octane were identical. Their gas chromatographic retention times were superimposable using a Perkin-Elmer 226 instrument with a 200-ft. silicone rubber capillary column operated isothermally at 200° and 12-p.s.i.g. helium pressure.

Acknowledgment.—We wish to thank Dr. John A. Favre for the determination and interpretation of the mass spectral data.

The Hydrolysis and Oxidation of α,ω-Bis(methylthio)polyfluoroalkanes

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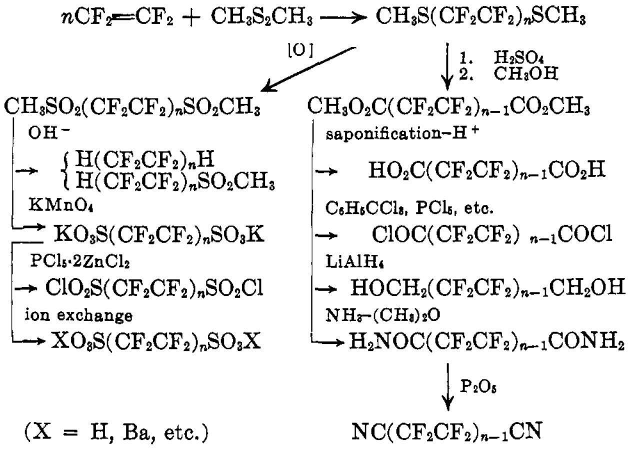
The α,ω-bis(methylthio)polyfluoroalkanes are shown to be sources of perfluoroalkanedioic acids, bis(methylsulfonyl)polyfluoroalkanes, αH,ωH-polyfluoroalkanes, and the new perfluoroalkanedisulfonic acids.

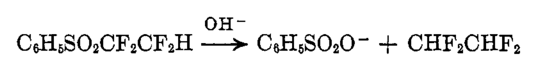
The telomerization of tetrafluoroethylene with methyl disulfide in the presence of *t*-butyl peroxide as a catalyst produces a series of telomers containing a straight perfluoroalkane chain having terminal methylthio groups.[1] These functional groups are utilized to prepare several difunctional fluorocarbons.[2]

Treatment of 1,6-bis(methylthio)dodecafluorohexane with concentrated sulfuric acid at temperatures of 150–180° in Hastelloy B pressure equipment causes hydrolysis of the terminal difluoromethylene groups, removal of the sulfur function, and formation of octafluorohexanedioic acid, isolated as the dimethyl ester. Similarly, the dimethyl esters of tetrafluorosuccinic, dodecafluorooctanedioic, and hexadecafluorodecanedioic acids were prepared, in yields as high as 80%. The free acids were obtained by saponification and the amides, nitriles,[3] and glycols[4] were prepared by standard techniques as shown below.



A convenient technique for isolating the dimethyl esters was used in which the acidic reaction product was suspended in water and methanol, and the ester was continuously extracted with 1,2-dichloroethane at 60°. The extract was dried and fractionally distilled.

Oxidation of 1,6-bis(methylthio)dodecafluorohexane with a variety of oxidizing agents, and especially with hydrogen peroxide in glacial acetic acid, gave high yields of the corresponding sulfone, 1,6-bis(methylsulfonyl)dodecafluorohexane. Treatment of the disulfone with aqueous alkali yielded sodium methanesulfonate and 1H,6H-dodecafluorohexane in high yield. An intermediate hydrolysis product, 1H-6-(methylsulfonyl)dodecafluorohexane, was isolable. The direction of this alkaline hydrolysis was indicated by the preparation of sodium 3,3,4,4-tetrafluoro-1-butanesulfonate from 2,2,3,3-tetrafluorothiolane 1,1-dioxide, and by the formation of 1,1,2,2-tetrafluoroethane from 2H-tetrafluoroethyl phenyl sulfone.



$$C_6H_5SO_2CF_2CF_2H \xrightarrow{OH^-} C_6H_5SO_2O^- + CHF_2CHF_2$$

Treatment of the disulfones with aqueous potassium permanganate gave the perfluoroalkanedisulfonic acids, isolated as the potassium salts. Thus, dipotassium dodecafluoro-1,6-hexanedisulfonate was obtained from 1,6-bis(methylsulfonyl)dodecafluorohexane. The salts showed surface-active properties, and were converted to the corresponding acid chlorides by treatment with phosphorus pentachloride–zinc chloride.[5] Attempts to prepare sulfonamide derivatives from the sulfonyl chlorides were unsuccessful; however, perfluoroalkane monosulfonyl chlorides have been converted to the amides.[6] In the case of tetrafluoro-1,2-ethanedisulfonyl chloride,[7] attempts to effect alkaline hydrolyses or reaction with amines in aqueous media resulted in the liberation of tetrafluoroethylene, while chloride, sulfate, and sulfite ions were formed. The reaction ran so smoothly that this particular sulfonyl chloride could be used as a laboratory source of pure tetrafluoroethylene (yield by weight 33%). A wash with aqueous alkali followed by drying gave material >99% pure by vapor phase chromatography.

