either at the same time or on different days to compare their reproducibility, and variations determined from measurements on a standard solution on a day-to-day basis, were corrected by insertion of the proper figure in the calculations.

Fluorescence and Chemiluminescence Measurements.—Data were recorded with an Aminco–Bowman spectrophotofluorometer (American Instrument Co., Inc.) using Vitroseal tubes. Dimethyl sulfoxide (Matheson Coleman and Bell) was stirred for several hours over KOH pellets and then distilled from the same flask at vacuum pump pressure. The fluorescence of the distillate was then checked; it could not be reduced by fractional freezing, but shaking with potassium superoxide appeared to reduce fluorescence. Solvent fluorescence was insignificant at the exciting wavelengths used to determine fluorescence of the species of interest.

Spectra in anhydrous dimethyl sulfoxide were recorded after the addition of about 50 mg of KO_2 (personal gift of Professor Paul H. Emmett) to a 3-ml sample of a standard solution. For the partially aqueous systems, standard 0.5 N NaOH was pipetted into the tube, the proper amount of standard hydrazide solution or corresponding anhydride solution in dimethyl sulfoxide pipetted in, the tube was swirled until no striations of light were noted, and the spectrum was recorded. The aqueous spectra were recorded in a solution 1 N in NH_4OH and 0.12 N in Cu^{2+}. To this chilled mixture, 30% H_2O_2 was added dropwise while the tube sat in the spectrophotofluorometer so that emission of light had ceased before addition of the succeeding drop. The spectrum of the final product was recorded after a second run in an ice bath, and the spectrum of the corresponding phthalate was recorded from a sample of a solution of the anhydride dissolved overnight in dilute Na_2CO_3 solution.

Acknowledgment.—We wish to thank the National Institutes of Health (GM-10849) for its support of this work.

Compounds of Phosphorus and Fluorine. IV. Reaction of 1-Chloro-2,3,3,4,4,5,5-heptafluorocyclopentene with Trialkyl Phosphites and Other Nucleophilic Reagents[1]

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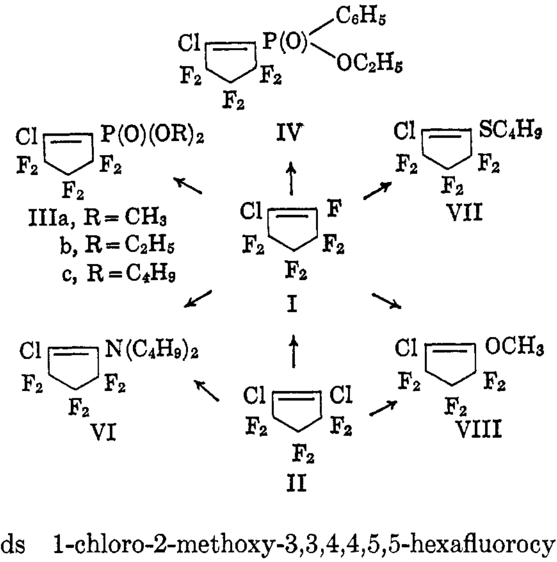
1-Chloro-2,3,3,4,4,5,5-heptafluorocyclopentene (I) reacts readily with nucleophilic reagents, giving the products of displacement of vinylic fluorine. The chlorine atom is retained in every case. The reaction of I with trialkyl phosphites provides a direct synthesis of the dialkyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonates (III), compounds first described in the preceding paper in this series. Diethyl phenylphosphonite reacts similarly, giving a phosphinate ester (IV). Dibutylamine reacts with I to give the same product (VI) which is obtained from dibutylamine and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (II), but under much milder conditions. I also reacts readily with methanol and with butyl mercaptan in ether solution in the presence of triethylamine, giving the known ether, VIII, or the new compound, butyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl sulfide (VII). The mechanism of the displacement of fluorine *vs.* chlorine is discussed.

In part II of this series it was shown that trialkyl phosphites cannot be made to react with 1,2-dichloroperfluorocycloalkenes in a 1:1 ratio. The products are diphosphonates, regardless of the order of addition or the ratio of reactants.[2] A monophosphonate was, however, later prepared by an indirect synthesis involving the cleavage of one of the C–P bonds in a diphosphonate.[1] In the present paper a direct synthesis of monophosphonates is described, employing 1-chloro-2,3,3,4,4,5,5-heptafluorocyclopentene (I) as the starting material. This and other reactions of I with various nucleophilic reagents to be discussed are sketched in Chart I.

