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# A NOVEL TELOMERIZATION* PROCEDURE FOR CONTROLLED INTRODUCTION OF PERFLUORO-n-ALKYL END GROUPS

W.H. GUMPRECHT and R.H. DETTRE

Jackson Laboratory - Organic Chemicals Department, E.I. du Pont de Nemours & Company, Deepwater, New Jersey 08023 (U.S.A.)

## SUMMARY

The combination of fully halogenated dialkanoyl peroxides and polybromo- or polyiodomethanes has been developed as an efficient, mild telogen system for telomerizing chlorotrifluoroethylene and vinylidene chloride. Some of these telomers have been converted to carboxylic acids for investigation of their surface properties as monolayers.

## INTRODUCTION

As part of a continuing program for studying surface properties of fluorinated groups there arose a need to prepare well-defined perfluoro-n-alkyl terminated telomers of chlorotrifluoroethylene ($CF_2$=CFCl) and vinylidene chloride ($CH_2$=$CCl_2$). The syntheses of telomers (I) of $CF_2$=CFCl using $R_fI$ as telogens

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* The principles of telomerization used in this work have been presented by Haszeldine[1].

(Tel-X) with either thermal or photochemical initiation have been described[2]. No similar synthesis of telomers from $CH_2=CCl_2$ is known, though kinetic data indicate[3] that this taxogen (Tax) readily adds $R_f\cdot$.

Attempts in this laboratory to telomerize $CF_2=CFCl$ thermally with $C_2F_5I$ have shown that this procedure suffers as a preparative method because of the formation of large amounts of iodine-free, coupled products (II). The photochemical telomerization procedure is also of limited preparative value because of the long reaction times required and the need for special equipment, though fewer by-products are formed.

$$\text{Tel-X} + n\ \text{Tax} \xrightarrow[\text{or } h\upsilon]{\Delta} \underset{\text{(I)}}{\text{Tel}\text{-(Tax)}_n\text{-X}} + \underset{\text{(II)}}{[\text{Tel}\text{-(Tax)}_n]_2} + X_2$$

## RESULTS AND DISCUSSION

### Dialkanoyl Peroxides as $R_f\cdot$ Sources

An alternative to the photolytic and thermal routes to $R_f\cdot$ is the homolytic decomposition of perfluorodialkanoyl peroxides (III) followed by loss of $CO_2$. This reaction would be expected to occur under relatively mild thermal inducement so that secondary radical processes should be minimized.

$$\underset{\text{(III)}}{(R_fCO)_2O_2} \xrightarrow{\Delta} 2[R_fCO_2\cdot] \longrightarrow 2[R_f\cdot] + 2CO_2$$

The use of this technique has apparently been limited by the lack of availability of the peroxides. Indeed, a maximum

yield of $(CF_3CO)_2O_2$ of only about 20% from $(CF_3CO)_2O$ could be attained under the most favorable conditions; the literature procedure[4] gave an even poorer yield. The inability in obtaining this peroxide in sufficient quantity prevented its use as a starting material in this work.

The yields of $(C_2F_5CO)_2O_2$[5] and $(CF_3CCl_2CO)_2O_2$ from the acyl chlorides[6,7], however, are in the 80% range. The half-lives of $(C_2F_5CO)_2O_2$ at 50° and 60°C. are 53 and 15 min., respectively; $(CF_3CCl_2CO)_2O_2$ would be expected to be less stable, being similar to $(CCl_3CO)_2O_2$[8]. The acyl chloride, $CF_3CCl_2COCl$, was prepared in an overall yield of 27% starting from $CF_3CCl{=}CCl_2$ by the published procedures[7]. A significant impurity encountered in this preparation was $CF_3CHClCO_2C_2H_5$[9] which could not be removed completely from the acyl chloride by distillation.

