to the lower constant value above 620°K. This behavior cannot be expressed by the usual type of power series equation for heat capacity. Accordingly, no attempt was made to fit the measured heat contents to an equation for this region. The experimental values were smoothed to give a good fit with the data above and below this region. The average deviation of the smoothed values from the experimental heat contents is 7.7 cal./mole (0.21%). Heat capacities in this region were determined by graphical differentiation of the smoothed data.

The heat content measurements of Kapustinsky and Novosel'tsev[8] were made over the temperature range 295–1395°K. with temperature intervals as large as 275°K. No indication of a specific heat anomaly was found. Mean specific heats, $H_t - H_0/t$, calculated from their data do not yield a smooth fit with the low temperature data of Seltz, *et al.*,[10] and in addition, are some 10% larger than those of this research. These results are shown graphically in Fig. 1. Inasmuch as the apparatus and method of this research gave excellent checks with the Bureau of Standards for the heat content of $Al_2O_3$, we consider our data to be more reliable.

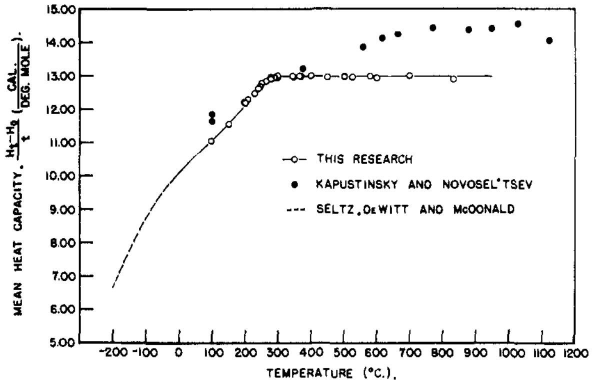

Fig. 1.—Mean heat capacity of nickel oxide.

**Thermodynamic Properties.**—In Table II are summarized the thermodynamic properties of NiO calculated at intervals of 50°. The values of $H_T - H_0$, $C_p$ and $S_T - S_0$ for 273.16°K. were calculated from the data of Seltz, *et al.*[10]

Table II

Thermodynamic Properties of NiO

| $T$, °K. | $H_T - H_0$, cal./mole | $C_p$, cal./deg. mole | $S_T - S_0$, cal./deg. mole | $-(F_T - H_0)$ $T$, cal./deg./mole |
|---|---|---|---|---|
| 273.16 | 1374 | 10.14 | 8.33 | 3.30 |
| 300.0 | 1652 | 10.57 | 9.30 | 3.79 |
| 350.0 | 2204 | 11.56 | 11.00 | 4.70 |
| 400.0 | 2810 | 12.70 | 12.62 | 5.59 |
| 450.0 | 3475 | 13.93 | 14.18 | 6.46 |
| 500.0 | 4204 | 15.21 | 15.72 | 7.31 |
| 523.16[a] | 4563 | 15.82 | 16.42 | 7.70 |
| 550.0 | 4953 | 13.9 | 17.15 | 8.14 |
| 600.0 | 5623 | 13.1 | 18.31 | 8.94 |
| 650.0 | 6270 | 12.91 | 19.34 | 9.69 |
| 700.0 | 6916 | 12.91 | 20.30 | 10.42 |
| 750.0 | 7561 | 12.91 | 21.19 | 11.11 |
| 800.0 | 8207 | 12.91 | 22.04 | 11.78 |
| 850.0 | 8852 | 12.91 | 22.82 | 12.41 |
| 900.0 | 9498 | 12.91 | 23.56 | 13.01 |
| 950.0 | 10143 | 12.91 | 24.26 | 13.58 |
| 1000.0 | 10789 | 12.91 | 24.92 | 14.13 |
| 1050.0 | 11434 | 12.91 | 25.55 | 14.66 |
| 1100.0 | 12080 | 12.91 | 26.15 | 15.17 |

[a] Antiferromagnetic Curie point.

Gulf Research & Development Co.
Pittsburgh, Pa.

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[Contribution No. 84 from the Central Research Department of Minnesota Mining and Manufacturing Company]

# The Free-radical Catalyzed Addition of Alcohols and Aldehydes to Perfluoroölefins[1]

By J. D. LaZerte and R. J. Koshar

Received August 30, 1954

Terminally unsaturated perfluoroölefins containing three or more carbon atoms have been found to undergo a free radical catalyzed addition with alcohols and aldehydes to give good yields of adducts. The addition of an alcohol $RCH_2OH$ to $R_fCF{=}CF_2$ yielded the fluorinated alcohol, $R_fCFHCF_2CHROH$. The aldehyde addition product was identified as the ketone, $R_fCFHCF_2CO{-}R$. No telomerization was observed.

