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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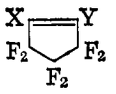
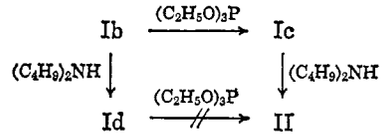
The title compound (Ic) reacts with dibutylamine, ethanol, 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, and aqueous base under very mild conditions giving in each case the product of displacement of the vinylic chlorine atom. The reaction with aqueous base is more complex. The results support a mechanism 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

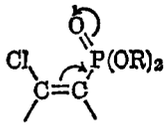
Analysis	Cl	F	NaOH
ml/g	18.7	38.8, 40.3	97.3
Per cent	6.63	7.38, 7.67	...
Equiv/mole	0.65	1.34, 1.39	3.37
Equiv/Cl	1	2.06, 2.13	5.18

(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).
(4) C. O. Parker, *J. Am. Chem. Soc.*, **81**, 2183 (1959), and references therein.
(5) (a) A. Henne, U. S. Patent 3,024,290 (March 6, 1962); *Chem. Abstr.*, **56**, 15333 (1962); (b) J. T. Maynard, *J. Org. Chem.*, **28**, 112 (1963).
(6) A. Ferretti and G. Tesi, *Chem. Ind.* (London), 1987 (1964).
(7) T. Mill, J. O. Rodin, R. M. Silverstein, and C. Woolf, *J. Org. Chem.*, **28**, 836 (1963).

The complexity of the reaction of Ic with hydroxide ion is perhaps to be expected, for the replacement of Cl by OH creates a vinyl alcohol which can rearrange to a ketone and then release hydrogen fluoride. The 1:2:5 ratio is best explained as a series of successive displacements of Cl, F, and F at C-2, C-5, and C-5, followed by a haloform cleavage at each carbonyl group. An attempt to isolate the intermediate diketone, diethyl 2,5-dioxo-3,3,4,4-tetrafluoro-1-cyclopentylphosphonate, by a reaction of Ic with water and triethylamine in ether solution was unsuccessful.

In contrast to Ic, the corresponding acid, 3,3,4,4,-5,5-hexafluoro-1-cyclopenten-1-ylphosphonic acid[2] [I, X = Cl; Y = $P(O)(OH)_2$], releases neither chloride nor fluoride on treatment with base. The chlorine atom in the acid is stable.

The foregoing experiments show that the displacement of chlorine from dialkyl 2-chloroperfluoro-1-cycloalken-1-ylphosphonates is not limited to trialkyl phosphites but takes place with nucleophilic reagents in general. The factor which makes this possible is believed to be the placement of the electron-withdrawing $P(O)(OR)_2$ substituent on C-1, as suggested in part II.[3] The function of the phosphonate group is to effect



a reversal of the polarization of the double bond, so that the attack of the nucleophile is at C-2 instead of C-1.

In principle, it should be possible to accomplish this polarization reversal with a variety of other electron-withdrawing groups such as C=O, C≡N, S→O, SO_2, N→O, etc. One such example is the carboxamide derivative referred to earlier.[7] Its reactivity was explained as being due to the greater conjugative capacity of the carboxamide group relative to chlorine. This explanation is not incompatible with the principle stated here.

Experimental Section[8]

Reagents.—The Ic used in all of this work, with the exception of the dibutylamine reaction, was the high-boiling fraction, bp 91–93° (2 mm), $n^{24}D$ 1.3988, obtained in the reaction of Ib with triethyl phosphite.[1] The product used in the dibutylamine reaction was from an earlier preparation with similar properties. Triethyl phosphite and 2,2,3,3,4,4-hexafluoro-1,5-pentanediol were Hooker products. The remainder of the reagents were obtained from other commercial sources and used without further purification.