Telomerizations

Treatment of taxogens, such as $CF_2{=}CFCl$, with dialkanoyl peroxides alone would not generate true telomers since the terminating group -X would not be controlled. For this purpose a chain transfer agent is needed. Initially, it was thought that $R_fI$ could serve this purpose. However, the combination of $CF_2{=}CFCl$, $(C_2F_5CO)_2O_2$ and $C_2F_5I$ (chosen to maintain the integrity of the initiating group Tel-) gave iodine-free, coupled products of the II type almost exclusively. This behavior clearly indicates the greater bond strength of $-CF_2{-}I$ in the chain transfer agent versus that in the expected telomers (IVa; X=I)[1].

$C_2F_5(CF_2CFCl)_n X$ (IV)

Steric crowding of the multiple, bulky halogens in polybromo- or polyiodomethanes should reduce the bond strength of any one of the $\rangle C - X$ bonds and, along with resonance stabilization, should reduce the radical reactivity of the resultant polyhalogenated methyl radicals toward electron-deficient taxogens*. Use of $CHI_3$ instead of $C_2F_5I$ in the $CF_2$=CFCl - $(C_2F_5CO)_2O_2$ reaction generated telomers which were sensitive to photochemical oxidation, as indicated by bands in their infrared spectra at 5.30μ for $-CF_2COF$ and at 5.64μ for $-CF_2CO_2H$. This characteristic suggests the presence of the -CFClI group in these telomers (IVa; X=I)[1]. There was no evidence for C-H absorption in these spectra, ruling out the possibility of significant incorporation of $-CHI_2$ groups. The pattern of infrared absorption was similar to that encountered with known $CF_2$=CFCl polymers[11a]. In addition, a band seen at 7.45μ has been attributed to the $C_2F_5$- group.

Carbon tetrabromide in place of $CHI_3$, gave similar telomers (IVb; X=Br). However, these were not prone to photochemical oxidation.

$^{19}F$ NMR spectroscopy is not particularly useful in analyzing these telomers in that their spectra (in $CFCl_3$) showed broad, overlapping absorptions with little-to-no fine structure. This complexity may well arise from the $-CF_2$-'s

*Walling[10] has presented data and a thorough discussion of factors influencing radical addition reactions of alkyl polyhalides.

in the repeating $-(CF_2CFCl)_n-$ since these two $^{19}F$'s are not equivalent, splitting each other and coupling to the $^{19}F$ on the assymetric -CFCl-. Based on analysis of spectra for some simple reference molecules, very tentative assignments can be made for the $^{19}F$'s in Br-terminated telomers (IVb; X=Br). Thus, the absorption at a chemical shift of about 81 ppm from $CFCl_3$ (internal standard) probably arises from $\underline{CF_3}CF_2$-, appearing as a triplet, plus $-CF_2\underline{CF}ClBr$. The broad, overlapping multiplets between 103 and 112 ppm may be due to the $-\underline{CF_2}CFCl$-'s in the repeating unit, with the two attached to the carbon next to $C_2F_5$- appearing separately at about 115 ppm. Still another set of broad, overlapping multiplets between 120 and 131 ppm may be caused by a combination of the -CFCl-'s in the repeating unit plus the $CF_3\underline{CF_2}$-. Assuming the 115 ppm absorption **in** the NMR spectrum of a typical Br-terminated telomer (IVb; X=Br) to total two $^{19}F$'s, the number of other $^{19}F$'s were, respectively, 4.1 $CF_3$ plus -CFClBr, 13.1 $-\underline{CF_2}CFCl$-'s in the repeating unit and 8.1 -CFCl-'s in the repeating unit plus $CF_3\underline{CF_2}$-. On this basis, the average value of "n" was, then, between 6.1 and 7.6. More meaningful NMR data are obtained for the carboxylic acids derived from these telomers which will be discussed later in this paper.

