and liquid air traps, the Dry Ice trap being made of copper since the COF_2 formed is very corrosive toward glass at elevated temperatures. When all the carbamyl fluoride had been run through, the system was flushed with dry nitrogen for several hours. Fractionation of the Dry Ice condensate gave $CF_3N{=}CF_2$, b.p. -33 to $-31°$, in 96% yield and 89% conversion. The liquid air condensate and forerun from the fractionation amounted to 97% of the theoretical COF_2. Both products gave the correct mol. wt. and the $CF_3N{=}CF_2$ showed the $C{=}N$ absorption band at 5.53 μ. Haszeldine reports b.p. $-33°$ and the $C{=}N$ band at 5.54 μ for this compound.[4]

Acknowledgment.—Much credit is due to those who investigated the NMR spectra of these compounds, as such studies, where possible, constitute the most reliable method for unequivocal assignment of structure. With the exception of $CF_3CON(CF_3)_2$, which was done by Dr. H. S. Gutowsky of the University of Illinois, all NMR spectra were taken and analyzed by Norbert Muller and George F. Svatos.

GAINESVILLE, FLORIDA

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[CONTRIBUTION NO. 103 FROM THE CENTRAL RESEARCH DEPARTMENT OF MINNESOTA MINING AND MANUFACTURING CO. AND THE UNIVERSITY OF COLORADO]

Perfluoroacrylonitrile and its Derivatives[1]

BY J. D. LAZERTE,[2] D. A. RAUSCH, R. J. KOSHAR, J. D. PARK, W. H. PEARLSON AND J. R. LACHER

RECEIVED MARCH 19, 1956

The carbon–carbon double bond in $CF_2{=}CFCN$ has been found to be very susceptible to attack. Hydrolysis with sulfuric acid yielded monofluoromalonic acid rather than perfluoroacrylic acid. Almost complete conversion of the fluorine in the molecule to fluoride ion occurred in the presence of aqueous base. Methanol added across the double bond in the absence of a catalyst to yield CH_3OCF_2CFHCN. When $CF_2{=}CFCN$ was heated in the presence of a catalyst, a dimer was formed. Butadiene-1,3 and $CF_2{=}CFCN$ reacted to yield $C_7H_6F_3N$. Bromination of $CF_2{=}CFCN$ give a high yield of $CF_2BrCFBrCN$. Many of the classical reactions of the nitrile group could be carried out if the $C{=}C$ was protected by the prior addition of bromine.

Earlier publications from these laboratories have reported on the chemical reactivity of perfluoroolefins, $CF_2{=}CF{-}R_f$,[3,4] and the fluorohaloölefins, $CF_2{=}CFX$.[5,6] The compound perfluoroacrylonitrile contains the $CF_2{=}CF{-}$ structure conjugated with the nitrile group. This unsaturated nitrile has been prepared and the chemistry of both the $CF_2{=}CF{-}$ and $-CN$ molecular groupings investigated.

Chaney[7] had prepared this monomer *via* a sequence of reactions which began with the conversion of $CF_2ClCF{=}CCl_2$ to $CF_2ClCFClCOCl$. He observed that the olefinic bond in $CF_2{=}CFCN$ was very susceptible to nucleophilic attack; alcohols added in the absence of a catalyst to yield R_HOCF_2CFHCN. Henne and Fox[8] prepared perfluoroacrylic acid from the same fluorochloropropene.

