site on the enzyme surface attacks the C-1 carbon atom, replacing the phosphate group with cleavage of the carbon–oxygen bond and formation of the glucose–enzyme intermediate. In the second step, the fructose molecule is the nucleophilic reagent which attacks the C-1 atom, displacing the enzyme and forming the final product, sucrose. The transglucosidase action of this enzyme,[30] the catalysis of phosphate exchange in glucose-1-phosphate[28] and fructose exchange in sucrose[31] are readily explained by analogous mechanisms.

There is a substantial amount of theoretical and experimental evidence to indicate that all single step nucleophilic displacements at a saturated carbon atom require "backside" attack by a nucleophilic reagent.[3,32] This appears to be true of "carbonium ion" mechanisms, which might be expected in the cleavage of an acetal type compound, as well as in the Walden inversion type of mechanism. The nucleophilic site on the enzyme would, therefore, make a backside attack leading to a glucose–enzyme intermediate of inverted configuration at the C-1 carbon atom. The fructose molecule would then displace the enzyme, again with inversion, to produce a final product, sucrose, having the same configurations as the initial glucose-1-phosphate substrate.

This mechanism leads to the suggestion that other enzymatic reactions which result in retention of configuration, *e.g.*, some glucosidase-catalyzed hydrolyses, may actually proceed in two steps, each involving an inversion. In all these cases a nucleophilic site on the enzyme surface takes direct part in the reaction to form an intermediate of greater or lesser stability depending on the particular system involved.

Acknowledgment.—The author wishes to express his gratitude to the du Pont Company for the award of a fellowship grant, and to Dr. Paul D. Bartlett for his encouragement of this research.

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE UNIVERSITY OF COLORADO]

Directed Chlorination of Fluorinated Aliphatic Ethers[1]

BY J. D. PARK, D. M. GRIFFIN[2] AND J. R. LACHER

A study was made of the photochemical chlorination of fluorinated aliphatic ethers of the type $ROCF_2CX_2H$ (R = CH_3– or C_2H_5–, X = chlorine, fluorine or hydrogen). Henne and co-workers had previously found that attack by chlorine on fluorinated aliphatic hydrocarbons is directed away from the hydrogen atom linked to a carbon alpha to a $-CF_2-$ or CF_3- group. The chlorination of the fluorinated aliphatic ethers was found to proceed in accord with the observations made by Henne and co-workers on the fluorinated aliphatic hydrocarbons. In all the ethers studied, chlorination was found to be directed away from the carbon atom adjacent to the $-CF_2-$ group of the fluorinated ethyl radical. The chloromethyl ethers were remarkably stable toward water, acids, methylmagnesium bromide and sodium. Physical properties determined for the chlorinated fluoroethers included boiling point, freezing point, refractive index, density, ultraviolet absorption spectrum and infrared absorption spectrum.

In a series of studies on the photochemical chlorination of fluorinated straight-chain aliphatic hydrocarbons, Henne and co-workers[3-8] found that methyl and methylene groups adjacent to CF_3- or $-CF_2-$ groups were protected from attack by chlorine. The lack of reactivity of hydrogen atoms adjacent to CF_3- and $-CF_2-$ groups was explained by Henne and Zimmerschied on the basis of the inductive effect of fluorine. Such an inductive effect was thought to increase the protonic character of hydrogen atoms adjacent to the CF_3- and $-CF_2-$ groups by a shift of C–H bonding electrons toward the carbon atom.

In the present work, a study was made of the photochemical, liquid-phase chlorination of the fluorinated ethers and their respective products in order to determine whether a directing effect on the entry of chlorine into the molecule might be observed. The chlorinations were carried out using a deficiency of chlorine to suppress the formation of polychlorinated products.

Parent compound	Chloro derivative
CH_3OCF_2CFHCl[9]	$ClCH_2OCF_2CFHCl$
$CH_3OCF_2CFH_2$[10]	$ClCH_2OCF_2CFH_2$
$CH_3OCF_2CF_2H$[11]	$ClCH_2OCF_2CF_2H$
$CH_3OCF_2CH_2Cl$[12]	$ClCH_2OCF_2CH_2Cl$
$CH_3OCF_2CHCl_2$[13]	$ClCH_2OCF_2CHCl_2$
$C_2H_5OCF_2CFHCl$[9]	$ClCH_2CH_2OCF_2CFHCl$ and $CH_3CCl_2OCF_2CFHCl$

In each case, chlorination was found to take place only in the unsubstituted radical of the ether. Thus, only chloromethyl ethers of the type CH_2Cl-

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(2) Atomic Energy Commission predoctoral Fellow, 1948–1949.

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(6) A. L. Henne and A. M. Whaley, *ibid.*, **64**, 1157 (1942).