Using the $^{19}F$ NMR spectra to obtain a rough estimate of the values of "n", it is possible to compare $CBr_4$ with $CHI_3$ in their effectiveness as chain transfer agents and to determine the effect of changes in the molar ratios of reactants on the

degree of telomerization. Thus, using 0.2 mole of $CBr_4$ or $CHI_3$ with 0.1 mole of $(C_2F_5CO)_2$ $O_2$ and 1 mole of $CF_2$=CFCl gave an average value for "n" = 7 with the former, compared with 13 with the latter. Also, increasing the amount of $(C_2F_5CO)_2$ $O_2$ from 0.13 to 0.146 mole per mole of $CF_2$=CFCl and keeping the concentration of $CBr_4$ constant at 0.2 mole per mole of the taxogen under essentially identical operating conditions, decreased the average value of "n" from 11-15 to 7-9.

The use of $(CF_3CCl_2CO)_2$ $O_2$ with $CF_2$=CFCl and $CBr_4$ also gave Br-terminated telomers. However, $^{19}F$ NMR of acids derived from them (vide infra) showed two types of $CF_3$-, at about 70 ppm and 77 ppm, with the latter predominating. Again, based on reference spectra of related, simple molecules, these $^{19}F$ absorptions are attributed to $\underline{CF_3}CCl_2CF_2$- and $\underline{CF_3}CF_2CFCl$-, respectively. Other spectral characteristics were consistent with $-(CF_2CFCl)_n-$. It would appear, then, that the generated $CF_3CCl_2\cdot$ is prone to expel $CCl_2$:, giving rise to two telomer structures (Va, VIa; X = Br).

$$CF_3CCl_2-(CF_2CFCl)_n\ X \qquad CF_3\cdot(CF_2CFCl)_n\ X$$

(V) (VI)

Vinylidene chloride also gave telomers (VIIa and b; X = Br and I) with $(C_2F_5CO)_2$ $O_2$ and either $CBr_4$ or $CI_4$. A broader molecular weight distribution occurred in these telomerizations than in those using $CF_2$=CFCl. Their infrared spectra were quite similar to those of known $CH_2$=$CCl_2$ polymers[11b] except for bands at 7.5 and 8.3μ indicative of $C_2F_5$- and >CF-.

Their $^{19}F$ NMR spectra (in hexafluorobenzene) were consistent with attack of $C_2F_5\cdot$ at the $CH_2=$ since the two major absorptions were, as a singlet for $\underline{CF_3}CF_2-$, near 87 ppm and, as a triplet for $-CF_2\underline{CH_2}-$, near 116 ppm. These spectra were of little use in obtaining average values of "n" for these telomers. More reliable values were determined from halogen ratios by elemental analysis.

$$C_2F_5-(CH_2CCl_2)_n-X$$
(VII)

The telomerization combination of $(C_2F_5CO)_2O_2$ and $CBr_4$ generally gave high conversions (80-95%) of these taxogens. Other combinations were less satisfactory.

In passing, it should be noted that the combination of $(C_2F_5CO)_2O_2$ and $CHI_3$ with hexafluoropropylene gave a complex mixture of I-containing telomers which were similar, by $^{19}F$ NMR, to those obtained[12] by thermal telomerization using $C_2F_5I$. Conversions in both cases were quite low (about 3%). However, the conditions were milder, and the molecular weight distribution was much narrower using the peroxide system.

## Conversion of $CF_2=CFCl$ and $CH_2=CCl_2$ Telomers to Carboxylic Acids

The conversion of polyhalogenated methyl groups into the carboxyl group by treatment with oleums of various strengths[13] or fuming nitric acid[14] has been described. The oleum procedure was quite effective with the $CF_2=CFCl$ telomers, giving telomeric carboxylic acids (IVc, Vb, VIb; X = $CF_2CO_2H$). These acids were

fractionated into low and high molecular weight components by vacuum distillation of their methyl esters (IVd, Vc, VIc; X = $CF_2CO_2CH_3$) which were readily saponified back to the acids. The infrared spectra of these acids showed, in addition to the same general absorptions as were found in the spectra of the halogen-terminated telomers, bands between 2.7 and 4.0μ and at 5.64μ for $-CF_2CO_2H$.

