TABLE IV

ANALYTICAL RESULTS FROM PURE ETHYNYLCARBINOLS

Parent ketone	B.p., °C.	M.p., °C.	Assay, %
Cyclohexanone	178	32–33	99.5 ± 0.1
Diisopropyl ketone	163–165	. . .	98.7 ± 0.2
Acetophenone	85 (3 mm.)	. . .	99.2 ± 0.1
2-Butanone	119–121	. . .	99.5 ± 0.1
2-Cyclohexylcyclohexanone	115 (1 mm.)	. . .	98.3 ± 0.2
Methyl vinyl ketone	50–51 (54 mm.)	. . .	99.9 ± 0.1
2-Octanone	72–73 (4 mm.)	. . .	99.9 ± 0.1
1-Indanone	. . .	70.1	99.9 ± 0.1
9-Fluorenone	. . .	107	98.4 ± 0.1

C. Procedure for Ketone Determinations.—A weighed sample of solution to be analyzed was placed in a 400-ml. beaker containing 200 ml. of water and equipped with a pH meter and magnetic stirrer. The solution was neutralized to pH 4.00 with 0.1 *N* hydrochloric acid and 0.8 *N* hydroxylamine hydrochloride was added (10 ml. per 40-ml. titration). The liberated hydrochloric acid was back-titrated with 0.1 N sodium hydroxide.

This method was applied to cyclohexanone, acetone, cyclopentanone, 2-butanone, 3-pentanone, and 2-octanone.

Acknowledgment.—We wish to thank Dr. Ralph G. Verdieck for determining the dielectric constants and John G. Maroski for his assistance in carrying out many of the analyses.

Fluoro Ketones. II. Reactions with Trialkyl Phosphites

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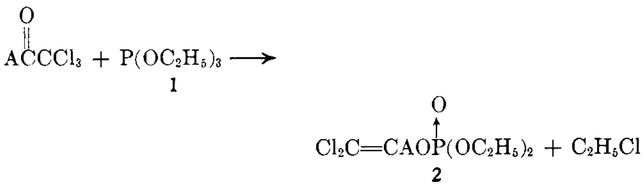
sym-Dichlorotetrafluoroacetone and *sym*-difluorotetrachloroacetone have been found to undergo the Perkow reaction with trialkyl phosphites to give the corresponding dialkyl perhaloisopropenyl phosphate and alkyl chloride. Perfluoro ketones undergo a new reaction with trialkyl phosphites to yield alkyl enol ethers of the ketones and dialkyl phosphorofluoridate.

The reaction of α-halogenated aldehydes, ketones, esters, and amides with phosphites containing at least one alkyl ester group yields vinyl phosphates.[1–3] For example, the reaction of chloral[2,3] or trichloroacetophenone[2] with triethyl phosphite (**1**) yields the dichlorovinyl esters **2** and ethyl chloride.

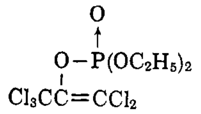


$$\mathrm{A\overset{O}{\overset{\|}{C}}CCl_3 + \underset{\mathbf{1}}{P(OC_2H_5)_3} \longrightarrow \underset{\mathbf{2}}{Cl_2C{=}CAO\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2} + C_2H_5Cl}$$

A = C_6H_5 or H

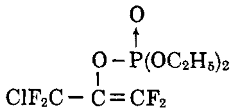
This paper describes some examples of reaction of alkyl phosphites with perhalogenated ketones and the abnormal reaction products from perfluorinated ketones.

When hexachloro-, *sym*-dichlorotetrafluoro-, or *sym*-difluorotetrachloroacetone react with triethyl phosphite, the corresponding diethyl perhaloisopropenyl phosphates (**3**, **4**, and **5**) are formed along with ethyl chloride. Interestingly, no ethyl fluoride was formed in the latter two reactions. With 3 moles of trimethylphosphite, hexachloro-1,3,5-cyclohexanetrione[4] gave the aromaticized product **6**. The isopropenyl phosphates are sensitive to water, react with bromine, and appear to undergo S_N2' reactions with anions such as iodide and cyanide.



