Experimental Section[6]

1,4-Dioxane–Pentafluoroaniline Complex.—To 27.5 g (0.15 mole) of pentafluoroaniline was slowly added 50 ml of 1,4-dioxane. The temperature of stirred reaction rose exothermically to 40° and was allowed to proceed for 15 min. The excess dioxane was stripped off at ambient temperature in a rotary vacuum evaporator. The white crystalline complex (28.3 g, 83%) was collected and sublimed twice at 40° (0.05 mm). The volatile crystalline complex, mp 55.5–56.5°, slowly turned blue on standing in an open container.

Anal. Calcd for $C_{16}H_{12}F_{10}N_2O_2$: C, 42.30; H, 2.66; F, 41.8; N, 6.17. Found: C, 42.09; H, 2.68; F, 42.1; N, 6.37.

The fluorine nmr spectrum in benzene (22.6% by weight) exhibits three multiplets at 86.2, 88.8, and 97.5 ppm from trifluoroacetic acid. Peak area ratios are 2:2:1, respectively.

Proton nmr spectra in benzene (22.6% by weight) and in carbon tetrachloride (19.2% by weight) show peaks at 3.40 and 3.03 ppm with area ratios of 4.0:1.6, and at 3.68 and 4.02 ppm with area ratios of 4.0:1.5, respectively.

1,4-Dioxane–Pentafluorophenol Complex.—Pentafluorophenol (0.15 mole) was treated with 1,4-dioxane, as above. The colorless crystalline complex, 28.0 g (82%) was sublimed twice at 55° (0.05 mm) affording the analytical sample, mp 50–51°.

Anal. Calcd for $C_{16}H_{10}F_{10}O_4$: C, 42.12; H, 2.21; F, 41.6. Found: C, 42.20; H, 2.18; F, 41.6.

The fluorine nmr spectrum in carbon tetrachloride (22.8% by weight) shows two multiplets at 86.0 and 91.6 ppm from trifluoroacetic acid. The peak area ratio is 4.0:1.0.

Proton nmr spectrum in carbon tetrachloride (22.8% by weight) has two peaks at 7.62 and 3.88 ppm with an area ratio of 1.0:4.0.

1,4-Dioxane–2,3,5,6-Tetrafluorophenol Complex.—2,3,5,6-Tetrafluorophenol (0.15 mole) was treated with 1,4-dioxane, as above. The colorless crystalline complex, 27.3 g (87%), was sublimed twice at 45° (0.1 mm) affording the analytical sample, mp 66–67°.

Anal. Calcd for $C_{16}H_{12}F_8O_4$: C, 45.72; H, 2.88; F, 36.2. Found: C, 45.54; H, 2.84; F, 35.6.

The fluorine nmr spectrum in carbon tetrachloride (16.0% by weight) exhibits two multiplets at 60.2 and 82.3 ppm, with a peak area ratio of 1.0:1.0.

Proton nmr spectrum in carbon tetrachloride (16.0% by weight) has peaks at 7.81, 6.60, and 3.85 ppm, with area ratios of 2.0:2.0:8.0.

Registry No.—1, 13811-14-8; 2, 13811-09-1; 3, 13811-10-4; pentafluorophenol, 771-61-9; 3,4-dioxane, 123-91-1.

(6) Melting points are corrected.

The Synthesis of Monobromoperfluoroalkanecarboxylic Acids and Derivatives

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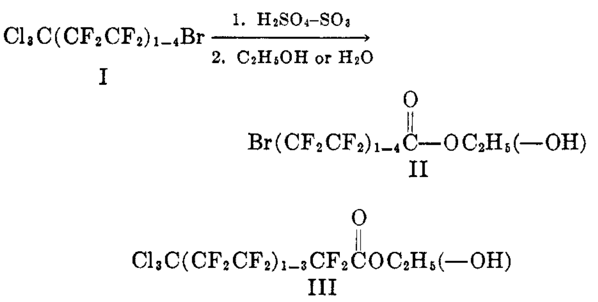
Received April 14, 1967