The synthesis of terminally unsaturated perfluoroölefins in high yield by the pyrolysis of the salts of the perfluorocarboxylic acids[2,3] has made many of these olefins available for the investigation of their chemical reactions. While many base-catalyzed nucleophilic addition reactions of these perfluoroölefins have been reported, the investigation of the free radical catalyzed addition of organic compounds has received less attention. Hanford and Joyce in a series of patents[4] have disclosed the free radical catalyzed addition of alcohols, carboxyl compounds, ethers and hydrocarbons to $C_2F_4$ to obtain $H(CF_2CF_2)_nZ$, where $n$ ranges from one up to as high as twenty-five, and Z is the radical formed from the organic reactant. The structures of the compounds formed from these reactions were not reported. The addition

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[1] Presented before the Fluorine Symposium, 124th Meeting of the American Chemical Society, Chicago, Ill., 1953.

[2] L. J. Hals, T. S. Reid and G. H. Smith, This Journal, 73, 4054 (1951).

[3] J. D. LaZerte, L. J. Hals, T. S. Reid and G. H. Smith, *ibid.*, 75, 4525 (1953).

[4] W. E. Hanford (to du Pont), U. S. Patent 2,411,158 (November 19, 1946); W. E. Hanford (to du Pont), U. S. Patent 2,411,159 (November 19, 1946); W. E. Hanford (to du Pont), U. S. Patent 2,433,844 (January 6, 1948); R. M. Joyce (to du Pont), U. S. Patent 2,559,638 (July 10, 1951).

TABLE I

THE ADDITION OF ALCOHOLS TO PERFLUOROÖLEFINS

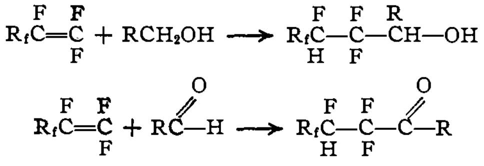
| Alcohol | Olefin | Addition product | Conv., %[a] | Yield, %[b] | B.p., °C.[c] | $n^{25}_D$ | Carbon, % Calcd. | Carbon, % Found | Fluorine, % Calcd. | Fluorine, % Found | OH, % Calcd. | OH, % Found |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $CH_3OH$ | $C_3F_6$ | $CF_3CFHCF_2CH_2OH$ | 70–75 | 90 | 114 | 1.3115 | 26.4 | 26.3 | 62.6 | 62.3 | 9.3 | 9.2 |
| $CH_3OH$ | $C_4F_8$-1 | $C_2F_5CFHCF_2CH_2OH$ | 72 | 76 | 124 | 1.3083 | 25.9 | 26.1 | 65.5 | 65.2 | 7.3 | 7.3 |
| $CH_3OH$ | $C_4H_8$-2 | $CF_3CFHCF(CH_2OH)CF_3$ | 95 | 70 | 118 | 1.3118 | 25.9 | 25.9 | 65.5 | 66.9 | .. | .. |
| $CH_3OH$ | $C_5F_{10}$-1 | $C_3F_7CFHCF_2CH_2OH$ | 89 | 85 | 138 | 1.3093 | 25.5 | 25.8 | 67.4 | 67.7 | 6.0 | 5.8 |
| $CH_3OH$ | $C_7F_{14}$-1 | $C_5F_{11}CFHCF_2CH_2OH$ | 50 | 90 | 170[d] | .... | .. | .. | 69.5 | 67.6 | 4.5 | 4.3 |
| $CH_3OH$ | $C_9F_{18}$-1 | $C_7F_{15}CFHCF_2CH_2OH$ | 33 | 90 | 201[e] | .... | 24.9 | 24.3 | 71.0 | 69.9 | 3.5 | 3.4 |
| $C_2H_5OH$ | $C_4F_8$-1 | $C_2F_5CFHCF_2CHOHCH_3$ | 38 | 66 | 130 | 1.3202 | 29.3 | 29.3 | 61.8 | 61.5 | 6.9 | 6.8 |
| $C_2H_5OH$ | $C_5F_{10}$-1 | $C_3F_7CFHCF_2CHOHCH_3$ | 70 | 60 | 145 | 1.3183 | 28.4 | 28.3 | 64.2 | 63.9 | 5.7 | 5.5 |
| $(CH_3)_2CHOH$ | $C_5F_{10}$-1 | $C_3F_7CFHCF_2COH(CH_3)_2$ | 40 | 55 | 152 | 1.3291 | 30.9 | 30.9 | 61.3 | 60.8 | .. | .. |

[a] Based on olefin reacted. [b] Distilled or recrystallized material. [c] 735–740 mm. [d] Melting point, 38–39°. [e] Melting point, 80–81°.

of $CF_3I$ to $C_2F_4$,[5] $C_3F_6$,[6] $C_2F_3Cl$[7−9] and $CF_3CH{=}CH$[10,11] also has been discussed.