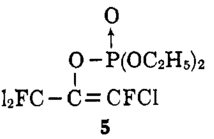
3

$$\mathrm{Cl_3C\overset{O-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2}{C}{=}CCl_2}$$



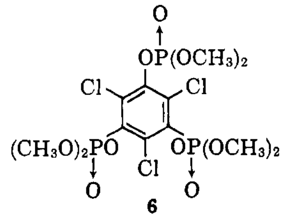
4

$$\mathrm{ClF_2C-\overset{O-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2}{C}{=}CF_2}$$



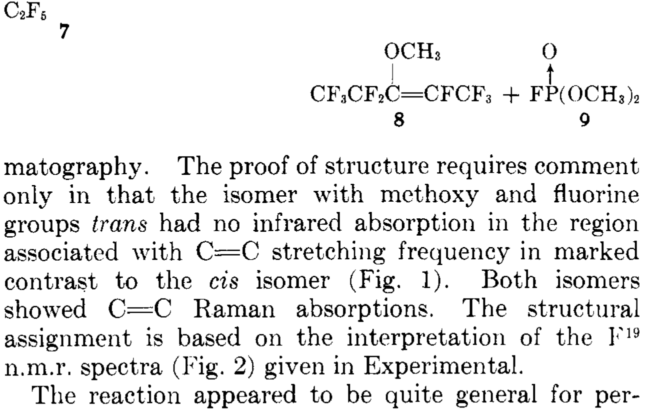
5

$$\mathrm{Cl_2FC-\overset{O-\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2}{C}{=}CFCl}$$



6

Surprisingly, the perfluorinated ketones were found to react exothermically at 0° with trialkyl phosphites with no alkyl fluoride evolution to give the alkyl enol ether of the starting ketone and a dialkyl phosphorofluoridate. For example, perfluoro-3-pentanone (**7**) reacted with trimethyl phosphite to give 3-methoxyperfluoro-2-pentene (**8**) and dimethyl phosphorofluoridate (**9**). The enol ether **8** was obtained as a 1:1 mixture of *cis* and *trans* isomers, separable by gas chromatography. The proof of structure requires comment only in that the isomer with methoxy and fluorine groups *trans* had no infrared absorption in the region associated with C=C stretching frequency in marked contrast to the *cis* isomer (Fig. 1). Both isomers showed C=C Raman absorptions. The structural assignment is based on the interpretation of the F^{19} n.m.r. spectra (Fig. 2) given in Experimental.



$$\mathrm{\underset{\mathbf{7}}{(C_2F_5)_2C{=}O} + P(OCH_3)_3 \longrightarrow \underset{\mathbf{8}}{CF_3CF_2\overset{OCH_3}{\overset{|}{C}}{=}CFCF_3} + \underset{\mathbf{9}}{F\overset{O}{\overset{\uparrow}{P}}(OCH_3)_2}}$$

The reaction appeared to be quite general for perfluoro ketones giving enol ethers with perfluoro-4-hep-

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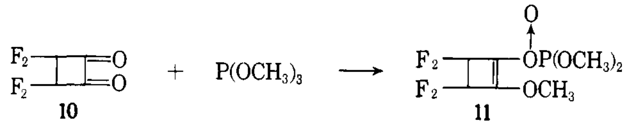
[1] F. Cramer, *Angew. Chem.*, **72**, 236 (1960); F. N. Lichtenhaler, *Chem. Rev.*, **61**, 607 (1961).

[2] M. S. Kharasch and I. S. Bengelsdorf, *J. Org. Chem.*, **20**, 1356 (1955).

[3] W. Perkow, *Ber.*, **87**, 755 (1954).

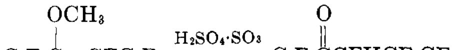
[4] T. Zincke and O. Kegel, *ibid.*, **22**, 1467 (1889).

tanone and hexafluoroacetone. Perfluorobutyraldehyde gave a low yield of the corresponding enol ether, and hexafluorocyclobutanone[5] gave the known 1-methoxypentafluorocyclobutene.[6] However, tetrafluoro-1,2-cyclobutanedione (**10**)[5] underwent an addition reaction with trimethyl phosphite to give **11**. The structure of **11** was assigned on the basis of its n.m.r. and infrared spectra.[7]



10 **11**

The enol ether **12** of perfluoro-4-heptanone could be hydrolyzed with fuming sulfuric acid to give α-hydroperfluoro-4-heptanone (**13**), thus giving an over-all reduction of an α-fluorine in a perfluoro ketone with trialkyl phosphite.