The chemistry of I reported in the literature is meager, as the compound has not been generally available. In our laboratories it is prepared by the partial fluorination of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (II) with potassium fluoride in dimethylformamide.[3,4] Further fluorination gives perfluorocyclopentene, with displacement of the remaining chlorine atom,[3,4] but in all of the other reactions the chlorine atom is preserved. The reaction of I with methanol in the presence of lithium chloride or potassium bifluoride yields 1-chloro-2-methoxy-3,3,4,4,5,5-hexafluorocyclopentene (VIII).[4c] Reduction of I with sodium borohydride or diborane and sodium fluoride gives 1-chloro-2H-3,3,4,4,5,5-hexafluorocyclopentene.[5] The reaction of I with hydrogen chloride gives II and trichloropentafluorocyclopentene.[6]

CHART I



In the present work, I was found to react smoothly with trimethyl phosphite, triethyl phosphite, tributyl

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[1] Part III: A. W. Frank, *J. Org. Chem.*, **31**, 1521 (1966).

[2] Part II: A. W. Frank, *ibid.*, **30**, 3663 (1965).

[3] Unpublished work by Dr. R. L. K. Carr.

[4] (a) A similar method was described by A. Henne and J. Sedlak, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., 1960, p 16 M. See also (b) A. Henne, U. S. Patent 3,024,290 (March 6, 1962); *Chem. Abstr.*, **56**, 15333 (1962); (c) N. A. Edelson, Ph.D. Thesis, Cornell University, 1962; (d) J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).

[5] (a) D. J. Burton and R. L. Johnson, *J. Am. Chem. Soc.*, **86**, 5361 (1964); (b) R. L. Johnson and D. J. Burton, *Tetrahedron Letters*, 4079 (1965).

[6] C. F. Baranauckas and R. L. K. Carr, U. S. Patent 3,193,587 (July 6, 1965); *Chem. Abstr.*, **63**, 14724 (1965).

phosphite, and diethyl phenylphosphonite at room temperature, giving the products of displacement of the vinylic fluorine atom (IIIa–c and IV). The identity of the products was established by analysis, which showed that the chlorine atom was retained; by the stoichiometry of the reaction; and, in one case (IIIb), by comparison with the product prepared by a different method.[1] The phosphinate ester IV was identified by hydrolysis to the acid, mp 171–172° (V). The three phosphonate esters (IIIa–c) were distillable liquids which fumed in air. The double bond was clearly evident in their infrared spectra and responded readily to permanganate and bromine tests. The permanganate solutions were completely decolorized. The monophosphonates were therefore stronger reducing agents than the diphosphonates which reduced permanganate only to the MnO_2 stage and did not decolorize bromine at all.[2]

In the triethyl phosphite reaction, a side reaction was observed leading to diethyl ether and ethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonofluoridate (IX). Similar side reactions have been observed between triethyl phosphite and other fluoro olefins, including perfluorocyclobutene.[7]

No evidence of reaction was seen when I was added to a solution of the sodium derivative of dibutyl phosphite in benzene. The expected product was IIIc.

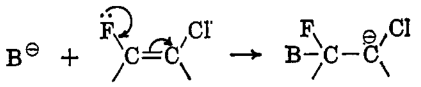
In view of the ease with which I reacted with phosphite and phosphonite esters, some further experiments were performed to determine its reactivity toward other nucleophilic reagents.

The reaction of I with dibutylamine took place readily in ether solution at room temperature, giving within a few minutes a 91% yield of a dibutylamine salt, mp 100–101°, identified as the hydrofluoride. The filtrate gave on distillation an 89% yield of N,N-dibutyl 2-chloro-3,3,4,4,5,5,-hexafluoro-1-cyclopenten-1-ylamine (VI) as a bright yellow oil. Parker[8] had previously prepared this compound from dibutylamine and II, but gave no specific details for its preparation. His reaction was repeated, using an excess of dibutylamine and ether as the solvent, and was found to be exceedingly slow by comparison with I; 76 hr of refluxing elapsed before the precipitation of dibutylamine hydrochloride ceased. The excess dibutylamine, as observed by Parker, did not participate in the reaction. In fact, VI could not be made to react further with dibutylamine even when a mixture of the two was heated in the absence of a solvent for 6 hr at 156°.