Data are available on the addition of alcohols and aldehydes to hydrocarbon olefins. Urry, *et al.*,[12] found that primary and secondary alcohols added to $C_8H_{16}$-1 in the presence of peroxides or light. All the monoaddition products could be explained by the addition of the RCHOH radical to the terminal carbon of the octene-1 and the hydrogen atom to the other carbon atom, *i.e.*, $C_6H_{13}CH_2CH_2{-}\underset{H}{\overset{R}{C}}{-}OH$. The reaction of an aldehyde with a non-halogenated terminally unsaturated olefin also has been investigated.[13] The products were identified as ketones which were postulated as being formed by the addition of the $RC{=}O$ radical to the terminal carbon atom of the olefin.

The results of the present investigation indicate that analogous reactions are obtained when the perfluoroölefins are substituted for the non-halogenated olefins. The general reactions involved are

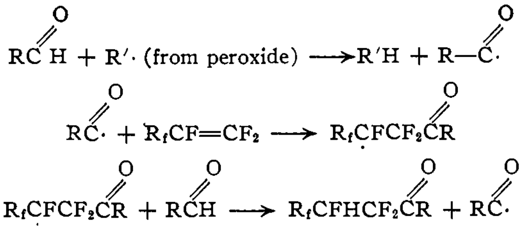


$$R_f\overset{F}{C}=\underset{F}{\overset{F}{C}} + RCH_2OH \longrightarrow R_f\underset{H}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\overset{R}{C}H-OH$$

$$R_f\overset{F}{C}=\underset{F}{\overset{F}{C}} + R\overset{O}{C}-H \longrightarrow R_f\underset{H}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\overset{O}{C}-R$$

The same radicals have apparently added to the perfluoroölefin as added to the non-halogenated olefins. The direction of addition is also identical. Only one product was obtained from a single reaction; no telomers or isomers were found in any of the products.

The mechanism described by Kharasch[13] satisfactorily explains the free radical catalyzed additions to the perfluoroölefins. Applied to the addition of an aldehyde to the fluorinated olefin the reaction can be written as



$$R\overset{O}{C}H + R'\cdot \text{ (from peroxide)} \longrightarrow R'H + R{-}\overset{O}{C}\cdot$$

$$R\overset{O}{C}\cdot + R_fCF{=}CF_2 \longrightarrow R_f\dot{C}FCF_2\overset{O}{C}R$$

$$R_f\dot{C}FCF_2\overset{O}{C}R + R\overset{O}{C}H \longrightarrow R_fCFHCF_2\overset{O}{C}R + R\overset{O}{C}\cdot$$

The addition of alcohols to perfluoroölefins was examined to determine what factors influenced the course of the reaction. The molecular weight of the terminally unsaturated perfluoroölefins did have some effect on the conversion to the 1,1,3-tri-H-alcohols. This may be due to the decreasing solubility of the olefins in the alcohol as the molecular weight of the olefin increases. While the conversion was decreased, the yield of addition product was not changed significantly as the molecular weight of the olefin increased. The conversion and yield values are listed as Table I. Only two perfluoroölefins having non-terminal unsaturation were used. Methanol added to $C_4F_8$-2 at least as rapidly as to $C_4F_8$-1. The expected saturated, fluorine-containing alcohol was obtained. When $c$-$C_6F_{10}$ was substituted for the $C_4F_8$-2, a low conversion to a mixture of addition products was obtained. Infrared spectral analysis indicated that a number of unsaturated compounds were present.

The effect of the structure of the alcohol on the addition also was investigated. Some of the results are summarized in Table II. While $CH_3OH$ and $C_2H_5OH$ reacted very readily with a terminally unsaturated olefin to give high conversions to the fluorine-containing alcohol, the extent of the conversion decreased very rapidly when $n$-$C_3H_7OH$ and $n$-$C_4H_9OH$ were employed. Solubility effects were not the cause of this behavior since the use of $i$-$C_3H_7OH$ and *sec*-$C_4H_9OH$ gave higher conversions in the addition than did their straight chain isomers. These differences in reactivity between isomeric alcohols can be explained on the basis of a greater ease of removal of the H atom on the secondary carbon by the attacking radical, or by the greater tendency of the $R{-}\underset{CH_3}{\dot{C}}{-}OH$ radical to attack the perfluoroölefin.

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[5] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949).

[6] R. N. Haszeldine and B. R. Steele, Abst. 122nd Meeting A.C.S., p. 11K, September, 1952.

[7] R. N. Haszeldine and B. R. Steel, *J. Chem. Soc.*, 1592 (1953).

[8] A. L. Henne and D. W. Kraus, THIS JOURNAL, **76**, 1175 (1954).

[9] W. T. Miller and J. Howald, Abst. 122nd Meeting A.C.S., p. 12K, September, 1952.

[10] A. L. Henne and M. Nager, THIS JOURNAL, **73**, 5527 (1951).

[11] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953).

[12] W. H. Urry, F. W. Stacey, O. O. Juveland and C. H. McDonnell, THIS JOURNAL, **75**, 250 (1953).