The methods of synthesis of perfluoroacrylonitrile emphasized in the present investigation used readily available starting materials. The following reaction sequence gave a 25% over-all yield

$$CF_2{=}CFCl + ICl \longrightarrow CF_2ClCFClI \xrightarrow{2C_2H_4}$$

$$CF_2ClCFClCH_2CH_2I \xrightarrow{\text{base}}$$

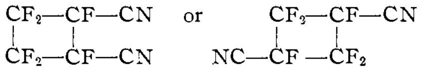
$$CF_2ClCFClCH{=}CH_2 \xrightarrow{KMnO_4} CF_2ClCFClCO_2H \longrightarrow$$

$$CF_2ClCFClCO_2C_2H_5 \longrightarrow CF_2ClCFClCONH_2 \longrightarrow$$

$$CF_2ClCFClCN \longrightarrow CF_2{=}CFCN$$

Another method reported earlier[9] involved the conversion of CF_3CFHCN to $CF_2{=}CFCN$. The CF_3CFHCN was prepared by the addition of ammonia to perfluoropropene.[10]

Some reactions of $CF_2{=}CFCN$ left the nitrile group intact. A reaction with methanol occurred in the absence of any catalyst to give the ether, CH_3OCF_2CFHCN. Bromination of $CF_2{=}CF{-}CN$ took place under mild conditions to give $CF_2BrCFBrCN$. In the presence of catalytic amounts of Terpene B, dimerization of $CF_2{=}CFCN$ occurred. The structure of the reactant product is either



or a mixture of these two compounds. The dimer of perfluoroacrylonitrile and 1,3-butadiene was obtained by heating the two reactants under pressure. The structure of this dimer has not been determined.

Perfluoroacrylonitrile is decomposed in both aqueous base and aqueous acid. The bulk of the fluorine in $CF_2{=}CFCN$ was recovered as fluoride ion when this compound was sealed in an ampoule with aqueous base. In the presence of H_2SO_4, monofluoromalonic acid was formed. It is postulated that the compound $HOCF_2CFHFCO_2H$ is probably an intermediate in this reaction.

To obtain derivatives of $CF_2{=}CFCN$ it was found necessary to protect the olefinic bond during the conversion of the nitrile group. The dibromide was used successfully for this purpose. The amide, $CF_2BrCFBrCONH_2$, was prepared by hydrolyzing

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[1] Presented before the Symposium on Fluorine Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., 1954.

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[7] D. W. Chaney, U. S. Patents 2,439,505 (April 13, 1948), 2,443,024 (June 8, 1948) and 2,456,768 (December 21, 1948).

[8] A. L. Henne and C. J. Fox, THIS JOURNAL, **76**, 479 (1954).

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$CF_2BrCFBrCN$ with 85% H_2SO_4. Debromination with zinc dust gave $CF_2{=}CFCONH_2$. Hydrolysis of the amide sulfate with dilute H_2SO_4 gave $CF_2BrCFBrCO_2H$. Alcoholysis of $CF_2BrCFBrCN$ occurred in the presence of concentrated H_2SO_4 and refluxing C_2H_5OH to give $CF_2BrCFBrCO_2C_2H_5$. Subsequent debromination with zinc dust yielded $CF_2{=}CFCO_2C_2H_5$. $CF_2{=}CFCO_2CH_2C_3F_7$ was prepared in the same manner.

Experimental

$CF_2ClCFClCH_2CH_2I$.—A 500-ml. autoclave was charged with 140 g. (0.5 mole) of $CF_2ClCFClI$[11] and pressured with 450 p.s.i.g. (0.55 mole) of ethylene. The autoclave was rocked for 15 minutes during which time the pressure dropped to 360 p.s.i.g. This was followed by a four-hour heating period at 210°. The liquid recovered from this preparation was fractionated to obtain 144 g. (94% yield) of $CF_2ClCFClCH_2CH_2I$, b.p. 65.1° at 25 mm., d^{20}_4 1.990, n^{20}D 1.4720.

Anal. Calcd. for $C_4H_4Cl_2F_3I$: C, 15.60; H, 1.30; I, 41.37. Found: C, 15.74; H, 1.39; I, 41.32.

Caution.—During an attempt to run this reaction on one molar quantities in a 500-ml. Parr bomb, a violent explosion occurred while heating to 210°. However, three successful reactions were carried out using half-molar quantities.