I also reacted readily with methanol or butyl mercaptan in ether solution at room temperature, with triethylamine present as an acid acceptor. Some interaction between I and the triethylamine was noted.[9] The reaction with butyl mercaptan gave the new compound, butyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl sulfide (VII), in 77% yield. Doubling the quantities of butyl mercaptan and triethylamine did not result in further substitution. The reaction of I with methanol gave a 24% yield of the known ether, VIII.[4c,10] Better results were obtained when the triethylamine was avoided. A 50% yield of VIII was obtained when I was treated with 1 equiv of potassium hydroxide in excess methanol at 25–30°.

In summation, the reaction of I with nucleophilic reagents results in every case in the displacement of the vinylic fluorine in preference to the chlorine.

The direction of this displacement is consistent with what is known of the chemistry of fluoro olefins which contain the $-CF{=}CCl-$ grouping. Chlorotrifluoroethylene, for example, reacts with triethyl phosphite giving diethyl 2-chloro-1,2-difluorovinylphosphonate,[11] and adds alcohols,[12] mercaptans,[13] and secondary amines[14] giving exclusively the 2-chloro isomers. Alkoxides displace vinylic fluorine from cyclobutene[15] and cyclopentene[16] derivatives containing the $-CF{=}CCl-$ grouping. Since the molecule I is otherwise symmetrical, the orienting effect may be ascribed to the difference in the $+E$ effect of the vinylic halogens (F > Cl). The initial attack of the nucleophilic reagent may be written as follows.



The phosphorus esters behave in this respect in the same manner as other nucleophilic reagents. Differences do not arise until the second group reacts, as was found in the two preceding papers.[1,2]

Experimental Section[17]

Reagents.—Diethyl phenylphosphonite[18] was prepared from phenylphosphonous dichloride by reaction with ethanol in the presence of dimethylaniline. 1-Chloro-2,3,3,4,4,5,5-heptafluorocyclopentene (I), bp 56–58°, was prepared by the reaction of 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (II) with potassium fluoride in dimethylformamide.[3,4,19] The remainder of the reagents were obtained from commercial sources and used without further purification.

Dimethyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (IIIa).—Trimethyl phosphite (49.6 g, 0.4 mole) was added dropwise over a 30-min period to 91.4 g (0.4 mole) of I, with external cooling as required to maintain the reaction temperature between 25 and 35°. The reaction was exothermic,

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[7] I. L. Knunyants, V. V. Tyuleneva, E. Ya. Pervova, and R. N. Sterlin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1797 (1964).

[8] C. O. Parker [*J. Am. Chem. Soc.*, **81**, 2183 (1959)] gave bp 69° (0.2 mm), $n^{20}\mathrm{D}$ 1.4342, for VI.

[9] An unexpected side reaction between triethylamine and a perfluoro olefin was encountered by K. E. Rapp [*ibid.*, **73**, 5901 (1951)], when the triethylamine was employed as a catalyst in the addition of butyl mercaptan to hexafluorocyclobutene.

[10] A. L. Henne and K. A. Latif [*J. Indian Chem. Soc.*, **30**, 809 (1953)] gave bp 130° (742 mm), $n^{20}\mathrm{D}$ 1.3750, for VIII.

[11] I. L. Knunyants, R. N. Sterlin, V. V. Tyuleneva, and L. N. Pinkina, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1123 (1963).

[12] (a) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (Oct 15, 1946); *Chem. Abstr.*, **41**, 982 (1947). (b) W. T. Miller, Jr., E. W. Fager, and P. H. Griswold, *J. Am. Chem. Soc.*, **70**, 431 (1948). (c) J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *ibid.*, **70**, 1550 (1948).

[13] K. E. Rapp, R. L. Pruett, J. T. Barr, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 3642 (1950).

[14] R. L. Pruett, J. T. Barr, K. E. Rapp, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 3646 (1950).

[15] J. D. Park, L. H. Wilson, and J. R. Lacher, *J. Org. Chem.*, **28**, 1008 (1963).