The $^{19}F$ NMR spectra (in hexafluorobenzene) of these acids, while complex, permitted a clearer interpretation than spectra of the halogen-terminated telomers. Thus, the spectrum of the acid IVc had absorptions at 81 ppm for $\underline{CF_3}CF_2-$, between 100 and 113 ppm for $-\underline{CF_2}CFCl-$, at 115 ppm for $-\underline{CF_2}CO-$, and at 123 ppm for $CF_3\underline{CF_2}CF_2-$ which was partially overlapped by -CFCl- bands between 121 and 138 ppm. (The spectra of the mixed acids Vb and VIb were described earlier.)

Average values for "n" in these telomers could be determined more accurately using these spectra. For instance, values of 3.2 and 3.3 were calculated, taking the three $^{19}F$ in the $CF_3-$ as the basis, from the sums of the $^{19}F$'s in $-\underline{CF_2}CFCl$ plus $-CF_2CO-$ and in -CFCl- plus $CF_3\underline{CF_2}CF_2-$, respectively, in the fractionated acid IVc from saponification of the lower boiling ester IVd.

The $CH_2=CCl_2$ telomers were prone to degradation, primarily through dehydrochlorination[15], during conversion into the acids (VIII), even under the mildest conditions[13a,14]. A large proportion of these telomers proved to be inert dimers of the II type. The infrared spectra of these acids had bands for $-CH_2CO_2H$ between

2.8 and 4.2μ and at 5.84μ, for $C_2F_5$- at 7.50μ and for >C=CH- at 6.14μ. The remainder of the spectra was consistent with $-(CH_2CCl_2)_n$ [11b].

The $^1H$ NMR spectra (in hexafluorobenzene) of these acids (VIII) were of poor quality. An absorption at a chemical shift of 11.5 ppm from tetramethyl silane (internal standard) was taken to indicate $-CO_2H$. There were intense, overlapping bands in the 3-4.4 ppm region which were tentatively assigned to $-(CH_2CCl_2)_n-$. In addition, there were a number of bands in the olefinic region. Integrating these two regions and taking $-CO_2H$ as one $^1H$ for a particular sample of the acid mixture VIII, the relative intensity ratios of these types were: $-(CH_2CCl_2)_{3.5}/-(CH=\overset{|}{C})_{0.6}/CO_2H$.

$$C_2F_5-(CH_2CCl_2)_m-(CH=CCl)_pCH_2CO_2H$$

(VIII)

Hexadecane Contact Angle Measurements on Monolayers of the Telomeric Acids from $CF_2$=CFCl and $CH_2$=$CCl_2$

Monolayers of the acids were deposited on glass from saturated hydrocarbon solutions using the retraction method[16,17]. Contact angle measurements were made by the sessile drop technique[16,18]. For the purpose of comparison, contact angles were also measured on monolayers of n-$C_3F_7CO_2H$ and n-$C_9F_{19}CO_2H$. The results of these measurements appear in Table 1.

A comparison of the contact angles for the $CF_2$=CFCl telomeric acids (IVc; X = $CF_2CO_2H$) with those for the two perfluorocarboxylic

acids indicates that the packing of the terminal $CF_3$ in the telomeric acid monolayer is less than that of n-$C_9F_{19}CO_2H$ and closer to that of n-$C_3F_7CO_2H$*. This behavior probably arises from the relatively large chlorine atoms along the chain of the telomeric acids. The somewhat lower angles for the $CH_2{=}CCl_2$

TABLE 1
HEXADECANE CONTACT ANGLES ON ACID MONOLAYERS

| Acid Monolayer (on glass) | Contact Angles (25°C.) Advancing | Receding |
|---|---|---|
| $C_2F_5(CF_2CFCl)_{3.3}CF_2CO_2H$* | 74° | 71° |
| $C_2F_5(CH_2CCl_2)_{3.5}(CH{=}CCl)_{0.6}CH_2CO_2H$* | 53° | 44° |
| n-$C_3F_7CO_2H$ | 73° | 69° |
| (Ref. 19) | (70°) | |
| n-$C_9F_{19}CO_2H$ | 80° | 76° |
| (Ref. 19) | (78°) | |

*Average compositions.

telomeric acids (VIII) reflect a still greater spacing between the terminal $CF_3$ in the monolayer, consistent with the greater chain bulkiness of these acids. While monolayers of these telomeric acids obviously contain components having different chain lengths, the chains were all sufficiently long that any effect chain length differences might have on the contact angle should have been small when compared with the effect of chain bulkiness on the packing of the terminal $CF_3$ groups.

