Synthesis and Chemistry of Ethynylsulfur Pentafluoride

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The new acetylene, $SF_5C \equiv CH$, has been synthesized. It readily adds methanol and diazomethane to give *cis*-2-methoxyvinylsulfur pentafluoride and isomeric pyrazoles, respectively, and it forms adducts with 1,3-butadienes. Dehydrogenation of these adducts affords SF_5 -substituted benzenes by a convenient new route. The silver salt of $SF_5C \equiv CH$ is unstable.

This paper describes the synthesis and chemistry of the new acetylene, $SF_5C \equiv CH$. The related acetylene, $SF_5C \equiv CCH_3$, has been reported,¹ but none of its chemical properties is described.

Synthesis.—Ethynylsulfur pentafluoride has been prepared in four steps, starting with sulfur chloride pentafluoride.

$$SF_{5}Cl + HC \equiv CH \xrightarrow{160-170^{\circ}} SF_{5}CH = CHCl$$

$$SF_{5}CH = CHCl \xrightarrow{Br_{2}, h\nu} SF_{5}CHBrCHBrCl$$

$$K_{2}CO_{3}, 25^{\circ}$$

 $SF_{\delta}CHBrCHBrCl \xrightarrow{K_{\delta}CO_{\delta}, z_{\delta}} \xrightarrow{SF_{\delta}} C = C < Cl + SF_{\delta} \\ Br = C = C < H + SF_{\delta} \\ Br = C = C < Cl \\ H + SF_{\delta}C = C < Cl \\ Cl \\ SF_{\delta}CBr = CHCl \xrightarrow{Zn, diglyme}_{90\%} SF_{\delta}C = CH (b.p. 6^{\circ})$

2-Chlorovinylsulfur pentafluoride, first synthesized^{1,2} photocatalytically, was prepared in this study by thermal addition of SF_5Cl to acetylene.³ The other SF_5 compounds in the four-step sequence are new and have been identified by elemental and spectral analyses. H^1 n.m.r. spectroscopy has served to elucidate the *cis* and trans configurations of these and other SF₅-substituted ethylenes obtained in this study (see Table I). The spectra of the cis and trans isomers having hydrogen on C-2 differ in that there is spin-spin coupling (3 c.p.s.) between this hydrogen and fluorines of the SF_5 group in one isomer and not the other. Judging by the spectra of the *cis* and *trans* isomers of SF₅CH=CHOCH₃ splitting occurs when the SF_5 group and hydrogen are trans. The configurations of the SF₅CH=CHOCH₃ isomers are unequivocally established by their dipole moments, cis 5.13 D. and trans 3.94 D., and also by the magnitudes of the spin-spin coupling constants of the cis and trans hydrogens, which are 6 and 13 c.p.s., respectively.⁴ Bromination of SF₅CH=CHCl also gave the highly toxic S_2F_{10} and CHBr₂CHBrCl. Diglyme was found to be a particularly good solvent for the zinc dehalogenation reaction because it gave a product of high purity.

Addition of Methanol to Ethynylsulfur Pentafluoride. —Base-catalyzed addition of methanol to ethynylsulfur pentafluoride occurs readily in the normal stereospecific

TABLE I				
Proton Magnetic Resonance Data on Certain SF_{δ} Compounds				
Compd.	Chemical shift, p.p.m. ^a	J-values (c.p.s.)		
SF ₅ C=CH		$J_{\rm FH} = 3$		
$SF_5 \sim Cl$ Br H	6.8 (5 peaks)	$J_{\rm FH} = 3.3$		
SF_{5} H >C=C< Br Cl	7.4 (no splitting)			
$SF_5 \qquad H_1 \ >C = C < H_1 \ H_a \qquad Cl$	$H_{a} = 6.7 (\sim 9 \text{ peaks} H_{b} = 7.1 \text{ (doublet)}$			
SF_{5} H_{1} $C=C<$ H_{a} OC	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{l} J_{\mathrm{H}_{a}\mathrm{H}_{b}} = 13 \\ J_{\mathrm{FH}_{a}} = 6 \\ J_{\mathrm{FH}_{b}} = \sim 0 \end{array}$		
$SF_5 OO = C < H_a H_b$	$\begin{array}{llllllllllllllllllllllllllllllllllll$			
SF_{δ} H >C=C< Br H Br H	$H_{a} = 6.4 \text{ (doublet)}$ $H_{b} = 5.9 \text{ (10 peaks)}$	$J_{\mathrm{H_aH_b}} = 4.5$ $J_{\mathrm{FH_b}} = 3.2$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Br H = 4.83	$J_{\rm FH} = 1.7$		
$\begin{array}{c} H_{a} \\ \\ SF_{5}C - CH_{b} < \\ \\ H_{a} \end{array} $	$\begin{array}{ll} H_{a} = 3.4 \ (10 \ \text{peaks}) \\ \text{OCH}_{c3} & H_{b} = 4.4 \ (3 \ \text{peaks}) \\ \text{OCH}_{c3} & H_{c} = 2.9 \end{array}$			