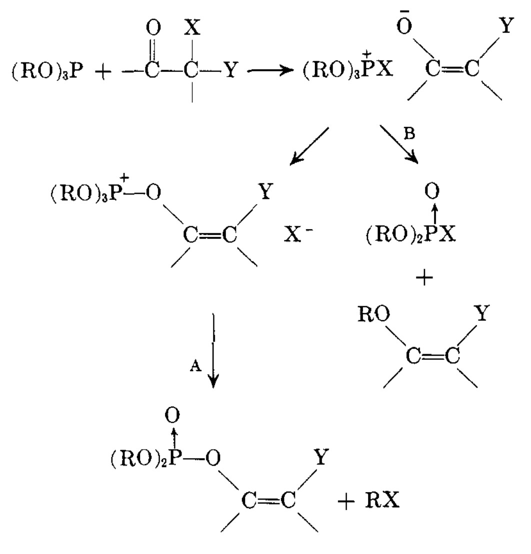


$$C_3F_7\overset{OCH_3}{\overset{|}{C}}{=}CFC_2F_5 \xrightarrow{H_2SO_4 \cdot SO_3} C_3F_7\overset{O}{\overset{\|}{C}}CFHCF_2CF_3$$

12 **13**

Although several mechanisms have been proposed for the reaction of α-chloro and α-bromo ketones with trialkyl phosphites, the recent studies of Hoffmann and Diehr[8] support path A in Scheme I.

Scheme I



This scheme suggests initial attack on halogen forming a resonance-stabilized anion and $(RO)_3PX^+$, which has precedent in the formation of pentachlorocyclopentadienide ion from hexachlorocyclopentadiene and triethyl phosphite.[9] When X = Cl and Y = Cl or F, attack must occur preferentially at X, and reaction proceeds *via* path A. When X = Y = F, the cation in the initially formed enolate complex now possesses the stronger P–F bond, and displacement at carbon rather than phosphorus occurs (path B).

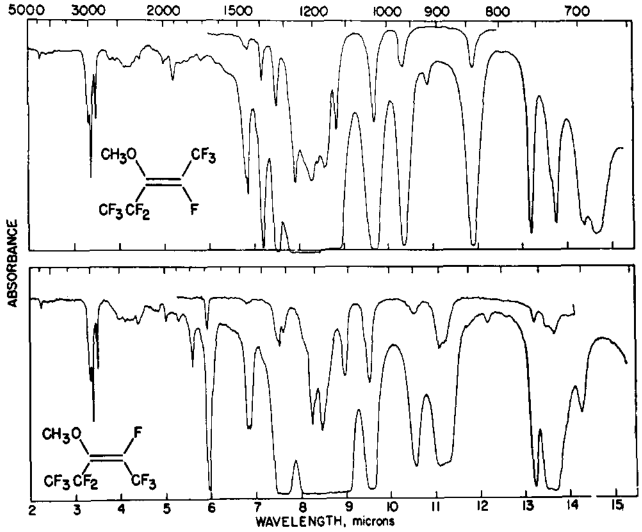


Fig. 1.—Infrared spectra of *cis*- and *trans*-3-methoxyperfluoro-2-pentene.

Experimental

sym-Difluorotetrachloroacetone and *sym*-dichlorotetrafluoroacetone were obtained from General Chemical Division, Allied Chemical and Dye Corp., Morristown, N. J., and were used without further purification. Perfluoro-4-heptanone and perfluoro-3-pentanone were prepared by the method of Wiley.[10] The phosphite esters were distilled just prior to use. *Caution. Many substituted vinyl phosphates are powerful cholinesterase inhibitors and are, therefore, highly toxic.*

3-Chloro-1,1,3,3-tetrafluoroisopropenyl Diethyl Phosphate (4).[11] —*sym*-Dichlorotetrafluoroacetone (50 g., 0.25 mole) was placed in a flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. The flask was cooled with an ice–water bath, and 42 g. (0.25 mole) of triethyl phosphite was added dropwise with vigorous stirring. The rate of addition was adjusted to maintain gentle reflux, and ethyl chloride was evolved. The reaction mixture was allowed to stand overnight at room temperature and then was distilled directly. There was obtained 61.0 g. (81%) of **3-chloro-1,1,3,3-tetrafluoroisopropenyl diethyl phosphate** (4), b.p. 69–71° (4 mm.), $n^{25}D$ 1.3880.