As a part of our program directed toward the synthesis of new versatile fluoroorganic intermediates, it was of interest to prepare the perfluorinated alkanecarboxylic acids and their derivatives containing a reactive substituent at the end of the chain.[1] Although perfluoroalkanecarboxylic acids and their derivatives containing a reactive substituent at the end of the chain are potentially useful organic intermediates, very little synthetic work in this area has been reported in the literature.[2]

In the present paper, a convenient method for the synthesis of a series of heretofore unreported ω-bromoperfluoroalkanecarboxylic acids and their derivatives is described. The synthesis is illustrated in eq 1.



$$\underset{\text{I}}{\mathrm{Cl_3C(CF_2CF_2)_{1-4}Br}} \xrightarrow[\text{2. } \mathrm{C_2H_5OH} \text{ or } \mathrm{H_2O}]{\text{1. } \mathrm{H_2SO_4{-}SO_3}} \underset{\text{II}}{\mathrm{Br(CF_2CF_2)_{1-4}\overset{O}{\overset{\|}{C}}{-}OC_2H_5({-}OH)}} \qquad (1)$$

$$\underset{\text{III}}{\mathrm{Cl_3C(CF_2CF_2)_{1-3}CF_2\overset{O}{\overset{\|}{C}}OC_2H_5({-}OH)}}$$

The free radical catalyzed telomerization of tetrafluoroethylene with bromotrichloromethane provided the required starting material, I.[3] The conversion of I to ω-bromoperfluoroalkanecarboxylic acid or to ester II was successfully effected by treatment with 30% oleum in the presence of a small amount of a mixture of mercuric sulfate and mercurous sulfate followed by hydrolysis or alcoholysis of the resulting mixture, respectively.[4] In no case was ω-trichloromethylperfluoroalkanecarboxylic acid or ester III detected. Under the conditions of the reaction employed, the exclusive product obtained was II in high yield.[5]

Assignment of the structure II rather than III was made on the basis of elemental analysis, infrared, and F^{19} resonance spectral properties. Also the treatment of the ester II ($n = 2$) with zinc dust in ethanol yielded the known ethyl ω-hydroperfluoropentanoate. The ester II could easily be converted to the corresponding amide which, in turn, gives rise to the corresponding nitrile upon dehydration with phosphorus pentoxide.

In the absence of the mercury salts, the rate of the reaction was found to be slow. This conclusion was based on the observation that under the identical reaction conditions, the presence of the salts led to the complete reaction of I ($n = 1$) while the absence of the salts gave only about 50% conversion of I ($n = 1$). The rate of the reaction also decreases with increasing the value of n in I. For example, a reaction temperature of 100–105° and a reaction time of about 45 hr are sufficient for the complete reaction of I ($n = 1$), whereas a reaction temperature of 115–120° and a reaction time of about 70 hr are required for I ($n = 2$).

Under conditions identical with those described above, a compound, arising from the free radical catalyzed addition of bromotrichloromethane to perfluoropropene, gave 3-bromoperfluorobutanoic ester (V) (see eq 2). The formation of V confirms that the com-

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[1] In general, compounds of the type R_fH and R_fCl (where R_f is a polyfluoro group) are chemically extremely inert and have not been reported to be useful for further synthetic work. For example, the free radical catalyzed addition of ethylene to R_fCl has not been reported, whereas R_fBr reacts with ethylene in the presence of free radical generating catalysts to yield $R_f(CH_2CH_2)_nBr$; K. C. Smeltz, U. S. Patent 3,055,953 (1962). For the information as to the relative reactivity of compounds of the type R_fX (X = H, Cl, Br, or I), see W. C. Francis and R. N. Haszeldine, *J. Chem. Soc.*, 2151 (1955).

[2] For a brief review of method of synthesis of polyfluorinated acids, see Chapter VII, A. M. Lovelace, D. A. Raush, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, and Chapter 3, R. E. Banks, "Fluorocarbons and Their Derivatives," Oldbourne Press, London, 1964.

[3] A. Sieglitz, *et al.*, German Patent 949,822 (1956).

[4] For the convenience of handling, all products were isolated as an ester rather than a free acid.

[5] In the acid hydrolysis using oleum of $Cl_3C(CF_2CFCl)_nBr$, it has been reported that -CFClBr group undergoes hydrolysis faster than the $-CCl_3$ group; W. S. Barnhart and R. H. Wade, U. S. Patent 2,806,865 (1957).