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 a Downfield from tetramethylsilane (external, 5% in carbon tetrachloride).

manner⁵ to give *cis*-2-methoxyvinylsulfur pentafluoride. Treatment of 2-chlorovinylsulfur pentafluoride with methanolic potassium hydroxide gives *trans*-2methoxyvinylsulfur pentafluoride⁶ with physical properties markedly different from those of the *cis* isomer.

$$\begin{split} & \mathrm{SF}_{\delta}\mathrm{C} = \mathrm{CH} + \mathrm{CH}_{3}\mathrm{OH} \xrightarrow{\mathrm{OH}^{-}} & \overset{\mathrm{OH}^{-}}{\overset{-}{\longrightarrow}} & \overset{\mathrm{OCH}_{3}}{\overset{-}{\longrightarrow}} & \overset{\mathrm{OCH}_{3}}{\overset{-}{\longrightarrow}} \\ & \mathrm{(b.p.\ 144^{\circ};\ n^{24}\mathrm{p}\ 1.3633;\ dipole\ moment,\ 5.13\ D.)} \\ & \mathrm{SF}_{\delta}\mathrm{CH} = \mathrm{CH}\mathrm{Cl} + \mathrm{CH}_{3}\mathrm{OH} \xrightarrow{\overset{\mathrm{OH}^{-}}{\longrightarrow}} & \overset{\mathrm{SF}_{\delta}}{\overset{-}{\longrightarrow}} & \overset{\mathrm{H}}{\overset{-}{\longrightarrow}} \\ & \mathrm{H} & \overset{\mathrm{OH}^{-}}{\overset{\mathrm{OCH}_{3}}{\overset{\mathrm{OH}^{-}}{\longrightarrow}} \\ & \mathrm{H} & \overset{\mathrm{OH}^{-}}{\overset{\mathrm{OH}_{3}}{\overset{\mathrm{OCH}_{3}}{\overset{\mathrm{OH}_{3}}{\longrightarrow}}} \\ & \mathrm{(b.p.\ 115^{\circ};\ n^{24}\mathrm{p}\ 1.3572;\ dipole\ moment,\ 3.94\ D.)} \end{split}$$

Addition of Diazomethane to Ethynylsulfur Pentafluoride.—The well-known addition of diazomethane

⁽¹⁾ J. R. Case, H. Ray, and H. L. Roberts, J. Chem. Soc., 2066 (1961).

⁽²⁾ H. L. Roberts, Quart. Rev. (London), 15, 42 (1961).

⁽³⁾ We are indebted to Dr. C. W. Tullock of this laboratory for this procedure.

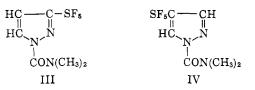
⁽⁴⁾ L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pregamon Press, Inc., New York, N. Y., 1959, p. 85.

⁽⁵⁾ W. E. Truce and D. L. Goldhamer, J. Am. Chem. Soc., 81, 5798 (1959).

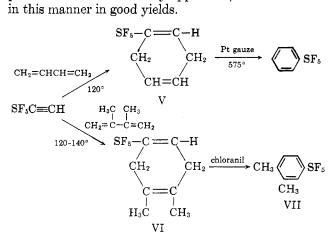
⁽⁶⁾ N. H. Ray, J. Chem. Soc., 1440 (1963). 2-Methoxyvinylsulfur pentafluoride, b.p. 114°, was obtained from SFsCH—CHCl and NaOCHs. Although the geometric structure was not determined, it apparently was the trans isomer.

to acetylene⁷ proceeded readily in ether at 0° with ethynylsulfur pentafluoride to give a mixture of the isomeric pyrazoles I and II.