Anal. Calcd. for $C_7H_{10}ClF_4O_4P$: C, 28.0; H, 3.4; F, 25.3. Found: C, 28.9; H, 3.8; F, 24.5.

The halogen-substituted isopropenyl phosphates are colorless oils, which produce marked respiratory effects on inhalation and should be considered toxic. Difficulties were encountered in securing acceptable analyses of the isopropenyl phosphates, which hydrolyzed readily with traces of moisture. The structures were assigned on the basis of the infrared and fluorine n.m.r. spectra. 3-Chloro-1,1,3,3-tetrafluoroisopropenyl diethyl phosphate showed bands in the infrared spectrum assignable to the terminal difluoromethylene (1767) and to the phosphate (1040 cm.⁻¹) groups.

In a similar manner, *sym*-difluorotetrachloroacetone and triethyl phosphite gave **1,3-difluoro-1,3,3-trichloroisopropenyl diethyl phosphate** (5), b.p. 81–82° (0.25 mm.), $n^{25}D$ 1.4437, in 80% yield. The infrared spectrum showed C=C at 1680 and phosphate at 1030 cm.⁻¹ (broad).

Anal. Calcd. for $C_7H_{10}Cl_3F_2O_4P$: C, 25.2; H, 3.0; F, 11.4. Found: C, 25.3; H, 2.7; F, 12.1.

Hexachloroacetone and triethyl phosphite gave **1,1,3,3,3-pentachloroisopropenyl diethyl phosphate** (3), b.p. 131–132° (0.8 mm.), $n^{25}D$ 1.4954, in 60% yield. The infrared spectrum showed C=C at 1600 and phosphate at 1010 cm.⁻¹ (broad). Pentachloroisopropenyl trichloroacetate shows similar C=C absorption (1603 cm.⁻¹).[12]

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[5] D. C. England, *J. Am. Chem. Soc.*, **83**, 2205 (1961).

[6] J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950).

[7] However, see V. A. Kukhtin, K. M. Kirillova, R. R. Shagidullin, Y. Y. Samilov, N. A. Lyazina, and N. F. Rakova, *J. Gen. Chem. USSR* (Eng. Transl.), **32**, 2020 (1962).

[8] H. Hoffmann and H. J. Diehr, *Tetrahedron Letters*, 583 (1962).

[9] V. Mark, *ibid.*, 295 (1961).

[10] D. W. Wiley, U. S. Patent 3,091,643 (1963).

[11] The reactions of the chlorofluoro ketones with trialkyl phosphites were carried out in conjunction with Dr. J. J. Drysdale.

[12] W. M. Wagner, H. Kloosterziel, and A. F. Bickel, *Rec. trav. chim.*, **81**, 933 (1962).

