OFC–CH=SF$_2$=O is also isoelectronic to OFC–N=SF$_2$=O. The latter does not show this kind of isomerism at all (NMR measurements are reported at temperatures as low as $-90\,^\circ$C). This is possibly a result of the higher polarity of the N=S bond versus the C=S bond, resulting in a lower N=S torsional barrier[33].

The second coalescence in OFC–CH=SF$_2$=O remains to be explained. In the first place it has been the existence of two coalescence temperatures that forced us to assume a rotational barrier around the C=S bond. The second rotation is certainly that of the OFC group, and is comparable to rotational barriers of C–C bonds in the sulfonium ylides previously mentioned.

It is also known that in OFC–CH=CH$_2$ and other substituted acryloyl fluorides the rotation of the OFC group can be frozen out at $-154\,^\circ$C[34]. The *s-trans* conformation of the OFC group is generally more populated, and the free activation energy between *s-cis* and *s-trans* has been found to be between 23 and 30 kJ mol^{-1}.

Interestingly, we see the splitting of **A** into two isomers **A**$_{cis}$ and **A**$_{trans}$ with quite different populations, chemical shifts, and coupling constants. The given assignment in Fig. 3 and the Table is again based on trends in coupling constants and therefore is again not unambigous. The free energy difference for these two isomers is 4.5 $\pm$ 2.0 kJ mol^{-1}, and the free energy of activation between the two is

calculated to 32.7 ± 2.0 from A_{cis} and 37.2 ± kJ mol^{-1} from A_{trans}, respectively.

Table ^{19}F- and ^{1}H-NMR data of the different isomers of OFC−CH=SF$_2$=O; as indicated in the text, the assignment of the sets of NMR signals to the different isomers is tentative

	A	**B**	**A$_{cis}$**	**A$_{trans}$**	**B$_{trans}$**
T[°C]	+50	−70	−70	−136	−136	−136
δ_F	58.3,	56.3,	62.2,	55.4,	63.5,	61.0,
	29.3	30.3	27.3	28.0	37.5	28.5
δ_H	4.8	4.9	4.6	− not resolved −		
$J_{H,F(S)}$ [Hz]	2.1	2.9	3.5	4.1	9.0	5.1
$J_{H,F(C)}$ [Hz]	2.9	7.3	23.2	7.4	5.0	24.5
$J_{F,F}$ [Hz]	12.3	7.3	15.1	7.1	21.0	15.3

Also, **B** seems to undero another coalescence, of which the broadening of the OFC signal in the ^{19}F-NMR spectra is a clear indication. But the crossover of the OFC signal of **A** by the OFC signal of **B** on cooling complicates the analysis. Since the chemical shifts of **B** at −70°C and **B**$_{trans}$ at −136°C change only a little, it can be concluded that the missing isomer **B**$_{cis}$ is either too low in concentration to be observed and/or has signals close to those of **B**$_{trans}$, so that they are obscured.

Experimental

Infrared spectra: Perkin-Elmer Model 885 infrared spectrometer; gases (pressure: 1−10 mbar) or liquids; the window material most commonly used was KCl. − Raman spectra: Cary 82 instrument using an Ar laser for excitation (Spectra Physics). − Mass spectra: Varian MAT 112 S high resolution mass spectrometer using either a solid inlet probe or a controlled gas flow inlet. Only the most important ions are reported. − ^{19}F- and ^{1}H-NMR spectra: JEOL FX 90 Q nuclear magnetic resonance spectrometer, CFCl$_3$ and (H$_3$C)$_4$Si were used as external standards, and chemical shifts follow IUPAC conventions. − Starting Materials: HOOC−CH$_2$−SF$_5$[18,35] and ClOC−CH$_2$−SF$_5$[18,35] were prepared according to literature methods; all other reagents were taken from laboratory stock and were purified (where necessary) before use.

