

# Synthesis and Chemistry of Ethynylsulfur Pentafluoride

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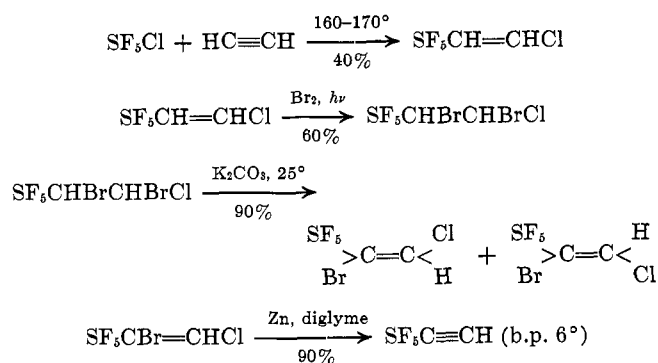
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The new acetylene,  $\text{SF}_5\text{C}\equiv\text{CH}$ , has been synthesized. It readily adds methanol and diazomethane to give *cis*-2-methoxyvinylsulfur pentafluoride and isomeric pyrazoles, respectively, and it forms adducts with 1,3-butadienes. Dehydrogenation of these adducts affords  $\text{SF}_5$ -substituted benzenes by a convenient new route. The silver salt of  $\text{SF}_5\text{C}\equiv\text{CH}$  is unstable.

This paper describes the synthesis and chemistry of the new acetylene,  $\text{SF}_5\text{C}\equiv\text{CH}$ . The related acetylene,  $\text{SF}_5\text{C}\equiv\text{CCH}_3$ , has been reported,<sup>1</sup> but none of its chemical properties is described.

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



2-Chlorovinylsulfur pentafluoride, first synthesized<sup>1,2</sup> photocatalytically, was prepared in this study by thermal addition of  $\text{SF}_5\text{Cl}$  to acetylene.<sup>3</sup> The other  $\text{SF}_5$  compounds in the four-step sequence are new and have been identified by elemental and spectral analyses.  $\text{H}^1$  n.m.r. spectroscopy has served to elucidate the *cis* and *trans* configurations of these and other  $\text{SF}_5$ -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  $\text{SF}_5$  group in one isomer and not the other. Judging by the spectra of the *cis* and *trans* isomers of  $\text{SF}_5\text{CH}=\text{CHOCH}_3$  splitting occurs when the  $\text{SF}_5$  group and hydrogen are *trans*. The configurations of the  $\text{SF}_5\text{CH}=\text{CHOCH}_3$  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.<sup>4</sup> Bromination of  $\text{SF}_5\text{CH}=\text{CHCl}$  also gave the highly toxic  $\text{S}_2\text{F}_{10}$  and  $\text{CHBr}_2\text{CHBrCl}$ . 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.

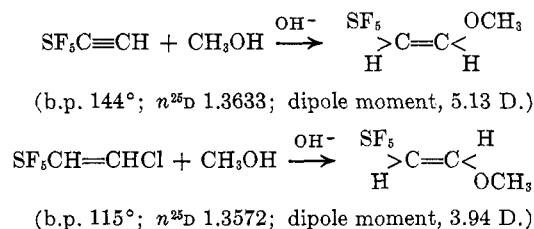
—Base-catalyzed addition of methanol to ethynylsulfur pentafluoride occurs readily in the normal stereospecific