[16] E. T. McBee, D. L. Crain, R. D. Crain, L. R. Belohlav, and H. P. Braendlin, *J. Am. Chem. Soc.*, **84**, 3557 (1962).

[17] Melting points were determined using a Fisher-Johns apparatus and are corrected. The infrared spectra were taken on a Beckman IR-4 instrument, and the ultraviolet spectra on a Cary Model 14 instrument. The analyses were all carried out in our analytical and instrumental laboratories, with the exception of the C, H, and F analyses on V which were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

[18] G. Kamai, *Zh. Obshch. Khim.*, **18**, 443 (1948); *Chem. Abstr.*, **42**, 7723 (1948).

[19] Pure I has bp 58°, $n^{25}\mathrm{D}$ 1.3244, and contains a strong C=C band in the infrared at 1710 cm^{-1}. The refractive index is quite sensitive to small amounts of II or perfluorocyclopentene which may be present. The physical properties given by J. A. Sedlak [Ph.D. Thesis, The Ohio State University, 1960, p 63] were bp 61.6° (741 mm), C=C band at 5.85 μ (1710 cm^{-1}), while Edelson (ref. 4c, p 116) gave bp 57–58°, $n^{20}\mathrm{D}$ 1.3250.

and a gas (methyl fluoride) was evolved which did not condense in a Dry Ice–acetone trap. Following the addition, the reaction mixture was stirred at room temperature until the exotherm subsided (3 hr) and was then heated briefly to 100°. The product weighed 130.0 g (theoretical wt 127.4 g) and gave a negative test for unreacted phosphite with 0.1 N iodine in benzene. Two distillations gave IIIa as a colorless, fuming liquid, bp 64–66° (4.5 mm), $n^{25}\text{D}$ 1.3817, $d^{20}{}_4$ 1.6669, in 38% yield.

Anal. Calcd for $C_7H_6ClF_6O_3P$: Cl, 11.13; P, 9.73. Found: Cl, 11.1; P, 9.9.

The infrared spectrum of this ester (neat) contained strong bands assigned to P=O (1288 cm^{-1}), P–O–(C) (1055 cm^{-1}), and C=C (1610 cm^{-1}), and the C–F heptad[1,2] (1010, 1104, 1166 1211, 1250, . . ., and 1334 cm^{-1}). The weak C–O–(P) band characteristic of methyl esters of phosphorus was masked by the strong C–F absorption.

Dibutyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (IIIc).—The dibutyl ester IIIc was similarly prepared from I and tributyl phosphite as a viscous, colorless liquid, bp 48–51° (0.0001 mm)(bath temperature), $n^{25}\text{D}$ 1.4091, in 88% yield.

Anal. Calcd for $C_{13}H_{18}ClF_6O_3P$: Cl, 8.81; P, 7.70. Found: Cl, 8.6; P, 8.28.

Its infrared spectrum (in carbon disulfide) contained strong bands assigned to P=O (1280 cm^{-1}), P–O–(C) (1020 cm^{-1}), and C=C (1602 cm^{-1}), and the C–F heptad at 1007, 1097, 1158, 1198, 1240, . . ., and 1332 cm^{-1}.

Diethyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (IIIb).—The reaction of 228.5 g (1.0 mole) of I with 166.0 g (1.0 mole) of triethyl phosphite, following the procedure described above for IIIa, gave 130.4 g of a high-boiling fraction, bp 91–93° (2 mm), which was taken up in ether, washed with water, dried, and redistilled, giving 114.0 g (33%) of IIIb, bp 87–88° (1.8 mm), $n^{25}\text{D}$ 1.3998, identical with the product described in the preceding paper.[1]

Anal. Calcd for $C_9H_{10}ClF_6O_3P$: C, 31.18; H, 2.91; F, 32.89; P, 8.94. Found: C, 31.05; H, 2.92; F, 32.64; P, 9.11.

The low-boiling fractions were combined and redistilled, giving 19.4 g (26%) of a fraction, bp 34–35°, $n^{23}\text{D}$ 1.3532, identified by its odor and physical properties as *diethyl ether,* and 90.5 g (28%) of another fraction, bp 50–51° (1.8 mm), $n^{25}\text{D}$ 1.3818, identified as **ethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonofluoridate (IX).**

Anal. Calcd for $C_7H_5ClF_7O_2P$: C, 26.23; H, 1.57; F, 41.49; P, 9.66. Found: C, 26.25; H, 1.50; F, 41.49; P, 9.96.

