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The Preparation and Some Properties of the C_4F_8 Olefins[1]

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The olefins C_4F_8-1, C_4F_8-2 (mixture of *cis* and *trans* isomers) and *i*-C_4F_8 have been prepared by pyrolytic reactions and a number of physical and chemical properties determined. Perfluoroisobutene differs markedly in its physical and chemical properties from the other isomers, which are quite similar to one another. *i*-C_4F_8 reacts with alcohols and bromine at much different rates than does C_4F_8-1 or C_4F_8-2; an attempt has been made to explain these differences.

The differences in the chemical and physical properties of isomeric hydrocarbon olefins have been extensively studied and are well-known. The isomeric C_4F_8 olefins afford the simplest group of compounds for a comparative study of the effects of isomerization on the properties of fluorocarbon olefins.

Of these olefins, perfluorobutene-2 has been prepared by Henne and Newby[2] by the dechlorination of $CF_3CFClCFClCF_3$ with zinc in alcohol. On the basis of the marked boiling point range, 0.4 to 3.0°, and the melting point range, -139 to $-129°$, they concluded that it was a mixture of the *cis* and *trans* isomers. Miller[3] prepared perfluorobutene-2 and its dibromide. Miller also reported that perfluorobutene-1 was one of the products of the pyrolysis of C_2F_4 or perfluorocyclobutane. No proof of structure was given. Perfluoroisobutene has not previously been reported.

Simple methods of synthesis from perfluorocarboxylic acids were found in each instance.

Perfluorobutene-1 was prepared conveniently and in high yield by the pyrolysis of dry sodium perfluorovalerate

$$CF_3CF_2CF_2CF_2CO_2Na \xrightarrow{ca.\ 250°} CF_3CF_2CF{=}CF_2 + CO_2 + NaF$$

This reaction is an example of a general process for preparing Δ^1-fluorocarbon olefins recently described by Hals, Reid and Smith.[4]

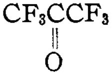
Perfluorobutene-2 was prepared by a variation of the method used for the preparation of perfluorobutene-1. It was found that the pyrolysis of the potassium salt of *n*-perfluorovaleric acid produced C_4F_8-2 and C_4F_8-1 in a ratio of about 4:1. The two olefins were separated by the selective bromination of C_4F_8-1. In addition, C_4F_8-2 has been identified as one of the co-products in the preparation of perfluoroisobutene. These two olefins could also be readily separated by selective bromination; in this instance C_4F_8-2 was the more reactive olefin and was separated as the dibromide.

Perfluoroisobutene was prepared by the uncatalyzed pyrolysis of perfluorocyclobutane in a carbon-lined reactor at 720°. Under optimum conditions, yields of about 70% have been obtained at 90% conversion. The formation of this olefin from *c*-C_4F_8 requires the cleavage and reformation of both carbon–carbon and carbon–fluorine bonds. The high yields obtainable show the preference for the branched chain structure instead of the straight chain or the ring.

Each of the olefins was shown to be free of isomeric contaminants and other impurities by examination of its infrared spectrogram.

The validity of the structural assignments made was established chemically by oxidation of the olefins with aqueous potassium permanganate and identification of the fragments.[5] The oxidation of the isomer believed to be perfluorobutene-2 gave the expected trifluoroacetic acid and no other fluorocarbon carboxylic acid. In a similar manner, the oxidation of the isomer believed to be perfluorobutene-1 resulted in the formation of the expected perfluoropropionic acid.

The structure of iso-C_4F_8 was also established by neutral permanganate oxidation to hexafluoroacetone isolated according to the procedure of Henne, Shepard and Young.[6] The ketone was identified by its boiling point and molecular weight, and by comparing its infrared spectrogram with that of an authentic sample. The reference spectrogram was kindly supplied by Professor A. L. Henne of The Ohio State University.

Another procedure was used in attempting to establish the structure of iso-C_4F_8. Oxidation with alkaline permanganate was attempted; a base-catalyzed addition of HF occurred instead and $(CF_3)_3CH$ was obtained in place of the expected  $CF_3\underset{\underset{\displaystyle O}{\|}}{C}CF_3$ cleavage products, CF_3CO_2H and CF_3H.