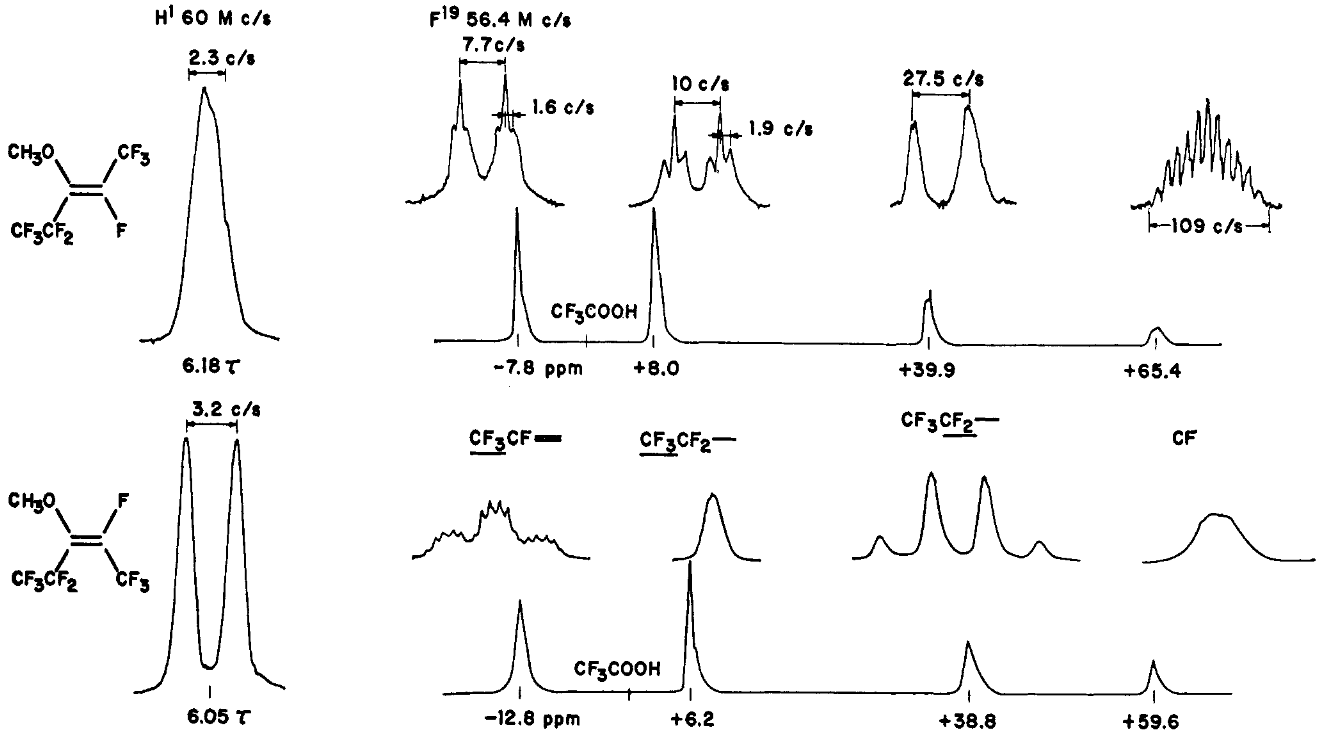

Fig. 2.—N.m.r. spectra of *cis*- (high boiling) and *trans*-3-methoxyperfluoro-2-pentene (low boiling). Enlarged regions are not drawn to same scale.

Anal. Calcd. for $C_7H_{10}Cl_5O_4P$: C, 22.9; H, 2.8. Found: C, 22.1; H, 2.8.

The fluorine and proton n.m.r. spectra of the isopropenyl phosphates were examined cursorily. The gross patterns were consistent with the assigned structures; however, no detailed analyses were attempted.

2,4,6-Trichlorophloroglucinoltris(dimethyl phosphate) (6).—2,2,4,4,6,6-Hexachloro-1,3,5-cyclohexanetrione, m.p. 48–49°, was prepared by the method of Zincke and Kegel.[4] The trione (20.0 g., 0.060 mole) was dissolved in anhydrous ether (50 ml.) in the apparatus described for the reactions of the chlorofluoro ketones. Trimethyl phosphite (22.3 g., 0.180 mole) was added over 1 hr., and after the exothermic reaction had subsided the mixture was allowed to stir at 25° for 48 hr. Evaporation of the ether gave a red crystalline mass, which was recrystallized from benzene to give 27.5 g. (83%) of the colorless **2,4,6-trichlorophloroglucinoltris(dimethyl phosphate)** (6), m.p. 155°.

Anal. Calcd. for $C_{12}H_{18}O_{12}Cl_3P_3$: C, 26.00; H, 3.28; Cl, 19.22. Found: C, 26.03; H, 3.37; Cl, 18.94.

The infrared spectrum of 6 showed aromatic C=C at 1565 and phosphate at 1050 cm.$^{-1}$ (broad). Hydrolysis of 6 with dilute base gave a good yield of trichlorophloroglucinol.