These pyrazoles were not separated; however, the 60:40 ratio of isomers was established by H^1 n.m.r. spectroscopy. Dimethylcarbamoylation of this isomeric mixture gave products III and IV, evidently derived from I and II, respectively. None of the isomer corresponding to acylation of I in the 2-position was observed.



Diels-Alder Reactions.—A simple two-step synthesis of SF_5 -substituted benzenes has been uncovered in the reaction of ethynylsulfur pentafluoride with 1,3butadienes followed by dehydrogenation. Alkyl-substituted phenylsulfur pentafluorides, for which previous procedures⁸ are not directly applicable, can be obtained in this manner in good yields.



Other new compounds prepared include SF₅CH₂CH- $(OAc)_2$, $SF_5CH_2CH(OCH_3)_2$, $SF_5CHBrCH_2Br$, SF_5 - CBr_2CHBr , and $SF_5CBr=CH_2$.

Experimental

H¹ n.m.r. spectra were obtained on a Varian A-60 n.m.r. spectrometer. Chemical shifts are given in p.p.m. downfield from tetramethylsilane employed as an external standard (5%)in carbon tetrachloride) unless stated otherwise. F19 n.m.r. spectra were obtained on a Varian HR 56.4-Mc./sec. spectrometer. Sulfur chloride pentafluoride, SF5Cl, was prepared in high yield by the reaction of sulfur tetrafluoride, chlorine, and cesium fluoride.9

2-Chlorovinylsulfur Pentafluoride.-A mixture of 12 g. of acetylene and 150 g. of SF5Cl was heated in a 400-ml. stainless steel pressure vessel for 1 hr. at 160° and 4 hr. at 175°. Distillation of the liquid product (69 g.) gave 33 g. (35%) of SF₅CH= CHCl, b.p. 65-67°,² 8 g. of SF₅CH=CHCH=CHCl, and 28 g.

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of a higher boiling residue. The volatile products recovered from these runs contained about 65% SF₅Cl, 20% C₂H₂, 10%SOF₂, 5% SO₂, and a trace of SiF₄. These can be recycled to afford better utilization of the SF₅Cl.

2-Chloro-1,2-dibromoethylsulfur Pentafluoride.—A mixture of 252 g. (1.33 moles) of SF₅CH—CHCl and 214 g. (1.33 moles) of bromine was irradiated for 13 hr. with a 275-w. G. E. sun lamp placed about 12 in. from the flask. The temperature was maintained at 20-25° by means of a water bath. Unreacted ${\rm SF}_5{\rm CH}{=}{\rm CHCl}$ (50 g.), ${\rm S}_2{\rm F}_{10}$ (10 g.), and other low boilers were removed by distillation at room temperature (10-20 mm.). The residue (321 g.) comprised about 92% SF₅CHBrCHBrCl and 8% CHBr₂CHBrCl. An analytical sample of SF₅CHBr-CHBrCl, b.p. 70° at 13 mm., n^{25} D 1.4610, was obtained by gas chromotography.

Anal. Caled. for C₂H₂Br₂ClF₅S: Br, 45.9; Cl, 10.2; F, 27.3. Found: Br, 45.2; Cl, 10.0; F, 27.3.

and cis-1-Bromo-2-chlorovinylsulfur Pentafluoride .trans Crude SF₅CHBrCHBrCl (321 g.) of the above step was mixed with 400 ml. of acetone and 150 g. of potassium carbonate (1.09 moles), and the resultant mixture was stirred for 12 hr.; the temperature stayed at about 35° for much of the time because of the heat of reaction. The solid was removed by filtration, and the filtrate was distilled through a precision still. About 149 g. of $SF_5CBr=CHCl$, b.p. 50° at 52 mm., was obtained. The over-all yield of steps 2 and 3 was approximately 56%.