Some physical properties of the olefins and their dibromides are shown in Table I. Perfluoroisobutene is considerably denser than the other two isomers and is also appreciably higher boiling. Both the physical and chemical properties of the olefins show marked differences between iso-C_4F_8 and the other two isomers.

Perfluoroisobutene should be handled with great caution and adequate ventilation since it is quite toxic.

The infrared absorption spectra of the olefins are shown in Fig. 1. Perfluorobutene-1 has a strong C=C absorption band at 5.58 μ; all of the straight chain fluorocarbon olefins containing a terminal double bond that have been prepared, except tetrafluoroethylene, have a sharp absorption

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[1] Presented in part before the Section on Physical and Inorganic Chemistry of the XII International Congress of Pure and Applied Chemistry, New York City, September, 1951.

[2] A. L. Henne and T. H. Newby, THIS JOURNAL, **70**, 130 (1948).

[3] W. T. Miller, Jr., of Slesser and Schram, "Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, Chapt. 32, p. 676.

[4] L. J. Hals, T. S. Reid and G. H. Smith, Jr., THIS JOURNAL, **73**, 4054 (1951).

[5] A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

[6] A. L. Henne, J. W. Shepard and E. J. Young, *ibid.*, **72**, 3577 (1950).

TABLE I

THE PHYSICAL PROPERTIES OF THE C_4F_8 OLEFINS AND THEIR DIBROMIDES

Compound	B.p.,[a] °C.	n^{25}D	$d^{25}{}_4$[b]	Mol. wt. Calcd.	Mol. wt. Found	Analysis Carbon Calcd.	Analysis Carbon Found	Analysis Fluorine Calcd.	Analysis Fluorine Found	Analysis Bromine Calcd.	Analysis Bromine Found
$CF_3CF_2CF{=}CF_2$	+1	....	1.5443 (0°)	200	198–202	24.0	24.3	76.0	75.5		
$CF_3CF{=}CFCF_3$	0[c]	....	1.5297 (0°)	200	198–202	24.0	24.0	76.0	75.9		
$CF_3C(CF_3){=}CF_2$	+6.5	....	1.5922 (0°)	200	198–202	24.0	24.1	76.0	76.1		
$C_2F_5CFBrCF_2Br$	95	1.3511	2.1279	360				42.2	41.5	44.4	44.5
$CF_3CFBrCFBrCF_3$	96[d]	1.3538[d]	2.2673	360							
$(CF_3)_2CBrCF_2Br$	96[e]	....	....	360	358[g]			42.2	41.3	44.4	42.8
$Br(CF_2)_4Br$	97[f]	1.3495	2.0979	360				42.2	40.7	44.4	44.6

[a] At *ca.* 740 mm. [b] The densities of the olefins are: C_4F_8-1, $d = 1.5443 - 0.0036t.$; C_4F_8-2, $d = 1.5297 - 0.0036t.$; *i*-C_4F_8, $d = 1.5922 - 0.0037t.$ Miller reports $d^{-20}{}_4$ 1.601 for C_4F_8-2. [c] Miller (ref. 3) reports b.p +1.2° at 764 mm. [d] Miller (ref. 3) reports b.p. 96°, n^{20}D 1.3574. [e] M.p. 41–45°; probably still contains impurities. [f] Prepared from silver perfluoroadipate and bromine. [g] Vapor density measurement in a high temperature Monel Dumas bulb. The design was based on a suggestion of Dr. J. D. Park of the University of Colorado.

band at this wave length. Perfluoroisobutene has a strong C=C band at 5.71 μ and perfluorobutene-2 (mixture of *cis* and *trans* isomers) has a weak band at 5.77 μ. The positions of the bands are consistent with the observations of Torkington and Thompson[7] and of Smith[8] on other fluorine-containing olefins. They found that the replacement of the hydrogen atoms attached to doubly bonded carbon atoms with fluorine atoms decreased the wave length of the C=C stretching absorption band about 0.2 μ per fluorine atom. Since this band is about 6.1 μ in hydrocarbons, the expected bands in perfluoroisobutene and perfluorobutene-2 were at about 5.75 μ and in perfluorobutene-1, 5.59 μ. The predicted values are in good agreement with the experimental results.

