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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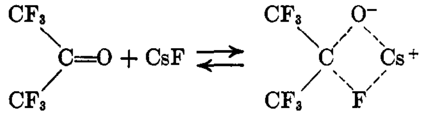
Discussion

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

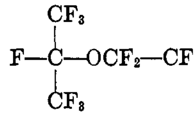
The perfluoro tertiary alcohol, tetradecafluoro-4-(heptafluoropropyl)-4-heptanol, has also been prepared in small yields by the reaction of tetradecafluoro-4-heptanone with sodium methoxide.[4]

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).

This preparation was also carried out with certain other catalyst systems. NaF, LiF, and RuF with diglyme produced small yields of the product but required higher temperatures and pressures. Acetonitrile and benzonitrile were used with KF to produce small to moderate yields. These last systems were characterized by the near absence of side-reaction TFE polymerization.

Synthesis of Decafluoro-3-trifluoromethyl-3-pentanol.—CsF (15.2 g, 0.10 mole) was slurried in diglyme (30 g) and octafluoro-2-butanone (perfluoro methyl ethyl ketone) (21.0 g, 0.098 mole)[6] was added at room temperature over 5–6 hr. The charge was heated to 98–100° and TFE (17 g, 0.17 mole) was added at pressures up to 25 psig over about 40 hr. Liquid fluorocarbon polymer (5.4 g) was separated and the balance of the charge was filtered. The diglyme was stripped from the filtrate under reduced pressure at 50–55°. The residual oily cake was cooled and acidified with 96% sulfuric acid (90 g) below 10°. The product was distilled at reduced pressure (20 mm) into a trap cooled by liquid nitrogen. The yield of product was 26.1 g (0.078 mole): bp 87.5°. The F^{19} resonance spectrum comprised three peaks at +3.21, +40.18, and −5.07 ppm. The relative areas were 6, 4, and 3, respectively, consistent with the structure, $(CF_3CF_2)_2C(CF_3)OH$. This product was also prepared by the addition (again in the presence of cesium fluoride and diglyme) of 2 moles of TFE to trifluoroacetyl fluoride, but with a somewhat less satisfactory yield.

A charge of diglyme (15 g), cesium fluoride (7 g, 0.046 mole), trifluoroacetyl fluoride (5 g, 0.045 mole), and TFE (25.5 g, 0.255 mole) yielded liquid perfluorocarbon polymer (19.5 g) and the desired perfluoro tertiary alcohol (4.5 g, 0.0134 mole).

Synthesis of Decafluoro-3-pentafluoroethyl-3-pentanol.—Cesium fluoride (22.8 g, 0.15 mole) was slurried in diglyme (40 g) in a stirred pressure bottle and, in the absence of air, decafluoro-3-pentanone (40 g, 0.15 mole) (prepared by treatment of the ethyl ester of perfluoropropionic acid with sodium methoxide)[10] was added at 30–35°. The charge was heated to 100° and, at 98–100°, tetrafluoroethylene (15 g, 0.15 mole) was added over about 15 hr. The charge was filtered to remove the cesium fluoride and the solvent was stripped from the filtrate under reduced pressure (less than 5 mm) at 55–60°. The residual cake was chilled in an ice and salt bath and acidified with 140 g of 96% sulfuric acid, keeping the temperature below 10°. The product was distilled into a trap cooled with liquid nitrogen at pressures below 5 mm. The crude distillate was purified by fractional distillation using a 20-cm packed column. The yield was 34.6 g (0.0895 mole): bp 104–105°. The F^{19} resonance spectrum was limited to two peaks at +2.91 and +38.19 ppm with areas in the ratio of 3 to 2, respectively. This spectrum was consistent with the structure, $(CF_3CF_2)_3COH$.