$CF_2ClCFClCH{=}CH_2$.—To 56 g. (1 mole) of KOH and 500 ml. of C_2H_5OH held at 0° was added slowly 144 g. (0.47 mole) of $CF_2ClCFClCH_2CH_2I$. Stirring was continued for two hours after the addition was completed. The product was washed with a large volume of water, rewashed until neutral, and dried over Drierite; 76 g. (91% yield) of $CF_2ClCFClCH{=}CH_2$ was recovered, b.p. 44.8° at 238 mm., d^{20}_4 1.348, n^{20}D 1.3769, mol. wt. by vapor density 180 (calculated value 179).

Anal. Calcd. for $C_4H_3Cl_2F_3$: C, 26.84; H, 1.67. Found: C, 26.91; H, 2.10.

$CF_2ClCFClCO_2C_2H_5$.—Ten grams (0.056 mole) of $CF_2ClCFClCH_2{=}CH_2$ was added to a 15% aqueous solution of $KMnO_4$ containing 30 g. of the oxidant. The temperature was controlled at 60°. The reaction mixture was cooled to 0° and acidified with 10% H_2SO_4. After removal of any excess $KMnO_4$ with SO_2, the crude $CF_2ClCFClCO_2H$ was extracted with ether. Distillation of a representative portion of this extract yielded 2.5 g. of $CF_2ClCFClCO_2H$. This acid was treated with 5 ml. of absolute ethanol and 2 ml. of concentrated H_2SO_4. After 24 hours in a refrigerator, the lower ester layer was separated. After water washing, drying and distilling, 2 g. (78% yield) of $CF_2ClCFClCO_2C_2H_5$ resulted, b.p. 138–139° at 630 mm., n^{23}D 1.3827. This compares with b.p. 142° at 1 atm., n^{20}D 1.3830 reported earlier.[12]

$CF_2ClCFClCONH_2$.—Anhydrous NH_3 was bubbled through 1.5 g. (0.0067 mole) of $CF_2ClCFClCO_2C_2H_5$. Evaporation of volatile material and sublimation of the resulting solid gave 1.0 g. (68% yield) of $CF_2ClCFClCONH_2$, m.p. 90.6–91.1°.

Anal. Calcd. for $C_3H_2Cl_2F_3NO$: C, 18.39; H, 1.03; N, 7.15. Found: C, 18.08; H, 1.22; N, 6.87.

$CF_2ClCFClCN$ **and** $CF_2{=}CFCN$.—These compounds were synthesized by the methods reported by Chaney.[7]

CH_3OCF_2CFHCN.—Fifty-five grams (0.47 mole) of $CF_2{=}CFCN$, 16.4 g. of CH_3OH and 1.0 g. of benzoyl peroxide were charged to a Magne-Dash autoclave. The mixture was heated to 75° for 16 hours. Fractionation yielded 33 g. of CH_3OCF_2CFHCN, b.p. 32–33° at 30 mm.

Anal. Calcd. for $C_4H_4F_3NO$: C, 34.5; N, 10.07. Found: C, 34.6; N, 10.02.

$CF_2BrCFBrCN$.—One hundred and four grams (0.97 mole) of $CF_2{=}CFCN$ was bubbled into 135 g. (0.85 mole) of bromine. Irradiation from an infrared lamp was required to start the reaction. At the completion of the reaction, the product became colorless. A yield of 224 g. of crude $CF_2BrCFBrCN$ resulted. Fractionation yielded 196 g. (77% yield) of dibromide, b.p. 98–99° at 740 mm., n^{25}D 1.4102.

Anal. Calcd. for $C_3F_3Br_2N$: Br, 59.9. Found: Br, 60.3.

Debromination with zinc dust in dioxane converted the $CF_2BrCFBrCN$ back to $CF_2{=}CFCN$ in 75% yield.