Separation of the cis and trans isomers (ratio about 1:4) was carried out by gas chromatography with a 12 ft. by 0.75 in. copper column packed with 30% Dow Corning silicone oil No. 703 on Chromosorb P. A column temperature of 125° and a helium flow of 625 ml./min. were used.

	cis	trans
Retention time of cut, min.	20	30
Density, g./ml.	2.06	2.06
n^{25} D	1.4150	1.4250

Anal. Calcd. for C2HBrClF5S: Br, 29.88; Cl, 13.26; F, 35.52; S, 12.02. Found (*cis* isomer): Br, 30.00; Cl, 12.97; F, 35.47; S, 11.79. Found (*trans* isomer): Br, 30.56; Cl, 12.91; F, 35.76; S, 11.46.

The mass spectrogram of these isomers showed an abundant parent peak of 266 m/e and other ions expected for these structures.

 F^{19} n.m.r. showed the presence of SF_5 groups and the absence of other types of fluorine. The H^1 n.m.r. (see Table I) of one isomer (RT = 20 min.) showed an unsplit hydrogen whereas the spectrum of the other isomer showed a quintuplet. These results indicate that these isomers were cis and trans, respectively.

Ethynylsulfur Pentafluoride.---A mixture of 200 ml. of the dimethyl ether of diethylene glycol (diglyme, freshly distilled over sodium) and 45 g. (0.69 mole) of zinc dust was placed in a thoroughly dried 500-ml., three-necked flask equipped with a stirrer, dropping funnel, nitrogen inlet tube, and reflux condenser $(45^\circ,\, {\rm condenser}\ {\rm water})$ to which was attached a trap cooled with Dry Ice-acetone. This mixture was heated to 140° and 76 g. (0.28 mole) of SF₅CBr=CHCl was added over a period of 30 min. Heating was continued for an additional 60 min. Nitrogen was bubbled through the mixture during the entire reaction. About 35 g. (22 ml.) of SF₅C=CH of 98% purity or better, indicated by gas chromatography, collected in the trap, b.p. 6°. Anal. Caled. for C2HF5S: F, 62.5; S, 21.1. Found: F, 62.1; S, 21.8.

The infrared spectrum showed absorption bands at 3.0 (--C \equiv C—H), 4.71 (—C=C—), 6.17, 6.62, 7.45, 11.12 (S—F very strong), 13.78, and 14.75 μ .

The mass spectrum had peaks at m/e = 152 (parent), 133 $(SF_4C_2H^+)$, 127 (SF_5^+) , 89 (SF_3^+) , and 44 (C_2HF^+) .

The proton magnetic resonance spectrum showed only one hydrogen split into a quintuplet by the SF5 group.

Ethynylsulfur Pentafluoride from 2-Chlorovinylsulfur Pentafluoride and Base.¹⁰—A mixture of 7 g. of SF₅CH=CHCl and 25 ml. of xylene was added rapidly with stirring to 9.2 g. of cesium hydroxide and 2.8 g. of a mineral oil dispersion of sodium hydride (53%) at room temperature. After an induction period of about 18 min., a rapid reaction set in, and the temperature rose from about 30 to 120°. About 0.7 ml. of volatile material was

⁽⁷⁾ J. D. Loudon, "Chemistry of Carbon Compounds," Vol. IV^A, E. H. Rodd, Ed., D. Van Nostrand Co., Inc., Princeton, N. J. chapter 4.

⁽⁸⁾ W. A. Sheppard, J. Am. Chem. Soc., 84, 3064 (1962).

⁽⁹⁾ C. W. Tullock, D. D. Coffman, and E. L. Muetterties, ibid., 86, 357 (1964).

⁽¹⁰⁾ Dr. C. W. Tullock of this laboratory carried out the first experiments.

collected in a trap cooled with Dry Ice-acetone. Gas chromatographic analysis of this volatile product indicated that 7% of it was SF₅C=CH (identified by mass spectrometry and infrared). The conversion of SF₅CH=CHCl to SF₅C=CH was 1-2\%.

cis-2-Methoxyvinylsulfur Pentafluoride.—To a mixture of 6 g. (0.0394 mole) of SF₅C=CH and 7.9 g. (0.25 mole) of methanol was added 1 ml. of 4 N methanolic potassium hydroxide at room temperature. The temperature rose to about 60° over a period of 8 min. and then subsided. At this point, the mixture was no longer basic (pH 6). Additional catalyst solution (1.0 ml.) was added whereupon the temperature rose to about $56\,^\circ$ and then slowly decreased to room temperature. The total reaction time was about 85 min. The mixture was still basic. Gas chromatographic analysis indicated that most of the SF₆C=CH had reacted. Water was added, and the product was separated in the lower layer. Gas chromatographic analysis of the crude product indicated that it was substantially all SF₅CH=CHOCH₃ (cis), although a small amount of the trans isomer and a trace of $\mathrm{SF}_3\mathrm{CH}_2\mathrm{CH}(\mathrm{\ddot{O}CH}_3)_2$ were also present. Distillation through a spinning-band column gave 4.7 g. of the cis isomer (65%), b.p. 50° at 20 mm. (144°, extrapolated), n^{25} D 1.3633.