Preparation of O=C=CH−SF$_5$: A glass tube (35 × 5 cm) is fully packed with several alternating layers of P$_4$O$_{10}$ and quartz sand. The upper end is connected to a glass bulb containing 15 g (80.6 mmol) HOOC−CH$_2$−SF$_5$, the lower end to a −196°C trap and subsequently to a vacuum line. The reactor has a temperature gradient of 60−80°C (top) to 140−160°C (bottom). The pentafluorosulfanylacetic acid is pumped through the reactor over a period of 2 d. The product is purified by trap-to-trap vacuum distillation (−20/−100/−196°C). Pure O=C=CH−SF$_5$ is found in the −100°C trap. The yield is 10.6 g (78%) of the colorless liquid, bp 47°C. Interestingly, the yield is much lower if the flow direction within the reactor is from bottom to top. − IR (gas): ṽ = 3135 cm^{-1} (w), 2177 (s), 1325 (w), 878 (vs), 720 (m). − MS (80 eV): m/z (%) = 167.96666 (100) [M$^+$] (calcd. for C$_2$HF$_5$OS 167.96683), 149 (17) [M$^+$ − F], 127 (77) [SF$_3^+$], and smaller fragments. − ^{19}F NMR (AB$_4$X pattern): δ_A = 80.2, δ_B = 88.7 (J_{AB} = 152.7, J_{BX} = 5.7 Hz). − ^{1}H NMR: δ = 5.5.

2,4-Bis(pentafluorosulfanyl)-3-butene-3-olide (Pentafluorosulfanylketene Dimer): O=C=CH−SF$_5$ (6.16 g, 36.8 mmol) is condensed into a 10-ml glass ampule, which is sealed off and kept at 80°C. The dimerization is monitored by ^{19}F-NMR spectroscopy. The product is contaminated with OFC−CH=SF$_4$ and a polymer. Distillation at 55°C/25 mbar affords pure ketene dimer in varying yields as a colorless liquid. − IR (liq.): ṽ = 3108 cm^{-1} (vw), 3000 (vw), 1990 (m), 1895 (m), 1718 (s), 1046 (m), 972 (s), 913 (vs), 850 (vs), 808 (s), 762 (s), 672 (s). − MS (80 eV): m/z (%) = 336 (14) [M$^+$], 297 (5) [C$_4$HF$_8$O$_2$S$_2^+$], 228 (10) [C$_4$H$_2$F$_6$O$_2$S$_2^+$], 208 (9) [C$_4$HF$_5$O$_2$S$^+$], 181 (19) [C$_3$H$_2$F$_5$OS$^+$], 168 (62) [C$_2$HF$_5$OS$^+$], 149 (100) [C$_2$HF$_4$OS$^+$], and smaller fragments. − ^{19}F-NMR (2 overlapping AB$_4$X spectra): δ_{A1} = 70.9, δ_{A2} = 76.3, δ_{B1} = 65.4, δ_{B2} = 69.1 (J_{A1B1} = 151.6, J_{A2B2} = 152.9, J_{B1X1} = 5.4, J_{B2X2} = 7.1 Hz). − ^{1}H-NMR (2 overlapping quint): δ = 5.42, 5.84.

Pentafluorosulfanylketene Polymer: Pentafluorosulfanylketene is condensed into a glass ampule, which contains a few mg of KF. Polymerization occurs at room temp. within a few minutes. Without fluoride catalyst polymerization requires several days at 80°C (see above). The colorless, rubberlike polymer is freed from volatile impurities by prolonged heating in vacuum. − IR (film): 3129 cm^{-1} (w), 3015 (w), 1786 (s), 1742 (sh), 1679 (m), 1345 (m), 1299 (m), 1206 (w), 1160 (5), 1119 (s), 1095 (w), 954 (s), 865 (vs), 824 (sh, 613 (s), 566 (s). − ^{19}F-NMR (DMSO; several overlapping AB$_4$ spectra): δ_A = 79−104, δ_B = 62−84, no C−F signals.

