centered at 1.8 ppm (J_{gem} = 11–12 cps, $J_{1a,6a}$ = 9 cps). The remaining ring protons and the side-chain methylene protons produced an overlapping series of patterns downfield (3.3–4.2 ppm) which have not been analyzed, but appeared to contain a badly perturbed one-proton triplet (3.85 ppm, sum of J = 5–6 cps), and a two-proton narrow multiplet at about 4.04 ppm (not appreciably broadened at 100 Mc/sec).

The spectrum in pyridine (internal TMS) at 60 and 100 Mc proved more useful (see Figure 2); a trace of deuterium oxide was added to cause exchange of hydroxylic protons. The multiplet of the tertiary proton H-1 was now cleanly separated from the ring-methylene proton signals at 100 Mc/sec, but not at 60 Mc/sec (see introductory section.) The equatorial ring-methylene proton produced a pair of triplets at 2.0 ppm (J_{gem} = 12 cps, J_{vic} = 3 to 4 cps). The axial ring-methylene proton produced a pattern centered at 2.40 ppm, consisting of a trio of doublets, on which two additional low-intensity lines were superimposed near the central lines (J_{gem} = 12 cps, J_{aa} = 12–13 cps, J_{ae} = 2.0–2.5 cps). The side-chain methylene spectrum (protons not equivalent) was observed as an eight-line pattern, consisting of two perturbed sets of four lines centered at 4.07 (J_{gem} = 10 cps, J_{vic} = 5.5 cps) and 4.27 ppm (J_{gem} = 10 cps, J_{vic} = 7 cps).

The remaining pyridine spectrum (4.4–4.9 ppm) has not been fully analyzed, but appears to include (1) a quartet at 4.68 ppm, shown by double resonance[18,19] experiments to correspond to H-5; (2) a perturbed triplet probably due to H-3 or H-4 at 4.5 ppm (J about 3 cps); and (3) an unresolved multiplet at 4.78 ppm probably broadened by long-range couplings (width at half-height about 6 cps), which may be produced by an equatorial proton (H-2 or H-4).

DL(1234/5) Diastereomer of 1-Triphenylmethoxymethyl-2,3,4,5-cyclohexanetetrol Tetraacetate (Pseudo-α-DL-talopyranose Trityl Ether Tetraacetate) (13).—A solution of 50 mg of the pentol and 80 mg of triphenylmethyl chloride in 1.5 ml of dry pyridine was kept at 25° for 36 hr. Acetic anhydride (0.15 ml) was added, and the solution was again kept for 36 hr. The orange solution was poured into a mixture of ice and water (stir 30 min). The precipitate was collected and dried.

This material was recrystallized from 2-propanol–petroleum ether, giving an 80-mg (50%) yield of colorless product, mp 174–175°. This product was recrystallized for analysis from 2-propanol–ethanol (3:1), giving 60 mg of product, mp 175–176°.

Anal. Calcd for $C_{34}H_{36}O_9$: C, 69.37; H, 6.16. Found: C, 69.01; H, 6.06.

Similar treatment of 0.6 g of the pentol gave a 1.5-g (76%) yield of once-recrystallized product, mp 174–175°.

The pmr spectrum was observed at 60 Mc/sec in chloroform-*d*. Aromatic signals (15 protons) were observed at 7.1–7.5 ppm. Acetate methyl singlets appeared at 2.10, 2.01, 1.92, and 1.83 ppm (three protons each). The side-chain methylene protons produced a doublet at 3.08 ppm (J about 7 cps), whose degree of perturbation indicated location of the tertiary proton H-1 signal at about 2.5 ppm. The ring-methylene protons produced a pattern at 1.55–1.80 ppm. The AcO–C*H* spectrum (H-2, H-3, H-4, and H-5) resembled that of compounds **10** and **12** (see above), and consisted of a poorly defined one-proton triplet at 5.52 ppm (J about 3 cps), and a three-proton pattern at 4.8–5.3 ppm.