Anal. Caled. for $C_3H_5F_5OS$: F, 51.6; S, 17.4; Found: F, 51.3; S, 17.5.

The infrared spectrum showed absorption bands at 3.14 (=CH), 3.37 and 3.48 (saturated CH), 5.98 (-C=C-), 7.29 (C-CH₃), and 11.95 μ (SF₅). The fluorine resonance spectrum showed the presence of an SF₅ group, and the proton resonance spectrum (see Table I for details) was consistent with the *cis* structure.

trans-2-Methoxyvinylsulfur Pentafluoride.—SF₆CH=CHCl (19.04 g.) was added dropwise to a mixture of 63 g. (2.0 mole) of methanol and 10 g. (0.16 mole) of KOH (85%) over a period of 18 min. with a temperature rise from 25 to 61°. The KCl formed (7.0 g., 0.094 mole) was removed by filtration. Neutralization of the filtrate with methanolic HCl gave additional KCl (3.4 g., 0.046 mole). On distillation of the filtrate through a Vigreux column, much of the product codistilled with methanol. Addition of water caused the product to separate as the lower layer. Distillation of the lower layer gave 7.3 g. (40%) of SF₅CH=CHOCH₃, b.p. 115°, n^{25} D 1.3572. The residue contained a small amount of SF₅CH₂CH(OCH₃)₂.

Anal. Caled. for $C_{3}H_{5}F_{5}OS$: C, 19.6; H, 2.7; F, 51.6; S, 17.4. Found: C, 20.3; H, 2.9; F, 51.5; S, 17.2.

The infrared spectrum showed bands at 3.2 and 3.5 (saturated CH), 6.1 (-C=C-), 8.1 (ether C-O), and 12.0 μ (S-F). The proton resonance spectrum showed no hydrogen *trans* to SF₅.

The proportion of SF₅CH₂CH(OCH₃)₂ in the product was increased by refluxing the reaction mixture for 2 hr. Also, SF₅-CH₂CH(OCH₃)₂ could be obtained, although quite slowly, by refluxing SF₅CH=CHOCH₃ with methanolic KOH. A sample of SF₅CH₂CH(OCH₃)₂, b.p. 63° at 50 mm., n^{25} D 1.3613, was purified by gas chromatography.

Anal. Caled. for $C_4H_9F_5O_2S$: F, 44.1; S, 14.8. Found: F, 43.9; S, 14.0.

Pentafluorosulfur Pyrazoles.—An ethereal solution (150 ml.) of $CH_2N_2^{11}$ (0.69 mole) was added portionwise with stirring over a period of 20 min. to a mixture of 10.8 g. (0.71 mole) of $SF_5C \equiv CH$ and 50 ml. of ether. The temperature was maintained at 0-5° with an ice bath. The diazomethane reacted almost as fast as it was added. After a total reaction time of about 30 min., the mixture was essentially colorless. Gas chromatographic analysis indicated that virtually all of the $SF_5C \equiv CH$ had undergone reaction. Removal of the ether under reduced pressure gave 13.8 g. (85%) of a white solid product, m.p. 45-55°. An analytical sample, m.p. 68-69°, was obtained by sublimation at 55° at 0.1 mm.

Anal. Calcd. for $C_3H_3F_5N_2S$: C, 18.6; H, 1.56; F, 48.9; N, 14.4. Found: C, 18.9; H, 1.67; F, 48.9; N, 14.2.