4-Methoxyperfluoro-3-heptene (12).—Trimethyl phosphite (5.58 g., 0.045 mole) was added to 18.30 g. (0.050 mole) of perfluoro-4-heptanone at a rate which maintained the vigorous reaction at reflux. After the addition was complete (30 min.), the colorless solution was heated to reflux (110°) for 15 min. The resulting liquid was then distilled to give 14.9 g. (91%) of 12, b.p. 104-109°, $n^{25}\mathrm{D}$ 1.2989, and 5.4 g. (95%) of dimethyl phosphorofluoridate (9), b.p. 150°, $n^{25}\mathrm{D}$ 1.3527 [lit.[13] b.p. 150.1° (759 mm.), $n^{23.8}\mathrm{D}$ 1.3540]. (*Caution! Extremely toxic.*) Redistillation of the olefin 12 gave 12.1 g. of pure 4-methoxyperfluoro-3-heptene, b.p. 105–106°, $n^{25}\mathrm{D}$ 1.2983.

Anal. Calcd. for $C_8H_3F_{13}O$: C, 26.5; H, 0.8; F, 68.2. Found: C, 26.7; H, 1.1; F, 68.2.

In a similar fashion using a Dry Ice condenser, 143 g. (0.537 mole) of perfluoropentanone was treated with 69 g. (0.556 mole) of trimethyl phosphite to give on distillation through a Heligrid column (736 mm.) a combined yield of 124 g. (88%) of *cis*- and ***trans*-3-methoxyperfluoro-2-pentene**. The lower boiling fractions, b.p. 69–71°, were predominantly (85%) one isomer, whereas the higher boiling fractions, b.p. 75–76°, were predominantly (95%) the other isomer. The ratio of the two isomers as determined by gas chromatography was essentially 1:1. Analytical samples were obtained by preparative gas chromatography using a column of 20% w./w. tetrakis(1H,1H,5H-octafluoropentyl and 1H,1H,7H-dodecafluoroheptyl) pyromellitate on 40–60-mesh firebrick at 50°; *trans* isomer, $n^{25}\mathrm{D}$ 1.290, d_{25} 1.453; and *cis* isomer, $n^{24.5}\mathrm{D}$ 1.298, d_{25} 1.504.

The infrared (Fig. 1) and Raman spectra of the higher boiling (*cis*) isomer showed strong absorption for C=C at 1690 and 1695 cm.$^{-1}$, respectively, whereas the corresponding spectra of the lower boiling (*trans*) isomer showed no absorption for C=C in the infrared (Raman, 1740 cm.$^{-1}$). The mass spectral analyses were consistent with both isomers having similar structures with identical parent mass peaks at 262. Also consistent with the assigned general structure was the presence of CF_3^+ and $C_2F_5^+$ fragments.

Anal. Calcd. for $C_6H_3F_9O$: C, 27.5; H, 1.2; F, 65.2. Found for *trans:* C, 27.8; H, 1.6; F, 65.3. Found for *cis:* C, 27.9; H, 1.6; F, 65.3.

The n.m.r. spectra are reproduced in Fig. 2. Assignments of each F multiplet are based on integrated intensities and on chemical shift comparisons with related compounds. The $\mathit{CF_3}CF_2$ multiplets are generally upfield from $\mathit{CF_3}C{=}C$ multiplets.[14] Further, it is noted that, in the high-boiling isomer (not in the low-boiling isomer), there is strong coupling (J = 17.5 c.p.s.) between the CF_2 multiplet and the downfield CF_3 multiplet. Considering that *cis*-trifluoromethyl fluorine nuclei generally are coupled (at long range) more strongly than *trans*-trifluoromethyl groups[15] argues that (1) the high-boiling isomer (with C=C infrared absorption) has the structure where the two perfluoroalkyl groups are *cis* to each other and (2) the downfield CF_3 multiplet is that of the CF_3 on the double bond. Using this structural assignment, interpretation of the spectra gave the nuclear spin-coupling constants diagramed schematically below. The F multiplets in the *cis* isomer could only be resolved to give the coupling constants listed. It is noted that the vinyl fluorine is also coupled (at long range) more strongly with *cis* groups than with *trans*.