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TABLE I

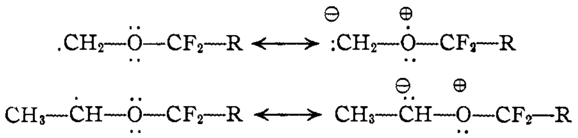
PHYSICAL PROPERTIES OF THE CHLORINATED FLUOROETHERS

Compound	B.p., °C.	B.p., Mm.	F.p., °C.	d^{20}_4	n^{20}_D	MR^a	MR^b	AR_F	Chlorine, % Calcd.	Chlorine, % Found
$ClCH_2OCF_2CFHCl$	104.5	624	Glass	1.5269	1.3768	27.46	27.52	1.12	37.76	38.75
$ClCH_2OCF_2CFH_2$	85	625	−51	1.4174	1.3514	22.59	22.62	1.11	24.37	24.35
$ClCH_2OCF_2CF_2H$	72	628	−78	1.4869	1.3311	22.60	22.92	1.19	21.29	22.73
$ClCH_2OCF_2CH_2Cl$	116	626	−44	1.4594	1.3974	27.45	27.25	1.00	43.03	42.99
$ClCH_2OCF_2CHCl_2$	137	627	−31	1.5679	1.4205	32.32	32.26	1.08	53.37	53.55
$ClCH_2CH_2OCF_2CFHCl$	80	100	Glass	1.4620	1.3935	32.08	32.44	1.23	36.04	37.15
$CH_3CCl_2OCF_2CFHCl$	59	100	Glass	1.4021	1.3776	36.95	37.96	1.45	46.00	45.62

[a] Calculated by adding the atomic increments. [b] Observed value, calculated by means of the Lorentz–Lorenz equation.

O-CF_2CX_3 were formed from the methyl ethers. Chlorination of $C_2H_5OCF_2CFHCl$ yielded two principal products, $ClCH_2CH_2OCF_2CFHCl$ (1 part) and $CH_3CCl_2OCF_2CFHCl$ (2 parts).

Two factors may explain the directed chlorination observed. First, the hydrogen atoms in the β-positions of the fluoroethyl groups of the ethers are made protonic by the inductive effect of fluorine, as postulated by Henne and Zimmerschied. Second, the radicals formed by removal of hydrogen from the methyl groups or from the α-position of the ethyl group may gain resonance stabilization as indicated



$$\cdot CH_2{-}\underset{..}{\ddot{O}}{-}CF_2{-}R \longleftrightarrow \overset{\ominus}{:}CH_2{-}\overset{\oplus}{\underset{..}{\dot{O}}}{-}CF_2{-}R$$

$$CH_3{-}\dot{C}H{-}\underset{..}{\ddot{O}}{-}CF_2{-}R \longleftrightarrow CH_3{-}\overset{\ominus}{\ddot{C}}H{-}\overset{\oplus}{\underset{..}{O}}{-}CF_2{-}R$$

These chloromethyl ethers exhibited a high degree of stability. These alpha chloro compounds did not undergo hydrolysis to esters in the presence of 96% sulfuric acid[14] as shown by Young and Tarrant for ethers of the type R-O-CF_2R' (where R is an alkyl group). The compounds resisted treatment with methylmagnesium bromide. Treatment with metallic sodium resulted in only slight reaction.

Formulas and physical constants of the chlorinated fluoroethers are given in Table I. Infrared absorption spectra of the compounds were taken.

Experimental

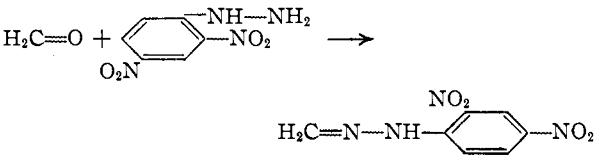
(1) **Chlorination of the Fluorinated Ethers.**—All the fluoroethers were chlorinated by the following procedure: One mole of the ether was placed in an apparatus consisting of a vertical Pyrex tube 40 cm. high and 50 mm. in diameter, fitted with a reflux condenser. Illumination was obtained by means of a 300-watt incandescent bulb. Chlorine was bubbled slowly into the ether through a sintered glass frit at the bottom of the reaction vessel until 0.9 mole of chlorine had been added. All of the chlorination reactions proceeded smoothly and rapidly with evolution of sufficient heat to cause refluxing.

When the addition of chlorine was complete, the reaction mixture was drained through a side arm at the bottom of the vessel into a dilute solution of sodium sulfite to remove unreacted chlorine. The product was washed with cold water, dried over calcium chloride, and fractionated in a small column packed with glass helices. Conversion to the chlorinated ether was 70 to 80%, and the yield was 90 to 95% of the theoretical yield.

