in vacuo, the oily residue was treated with benzene (3 \times 70 ml), and the solvent was removed in vacuo after each addition.

The residue was dissolved in hexane and, upon standing, a crystalline product (23.6 g, m.p. 91.3-93.3°) was collected; a second crop (14.0 g, m.p. 60.3-83.2°) was also obtained. Recrystallization of the first crop from chloroform yielded 1b: m.p. 96.8–98.3°;² λ_{max} (*p*-dioxane) 224 m μ (ϵ 74.5); v_{max} (chloroform) 3571, 3425 (O—H stretching),² 1736 cm⁻¹ (ester carbonyl). Anal. Calcd. for C₂₈H₅₂O₈: C, 65.09; H, 10.14.

Found: C, 65.25; H, 10.27.

After refluxing 1b in 95% ethanol for 2 h, and two recrystallizations from the same solvent, 1a was obtained: m.p. 44.8-46.1°; λ_{max} (*p*-dioxane) 224 (ε 39.7), 274.5 mμ (ϵ 19.8); v_{max} (chloroform) 3509 (O—H stretching), 1736 cm⁻¹ (ester and ketone carbonyl).

Anal. Calcd. for C14H26O4: C, 65.09; H, 10.14. Found: C, 65.18; H, 10.27.

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Nucleophilic displacement of vinylic halogen in fluorinated cycloalkenes. II. **Reaction with triphenylphosphine**

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1,2-Dichloroperfluorocyclobutene and the corresponding cyclopentene react with triphenylphosphine under hydrolytic conditions in wet acetic acid to yield novel triphenyl(fluorocycloalkenyl)phosphonium betaines. Structural assignments are made on the basis of elemental analysis, ¹H and ¹⁹F nuclear magnetic resonance spectra, infrared spectra, and degradation studies. Triphenylphosphine and 1,2-dichloroperfluorocyclohexene yield triphenylphosphine oxide and a product which appears to be 1-chloro-2hydrooctafluorocyclohexene

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Displacement of both vinyl chlorines from the olefins 1a-c with trialkyl phosphites, phosphonites, and phosphinites yields products substituted in the 1- and 2-positions with phosphorus (1). Depending on the type of nucleophile used,



certain secondary phosphines or diphosphines were reported to yield either mono- or disubstitution products (2).

It has now been found that reaction of triphenylphosphine with 1a and 1b in acetic acidwater yields the triphenylphosphonium betaines 2a and 2b, respectively, in low yield (3). These are the phosphorus analogues of the quaternary ammonium betaines 3 obtained when the nucleophile is tertiary amino nitrogen (4a-c). The structures 2 are assigned on the basis of elemental analysis, molecular weight, infrared, ¹H and ¹⁹F

²The melting point and the O-H stretching frequencies reported for 1 in our preceding paper (1) are indicative of a monomer-dimer mixture.

nuclear magnetic resonance spectra, and oxidation of 2b to the expected dicarboxylic acid with CrO_3 .

The infrared spectra of the betaines 2 in the $1540-1820 \text{ cm}^{-1}$ region were quite similar to those of 3b of the same ring size (4a). Strong bands were present in 2a at 1779, 1669, and 1637 cm⁻¹ for the O_C_C_C_C_O system, while in 2b a strong band was present at 1653 cm⁻¹, with much weaker absorption at 1721 and 1686 cm⁻¹.

Absorptions due only to aromatic protons at δ 7.56–7.95 and 7.52–7.95 p.p.m., respectively, were present in the ¹H spectra of **2***a* and **2***b* (acetone-*d*₆, TMS as internal reference). The ¹⁹F spectrum of **2***a* in dimethyl formamide (relative to internal CFCl₃) consisted of a doublet at δ +118.1 p.p.m., *J*_{PF} = 20.5 Hz; the chemical shift for **2***b* in the same solvent was at δ +127.2 p.p.m., *J*_{PF} = 1.1 Hz. These chemical shifts are very close to those of the corresponding **3***b*¹ and a related system studied by Stockel and co-workers

(5). The larger J_{PF} in 2a relative to that in 2b may result from strong through-space coupling, reflecting the highly strained nature of the four-membered ring (6).