Fluorocarbonylmethylidenesulfur Tetrafluoride, OFC−CH=SF$_4$: 2.0 g (11.9 mmol) O=C=CH−SF$_5$ are slowly pumped in vacuum through a 270−290°C hot quartz tube filled with several millimeter-sized glass splinters. The yields are much lower if quartz splinters are used. The products are trapped at −196°C and subsequently pumped in vacuum through a 30 cm long tube cooled to −70°C. OFC−CH=SF$_4$ crystallizes, while the impurities (O=C=CH−SF$_5$, OFC−CH$_2$−SF$_5$) are condensed into a −196°C trap. After the separation the product is pumped into a separate trap. 1.0 g (50%) of OFC−CH=SF$_4$ is obtained as a colorless liquid, mp −29°C. − IR (gas): ṽ = 3154 cm^{-1} (vw), 1859 (vs), 1818 (m), 1372 (s), 1254 (w), 1155 (s), 1116 (m), 1089 (m), 932 (s), 860 (vs), 798 (s), 719 (w), 678 (w), 614 (w), 582 (w). − MS (80 eV): m/z (%) = 168 (56) [M$^+$], 149 (14) [M$^+$ − F], 89 (100) [SF$_3^+$, and smaller fragments. − ^{19}F-NMR (A$_2$BCDX pattern by computer simulation and decoupling experiments): δ_A = 60.89, δ_B = 59.09, δ_C = 56.97, δ_D = 42.88 (J_{AB} = 165.29, J_{AC} = 165.86, J_{AD} = −4.20, J_{AX} = 8.18, J_{BC} = 11.79, J_{BD} = −34.18, J_{BX} = −11.15, J_{CD} = −14.06, J_{CX} = −38.79, J_{DX} = −1.27 Hz). − ^{1}H-NMR: δ = 4.4. The numerical values above are those of a CD$_3$CN solution; solutions in CDCl$_3$ or sulfolane exhibit slightly different chemical shifts.

cis-Ethoxy(ethoxycarbonylmethyl)sulfur Tetrafluoride, H$_5$C$_2$O−SF$_4$−CH$_2$−COOC$_2$H$_5$: OFC−CH=SF$_4$ (0.24 g, 1.43 mmol) is dissolved in 7.5 ml of ethanol (p.a., free of H$_2$O). A solution of 7.5 ml of 0.2 M KOH in ethanol is added dropwise. KF is precipitated immediately. Slow vacuum distillation through cold traps (−40°C and −196°C) affords pure cis-H$_5$C$_2$O−SF$_4$−CH$_2$−COOC$_2$H$_5$ in the −40°C trap as a colorless liquid. The reaction is essentially quantitative. − MS (80 eV): m/z (%) = 195 (58) [C$_4$H$_7$F$_4$O$_2$S$^+$], 172 (21) [C$_4$H$_6$F$_2$O$_3$S$^+$], 167 (15) [C$_3$H$_7$F$_4$OS$^+$], 147 (62) [C$_3$H$_6$F$_3$OS$^+$], 127 (62) [C$_3$H$_6$F$_3$OS$^+$], 127 (100) [C$_3$H$_5$F$_2$OS$^+$], and smaller fragments. − ^{19}F-NMR (A$_2$BCX$_2$ pattern): δ_A = 77.5, δ_B = 77.6, δ_C = 94.2 (J_{AC} = J_{BC} = 120.7, J_{CX} = 12 Hz). − ^{1}H-NMR: δ(CH$_3$) = 1.74, 1.75, δ(CH$_2$) = 4.60, 4.60 4.62.