The high intensities of the C=C absorption bands in perfluorobutene-1 and perfluoroisobutene as compared to that of perfluorobutene-2 are believed to be reasonable. The *trans* isomer of C_4F_8-2 should have at best a very weak C=C band while the *cis* isomer would be expected to have a more intense but still weak C=C band. The intensity of the C=C band of a mixture containing a considerable amount of the *trans* isomer, as is believed to be the case here, would then have a less intense C=C absorption band than the two highly unsymmetrical isomers C_4F_8-1 and iso-C_4F_8.

Perfluorobutene-2.—The perfluorobutene-2 obtained by the pyrolytic reactions was investigated to determine whether two isomers were present, and, if so, the probable composition of the mixture.

It has been found in hydrocarbon chemistry that *cis*-butene-2 and *trans*-butene-2 differ in boiling point by 2.57°.[9,10] It was hoped that the boiling point difference between the *cis* and *trans* isomers of perfluorobutene-2 might be large enough so that enrichment of the isomers by distillation would be possible.

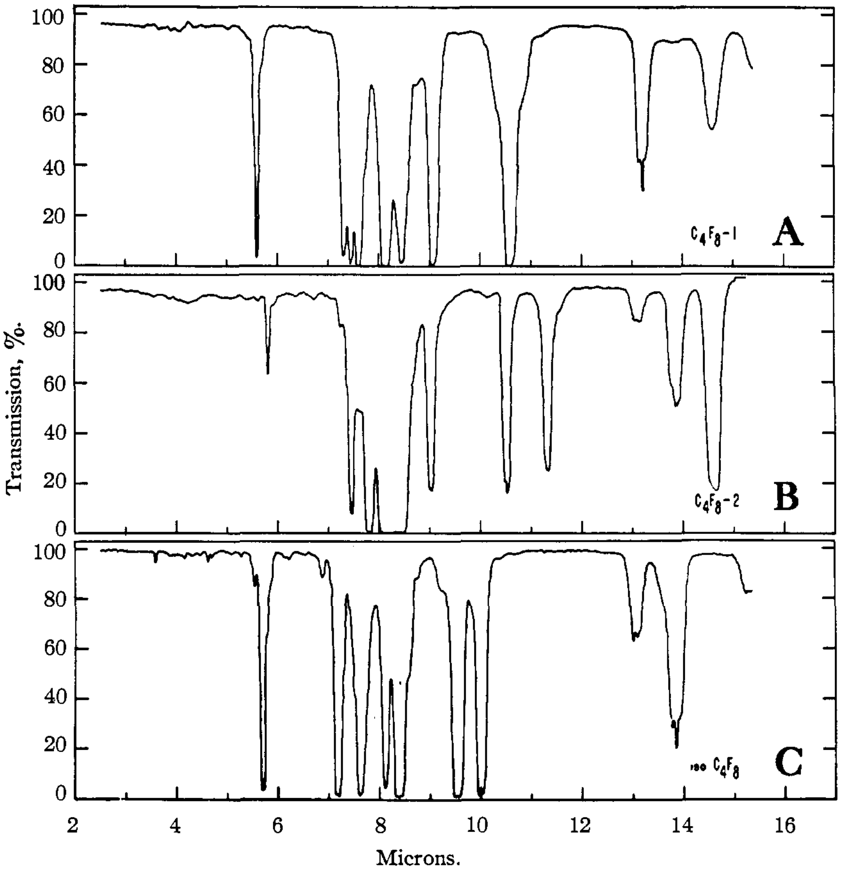

Fig. 1.—The infrared spectrograms of A, C_4F_8-1; B. C_4F_8-2; C. *i*-C_4F_8.

Examination of the infrared spectrograms of a series of fractions from the distillation of perfluorobutene-2 showed that there were noticeable and

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(7) P. Torkington and H. W. Thompson, *Trans. Faraday Soc.*, **41**, 236 (1945).

(8) D. C. Smith, J. R. Nielsen, L. H. Berryman, H. H. Claassen and R. L. Hudson, NRL Report 3567, September 15, 1949.

(9) G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **57**, 876 (1935).

(10) A. B. Lamb and E. E. Roper, *ibid.*, **62**, 811 (1940).

systematic variations in the intensities of certain bands which could not be attributed to impurities. The bands at 5.77, 9.05, 10.53 and 13.83 μ increased in intensity as the fractionation proceeded while the bands at 11.33 and 14.60 μ decreased in intensity. None of the variations were large. This indicated that two components were present, *cis-* and *trans*-perfluorobutene-2, which could not be completely separated by distillation.