*See Ref. 17 for a discussion of the relationship between chain length, chain packing and contact angles of monolayers.

EXPERIMENTAL

Commercial supplies of $CF_2$=CFCl, $CHI_3$, $CBr_4$, $CI_4$, $(CF_3CO)_2O$ (which contained the usual 10% $CF_3CO_2H$) and $C_2F_5COCl$ were used without purification. The $CH_2$=$CCl_2$ was passed through a column of alumina just prior to use to remove any peroxidic or acidic impurities. Perfluoropropionyl peroxide[5] was used as ca. a 10% solution in "Freon" 113; its half-life at various temperatures was determined by measuring the rate of disappearance of the 5.46μ band in the IR.

IR spectra of the intermediates and products were determined through NaCl windows using a Perkin-Elmer Model 337 Infracord Spectrophotometer. The $^{19}F$ and $^{1}H$ NMR spectra were obtained with a Varian A 56-60 Spectrometer operating at 56.5mHz and 60mHz, respectively.

Preparation of $(CF_3CO)_2O_2$[4]

A solution of 8.0 g. (0.10 mole) of 97.8% $Na_2O_2$ in 100 ml. of water was prepared below 10°C. to prevent oxygen loss. To this solution was added slowly with stirring and ice-cooling 30 g. of reagent-grade NaCl. A turbid solution was obtained after 10 min. To this mixture was added 16.8 g. (0.20 mole) of $NaHCO_3$. To the milky, syrupy suspension was added 250 ml. of ice-cold "Freon" 113. The mixture was cooled to -15°C. in a salt-ice mixture. The agitation rate was increased to its maximum, and full salt-ice cooling was maintained while 46.6 g.

(0.20 mole) of $(CF_3CO)_2O$, precooled to -10°C. in a jacketed addition funnel, was added in 55 sec. The temperature increased to -2°C. during the addition. The temperature was allowed to fall to -10°C. and remain there for 5 min. The reaction mixture was transferred to a cold separatory funnel and diluted with ice water to facilitate layer separation. The "Freon" 113 layer, which had a strong bleach-like odor, was withdrawn into an ice-cold container and stored in a refrigerator below -20°C.

This solution, weighing 411 g., contained 1.1% of $(CF_3CO)_2O_2$ (by iodometric titration) which corresponds to a 20% yield based on $Na_2O_2$. It showed no IR evidence for unreacted $(CF_3CO)_2O$. Higher yields could not be achieved under a variety of conditions.

Preparation of $(CF_3CCl_2CO)_2O_2$

In a similar manner, a solution of 4.0 g. (0.05 mole) of $Na_2O_2$ in 300 ml. of 20% NaCl solution plus 200 ml. of "Freon" 113 was prepared at -15°C. To this mixture was added, in 45 sec. with high-speed agitation and full salt-ice cooling, 26 g. (0.10 mole) of 83.5% (by GLC) $CF_3CCl_2COCl$[7] precooled to -25°C. The mixture was kept below -10°C. for 30 min., and then the "Freon" 113 layer was separated and stored below -20°C. The concentration of $(CF_3CCl_2CO)_2O_2$ (by iodometric titration) in this solution, weighing 371 g., was 4.2% corresponding to an 80% yield.

