was prepared and purified by the method of Booth and Morris.[8] Hexaphenylcyclotriphosphazene (m.p. 228–229°; lit.[9] 228°, 230–232°) was prepared by the reaction of diphenylchlorophosphine and hydrazine monohydrochloride.[9] A sample of 2,4,6-trichloro-2,4,6-triphenylcyclotriphosphazene (m.p. 155–156°) was kindly furnished by W. R. Grace and Company.

$[(C_6H_5)_2PN]_3\cdot HICl_2$.—Iodine monochloride was added to CCl_4 which had been saturated with HCl. The resulting solution of $HICl_2$ (*ca.* 0.1 *M*) was slowly added with stirring to a saturated solution of $[(C_6H_5)_2PN]_3$ in CCl_4 (*ca.* 0.02 *M*) until precipitation was complete. The yellow powder was collected by suction filtration, washed with pure solvent until the washings were colorless, and dried in a desiccator. The melting point was 197–199° and the yield was 65% based on the phosphazene. The infrared spectrum of this substance proved that the hexaphenylcyclotriphosphazene ring system remained intact.

Anal. Calcd. for $[(C_6H_5)_2PN]_3\cdot HICl_2$: C, 54.29; H, 3.93; Cl, 8.9; N, 5.28. Found: C, 54.20; H, 3.83; Cl, 8.4; N, 5.21.

$[(C_6H_5)_2PN]_3\cdot 2ICl$.—An excess of liquid ICl was added to a small amount (*ca.* 0.25 g.) of $[(C_6H_5)_2PN]_3$, the mixture placed in a vacuum desiccator, and the pressure reduced to 0.1–0.2 mm. for a period of 40 hr. During this time, the excess ICl evaporated and the melting point of the product slowly increased. The mixture also changed from a dark red liquid to a yellow powder during the first 10–12 hr. The final melting point was 181–183° (dec.). The infrared spectrum of this substance showed the presence of the hexaphenylcyclotriphosphazene ring system.

Anal. Calcd. for $[(C_6H_5)_2PN]_3\cdot 2ICl$: C, 46.88; H, 3.28; Cl, 7.7; N, 4.56. Found: C, 45.21; H, 3.38; Cl, 8.8; N, 4.65.

---

[8] H. S. Booth and W. C. Morris, *Inorg. Syn.*, **1**, 167 (1939).

[9] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY 4, CALIFORNIA

On the Reaction of Pentafluorosulfur Hypofluorite with Unsymmetrical Two-Carbon Alkenes

BY STANLEY M. WILLIAMSON

Received September 24, 1962

The reaction of pentafluorosulfur hypofluorite with some simple alkenes and some other compounds has been reported recently.[1] It was found in that work that F_5SOF reacts with vinyl chloride to give exclusively 2-chloro-2-fluoroethyl pentafluorosulfur oxide. This specificity for the addition now has been further confirmed by the use of vinyl fluoride and vinylidene fluoride as reactants. The preparation and physical properties of and structural evidence for 2,2-difluoroethyl pentafluorosulfur oxide and 2,2,2-trifluoroethyl pentafluorosulfur oxide are presented. The equations for the reactions and Roman numeral symbols for the new compounds are

$$FCH{=}CH_2 + FOSF_5 \longrightarrow \underset{\text{I}}{F_2CH{-}CH_2{-}O{-}SF_5} \qquad (1)$$

$$F_2C{=}CH_2 + FOSF_5 \longrightarrow \underset{\text{II}}{F_3C{-}CH_2{-}O{-}SF_5} \qquad (2)$$

Experimental

Preparation.—The general description of the gas phase reaction is given elsewhere.[1] The molecular weights of the $CFH{=}CH_2$[2] and $CF_2{=}CH_2$[3] indicated high purity. The extreme reactivity of the F_5SOF toward either of the alkenes made it difficult to follow the reaction quantitatively by means of a pressure drop. A careful product analysis was necessary to determine the presence of any side reaction products or the other isomer of the addition compound. By means of ordinary vapor phase chromatography and fractional co-distillation,[4] there was observed to be essentially no carbon-containing fractions except the one which was the addition product.

Physical Properties.—Some of the physical properties of the compounds are listed in Table I.

TABLE I
PHYSICAL PROPERTIES

	$F_2CH{-}CH_2{-}O{-}SF_5$	$F_3C{-}CH_2{-}O{-}SF_5$
Phase description at room temp.	"Water-clear" liquid	"Water-clear" liquid
Boiling point[a]	62.4°	41.7°
ΔH_{vap}, kcal. mole^{-1}	7.86	7.08
Melting point[b]	$-93 \pm 1°$	$-108 \pm 1°$
Infrared frequencies,[c] cm.$^{-1}$	890 (s), 905 (s), 960 (w) 1079 (m), 1103 (m), 1141 (w) 1372 (w), 1420 (w), 1463 (w) 2987 (w)	891 (s), 916 (s) 975 (w), 1100 (m) 1187 (s), 1299 (m) 1415 (w), 2988 (w)
Liquid density, g./ml. at 25.0°	1.680	1.670