Neither 2a nor 2b decolorized bromine in CCl₄ or permanganate in acetone, and neither reacted with *m*-nitrobenzaldehyde after 18 h in refluxing tetrahydrofuran. With methyl iodide for 7 h in refluxing acetone 2a and 2b were unreactive, as was 2b with refluxing 50% sulfuric acid for 15 h.

Upon refluxing 2a with concentrated HCl for 15 h and recrystallizing the product from ethanol-acetone-water, there was obtained a material of empirical formula $C_{21}H_{17}F_2OP$, to which the structure 4 is assigned on the basis of its infrared and ¹H nuclear magnetic resonance spectra. A pair of strong bands at 1587 and 1562 $\rm cm^{-1}$ is indicative of the proposed betaine structure (7): no absorption due to OH or C=O stretch was evident. In the nuclear magnetic resonance spectrum (dimethyl sulfoxide- d_6), absorption was present at δ 4.12 (PCH, doublet, $J_{PH} = 22$ Hz) (8), 5.98 (CF₂H, triplet, $J_{\rm FH} = 56$ Hz), and at 7.38–7.93 p.p.m. (aryl H). The peaks of the doublet and triplet were broad, possibly because of allylic couplings. Integration of the spectrum was in fair agreement with that expected for 4. Stereochemistry about the C=C bond was not assigned.



In contrast to the behavior of 1a and 1b with triphenylphosphine, 1c gave an 81% yield of triphenylphosphine oxide but no product analogous to 2 was isolated. Distillation of the reaction mixture prior to phosphine oxide isolation gave a mixture of acetic acid, unchanged 1c, and a material having infrared absorption at 1658 cm⁻¹ in CCl₄ and a complex multiplet at δ 6.45



p.p.m. in its ¹H nuclear magnetic resonance spectrum. Although difficulties in separation prevented full characterization, spectral data for the latter compound are in accord with 1-chloro-2hydrooctafluorocyclohexene, **5**, which reportedly

¹D. F. Keeley, private communication.

has C==C absorption at 1660 cm⁻¹ (9). A reason for the apparent change in mode of attack by phosphorus is not known at this time.

Experimental

The olefins 1a and 1c were obtained from Peninsular ChemResearch, Inc.² 1b was from either the latter source or Hooker Chemical Corporation. Triphenylphosphine was a product of Eastman Kodak.

Infrared spectra were obtained from KBr disks with a Perkin–Elmer model 137 spectrophotometer (NaCl optics). The nuclear magnetic resonance spectra were recorded on Varian spectrometer models A-60A and HR-60 (56.4 MHz).

Triphenyl(3,3-difluoro-2-hydroxy-4-oxo-1-cyclobuten-

1-yl)phosphonium Hydroxide, Inner Salt (2a)

A mixture of 5.85 g (0.03 mole) of 1*a* and 8.66 g (0.033 mole) of triphenylphosphine in 50 ml of acetic acid and 2 ml of water was refluxed for 3 h. The gaseous products gave positive tests for F^- and Cl^- . After refluxing, about 10 ml of the mixture were distilled at 100–116° but gas-liquid partition chromatography (g.l.p.c.) analysis indicated only solvent and traces of other compounds. The remainder of the reaction mixture was poured into about 150 ml of water and ice and the precipitate was filtered and washed with water, 6.71 g, m.p. ca. 120–200°. The solid was washed with two 25 ml portions of ethanol, followed by 25 ml of ether, to give 3.27 g (29%) of 2*a*, m.p. 228–233°. Recrystallization from acetone–water gave an analytical sample, m.p. 230–231°.

Anal. Calcd. for $C_{22}H_{15}F_2O_2P$ (mol. wt., 380): C, 69.47; H, 3.98; F, 9.99; P, 8.14. Found (mol. wt., 375 osmometric in acetone): C, 69.67; H, 3.97; F, 9.59; P, 8.18.