The fluorine magnetic resonance spectrum in $CDCl_{3}$ showed two different SF_{5} groups. The proton magnetic resonance in $CDCl_{3}$ (internal standard) showed absorption at 13.1 (NH), 8.0 (no splitting), 7.8 (triplet split slightly by SF_{5}), and 6.8 p.p.m. (doublet). These data indicate the presence of two isomeric pyrazoles having SF_{5} groups in the 3- or 4-positions. The peak at 8.0 p.p.m. corresponded to the hydrogens of II (these would not be split), and the peaks at 7.8 and 6.8 p.p.m. corresponded to the H-4 and H-5 of I. In I the spin-spin coupling of hydrogens (J = 2.5 c.p.s.) led to a weak-strong-strong-weak pattern. One hydrogen (apparently the H-5 of II) was slightly coupled to the SF₅ group.

From the intensities obtained in this spectrum the ratio of I to II was about 3:2. Gas chromatographic analysis also indicated two main components in this product in about a 3:2 ratio, confirming the proton magnetic resonance data.

Carbamoylated Pyrazoles.—To a solution of 11.8 g. (0.06 mole) of pentafluorosulfur pyrazole and 50 ml. of tetrahydrofuran was added, at 0-5°, 3.0 g. of a 53% dispersion of NaH in mineral oil suspended in 10 ml. of tetrahydrofuran. The mixture was heated to reflux during which time about 1.5 ml. of H₂ was collected over water. Dimethylcarbamoyl chloride (7.5 g.) was then added at room temperature, and the mixture was stirred overnight, filtered, and distilled through a molecular still. There was obtained 8.5 g. (56%) of carbamoylated pentafluorosulfur pyrazole, b.p. 70° (pot temperature) at 0.2 μ .

Anal. Calcd. for $C_6H_8F_5N_3OS$: C, 27.2; H, 3.04; F, 35.8; N, 15.8; S, 12.1. Found: C, 27.9; H, 3.06; F, 34.8; N, 15.8; S, 12.1.

Both F^{19} and H^1 n.m.r. spectra were in accord with the isomeric pyrazole structures. The H^1 n.m.r. spectrum (tetramethylsilane) showed peaks at 3.2 (CH₃), 6.8 (doublet, J = 3.2 c.p.s.), 8.0, 8.4 (multiplet), and 8.8 p.p.m. The intensities of the 8.0 and 8.8 p.p.m. peaks were equal and corresponded to the H-5 and H-3, respectively, in the 4-SF₅ pyrazole. The 6.8- and 8.4-p.p.m. peaks were of equal intensities and corresponded to the H-4 and H-5, respectively, in the 3-SF₅ pyrazole. The ratio of the ratio of the ratio of the hydrogens to methyl hydrogens was 1:3.

Adduct of Ethynylsulfur Pentafluoride and 1,3-Butadiene.—A mixture of 4.7 g. (0.031 mole) of SF₅C=CH, 1.9 g. (0.05 mole) of butadiene, and 0.1 g. of hydroquinone was heated in a Carius tube for 2 days at 140°. The product was dark in color and somewhat viscous. Distillation through a 6-in. spinning-band column gave 4.97 g. (78%) of the 1,4-adduct, b.p. 48-50° at 10 mm., $n^{24.8}$ D 1.4109.

Anal. Caled. for $C_6H_7F_5S$: F, 46.1; S, 15.6. Found: F, 45.7; S, 15.8.

The infrared spectrum showed bands at 3.28 (=-CH), 4.46 and 4.57 (saturated CH), 5.93 (--C==C--), 6.05 (CH==C--S--), and 12.0 μ (S-F).

The proton resonance spectrum showed absorptions (internal standard) at 6.20 (one hydrogen), 5.33 (three peaks, -CH=CH-), and 2.76 p.p.m. (four methylene hydrogens).

When this adduct was passed over platinum gauze at 575°, it was converted to $C_6H_5F_5S$ and hydrogen as judged by gas chromatographic analysis in comparison with an authentic sample.⁸

Adduct of Ethynylsulfur Pentafluoride and 2,3-Dimethylbutadiene.—A mixture of 3.34 g. (0.022 mole) of SF₅C=CH, 2.22 g. (0.027 mole) of 2,3-dimethylbutadiene, and 0.1 g. of hydroquinone was heated in a Carius tube for 3 hr. at 70–100° and for 16 hr. at 100–110°. Distillation of the product through a 6-in. spinning-band column yielded 2.61 g. (50.5%) of crude 1,4-adduct, b.p. 65° at 4 mm.