TABLE I  
PROTON MAGNETIC RESONANCE DATA ON CERTAIN  $\text{SF}_5$  COMPOUNDS

Compd.	Chemical shift, p.p.m. <sup>a</sup>	J-values (c.p.s.)
$\text{SF}_5\text{C}\equiv\text{CH}$	2.25 (5 peaks)	$J_{\text{FH}} = 3$
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{Br} \quad \text{H} \end{array}$	6.8 (5 peaks)	$J_{\text{FH}} = 3.3$
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{Br} \quad \text{Cl} \end{array}$	7.4 (no splitting)	
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{H}_a \quad \text{H}_b \\ \quad \quad \text{Cl} \end{array}$	$\text{H}_a = 6.7$ (~9 peaks) $\text{H}_b = 7.1$ (doublet)	$J_{\text{H}_a\text{H}_b} = 13$ $J_{\text{FH}_a} = 5$ $J_{\text{FH}_b} = \sim 0$
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{H}_a \quad \text{H}_b \\ \quad \quad \text{OCH}_3 \end{array}$	$\text{H}_a = 5.7$ (7 peaks) $\text{H}_b = 7.0$ (doublet) $\text{H}_c = 3.3$	$J_{\text{H}_a\text{H}_b} = 13$ $J_{\text{FH}_a} = 6$ $J_{\text{FH}_b} = \sim 0$
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{H}_a \quad \text{H}_b \\ \quad \quad \text{OCH}_3 \end{array}$	$\text{H}_a = 6.3$ (10 peaks) $\text{H}_b = 7.7$ (7 peaks) $\text{H}_c = 3.5$	$J_{\text{H}_a\text{H}_b} = 6.0$ $J_{\text{FH}_a} = 8.7$ $J_{\text{FH}_b} = 3$
$\begin{array}{c} \text{SF}_5 \\ >\text{C}=\text{C}< \\ \text{Br} \quad \text{H}_a \\ \quad \quad \text{H}_b \end{array}$	$\text{H}_a = 6.4$ (doublet) $\text{H}_b = 5.9$ (10 peaks)	$J_{\text{H}_a\text{H}_b} = 4.5$ $J_{\text{FH}_b} = 3.2$
$\begin{array}{c} \text{SF}_5\text{C} \\   \\ \text{Br} \quad \text{H} \\   \quad   \\ \text{Br} \quad \text{H} \end{array}$	$\text{H} = 4.83$	$J_{\text{FH}} = 1.7$
$\begin{array}{c} \text{SF}_5\text{C} \\   \\ \text{H}_a \quad \text{H}_b \\   \quad   \\ \text{H}_a \quad \text{H}_b \\ \quad \quad \text{OCH}_3 \\ \quad \quad \text{OCH}_3 \end{array}$	$\text{H}_a = 3.4$ (10 peaks) $\text{H}_b = 4.4$ (3 peaks) $\text{H}_c = 2.9$	$J_{\text{FH}_a} = 8.6$ $J_{\text{H}_a\text{H}_b} = 5$ $J_{\text{FH}_b} = 0$

<sup>a</sup> Downfield from tetramethylsilane (external, 5% in carbon tetrachloride).

manner<sup>5</sup> to give *cis*-2-methoxyvinylsulfur pentafluoride. Treatment of 2-chlorovinylsulfur pentafluoride with methanolic potassium hydroxide gives *trans*-2-methoxyvinylsulfur pentafluoride<sup>6</sup> with physical properties markedly different from those of the *cis* isomer.



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

(5) W. E. Truce and D. L. Goldhamer, *J. Am. Chem. Soc.*, **81**, 5793 (1959).

(6) N. H. Ray, *J. Chem. Soc.*, 1440 (1963). 2-Methoxyvinylsulfur pentafluoride, b.p.  $114^\circ$ , was obtained from  $\text{SF}_5\text{CH}=\text{CHCl}$  and  $\text{NaOCH}_3$ . Although the geometric structure was not determined, it apparently was the *trans* isomer.

(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," Pergamon Press, Inc., New York, N. Y., 1959, p. 85.



collected in a trap cooled with Dry Ice-acetone. Gas chromatographic analysis of this volatile product indicated that 7% of it was  $\text{SF}_5\text{C}\equiv\text{CH}$  (identified by mass spectrometry and infrared). The conversion of  $\text{SF}_5\text{CH}=\text{CHCl}$  to  $\text{SF}_5\text{C}\equiv\text{CH}$  was 1-2%.

**cis-2-Methoxyvinylsulfur Pentafluoride.**—To a mixture of 6 g. (0.0394 mole) of  $\text{SF}_5\text{C}\equiv\text{CH}$  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° 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  $\text{SF}_5\text{C}\equiv\text{CH}$  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  $\text{SF}_5\text{CH}=\text{CHOCH}_3$  (*cis*), although a small amount of the *trans* isomer and a trace of  $\text{SF}_5\text{CH}_2\text{CH}(\text{OCH}_3)_2$  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),  $n_D^{20}$  1.3633.

*Anal.* Calcd. for  $\text{C}_3\text{H}_5\text{F}_5\text{OS}$ : F, 51.6; S, 17.4; Found: F, 51.3; S, 17.5.

The infrared spectrum showed absorption bands at 3.14 ( $=\text{CH}$ ), 3.37 and 3.48 (saturated CH), 5.98 ( $-\text{C}=\text{C}-$ ), 7.29 ( $\text{C}-\text{CH}_3$ ), and 11.95  $\mu$  ( $\text{SF}_5$ ). The fluorine resonance spectrum showed the presence of an  $\text{SF}_5$  group, and the proton resonance spectrum (see Table I for details) was consistent with the *cis* structure.

**trans-2-Methoxyvinylsulfur Pentafluoride.**— $\text{SF}_5\text{CH}=\text{CHCl}$  (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  $\text{SF}_5\text{CH}=\text{CHOCH}_3$ , b.p. 115°,  $n_D^{25}$  1.3572. The residue contained a small amount of  $\text{SF}_5\text{CH}_2\text{CH}(\text{OCH}_3)_2$ .