Infrared Spectra.—The spectrum for each intermediate and product, using potassium bromide pellets, was recorded with a Perkin-Elmer Model 137 Infracord spectrometer, and in each case was consistent with the assigned structure.

Acknowledgment.—This research was made possible by a generous grant (CA-07250) to the University of San Francisco from the National Cancer Institute, Public Health Service. We wish to thank Professor Edward E. Smissman, University of Kansas, and Professor Henry Z. Sable, Western Reserve University, for helpful discussions.

Compounds of Phosphorus and Fluorine. III. Preparation of Mono- and Diphosphonate Derivatives from Tetraethyl 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate[1]

ARLEN W. FRANK

Research Center, Hooker Chemical Corporation, Niagara Falls, New York 14302

Received December 1, 1965

A diphosphonic acid, 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonic acid (II), and a monophosphonic acid, 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonic acid (V), were prepared from a common intermediate, the title compound Ia, and converted to various derivatives. Noteworthy reactions were (1) a C–P bond cleavage which occurred when Ia was treated with phosphorus pentachloride and which provided the access to the monophosphonate derivatives; (2) an ester dealkylation which occurred when Ia was refluxed in ethanol; and (3) the preparation of an unsymmetrical diphosphonate (Ib) by the reaction of diethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (VI) with tributyl phosphite.

The preparation of tetraalkyl perfluoro-1-cycloalken-1,2-ylenediphosphonates from trialkyl phosphites and 1,2-dichloroperfluorocycloalkenes was described in part II of this series.[1] The present paper is concerned with their reactions. A key step in this work was a reaction in which a cleavage of one of the C–P bonds occurred, providing an entry to a class of compounds, the 2-chloroperfluoro-1-cycloalken-1-ylphosphonates, which were not directly accessible from the 1,2-dichloroperfluorocycloalkenes.

The relationships between the various compounds described in this paper are sketched in Chart I.

An attempt to prepare 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonic tetrachloride (III) directly from tetraethyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ia) by reaction with phosphorus pentachloride, a reaction often used for the preparation of dichlorides of phosphonic acids,[2] gave a single product identified by its analyses and chemical reactions as 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonic dichloride (IV), a product containing only one C–P bond. Fairly forcing conditions were used, but under milder conditions the reaction was incomplete. If III had indeed been formed, it must have reacted further with the phosphorus pentachloride, probably through an exchange of chlorine for oxygen and thermal decomposition of the resulting tetrachlorophosphorane.[3] The presence of phosphorus trichloride in the distillate confirmed this.

