The anomalous experiment referred to in reference 9 involved the reaction of triphenylchromium with a 6-fold excess of phenylmagnesium bromide in tetrahydrofuran for 2 hours. After hydrolysis of the dark solution, the sole product isolated was the bis-biphenyl-chromium(I) cation in 16% yield.

Reaction of Black Solid with Phenylmagnesium Bromide.—A 10.4-g. sample of triphenylchromium-magnesium halide salt was rearranged to black solid at 50° (0.05 mm.). This material then was dissolved in 70 ml. of a 1.1 *M* solution of phenylmagnesium bromide in THF and refluxed for 2 hours. After hydrolysis of the reaction solution according to the previously described procedure, 0.61 g. (12%) of a mixed tetraphenylboron salt was precipitated which consisted of a 20:80 mixture of bis-benzenechromium(I) and benzene-biphenylchromium(I) salts.

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[CONTRIBUTION NO. 528 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO.]

Addition of Phosphines to Fluoroölefins

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Phosphine and phenylphosphine undergo thermal addition to fluoroölefins to give fluoroalkylphosphines. Reaction of phosphine with tetrafluoroethylene gave the mono- and bis-(1,1,2,2-tetrafluoroethyl)-phosphines and, unexpectedly, tetrafluoroethylenediphosphine. Similar products were obtained with phosphine and chlorotrifluoroethylene and dichlorodifluoroethylene, but only monoaddition products resulted from reaction with 1,1-difluoroethylene, 1,1-difluoroisobutylene and hexafluoropropene.

Silanes have been reported to add to fluoroolefins in the presence of free-radical catalysts and the extension of this type of reaction to other metalloid hydrides has been considered.[1] Tin hydrides have since been added to tetrafluoroethylene[2] and free-radical-,[3] acid-[4] and base-[5] catalyzed additions of phosphine to non-fluorinated olefins have been reported.

Phosphine has now been found to react with fluoroölefins in the absence of a catalyst to give fluoroalkylphosphines. Phosphine and tetrafluoroethylene, for example, react at 150° in a sealed glass tube to give 1,1,2,2-tetrafluoroethylphosphine (I), bis-(1,1,2,2-tetrafluoroethyl)-phosphine (II) and, surprisingly, tetrafluoroethylenediphosphine (III). Octafluorocyclobutane and

$HCF_2CF_2PH_2$ I $(HCF_2CF_2)_2PH$ II $H_2PCF_2CF_2PH_2$ III

1,1,2,2-tetrafluoroethane were also detected among the gaseous products. A similar range of products was obtained by the addition of phosphine to chlorotrifluoroethylene and to dichlorodifluoroethylene as shown in Table I. The reaction of phosphine with 1,1-difluoroethylene, 1,1-difluoroisobutylene and hexafluoropropene gave only the monoaddition products.

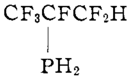
The reaction of phenylphosphine with tetrafluoroethylene gave phenyl-1,1,2,2-tetrafluoroethylphosphine (IV) in 45% yield and a trace of bis-(1,1,2,2-tetrafluoroethyl)-phenylphosphine (V).

$C_6H_5PHCF_2CF_2H$ IV $C_6H_5P(CF_2CF_2H)_2$ V

The fluoroalkylphosphines obtained in these reactions are clear, colorless, spontaneously flammable liquids. These compounds are much less basic than the corresponding alkylphosphines and undergo conventional phosphine reactions, such as quaternization, slowly, if at all.

TABLE I

PRODUCTS OF THE ADDITION OF PHOSPHINE TO FLUOROÖLEFINS

Olefin	Product	B.p., °C.	Yield[c]
$CF_2{=}CF_2$	$HCF_2CF_2PH_2$	20–22	53
	$(HCF_2CF_2)_2PH$	91–92	7
	$H_2PCF_2CF_2PH_2$	69–72	9
	HCF_2CF_2H	....	[a]
	C_4F_8	....	[a]
$CFCl{=}CF_2$	$HCFClCF_2PH_2$	67	54
	$(HCFClCF_2)_2PH$	138–142	6
	$H_2PCFClCF_2PH_2$	107–109	1
	$HCFClCF_2H$	20	[a]
$CCl_2{=}CF_2$	$HCCl_2CF_2PH_2$	109.5–110.5	30
	$(HCCl_2CF_2)_2PH$	180–184	3
	$H_2PCCl_2CF_2PH_2$	*ca.* 140	[a]
	$HCCl_2CF_2H$	45–47	[a]
$CH_2{=}CF_2$	$HCF_2CH_2PH_2$[b]	52–53.5	1
$(CH_3)_2C{=}CF_2$	$(CH_3)_2CHCF_2PH_2$[b]	75–77	6
$CF_3CF{=}CF_2$	 $CF_3\underset{\displaystyle PH_2}{\underset{\vert}{C}}FCF_2H$[b]	45–48	36

[a] Product not isolated in pure form; characterized only by infrared or nuclear magnetic resonance analysis. [b] Structure tentatively assigned by nuclear magnetic resonance analysis. [c] Per cent. based on the amount of phosphine charged.