(8) Melting points were determined using a Fisher-Johns apparatus and are corrected. The infrared spectra were taken on a Beckman IR-4 instrument. The analyses were performed in our analytical and instrumental laboratories, with the exception of the C, H, and F analyses which were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Diethyl 2-Dibutylamino-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (II). A. From Ic.—Dibutylamine (12.9 g, 0.1 mole) was added dropwise over a 20-min period to a solution of 17.3 g (0.05 mole) of Ic in 200 ml of anhydrous ether. The temperature rose to 37° during the addition and crystals of the amine salt separated. The crystals were collected on a filter, washed with ether, and dried, giving 8.8 g (theoretical wt 8.3 g) of dibutylamine hydrochloride,[9] mp 284° (the hydrofluoride[1] melts at 100–101°). The filtrate and washings were combined and distilled, giving 14.0 g (64%) of II as a yellow oil, bp 136–138° (0.2 mm), $n^{25}D$ 1.4428.

Anal. Calcd for $C_{17}H_{28}F_6NO_3P$: C, 46.47; H, 6.42; N, 3.19; P, 7.05. Found: C, 46.48; H, 6.44; N, 3.49; P, 6.83; Cl, 0.2.

The infrared spectrum of II (neat) contained strong bands at 1590 (C=C), 1260 (P=O), and 1024 cm^{-1} (P–O–(C)), and the C–F heptad[3] at 1008 (sh), 1120, ..., 1184, 1230, 1288, and 1340 cm^{-1}.

B. From Id.—A mixture of 10.1 g (0.03 mole) of Id[1] and 5.0 g (0.03 mole) of triethyl phosphite was heated in a small reflux assembly for 6 hr at reflux (154°). The iodine titer of the phosphite did not change and a test of fluoride ion with cerous nitrate was negative.

Diethyl 2-Ethoxy-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (IIIa).—A mixture of 17.3 g (0.05 mole) of Ic, 5.1 g (0.05 mole) of triethylamine, and 100 ml of anhydrous ether was treated dropwise over a 2-min period at room temperature with 4.6 g (0.1 mole) of anhydrous ethanol. After 2-hr. stirring, the solid which precipitated was collected on a filter, washed with ether, and dried, giving 5.9 g (87%) of triethylamine hydrochloride,[10] mp 243–250° (*Anal.* Calcd: Cl, 25.6. Found: Cl, 24.0.). The filtrate and washings were combined and distilled, giving 13.8 g (78%) of IIIa, bp 122–124° (3.5 mm), $n^{25}D$ 1.4049, fp −78°.

Anal. Calcd for $C_{11}H_{15}F_6O_4P$: C, 37.09; H, 4.24; F, 32.00; P, 8.70. Found: C, 36.10; H, 4.06; F, 33.41; P, 8.80; Cl, nil.

The infrared spectrum of IIIa (neat) contained strong bands at 1620 (C=C), 1275 (P=O), and 1020 cm^{-1} (P–O–(C)), and the C–F heptad at ..., 1105, ..., 1196, 1242, ..., and 1338 cm^{-1}. The bands[3] at 1010, 1155 and 1293 cm^{-1} were masked by stronger absorption.

1,5-Bis(2-diethoxyphosphinyl-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yloxy)-2,2,3,3,4,4-hexafluoropentane (IIIb).—A similar reaction between 34.7 g (0.1 mole) of Ic, 10.6 g (0.05 mole) of 2,2,3,3,4,4-hexafluoro-1,5-pentanediol, and 10.1 g (0.1 mole) of triethylamine in 200 ml of anhydrous ether gave 12.3 g (90%) of triethylamine hydrochloride and 40.4 g (91%) of IIIb as a pale yellow oil. A portion of this product was distilled in a Hickman molecular still at 125–160° (0.007 mm), giving an analytical sample, $n^{25}D$ 1.4039.

Anal. Calcd for $C_{23}H_{24}F_{18}O_8P_2$: C, 33.17; H, 2.91; F, 41.09; P, 7.44. Found: C, 33.04; H, 2.91; F, 39.91; P, 7.37.

The infrared spectrum of IIIb (neat) contained strong bands at 1640 (C=C), 1280 (P=O), and 1037 cm^{-1} (P–O–(C)), and strong C–F absorption in the 1000–1350-cm^{-1} region.

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.

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

(10) L. Wagner [*Z. Krist.*, **43**, 148 (1907)] gave mp 253–254°, subl 245°; *Beilstein*, **H IV**, 101.