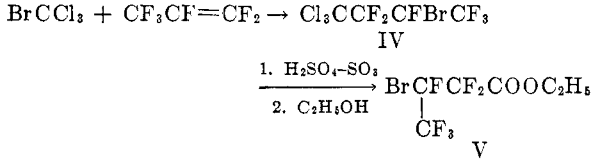
TABLE I

ETHYL MONOBROMOPERFLUOROALKANOATES AND DERIVATIVES

Product	Bp (mm) or mp, °C	n^{25}D	Yield, %	Formula	Calcd, % Br	C	F	H	Found, % Br	C	F	H
$BrCF_2CF_2CO_2C_2H_5$	127 (739)	1.3670	73	$BrC_5F_4H_5O_2$	31.59	23.73	30.04	1.99	30.5	23.8	30.0	2.06
$Br(CF_2CF_2)_2CO_2C_2H_5$[a]	157 (729)	1.3525	75	$BrC_7F_8H_5O_2$	22.64	23.81	43.06	1.43	22.2	23.86	44.3	1.49
$Br(CF_2CF_2)_3CO_2C_2H_5$[b]	63 (3.3)	1.3450	67	$BrC_9F_{12}H_5O_2$		23.86	50.33	1.11		23.9	49.6	1.22
$Br(CF_2CF_2)_4CO_2C_2H_5$[c]	60–74 (0.7)											
$CF_3CFBrCF_2CO_2C_2H_5$	55–56 (26)	1.3590	82	$BrC_6F_6H_5O_2$	26.37	23.79	37.62	1.67	27.0	23.95	37.3	1.67
$BrCF_2CF_2CONH_2$	112–113		87	$BrC_3F_4H_2NO$	35.65	16.09		0.93	35.1	16.0		1.13
$Br(CF_2CF_2)_2CONH_2$	129–130		89	$BrC_5F_8H_2NO$	24.67	18.53	46.91	0.62	24.7	18.9	47.0	0.80
$Br(CF_2CF_2)_3CONH_2$	143–144		89	$BrC_7F_{12}H_2NO$	18.85	19.83		0.48	18.1	20.1		0.78
$Br(CF_2CF_2)_4CONH_2$	155–156			$BrC_9F_{16}H_2NO$	15.25	20.63		0.39	15.9	20.9		0.71
$CF_3CFBrCF_2CONH_2$	66–67		83	$BrC_4F_6H_2NO$	29.17	17.53		0.74	29.9	18.1		0.88
$BrCF_2CF_2CN$	28–29 (740)	1.3570	91	BrC_3F_4N	38.83	17.47	36.89		37.8	17.3	37.4	
$Br(CF_2CF_2)_2CN$	78–79 (743)	1.3170	92	BrC_5F_8N	26.12	19.62	49.68		26.6	19.8	50.0	
$Br(CF_2CF_2)_3CN$	123 (739)	1.3185	72	$BrC_7F_{12}N$	19.68	20.71			19.70	20.45		

[a] The reaction was run at 115–120° (70 hr) using 200 g of I ($n = 2$), 150 ml of 30% oleum, and catalysts. [b] The reaction was run at 145–155° (95 hr) using 124 g of I ($n = 3$), 150 ml of 30% oleum, and catalysts. [c] The product is impure, as prepared and isolated from the reaction of a mixture of I (n = 1, 2, 3, and 4), and characterized as the amide.

pound obtained from the addition of bromotrichloromethane to perfluoropropene was IV, *the anticipated product.*[6] Assignment of the structure V was based on elemental analysis, infrared, and F^{19} resonance spectral properties.



$$BrCCl_3 + CF_3CF{=}CF_2 \rightarrow \underset{IV}{Cl_3CCF_2CFBrCF_3} \xrightarrow[2.\ C_2H_5OH]{1.\ H_2SO_4\text{–}SO_3} \underset{V}{Br\underset{\displaystyle CF_3}{\underset{|}{C}}FCF_2COOC_2H_5} \quad (2)$$