The first group of bands, including the double bond band at 5.77μ, is associated with the higher boiling isomer. The *cis* form would be expected to have the more intense C=C absorption band so the higher boiling isomer was assigned the *cis* configuration. *cis*-Isomers have been found to have the more intense C=C bands.[11]

The bands in the C_4F_8-2 mixture that decrease in intensity are characteristic of the lower-boiling isomer, *trans*-C_4F_8-2.

The relative amounts of the *cis* and *trans* isomers were tentatively established by the study of a bromination–debromination cycle.

The photochemical bromination of perfluorobutene-2 containing any ratio of *cis* and *trans* isomers was expected to form approximately equal amounts of the *meso* and racemic dibromides. The expectation was based on the results obtained in the photochemical chlorination of *trans*-stilbene[12] which was found to give approximately equal amounts of the *meso* and racemic dichlorides. The first step is believed to be the attack of a chlorine atom on the double bond with the formation of $C_6H_5CHCl\dot{C}HC_6H_5$.

There is then about an equal chance for *cis* or *trans* addition of the second chlorine atom. Any ratio of *cis* to *trans* forms would be expected to lead to equal amounts of the *meso* and racemic dichlorides.

Assuming that the $C_4F_8Br_2$ was an equimolar mixture of the *meso* and racemic dibromides, debromination by either a *cis* or a *trans* mechanism would produce equimolar amounts of the *cis* and *trans* isomers of C_4F_8-2. The debromination of the 2,3-dibromobutanes by zinc and alcohol has been shown to proceed by a *trans* mechanism.[13,14]

The debromination of $C_4F_8Br_2$ with zinc in acetic acid was then assumed to proceed by a *trans* mechanism only. The bromination–debromination cycle was carried out with C_4F_8-2 from the pyrolysis of perfluorocyclobutane and C_4F_8-2 was obtained which should have been half *cis* and half *trans*. The infrared spectrograms of the final product and the starting material were very nearly the same. The C_4F_8-2 formed by high temperature pyrolytic reactions then has essentially the same isomer ratio as the product of the bromination–debromination cycle and, on the basis of the preceding argument and evidence presented below, is considered to consist of nearly equal amounts of the *cis* and *trans* isomers.

One difficulty that might arise in the cycle experiment is that the ratio of *cis* to *trans* C_4F_8-2 presumed to exist in the initial debromination products might be altered by an acid (acetic acid or $ZnBr_2$) catalyzed isomerization; this would lead to a false conclusion about the composition of both the final product and the initial pyrolysis products.

However, it has been possible by the use of very strong acid catalysts to obtain C_4F_8-2 with much higher *trans* to *cis* ratios than the debromination products possess, indicating that the *trans* to *cis* equilibrium ratio is higher than in the debromination products. It would seem fortuitous, if isomerization was occurring during debromination, that the *cis–trans* ratio always stopped at the same intermediate position between the 1:1 and the equilibrium ratios. It seems more likely that little, if any, isomerization was occurring during debromination. It has also been possible to take a C_4F_8-2 mixture containing a higher *trans–cis* ratio than the usual debromination products, put it through the cycle and emerge with C_4F_8-2 having the usual *trans–cis* ratio of debromination products. This shows that mixtures having different compositions than the pyrolysis products still give the same debromination products, as would be expected if the original assumptions about the reactions were correct.

Chemical Reactions of the Perfluorobutenes.—The three olefins undergo, in general, the same types of chemical reactions, but there are marked differences in the ease of reaction.

Bromine adds rapidly to perfluorobutene-1 at room temperature, more slowly to perfluorobutene-2, and with great difficulty to perfluoroisobutene. The differences in rates of reaction and the conditions needed are great enough to allow a virtually complete separation of any mixture of isomers by selective bromination.

A mixture of C_4F_8-1 and C_4F_8-2 was separated by mixing the olefins with enough bromine to brominate the C_4F_8-1; C_4F_8-1 was absorbed rapidly and completely at room temperature while little of the C_4F_8-2 reacted. C_4F_8-2 brominated rapidly, however, when irradiated with ultraviolet light from a mercury arc lamp; under these conditions iso-C_4F_8 did not brominate at all. The bromination of iso-C_4F_8 was finally accomplished by adding water and acetamide to the iso-C_4F_8 and bromine and irradiating the mixture with ultraviolet light.

