

and sodium (2.1 g, 0.11 mol) in THF (150 mL). After an 18-h reaction at 61 °C, the polymer was isolated by precipitation in dilute aqueous hydrochloric acid, followed by sequential precipitation from THF into water, acetone, and hexane (yield 41%). The white, flexible, film-forming polymer had a glass transition temperature (T_g) of 60 °C. Infrared and NMR spectra were compatible with structure VI. ^{31}P NMR spectra showed a peak at +2.16 ppm with a shoulder at +7.69 ppm.¹³ Gel permeation chromatography (GPC)¹⁴ suggested a molecular weight near 1.2×10^6 . Elemental analysis¹⁵ indicated that 62% of the side groups were phenyl and 38% were $\text{CF}_3\text{CH}_2\text{O}$. Comparative tests indicated that this polymer showed a greater resistance to molecular weight decline at 300 °C than did $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. Prolonged reaction of IV with phenyllithium (for example, for 12 h at 20 °C) raised the phenyl side group content to 84%,¹⁶ while the molecular weight declined to $\approx 80\,000$. More vigorous reaction conditions yielded fully substituted¹⁷ but lower molecular weight materials ($\bar{M}_n \approx 2500$).

Similar techniques were employed for the interaction of diethylmagnesium or dibutylmagnesium in THF or glyme with solutions of IV in perfluorobutyltetrahydrofuran. After a 2-day reaction with Et_2Mg at 25 °C, followed by treatment with $\text{CF}_3\text{CH}_2\text{ONa}/\text{CH}_3\text{CH}_2\text{OH}$ at 60 °C for 24 h, a highly elastomeric polymer was isolated (yield 20%). It was soluble in THF and chloroform. The \bar{M}_n molecular weight by GPC analysis¹⁴ was 6×10^5 , and microanalysis indicated that 90% of the side groups were ethyl and 10% were $\text{CF}_3\text{CH}_2\text{O}$.¹⁸ ^{31}P NMR analysis showed one peak at -15.99 ppm.¹³ The T_g value was -50 °C.

It is clear that this synthetic method via polymer IV provides a valuable route to the synthesis of a new class of potentially useful macromolecules.

Acknowledgment. We thank the Office of Naval Research for the support of this work.

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- Relative to aqueous 85% H_3PO_4 . The ^{31}P spectrum for $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$ shows a peak at +8.2 ppm.
- The \bar{M}_n molecular weights were estimated by gel permeation chromatography comparison with polystyrene standards with the use of 10^6 Styragel columns. The solvent was THF.
- Anal. Calcd for $[\text{NP}(\text{C}_6\text{H}_5)_{1.24}(\text{OCH}_2\text{CF}_3)_{0.76}]_n$: C, 49.88; H, 3.58; N, 6.49; P, 14.35; F, 20.07. Found: C, 50.20; H, 3.55; N, 6.43; P, 14.30; F, 19.60.
- Anal. Calcd for $[\text{NP}(\text{C}_6\text{H}_5)_{1.68}\text{F}_{0.32}]_n$: C, 67.00; H, 4.65; N, 7.76; P, 17.20; F, 3.37. Found: C, 66.87; H, 4.70; N, 7.67; P, 17.02; F, 3.40.
- Anal. Calcd for $[\text{NP}(\text{C}_6\text{H}_5)_2]_n$: C, 72.36; H, 5.85; N, 7.03; P, 15.59. Found: C, 71.27; H, 5.85; N, 6.31; P, 16.33.
- Anal. Calcd for $[\text{NP}(\text{CH}_2\text{CH}_3)_{1.60}(\text{OCH}_2\text{CF}_3)_{0.20}]_n$: C, 41.00; H, 8.03; N, 11.97; P, 26.49; F, 9.74. Found: C, 41.80; H, 7.89; N, 11.79; P, 26.35; F, 9.78.

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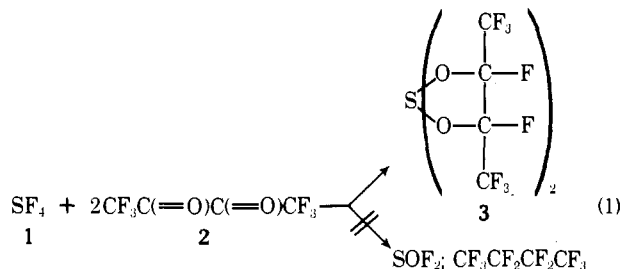
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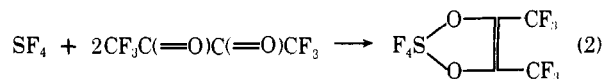
An Unusual Reaction of Sulfur Tetrafluoride with a Carbonyl Compound

Sir:

The reaction of sulfur tetrafluoride with organic compounds containing oxygen functions, such as carbonyl or carboxyl groups, provides a well-established synthesis method of carbon-fluorine compounds.¹ We wish to report a reaction of SF_4 which is in notable contrast to common experience and which takes a highly unexpected course: when SF_4 and perfluorobiacetyl (PFBA) were allowed to react in a 1:2 molar ratio during a period of several days at room temperature, a quantitative yield of a crystalline 1:2 adduct, $\text{SF}_4 \cdot 2\text{PFBA}$, was obtained, while the expected product, resulting from the fluorination of carbonyl groups, perfluoro-*n*-butane, was not observed (i.e., eq 1). No evidence for the oxidative addition of



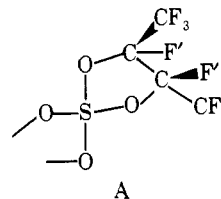
PFBA to SF_4 , with formation of a sulfur(VI)-dioxasulfolene derivative (eq 2), was obtained, either.²



As will be discussed below our SF_4/PFBA adduct proved to be a spiro-sulfurane, resulting from transfer of fluorine from sulfur to carbon, with formation of the 1,3,2-dioxasulfolene ring system, as in 3.³

The spiro-sulfurane 3 was obtained as a white solid of mp 60 °C, stable at room temperature and sufficiently volatile to be sublimed in vacuo (25 °C (1 mm)) without decomposition. The identity of 3 was established by elemental analysis,⁴ mass spectroscopy,⁵ NMR spectroscopy, and a single-crystal x-ray structure determination.

For the discussion of the NMR data, part of the molecule is drawn as shown in A. The discussion is based on the as-



sumption of a geometry at sulfur approximating to trigonal-bipyramidal, with the two oxygen-containing rings spanning one axial and one equatorial position each, while the lone pair of electrons occupies an equatorial position.³

In the ^{19}F NMR spectrum of 3 in acetone a second-order multiplet at δ 76.4 ppm⁶ is observed for the two nonequivalent CF_3 groups; two signals at δ 122.0 and 129.3 ppm⁶ correspond to the nonequivalent fluorine atoms, F'. No change with temperature was observed in the ^{19}F NMR spectrum between 30 and 100 °C (toluene solvent) and between 30 and -70 °C (in acetone). The nonequivalence at room temperature of both CF_3 and F' substituents is in line with observations on the related sulfurane, $\text{S}[\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}]_2$.⁷ It is believed that the molecule undergoes fast pseudorotation which does not, however, lead to CF_3 and CF fluorine substituents becoming equivalent. Further, our observations suggest trans geometry

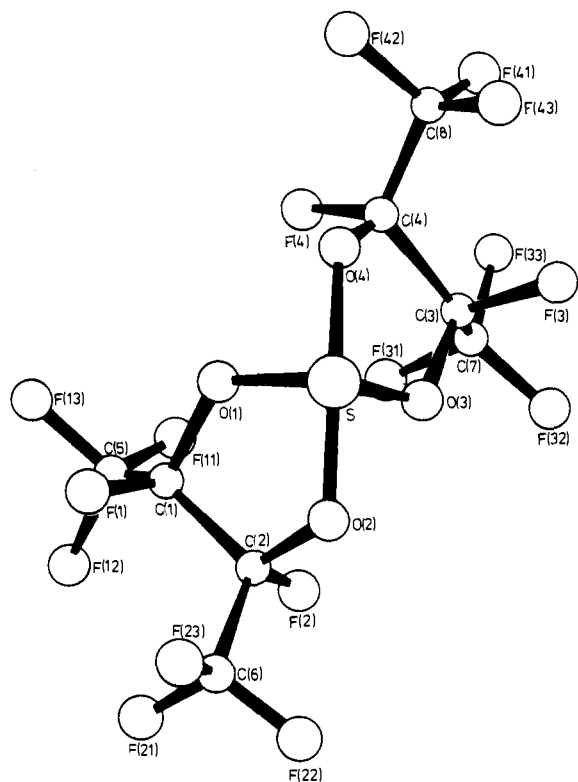


Figure 1. Stereoscopic view of a single molecule of **3**; the lone pair of electrons is directed toward the viewer out of the plane of the paper.

of substituents in **3**, rather than *cis*; for the latter, pseudorotation should lead to positional averaging. These conclusions are supported by the x-ray crystal structure determination (vide infra).

The ^{13}C NMR spectra⁸ supplement and confirm the findings from the ^{19}F spectra. At room temperature two quartets with a shift difference of 0.51 ppm were observed for the carbon atoms of the two CF_3 groups. Each line of these quartets, as a result of coupling to the two nonequivalent fluorine substituents, F' , appears as a doublet of doublets.⁹ A complicated multiplet is observed for the carbon atoms of the dioxasulfane rings whose signals partially overlap with those of the CF_3 groups. In the ^{13}C ($^{19}\text{F}_3\text{C}$) NMR spectrum, a doublet at 79.2 ppm with still relatively broad lines is observed, $^1J_{\text{CF}} = 184.8$ Hz.