The products obtained from 1,1-difluoroethylene and from 1,1-difluoroisobutylene were characterized only by their mass spectra and H^1 and F^{19} magnetic resonance spectra. The choice of isomers of these products was made on the basis of the presence or absence of CF_2H groups in the H^1 and F^{19} magnetic resonance and mass spectra.

Experimental[6]

General Procedure.—All the phosphine addition reactions were carried out in sealed glass tubes which were heated at 150° for 8 hours. Equimolar quantities of phosphine and fluoroölefin were used and the products were isolated by distillation of the reaction mixture as described in the phosphine–tetrafluoroethylene reaction below. The products

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(1) A. M. Geyer and R. N. Haszeldine, *Nature*, **178**, 808 (1956).

(2) C. G. Krespan and V. A. Engelhardt, *J. Org. Chem.*, **23**, 1565 (1958).

(3) A. R. Stiles, F. F. Rust and W. E. Vaughan, THIS JOURNAL, **74**, 3282 (1952).

(4) H. C. Brown, U. S. Patent 2,584,112, Feb. 5, 1952.

(5) I. Hechenbleickner and M. M. Rauhut, U. S. Patent 2,822,376, Feb. 4, 1958.

(6) Melting and boiling points are uncorrected.

were protected from atmospheric oxygen by carrying out all transfers under reduced pressure or in a nitrogen atmosphere.

Reaction of Phosphine with Tetrafluoroethylene.—Each of eight 165-ml. Carius tubes was cooled in liquid nitrogen and evacuated to 0.1 mm., and 3 g. of phosphine and 9 g. of tetrafluoroethylene were condensed in each tube. The tubes were sealed and heated at 150° for 8 hours. The tubes were cooled in liquid nitrogen, opened, evacuated to 0.1 mm. and allowed to warm to −80°. The gaseous products which distilled were found by infrared analysis to contain octafluorocyclobutane and 1,1,2,2-tetrafluoroethane in addition to unreacted phosphine and tetrafluoroethylene. The residual liquid products were combined by distillation under reduced pressure into the pot of a 12-inch spinning-band column. Little or no solid residue remained in the tubes.

Distillation of the liquid products in an atmosphere of nitrogen gave 38.5 g. (53% yield) of 1,1,2,2-tetrafluoroethylphosphine (I), b.p. 20–22°. The phosphine is a clear, colorless, spontaneously flammable liquid with an extremely vile odor. The parent peak in the mass spectrum was 134 and the most abundant species was 51, probably the CF_3 ion.

Anal. Calcd. for $C_2H_3F_4P$: F, 56.7; P, 23.1. Found: F, 54.7; P, 22.4.

Tetrafluoroethylenediphosphine (III), also a colorless, spontaneously flammable liquid, distilled at 69–72°, yield 4.2 g. (9%). Extreme difficulty was encountered in separating the diphosphine from bis-(1,1,2,2-tetrafluoroethyl)-phosphine (II) because the two compounds tend to codistil. The parent peak in the mass spectrum was 166 with lesser peaks at 165, 164, 163 and 162.

Anal. Calcd. for $C_2H_4F_4P_2$: C, 14.5; H, 2.4; P, 37.3. Found: C, 16.0; H, 2.4; P, 32.1.

Bis-(1,1,2,2-tetrafluoroethyl)-phosphine (II) distilled at 91–92°, yield 8.1 g. (7% based on phosphine charged).

Anal. Calcd. for $C_4H_3F_8P$: C, 20.5; H, 1.3; P, 13.2; mol. wt., 234.04. Found: C, 20.8; H, 1.5; P, 14.0; parent mass, 234.

1,1,2,2-Tetrafluoroethyltrimethylphosphonium Iodide.—A mixture of 3.1 ml. of 1,1,2,2-tetrafluoroethylphosphine and 4.5 ml. of methyl iodide was heated at 100° in a sealed glass tube for 88 hours. The tube was opened and the unreacted starting materials were evaporated under reduced pressure. The residual white crystalline 1,1,2,2-tetrafluoroethyltrimethylphosphonium iodide melted at 215–222° with decomposition.