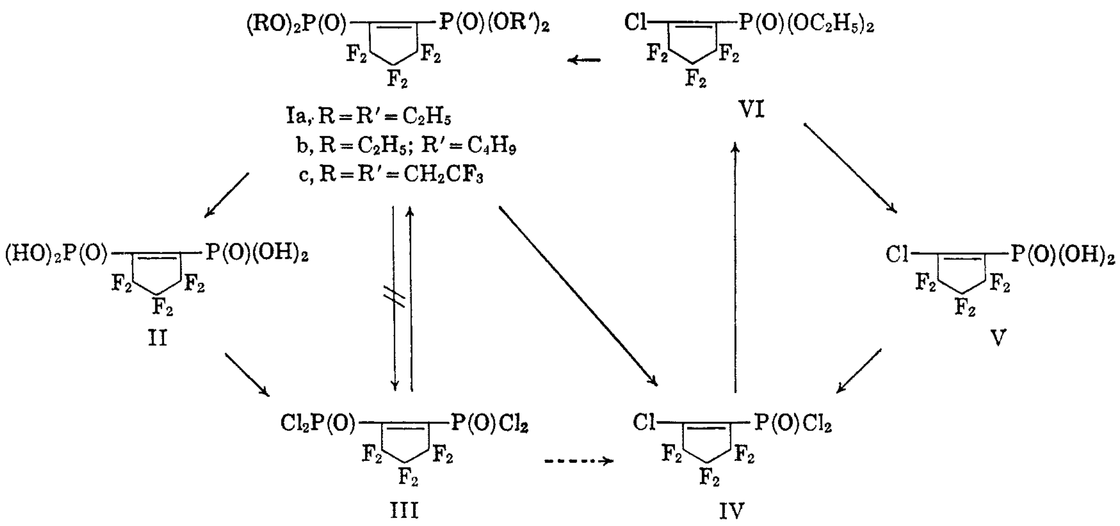
---

(1) Part II: A. W. Frank, *J. Org. Chem.*, **30**, 3663 (1965).

(2) See, *e.g.*, its use with diethyl ω-hydroperfluoroalkylphosphonates: N. O. Brace, *ibid.*, **26**, 3197 (1961).

(3) For recent examples of the thermal cleavage of fluoroalkyl tetrachlorophosphoranes, see G. M. Burch, H. Goldwhite, and R. N. Haszeldine, *J. Chem. Soc.*, 1083 (1963).

CHART I



The reaction may be thought of as occurring in the following stages.[4]

$$\text{Ia} + 4\text{PCl}_5 \longrightarrow \text{III} + 4\text{POCl}_3 + 4\text{C}_2\text{H}_5\text{Cl}$$

$$\text{III} + \text{PCl}_5 \longrightarrow \text{IV} + \text{PCl}_3 + \text{POCl}_3$$

The identity of IV was established by hydrolysis with water to 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-yl-phosphonic acid (V), mp 107–109°, and by esterification with ethanol and triethylamine to diethyl 2-chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (VI). Hydrolysis of VI with hydrochloric acid gave the same acid, V.

The monophosphonate ester VI was a presumed intermediate in the preparation of Ia from triethyl phosphite and 1,2-dichloro-3,3,4,4,5,5-hexafluorocyclopentene.[1] It should, therefore, react readily with triethyl phosphite to give Ia, or with other trialkyl phosphites to give unsymmetrical diphosphonate esters. An experiment with tributyl phosphite confirmed this. The reaction of VI with tributyl phosphite gave an 84% yield of *unsym* dibutyl diethyl 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ib) in just 15 min at 120°.

The diacid chloride III was finally prepared in two steps *via* the diacid, 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonic acid (II). Hydrolysis of Ia with hydrochloric acid gave a quantitative yield of II, a very hygroscopic solid, mp 194–199° dec. Attempts to prepare II by thermal dealkylation of the ester[5] Ia were unsuccessful as the product was not stable at the 250° temperature required for the dealkylation.

The diacid II was recovered unchanged after treatment with thionyl chloride at room temperature or at reflux, but with phosphorus pentachloride a 65% yield of III was obtained, together with 25% of IV. Some cleavage occurred even though the temperature did not exceed 76° at any point in the reaction. Compound III was obtained as a high-boiling liquid which crystallized on cooling: mp 78.5–81.5°.

Esterification of III with trifluoroethanol gave tetrakis(2,2,2-trifluoroethyl) 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ic) in 51% yield. An attempt to prepare the dithio analog of III by exchange of oxygen for sulfur with P_4S_{10}[6] was unsuccessful.

A qualitative measure of the effect of the fluorine substitution on the alkylating power of the phosphonate ester groups was obtained in a reaction between Ia and ethanol. The ester (Ia) required 72 hr of refluxing in ethanol for complete conversion to *sym* diethyl dihydrogen 3,3,4,4,5,5-hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (VII, not shown in Chart I). Under these conditions, diethyl trichloromethylphosphonate was converted to ethyl hydrogen trichloromethylphosphonate in 26 hr, but diethyl ethylphosphonate and diethyl acetylphosphonate were unaffected.[7]

The monophosphonate and diphosphonate derivatives were clearly differentiated by their infrared spectra. The monophosphonate derivatives all contained a strong C=C band at about 1640 cm^{-1}, but the diphosphonate derivatives, *including the unsymmetrical ester Ib*, showed no trace of absorption in the double bond region. Since the only feature common to all of the diphosphonate derivatives—Ia, Ib, Ic, II, III, and VII—was the presence of two P=O groups on the double bond, the absence of C=C bands in their infrared spectra must be due to a dampening effect of the P=O groups on the stretching vibration of the double bond.

