Notes

Synthesis and Structure of (Difluoromethyl)triphenylphosphonium Fluorosulfite. Evidence for Formation of Difluorosulfene as an Intermediate

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Introduction

In previous studies on the formation and reactions of difluorocarbene, we have reported that α-(fluorosulfonyl)-difluoroacetic acid and its derivatives FO_2SCF_2Y (Y = CO_2H, CO_2R, H) are good precursors.[1−3] Under various reaction conditions these compounds decomposed readily to give the difluorocarbene intermediate, for example:

$$FO_2SCF_2CO_2R \xrightarrow{Nu^-} RNu + CO_2 + SO_2 + :CF_2 + F^-$$

$$FO_2SCF_2H \xrightarrow{B^-} HB + :CF_2 + SO_2 + F^-$$

It was of interest to us to determine whether difluorosulfene is initially formed during these processes, i.e.:

$$FO_2SCF_2^- \xrightarrow{-F^-} [CF_2{=}SO_2] \rightarrow :CF_2 + SO_2$$

It is well know that isolation of a sulfene in the free form is very difficult owing to the exceptional reactivity of the C=S double bond.[4] Success has been achieved only by demonstrating indirectly the existence of such a species through capture by addition reactions.[5,6]

Recently, Sundermeyer has reported the isolation of an amine-stabilized difluorosulfene:[7]

$$\overline{CF_2SO_2CF_2SO_2} \xrightarrow[-70\ ^\circ C]{Et_3N/THF} 2Et_3N^+CF_2SO_2^- \xrightarrow{H_2O} [Et_3NCF_2H]HSO_3^-$$

Here we wish to report a new example demonstrating the formation of difluorosulfene as an unstable intermediate.

Results and Discussion

Treatment of α-(fluorosulfonyl)difluoromethylacetic acid with triphenylphosphine in acetonitrile at room temperature afforded (difluoromethyl)triphenylphosphonium fluorosulfite, $Ph_3P^+HCF_2$ FSO_2^- (**3**). The gas evolved during the reaction process was determined to be CO_2 by GC−MS.

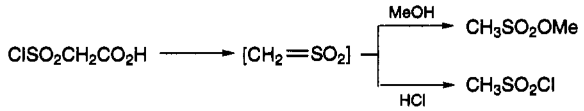
$$\underset{\mathbf{1}}{FO_2SCF_2CO_2H} + \underset{\mathbf{2}}{Ph_3P} \xrightarrow[\text{room temp, 3 h}]{CH_3CN} \underset{\mathbf{3}}{Ph_3PHCF_2^+FSO_2^-} + CO_2$$

The formation of **3** may be proposed to occur via difluorosulfene as an intermediate, that was captured by Ph_3P to give **3** by the sequence of reactions depicted in Scheme 1.

Scheme 1

$$\mathbf{1} + \mathbf{2} \xrightarrow[-CO_2]{CH_3CN} Ph_3PH^+FSO_2CF_2^- \xrightarrow[-Ph_3P^+HF^-]{} [CF_2{=}SO_2] \xrightarrow{Ph_3P} Ph_3P^+CF_2SO_2^- \xrightarrow[-Ph_3P]{Ph_3P^+HF^-} \mathbf{3}$$

This is similar to the thermolysis of $ClSO_2CH_2CO_2H$ to yield sulfene, $CH_2{=}SO_2$, as an intermediate as reported by King:[8]



Another possible reaction path is the nucleophilic attack by Ph_3P at the carbon atom of HCF_2SO_2F, as shown in Scheme 2.

Scheme 2

$$\mathbf{1} \xrightarrow{Ph_3P} FO_2SCF_2CO_2^-Ph_3PH^+ \xrightarrow{-CO_2,\ Ph_3P} FO_2SCF_2H \xrightarrow{Ph_3P} \mathbf{3}$$

To test this possibility, HCF_2SO_2F was prepared independently and treated with Ph_3P in CH_3CN. However, after the mixture had been stirred for 4 h at room temperature and then at 40 °C for another 2 h, no evidence of reaction could be found. According to this result, this sequence of reactions to give **3** must be ruled out.

Compound **3** is a white solid having a high melting point (239−242 °C). It does not dissolve in CH_2Cl_2, and its solubility

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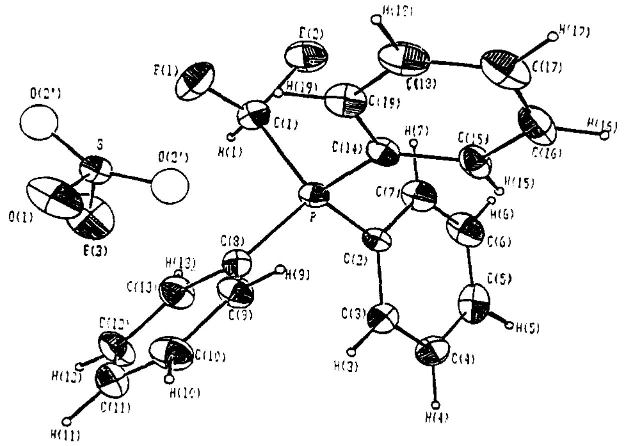

Figure 1. The molecular structure of **3**. Selected bond lengths (Å) and bond angles (deg): P—C1 = 1.853(8), P—C2 = 1.787(7), P—C3 = 1.757(7), S—F3 = 1.516(6), S—O1 = 1.436, S—O2 = 1.41(1); C1—P—C2 = 107.5(3), C1—P—C3 = 107.4(3), C1—P—C14 = 108.0(3), C2—P—C8 = 111.5(3), C2—P—C14 = 110.7(3), F3—S—O1 = 110.5(5).

in CH_3CN and $(CH_3)_2CO$ is low. Recrystallization from a mixture of tetrahydrofuran and CH_3CN gave crystalline material. Its X-ray diffraction analysis confirms the molecular structure (see Figure 1).

