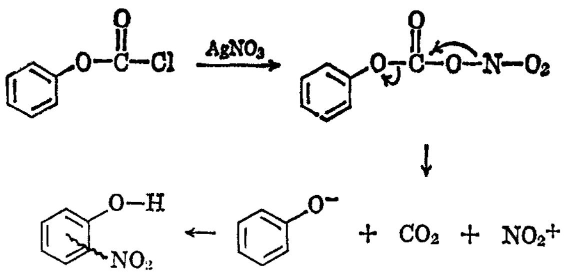

(3)

product nitrophenols. This is probably a gross oversimplification of the process, considering the complications in the thoroughly studied acyl nitrate nitrations.[7] However, the data presented herein and the attractive analogy with the reactions of acyl and aroyl nitrates suggests that there is an ionic dissociation in which substrate and nitrating agent are both generated from an intermediate nitratoformate ester. When an alternate substrate is available, this will also be nitrated depending on its reactivity. There seems to be little evidence for a concerted S_Ni rearrangement. This reaction scheme is also similar to the suggestion put forth by Kevill and Johnson[3] for the alkyl chloroformates.

Experimental Section[8]

Nitrophenols.—All of the nitrophenols used as infrared and vpc standards were commercially available and were used as received.

Aryl Chloroformates.—These materials were prepared by reaction of the corresponding phenol with *ca.* 10% excess phosgene in toluene solution and cold aqueous base. After washing the product solution with water and drying over sodium sulfate, the product was distilled through an efficient column.

A. Phenyl chloroformate was obtained in 52% yield: bp 84–87° (22 mm), $n^{25}\mathrm{D}$ 1.5101 [lit.[9] bp 80° (22 mm)].

B. *p*-Cresyl chloroformate was obtained in 73% yield: bp 93–96° (15 mm), $n^{25}\mathrm{D}$ 1.5020 [lit.[10] bp 108° (30 mm)].

Reactions with Silver Nitrate. A. Phenyl Chloroformate.—A solution of 31.4 g (0.20 mole) of phenyl chloroformate and 34.0 g (0.20 mole) of silver nitrate in 450 ml of acetonitrile (cooled to 0° before mixing) was stirred for 1 hr at 0°, then for 2 hr at room temperature. Precipitated silver chloride was removed by filtration, and the dark filtrate was diluted with water and made basic. Acetonitrile was removed by distillation, and the product solution was acidified and steam distilled to yield 9.4 g (34%) of *o*-nitrophenol melting at 42–45°. The infrared spectrum of this material was identical with that of an authentic sample of that material. The pot residue from the steam distillation was refluxed shortly with hydrochloric acid (to coagulate tars), treated with decolorizing carbon, and extracted with ether. The residue from solvent evaporation was treated with 50% sodium hydroxide solution to obtain the solid salt of *p*-nitrophenol. This was slurried with water and acidified to yield 7.8 g (28%) of *p*-nitrophenol melting at 112–115° (from benzene). The infrared spectrum of this material was identical with that of an authentic sample of that material.

In a similar experiment on one-half the above scale, vpc analysis of the crude reaction mixture showed the yields to be 19% *o*-nitrophenol, 33% *p*-nitrophenol, and less than 0.01% *m*-nitrophenol.

B. Reaction of Phenyl Chloroformate with Silver Nitrate in the Presence of *p*-Cresol.—A mixture of 21.3 g (0.13 mole) of silver nitrate, 15.7 g (0.10 mole) of phenyl chloroformate, and 10.8 g (0.10 mole) of *p*-cresol in acetonitrile solution were stirred for 1 hr at 0°. Vpc analysis of the crude reaction mixture showed it to contain 3.6% *o*-nitrophenol, 2.9% *p*-nitrophenol, and 43% *o*-nitro-*p*-cresol (based on silver nitrate). Steam distillation of the product yielded 10.2 g of yellow oil, the infrared spectrum of which was essentially identical with that of an authentic sample of *o*-nitro-*p*-cresol. Distillation gave one cut, bp 100° (4 mm), that crystallized and melts at 32–35°.