Experimental Section[8]

2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonic Dichloride (IV).—Phosphorus pentachloride (876 g; 4.2 moles) was added in portions to 448 g (1.0 mole) of Ia[1] at 75–100° at a rate sufficient to maintain a vigorous evolution of ethyl chloride. When the evolution of gas subsided (14 hr), the mixture was distilled at atmospheric pressure until most of the phosphorus oxychloride was removed. The distillate gave a positive iodine test for P(III). The temperature was then raised to 140°, and more phosphorus pentachloride was added from time to time until

---

[4] The intermediacy of III was not proved, but a C–P bond cleavage at some other stage, *e.g.*, to give VI, seemed less likely.

[5] A. E. Canavan, B. F. Dowden, and C. Eaborn, *J. Chem. Soc.*, 331 (1962).

[6] E. Uhing, K. Rattenbury, and A. D. F. Toy, *J. Am. Chem. Soc.*, **83**, 2299 (1961).

[7] A. W. Frank, *J. Org. Chem.*, **29**, 3706 (1964).

[8] Melting points were determined using a Fisher-Johns apparatus, and are corrected. The infrared spectra were taken on a Beckman IR-4 spectrophotometer. The C, H, and F analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

either no more ethyl chloride evolution could be induced[9] or phosphorus oxychloride distilled. The reaction mixture was cooled to 70°, purged with sulfur dioxide and then with nitrogen, and distilled, giving 140.5 g (45%) of IV, bp 49–50° (0.6 mm), n^{24}_{D} 1.4299.

Anal. Calcd for $C_5Cl_3F_6OP$: Cl (t),[10] 32.5; Cl (h), 21.7; P, 9.4. Found: Cl (t), 32.6; Cl (h), 22.7; P, 9.04.

The infrared spectrum of this product (neat) contained a strong P=O band at 1302 cm^{-1}, a strong C=C band at 1600 cm^{-1}, and the C–F heptad[1] at 1009, 1102, 1168, 1213, 1237, 1285, and 1340 cm^{-1}.

Further distillation gave a second fraction, 12.0 g, bp 53–64° (0.7 mm), n^{24}_{D} 1.4352, leaving only 7.1 g of residue. The balance of the reaction products were more volatile than IV.

2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonic Acid (V). A. From IV.—The acid chloride IV (32.8 g; 0.1 mole) was added dropwise to 200 ml of water over a 25-min period at 25–30° with external cooling, heated to boiling for 15 min to complete the hydrolysis, and then stripped to dryness under vacuum. The residue (30.3 g; calcd 29.0 g) was recrystallized three times from carbon tetrachloride, giving the acid, V, as a hygroscopic, crystalline solid, mp 107–109°.

Anal. Calcd for $C_5H_2ClF_6O_3P$: C, 20.67; H, 0.69; Cl, 12.22; P, 10.06; mol wt, 290.51. Found C, 20.77; H, 0.87; Cl (t), 12.6; P, 10.26; neut equiv, 288.90.

The acid was soluble in water, ethanol, and acetone, and insoluble in benzene, hexane, and chloroform. Titration of a 0.03 *M* aqueous solution of the acid with 0.1 *N* sodium hydroxide at 25° gave a curve with inflections at pH 3.3 and 8.8 (Figure 1). The apparent dissociation constants (p*K'*), calculated from points along the titration curve,[11] were —, 5.10.

The infrared spectrum of V (in Nujol) contained a P=O band at 1130 cm^{-1}, a strong C=C band at 1618 cm^{-1}, and the C–F heptad at 1010, 1104, 1163, 1212, 1250, 1288, and 1341 cm^{-1}. In this compound and in the other monophosphonate derivatives, the 1250-cm^{-1} band was not a doublet, as it was in the diphosphonates.