[13] M. S. Kharasch, W. H. Urry and B. M. Kuderna, *J. Org. Chem.*, **14**, 248 (1949).

When isobutyl and *t*-butyl alcohols were used no significant amount of addition occurred. Cyclohexanol, β-chloroethanol, ethylene glycol, phenol, benzyl alcohol, hexahydrobenzyl alcohol, benzoin and allyl alcohol did not give addition products under our reaction conditions.

TABLE II

FREE-RADICAL CATALYZED ADDITION OF ALCOHOLS TO $C_5F_{10}$-1

| Alcohol | Conversion to fluorinated alcohol, % | Alcohol | Conversion to fluorinated alcohol, % |
|---|---|---|---|
| Methyl | 89 | *n*-Butyl | <5 |
| Ethyl | 70 | *s*-Butyl | 20 |
| *n*-Propyl | 20 | *i*-Butyl | <5 |
| *i*-Propyl | 40 | *t*-Butyl | <5 |

The addition of $CH_3OH$ to $C_3F_6$ was investigated in some detail to determine the effect of the reaction conditions on conversion and yields. The mole ratio of alcohol to olefin was found to have a considerable influence on the conversion which could be obtained. When this ratio was one, or less than one, the conversion of the olefin was less than 50%. However, a 3:1 or 5:1 mole ratio of reactants gave conversions of 70–75% under similar experimental conditions (see Fig. 1).

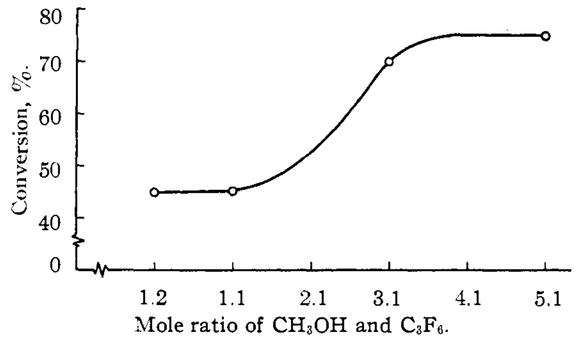


Fig. 1.—Preparation of $CF_3CFHCF_2CH_2OH$: time, eight hours; temperature, 100°; catalyst, one mole % benzoyl peroxide.

The purity of the $CH_3OH$ had a very noticeable effect on the rate of the addition reaction. A technical grade of $CH_3OH$ thought to contain very minor amounts of aldehyde reacted more rapidly with $C_3F_6$ than did $CH_3OH$ which had been dried carefully and fractionated. When the technical grade $CH_3OH$ was employed 70% conversion of the olefin was obtained in a two-hour period. A six to seven hour reaction time was necessary to obtain this same conversion when the purified $CH_3OH$ was used (see Fig. 2).

Benzoyl peroxide was found to be a very satisfactory catalyst. The quantities used varied from 0.5 to 1.0% by weight of the reactants. Some of the alcohol addition reactions were attempted with other peroxides, but comparable results were not obtained. Acetyl peroxide, *t*-butyl perbenzoate and *t*-butyl hydroperoxide gave much lower conversions.

The optimum reaction temperature for the addition of $CH_3OH$ to $C_3F_6$ was found to be 115–120°. Below this temperature longer reaction times were necessary. Above 120° the conversion to the adduct decreased significantly (see Fig. 3).

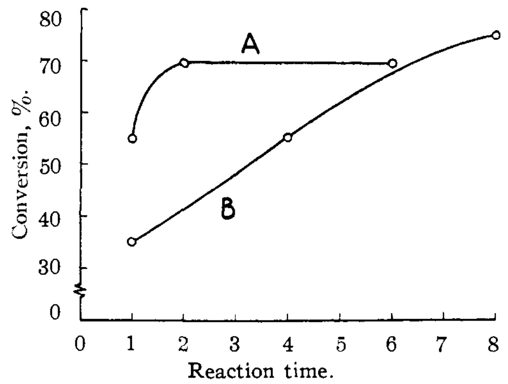


Fig. 2.—Preparation of $CF_3CFHCF_2CH_2OH$: curve A, technical grade $CH_3OH$; curve B, chemically pure $CH_3OH$; mole ratio of $CH_3OH$ and $C_3F_6$ = 5:1; temperature, 120°; catalyst, one mole % benzoyl peroxide.

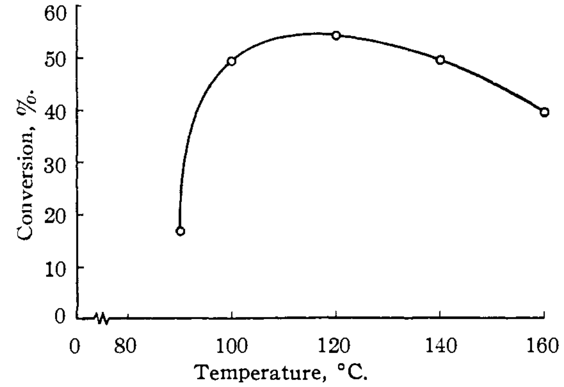


Fig. 3.—Preparation of $CF_3CFHCF_2CH_2OH$: mole ratio of $CH_3OH$ and $C_3F_6$ = 5:1; time, 1 hr.; catalyst, one mole % benzoyl peroxide.

