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).

The cake was washed with diethyl ether and dried under vacuum at room temperature. The product (the cesium salt of perfluoropropionic acid) was a white crystalline solid: yield 175 g. This salt (174.5 g) was added slowly to 96% sulfuric acid (180 g) at 0–5°. The slurry was allowed to stand overnight at room temperature, separating into two layers. The upper layer (62 cc in volume, 93 g) was separated and distilled at 50° (112–113 mm) to yield 88.5 g (0.42 mole). It was identified by infrared spectrum[3] as pentafluoropropionic acid. The F^{19} resonance spectrum comprised a triplet at +7.27 ppm and a quartet at +46.14 ppm with relative areas of 3 and 2. The proton resonance showed only a singlet at +11.58 ppm. These spectra support the infrared characterization of the product as pentafluoropropionic acid. The same product was prepared, using potassium fluoride and acetonitrile in a steel bomb. The TFE and CO_2 were added cold and the bomb was heated to 150° with shaking for 10 hr. The excess KF was filtered off. The solvent was stripped off at 50° under reduced pressure, and the resulting cake was acidified cold (0–5°) with 96% sulfuric acid. The product was distilled off under reduced pressure and obtained in a yield of 75% of theory based on TFE charged.

B. The Condensation of Chlorotrifluoroethylene with Carbon Dioxide.—Cesium fluoride (15 g, 0.1 mole) was slurried in diethylene glycol dimethyl ether (diglyme) and TFE and CO_2 were added in the absence of air as in A but at a temperature of 50°. The completed charge was drowned in diethyl ether (500 g), chilled, and filtered. The cake, washed with ether and dried, weighed 19.5 g. Acidification of a small portion of this material with cold 96% sulfuric acid yielded a clear liquid identified by nmr spectrum as $CF_3CClFCOOH$. On the basis of previous observations, the two possible structures were I, $CF_3CCl\text{-}FCOOH$, and II, $CClF_2CF_2COOH$. The F^{19} resonance spectrum consisted of two multiplets, a doublet and a quartet with an area ratio of 3 to 1. This was sufficient to resolve the question in favor of structure I.

C. Preparation of Perfluoroisobutyric Acid by Condensation of Hexafluoropropene with Carbon Dioxide.—Although TFE was condensed with CO_2 at 100° to yield a stable salt, in the case of hexafluoropropene (HFP), it was necessary to drop the reaction temperature to 70° to avoid reversal of the reaction. Otherwise, the procedure was similar to that employed in the condensation of TFE with CO_2.

Cesium fluoride (90 g, 0.59 mole) was slurried in triethylene glycol dimethyl ether (triglyme) (180 g), and hexafluoropropene (118 g, 0.79 mole) and carbon dioxide (26 g, 0.59 mole) were added together at 70° and 20–25-psig pressure. A liquid fluorocarbon layer of 21 g (dimers and trimers of HFP) was separated off. The triglyme layer was filtered and drowned in benzene, and the cesium salt of perfluoroisobutyric acid (132 g) was separated and dried. Acidification yielded the free acid (72 g, 0.33 mole). The structure was confirmed by an infrared spectrum which matched an earlier result[3] and by nmr spectra. The F^{19} spectrum showed a doublet at +1.63 ppm and a septet at +107.8 ppm with relative areas of 6 and 1. The proton resonance showed a singlet at 11.76 ppm. These results were consistent with the assigned structure.

D. Attempted Condensation of Perfluoroisobutylene with Carbon Dioxide.—Perfluoroisobutylene (PFIB) added readily to cesium fluoride in dry diglyme at room temperature to form a complex soluble in the diglyme, presumably perfluoro-*t*-butylcesium. Acidification by addition of dry HCl to a portion of the charge yielded a small quantity of a product which was removed under vacuum, trapped at liquid nitrogen temperature, and characterized by nmr spectra. The F^{19} resonance spectrum was a doublet at −11.7 ppm and the proton resonance spectrum was a group of ten peaks at +3.13 ppm, indicating that the product was 2H-hexafluoro-2-(trifluoromethyl)propane, $(CF_3)_3CH$.