Fluorocarbonylmethylidenesulfur Difluoride Oxide, OFC−CH=SF$_2$=O: OFC−CH=SF$_4$ (0.29 g, 1.73 mmol) is dissolved in

5 ml of freshly distilled and dried sulfolane. Sulfolane (0.62 ml) containing 5 mol% of H$_2$O (1.73 mmol) is added dropwise at room temp. over a period of 2.5 h. The reaction is monitored by ^{19}F-NMR spectroscopy in order to detect the precise end point of the hydrolysis. Too slow addition of water or excess of it results in the formation of larger quantities of OFC−CH$_2$−SF$_5$, HOOC−CH$_2$−SF$_5$, H$_3$C−SFO$_2$, and HOOC−CH$_2$−SFO$_2$. When the ^{19}F-NMR resonances due to the starting material have completely disappeared, the reaction mixture is pumped in vacuum through cold traps (−30/−78/−196°C). The contents of the −78°C trap are redistilled in static vacuum. Such purified product contains traces of OFC−CH$_2$−SF$_5$ and OFC−CH=SF$_4$ as the only impurities. It is a colorless liquid, mp ca. −35°C (mixture of isomers), 39% yield. − IR (gas): $\tilde{\nu}$ = 3131 cm^{-1} (w), 1845 (sh), 1822 (vs), 1407 (vs), 1328 (s), 1186 (m), 1099 (m), 1058 (s), 1027 (m), 947 (s), 841 (s), 795 (m). − Raman (liquid): 3111 cm^{-1} (m), 1800 (s), 1327 (m), 1297 (w), 1215 (w), 1111 (w), 1057 (m), 949 (w), 919 (w), 739 (w), 735 (w), 683 (s), 573 (w), 564 (w), 463 (m), 395 (m), 364 (m), 317 (m), 149 (w). − MS (80 eV): m/z (%) = 145.96549 (100) [M$^+$] (calcd. for C$_2$HF$_3$O$_2$S 145.96494), 126.96655 (31) [M$^+$ − F] (calcd. for C$_2$HF$_2$O$_2$S 126.96654), 67 (15) [SOF$^+$], 60 (14) [C$_2$HFO$^+$], and smaller fragments. − NMR data see the Table and Fig. 2.

CAS Registry Numbers

O=C=CHSF$_5$: 109907-07-5 / HOOCCH$_2$SF$_5$: 762-59-4 / OFC-CH=SF$_4$: 109907-09-7 / H$_5$C$_2$OSF$_4$CH$_2$COOC$_2$H$_5$: 115983-28-3 / OFCCH=SF$_2$=O: 115983-29-4 / OFCCH$_2$SF$_5$: 115983-30-7 / H$_3$CSFO$_2$: 558-25-8 / HOOCCH$_2$SFO$_2$: 41505-90-2 / pentafluorosulfanyl ketene dimer: 109907-08-6

[1] C. K. Ingold, J. A. Jessop, *J. Chem. Soc.* **1930**, 713.

[2] E. F. Perozzi, I. C. Paul in *The Chemistry of the Sulfonium Group*, (C. J. M. Sterling, Ed.), p. 15, John Wiley & Sons Ltd., Chichester, New York, Brisbane, Toronto 1981.

[3] B. M. Trost, L. S. Melvin, jr., *Organic Chemistry*, Vol. 31, Sulfur Ylides, Academic Press, New York 1975.

[4] The zwitterionic formulation S$^{\oplus}$−$^{\ominus}$C of ylides is more often used than the double bond formula (S=C). Throughout this paper we use the formula that has been previously used for the given compound. Thus it happens that the double bond formula is used only for ylides with considerable double bond character.

[5] E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **87** (1968) 1353.

[6] G. Kleemann, K. Seppelt, *Angew. Chem.* **90** (1975) 547; *Angew. Chem., Int. Ed. Engl.* **17** (1978) 516.

[7] B. Pötter, K. Seppelt, *Angew. Chem.* **96** (1984) 138; *Angew. Chem., Int. Ed. Engl.* **23** (1984) 150.