Reactions of the olefins with alcohols in the presence of basic catalysts have been carried out. Here the order of reactivity is reversed; iso-C_4F_8 is much more reactive than either of the other two isomers. All three will add alcohols in the presence of basic catalysts to form alkyl β-H-perfluoroalkyl ethers, a familiar reaction of fluorocarbon olefins. Only perfluoroisobutene will add alcohols in neutral or weakly acidic media.

The structures of ethers formed by the addition of alcohols to iso-C_4F_8 and C_4F_8-1 are $(CF_4)_2CHCF_2$-OR and $CF_3CF_2CHFCF_2OR$. It has been shown in the case of ethylene derivatives that the OR group becomes attached to the carbon atom bearing the largest number of fluorine atoms.[15] In C_3F_6 the same rule applies, the OR group adding to the

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(11) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, pp. 329-332.

(12) S. Winstein and D. Seymour, This Journal, **68**, 119 (1946).

(13) W. G. Young and H. J. Lucas, *ibid.*, **52**, 1964 (1930).

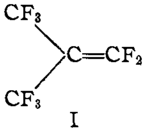
(14) W. G. Young and S. Winstein, *ibid.*, **58**, 102 (1936).

(15) W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (October 15, 1946).

CF_2 group. The rule is assumed to apply to the C_4F_8 olefins.

The yields of saturated ethers from iso-C_4F_8 were usually about 60%; the yields from C_4F_8-1 were very low due largely to the loss of hydrogen fluoride and to other side reactions. The ether from C_4F_8-2 and methanol was not definitely characterized; it appeared to be a diaddition product, possibly similar to the dialkoxy compounds prepared by Park, *et al.*,[16] from perfluorocyclobutene.

The mechanism of the addition of alcohols (and other bases such as amines) may be pictured as involving an initial attack of a nucleophilic group, OR^- in this instance, on the double bond. If this is the case, any factor tending to decrease the effective electron density at the carbon atom being attacked will increase the ease of addition. The strongly electronegative fluorine atom can do this by a simple inductive effect as in C_2F_4. Another manner of decreasing the electron density which is operative when a CF_3 (or $R_fCF_2^-$) group is attached to a carbon atom of the double bond may be considered. The perfluoroisobutene molecule (I) may be pictured as having structures of the type II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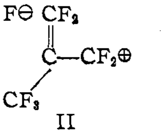
II

Such forms would reduce the electron density at the carbon atom bearing the formal positive charge. The sixfold multiplicity of this form should greatly enhance the effect; attack by a negative group should then take place readily.

Perfluorobutene-2 could similarly have the structures $CF_3\overset{+}{C}F{-}CF{=}CF_2\overset{-}{F}$. The formal positive charge would alternate between the two central carbon atoms with three identical structures in each case. The olefin would be expected to be quite susceptible to base attack, though perhaps less so than iso-C_4F_8.

Perfluorobutene-1 can have similar structures: $CF_3CF(F^-){=}\overset{+}{B}FCF_2$. Only two identical structures are possible and they could well be expected to have a lesser effect on the reactivity of the olefin.

A similar approach has previously been used by Roberts, Webb and McElhill[17] in explaining the ready hydrolysis of the CF_3 groups in *o*- and *p*-trifluoromethylphenol.

Experimental

Low Temperature Distillation Columns.—Two columns were used, both vacuum jacketed and silvered. One column had an 18 mm. × 60 cm. packed section filled with No. 2916 Nichrome Heli-Pak Podbielniak packing. The second column had a 14 mm. × 65 cm. packed section filled with $^3/_{64}''$ stainless steel single-turn helices. Both columns are believed to have 50–75 plates.

Infrared Spectrograms.—The spectrograms were obtained on a Perkin–Elmer Model 21 spectrophotometer; they were run at 50 mm. pressure in a 2.5-cm. cell. A sodium chloride prism was used.

The Preparation of $CF_3CF_2CF{=}CF_2$.—The starting material for this preparation was perfluoro-*n*-valeric acid prepared by the electrochemical process. Only refractionated acid was used; b.p. 140°, $n^{25}D$ 1.294, neutral equivalent, 262–264.