General Telomerization Procedure

The telomerizations were carried out in pressure vessels which were lined with Hastelloy, and were clean and dry. The air in the tubes was displaced with $N_2$ while the tubes were being cooled in ice-water. The liquid and solid reactants were added to the tubes which were then closed, cooled in Dry Ice and evacuated. Gaseous reactants were then distilled into the tubes. The tubes, while being shaken, were heated for a period of time sufficient to decompose essentially all of the peroxides. The tubes were cooled, vented and discharged using a "Freon" 113 rinse.

The telomers were isolated by removing the solvent under vacuum. Attempts to fractionate them by vacuum distillation met with limited success because of the liberation of either bromine or iodine. This characteristic precluded meaningful gas chromatographic analysis.

Conditions and results for the specific telomerizations are given in Table 2.

Preparation of $C_2F_5(CF_2CFCl)_nCF_2CO_2H$ (IVc)

The telomer $C_2F_5(CF_2CFCl)_nX$ (IVb), where "n" = 7-9 and X = Br (see Table 2), was stirred and heated for 17 h at 150-170°C. with about an equal volume of 20% oleum[13]. Bromine was evolved during this period. The mixture was allowed to cool without stirring, and the lighter oleum layer was decanted and discarded. The waxy telomeric acid wafer was

TABLE 2

TELOMERIZATION REACTIONS

| Telomer | Moles of: Taxogen | Peroxide[a] | Chain Transfer Agent | Reaction: Temp. (°C) | Time (h) | Telomer Yield (g) | Conversion of Taxogen[b] (%) | Approx. "n" |
|---|---|---|---|---|---|---|---|---|
| IVa | 1 $CF_2$=CFCl | 0.1 $(C_2F_5CO)_2O_2$ | 0.2 $CHI_3$ | 50-55 | 12 | 78-grease | 58 | 13[c] |
| IVb | 1 " | 0.1 " | 0.2 $CBr_4$ | " | " | 115-oil | 79 | 7[c] |
| " | 2 " | 0.26 " | 0.4 " | 60-65 | 8 | 238- " | 88-92 | 11-15[d] |
| " | 3 " | 0.44 " | 0.6 " | " | " | 384- " | 88-92 | 7-9[d] |
| Va, VIa | 0.257 $CF_2$=CFCl | 0.0343 $(CF_3CCl_2CO)_2O_2$ | 0.054 " | 55-60 | 17 | 12- " | 20-24 | 2-3[c] |
| VIIa | 3.75 $CH_2$=$CCl_2$ | 0.615 $(C_2F_5CO)_2O_2$ | 0.935 " | 60-65 | 8 | 104-solid[e] 334-viscous oil | 95 | 25[f] 6[f] |
| VIIb | 0.7 $CH_2$=$CCl_2$ | 0.123 " | 0.096 $CI_4$ | " | " | 64-oil | 54 | 3[g] |

a - In "Freon"-113 solutions. 1 mole $(R_fCO)_2O_2$ gives 2 moles $R_f$.

b - Based on value of "n" in the repeating unit.

c - Based on NMR ratios of $^{19}F$ in $R_f$- and $\{Tax\}_n$ in the corresponding acids.

d - Based on NMR ratios of $^{19}F$ in $R_f$- and $\{Tax\}_n$ in the bromine or iodine-terminated telomers.

e - Insoluble in "Freon"-113.

f - Based on halogen ratios from elemental analyses.

g - Based on NMR ratio of $^1H$ in $-CO_2H$ and $\{Tax\}_n$ in the corresponding acid.

treated with ice, then rinsed thoroughly with water and dried by heating to 150°C. while purging with dry argon.

The pale yellow, sticky wax was dried further by dissolving it in toluene and distilling toluene from the solution until no water collected in a Dean-Stark trap. The toluene solution was treated at the boil for 4 h with $CH_3OH$ and a catalytic amount of $H_2SO_4$ to effect esterification. The acid in the solution was destroyed with $Na_2CO_3$, and the toluene was distilled*.