[8] A. Simon, E. M. Peters, D. Lentz, K. Seppelt, *Z. Anorg. Allg. Chem.* **468** (1980) 7.

[9] H. Bock, J. E. Boggs, G. Kleemann, D. Lentz, H. Oberhammer, E. M. Peters, K. Seppelt, A. Simon, B. Solouki, *Angew. Chem.* **91** (1979) 1008; *Angew. Chem. Int. Ed. Engl.* **18** (1979) 944.

[10] B. Pötter, K. Seppelt, A. Simon, E. M. Peters, B. Hettich, *J. Am. Chem. Soc.* **107** (1985) 980.

[11] D. Christen, H. G. Mack, C. J. Marsden, H. Oberhammer, G. Schatte, K. Seppelt, H. Willner, *J. Am. Chem. Soc.* **109** (1987) 4009.

[12] D. A. Dixon, B. E. Smart, *J. Am. Chem. Soc.* **108** (1986) 2688.

[13] J. Svara, E. Fluck, *Phosphorus Sulfur* **25** (1985) 129.

[14] T. Krügerke, J. Buschmann, G. Kleemann, P. Luger, K. Seppelt, *Angew. Chem.* **99** (1987) 808; *Angew. Chem. Int. Ed. Engl.* **26** (1987) 799.

[15] D. C. England, C. G. Krespan, *J. Am. Chem. Soc.* **88** (1966) 5582.

[16] B. Pötter, K. Seppelt, *Inorg. Chem.* **21** (1982) 3147.

[17] B. Pötter, G. Kleemann, K. Seppelt, *Chem. Ber.* **117** (1984) 3255.

[18] G. Kleemann, K. Seppelt, *Chem. Ber.* **116** (1983) 645.

[19] J. Casanova, jr., D. A. Rutolo, jr., *J. Chem. Soc., Chem. Commun.* **1967**, 1224.

[20] K. Kondo, D. Tunemoto, *J. Chem. Soc. Chem. Commun.* **1970**, 1361.

[21] A. T. Christensen, W. G. Witmore, *Acta Crystallogr., Part B*, **25** (1969) 73.

[22] V. G. Adrianov, Y. T. Struchkov, *Izv. Akad. Nauk SSSR* **26** (1977) 687; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **26** (1977) 624.

[23] A. T. Christensen, E. Thom, *Acta Crystallogr., Sect. B*, **27** (1971) 581.

[24] J. L. Atwood, H. T. Mayfield, *Cryst. Struct. Commun.* **7** (1978) 739.

[25] H. Shanan-Atidi, K. H. Bar-Eli, *J. Phys. Chem.* **74** (1970) 961.

[26] U. Thimopoulos, H. Oertel, H. Baumgärtel, unpublished results.

[27] T. Grelbig, B. Pötter, K. Seppelt, *Chem. Ber.* **120** (1987) 815.

[28] E. A. V. Ebsworth, T. E. Fraser, D. W. H. Rankin, *Chem. Ber.* **110** (1977) 3494.

[29] J. C. J. Bart, *Angew. Chem.* **80** (1968) 697; *Angew. Chem., Int. Ed. Engl.* **7** (1968) 730.

[30] H. L. Ammon, G. L. Wheeler, P. H. Watts, jr., *J. Am. Chem. Soc.* **95** (1973) 6158.

[31] M. A. Howells, R. D. Howells, N. C. Howells, N. C. Baenziger, D. J. Burton, *J. Am. Chem. Soc.* **95** (1973) 5366.

[32] B. Neumüller, E. Fluck, *Phosphorus Sulfur*, **29** (1986) 23.

[33] J. K. Ruff, *Inorg. Chem.* **5** (1966) 1787.

[34] F. S. Lin, K. L. Servis, *J. Am. Chem. Soc.* **94** (1972) 5794.

[35] D. D. Coffman, C. W. Tullock, *U. S. Pat.* 3102903 (Sept. 3, 1963).

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