C. Reaction of Phenyl Chloroformate and *p*-Cresol with a Deficiency of Silver Nitrate.—A solution of 15.7 g (0.10 mole) of phenyl chloroformate, 10.8 g (0.10 mole) of *p*-cresol, and 8.5 g (0.050 mole) of silver nitrate in acetonitrile was stirred for 1 hr at 0° and *ca.* 2 hr at room temperature. The silver chloride (7.0 g, 98%) was removed by filtration. Vpc analysis of the crude product solution showed it to contain 8.7 g (55%) of phenyl chloroformate and less than 0.1% *p*-cresyl chloroformate. No attempt was made to analyze for other products.

D. Attempted Reaction of *o*-Nitrophenol with Silver Nitrate.—A mixture of 2.8 g (0.020 mole) of *o*-nitrophenol and 6.8 g (0.040 mole) of silver nitrate was stirred in acetonitrile solution for 3 hr at room temperature. Vpc analysis of the reaction product showed that it contained only starting material and there was no *p*-nitrophenol present.

E. *p*-Cresyl Chloroformate.—An acetonitrile solution of 34 g (0.20 mole) of *p*-cresyl chloroformate and 68 g (0.40 mole) of silver nitrate was stirred for *ca.* 1 hr at 0° and 2 hr at room temperature. Distillation of the crude product from filtration of the silver chloride yielded 12.5 g (44%) of *o*-nitro-*p*-cresol melting at 34–35° (from cold hexane). The infrared spectrum of this material was identical with that of an authentic sample of material.

Fluoride Ion Initiated Reactions of Perfluoro α-Olefins. I. Reaction of the Pentafluoroethyl Carbanion with Tetrafluoroethylene

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The polymerization of tetrafluoroethylene (TFE) has usually followed a free-radical mechanism and yielded solid polymers. Anionic catalysis has been successfully used in the limited polymerization of other fluoro olefins to produce liquids, but TFE has been unreactive, presumably owing to its symmetry. This suggested a possible advantage in the use of a solid catalyst. Cesium fluoride on an active-carbon support did catalyze the reaction of TFE with itself, but the products were so tightly bound to the catalyst that elevated temperatures (exceeding 100°) were required for their removal. The product was an extensive mixture of saturated compounds, olefins, and diolefins. Some of the compounds formed contained an uneven number of carbon atoms, indicating rupture of the carbon-to-carbon bond. A milder reaction, avoiding rupture of the bond between carbon atoms, was obtained with a catalyst system comprising cesium fluoride suspended in an activating solvent such as di-, tri-, or tetraethylene glycol dimethyl ether (hereinafter called di-, tri-, or tetraglyme).

The condensation of TFE with itself in the presence of solvent-activated cesium fluoride presumably follows a cycle comprising the following steps: (1) formation

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(7) (a) G. Drefahl and H. Cramer, *Chem. Ber.*, **91**, 745 (1958); (b) M. A. Paul, *J. Am. Chem. Soc.*, **80**, 5332 (1958); (c) H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 729 (1955); (d) V. Gold, F. D. Hughes, and C. K. Ingold, *ibid.*, 2467 (1950); F. G. Bordwell and E. W. Garbisch, *J. Am. Chem. Soc.*, **82**, 3588 (1960).

(8) Infrared spectra were obtained as Nujol mulls or neat smears using a Perkin-Elmer Model 337 spectrophotometer. Vpc analyses were performed using a column comprised of SE 30 silicone oil on Anakrom ABS support. An internal standard was 1,2,3,4-tetrachlorobenzene.

(9) Y. Iwakura and A. Nobeya, *J. Org. Chem.*, **25**, 1118 (1960).

(10) M. Capisarow, *J. Chem. Soc.*, 251 (1929).

of the perfluoro carbanion $CF_3CF_2^-$; (2) addition of the perfluoro carbanion to a molecule of TFE; (3) elimination of fluoride ion to yield an olefin; and (4) addition of another perfluoro carbanion, etc.

In the buildup of the larger molecules, the olefins or the carbanion may contain two or more ($-CF_2-CF_2-$) units.

An interesting aspect of this reaction is that the reaction velocity is roughly proportional to the amount of CsF added, although the CsF is only very slightly soluble in the solvent employed. This suggests that the surface of the CsF crystal must be involved in the initial polarization of the TFE forming the perfluoro carbanion, and that the Cs atom of the ion pair $CF_3CF_2^-Cs^+$ may retain its position in the lattice of the CsF crystal.

Experimental Section

Caution! Tetrafluoroethylene is usually stored in the presence of a terpene to inhibit spontaneous polymerization. At pressures above 40 psig, uninhibited tetrafluoroethylene may explode spontaneously. The inhibited monomer will also explode if ignited.[1,2] In the work reported here, the TFE was freed from the terpene inhibitor just before use by passage through a tube filled with silica gel.