The infrared spectrum of this compound (neat) contained strong bands assigned to P=O (1290 cm^{-1}), P–O–(C) (1012 cm^{-1}), and C=C (1623 cm^{-1}), a weak P–F band at 900 cm^{-1}, and the C–F heptad at . . . (masked), 1107, 1170, 1226, 1256, . . . (masked), and 1342 cm^{-1}.

This by-product was consistently obtained in later preparations of IIIb.

2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphenylphosphinic Acid (V).—The reaction of 22.9 g (0.1 mole) of I with 19.8 g (0.1 mole) of diethyl phenylphosphonite, following the procedure described above for IIIa, gave 43.1 g (theoretical wt 39.5 g) of ethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphenylphosphinate (IV) as a crude, low-melting solid, mp 30–42°, which decomposed when distilled at 0.3 mm and resisted efforts at recrystallization.

A portion of the ester (15.9 g, 0.04 mole) was hydrolyzed by boiling with 200 ml of 19% hydrochloric acid for 9 hr. The crystalline solid which separated was collected on a filter, washed with water, and dried, giving 10.3 g (70%) of V, mp 171–172° after two recrystallizations from benzene.

Anal. Calcd for $C_{11}H_6ClF_6O_2P$: C, 37.68; H, 1.73; Cl, 10.11; F, 32.52; P, 8.84; mol wt, 350.6. Found: C, 38.28; H, 1.95; Cl, 9.9; F, 33.02; P, 9.03; neut equiv, 351.

Its infrared spectrum (in Nujol) contained a strong C=C band at 1610 cm^{-1}, a weaker aromatic C=C band at 1589 cm^{-1}, and the C–F heptad at 1006, 1103, 1163, 1207, 1252, 1278, and 1327 cm^{-1}. There were broad, shallow bands at 2150, 2260, and 2500–2600 cm^{-1} (P-OH). The multiplicity of bands in the 1100–1300-cm^{-1} region made an assignment of the P=O band uncertain.

Titration of a 0.03 M aqueous solution of V with 0.1 N sodium hydroxide at 25° gave a curve with a single inflection at pH 5.6. The acid was too strong to permit a calculation of its apparent dissociation constant at this concentration, and not sufficiently soluble in water to permit higher concentrations.

N,N-Dibutyl-2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylamine (VI). A. From I.—Dibutylamine (25.8 g, 0.2 mole) was added dropwise over a 10-min period to a solution of 22.9 g (0.1 mole) of I in 200 ml of ether. Precipitation of dibutylamine hydrofluoride commenced immediately, and the exotherm caused the solution to boil. After an additional 5 min, the reaction subsided. The mixture was allowed to cool and filtered, and the filter cake was washed with ether and dried, giving 13.6 g (91%) of dibutylamine hydrofluoride, mp 101–104°. One recrystallization from acetone gave an analytical sample of mp 100–101°.

Anal. Calcd for $C_8H_{20}FN$: F, 12.73; N, 9.39. Found: F, 13.01; N, 9.45.

This salt is not described in the literature. Its infrared spectrum (in Nujol) contained bands at 742 (s), 807 (m), 926 (s), 1029 (m), 1066 (m), 1148 (w), 1340 (vs), 1405 (s), 1545 (m), 1633 (s), 1975 (vs), 2100 (vs, broad), 2580 (s), 2700 (s) cm^{-1}.

The filtrate and washings were combined and distilled, giving 29.9 g (89%) of VI, bp 73–76° (0.2 mm), $n^{24}\text{D}$ 1.4337, as a bright yellow oil.[8]

Anal. Calcd for $C_{13}H_{18}ClF_6N$: Cl, 10.50; N, 4.15. Found: Cl, 10.2; N, 3.96.

Its infrared spectrum (neat) contained a strong C=C band at 1635 cm^{-1} and the C–F heptad at 1003 (sh), 1115, 1170 (sh), 1187, 1232, 1278, and 1333 cm^{-1}. No fluorinated C=C absorption appeared in either the pure VI or the crude ether residue before distillation. Ultraviolet spectrum (in methanol) showed λ_{max} 258 mμ (ϵ 12,340).