(2) **Structures of the Chlorinated Ethers.** (A) $ClCH_2OCF_2CFHCl$.—Forty-six grams (0.25 mole) of the chloroether was added to 15 g. (0.27 mole) of potassium hydroxide in 150 ml. of methanol. Potassium chloride was precipitated immediately. A portion of the resulting mixture (after filtration to remove potassium chloride), when heated with an acidic solution of 2,4-dinitrophenylhydrazine, yielded formaldehyde-2,4-dinitrophenylhydrazone, m.p. 163°. The postulated equations for the reactions are

$$ClCH_2OCF_2CFHCl + KOH \xrightarrow{CH_3OH} KCl + HOCH_2OCF_2CFHCl$$

$$HOCH_2OCF_2CFHCl \xrightarrow[H_2O]{H^+} H_2C{=}O + 2HF + CFHCl{-}COOH$$



The hydrolysis to yield formaldehyde indicated that the structure of the compound was $ClCH_2OCF_2CFHCl$.

(**B**) $ClCH_2OCF_2CF_2H$ **and** (**C**) $ClCH_2OCF_2CHCl_2$.—These ethers were assigned their respective structures from the fact that both yielded formaldehyde when treated in the same manner as in A.

(**D**) $ClCH_2OCF_2CFH_2$.—Monochlorination of $CH_3OCF_2CFH_2$ could theoretically yield either $ClCH_2OCF_2CFH_2$ or CH_3OCF_2CFHCl, or both. CH_3OCF_2CFHCl is a known compound boiling at 64° at 625 mm.[3] The only monochlorinated fluoroether isolated from the chlorination of $CH_3OCF_2CFH_2$ boiled at 85–85.5° at 625 mm. By elimination the compound was assigned the structure $ClCH_2OCF_2CFH_2$.

(**E**) $ClCH_2OCF_2CH_2Cl$.—Monochlorination of $CH_3OCF_2CH_2Cl$ could theoretically yield either $ClCH_2OCF_2CH_2Cl$ or $CH_3OCF_2CHCl_2$, or both. $CH_3OCF_2CHCl_2$ is a known compound[13] having a boiling point of 97° at 625 mm. pressure. The compound obtained from the monochlorination of $CH_3OCF_2CH_2Cl$ boiled at 135–136° at 626 mm. Hence, the compound was assigned the structure $ClCH_2OCF_2CH_2Cl$.

(**F**) $CH_3CCl_2OCF_2CFHCl$.—Analysis and molar refraction indicated that the compound contained three atoms of chlorine per molecule, indicating that dichlorination had taken place. When 20 g. of the compound was treated with 50% hydriodic acid in a sealed tube at 170° for five hours, the resulting products included carbon and acetic acid. Acetic acid was identified by extracting the reaction mixture with ether, evaporation of the ether and treatment of the residual material with *p*-nitrobenzyl bromide[15] to form *p*-nitrobenzyl acetate, m.p. 76°. An equation for the reaction may be postulated

$$CH_3CCl_2OCF_2CFHCl + H_2O \xrightarrow{H^+} CH_3COOH + C + \text{other products}$$

The formation of carbon from fluorinated olefins when heated under pressure has been noted by Benning and Park[16]

$$CF_2{=}CF_2 \xrightarrow{\text{heat}} CF_4 + C$$

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(14) J. A. Young and P. Tarrant, THIS JOURNAL, **71**, 2432 (1949).

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 229.

(16) A. F. Benning and J. D. Park, U. S. Patent 2,351,390 (to E. I. du Pont de Nemours & Co.) (September 15, 1942).

A similar disproportionation is thought to have taken place in the present reaction, but further study is necessary before a definite statement of the reaction mechanism can be given. The fact that acetic acid was obtained as a product of the reaction, however, led to the assignment of the structure $CH_3CCl_2OCF_2CFHCl$ to the compound.

(G) $ClCH_2CH_2OCF_2CFHCl$.—The structure of this compound was determined by synthesis according to the equations

$$HOCH_2CH_2OH + CF_2{=}CFCl \xrightarrow{HOCH_2CH_2O^-} HOCH_2CH_2OCF_2CFHCl$$

$$HOCH_2CH_2OCF_2CFHCl + PCl_5 \longrightarrow ClCH_2CH_2OCF_2CFHCl + HCl + POCl_3$$

Ethylene glycol was added to trifluoroethylene under autogenous pressure[17] in the presence of sodium 2-hydroxyethoxide in a Parr hydrogenation apparatus. The resulting 1-(2-hydroxyethoxy)-1,1,2-trifluoro-2-chloroethane was fractionated under reduced pressure, the principal fraction boiling at 40° (1 mm.). Identity of the hydroxy ether was checked by molar refraction.