An additional hazard lies in the toxicity of the explosion products. Also, some of the branched-chain olefins prepared by the reaction described in this paper are believed to be very toxic, even at concentrations of only a few parts per million.

The condensations were run in pressure bottles (Fischer-Porter Aerosol Compatibility Tubes) in 3-, 6-, and 12-oz sizes. Pressures were measured with Bourdon gauges and the reaction temperature was maintained by a water bath. In some cases, the pressure tube was modified as shown in Figure 1 to permit withdrawal of the material condensing in the upper part of the tube and return of the solvent to the reaction zone. The products obtained were mixed branched-chain olefins. Molecular weights of the individual components and some information regarding their structure were obtained with a Bendix "Time of Flight" mass spectrometer operated in conjunction with a vapor phase chromatograph.

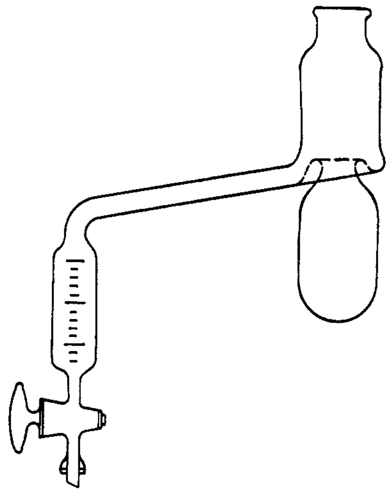


Figure 1.—Pressure bottle, modified for product removal.

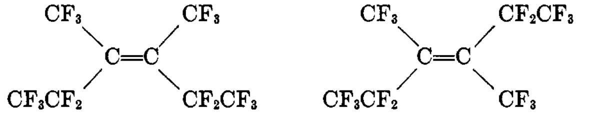
Further structural information was obtained from infrared and nmr spectra. Infrared spectra were obtained with a Perkin-Elmer Model 21 split-beam spectrometer. The F^{19} spectra were obtained on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts are expressed in parts per million *vs.* external trifluoroacetic acid, with the positive direction on the high-field side. Calibrations were made by the usual audiomodulation side-band technique.

In general, the magnitude of the CF_3 bands in relation to that of the CF_2 bands indicated a high degree of branching. CF_3 areas were identified by characteristic shifts of -15 to -20 ppm when attached to a double-bonded carbon, and of -3 to $+5$ ppm when attached to a $-CF_2-$ group.

Condensation of TFE.—CsF (10 g) was ground in a dry atmosphere and slurried under dry conditions in 150 g of diethylene glycol dimethyl ether (Ansul Ether 141 or diglyme) in a pressure bottle with a magnetic stirrer. The atmosphere in the bottle was replaced with TFE and more TFE was added to a pressure of 5 psig. The charge was then heated with stirring to 99–100° and a total of 45 g of TFE was added at 10–20 psig over a period of about 80 hr. The charge was allowed to cool to room temperature and the residual solid (principally CsF) was removed by filtration. A heavy fluorocarbon oil (27 g) was separated and fractionated by distillation into cuts representing C_8, C_{10}, C_{12}, and C_{14} olefins. The lighter portions (traces only) were allowed to escape and the heavier products were retained as still residue. Reduced pressures were used to avoid the necessity for temperatures above 100°. The boiling ranges of the various cuts were C_8F_{16}, 95–96°; $C_{10}F_{20}$, 135–138°; $C_{12}F_{24}$, 175–178°; and $C_{14}F_{28}$, 209–211°.

The magnitudes of these cuts and the number of isomers in each as indicated by vapor phase chromatography were as follows: C_8F_{16}, 11% of total (two isomers in approximately equal quantities); $C_{10}F_{20}$, 58% of total (one strong band and two weak bands); $C_{12}F_{24}$, 12% of total (two strong bands and two weak bands); $C_{14}F_{28}$, 14% of total (two strong bands and two weak bands); and residue, 5%.