B. From II.—Dibutylamine (258.0 g, 2.0 moles) was added dropwise over a 2.5-hr period to a solution of 122.5 g (0.5 mole) of II in 1000 ml of ether. No exotherm was observed, but the reaction mixture became yellow and cloudy. It was then heated at reflux and filtered from time to time to remove the amine salts. After 76 hr, the reaction appeared to be over. The reaction mixture was concentrated to low volume, filtered, and distilled, giving 142.4 g (84%) of VI as a bright yellow oil, bp 79–82° (0.25 mm), $n^{24}\text{D}$ 1.4328. A comparison of the infrared spectra of the products prepared by the two methods showed that they were identical.

The amine salts obtained in this reaction were collected, washed with ether, and dried, giving 83.0 g (theoretical wt 82.8 g) of dibutylamine hydrochloride, mp 283° dec.[20]

C. Reaction with Excess Dibutylamine.—VI (16.9 g, 0.05 mole) was heated with a tenfold excess (38.7 g, 0.5 mole) of dibutylamine for 6 hr at 156°. No reaction was observed. The VI was recovered unchanged when the dibutylamine was stripped off under vacuum.

Butyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl Sulfide (VII).—Butyl mercaptan (9.0 g, 0.1 mole) was added dropwise over an 11-min period to a solution of 22.9 g (0.1 mole) of I and 10.1 g (0.1 mole) of triethylamine in 100 ml of ether at 25–30°. The precipitation of triethylamine hydrofluoride commenced immediately. After 1 hr, the mixture was filtered and distilled, giving 22.9 g (77%) of VII as a pale yellow liquid, bp 79–81° (10 mm), $n^{25}\text{D}$ 1.4330.

Anal. Calcd for $C_9H_9ClF_6S$: Cl, 11.87; S, 10.73. Found: Cl, 11.84; S, 10.68.

Its infrared spectrum (neat) contained a strong C=C band at 1586 cm^{-1} and the C–F heptad at 1008, 1104, 1150, 1200, 1254, 1286, and 1328 cm^{-1}.

The same product was obtained when the quantities of butyl mercaptan and triethylamine employed in the reaction were doubled.

1-Chloro-2-methoxy-3,3,4,4,5,5-hexafluorocyclopentene (VIII). A. Triethylamine Method.—Methanol (6.4 g, 0.2 mole) was added dropwise over a 30-min period to a solution of 22.9 g (0.1 mole) of I and 10.1 g (0.1 mole) of triethylamine in 100 ml of anhydrous ether, with ice cooling to maintain the reaction temperature between 25 and 30°. After the addition, the reaction mixture, which had separated into two layers, was allowed to stir for 2.5 hr and filtered. Only 0.6 g of salt was obtained. The lower layer was then removed, washed with ether, and discarded. The washings were combined with the upper layer, stripped of solvent, and twice distilled, giving 5.8 g (24%) of VIII[10] as a colorless liquid, bp 130–131°, $n^{25}\text{D}$ 1.3740.

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(20) A. Skita and F. Keil [*Monatsh.*, **53/54**, 753 (1929)] gave mp 283–284° for dibutylamine hydrochloride.

Anal. Calcd for $C_6H_3ClF_6O$: Cl, 14.7. Found: Cl, 13.6.

Its infrared spectrum (neat) contained a strong C=C band at 1671 cm^{-1} and strong absorption in the C–F region at 994, 1007 (doublet), 1070, 1087, 1136, 1143, 1203, and 1288 cm^{-1}.

B. **Potassium Hydroxide Method.**—A solution of 6.5 g (0.1 mole) of 86% potassium hydroxide pellets in 50 ml of methanol was added dropwise over a 30-min period to 22.9 g (0.1 mole) of I in 50 ml of methanol, with ice cooling to maintain the reaction temperature between 25 and 30°. After the addition, the reaction mixture was stirred for 1.5 hr and then poured into 500 ml of water. The product (VIII) was isolated by extraction with ether. One distillation gave 12.0 g (50%) of VIII as a colorless oil, bp 130°, $n^{25}D$ 1.3733.

Anal. Calcd for $C_6H_3ClF_6O$: Cl, 14.7. Found: Cl, 13.7.