The acid was converted to its anilinium salt by adding aniline dropwise to a portion of V in acetone: mp 222.5–224°, after recrystallization from ethanol.

Anal. Calcd for $C_{11}H_9ClF_6NO_3P$: N, 3.65. Found: N, 3.72.

The infrared spectrum of this salt (in Nujol) contained a strong P=O band at 1147 cm^{-1}, a P–OH band at 2600 cm^{-1}, a sharp C=C band at 1618 cm^{-1}, and the C–F heptad at 1005, 1100 and 1115 (doublet), 1160 sh, 1207, 1255, 1285, and 1336 cm^{-1}.

B. From VI.—The ester VI (58.0 g; 0.17 mole) was added dropwise over a 45-min period to 500 ml of boiling 19% hydrochloric acid, heated at reflux until the gas evolution subsided (75 min), and then stripped to dryness under vacuum. The residue (50.0 g) was a liquid. Its infrared spectrum and analysis (Found: Cl, 10.8; P, 10.5) indicated that the hydrolysis was incomplete. Further refluxing for 5 hr with 400 ml of 19% hydrochloric acid gave a semisolid mass from which V was isolated as a crystalline solid, mp 97–99° after four recrystallizations from carbon tetrachloride.

Anal. Calcd for $C_5H_2ClF_6O_3P$: Cl, 12.22; mol wt, 290.51. Found: Cl (t), 11.7; Cl (h), nil; neut equiv, 283.

Diethyl 2-Chloro-3,3,4,4,5,5-hexafluoro-1-cyclopenten-1-ylphosphonate (VI).—To a solution of 4.6 g (0.1 mole) of anhydrous ethanol and 10.1 g (0.1 mole) of triethylamine in 100 ml of dry ether was added 16.4 g (0.05 mole) of IV over a 30-min period at 25–30°. Another 100 ml of ether was added to facilitate stirring. After 1 hr, the mixture was filtered and distilled, giving 14.7 g (85%) of VI, bp 90–92° (1.5 mm), n^{24}_{D} 1.4010.

Anal. Calcd for $C_9H_{10}ClF_6O_3P$: Cl, 10.23; P, 8.94. Found: Cl (t), 10.3; P, 8.62.

The infrared spectrum of this ester (neat) contained a strong P=O band at 1288 cm^{-1}, a strong P–O–(C) band at 1020 cm^{-1}, a sharp C=C band at 1610 cm^{-1}, and the C–F heptad at — (masked), 1100, 1163, 1205, 1244, — (masked), and 1340 cm^{-1}.

unsym **Dibutyl Diethyl 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ib).**—Tributyl phosphite (12.5 g; 0.05 mole) was added dropwise over a 15-min period to 17.3 g (0.05 mole) of VI which had been preheated to 120°. The reaction was exothermic. Distillation of the product gave 1.5 g of butyl chloride,[12] bp 76.5–78°, n^{23}_{D} 1.3991 (which, together with 1.8 g, n^{23}_{D} 1.4001 recovered from the trap after distillation, brought the yield to 72.5%), and 21.1 g (84%) of Ib, bp 150–152° (0.35 mm), n^{23}_{D} 1.4208.