The sodium salt was prepared by neutralization of an aqueous solution of the acid with aqueous NaOH and finally vacuum-dried at 80–100°. Careful neutralization is essential since excess base may materially decrease the subsequent yield of olefin.

The salt was pyrolyzed in a round-bottom flask heated by a Glas-Col mantle. In one experiment 615 g. of the salt was heated at 290–300° (outside temperature). The gaseous products were collected, scrubbed with 30% KOH, dried over phosphorus pentoxide and collected in a liquid air-cooled trap; yield of crude olefin, 386 g., 90%. The material was virtually all C_4F_8-1, with only minor amounts of C_3F_8, C_2F_4, CF_3H and C_2F_5H. A center cut, 94 g., 55% of the 170 g. fractionated, had b.p. 0° at 740 mm., mol. wt., 199–201.

The Preparation of $CF_3CF{=}CFCF_3$.—$C_4F_9CO_2K$ was prepared by neutralization of an aqueous solution of $C_4F_9CO_2H$ to *p*H 5 and evaporation to dryness at 100°.

The salt, 78.5 g. (0.26 mole), was pyrolyzed at 165–200° and the gases scrubbed and dried to yield 42 g. (0.21 mole) of C_4F_8 olefins. Distillation gave 27.6 g. of a mixture of C_4F_8-2 (80%) and C_4F_8-1 (20%). 11.6 g. (0.058 mole) was sealed in an ampoule with 3.0 g. (0.02 mole) of bromine and allowed to stand *ca.* six hours until nearly all of the bromine had been consumed. The ampoule was cooled, opened and excess mercury added to destroy residual bromine. Infrared analysis of the recovered olefin (8.0 g., 80% of the original C_4F_8-2) showed that there was no C_4F_8-1 left and that, aside from traces of SiF_4, the material was all C_4F_8-2. The over-all yield of C_4F_8-2 from $C_4F_9CO_2K$ was 36%.

The Preparation of Perfluoroisobutene.—Perfluoroisobutene was prepared by the pyrolysis of c-C_4F_8. The reactor consisted of a carbon tube of 0.5″ i.d. fitted tightly inside a length of 0.75″ iron pipe; the reactor was heated over a 14″ section by an electric furnace. Refractionated c-C_4F_8, b.p. −4°, was passed through the reactor at 700–725° at the rate of 30 g. per hour. Under these conditions there was a 90% conversion of c-C_4F_8. The products were scrubbed with dilute base, dried over phosphorus pentoxide and fractionated. Seventy per cent. of the product was *iso*-C_4F_8, b.p. 5–6° at 740 mm. Infrared analysis showed this material to be free of other C_4 fluorocarbons. The olefin is destroyed by strong aqueous base and must be handled accordingly. C_4F_8-2 was obtained as a by-product in 5–10% yield.

The Oxidation of C_4F_8-1.—A Pyrex ampoule was charged with 11.7 g. of C_4F_8-1, 8.0 g. of $KMnO_4$, *ca.* 12 g. of KOH and sufficient water to form a slurry. The ampoule was sealed, then heated for five days with shaking at 85°. The low-boiling gases were removed and the contents of the ampoule filtered. The filtrate was evaporated to dryness and extracted with ethanol to remove the potassium salts of fluorocarbon carboxylic acids. Upon evaporation of the alcohol solution, there was obtained 4.8 g. (63% based on the permanganate) of $C_2F_5CO_2K$.

The Oxidation of $CF_3CF{=}CFCF_3$.—An aqueous solution of 10.2 g. of $KMnO_4$ and 2 g. of KOH was sealed in an ampoule with 4.6 g. of C_4F_8-2 and the ampoule heated at 85° for 48 hours. One and a half grams of unreacted material was recovered. The aqueous solution was filtered and then treated to recover CF_3CO_2Na in high yield.

The Oxidation of *i*-C_4F_8.—38.8 g. of *i*-C_4F_8 was charged to a one-liter autoclave containing 76 g. of $KMnO_4$ and 400 cc. of water. The reaction mixture was heated for eight hours at 100° with stirring. The reactor was then cooled and the volatile materials bled off and collected. They consisted largely of unreacted *i*-C_4F_8, *ca.* 12 g., and a smaller amount of CO_2. The aqueous solution in the autoclave was treated by the procedure described by Henne[6]; yield 5.8 g., 27%, conversion 67%. A purified sample of hexafluoroacetone boiled at −26.5° at 746 mm., mol. wt., 163–168 (vapor density). Calcd. for C_3F_6O: mol. wt., 166.