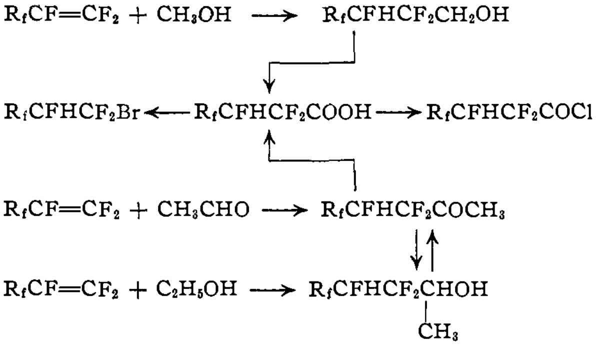
The chemical stability of the fluorine-containing alcohols and ketones to acidic and basic conditions was determined. The alcohols of the type $R_fCFHCF_2CH_2OH$ were found to be stable in the presence of 0.5 *N* HCl at 100°. Decomposition was obtained in the presence of 0.2 *N* NaOH solution at the same temperature. A similar base stability test carried out with a dihydroperfluoro alcohol, $R_fCH_2OH$, gave no decomposition. The hydrogen atom on the γ-carbon atom apparently contributes to the base instability of the 1,1,3-trihydroperfluoro alcohols. The hydrolytic stability of one of the fluorine-containing ketones indicated that no decomposition occurred when the ketone was heated to 80–90° with 5% $H_2SO_4$. Extensive decomposition did occur, however, when the ketone was mixed with 5% NaOH or 10% $(C_2H_5)_3N$ at 80–90°.

The chemical reactions used to help determine the structure of the adducts and to illustrate their reactivity are shown in Chart I. Oxidation of alcohols of the general formula $R_fCFHCF_2CH_2OH$ or the ketones $R_fCFHCF_2COCH_3$ gave a high yield of β-hydroperfluoro acid.[7] Pyrolyses of the sodium salts of these β-hydro acids resulted in a convenient synthesis of the olefins, $R_fCH{=}CF_2$.

Dehydration of the secondary and tertiary alcohols, $R_fCFHCF_2CHOHCH_3$ and $R_fCFHCF_2CROHCH_3$, yielded $R_fCFHCF_2CH{=}CH_2$ and $R_fCFHCF_2CR{=}CH_2$.

CHART I

INTERCONVERSION OF ADDUCTS



Several other tests were conducted to determine that the acetaldehyde addition product was $R_fCFHCF_2COCH_3$ rather than $R_fCFHCF_2CH_2COH$. Treatment of the addition compound with a basic iodine–potassium iodide solution yielded a small quantity of iodoform. The compound gave a negative Schiff test, and was oxidized very slowly with $KMnO_4$ at 25°. No oxidation occurred when the adduct was refluxed with aqueous dichromate.

The direction of the additions was firmly established by both nuclear magnetic resonance measurements[14] and chemical reactions conducted on compounds which had been prepared from the adducts. A sample of acid was prepared by oxidation of the methanol–perfluoropropene adduct ($CF_3CFHCF_2CH_2OH$ or $CF_3CF(CH_2OH)CF_2H$). This acid was then converted into the acid chloride ($CF_3CFHCF_2COCl$ or $CF_3CF(COCl)CF_2H$) and the bromide ($CF_3CFHCF_2Br$ or $CF_3CFBrCF_2H$). The nuclear magnetic resonance spectra for the acid chloride showed that the proton peak was split into a doublet by spin–spin interaction with one fluorine atom on the same carbon atom as the hydrogen. If a $-CF_2H$ group had been present the proton peak would have been split into three peaks. The compound then has the formula $CF_3CFHCF_2COCl$. The fluorine resonance peaks were also in agreement with this structural assignment.

The structure of the bromide was proved to be $CF_3CFHCF_2Br$. The product from the vapor phase addition of HBr to $C_3F_6$ has been shown[6] to be $CF_3CFHCF_2Br$. This reaction was repeated and the infrared spectrum of the product compared with the spectrum of the bromide prepared from the methanol–perfluoropropene adduct. The two spectra were identical. The structure of the adduct must be $CF_3CFHCF_2CH_2OH$. Because of the interrelation of the reaction products shown in Chart I, the structures as written in this figure are correct.

## Experimental

**Materials.**—The terminally unsaturated perfluoroölefins were prepared by the pyrolysis of salts of perfluorocarboxylic acids. All of the alcohols and aldehydes used, with the exception of certain specified samples of methanol, were either analytical reagent grade or were purified by fractionation. Technical grade methanol was obtained from the Aloe Company. Benzoyl peroxide was obtained from the Novadel–Agene Corporation.