Acknowledgment.—The author is indebted to Mr. Leon A. Zengierski for capable technical assistance and to Dr. Charles F. Baranauckas for his guidance and encouragement.

Compounds of Phosphorus and Fluorine. V. Displacement of Chlorine from Diethyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate by Nucleophilic Reagents[1]

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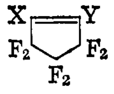
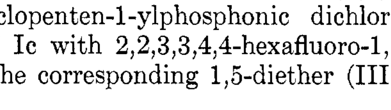
The title compound (Ic) reacts with dibutylamine, ethanol, 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, and aqueous base under very mild conditions giving in each case the product of displacement of the vinylic chlorine atom. The reaction with aqueous base is more complex. The results support a mechanism involving the reversal of polarization of the double bond by the phosphonate group, suggested earlier to explain the displacement of the vinylic chlorine atom in Ic by trialkyl phosphites.

In part III of this series it was shown that a trialkyl phosphite displaces chlorine from diethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (Ic), giving a tetraalkyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate.[2] In fact, this reaction occurs so readily that Ic cannot be prepared directly from 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene (Ia),[3] though Ia gives monosubstitution products with most other nucleophilic reagents.[4] The displacement of the second chlorine atom in compounds of this type is a fairly rare occurrence, having been observed only in the reactions of Ia with potassium fluoride[5] and cuprous mercaptides,[6] and of 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylcarboxamide (I, X = Cl; Y = $CONH_2$) with ammonia, aniline, or lithium aluminum hydride.[7] The chemistry of Ic has therefore been investigated further, particularly with respect to the reactivity of its chlorine atom toward other nucleophilic reagents. The principal compounds to be discussed are the following.



Ia, X = Y = Cl
b, X = Cl; Y = F
c, X = Cl; Y = $P(O)(OC_2H_5)_2$
d, X = Cl; Y = $N(C_4H_9)_2$
II, X = $N(C_4H_9)_2$; Y = $P(O)(OC_2H_5)_2$
IIIa, X = OC_2H_5; Y = $P(O)(OC_2H_5)_2$
b, X = $-OCH_2(CF_2)_3CH_2O-$; Y = $P(O)(OC_2H_5)_2$

Dibutylamine reacted readily with Ic in ether solution at room temperature, giving a quantitative precipitate of dibutylamine hydrochloride and a 64% yield of diethyl 2-dibutylamino-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (II). The converse reaction, between triethyl phosphite and N,N-dibutyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylamine (Id),[1] did not take place even on heating for 6 hr at 154°.



Alcohols also reacted with Ic in ether solution at room temperature, with triethylamine present as an HCl acceptor. The reaction with ethanol gave a 78% yield of diethyl 2-ethoxy-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (IIIa) under conditions very similar to those used for the esterification of 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonic dichloride.[2] The reaction of Ic with 2,2,3,3,4,4-hexafluoro-1,5-pentanediol gave the corresponding 1,5-diether (IIIb) in 91% yield.

The ease with which these reactions took place suggested that Ic might respond to an active chlorine titration. In our laboratories, active chlorine is determined by hydrolyzing a test sample with excess 0.1 *N* sodium hydroxide at room temperature and titrating the released chloride ion with 0.1 *N* silver nitrate. The consumption of sodium hydroxide was considerably in excess of what was expected, but only two-thirds of the chlorine was released (Table I). An active fluorine analysis, in which the released fluoride ion was precipitated as lead chlorofluoride, made up the difference. The Cl:F:NaOH ratio was found to be 1:2:5 (Table I).

TABLE I

ANALYSIS OF Ic FOR ACTIVE HALOGEN

Analysis	Cl	F	NaOH
ml/g	18.7	38.8, 40.3	97.3
Per cent	6.63	7.38, 7.67	...
Equiv/mole	0.65	1.34, 1.39	3.37
Equiv/Cl	1	2.06, 2.13	5.18

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[1] Part IV: A. W. Frank, *J. Org. Chem.*, **31**, 1917 (1966).

[2] Part III: A. W. Frank, *ibid.*, **31**, 1521 (1966).

[3] Part II: A. W. Frank, *ibid.*, **30**, 3663 (1965).

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