Dimer of $CF_2{=}CFCN$.—Approximately a tenth of a drop of Terpene B was put into a 10-ml. tube, which was then attached to the vacuum system. After evacuation, 7 g. (0.065 mole) of $CF_2{=}CFCN$ was distilled into the tube. The tube was then sealed and heated in an oil-bath at 230° for approximately 72 hours. After cooling in liquid nitrogen, the reactor was opened and the contents distilled in the vacuum system. Five grams of $CF_2{=}CFCN$ and 2 g. of a higher boiling material were obtained. This higher boiling material had a reflux boiling point of 73.5° at 634 mm. pressure, n^{20}D 1.3300, d^{20}_4 1.462, molecular weight by vapor density 212 (calculated value 214). The infrared absorption spectrum on the liquid indicated a band at 4.49 μ which is normally associated with the nitrile group. No band associated with —C═C— was evident. The conversion was 30% and the yield was 100%.

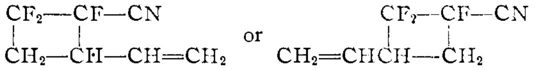
Reaction of $CF_2{=}CFCN$ **with** $CH_2{=}CH{-}CH{=}CH_2$.—The procedure followed was similar to the ones described by Coffman, *et al.*[13] A tube of about 10-ml. capacity was evacuated. Four grams (0.037 mole) of $CF_2{=}CFCN$ and 2.7 g. (0.05 mole) of $CH_2{=}CHCH{=}CH_2$ were then distilled into the tube which was then sealed under vacuum and then placed in an oil-bath at 40–50° for approximately eight hours. A "pot to pot" distillation of the reaction mixture in the vacuum system yielded 5.1 g. (88%) of product, b.p. 137.3° at 633.8 mm., n^{20}D 1.3891, d_4^{20} 1.173.

Anal. Calcd. for $C_7H_6F_3N$: C, 52.2; H, 3.72; N, 8.7. Found: C, 53.2; H, 4.22; N, 9.4.

This compound was oxidized with a basic solution of $KMnO_4$ to yield NH_3, CO_2 upon acidification, and a resinous material. All attempts to isolate an organic acid from this resinous material failed.

The infrared spectrum of the dimer showed the absorption at 4.48 μ associated with the nitrile group along with a band at 6.12 μ which is probably due to the presence of the $CH_2{=}CH{-}$ group.

The probable structure of this compound is either



Basic Hydrolysis of $CF_2{=}CFCN$.—A sample of $CF_2{=}CFCN$ was introduced into an evacuated glass bulb and a large measured excess of 0.5 *N* base added. This mixture was heated to 80° for 30 minutes. Back titration with acid indicated that 2.93 moles of alkali was consumed per mole of nitrile present. Two and one-half moles of fluoride ion per mole of $CF_2{=}CFCN$ was released under these conditions.

Acid Hydrolysis of $CF_2{=}CFCN$.—Fifteen grams of 70% sulfuric acid, 0.5 g. each of Cu powder and hydroquinone were placed in a 30-ml. combustion tube, the tube evacuated, 6 g. (0.056 mole) of $CF_2{=}CFCN$ was added and the tube sealed. This was then heated at 70° in a furnace until all the nitrile had reacted. This required approximately 72 hours. The combustion tube was then cooled in liquid nitrogen and opened. The solid reaction material was dissolved in a minimum amount of water and the water solution extracted with five 5-ml. portions of ether. The ether extracts were combined and upon evaporation a solid was obtained. This solid was redissolved in ether and decolorized twice with carbon. After evaporation of the ether, 3 g. of monofluoromalonic acid was obtained (45% of theory), m.p. 135.8–136.5°, neutral equivalent 123 (calcd. value 122). The infrared spectrum showed strong absorption at 3.45, 3.96, 5.77 and 8.99 μ.

Anal. Calcd. for $C_3H_3FO_4$: C, 29.52; H, 2.48; F, 15.57. Found: C, 30.01; H, 2.82; F, 16.20.