With the results observed in this work and together with the findings of Barnhart and Wade,[5] the qualitative order of the relative ease of acid hydrolysis of the perhalomethyl groups attached to a polyfluoroalkane chain is suggested to be

$$-CFClBr > -CCl_3 > -CF_2Br \quad (-\overset{|}{C}FBr)$$

Experimental Section

All melting points and boiling points are uncorrected. All melting points were taken on a Thomas–Hoover capillary melting point apparatus. Infrared absorption spectra were determined on a Perkin-Elmer Model 137 Infracord. The F^{19} resonance spectra were measured on a Varian high-resolution nmr spectrometer operating at 56.4 Mc. Chemical shifts are determined in parts per million using CCl_3F as an internal standard (δ = 0 ppm) with the positive direction on the high-field side. The proton resonance spectra were obtained on a Varian A-60 nmr spectrometer using tetramethylsilane as an internal standard (δ = 0 ppm) with the positive direction in this case on the low-field side.

Materials.—Tetrafluoroethylene was purchased from Peninsular ChemResearch Inc. and used without removing the polymerization inhibitor. Bromotrichloromethane was Eastman Organic Chemicals technical grade and was used without further purification. The telomer I was prepared according to the reported method.[3]

2-Bromo-4,4,4-trichloroperfluorobutane (IV).—Into an evacuated 1.4-l. stainless steel autoclave were placed, *in vacuo*, 1000 g (5.05 moles) of bromotrichloromethane and 15 g (0.103 mole) of di-*t*-butyl peroxide. The autoclave was cooled at −78° and charged with 1000 g (6.67 moles) of perfluoropropene. The autoclave was agitated and heated at 110° for 85 hr, during which period the pressure dropped from about 1000 psi to about 300 psi. The autoclave was cooled to room temperature, and the excess perfluoropropene was recovered. The remainder of the liquid contents (1250 g) was distilled to yield 681 g (68.1% recovery) of bromotrichloromethane and 448 g (77% yield based on unrecovered bromotrichloromethane) of analytically pure IV, bp 54° (26 mm), n^{25}D 1.4045.

Anal. Calcd for $BrC_4Cl_3F_6$: Br, 22.94; C, 13.79; F, 32.73. Found: Br, 22.1; C, 13.92; F, 32.7.

Ethyl Monobromoperfluoroalkanoates.—The preparation of ethyl 3-bromoperfluoropropionate (II, n = 1) is described as a typical example of the procedure. The results of other preparations are summarized in Table I.

A stirred mixture of 700 g (2.35 moles) of I (n = 1), 35 g of mercuric sulfate, 7 g of mercurous sulfate, and 525 ml of 30% oleum was heated for 45 hr by a heating mantle set at 100–105°. The reaction mixture was cooled to room temperature, and the solid was filtered. The filtrate was added slowly into 600 ml of ethanol at 0–5° while stirring. After completion of the addition, the mixture was brought to room temperature, kept overnight, and poured into about 2 l. of ice cold water. The organic layer that separated was collected and dried over Drierite to yield 446 g (75% yield) of crude ester. A fractional distillation gave 435 g (73% yield) of analytically pure ester II (n = 1), bp 127° (739 mm), n^{25}D 1.3670.

The infrared spectrum (CCl_4) showed the presence of a carbonyl function (~1765 cm^{-1}) and no absorption attributable to the Cl_3C– group in the 700–850-cm^{-1} range. The F^{19} resonance spectrum (neat) consisted of two triplets (J = 5.85 cps), centered at δ = +66.74 ppm ($BrCF_2$–) and +115.48 ppm (–CF_2CO–), with an area ratio of one to one. The proton resonance spectrum (neat) showed a triplet centered at δ = +1.40 ppm (J = 7 cps, integrated intensity of three protons) and a quartet centered at δ = +4.44 ppm (J = 7 cps, integration of two protons). These results are consistent with the assigned structure II (n = 1).

Monobromoperfluoroalkanamides.—All amides (Table I) were prepared by treatment of the ester with anhydrous ammonia in methylene chloride solution and purified by recrystallization from the same solvent. Infrared spectra of all amides reported showed absorption in 1700–1710 (C=O) and 3190–3390 cm^{-1} (NH) regions. The F^{19} resonance spectra were consistent with the assigned structures.