The x-ray crystal structure determination of **3** was conducted at -110°C because of excessive motion of CF_3 groups at higher temperatures. **3** forms triclinic crystals, $P1$ or $P1$; subsequent refinement has confirmed the latter space group. The cell constants derived from the 2θ settings of 15 strong reflections ($\pm(hkl)$) were as follows: $a = 9.425$ (6), $b = 10.691$ (3), $c = 7.219$ (3) Å; $\alpha = 90.72$ (5), $\beta = 92.65$ (5), $\gamma = 78.57$ (5)°; $z = 2$; calculated density 2.31 g cm^{-3} .¹⁰

The main structural features of **3**, the first tetraoxysulfurane to be studied by x-ray diffraction, may be explained in terms of approximately trigonal-bipyramidal geometry with a stereochemically active lone pair of electrons at sulfur (Figure 1). All the bonds are bent away from the lone pair: $\text{O}_{\text{ax}}\text{-S-O}_{\text{ax}}$, 171.5 (2)°; $\text{O}_{\text{eq}}\text{-S-O}_{\text{eq}}$, 104.6 (2)°. The axial S-O bond lengths (1.754 (3) and 1.756 (3) Å, respectively) are significantly shorter than those in some dioxy-diaryl sulfuranes previously studied¹¹⁻¹³ where values ranging between 1.82 and 1.92 Å were observed. Equatorial bond lengths were found as 1.630 (4) and 1.633 (3) Å; no such values for related compounds for comparison are available from the literature. The sulfone rings are puckered with one carbon atom ~ 0.35 Å displaced from the plane of the four other ring atoms. The CF_3 groups are situated *trans* to one another in each ring, thus

minimizing nonbonded interactions.

Our findings in the SF_4/PFBA system suggest that sulfurane formation may be of importance in reactions of SF_4 with carbonyl compounds. It has already been established that the reaction of PFBA with sulfur(IV) fluorides may be extended to, for example, R_2NSF_3 , with similar results. The investigation of the chemistry of **3** and related sulfuranes is in progress.¹⁴

Acknowledgments. We are indebted to NATO Scientific Affairs Division for a grant in support of the study of hypervalent molecules, in collaboration with the late Professor J. I. Musher of Yeshiva University, New York. Support by Deutsche Forschungsgemeinschaft (K.C.H. and J.V.W.) and by Fonds der Chemischen Industrie, Frankfurt am Main, is gratefully acknowledged. Perfluorobiacetyl was generously supplied by Dr. F. Kluge, Höchst A.G., Frankfurt am Main-Höchst, Germany. D.S. thanks Gesellschaft für Biotechnologische Forschung mbH., Stöckheim-Braunschweig, for providing x-ray facilities. Drs. V. Wray and W. S. Sheldrick of the same institution are thanked for ^{13}C NMR spectra and assistance with the x-ray structure determination, respectively.

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- (3) A number of sulfuranes, including spiro derivatives of a type similar to **3** have been described in the literature; for a recent review see J. C. Martin and E. F. Perozzi, *Science*, **191**, 154 (1976).
- (4) Calcd for $\text{C}_8\text{F}_{16}\text{O}_4\text{S}$: C, 19.37; F, 61.27. Found: C, 19.50; F, 60.80.
- (5) The ion of highest mass number corresponded to m/e 477, originating from loss of fluorine from the parent molecule. Besides, numerous other characteristic fragments were observed.
- (6) For ^{19}F nmr spectra internal CCl_3F was used as a standard. Acetone was used as a solvent for the ^{19}F NMR measurements. Very slow decomposition of **3** was noted in this solvent.
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- (9) The following parameters were observed: $\delta_{\text{C}1}$ 89.82 ppm ($^1J_{\text{CF}} = 285.9$ Hz, $^2J_{\text{CF}} = 36.9$ Hz, $^3J_{\text{CF}} = 1.4$ Hz), $\delta_{\text{C}2}$ 89.31 ppm ($^1J_{\text{CF}} = 286.3$ Hz, $^2J_{\text{CF}} = 35.1$ Hz, $^3J_{\text{CF}} = 2.7$ Hz).
- (10) Intensity data were collected using Mo $K\alpha$ radiation by the θ - 2θ scan technique at a variable scan rate of 4–30°/min, depending on the intensity of the reflection; 2436 unique reflections were measured in the range of $3^\circ \leq 2\theta \leq 50^\circ$. The positions of all atoms were located by automatic centrosymmetric direct methods (SHELX-76, G.M. Sheldrick). Least-square refinement using 1845 reflections with $F_o > 2.5\sigma(F_o)$ led to reliability factors of $R = 0.067$, $R_w = [\sum w^0 F_o - F_c] / \sum w^0 F_o$, $R_G = [\sum w |F_o - F_c| / \sum w F_o^2]^{0.5} = 0.078$.
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Received March 14, 1977

In Situ Generation and Reactions of $(\text{CO})_5\text{WC}(\text{C}_6\text{H}_5)_2$ with Alkenes—Role of Puckered Metallocyclobutanes in Determining the Stereochemistry of Cyclopropane Formation

Sir:

$(\text{CO})_5\text{WC}(\text{C}_6\text{H}_5)_2$ (**1**) reacts with alkenes to give cyclopropanes, olefin scission products, and new carbene complexes.¹ A mechanistic scheme involving the equilibrium be-