Anal. Caled. for $C_8H_{11}F_5S$: C, 41.0; H, 4.7; F, 40.6; S, 13.7. Found: C, 42.6; H, 5.0; F, 39.2; S, 14.1.

The elemental analysis indicated that this product contained about 3% of the dimer of 2,3-dimethylbutadiene as an impurity.

The infrared spectrum of this product was in agreement with the proposed structure and showed the following absorption bands: 3.35, 3.44, 3.49 (saturated CH), 6.02 (-C=C-), 7.23 ($C-CH_3$), and 12.0 μ (S-F).

The fluorine resonance spectrum showed the presence of an SF_5 group. The proton resonance spectrum showed hydrogens at 3.66 (internal standard), 6.14 (fairly broad), 3.66, and 2.34 p.p.m. in the ratio of 4:1:2:6, respectively.

Dehydrogenation was effected by refluxing a mixture of 2.0 g. of adduct (0.0085 mole), 3.0 g. (0.014 mole) of chloranil, and 20 ml. of *p*-xylene for 2 hr. The solid formed was removed by filtration, and the filtrate was distilled through a 6-in. spinning-band column to obtain 1.4 g. of 3,4-dimethylphenylsulfur pentafluoride, b.p. 62° at 5 mm., n^{25} D 1.4501. The analytical sample was purified by gas chromatography.

Anal. Caled. for $C_8H_7F_5S$: C, 41.4; H, 3.91; F, 40.9; S, 13.8. Found: C, 41.8; H, 3.78; F, 40.8; S, 13.8.

The proton magnetic resonance spectrum showed aromatic hydrogens at 7.1 (internal standard) and methyl groups at 1.7 p.p.m. in the ratio of 1:2 as required.

⁽¹¹⁾ J. S. Moore and D. E. Reed, Org. Syn., 41, 16, 1961.

1,2-Dibromoethylsulfur Pentafluoride.—Bromine reacted very slowly with SF₅CH=CH₂ at room temperature. The addition of bromine was effected readily by exposing a mixture of 20.8 g. (0.135 mole) of SF₅CH=CH₂¹ and 21.6 g. (0.135 mole) of Br₂ to a 275-w. G. E. sun lamp (about 12 in. away) for 37 min. during which time the reflux temperature rose from 42 to 85°. Distillation gave 34.6 g. (82%) of SF₅CHBrCH₂Br, a yellowish liquid, b.p. 50-52° at 20 mm., n^{25} D 1.4433.

Anal. Caled. for C₂H₃Br₂F₅S: Br, 50.9; F, 30.2; S, 10.2. Found: Br, 50.8; F, 29.4; S, 10.1.

2,2-Bis(acetoxy)ethylsulfur Pentafluoride.—To a mixture of 3.53 g. (0.0207 mole) of SF₅CH₂CHO⁶ and 11.0 g. (0.108 mole) of acetic anhydride was added 1 drop of concentrated sulfuric acid whereupon the temperature rose to about 40°. Distillation of the mixture after standing for 4 hr. gave 5.5 g. (98%) of SF₅-CH₂CH(O₂CCH₃)₂, b.p. 49° at 0.15 mm., n^{25} p 1.3793.

Anal. Caled. for C₆H₉F₅O₄S: C, 26.5; H, 3.31; S, 11.8. Found: C, 26.9; H, 3.38; S, 11.8.

1-Bromovinylsulfur Pentafluoride.—A mixture of 119 g. (0.38 mole) of SF₅CHBrCH₂Br, 58 g. of powdered K_2CO_3 (0.42 mole), and 200 ml. of acetone was stirred for 75 min. during which time the temperature rose to 33°. Gas chromatographic analysis of the reaction mixture indicated that virtually all of the starting material had reacted after 75 min. Distillation through a precision still gave 71 g. of SF₅CBr=CH₂, b.p. 86°, n^{25} p. 1.3814. Anal. Calcd. for C₂H₂BrF₅S: Br, 34.3; F, 40.8; S, 13.8.

Anal. Calcd. for $C_2H_2BrF_5S$: Br, 34.3; F, 40.8; S, 13.8. Found: Br, 34.4; F, 39.9; S, 13.6.

The fluorine and proton resonance spectra (see Table I) of this compound were consistent with the proposed structure.