The Preparation of $C_2F_5CFBrCF_2Br$.—One hundred and twenty grams (0.6 mole) of C_4F_8-1 was bubbled at room temperature through 80 g. (0.5 mole) of bromine contained in a glass trap. Bromination took place rapidly; the dibromide remained in the trap while the unreacted olefin passed through and was collected in a liquid air-cooled trap.

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[16] J. D. Park, M. L. Sharrah and J. R. Lacher, THIS JOURNAL, **71**, 2337 (1949).

[17] J. D. Roberts, R. L. Webb and E. A. McElhill, *ibid.*, **72**, 408 (1950).

The product, 188 g., was scrubbed, dried and fractionated. Of the 173 g. charged to the column, 100 g. (58%) of $C_4F_8Br_2$ boiled at 94–95°; there was an additional 25.6 g., b.p. 91–94°; total yield of dibromide, 73%.

The Preparation of $(CF_3)_2CBrCF_2Br$.—9.3 g. of i-C_4F_8 (0.047 mole), 5.7 g. of bromine (0.035 mole), 3 drops of water and a few crystals of acetamide were sealed in a Pyrex ampoule. There was no evident reaction in the dark at room temperature, but after three hours of exposure to an ultraviolet lamp, reaction appeared to be complete. The 8 g. of high-boiling products was separated in the vacuum system. There was obtained 4.0 g. (35%) of a white solid identified as the dibromide.[18]

Attempts to brominate i-C_4F_8 thermally at 100° or with ultraviolet light at room temperature in the absence of acetamide were unsuccessful.

The Preparation of $CF_3CFBrCFBrCF_3$.—The C_4F_8-2 used for the preparation of the dibromide was contained in intercuts from a series of i-C_4F_8 preparations. The amount of C_4F_8-2 in each fraction was determined by infrared analysis; the fraction was sealed up with slightly more than enough bromine to convert all of the C_4F_8-2 to dibromide and exposed to ultraviolet light until no further reaction was observed. Bromination was found to be rapid and quantitative; the recovered i-C_4F_8 did not contain any C_4F_8-2 and the C_4F_8-2 later recovered from the dibromide did not contain i-C_4F_8. After bromination of C_4F_8-2 the unreacted i-C_4F_8 was boiled off and collected, and mercury was added to the dibromide to remove excess bromine. The products from the various dibromide preparations were collected and fractionated.

The Debromination of $CF_3CFBrCFBrCF_3$.—$C_4F_8Br_2$ from the preparation described above was used; it had b.p. 96°, $n^{25}D$ 1.3538. Fifty-two grams of the dibromide was added slowly to a mixture of 200 cc. of boiling glacial acetic acid and 20 g. of zinc dust; the mixture was refluxed for about three hours. The volatile product, C_4F_8-2, was collected in a liquid air-cooled trap: yield 33 g. The olefin was separated from a small amount of entrained acetic acid by distillation in the vacuum system. The infrared spectrogram of this sample of C_4F_8-2 was quite similar to those of samples of C_4F_8-2 from pyrolytic reactions.

A larger quantity of C_4F_8-2 was prepared by the same process, treated with KOH and P_2O_5, and fractionated; the product was virtually the same as the C_4F_8-2 that had not been base treated, indicating that neither the base nor P_2O_5 changed the *cis–trans* ratio. This point is of interest since nearly all of the pyrolytic C_4F_8-2 had been treated with these reagents.

The Addition of Ethanol to i-C_4F_8.—A glass bubbler was charged with 65 g. (1.4 moles) of ethanol. The reactor was kept at about 9° while 50 g. (0.24 mole) of i-C_4F_8 was bubbled into the reactor. The reaction mixture was poured over ice and the water-insoluble layer separated and dried over $CaSO_4$ and CaO.