*Anal.* Calcd. for  $\text{C}_3\text{H}_5\text{F}_5\text{OS}$ : 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 ( $-\text{C}=\text{C}-$ ), 8.1 (ether  $\text{C}-\text{O}$ ), and 12.0  $\mu$  (S-F). The proton resonance spectrum showed no hydrogen *trans* to  $\text{SF}_5$ .

The proportion of  $\text{SF}_5\text{CH}_2\text{CH}(\text{OCH}_3)_2$  in the product was increased by refluxing the reaction mixture for 2 hr. Also,  $\text{SF}_5\text{CH}_2\text{CH}(\text{OCH}_3)_2$  could be obtained, although quite slowly, by refluxing  $\text{SF}_5\text{CH}=\text{CHOCH}_3$  with methanolic KOH. A sample of  $\text{SF}_5\text{CH}_2\text{CH}(\text{OCH}_3)_2$ , b.p. 63° at 50 mm.,  $n_D^{25}$  1.3613, was purified by gas chromatography.

*Anal.* Calcd. for  $\text{C}_4\text{H}_7\text{F}_5\text{O}_2\text{S}$ : F, 44.1; S, 14.8. Found: F, 43.9; S, 14.0.

**Pentafluorosulfur Pyrazoles.**—An ethereal solution (150 ml.) of  $\text{CH}_2\text{N}_2$  (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  $\text{SF}_5\text{C}\equiv\text{CH}$  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  $\text{SF}_5\text{C}\equiv\text{CH}$  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  $\text{C}_3\text{H}_5\text{F}_5\text{N}_2\text{S}$ : 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  $\text{CDCl}_3$  showed two different  $\text{SF}_5$  groups. The proton magnetic resonance in  $\text{CDCl}_3$  (internal standard) showed absorption at 13.1 (NH), 8.0 (no splitting), 7.8 (triplet split slightly by  $\text{SF}_5$ ), and 6.8 p.p.m. (doublet). These data indicate the presence of two isomeric pyrazoles having  $\text{SF}_5$  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 hydro-

gens ( $J = 2.5$  c.p.s.) led to a weak-strong-strong-weak pattern. One hydrogen (apparently the H-5 of II) was slightly coupled to the  $\text{SF}_5$  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  $\text{H}_2$  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  $\mu$ .

*Anal.* Calcd. for  $\text{C}_6\text{H}_8\text{F}_5\text{N}_2\text{OS}$ : 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  $\text{F}^{19}$  and  $\text{H}^1$  n.m.r. spectra were in accord with the isomeric pyrazole structures. The  $\text{H}^1$  n.m.r. spectrum (tetramethylsilane) showed peaks at 3.2 ( $\text{CH}_3$ ), 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- $\text{SF}_5$  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- $\text{SF}_5$  pyrazole. The ratio of the ring 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  $\text{SF}_5\text{C}\equiv\text{CH}$ , 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.,  $n_D^{24.5}$  1.4109.

*Anal.* Calcd. for  $\text{C}_6\text{H}_7\text{F}_5\text{S}$ : F, 46.1; S, 15.6. Found: F, 45.7; S, 15.8.

The infrared spectrum showed bands at 3.28 ( $=\text{CH}$ ), 4.46 and 4.57 (saturated CH), 5.93 ( $-\text{C}=\text{C}-$ ), 6.05 ( $\text{CH}=\text{C}-\text{S}-$ ), and 12.0  $\mu$  (S-F).

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

When this adduct was passed over platinum gauze at 575°, it was converted to  $\text{C}_6\text{H}_5\text{F}_5\text{S}$  and hydrogen as judged by gas chromatographic analysis in comparison with an authentic sample.<sup>8</sup>

**Adduct of Ethynylsulfur Pentafluoride and 2,3-Dimethylbutadiene.**—A mixture of 3.34 g. (0.022 mole) of  $\text{SF}_5\text{C}\equiv\text{CH}$ , 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.* Calcd. for  $\text{C}_8\text{H}_{11}\text{F}_5\text{S}$ : 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 ( $-\text{C}=\text{C}-$ ), 7.23 ( $\text{C}-\text{CH}_3$ ), and 12.0  $\mu$  (S-F).

The fluorine resonance spectrum showed the presence of an  $\text{SF}_5$  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.,  $n_D^{25}$  1.4501. The analytical sample was purified by gas chromatography.

*Anal.* Calcd. for  $\text{C}_8\text{H}_7\text{F}_5\text{S}$ : 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.