This same product was also prepared by condensing 3 moles of TFE with 1 mole of carbonyl fluoride. A charge of diglyme (100 g), cesium fluoride (50 g, 0.33 mole), carbonyl fluoride (17 g, 0.26 mole), and TFE (86 g, 0.86 mole) yielded 35 g of perfluorocarbon polymer plus 13 g of the desired perfluoro tertiary alcohol, decafluoro-3-pentafluoroethyl-3-pentanol.

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[10] D. W. Wiley, U. S. Patent 3,091,643 (May 28, 1963).

Fluoride Ion Initiated Reactions of Perfluoro α-Olefins. III. The Condensation of Perfluoro α-Olefins with Carbon Dioxide to Yield Perfluoro Carboxylic Acids

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Discussion

Perfluoro carboxylic acids have been prepared in the past by methods involving electrolytic fluorination, oxidation, or hydrolysis. The synthesis reported here comprises the direct addition of a metal fluoride complex of a perfluoro olefin to carbon dioxide followed by separation of the free acid by acidification and distillation. The condensation proved to be reversible, the stability of the carboxylic acid metal salt decreasing with increasing complexity of the olefin. The condensation of tetrafluoroethylene (TFE) with CO_2 was essentially quantitative at 100° and the free acid was stable to distillation at its normal boiling point. In the case of hexafluoropropene (HFP), however, it was necessary to drop the temperature to 70° to avoid thermal decarboxylation, an effect accentuated by the tendency of HFP to form dimers and trimers irreversibly.

Perfluoroisobutylene (PFIB) complexed readily with cesium fluoride in diethylene glycol dimethyl ether (diglyme) at room temperature, but it was necessary to cool the charge to below −25° for a quantitative addition to CO_2. Attempts to isolate free perfluoropivalic acid from this adduct were unsuccessful.

Some but not all perhalo olefins in which part of the fluorine is replaced with chlorine add to carbon dioxide. Chlorotrifluoroethylene yielded 2-chlorotetrafluoropropionic acid, but 1,1-dichlorodifluoroethylene failed to add to CO_2 under the conditions employed.

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.[1,2] A possible additional hazard lies in the toxicity of some of the explosion products.

In the work reported here, the terpene inhibitor was removed from the TFE by passage through a tube filled with silica gel just before entering the reaction vessel.

The perfluoro olefins themselves vary widely in toxicity. Approximate lethal doses for 4- to 6-hr exposure (LC_{50} for rats in parts per million by volume) are tetrafluoroethylene, 40,000 ppm or 4%; hexafluoropropene, 3000 ppm; and perfluoroisobutylene, 0.5 ppm. Allowable concentrations for continued exposure would be considerably lower.

The condensations were run in pressure bottles (marketed as Fisher-Porter Aerosol Compatibility Tubes) fitted with the necessary lines and gauges. They were stirred magnetically and temperatures were controlled by liquid baths.

The products were characterized by infrared and nmr spectra. The infrared spectra were obtained on a Perkin-Elmer Model 21 split-beam spectrometer. The F^{19} resonance spectra were measured on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts were determined in parts per million *vs.* external trifluoroacetic acid with the positive direction on the high-field side. Calibrations were made by the audiomodulation technique. Supplementary proton resonance spectra were obtained on a Varian A-60 magnetic resonance spectrometer, operating at 60 Mc *vs.* external tetramethylsilane with the positive direction in this case on the low-field side.

A. The Condensation of TFE with Carbon Dioxide.—Cesium fluoride (100 g, 0.66 mole) was slurried in distilled triethylene glycol dimethyl ether or triglyme (200 g) in a stirred pressure bottle. The atmosphere in the bottle was replaced with TFE at a pressure of 10 psig, and CO_2 was added to bring the pressure to 12 psig. The charge was heated with stirring to 100°. The pressure fell as the reaction proceeded and was brought up to 20 psig intermittently by addition of equal molar quantities of TFE and CO_2 (equal pressure increments). The reaction stopped when all of the cesium fluoride had been dissolved. The observed weight gain from addition of TFE and CO_2 was 97 g.

The charge was drowned in benzene (2000 g) and filtered.

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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).