The combined ethanol and ether washes were evaporated and the residue washed with petroleum ether, b.p. $30-60^\circ$. The soluble fraction yielded 1.13 g (13% recovery) of triphenylphosphine (mixture m.p. and infrared spectrum); the insoluble fraction yielded 0.56 g of the crude betaine and 0.75 g (9%) of crude triphenylphosphine oxide (m.p. and infrared spectrum).

2a could be distilled unchanged (92% recovery) in a sublimation apparatus at 3-3.5 mm, bath temperature 285-295°.

Triphenyl (3,3,4,4-tetrafluoro-2-hydroxy-5-oxo-1-cyclo-

penten-1-yl)phosphonium Hydroxide, Inner Salt (2b) A mixture of 7.08 g (0.027 mole) of triphenylphosphine and 6.12 g (0.025 mole) of 1b was refluxed for 20 h in 50 ml of acetic acid containing 1 ml of water. Distillation of the reaction mixture until the vapor temperature was about 117° gave no starting material; on g.l.p.c. analysis only acetic acid and an impurity originally present in the olefin were noted. After pouring the distillation residue into water and ice, a dark emulsion formed and was coagulated by heating on a steam cone. The tarry semisolid was recrystallized twice from ethanol–water to yield 3.75 g (35%) of product, m.p. 173–174°. Further recrystallization gave a product melting mostly at $176-178^\circ$, but with some melting at 166° . If the melted material was cooled rapidly with ice and then placed in the bath preheated to 165° , it melted at $181-182^\circ$. Allowing the melt to cool slowly to room temperature in the bath gave a solid, m.p. $175-176^\circ$. The infrared spectra of all the forms were identical.

Anal. Calcd. for $C_{23}H_{15}F_4O_2P$ (mol. wt., 430): C, 64.19; H, 3.51; F, 17.66; P, 7.20. Found (mol. wt., 422 osmometric in acetone): C, 64.34; H, 3.62; F, 17.81; P, 7.34.

The tarry, semisolid residue obtained from the filtrate of the first recrystallization of 2b was chromatographed in benzene on a column of Alcoa F-20 alumina and eluted with ethanol and acetone. From the eluate there was obtained 2.15 g of a solid, m.p. 148–153°, which yielded 0.51 g (7%) of triphenylphosphine oxide (infrared spectrum), m.p. 156–157°, and some tar.

Evaporation of the original reaction mixture filtrate gave a few grams of tarry material.

Oxidation of 2b with CrO_3

A solution of 3.01 g (0.007 mole) of 2b in acetic acid at 75–80° was treated with a solution of 2.00 g (0.02 mole) of CrO_3 in acetic acid and water and held at 75–80° for 30 min. From this solution was obtained 1.14 g (38%) of recovered 2b and 0.54 g (40%) of perfluorosuccinic acid, m.p. 88–90° (from benzene). Identification of this acid was by means of infrared spectrum and neutralization equivalent.

Reaction of 2a with HCl

A stirred slurry of 1.14 g (0.003 mole) of 2a in 30 ml of concentrated HCl was refluxed 15 h, cooled, filtered, and the product was washed with tetrahydrofuran and acetone, 0.63 g. It had no sharp melting point and gave a positive test for Cl⁻ with silver nitrate, but upon recrystallization from ethanol – acetone – water, colorless needles of a chlorine-free product, m.p. 210–211° (decomp.), were obtained.

Anal. Calcd. for C₂₁H₁₇F₂OP: C, 71.18; H, 4.84; F, 10.72; P, 8.74. Found: C, 70.89; H, 4.83; F, 10.50; P, 8.63.

The infrared spectrum of the tetrahydrofuran- and acetone-washed product was quite different from that of the recrystallized material. Strong bands at 1587 and 1562 cm⁻¹ in the latter were absent in the former; very broad and strong absorption at about 3226 cm⁻¹ in the initial product was absent in the recrystallized solid.