**Apparatus.**—The addition reactions were carried out either in sealed Pyrex ampoules or in a 250-cc. glass-lined stainless steel Magne Dash autoclave, depending on the boiling point of the perfluoroölefin and the quantity of product desired. When the autoclave was used, it was necessary to repeat the reaction several times until a high, constant conversion was attained. Traces of impurities apparently interfered with the propagation of the free radical reaction.

**The Addition of Methanol to Perfluoropropene.**—A mixture of 65.5 g. (2.05 moles) of technical grade methanol and 1.5 g. of benzoyl peroxide was charged to the autoclave. The autoclave was cooled with liquid air, evacuated and 56 g. (0.37 mole) of perfluoropropene introduced. The autoclave was then closed and the contents agitated at 110–120° for 3 hours. Only 15 g. of unreacted perfluoropropene was bled from the autoclave at room temperature. Any undecomposed peroxide was destroyed by the addition of ferrous sulfate or sodium bisulfite to the reaction mixture. Fractionation of the reaction mixture gave 45 g. (90% yield) of $CF_3CFHCF_2CH_2OH$, b.p. 114.5° (740 mm.), $n^{25}{}_D$ 1.3115. *Anal.* Calcd. for $C_4F_6H_4O$: C, 26.4; F, 62.6; OH, 9.3. Found: C, 26.3; F, 62.3; OH, 9.2. No other addition products were obtained. Infrared spectral analysis showed a characteristic C–OH absorption band at 2.9 $\mu$.

**The Addition of Methanol to Perfluorononene-1.**—Eighteen and three-tenths grams (0.04 mole) of perfluorononene-1, 1.6 g. (0.05 mole) of refined methanol and 0.2 g. of benzoyl peroxide were sealed in an evacuated Pyrex ampoule. The reactants were shaken at 80–90° for 15 hours. Distillation of the reaction mixture under reduced pressure yielded a solid residue. Vacuum sublimation of this solid gave 3.4 g. of $C_7F_{15}CFHCF_2CH_2OH$, m.p. 80–81°, b.p. 201–202° (740 mm.). *Anal.* Calcd. for $C_{10}F_{18}H_4O$: C, 24.9; F, 71.0; OH, 3.5. Found: C, 24.3; F, 69.9; OH, 3.4.

Table I summarizes the yields and physical properties of the adducts prepared by the addition of $CH_3OH$, $C_2H_5OH$, and $(CH_3)_2CHOH$ to the perfluoroölefins. The addition of $n$-$C_3H_7OH$, $n$-$C_4H_9OH$, $n$-$C_5H_{11}OH$, $ClCH_2CH_2OH$, $CH_2{=}CHCH_2OH$, $OHCH_2CH_2OH$, $C_6H_5OH$, $c$-$C_6H_5CH_2OH$, $c$-$C_6H_{11}CH_2OH$ and $C_6H_5COCHOHC_6H_5$ also was carried out under similar conditions.

**The Addition of Acetaldehyde to Perfluorobutene-1.**—To the evacuated Magne Dash autoclave was charged 108 g. (0.54 mole) of perfluorobutane-1, 26 g. (0.59 mole) of acetaldehyde and 0.5 g. of benzoyl peroxide. The contents of the autoclave were agitated at 100° for 15 hours. Fractionation of the reaction mixture gave 100 g. (76% yield) of $C_2F_5CFHCF_2COCH_3$, b.p. 91–92° (740 mm.), $n^{25}{}_D$ 1.2988, $d^{25}{}_4$ 1.693. *Anal.* Calcd. for $C_6F_8H_4O$: C, 29.7; F, 61.9. Found: C, 29.5; F, 62.3. Infrared spectral analysis showed a characteristic C=O absorption band at 5.68 $\mu$.

This product was dissolved in dioxane, made basic and then treated with an iodine–potassium iodide solution at 60°. $CHI_3$ was isolated and identified. The adduct also gave a negative Schiff test, did not discolor bromine in $CCl_4$ and was oxidized very slowly with $KMnO_4$ dissolved in acetone. Oxidation with aqueous acid–dichromate at 100° did not occur.

**The Addition of Butyraldehyde to Perfluoropropene.**—A mixture of 95 g. (0.63 mole) of perfluoropropene, 46 g. (0.64 mole) of butyraldehyde and 0.75 g. of benzoyl peroxide was charged to the Magne Dash autoclave and then agitated at 80° for 16 hours. Fifteen grams of unreacted perfluoropropene was bled from the autoclave at room temperature. Fractionation of the reaction mixture gave 65.5 g. (70% yield) of $CF_3CFHCF_2COC_3H_7$, b.p. 111.0–111.5° (738 mm.), $n^{25}{}_D$ 1.3268. *Anal.* Calcd. for $C_6F_6H_8O$: C, 37.8; F, 51.4. Found: C, 37.9; F, 51.4. The adduct had a strong C=O infrared absorption band at 5.71 $\mu$.