[a] The normal boiling points were determined from the vapor pressure *vs.* temperature data. The constancy of the vapor pressure *vs.* temperature from various fractions of the sample was taken as additional evidence of the purity of the compounds. The other evidence seemed to rule out the possibility of having azeotrope formation. [b] The melting points were observed under autogenous pressure. The visual observation was made on the sample as it warmed slowly in a *n*-propyl alcohol cold bath. The compounds have a strong tendency to form glasses when the liquid is cooled. When the compounds were distilled slowly into a cold trap at −183°, the condensing vapor usually would crystallize instead of forming a glass. [c] The infrared spectra were taken on a Perkin-Elmer 421 grating spectrophotometer at 2 mm. gas pressure in a 10-cm. glass cell with NaCl windows. The relative intensities of the absorptions are in parentheses following the frequency.

Structural Evidence.—Chemical analyses and vapor densities confirmed the formation of an addition compound.

Anal. Calcd. for $C_2H_3SOF_7$: C, 11.6; H, 1.5; S, 15.4; F, 64.0. Found: C, 11.9; H, 1.7; S, 15.2; F, 65.0. The theoretical vapor density of $C_2H_3SOF_7$ is 208.1 g./g.m.v. The experimental value was 209.8, which was measured at 142.0 mm. pressure and 299.5°K.

Anal. Calcd. for $C_2H_2SOF_8$: C, 10.6; H, 0.9; S, 14.2; F, 67.3. Found: C, 10.6; H, not determined; S, 14.5; F, 68.4. The theoretical vapor density of $C_2H_2SOF_8$ is 226.1 g./g.m.v. The experimental value was 227.8, which was measured at 238.0 mm. pressure and 298.8°K.

The observed frequencies of infrared absorptions are consistent with those which have been observed before for similarly structured compounds.[1] ($FCH_2{-}CH_2{-}O{-}SF_5$ has infrared absorption frequencies for carbon–fluorine at 1068 and 1098 cm.$^{-1}$, whereas for $CF_3{-}CF_2{-}O{-}SF_5$ they are at 1110, 1196, and 1246 cm.$^{-1}$.) The main pentafluorosulfur oxide frequencies for the compounds reported in this note are well within the range of 888 and 935 cm.$^{-1}$ reported for F_5SOF.[5] It appears now that with the growing number of F_5SO derivatives, the original assignment[5] in F_5SOF of the 888 cm.$^{-1}$ frequency to the O–F stretch was not correct. A more thorough study of these spectra will be required before a definite assignment can be made.

---

[1] S. M. Williamson and G. H. Cady, *Inorg. Chem.*, **1**, 673 (1962).

[2] A gift from Dr. J. Nelson, Jackson Laboratory, E. I. du Pont de Nemours Company, Wilmington, Delaware.

[3] Purchased from Peninsular Chemresearch Inc., Gainesville, Florida.

[4] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

[5] F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Am. Chem. Soc.*, **78**, 1553 (1956).