The residue was distilled using a short-path still under vacuum. About half of telomeric ester mixture (IVd; $X=CO_2CH_3$) distilled between 25 and 210°C. at 0.02 mm. Hg. This mixture was fractionated by vacuum distillation using a 10-cm. Hastelloy Helipak column.

The fraction boiling between 77 and 87°C. at 0.05 mm. Hg was heated with dilute aqueous KOH just below the boil (to prevent foaming) for 1 h. The small amount of insoluble oil present was separated; its IR spectrum showed little, if any, functionality indicating that it may have been a coupled product (II). The surface-active, alkaline solution was made strongly acid with HCl and evaporated to dryness under vacuum. The gummy residue was extracted with boiling "Freon" 113. The

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* Traces of lower mol. wt. esters codistilled with the toluene.

extract was dried with $Na_2SO_4$*, and the solvent was removed leaving a colorless, viscous oil.

Preparation of the Mixed Telomeric Acids Vb plus VIb ($X=CF_2CO_2H$)

The mixture of telomers (Va, VIa - see Table 2) was treated with excess 20% oleum at 150-170°C. overnight. The oleum layer was withdrawn, drowned into ice-water, and the turbid solution was extracted with "Freon" 113. The extract was combined with the telomeric acid mixture, and the solvent was evaporated.

The acidic materials were separated from inert materials in the residue by extraction with hot, aqueous KOH and centrifugation. The acid mixture was isolated from the clear, alkaline solution by the method described earlier and further purified by vacuum distillation using a short-path still. A pale yellow, viscous oil was collected.

Preparation of $C_2F_5-(CH_2CCl_2)_m-(CH=CCl)_p-CH_2CO_2H$ (VIII)

A two-phase mixture of 50 g. of the telomer $C_2F_5-(CH_2CCl_2)_n$ (VIIa), where "n" = 6 and X = Br (see Table 2) and 100 ml. of 90% $HNO_3$ was stirred with $NO_2$ bubbling into it and heated over a 4-h period to 72°C.[14]. Low boiling materials were removed under vacuum in a hot water bath. The mixture was cooled without stirring, and the nitric acid layer was decanted and discarded. The viscous residue was washed with water by decantation.

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* The acid strength of the telomeric acids is such that they will be converted to salts by drying agents, such as molecular sieves, which are salts of weak inorganic acids.

The acidic materials were removed by dissolving them in aqueous $NaHCO_3$ at 60°C. and clarifying the solution using filter-aid; about 32 g. was insoluble, dimeric material (II). The solution was acidified with HCl and extracted with "Freon" 113. The combined extracts were dried with $Na_2SO_4$, and the solvent was removed leaving 2.7 g. of an amber syrup.

Preparation of Acid Monolayers and Hexadecane Contact Angle Measurements

Monolayers of $C_2F_5(CF_2CFCl)_{3.3}CF_2CO_2H$ (IVc), $C_2F_5(CH_2CCl_2)_{3.5}(CH{=}CCl)_{0.6}CH_2CO_2H$ (VIII), described earlier, and the commercially available perfluoroacids were deposited on cover glass slides by absorption from saturated solutions in decane or hexadecane at 25°C. using the retraction method of Zisman and coworkers[16,17]. The glass slides had been cleaned with acetone and "Freon" 113 followed by a gentle flaming, and were immersed into the solutions immediately after cooling to room temperature. Immersion time was varied from a few sec. to about 30 min. without any noticeable variation in contact angle.

Contact angles were measured on the monolayers at 25°C. on profiles of sessile drops using a telescope fitted with a goniometer eyepiece[16,18]. The drops of hexadecane* were deposited on the monolayers using a hypodermic syringe.

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*The surface tension of the hexadecane used in these measurements was 27.1 dynes/cm. at 25°C.

Advancing and receding angles were obtained by increasing and decreasing the drop size. The angles were measured within 10 sec. after movement of the drop periphery. At least 12 readings were made on three separate monolayers and averaged. The standard deviation of the average was less than 1°. The small differences between advancing and receding angles in Table 1 indicate that the monolayers were reasonably homogeneous[20].

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