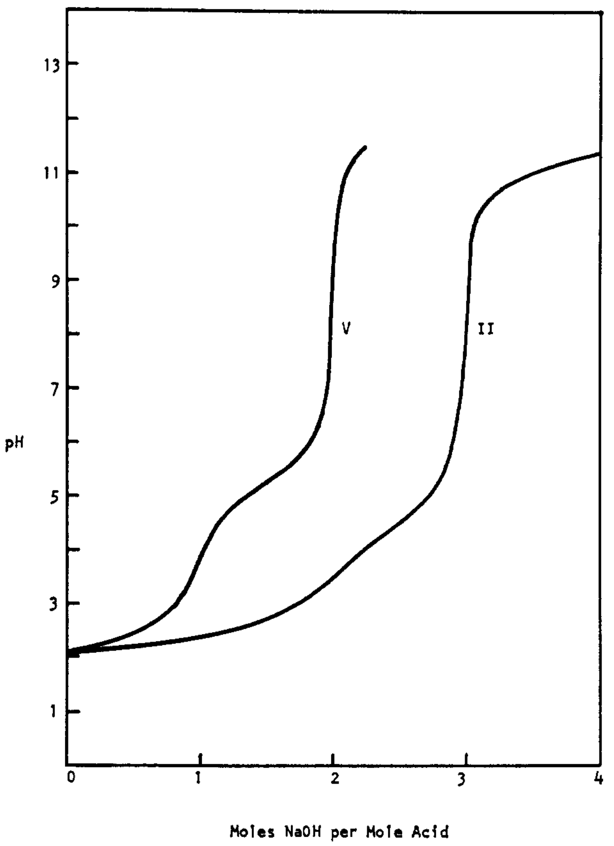


Figure 1.—Titration of phosphonic acids with 0.1 *N* sodium hydroxide.

Anal. Calcd for $C_{17}H_{28}F_6O_6P_2$: C, 40.48; H, 5.60; Cl, nil; F, 22.60; P, 12.28. Found: C, 40.28; H, 5.81; Cl (t), 0.1; F, 22.87; P, 12.2.

The infrared spectrum of this product (neat) contained a P=O band at 1282 cm^{-1}, a broad P–O–(C) band at 1020 cm^{-1}, and the C–F heptad at — (masked), 1100, 1155, 1200, 1237 and 1255 (doublet), — (masked), and 1343 cm^{-1}.

3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonic Acid (II).—The tetraethyl ester Ia[1] (448 g; 1.0 mole) was added over a 6-hr period to 4000 ml of boiling 19% hydrochloric acid contained in a 12-l. flask equipped with a mechanical stirrer, a dropping funnel, and a reflux condenser. The progress of the reaction was followed by observing the evolution of ethyl chloride through a bubbler attached to the top of the condenser. After the addition, heating was continued until the gas evolution subsided (8 hr). The solution was then stripped to dryness, leaving the acid, II, as an extremely hygroscopic, crystalline solid. After drying to constant weight in a vacuum desiccator over phosphorus pentoxide, it weighed 334 g (99.5% yield): mp 194–199° dec.

Anal. Calcd for $C_5H_4F_6O_6P_2$: P, 18.5; Cl, nil. Found: P, 17.6; Cl (t,h), nil.

The acid was soluble in polar solvents (water, ethanol, acetone, ether) and insoluble in hydrocarbon solvents (hexane, benzene) or chlorinated hydrocarbon solvents (methylene chloride, chloroform, carbon tetrachloride). Attempts to recrystallize it from various solvent pairs or by vacuum sublimation were unsuccessful. Titration of 0.03 *M* aqueous solution of II with 0.1 *N* sodium hydroxide at 25° gave a curve with a minor inflection at pH 2.8 and a major inflection at pH 8.2, corresponding to the 0.5 and 0.75 point in the titration, respectively (Figure 1). The apparent dissociation constants (p*K'*) for the four acid groups, calculated from points along the titration curve,[11] were —, —, 4.24, and 11.98.

---

[9] When this step was omitted, the product was low in chlorine and its infrared spectrum contained strong C–H absorption.

[10] Analysis for chlorine: t = total, h = hydrolyzable.

[11] C. Tanford and S. Wawzonek, "Technique of Organic Chemistry," Vol. I, Part 4, A. Weissberger, Ed., 3rd ed, Interscience Publishers, Inc., New York, N. Y., 1960, p 2953–2957.

[12] A. I. Vogel, *J. Chem. Soc.*, 636 (1943), gave bp 78.0° (762 mm), n^{20}_{D} 1.40223, for butyl chloride.