Monobromoperfluoroalkanenitriles.—Dehydration of the amide with phosphorus pentoxide at about 250° gave the corresponding nitrile (Table I). Infrared spectra (CCl_4) of all nitriles reported showed an absorption at ~2225 cm^{-1} (C≡N). The F^{19} resonance spectra were in agreement with the assigned structures.

Reaction of II (n = 2) with Zinc in Ethanol.—A mixture of 48 g (0.136 mole) of II (n = 2) and 16.2 g (0.248 g-atom) of zinc dust in 200 ml of absolute ethanol was first stirred at room temperature for 1 hr and then at 60° for 66 hr. The reaction mixture was filtered to remove solid materials. Distillation of the filtrate gave 22 g (59% yield) of analytically pure ethyl 5-hydroperfluoropentanoate, bp 59° (23 mm), n^{25}D 1.3220 (lit.[7] bp 140–142°, n^{20}D 1.3261).

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(6) The photochemical reaction of perfluoropropene–trifluoromethyl iodide gave 2-iodoperfluorobutane, $CF_3CF_2CFICF_3$; R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953).

(7) E. T. McBee, *et al.*, *Ind. Eng. Chem.*, **39**, 415 (1947).

Anal. Calcd for $C_7F_8H_6O_2$: C, 30.67; H, 2.21. Found: C, 30.75; H, 2.38.

Registry No.—II ($n = 1$), 13811-24-0; IV, 4259-30-7; $Br(CF_2CF_2)_2CO_2C_2H_5$, 424-35-1; $Br(CF_2CF_2)_3CO_2C_2H_5$, 13811-27-3; $Br(CF_2CF_2)_4CO_2C_2H_5$, 13811-28-4; $CF_3CFBrCF_2CO_2C_2H_5$, 13952-49-3; $BrCF_2CF_2CONH_2$, 13811-29-5; $Br(CF_2CF_2)_2CONH_2$, 13811-30-8; $Br(CF_2CF_2)_3CONH_2$, 13811-31-9; $Br(CF_2CF_2)_4CONH_2$, 13811-32-0; $CF_3CFBrCF_2CONH_2$, 13811-33-1; $BrCF_2CF_2CN$, 421-97-6; $Br(CF_2CF_2)_2CN$, 13811-35-3; $Br(CF_2CF_2)_3CN$, 13811-36-4.

Acknowledgment.—The author wishes to thank Mr. J. C. Lavis for his technical assistance.

Radical Reactions of Tetrafluorohydrazine. Diallyl Ether[1]

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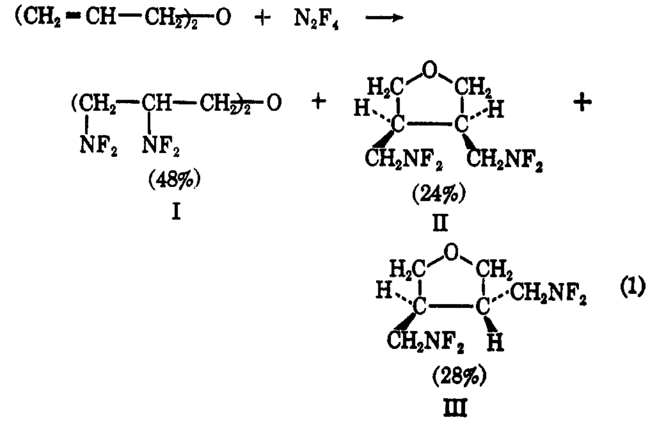
Received February 10, 1967

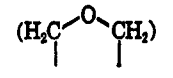
Studies on the radical reactions of tetrafluorohydrazine have now included the reaction with diallyl ether. The expected addition reaction[2] would yield di[2,3-bis(difluoramino)propyl] ether (I); however, it followed, in part, an unexpected course yielding two isomeric cyclic bis(difluoramino)-substituted compounds II and III (eq 1). The ratio of bis- to tetrakis(difluoramino) derivatives was approximately 1:1 under our reaction conditions.