2-Ethoxyperfluoropropene.[16]—Triethyl phosphite (42 g., 0.25 mole) was added dropwise to 42 g. (0.25 mole) of hexafluoro-

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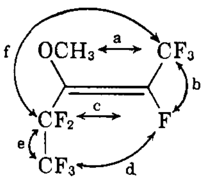
[13] W. Lange and G. V. Krueger, *Ber.*, **65B**, 1598 (1932).

[14] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 323.

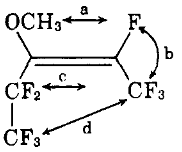
[15] S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962).

[16] This experiment was carried out by Dr. W. J. Middleton.



Low-boiling isomer (*trans*)

a, J_{HF} = ~0.6 c.p.s.
b, J_{FF} = 7.7 c.p.s.
c, J_{FF} = 27.5 c.p.s.
d, J_{FF} = 10.0 c.p.s.
e, J_{FF} = 1.9 c.p.s.
f, J_{FF} = 1.6 c.p.s.



High-boiling isomer (*cis*)

a, J_{HF} = 3.2 c.p.s.
b, J_{FF} = 4.9 c.p.s.
c, J_{FF} = 17.5 c.p.s.
d, J_{FF} = 2.8 c.p.s.

acetone contained in a flask equipped with a Dry Ice-cooled condenser. The rate of addition was adjusted so that a gentle reflux was maintained. The reaction mixture was distilled to give 22 g. (50%) of **2-ethoxy-1,1,3,3,3-pentafluoropropene** as a colorless liquid, b.p. 53–54°, $n^{25}D$ 1.3027. The infrared spectrum contained a band at 1760 cm.$^{-1}$ for C=C. The fluorine n.m.r. was consistent with an ABX_3 pattern for splitting.

Anal. Calcd. for $C_5H_5F_5O$: C, 34.1; H, 2.9; F, 53.9. Found: C, 34.7; H, 3.5; F, 53.8.

1-Ethoxy-2,3,3,4,4,4-hexafluoro-1-butene.—To 11.0 g. (0.066 mole) of triethyl phosphite, 20 g. (0.067 mole) of perfluorobutyraldehyde was added while cooling to 0°. The resulting semigelatinous (fluoroaldehyde polymer) mixture was then heated cautiously. Near 80°, a vigorous exothermic reaction occurred resulting in some loss of the volatile aldehyde. Distillation of the residue gave 8.2 g. (40%) of a mixture of the *cis* and *trans* isomers of **1-ethoxy-2,3,3,4,4,4-hexafluoro-1-butene,** b.p. 96.5–104°. An analytical sample of the pure *trans* isomer was obtained from a cut and had b.p. 103.5–104°, $n^{25}D$ 1.3282. The infrared spectrum contained a band at 1745 cm.$^{-1}$ for C=C. The fluorine n.m.r. (40 Mc.p.s., CF_3COOH ext.) spectrum consisted of three complex bands at +7.7 (CF_3), +43.0 (CF_2), and +86.0 p.p.m. (CF) in a ratio of 3:2:1; and the proton n.m.r. (40 Mc.p.s., tetramethylsilane ext.) spectrum consisted of three bands at τ 3.88 (—CF=C*H*O—, doublet, J_{HF} = 21 c.p.s.), 6.35 (—OCH_2CH$_3$, quadruplet, J = 7 c.p.s.), and 9.12 (CH$_2$CH_3, triplet, J = 7 c.p.s.) in a ratio of 1:2:3. The *trans* configuration was assigned on the basis of the observed 21-c.p.s. proton–fluorine coupling constant.[17]

Anal. Calcd. for $C_6H_6F_6O$: C, 34.6; H, 2.9; F, 54.8. Found: C, 34.4; H, 2.8; F, 55.3.

1-Methoxyperfluorocyclobutene.[18]—Perfluorocyclobutanone (34 g., 0.2 mole) was bubbled into a solution of 12.4 g. (0.1 mole) of trimethyl phosphite in 50 ml. of dry ether at room temperature. There was recovered 8 g. of perfluorocyclobutanone and after removal of the ether distillation gave 9.5 g. (55%) of 1-methoxyperfluorocyclobutene, b.p. 85°, $n^{25}D$ 1.3292 (lit.[6] b.p. 87°, $n^{25}D$ 1.3300).