Fifty-four grams (0.3 mole) of the β-hydroxy ether was treated with 73 g. (0.35 mole) of phosphorus pentachloride and 25 ml. of phosphorus oxychloride in a flask equipped with a reflux condenser and stirrer. The reaction was quite vigorous at first. After the initial reaction subsided, the mixture was warmed for 30 minutes, cooled, and poured over cracked ice. After being washed with water and dried over calcium chloride, the product was fractionated at 100 mm. pressure. The principal product boiled at 80° (100 mm.). The refractive index of the compound was 1.3929 at 20°. The boiling point of the chloroether obtained by chlorination of $CH_3CH_2OCF_2CFHCl$ was 80° (100 mm.) and its refractive index was 1.3935. The structure assigned the compound was therefore $ClCH_2CH_2OCF_2CFHCl$.

BOULDER, COLORADO RECEIVED OCTOBER 10, 1951

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[17] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (to du Pont) (October 15, 1946).

[CONTRIBUTION NO. 116 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Structure of Alkali Metal-catalyzed Butadiene Polymers[1,2]

BY A. W. MEYER, R. R. HAMPTON AND J. A. DAVISON

The structures of various sodium and potassium-catalyzed butadiene polymers were determined from infrared absorption measurements. All of the polymers had a higher proportion of butadiene in the 1,2-configuration (45–80%) than emulsion polybutadiene (18–23%). Polybutadienes catalyzed by potassium had 15–20% less butadiene in the 1,2-configuration than those in which sodium was the catalyst. When a mixture of sodium and potassium was used, the results were nearly the same as with the potassium catalyst alone. Polybutadienes made at 5° had 10 to 15% more butadiene in the 1,2-configuration than those made at 45°. Diluent type had little or no effect on the structure of the polybutadienes. The butadiene portions of butadiene–styrene copolymers were found to have the same relative proportions of 1,2-, *cis*-1,4- and *trans*-1,4-configurations as the butadiene homopolymers. The second order transition temperature of sodium-catalyzed polybutadiene polymerized at 30° was −45° whereas the 75° polybutadiene had a value of −64°.

Introduction

Considerable information has been obtained concerning the structure of butadiene polymers prepared by the free radical mechanism. The effects of variables such as polymerization temperature and ingredients of the polymerization recipe on the polymer structure were determined.[3,4] It was found that the polymerization temperature governed the resulting structure. Thus with decreasing temperature of polymerization there was an increase in the proportion of *trans*-1,4-butadiene configuration with an accompanying decrease in *cis*-1,4 and little change in 1,2. It has been widely shown that the reduction in polymerization temperature has the effect of increasing tensile strength, abrasion resistance and other properties of the polymer.[5] However the changes in structure obtained by altering the variables of the emulsion polymerization were relatively limited. In order to complete the knowledge regarding obtainable polybutadiene structures, it appeared to be of interest to determine variations in structure produced by polymerizations having a carbanion type of mechanism such as that obtained with alkali metal catalysts.

Previous work has shown[6] that sodium-catalyzed polybutadiene polymers contained about 70% of 1,2-configuration as compared to about 20% for emulsion polybutadiene. These sodium polymers were found to have advantages in processing quality and in balance between flex crack growth and hysteresis properties.[7]

The Government Laboratories at the University of Akron prepared alkali metal-catalyzed polybutadiene and butadiene–styrene copolymers in order to investigate the effects of type of catalyst, polymerization temperature, diluents and rate-retarding modifiers upon the structure and the physical properties of the polymers.[8]

Experimental Procedure and Results

Several series of polybutadienes were made at the Government Laboratories in 8-oz. bottles at 5, 30 and 45°. Three types of catalyst, sodium, potassium and equimolar mixtures of sodium and potassium were used in the following basic formula:

Ingredients	Parts
Monomers	100
Diluent	0–300
Rate modifier	0–1.0
Catalyst	0.16–0.30

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[1] Presented before the Symposium on Synthetic Rubber, Division of Rubber Chemistry of the American Chemical Society, New York, N. Y., September 3–7, 1951.

[2] This work was carried on under Quartermaster Contract W44-109-qm-2030.

[3] E. J. Hart and A. W. Meyer, THIS JOURNAL, **71**, 1980 (1949).

[4] A. W. Meyer, *Ind. Eng. Chem.*, **41**, 1570 (1949).

[5] L. M. White, *ibid.*, **41**, 1554 (1949).

[6] C. S. Marvel, W. J. Bailey and G. E. Inskeep, *J. Polymer Sci.*, **1**, 275 (1946).

[7] A. E. Juve, M. M. Goff, C. H. Schroeder, A. W. Meyer and M. C. Brooks, *Ind. Eng. Chem.*, **39**, 1490 (1947).

[8] W. K. Taft, H. Goldsmith, *et al.*, private communication to the Office of Rubber Reserve.