**1,2-Dibromoethylsulfur Pentafluoride.**—Bromine reacted very slowly with  $\text{SF}_5\text{CH}=\text{CH}_2$  at room temperature. The addition of bromine was effected readily by exposing a mixture of 20.8 g. (0.135 mole) of  $\text{SF}_5\text{CH}=\text{CH}_2^1$  and 21.6 g. (0.135 mole) of  $\text{Br}_2$  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  $\text{SF}_5\text{CHBrCH}_2\text{Br}$ , a yellowish liquid, b.p. 50–52° at 20 mm.,  $n_D^{25} 1.4433$ .

*Anal.* Calcd. for  $\text{C}_2\text{H}_2\text{Br}_2\text{F}_5\text{S}$ : 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  $\text{SF}_5\text{CH}_2\text{CHO}^6$  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  $\text{SF}_5\text{CH}_2\text{CH}(\text{O}_2\text{CCH}_3)_2$ , b.p. 49° at 0.15 mm.,  $n_D^{25} 1.3793$ .

*Anal.* Calcd. for  $\text{C}_6\text{H}_8\text{F}_5\text{O}_4\text{S}$ : 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  $\text{SF}_5\text{CHBrCH}_2\text{Br}$ , 58 g. of powdered  $\text{K}_2\text{CO}_3$  (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  $\text{SF}_5\text{CBr}=\text{CH}_2$ , b.p. 86°,  $n_D^{25} 1.3814$ .

*Anal.* Calcd. for  $\text{C}_2\text{H}_2\text{BrF}_5\text{S}$ : 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  $\text{SF}_5\text{CBr}=\text{CH}_2$  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 275-watt G. E. sun lamp located about 12 in. from the flask. Distillation of the product through a Vigreux column gave 74 g. (88%) of  $\text{SF}_5\text{CBr}_2\text{CH}_2\text{Br}$ , b.p. 42° at 0.5 mm.,  $n_D^{25} 1.4973$ .

*Anal.* Calcd. for  $\text{C}_2\text{H}_2\text{Br}_3\text{F}_5\text{S}$ : 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  $\text{AgNO}_3$ , 3.5 ml. of water, 2.5 ml. of  $\text{CH}_3\text{OH}$ , and 2.2 ml. of concentrated  $\text{NH}_4\text{OH}$  contained in a flask equipped with a magnetic stirrer and a Dry Ice-cooled condenser was added by distillation 0.7 g. of  $\text{SF}_5\text{C}\equiv\text{CH}$ . 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 ( $\text{C}\equiv\text{C}$ ), at 10–11 ( $\text{S}-\text{F}$ ), and at 2.9 and 6.0  $\mu$  owing to water. When this product was dried in a desiccator over  $\text{P}_2\text{O}_5$ , it decomposed.

$\text{F}^{19}$  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  $\text{SF}_5$ .

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%).

**Acknowledgment.**—We wish to thank Messrs. C. B. Matthews, H. Foster, R. J. Berndt, and C. G. Wortz and Miss N. E. Schlichter for help in obtaining and interpreting spectral and dipole moment data. We are indebted to Dr. C. W. Tullock for uncovering the first lead to a synthesis of  $\text{SF}_5\text{C}\equiv\text{CH}$ .

## The Pyridinolysis of Diaryl Methyl Phosphates

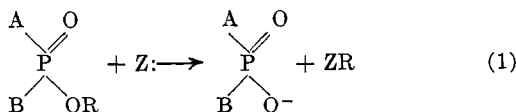
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Di(*para*-substituted phenyl) methyl phosphates (I) containing  $\text{NO}_2$ ,  $\text{CN}$ ,  $\text{Br}$ ,  $\text{Cl}$ ,  $\text{H}$ , and  $\text{OCH}_2\text{C}_6\text{H}_5$  groups have been synthesized and their reaction with pyridine to form *N*-methylpyridinium di(*para*-substituted phenyl) phosphates studied. The reaction is facilitated by electron-withdrawing groups and has a Hammett  $\rho$ -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,<sup>1</sup> phenols,<sup>2</sup> thiourea,<sup>3</sup> and mercaptide ions<sup>4</sup> by displacement on carbon to form alkylated products (reaction 1). Al-



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.<sup>5–8</sup> For example, dimethyl phosphoramidates

react with triethylamine faster than do methyl phosphorodiamidates,<sup>5</sup> and the relative rates of reaction of  $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{Y}$  with tertiary amines fall in the order  $\text{Y} = \text{H} > \text{SCH}_3 > \text{OCH}_3 > \text{CH}_3$ .<sup>7</sup> 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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