The F^{19} nmr spectrum of the C_8F_{16} fraction consists of three groups of peaks with relative areas of 6:6:4. The first is a composite of two peaks at -19.5 and -18.8 ppm, characteristic of $CF_3\overset{|}{C}{=}$. The second is at -2.2 ppm, characteristic of CF_3CF_2-. The third group is centered at $+22.3$ ppm, characteristic of $CF_3-CF_2\overset{|}{C}{=}$. Both the second and third groups are slightly asymmetric, indicating that they are superpositions of two peaks with a small chemical shift between them. These facts (combined with the formula, C_8F_{16}, established separately by mass spectrometry) indicate that this fraction is a mixture of *cis*- and *trans*-decafluoro-3,4-bis(trifluoromethyl)-3-hexene.



Analogous characterizations of the higher fractions were less conclusive but did show extensive branching and asymmetry.

The balance of the TFE charged reacted with the solvent and it may have been this reaction that finally stopped the consumption of TFE. Fractional distillation of the diglyme layer yielded 86% of unchanged diglyme. The residue contained 38% fluorine (a 1:1 adduct of diglyme–TFE would contain 32.5% F and a 1:2, 45.5%). A boiling point test in benzene indicated a molecular weight of ~370.

The diglyme layer from a similar run was washed with water to yield 18 g of a water-insoluble liquid which was fractionally distilled to yield 10 g containing 31.0% F (1:1 = 32.5% F) and 8 g containing 50.6% F (1:3 = 52.5% F). The structures of these adducts were not determined but the analyses suggest a mixture of at least the adducts of 1, 2, and 3 moles of TFE/mole of diglyme.

Substitution of ethylene glycol dimethyl ether (glyme) for diglyme resulted in a tenfold rate reduction. Triglyme and tetraglyme gave increased reaction rates with a change in the product distribution favoring the C_{10} fraction largely at the expense of the C_{14} fraction.

An increase in the TFE pressure to 150–200 psig (in a steel bomb on a shaker) had little effect on the rate, but did increase the yield of the C_{14} fraction.

Use of the modified pressure tube favored the C_{12} and C_{14} fractions.

The quantitative effects of these variables are shown in Table I. Water tended to prevent the condensation.

Doubling the amount of cesium fluoride used increased the rate of TFE takeup roughly 50%. Since the amount of cesium fluoride present in all cases far exceeded its solubility in the diglyme, a surface reaction was indicated.

The reaction rate was approximately doubled by a 25° increase in temperature.

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[1] D. D. Coffman, *et al.*, *J. Am. Chem. Soc.*, **71**, 490 (1949).

[2] H. C. Duus, *Ind. Eng. Chem.*, **47**, 1445 (1955).

Table I

Effects of Solvent, Pressure, and Reaction Vessel Design on Product Distribution in the Branched Polymerization of TFE

Solvent	Vessel	Product[a] C_8F_{16}	$C_{10}F_{20}$	$C_{12}F_{24}$	$C_{14}F_{28}$	Residue
Diglyme	Regular bottle	11	58	12	14	5
Triglyme	Regular bottle	3	65	21	2	9
Tetraglyme	Regular bottle	6	80	12	0.5	1.5
Diglyme	Modified bottle	3	42	15	39.5	0.5
Triglyme	Modified bottle	7	63	12	12	6
Tetraglyme	Modified bottle	11	47	23	17.5	1.5
Triglyme	Shaker bomb[b]	6	21	25	42	6

[a] Values are given as per cent of the total yield. [b] At 150–200 psig.

Condensation also occurred with other perfluoro terminal olefins in which structure precluded a shift of the double bond, but the extent was limited. Hexafluoropropene yielded only dimers and trimers, and perfluoroisobutylene gave only dimers.

Fluoride Ion Initiated Reactions of Perfluoro α-Olefins. II. The Condensation of Tetrafluoroethylene with Perfluoro Ketones to Yield Perfluoro Tertiary Alcohols

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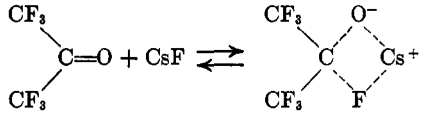
Discussion

A small number of perfluoro tertiary alcohols (not including those reported here) have been prepared in small yields by Grignard-type reactions.[1–3]

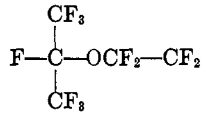
The perfluoro tertiary alcohol, tetradecafluoro-4-(heptafluoropropyl)-4-heptanol, has also been prepared in small yields by the reaction of tetradecafluoro-4-heptanone with sodium methoxide.[4]