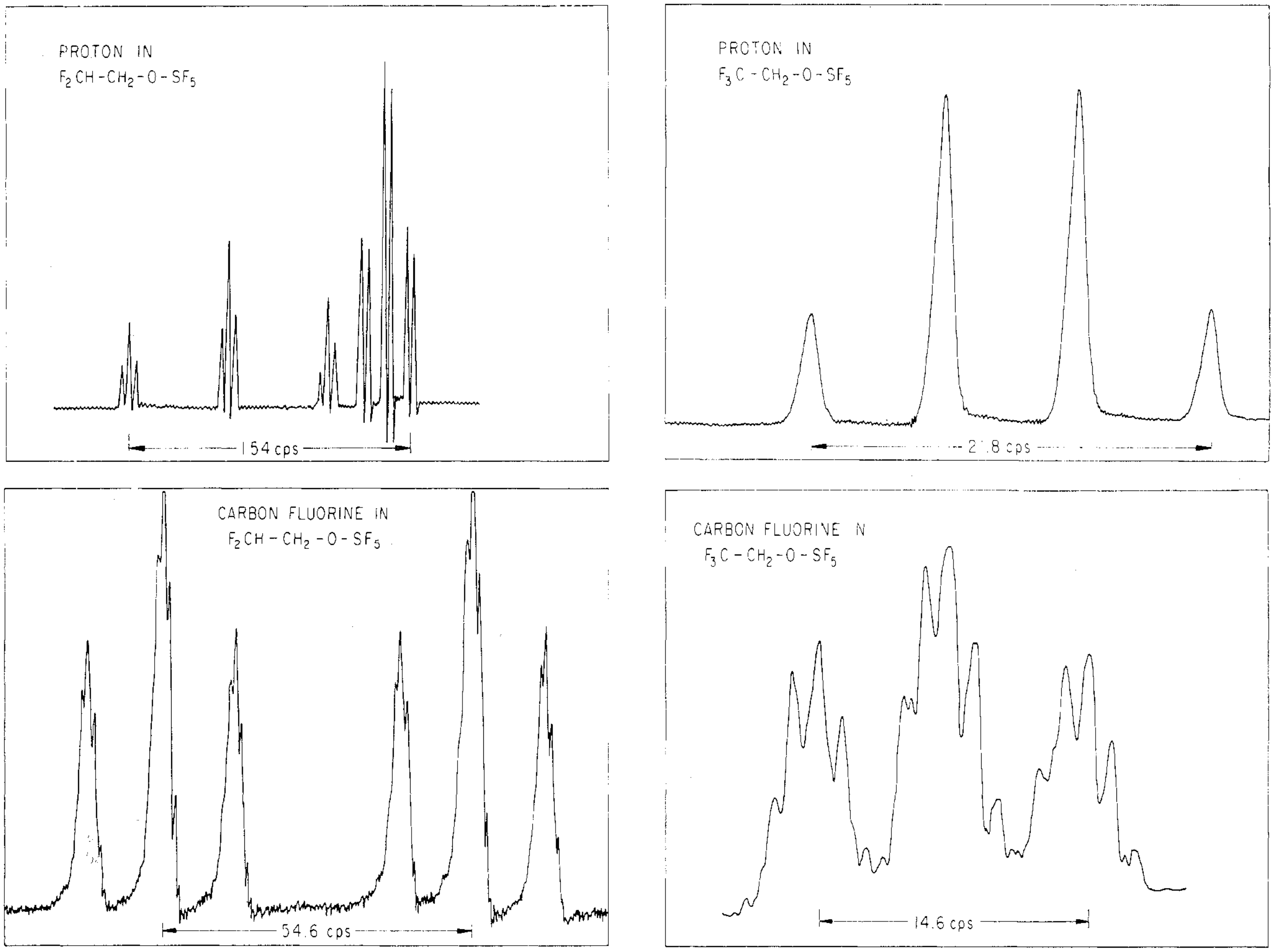

Fig. 1.—Nuclear magnetic resonance spectra of the protons and fluorine atoms of the carbon portions of the molecules, using a Varian Associates A-60 spectrometer for the proton spectra and a Varian Associates HR-56.4 spectrometer for the fluorine spectra.

The mass spectra show the production of the $F_5S^{32}OC^{12}H_2^+$ ion in yields of 26.1 and 22.2% relative to SF_5^+, respectively, from compounds I and II. $C^{12}F_2H-C^{12}H_2^+$ in a 41.0% yield from I and $C^{12}F_3C^{12}H_2^+$ in a 73.2% yield from II also were obtained. Also present were the correct isotopic species in the proper abundances for these and other ions. Ions which might have come from other isomeric structures or impurities were at a minimum. Each spectrum also exhibited a trace amount of its respective molecule ion.

The n.m.r. spectra presented in Fig. 1 show well the orientation of the added fluorine atom with respect to the fluorine and hydrogen atoms of the respective reactant alkene. The proton spectra do not indicate any spin–spin coupling among the fluorine atoms bonded to the sulfur with the protons; however, in the fluorine spectra, the fluorine atoms which are bonded to the carbon are significantly coupled with the equatorial sulfur fluorine atoms. A summary of the spin–spin coupling constants is given in Table II. The spectra of the SF_5 group have been omitted, because they are not relevant to this discussion, but the coupling constants between the two types of fluorine atoms in the group are included.

TABLE II

SPIN–SPIN COUPLING CONSTANTS IN C.P.S.

1 2 3 4 5 $F_2CH-CH_2-O-SF_4F$		1 2 3 4 $F_3C-CH_2-O-SF_4F$	
$J_{12} = 54.6$	$J_{24} \sim 0$	$J_{12} = 7.3$	$J_{23} \sim 0$
$J_{13} = 12.9$	$J_{25} \sim 0$	$J_{13} = 1.2$	$J_{24} \sim 0$
$J_{14} = 0.9$	$J_{34} \sim 0$	$J_{14} \sim 0$	$J_{34} = 144.1$
$J_{15} \sim 0$	$J_{35} \sim 0$		
$J_{23} = 4.0$	$J_{45} = 155.8$		

Summary

From these data it seems that the addition of F_5SOF to unsymmetrical two-carbon alkenes, where one carbon is an unsubstituted methylene-type carbon atom, is a clean, quantitative reaction, which gives a product which is the structural isomer with the F_5SO group bonded to the methylene-type carbon. This observation is consistent with the direction of addition that has been observed for CF_3I[6] and SF_5Cl[7] in reactions with similar alkenes, although the reaction condition for and reactivity of SF_5OF are not similar to those of CF_3I or SF_5Cl.

Acknowledgment.—Appreciation is expressed to Professor C. H. Sederholm and Dr. A. Newton, respectively, for their assistance in obtaining the n.m.r. and mass spectra.

---

(6) R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957).

(7) J. R. Case, N. H. Ray, and H. L. Roberts, *ibid.*, 2066 (1961).