$CF_2BrCFBrCONH_2$.—To 2.6 g. (0.0224 mole) of 85% sulfuric acid, heated to 150°, 6 g. (0.022 mole) of $CF_2BrCFBrCN$ was added over a period of three hours. Heating was continued for eight additional hours. The reaction mixture was then cooled and poured into a flask containing 10 ml. of dry ether. The ether solution was made alkaline

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(13) D. D. Coffman, P. L. Varrick, R. D. Cramer and M. W. Raasch, "Synthesis of Tetrafluorocyclobutanes by Cycloalkylation," This Journal, **71**, 490 (1949).

by bubbling anhydrous ammonia through it for ten minutes. The precipitated $(NH_4)_2SO_4$ was filtered and the solvent removed by evaporation under reduced pressure. The solid thus obtained was sublimed to yield 5.8 g. (90%) of $CF_2BrCFBrCONH_2$, m.p. 60.6–61.0°.

Anal. Calcd. for $C_3H_2Br_2F_3NO$: N, 4.92. Found: N, 4.86.

$CF_2{=}CFCONH_2$.—Two grams (0.03 mole) of zinc dust, a trace of zinc chloride and 100 ml. of dry acetone were mixed, heated to reflux, and 2 g. (0.007 mole) of $CF_2BrCFBrCONH_2$ dissolved in 20 ml. of acetone added slowly to this mixture. Reflux was maintained for two hours after the addition was completed. The solid obtained by solvent evaporation was sublimed to yield 0.55 g. (65%) of $CF_2{=}CFCONH_2$, m.p. 121.4–121.9°.

Anal. Calcd. for $C_3H_2F_3NO$: C, 28.81; N, 11.20. Found: C, 28.58; N, 11.18.

$CF_2BrCFBrCO_2H$.—This reaction was carried out in a manner similar to the reaction described by Wiley, *et al.*[14]; 4.4 g. (0.039 mole) of 85% sulfuric acid was heated to 150° and 10 g. (0.039 mole) of $CF_2BrCFBrCN$ added through the reflux condenser over a period of four hours. The temperature was kept at 150° for two hours after the addition of the nitrile. The bath was then allowed to cool to 90° and 10 ml. of water was added. The temperature was kept at 90° for about 15 hours. After the reaction mixture had cooled to room temperature, it was extracted with five 10-ml. portions of ether. The ether extracts were combined and neutralized with a solution of sodium carbonate. After separation of the water layer, the ether layer was extracted with two 10-ml. portions of water. The combined water layers were evaporated, yielding 6 g. of crude $CF_2BrCFBrCO_2Na$. Evaporation of the ether solution yielded 5 g. of $CF_2BrCFBrCONH_2$. The crude $CF_2BrCFBrCO_2Na$ was finely ground and suspended in 15 ml. of dry ether. Anhydrous HCl was then passed through the ether suspension of the salt for six hours. The reaction mixture was filtered and the ether then removed by distillation at atmospheric pressure. Distillation of the crude acid gave 3.8 g. of $CF_2BrCFBrCO_2H$, b.p. 72–73° at 2.5 mm. pressure, n^{20}_D 1.4458, d^{20}_4 2.191, neutral equivalent 287 (calculated 286).

Anal. Calcd. for $C_3HBr_2F_3O_2$: C, 12.60; Br, 55.91. Found: C, 13.99; Br, 54.20.

$CF_2BrCFBrCO_2C_2H_5$.—Forty grams (0.15 mole) of $CF_2BrCFBrCN$, 29 g. of 90% H_2SO_4 and 35 g. of C_2H_5OH were heated at reflux for nine hours. Ether extraction of the product followed by fractionation gave 28 g. (60% yield) of $CF_2BrCFBrCO_2C_2H_5$, b.p. 81–84° at 18–19 cm., n^{25}_D 1.426.