**The Oxidation of $C_2F_5CFHCF_2CH_2OH$.**—Eight grams (0.03 mole) of $C_2F_5CFHCF_2CH_2OH$, 10 g. (0.03 mole) of potassium dichromate, 12 g. of concentrated sulfuric acid and 25 cc. of distilled water were stirred under reflux for 4 hours. The mixture was filtered and the filtrate extracted with diethyl ether. Neutralization of the extracts with

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[14] Varian Associates, Palo Alto, California.

aqueous KOH yielded 9 g. of ethanol-soluble salt. The salt was acidified with concentrated sulfuric acid and the acid mixture distilled. Fractionation yielded 5 g. (0.02 mole) of $C_2F_5CFHCF_2COOH$, b.p. 152–153° (740 mm.), $n^{25}_D$ 1.3073, neut. equiv., 247 (calculated 245).

Using the above procedure, $CF_3CFHCF_2COOH$, b.p. 140° (740 mm.), $n^{25}_D$ 1.3100, neut. equiv. 197 (calculated 196) and $C_3F_7CFHCF_2COOH$, b.p. 166–167° (740 mm.), $n^{25}_D$ 1.3120, neut. equiv. 285 (calcd. 296) were prepared by the oxidation of $CF_3CFHCF_2CH_2OH$ and $C_3F_7CFHCF_2CH_2OH$, respectively.

**The Pyrolysis of $C_3F_7CFHCF_2COONa$.**—Pyrolysis of 9.3 g. (0.03 mole) of vacuum-dried $C_3F_7CFHCF_2COONa$ occurred at 220° to give 4 g. of $C_3F_7CH{=}CF_2$, b.p. *ca.* 30° (740 mm.). *Anal.* Calcd. for $C_5F_9H$: mol. wt., 232; C, 25.8; F, 73.7. Found: mol. wt., 235 (vapor density); C, 25.9; F, 73.1. The compound had a C=C infrared absorption band at 5.68 $\mu$.

**The Oxidation of $C_2F_5CFHCF_2CHOHCH_3$.**—A mixture of 8 g. (0.03 mole) of $C_2F_5CFHCF_2CHOHCH_3$, 9 g. (0.03 mole) of potassium dichromate, 8.5 g. of concentrated sulfuric acid and 50 cc. of water was stirred at 100° for 20 hours. Six grams of water-insoluble product was isolated. Infrared spectral analysis showed that the product contained a strong C=O absorption band but no C-OH band. The properties and spectrum of this product compared with those of $C_2F_5CFHCF_2COCH_3$ which was prepared by the addition of acetaldehyde to perfluorobutene-1.

**The Dehydration of $C_3F_7CFHCF_2CHOHCH_3$.**—To a flask containing 6 g. (0.04 mole) of $P_2O_5$ was added 11 g. (0.04 mole) of $C_3F_7CFHCF_2CHOHCH_3$. The reaction was very exothermic. Fractionation of the mixture yielded 7.5 g. of product, b.p. 91–92° (740 mm.), $n^{25}_D$ 1.3005, thought to be $C_3F_7CFHCF_2CH{=}CH_2$. *Anal.* Calcd. for $C_7F_{10}H_4$: C, 30.1; F, 68.3. Found: C, 30.5; F, 67.1. The compound appeared to undergo decomposition on standing. Infrared spectral analysis showed no absorption bands due to C=C or C-OH. However, the presence of the C=C bond was indicated by the rapid absorption of bromine in the presence of ultraviolet irradiation.

**The Dehydration of $C_3F_7CFHCF_2C(CH_3)_2OH$.**—A mixture of 12 g. (0.08 mole) of $P_2O_5$ and 19.4 g. (0.06 mole) of $C_3F_7CFHCF_2C(CH_3)_2OH$ was heated under reflux for 2 hours. A one-plate distillation gave 17 g. of distillate boiling at 110–120°. Fractionation yielded 11 g. of $C_3F_7CFHCF_2C(CH_3){=}CH_2$, b.p. 113–114° (740 mm.), $n^{25}_D$ 1.3143. *Anal.* Calcd. for $C_8F_{10}H_6$: C, 32.8; F, 65.1. Found: C, 33.0; F, 65.3. Again, infrared spectral analysis showed no absorption due to C=C or C-OH. The existence of the double bond was indicated by bromination in the presence of ultraviolet light.