Reaction of 1c with Triphenylphosphine

A mixture of 7.38 g (0.025 mole) of 1c and 7.08 g (0.027 mole) of triphenylphosphine in 50 ml of acetic acid containing 1 ml of water was refluxed for 43 h. Positive tests for \tilde{F}^- and Cl^- were obtained on the effluent gases. About 20 ml were distilled from the mixture and the distillate was dried over sodium sulfate and redistilled. A fraction weighing 5.68 g was collected at 83-84°. Gasliquid partition chromatographic analysis indicated about 21% starting olefin and about 75% of an unknown component, in addition to minor peaks. An infrared spectrum of this mixture in CCl₄ showed C=O at 1721 (acetic acid), C=C at 1658 (5), and C=C at 1626 cm⁻¹ (1c). Further washing with water and redistillation removed the acetic acid; the ¹H nuclear magnetic resonance spectrum (CCl₄) showed a broad multiplet at δ 6.45 p.p.m., in addition to signals due to ether used in the work-up.

²Mention of a product or company name does not imply endorsement by the Department to the exclusion of others which may also be suitable.

The residue from the first distillation was diluted with water to give 6.88 g of solid which yielded 5.63 g (81%) of triphenylphosphine oxide and 0.79 g (11% recovery) of crude triphenylphosphine, both of which were identified by comparison of their infrared spectra with those of authentic samples.3

Acknowledgments

¹H nuclear magnetic resonance spectra were recorded by Gordon J. Boudreaux of this Laboratory and the ¹⁹F spectra were obtained through the courtesy of Dr. Dean F. Keeley and Judith A. O'Connor, University of Southwestern Louisiana, Lafayette, Louisiana. Elemental analyses

Anal. Calcd. for C₆HClF₈: Cl, 13.61; F, 58.34. Found: Cl, 13.39; F, 57.80.

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New nitrochalcones. IX¹

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A number of new nitrohydroxychalcones are reported. Electron-donating groups in the aldehyde favor condensation by HCl, and electron-withdrawing substituents favor condensation by NaOH.

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A number of chalcones have been synthesized from acetophenones and benzaldehydes and the yields compared. Table I lists the results of condensations carried out in the presence of NaOH. The substituents in the aldehyde component increase the yield of chalcone formation in aqueous ethanol in the following way:

2,3-diOMe \gtrsim 2,5-diOMe > H > 2-OMe > 2,4-diOMe

Table II records the results of experiments carried out in ethanol in the presence of HCl. The order of effectiveness of reactants with substituents other than ortho can be established as follows:

4-OH \gtrsim 4-OMe \gtrsim 3-OMe-4-OH > 3,4-diOMe

 \approx 3,4-diOEt \gtrsim 4-Me > H > 4-Cl > 4-NO₂ > 2,4-diNO₂

and for ortho substituents:

2,4-diOMe \gtrsim 2-OMe > H > 2,3-diOMe = 2,5-diOMe

¹For Part VII see ref. 4a and for Part VIII see ref. 10,

On page 1254, in the left-hand column, the order of effectiveness of reactants with substituents should read 4-Cl > H and not H > 4-Cl.

The yields show a rough parallelism with Hammett's substituents constants (1), and with basicities (pK_{BH^+}) (2). These results are in accordance with earlier observations (3-5). It can be concluded that electron-donating substituents favor condensation by acid catalysts and that electron-withdrawing groups favor condensation by bases. The choice of condensing agent for the synthesis of chalcones can generally be decided on this basis.

Experimental

Aldehydes and acetophenones were obtained from Aldrich Chemical Co. Inc.; Columbia Organic Chemical Co.; and from Distillation Products. After having checked their purity most of them were used without further purification. Nitrohydroxyacetophenones were prepared as described earlier (4). Syntheses of chalcones in the presence of NaOH were the same as previously reported (4). The acidic condensation was carried out as follows.

An ethanolic solution of the appropriate acetophenone and aldehyde was kept ice-cold while being saturated with HCl gas for 30 min. It was kept in a thermostat at 30° for 1 h, and after allowing it to stand at room temperature



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³Note Added in Proof: While this note was in press a report (10) appeared which substantially confirmed the present results, although the transformation of 1c into 5 went unnoticed. In the present work the formation of 5 was confirmed by analysis of a sample obtained by preparative gas-liquid chromatography.