The ionization constants of these perfluoro tertiary alcohols are 1–3 × 10^{-10} compared with 1 × 10^{-9} for phenol, but their exploitation as chemical intermediates has awaited more ready availability. Steps in this direction are found in the observation that fluoroalkanoyl fluorides are formed by the reaction of a fluoro olefin with carbonyl fluoride in the presence of a fluoride ion catalyst,[5] and that hexafluoropropene may be similarly added to a fluoroalkanoyl fluoride to form a fluoro ketone.[6]

We have recently found that tetrafluoroethylene (TFE), in the presence of a suitable metal fluoride–polar solvent combination, will condense with certain perfluoro ketones to yield the corresponding perfluoro tertiary alcohols. In the actual conduct of the experiment, the ketone is added to the metal fluoride–solvent slurry followed by the TFE. For example, hexafluoroacetone is added to a slurry of cesium fluoride in diethylene glycol dimethyl ether (diglyme). The ketone and cesium fluoride form a soluble complex.



Subsequent addition of TFE produces the perfluoro-*t*-pentyl alcohol. No evidence of formation of the ether anion



$$F-C(CF_3)_2-OCF_2-CF_2^-$$

was found, indicating that the anion related to the ketone–cesium fluoride complex is too feeble as a nucleophile to attack TFE. Thus the assumption that the reaction producing the alcohol involves attack by the anion $CF_3CF_2^-$ (from TFE + CsF) upon the equilibrium concentration of the ketone is strongly favored.

It is interesting to note that, when the CsF is completely complexed by the ketone (dissolved), the addition of TFE produces no by-product liquid perfluoro olefin polymer. However, when excess (undissolved) CsF is present, the rate of formation of the alcohol is greatly increased, but there is also some polymerization of the TFE.[7]

Experimental Section

Caution! Tetrafluoroethylene (TFE) is usually stored in the presence of a terpene to inhibit spontaneous polymerization. At pressures above 40 psig, uninhibited TFE may explode spontaneously. The inhibited monomer will also explode if ignited.[8,9] A possible additional hazard lies in the toxicity of some of the explosive products.

Synthesis of Perfluoro-*t*-pentyl Alcohol.—Cesium fluoride (100 g, 0.66 mole) was slurried in diethylene glycol dimethyl ether (diglyme) (200 g) in a pressure bottle (marketed as the Fischer-Porter Aerosol Compatibility Tube). In the absence of air, hexafluoroacetone (108 g, 0.65 mole) was added at room temperature and at pressures up to 20 psig. The charge was then heated in a water bath to 98–100° and tetrafluoroethylene (98 g, 0.98 mole), with terpene inhibitor removed by passage through a tube filled with silica gel, was added at 98–100° and at pressures of 20–25 psig over a period of up to 50 hr. The charge was filtered and a by-product fluorocarbon layer (33 g) was separated. The remaining filtrate was cooled and the bulk of the solvent (diglyme) was removed by distillation at room temperature under a reduced pressure of 0.1–0.3 mm. The remaining soft cake was slurried in cold (0–5°) 96% sulfuric acid and the released alcohol was distilled off rapidly at atmospheric pressure and pot temperatures up to 100°. The product (160 g, 0.56 mole), purified by redistillation, was a water-white liquid boiling at 67°. Its structure, $CF_3CF_2C(CF_3)_2OH$, was established by means of the F^{19} resonance spectrum obtained on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts are expressed in parts per million *vs.* external trifluoroacetic acid with the positive direction on the high-field side. Calibrations were made by the audiomodulation side-band technique. The F^{19} resonance spectrum comprised three peaks at +4.08, +42.73, and −3.37 ppm with relative areas of 3, 2, and 6.

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[1] R. N. Haszeldine, *Nature*, **168**, 1028 (1951).

[2] R. N. Haszeldine, *J. Chem. Soc.*, 1748 (1953).

[3] O. R. Pierce, E. T. McBee, and G. F. Judd, *J. Am. Chem. Soc.*, **76**, 479 (1954).

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

[5] F. S. Fawcett, C. W. Tullock, and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

[6] R. D. Smith, F. S. Fawcett, and D. D. Coffman, *ibid.*, **84**, 4285 (1962).

[7] D. P. Graham, *J. Org. Chem.* **31**, 955 (1966).

[8] D. D. Coffman, *et al.*, *J. Am. Chem. Soc.*, **71**, 490 (1949).

[9] H. C. Duus, *Ind. Eng. Chem.*, **47**, 1445 (1955).