Carbon dioxide was added to the unacidified remainder of the charge at −25 to −30° in approximately stoichiometric quantity. The charge was then acidified with sulfuric acid (85%). A heavy precipitate was formed and it was necessary to thin the charge by addition of CCl_2FCClF_2. The charge was filtered and the cake (cesium sulfate) was washed with CCl_2FCClF_2. The filtrate was then washed repeatedly with 25% sulfuric acid to remove as much of the diglyme as possible. The major portion of the CCl_2FCClF_2 was distilled off quickly and the balance of the charge was fractionated to obtain the product. Instead of perfluoropivalic acid, the product was found to be 2H-trifluoro-2-(trifluoromethyl)propionic acid, $(CF_3)_2CHCOOH$, which might be considered a hydrolysate of PFIB. The product was characterized by direct comparison with a sample of this structure which has been disclosed previously.[4] Its F^{19} resonance spectrum consists of a doublet at −13.65 ppm. The proton resonance spectrum comprised a septet at +4.03 ppm and a singlet at +11.60.

In an attempt to avoid the hydrolytic action of aqueous sulfuric acid, the run was repeated using dry HCl for the acidification. In this case, the product was again not perfluoropivalic acid but, instead, a perfluoro olefin identical with the product obtained by the cesium fluoride–diglyme dimerization of PFIB.[5] It was believed to be a mixture of two dimers of PFIB, heptafluoro-2,4,4-tris(trifluoromethyl)-1-pentene, $(CF_3)_3CCF_2C(CF_3)\text{=}CF_2$, and heptafluoro-2,4,4-tris(trifluoromethyl)-2-pentene, $(CF_3)_3CCF\text{=}C(CF_3)_2$. Although PFIB forms a stable complex with cesium fluoride in diglyme, the CO_2 adduct is apparently not a stable carboxylic acid salt.

Attempts to add carbon dioxide to long-chain perfluoro α-olefins were unsuccessful owing to a tendency for the cesium fluoride–diglyme system to catalyze a shift of the double bond toward the center of the chain. This shift was apparently much more rapid than the addition of CO_2 and no carboxylic acid was isolated.

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[3] J. H. Simons, *Fluorine Chem.*, **2**, 491 (1954).

[4] I. L. Kunyants, L. S. German, and B. L. Dyatkin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1931 (1956).

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

Amino-N-cyanocarboxamides. I. *m*- and *p*-N,N-Dimethylamino-N-cyanobenzamide[1,2]

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Amino-N-cyanocarboxamides present a new, interesting, and possibly useful field of investigation. None of these compounds has been reported despite the fact that their amphoteric properties make them analogs (and potential antimetabolites) of the amino acids.

Since N-cyanocarboxamides are known to be stronger acids than carboxylic acids,[3] it seemed probable that some aromatic amino-N-cyanocarboxamides would exist as inner salts. We chose to investigate this possibility by preparing *m*- and *p*-N,N-dimethylamino-N-cyanobenzamide and comparing their second dissociation constants and infrared spectra with those of the corresponding carboxylic acids.

The two compounds were synthesized from their acid chlorides by allowing them to react with sodium hydrogen cyanamide in dimethylformamide. The melting points and analysis of these and several other N-cyanobenzamides are listed in Table I.

Their infrared spectra, and the spectra of the related acids as mineral oil mulls (Figure 1) clearly show that the *para* isomer **1** exists in the solid state as the uncharged species, but that the *meta* isomer **2** exists as the inner salt. This is in contrast to the analogous

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[1] This work was supported by Grant GM 11408 from the National Institutes of Health.

[2] Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

[3] R. Bader, *Z. Physik. Chem.*, **6**, 304 (1890).