On examination of the crude product fraction by gas chromatography, three components were noted to be present in a ratio of 2:1:1 based on peak areas. Attempts to effect separation of the products by distillation were not successful in yielding the pure components, and small quantities of the three products were separated by gas chromatography for purposes of characterization.

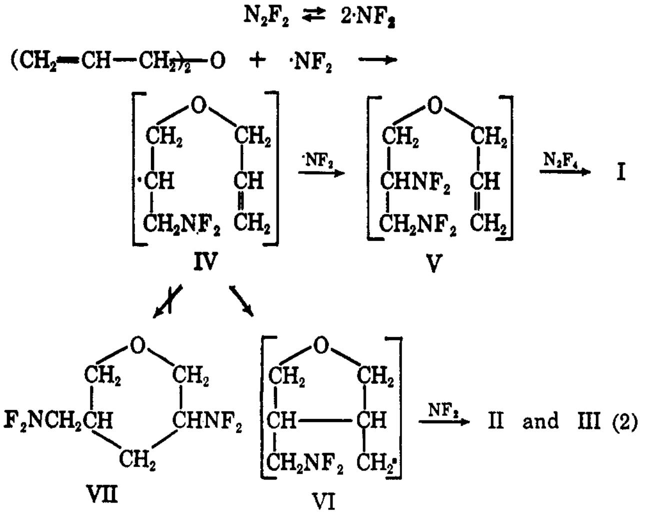
The F^{19} nmr spectrum of I showed a triplet centered at ϕ -56.8 ($J = \sim 27$ cps) and a multiplet centered at -42.0 representing the $-CH_2NF_2$ and $>CHNF_2$ groups, respectively. The proton resonance included superimposed triplets at τ 6.07 ($J = 27$ cps) due to the $-CH_2NF_2$ and $>CHNF_2$ protons. The methylene protons adjacent to the oxygen atom coincided with the center of the above triplet. These data are indicative of a compound with the structure of I.

Products II and III were identified as the indicated *cis, trans* isomers by elemental analysis and the following data. The F^{19} nmr spectra showed only triplets typical of primary alkyl difluoramines centered at ϕ -55.8 ($J = 26$ cps) and ϕ -56.5 ($J = 27$ cps) for II and III, respectively, indicating the presence of $-CH_2NF_2$ groups. The resonance signals in the pmr spectrum of II occurred as a triplet of multiplets centered at τ 6.42 ($-CH_2NF_2$), a multiplet centered at 6.04


$(H_2C{-}O{-}CH_2)$

and also a multiplet centered at 7.58 ($>CH{-}CH<$). Peak areas of methylene to methine protons was 4:1. The proton nmr spectrum of III showed a very complicated multiplet centered at τ 6.22 assigned as the signal arising from ring methylenes as well as part of the triplet from the $-CH_2NF_2$ groups. Also present was a multiplet centered at τ 7.23 attributed to the ring methine protons.

Tetrafluorohydrazine is known[2,3] to undergo a number of radical reactions with various substrates. In this instance the reaction mechanism is considered to involve the sequence given in eq 2. After initial disassociation of tetrafluorohydrazine, the difluoramino radical attacks at the terminal carbon atom of one of the carbon–carbon double bonds of diallyl ether to give the intermediate (IV), a 3-oxa-5-hexen-1-yl radical, which may react in either of two ways to give the 2,3-bis(difluoraminopropyl) allyl ether (V), or by an intramolecular attack of the radical on the remaining carbon–carbon double bond to give the cyclic intermediate (VI). In either instance the intermediates, V and VI, react further to yield the observed products, since V will ultimately give I by its further reaction with tetrafluorohydrazine, and VI, by reacting with a difluoramino radical, may give products II and III depending upon its configuration during cyclization.



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[1] This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Alabama under Contract Number DA-01-021 ORD-11909 (Z).

[2] A. L. Logothetis, U. S. Patents 3,196,167, (July 1965) and 3,215,709, (Nov 1965); H. Certontain, *J. Chem. Soc.*, 6602 (1965); A. J. Dijkstra, Ph.D. Thesis, "Kinetic Study of the Addition of Tetrafluorohydrazine to Olefins," University of Leiden, 1965; and R. C. Petry and J. P. Freeman, unpublished work.

[3] J. P. Freeman, Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, p 128.