The infrared spectrum of II (in Nujol) contained a P=O band at 1152 cm^{-1} and the C–F heptad at 998, 1100, — (masked), 1214, 1242 and 1260 (doublet), 1295, and 1348 cm^{-1}.

The acid was converted to its dianilinium salt by adding aniline dropwise to a portion of the acid in acetone; mp 267° dec, after recrystallization from ethanol.

Anal. Calcd for $C_{17}H_{18}F_6N_2O_6P_2$: C, 39.09; H, 3.47; N, 5.36. Found: C, 38.83; H, 3.34; N, 5.47.

The infrared spectrum of this salt (in Nujol) contained a P=O band at 1154 cm^{-1}, a P–OH band at 2645 cm^{-1}, and the C–F heptad at 998, 1095, — (masked), 1180, 1246 and 1256 (doublet), 1293, and 1343 cm^{-1}.

3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonic Tetrachloride (III).—A solution of 114.0 g (0.34 mole) of II in 500 ml of phosphorus oxychloride was treated with 298.0 g (1.43 mole) of phosphorus pentachloride in portions over a 30-min period at 30–40°. Gas evolution was brisk. The temperature was then raised gradually to 76°, and when the gas evolution subsided (3.5 hr) the solvent was stripped off under vacuum. The pot temperature was not allowed to rise above 70° during the stripping. The residue, 139.5 g, which was partly solid, gave on distillation 11.6 g of a fraction, bp 52–55° (1.3 mm), 16.6 g of an intermediate fraction, bp 53–58° (1.3–0.8 mm), $n^{26}D$ 1.4313, and 90.2 g of a fraction, bp 89–90° (0.45 mm). The low-boiling fraction, bp 52–55° (1.3 mm), $n^{26}D$ 1.4281, was identified by analysis and by its infrared spectrum as IV (25% yield).

Anal. Calcd for $C_5Cl_3F_6OP$: Cl (t), 32.5; Cl (h), 21.7. Found: Cl (t), 32.0; Cl (h), 22.6.

The high-boiling fraction, bp 89–90° (0.45 mm), was the desired III (65% yield). It crystallized on cooling: mp 78.5–81.5°.

Anal. Calcd for $C_5Cl_4F_6O_2P_2$: Cl, 34.6; P, 15.1. Found: Cl (t), 33.2; Cl (h), 33.3; P, 15.2.

The infrared spectrum of this product (in carbon tetrachloride) contained a P=O band at 1303 cm^{-1} and the C–F heptad at 1007, 1096, 1168, 1213, 1246 and 1272 (doublet), — (masked), and 1332 and 1342 (doublet) cm^{-1}.

Tetrakis(2,2,2-trifluoroethyl) 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (Ic).—A solution of 29.8 g (0.073 mole) of III in 100 ml of benzene was treated dropwise with 29.1 g (0.291 mole) of trifluoroethanol over a 24-min period at room temperature. Hydrogen chloride began to evolve during the addition and subsided after 7 hr of stirring at room temperature. The solvent was stripped off under vacuum, leaving 43.1 g of residue which gave on distillation a small forecut, 2.2 g, followed by 24.6 g (51%) of Ic: bp 84–86° (0.1 mm), $n^{24}D$ 1.3591, fp −28°. The undistilled residue was substantial.

Anal. Calcd for $C_{13}H_8F_{18}O_6P_2$: Cl, nil; P, 9.3. Found: Cl (t), 1.6; P, 9.2.

The infrared spectrum of this product (neat) contained a P=O band at 1280 cm^{-1}, a much-displaced P–O–(C) band at 1070 cm^{-1}, and the C–F heptad at 1012, 1102, 1166–1200 (not resolved), 1243 and 1260 sh (doublet), 1300, and 1348 cm^{-1}.