1,1,2-Tribromoethylsulfur Pentafluoride.—A mixture of 50 g. (0.21 mole) of $SF_5CBr=CH_2$ and 34 g. (0.21 mole) of bromine was prepared at room temperature. An exothermic reaction occurred almost immediately, and cooling was applied to lower the temperature to about 5°. The mixture was gradually warmed from 5 to 25° over a period of 1.5 hr., allowed to stand at room

temperature overnight, and then irradiated for 2 hr. with a 275watt G. E. sun lamp located about 12 in. from the flask. Distillation of the product through a Vigreux column gave 74 g. (88%) of SF₅CBr₂CH₂Br, b.p. 42° at 0.5 mm., n^{27} D 1.4973.

Anal. Calcd. for $C_2H_2Br_3F_5S$: Br, 61.03; F, 24.19; S, 8.16. Found: Br, 60.46; F, 24.33; S, 7.98.

Both the infrared spectrum and n.m.r. spectra were consistent with this structure.

Silver Salt of Ethynylsulfur Pentafluoride.—To a mixture of 1.7 g. of AgNO₃, 3.5 ml. of water, 2.5 ml. of CH₃OH, and 2.2 ml. of concentrated NH₄OH contained in a flask equipped with a magnetic stirrer and a Dry Ice-cooled condenser was added by distillation 0.7 g. of SF₅C==CH. A white precipitate formed immediately. The solid was removed by filtration and washed with water. There was obtained 1.1 g. of product after air drying for 2 hr.; it decomposed rapidly when heated to 60°. The infrared spectrum showed strong absorption at 4.85 (C==C), at 10–11 (S-F), and at 2.9 and 6.0 μ owing to water. When this product was dried in a desiccator over P₂O₅, it decomposed.

 F^{19} n.m.r. showed absorptions in acetone at -8485, -8460, and -8440 c.p.s. from 1,2-difluoro-1,1,2,2-tetrachloroethane (external) which indicated SF₅.

Attempts to obtain good elemental analyses were thwarted by the decomposition of the silver salt on drying. A sample dried in high vacuum at room temperature for 1 hr. gave 35.0% Ag (calcd., 41.5%). A sample air dried for 1 week gave 33.7%Ag and 14.7% F (calcd., 36.7%).

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The Pyridinolysis of Diaryl Methyl Phosphates

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Di(*para*-substituted phenyl) methyl phosphates (I) containing NO₂, CN, Br, Cl, H, and OCH₂C₆H₅ groups have been synthesized and their reaction with pyridine to form N-methylpyridinium di(*para*-substituted phenyl) phosphates studied. The reaction is facilitated by electron-withdrawing groups and has a Hammett ρ -value of +1.10. It is characterized by a small activation energy and log *PZ* of about 10.2 kcal./mole and 4.7, respectively. The n.m.r. chemical shifts of the methyl groups of I also generally increase with the electron-attracting ability of the substituent.

Aliphatic esters of phosphoric acid react with many nucleophilic reagents including amines,¹ phenols,² thiourea,³ and mercaptide ions⁴ by displacement on carbon to form alkylated products (reaction 1). Al-

> $A \xrightarrow{O} A \xrightarrow{O} P + Z: \longrightarrow P + ZR$ (1) B OR B O⁻

though these alkylation reactions are well known, very little has been reported about the effect of the substituents attached to phosphorus on them. Qualitatively, it has been observed that the rate of reaction increases with the electron-attracting ability of the substituents.⁵⁻⁸ For example, dimethyl phosphoramidates react with triethylamine faster than do methyl phosphorodiamidates,⁵ and the relative rates of reaction of $(CH_3O)_2P(O)Y$ with tertiary amines fall in the order $Y = H > SCH_3 > OCH_3 > CH_3$.⁷ There is, however, a scarcity of quantitative data and the studies are greatly complicated by uncertainty in assigning relative steric and electronic properties to substituents attached directly to phosphorus.

In order to obtain quantitative information about the effect of substituents on the reactivity of phosphate esters as alkylating agents, the reaction of a series of di(para-substituted phenyl) methyl phosphates, I, with pyridine has been studied. Since the substituents in this series cannot interact directly with the phosphorus atom and steric effects are essentially constant, the relative rates of reaction should be a reflection of only the electronic effect of the substituents. This system also doubles the electronic effect, which was expected to be

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