Thus it was demonstrated that, by the reaction of $FO_2SCF_2CO_2H$ with Ph_3P, difluorosulfene was probably involved as a highly reactive intermediate that was easily captured by Ph_3P to give eventually **3**. The possibility that **3** can be converted to the corresponding ylide and utilized in Witting reactions is being investigated.[9,10]

Experimental Section

^1H NMR and ^{19}F NMR spectra were recorded on a Varian 360L instrument using Me_4Si and CF_3COOH as internal and external standards respectively. $\delta_{TFA} = \delta_{F11} + 76.8$ ppm. (positive upfield). IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution MS spectra were obtained on a Finnigan GC-MS 4021 instrument. Elemental analyses were performed by the Analysis Department of the Shanghai Institute of Organic Chemistry.

$FO_2SCF_2CO_2H$ (1.8 g, 10 mmol) was added dropwise into a solution of Ph_3P (2.6 g, 10 mmol) in 50 mL of CH_3CN at room temperature. The gas evolved was collected in a syringe and detected by GC−MS to be CO_2. The reaction mixture was stirred for 4 h. The precipitate that had formed was filtered off and recrystallized from a mixed solvent of THF and CH_3CN to give fine crystals of **3** (2.6 g, 66%); mp 239−242 °C.

IR (KBr) γ (cm^{-1}): 3020 (m); 2860 (m); 1592 (s); 1483 (m); 1443 (s); 1340 (m); 1320 (m); 1220 (s); 1193 (s); 1113 (s); 1083 (s); 1060 (s); 760 (s); 692 (s); 621 (m); 520 (s); 500 (s). ^1H NMR $(CD_3)_2CO$ (δ): 7.86 (s, C_6H_5); 7.43 (d−t, HCF_2). ^{19}F NMR (δ): 49.3 (d-d, HCF_2, $^2J_{HF}$=54Hz, $^2J_{FP}$=82Hz); −114.3 (s, FSO_2). MS (*m/z*): 479 (M^+ + FSO_2, 0.38); 463 (M^+ + FSO, 2.03); 447 (M^+ + HCF_2, 4.96); 319 (M^+ − C_6H_5, 0.51); 313 (M^+ − FSO_2, 0.53); 279 ($Ph_3P^+(O)H$, 8.31); 263 (M^+ − CF_2 − FSO_2, 100.00); 185 (Ph_2P^+, 17.82); 133 (M^+ − H − Ph_3P, 1.80); 115 (FSO_2PH^+, 2.44); 108 (PhP^+, 13.79); 83 ($FSO2^+$, 2.86); 82 (HCF_2P^+, 1.47); 77 ($C_6H_5^+$, 4.86); 67 (FSO^+, 1.68); 51 (HCF_2^+, 7.19). Anal. Calcd for $C_{19}H_{16}F_3O_2PS$: C, 57.58; H, 4.04; S, 8.08. Found: C, 57.31; H, 3.78; S, 8.12.

Crystal data: $C_{19}H_{16}O_2F_3PS$, $M = 396.47$. Monoclinic, space group $P2_1/c$; $a = 9.749(2)$ Å, $b = 17.456(4)$ Å, $c = 11.209(3)$ Å, $\beta = 99.08(3)$°, $V = 1883.6$ Å^3, $Z = 4$; $D_c = 1.398$ g/cm^3; $F(000) = 816$; λ(Mo Kα) = 2.848 cm; crystal dimensions 0.20 × 0.10 × 0.10 mm. Intensity data were collected at 20 °C with a Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 3712 unique reflections were measured in the range $0 < 2\theta < 50$ with $0 < h < 11$, $0 < k < 20$, $-13 < l < 13$. Corrections for LP and absorption were applied for the reflection data. The structure was solved via a direct method. The positions for all H atoms were determined by theoretical calculations. Except for the O2 atom, all positional parameters and anisotropic thermal parameters for non-H atoms were refined by the full-matrix least-squares technique. The O2 atom is disordered and is located in the positions O2′ and O2″, the occupies were 0.55 and 0.45 respectively. The final R, R_w, and S values were 0.088, 0.097, and 2.49, respectively, on the basis of 1573 observed reflections ($F > 3\sigma(F)$). All calculations were performed on a MICROVAX II computer with SDP, MULTAN82, and ORTEP programs. Scattering factors were taken from ref 11.

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Supplementary Material Available: Tables giving summaries of the X-ray crystallographic results for **3**, including positional and thermal parameters general displacement parameter, bond lengths, and bond angles (3 pages). Ordering information is given on any current masthead page.

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