***sym* Diethyl Dihydrogen 3,3,4,4,5,5-Hexafluoro-1-cyclopenten-1,2-ylenediphosphonate (VII).**—A solution of 44.8 g (0.1 mole) of Ia[1] in 750 ml of anhydrous ethanol was heated to reflux in a distillation apparatus. Distillate was drawn off only as required to maintain the vapor temperature at 78°. When no further depression in the vapor temperature was observed (72 hr), the remainder of the ethanol was stripped off under vacuum, leaving 40.5 g (calcd 39.2 g) of VII as a slightly yellow, viscous liquid.

Anal. Calcd for $C_9H_{12}F_6O_6P_2$: P, 15.8; mol wt, 392. Found: P, 15.2; neut equiv, 416.

The infrared spectrum of this product (neat) contained a P=O band at 1157 cm^{-1}, three broad, shallow P–OH bands at 1600, 2200, and 2650 cm^{-1}, and the C–F heptad at 1010, 1100, — (masked), 1205, 1239–1252 (not resolved), 1295, and 1343 cm^{-1}.

The acid ester was converted to its bis(dicyclohexylammonium) salt by adding dicyclohexylamine to a portion of VII in acetone. No immediate reaction was observed, but crystals separated on standing overnight: mp 221–222° after one recrystallization from ethanol.

Anal. Calcd for $C_{33}H_{58}F_6N_2O_6P_2$: N, 3.71; P, 8.21. Found: N, 4.15; P, 8.09.

The infrared spectrum of this salt (in Nujol) contained a P=O band at 1215 cm^{-1} and the C–F heptad at 1006, 1100 sh, 1132, 1145 sh, 1200 sh, 1242, 1292, and 1340 cm^{-1}.

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.

Rates of Alkaline Hydrolysis of *meta*- and *para*-Substituted Ethyl β-Phenylpropionates and Correlation with σ^0 [1]

RICHARD FUCHS AND JOSEPH A. CAPUTO

Department of Chemistry, University of Houston, Houston, Texas 77004

Received November 1, 1965

A series of twenty *meta*- and *para*-substituted ethyl β-phenylpropionates have been prepared, and the rates of alkaline hydrolysis in 87.8% ethanol at 30° have been measured. The rates generally follow the σ^0 values for the substituents estimated from other reactivities and from F^{19} nmr shielding in similar solvents. The unexpectedly high rate of the m-$(CH_3)_3N^+$ compound may be due to a direct, short-range electrostatic interaction in the transition state for hydroxide ion attack of the ester.

Although the rates of alkaline hydrolysis of several *meta*- and *para*-substituted ethyl β-phenylpropionates had previously been reported,[2,3] the present, more extensive study was carried out with the following objectives: (1) to furnish an extensive group of σ^0 data (appropriate to benzene derivatives lacking direct resonance interactions between substituent and functional group[4]) based on a single reactivity series in one solvent, for comparison with values obtained from assorted reactivities[4] and from F^{19} nmr shifts;[5] (2) to establish σ^0 values for certain disubstitutions (3,4-methylenedioxy- and 3,4-dichloro-) which give readily purified, crystalline derivatives in a number of series; and (3) to determine the σ^0 values for the charged substituents *m*- and *p*-$(CH_3)_3N^+$.[6] The results are given in Table I.

The value of ρ is +0.63. This is based on six *meta* substituents having nearly invariant σ values.[7] The original value[3] of 0.591, based on *meta* and *para* sub-

---

[1] The support of this work by the Robert A. Welch Foundation under Grant E-136 is gratefully acknowledged.

[2] K. Kindler, *Ann.*, **452**, 90 (1927).

[3] R. Fuchs and J. J. Bloomfield, *J. Org. Chem.*, **28**, 910 (1963).

[4] R. W. Taft, S. Ehrenson, I. C. Lewis, and R. E. Glick, *J. Am. Chem. Soc.*, **81**, 5352 (1959).

[5] R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *ibid.*, **85**, 709, 3146 (1963).

[6] Values have been reported based on nmr data[5] but not on reactivities, nor in the solvent 87.8% ethanol.

[7] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).