Anal. Calcd. for $C_5H_{10}F_4IP$: I, 41.8. Found: I, 41.7.

Reaction of Phenylphosphine with Tetrafluoroethylene.—A 150-ml. Carius tube was charged with 7 g. of phenylphosphine[7] and 12 g. of tetrafluoroethylene and was heated at 150° for 8 hours. The tube was opened and the unreacted gases (80% tetrafluoroethylene and 15% octafluorocyclobutane by infrared analysis) were vented. The residual liquids were distilled under reduced pressure in a 12-inch spinning-band column. Phenyl-1,1,2,2-tetrafluoroethylphosphine (IV) distilled at 28° (0.5 mm.), $n^{25}D$ 1.4758, yield 6 g. (45%). Infrared and proton magnetic resonance analysis of this colorless, spontaneously flammable liquid showed the presence of three types of hydrogen in the molecule corresponding to PH, CF_2H and aromatic CH.

Anal. Calcd. for $C_8H_7F_4P$: C, 45.7; H, 3.4; P, 14.7. Found: C, 45.3; H, 3.7; P, 14.5.

Bis-(1,1,2,2-tetrafluoroethyl)-phenylphosphine (V) distilled at 42° (0.5 mm.), yield 0.3 ml.

Anal. Calcd. for $C_{10}H_{17}F_8P$: C, 38.7; H, 2.3; P, 10.0. Found: C, 39.0; H, 2.4; P, 10.0.

Reaction of Phosphine with Chlorotrifluoroethylene.—Distillation of the liquid products obtained from seven tubes containing a total of 63 g. of chlorotrifluoroethylene and 21 g. of phosphine gave 45.5 g. of clear, colorless 2-chloro-1,1,2-trifluoroethylphosphine, b.p. 67.0°. The proton and fluorine magnetic resonance spectra were compatible with the assigned structure and did not contain the triplet H^1 and doublet F^{19} associated with the CF_2H group. The mass spectrum contained parent mass peaks at 150 and 152.

Anal. Calcd. for $C_2H_3ClF_3P$: P, 20.6. Found: P, 20.1.

An extremely air-sensitive fraction which boiled at 109–129° was redistilled to give 0.2 g. of 1-chloro-1,2,2-trifluoroethylenediphosphine. The n.m.r. and mass spectra were compatible with this structure but the mass spectrum also contained peaks assignable to $HCFClCF_2PH_2$.

Bis-(2-chloro-1,1,2-trifluoroethyl)-phosphine distilled at 138–142°, yield 5.2 g. The n.m.r. and mass spectra were compatible with this structure.

Reaction of Phosphine with *unsym*-Dichlorodifluoroethylene.—Distillation of the liquid products from two Carius tubes containing a total of 22 g. of *unsym*-dichlorodifluoroethylene and 6 g. of phosphine gave 8.4 g. of 2,2-dichloro-1,1-difluoroethylphosphine, b.p. 109.5–110.5°. The proton and fluorine magnetic resonance spectra were compatible with the assigned structure and did not contain the triplet H^1 and doublet F^{19} associated with the CF_2H group.

Anal. Calcd. for $C_2H_3Cl_2F_2P$: C, 14.4; H, 1.8; P, 18.5. Found: C, 14.8; H, 1.8; P, 18.0.

A trace of colorless liquid distilled at about 140°. The H^1 and F^{19} magnetic resonance of this product were compatible with 1,1-dichloro-2,2-difluoroethylenediphosphine.

A clear, colorless liquid, believed to be bis-(2,2-dichloro-1,1-difluoroethyl)-phosphine, distilled at 180–184°, yield 0.8 g. The proton and fluorine magnetic resonance spectra, though not clean, were compatible with this structure.

Reaction of Phosphine with Hexafluoropropene.—Distillation of the liquid product obtained from 18 g. of hexafluoropropene and 4 g. of phosphine gave only one fraction, a clear, colorless, air-sensitive liquid, b.p. 45–48°, yield 8 g. The mass spectrum suggests that the product is a mixture of two hexafluoropropylphosphine isomers since it contains peaks assignable to both CF_2H and CF_2PH_2 ions in addition to the parent molecules (mass 184). The proton magnetic resonance indicates that 1,1,1,2,3,3-hexafluoro-2-propylphosphine is the chief isomer present since the strongest peaks are a pair of doublets assignable to the protons of a $FC{-}PH_2$ group.

Anal. Calcd. for $C_3H_3F_6P$: P, 16.8. Found: P, 15.4.

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[7] R. J. Horvat and A. Furst, THIS JOURNAL, **74**, 562 (1952).