Anal. Calcd. for $C_5F_3Br_2O_2H_5$: C, 19.1; Br, 50.95. Found: C, 19.1; Br, 50.97.

Preparation of $CF_2{=}CFCO_2C_2H_5$.—About 23.6 g. (0.075 mole) of $CF_2BrCFBrCO_2C_2H_5$ was added to 8.0 g. (0.12 mole) of zinc dust and anhydrous alcohol-free ether with stirring. After the initial exothermic reaction ceased, the ether was refluxed for five hours. Isolation of the product and fractionation yielded 6.0 g. (52% yield) of $CF_2{=}CFCO_2C_2H_5$, b.p. 100.0–100.5° at 750 mm., n^{25}_D 1.3615–1.3619.

Anal. Calcd. for $C_5H_5F_3O_2$: C, 39.0; F, 37.1. Found: C, 39.0; F, 37.0.

Preparation of $CF_2BrCFBrCO_2CH_2C_3F_7$.—This ester was prepared *via* the same method used to make the saturated ethyl ester. Fractionation of the crude product gave a 67% yield of $CF_2BrCFBrCO_2CH_2C_3F_7$, b.p. 72–73° at 10 mm., n^{25}_D 1.3676–1.3680.

Anal. Calcd. for $C_7F_{10}Br_2H_2O_2$: Br, 34.2; C, 17.9; F, 40.6. Found: Br, 34.3; C, 18.1; F, 40.7.

Preparation of $CF_2{=}CFCO_2CH_2C_3F_7$.—A 71% yield of $CF_2{=}CFCO_2CH_2C_3F_7$, b.p. 61.0–61.5° at 50 mm., n^{25}_D 1.3189, was obtained from the debromination reaction.

Anal. Calcd. for $C_7F_{10}O_2H_2$: C, 27.24; F, 61.68. Found: C, 27.3; F, 61.0.

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[14] P. F. Wiley and G. A. Nesty, "Process for Producing Esters of Acrylic Acid," U. S. Patent 2,526,310 (1950).

[CONTRIBUTION FROM THE MEDICAL BIOLOGICAL LABORATORY OF THE NATIONAL DEFENCE RESEARCH COUNCIL T.N.O.]

Synthesis of P^{32} Labeled Diisopropylphosphorofluoridate

BY R. A. OOSTERBAAN AND J. VAN ROTTERDAM

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A method is described for the preparation of P^{32} labeled diisopropylphosphorofluoridate in water or oil solution starting from radioactive phosphoric acid. The specific radioactivity amounts to 200 microcuries/mg.

Introduction

The synthesis of P^{32} labeled diisopropylphosphorofluoridate (DFP) of high specific activity (200 microcuries/mg.) has proved to be valuable in medical work; it has been used for the study of the metabolic fate of DFP and for the determination of plasma protein turnover and the life span of erythrocytes and thrombocytes.[1–3] Moreover the material has been used for studies with the purpose of collecting information on the chemical groups of esterases which are responsible for the enzymatic and DFP binding properties of these proteins.[4–6]

A number of methods for the synthesis of DFP[7–10] and DFP^{32} [11,12] have been published. These methods could not be used unmodified for our purpose. Either starting material of sufficient specific activity cannot be obtained readily or the methods are not designed for the desired microscale operation.

The present method is based on the conversion of phosphoric acid, which is obtainable in carrier-free form, into P^{32} and consequently into $P^{32}Cl_3$. The further synthesis is a micro-scale adaptation of Saunders' method,[11] according to the reaction scheme

$$3ROH + PCl_3 \longrightarrow (RO)_2POH + RCl + 2HCl$$

$$(RO)_2POH + Cl_2 \longrightarrow (RO)_2P(O)Cl + HCl$$

$$(RO)_2P(O)Cl + NH_4F \longrightarrow (RO)_2P(O)F + NH_4Cl$$

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