The crude ether, 54 g., was fractionated and 25 g. of $(CF_3)_2CHCF_2OC_2H_5$ obtained. This is a 41% yield based on the i-C_4F_8; b.p. 83° at 743 mm., $n^{25}D$ 1.2908, d^{25}_4 1.3946, γ^{25} 16.3 dynes/cm. *Anal.* Calcd. for $C_6F_8H_6O$: C, 29.3; F, 61.7. Found: C, 29.6; F, 60.4.

The Attempted Alkaline Oxidation of i-C_4F_8.—The attempted alkaline oxidation of i-C_4F_8 gave neither hexafluoroacetone nor the expected cleavage product CF_3H. Instead, $(CF_3)_3CH$ was produced. It was considered to result from the addition of HF to i-C_4F_8; the decomposition of some of the i-C_4F_8 must occur to furnish the necessary HF.

A mixture of 80 g. of $KMnO_4$ (0.51 mole), 50 g. of KOH (0.9 mole), 100 g. of i-C_4F_8 (0.5 mole) and 300 cc. of water was sealed in glass ampoules and heated at 90° overnight. The ampoules were opened and the volatile products charged to a low temperature fractionating column. There was no material boiling below about 0°. There was isolated 12.6 g., b.p. +11 to +12°, mol. wt., 216–218. *Anal.* Calcd. for C_4F_9H: mol. wt., 220; F, 77.7; C, 21.9. Found: F, 76.3; C, 22.3. The boiling point is about the same as that of its isomer $CF_3CF_2CF_2CF_2H$ which is 14° at 740 mm. Infrared analysis showed that there was virtually no i-C_4F_8 left and no other compounds containing C=C or C=O groups. The spectrogram matched that of the compound prepared by the direct addition of HF to i-C_4F_8.

The direction of addition is assumed to be the same as that of HX to other fluorocarbon olefins.

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[18] The addition of acetamide and water to the bromine to provide a more powerful brominating mixture was suggested by Dr. J. D. Park of the University of Colorado.

[CONTRIBUTION NO. 578 FROM THE CHEMISTRY LABORATORY OF INDIANA UNIVERSITY]

3-Substituted Thiophenes. V. Alkamine Esters of Phenyl-3-thienylglycolic Acid[1]

BY E. CAMPAIGNE AND R. C. BOURGEOIS[2]

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Phenyl-3-thienylglycolic acid has been synthesized *via* a benzilic acid rearrangement of benz-3-thenil, which was obtained from the product of a mixed benzoin condensation of benzaldehyde and 3-thenaldehyde. This product was shown to be phenyl-3-thenoylcarbinol by rearrangement of the oxime. During the course of the investigation, 3-thienylglycolic acid and 3,3′-thenil were prepared. 3,3′-Thenilic acid proved too unstable to characterize well. The alkamine esters of phenyl-3-thienylglycolic acid have approximately the same antispasmodic activity as the corresponding 2-thienyl isomers.

In continuing studies on the comparison of the properties of physiologically active 2- and 3-thienyl isomers,[3] attention was turned to the alkamine esters of phenylthienylglycolic acid, the 2-isomers of which have been shown[4] to be potent substitutes for the clinically useful antispasmodic drug, Trasentin (β-diethylaminoethyl diphenylacetate).

Blicke and Tsao[5] prepared phenyl-2-thienylglycolic acid in two ways: by the reaction of phenylmagnesium bromide with 2-thienylglyoxylic acid, and by the reaction of 2-thienylmagnesium bromide on phenylglyoxylic acid. Neither of these methods can be readily applied in the 3-thiophene series because of the difficulty of obtaining the appropriate substitutions in the 3-position. Several attempts were made to obtain 3-thienylglyoxylic acid. Efforts to oxidize 3-acetothienone led only

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[1] Taken in part from the Thesis submitted by R. C. B. in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Indiana University, June, 1951.

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[3] For previous papers in this series see R. G. Garst, E. Campaigne and H. G. Day, *J. Biol. Chem.*, **180**, 1013 (1949); or E. Campaigne and W. M. LeSuer, THIS JOURNAL, **71**, 333 (1949).

[4] *Cf.* (a) F. A. Lands, V. Nash and K. Hooper, *J. Pharm. Exp. Ther.*, **86**, 129 (1946); (b) R. F. Feldkamp and J. A. Faust, THIS JOURNAL, **71**, 4012 (1949).

[5] F. F. Blicke and M. Tsao, *ibid.*, **66**, 1645 (1944).