**The Oxidation of $C_2F_5CFHCF_2COCH_3$.**—Six grams (0.02 mole) of $C_2F_5CFHCF_2COCH_3$, 4 g. (0.02 mole) of $KMnO_4$ and 25 cc. of analytical grade acetone were stirred at 60° for 3 hours. The reaction mixture was diluted with $H_2O$ and filtered to remove $MnO_2$. The filtrate was acidified, and extracted with diethyl ether. Neutralization with aqueous base yielded an ethanol-soluble salt. The salt was acidified with concentrated sulfuric acid and the acid mixture distilled. Fractionation gave 3 g. of acid product, b.p. 150–152°, $n^{25}_D$ 1.3070, neut. equiv. 240 (calcd. 245). These physical properties and the infrared spectrum were the same as that of $C_2F_5CFHCF_2COOH$ prepared by the oxidation of $C_2F_5CFHCF_2CH_2OH$.

**The Oxidation of $CF_3CFHCF_2COC_3H_7$.**—The procedure was similar to that described for the oxidation of $CF_3CFHCF_2COCH_3$. A mixture of 10 g. (0.05 mole) of $CF_3CFHCF_2COC_3H_7$, 15.5 g. (0.09 mole) of $KMnO_4$ and 50 cc. of reagent grade acetone was heated under reflux for 4 hours. There was isolated 8.4 g. of acid, b.p. 139–142°, neut. equiv. 155 (calcd. 196). Comparison of its infrared spectrum with that of a sample of $CF_3CFHCF_2COOH$ prepared by the oxidation of $CF_3CFHCF_2CH_2OH$ indicated this product to be mostly $CF_3CFHCF_2COOH$. A second unidentified component also was present.

**The Hydrogenation of $C_2F_5CFHCF_2COCH_3$.**—A 43-cc. stainless steel autoclave was charged with 15.3 g. (0.06 mole) of $C_2F_5CFHCF_2COCH_3$ and 1.6 g. of copper chromite catalyst. The autoclave was pressurized with hydrogen to 2,000 p.s.i. and then heated at 150° for 8 hours. Fractionation yielded 6 g. of fluorine-containing alcohol, b.p. 128–130°, $n^{25}_D$ 1.3190. The physical properties and infrared spectrum of the product were the same as that of $C_2F_5CFHCF_2CHOHCH_3$ prepared by the addition of ethanol to perfluorobutene-1.

**The Preparation of $CF_3CFHCF_2COCl$.**—Five grams (0.02 mole) of $CF_3CFHCF_2COONa$ and 10 g. (0.08 mole) of benzoyl chloride were heated at 200° under reflux. Fractionation yielded 3 g. of $CF_3CFHCF_2COCl$, b.p. 54.5–55.0° (735 mm.), $n^{25}_D$ 1.3056. *Anal.* Calcd. for $C_4F_6HOCl$: C, 22.4; F, 53.2. Found: C, 22.6; F, 52.8.

**The Preparation of $CF_3CFHCF_2Br$.**—A mixture of 10 g. (0.03 mole) of dry $CF_3CFHCF_2COOAg$ and 5.3 g. (0.03 mole) of bromine reacted at room temperature to give $CO_2$ and 5.5 g. of crude $CF_3CFHCF_2Br$. Separation of the mixture by means of a one-plate distillation gave 2 g. of $CF_3CFHCF_2Br$, mol. wt. 222–229 (calcd. 231). The infrared spectrum was the same as a sample of $CF_3CFHCF_2Br$ prepared by the vapor phase addition of HBr to perfluoropropene.

In this latter reaction a total of 56 g. of $C_3F_6$ and 91 g. of HBr were passed through a hot tube at 120° over 25% $CaSO_4$–carbon catalyst. There was isolated 3.5 g. of $CF_3CFHCF_2Br$.

**The Hydrolytic Stability of $C_2F_5CFHCF_2CH_2OH$ and $C_2F_5CFHCF_2COCH_3$.**—The stability of $C_2F_5CFHCF_2CH_2OH$ and $C_2F_5CFHCF_2COCH_3$ was investigated in aqueous acid and base. In each case, several grams of the compound was heated at 100° in an acidic or alkaline solution. The aqueous phase was then titrated for total fluoride ion. The results of the experiments are shown in Tables III and IV.

Table III

Hydrolytic Stability of $C_2F_5CFHCF_2CH_2OH$ at 100°

| $C_2F_5CFHCF_2CH_2OH$, mole | Reagent | Time, hr. | Total fluoride ion (equiv.) |
|---|---|---|---|
| 0.15 | 10% $(C_2H_5)_3N$ | 20 | 0.006 |
| .12 | 10% $Na_2CO_3$ | 15 | .108 |
| .01 | 0.2 *N* NaOH | 4 | .040 |
| .01 | 0.5 *N* HCl | 20 | < .0003 |

Table IV

Hydrolytic Stability of $C_2F_5CFHCF_2COCH_3$ at 100°

| $C_2F_5CFHCF_2COCH_3$, mole | Reagent | Time, hr. | Total fluoride ion (equiv.) |
|---|---|---|---|
| 0.015 | $H_2O$ | 21 | <0.0001 |
| .017 | 10% $(C_2H_5)_3N$ | 20 | .013 |
| .023 | 5% NaOH | 15 | .054 |

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