Dimethyl 2-Methoxy-3,3,4,4-tetrafluorocyclobuten-1-yl Phosphate.[18]—To a solution of 11 g. (0.09 mole) of trimethyl phosphite in 50 ml. of dry ether, was added dropwise 10 g. (0.06 mole) of perfluoro-1,2-cyclobutanedione with stirring and cooling in a Dry Ice-acetone bath at −70°. The blue diketone was rapidly decolorized. An additional 5 g. of trimethyl phosphite was then added, but no exothermic reaction occurred. The mixture was distilled to give 8.5 g. of dimethyl methylphosphonate, b.p. 69° (10 mm.), $n^{25}D$ 1.4069, and 6.5 g. (36%) of **dimethyl 2-methoxy-3,3,4,4-tetrafluorocyclobuten-1-yl phosphate,** b.p. 90° (1 mm.), $n^{25}D$ 1.3950. Proton n.m.r. indicated the presence of two different methoxyl groups in the ratio of 2:1, and the infrared spectrum contained an absorption band at 1750 cm.$^{-1}$ for the enol ether C=C stretch.[7]

Anal. Calcd. for $C_7H_9F_4O_5P$: C, 30.0; H, 3.2; P, 11.0; F, 28.6. Found: C, 30.5; H, 3.4; P, 11.0; F, 24.0.

3-Hydroperfluoro-4-heptanone.—A mixture of 23.3 g. (0.064 mole) of the 4-methoxyperfluoro-3-heptene and 35 ml. of 20% fuming sulfuric acid was heated at reflux for 22 hr. The reaction mixture was cooled to room temperature and carefully poured onto 300 g. of ice. Extraction of the solution with five 40-ml. portions of ether followed by careful distillation from phosphorus pentoxide gave 18 g. (81%) of **3-hydroperfluoro-4-heptanone,** b.p. 90°. An analytical sample was obtained by gas chromatography.

Anal. Calcd. for $C_7HF_{13}O$: C, 24.2; H, 0.3; F, 71.0. Found: C, 24.9, 24.6; H, 0.8, 0.7; F, 71.1, 71.4.

When dissolved in 1:1 ethanol–water, the ketone apparently formed a hemiketal, which titrated at 0° as a weak acid with pK_a 8.5 (neut. equiv.: calcd., 348; found, 329).

The proton n.m.r. showed a complex pattern centered at τ 4.80 consisting of a doublet with each component split further into two pairs of doublets (J's = 46, 15, and 5.6 c.p.s.). The fluorine n.m.r. (56.4 Mc.p.s., CF_3COOH, ext.) contained two CF_3 peaks at +5.0 (triplet, J = 9.3 c.p.s.) and +7.3 p.p.m. (doublet, J = 10 c.p.s.). The CF_2 region consisted of a peak at +43.5 (broad unresolved), a w,s,s,w quartet centered at +48.6 (|w,s| = 290 c.p.s., |s,s| = 143 c.p.s., individual peaks unresolved), and a peak at 50.0 p.p.m. (complex multiplet, partially overlapped by a portion of the w,s,s,w quartet). The CF absorption was at +132.4 p.p.m. (complex multiplet). The spectrum has been interpreted as being consistent with the CF_2, adjacent to the asymmetric -CFH-, having nonequivalent fluorine atoms.[19] Thus the proton n.m.r. is the X portion (quartet) of an ABX pattern, further split by the fluorine on the same carbon, with the AB portion being the w,s,s,w CF_2 absorption. The CF_3 splitting patterns are interpreted as long-range F–F coupling with the fluorines on the carbons β to the CF_3's.[20]

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(17) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," Pergamon Press, New York, N. Y., 1959.

(18) This experiment was carried out by Dr. D. C. England.

(19) Ref. 14, pp. 377–381.

(20) N. Muller, P. C. Lauterbur, and G. F. Svatos, *J. Am. Chem. Soc.*, **79**, 1808 (1957).