When 1,4-bis(methylsulfonyl)octafluorobutane was oxidized with aqueous sodium dichromate, the main products were 1H,4H-octafluorobutane and 1H-4-(methylsulfonyl)octafluorobutane. When chromium trioxide and concentrated sulfuric acid were used, sodium 4-(methylsulfonyl)octafluoro-1-butanesulfonate was isolated.

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(1) W. E. Hanford, U. S. Patent 2,443,003 (June 8, 1948).

(2) I. L. Knunyants, L. Chih-yüan, and V. V. Shokina, *Russ. Chem. Rev.* (Eng. Transl.), **32**, 462 (1963): a review on difunctional fluorocarbons.

(3) E. T. McBee, P. A. Wiseman, and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

(4) M. P. Krasuskaya and I. L. Knunyants, Russian Patent 132,212 (Oct. 5, 1960).

(5) G. V. D. Tiers, *J. Org. Chem.*, **28**, 1244 (1963).

(6) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(7) C. G. Krespan, U. S. Patent 3,099,688 (July 30, 1963).

Experimental

1,2-Bis(methylthio)tetrafluoroethane and Higher Telomers.[1]—Methyl disulfide, containing 1% w./w. *t*-butyl peroxide (4.63 moles/hr.) was pumped into a 1.5-l., barricaded, stirred, pressure vessel. Tetrafluoroethylene[8] (13.89 moles/hr.), containing *d*-limonene inhibitor, was simultaneously fed to the reactor which was maintained at 135° and 600 p.s.i.g. The latter condition was maintained by pressure-controlled exit valves. The emerging product was cooled and fractionally distilled to yield the methyl disulfide telomers (Table I).

TABLE I

TETRAFLUOROETHYLENE–METHYL DISULFIDE TELOMERS

$CH_3S(CF_2CF_2)_nSCH_3$

n	B.p., °C. (mm.)	Yield, % (based on C_2F_4)
1	67–70 (40)	15.7
2	80–83 (20)	16.4
3	81–84 (4)	15.6
4	102–106 (4)	12.2
5	90–94 (0.7)	9.6
6	118–122 (0.7)	6.6
7	...	4.7
>7	...	10.5
	Total yield	91.3

1,2-Bis(methylsulfonyl)tetrafluoroethane.—1,2-Bis(methylthio)tetrafluoroethane (194 g.) was heated at 100–110° while a mixture of 30% hydrogen peroxide (450 ml.) and glacial acetic acid (300 g.) was added during 4 hr. The solution was boiled under reflux for 2 hr., poured into ice–water (10 l.), filtered, and recrystallized from methanol to yield the disulfone, m.p. 125°.

Anal. Calcd. for $C_4H_6F_4O_4S_2$: C, 18.6; H, 2.3; F, 29.4; S, 24.8. Found: C, 18.6; H, 2.4; F, 29.6; S, 24.8.

The same product was obtained when the telomer was treated with chromic acid at 100° or refluxing fuming (90%) nitric acid. The corresponding disulfone was prepared from each telomer up to 1,10-bis(methylthio)eicosafluorodecane (Table II).

TABLE II

PROPERTIES OF α,ω-BIS(METHYLSULFONYL)POLYFLUOROALKANES AND αH,ωH-POLYFLUOROALKANES

	$CH_3SO_2(CF_2CF_2)_nSO_2CH_3$		$H(CF_2CF_2)_nH$		
n	M.p., °C.	Yield, % (from methyl disulfide telomer)	B.p., °C.	M.p., °C.	Yield, % (from disulfone)
1	125	92	Not isolated	...	>90[a]
2	151	90	39.5–40.5	...	93
3	168	92	84.5–85.5	...	>90
4	171	75[b]	Not isolated	...	>90[a]
5	187	88	153–154	42–43	94

[a] Yield calcd. from v.p.c. [b] From crude (85% pure) telomer.

Dimethyl Tetrafluorosuccinate.—1,4-Bis(methylthio)octafluorobutane (2794 g., 85%) was heated in a stirred Inconel reactor with concentrated (98%) sulfuric acid (2.7 l.) to 165° during 4 hr., and this temperature was held for a further 4 hr. The product was discharged into water (3 l.) and filtered hot. The filtrate was diluted with methanol (1.5 l.) and was continuously extracted at 60° with 1,2-dichloroethane. The organic phase was separated, filtered with charcoal, dried, and fractionally distilled to yield dimethyl tetrafluorosuccinate (1390 g., 79%), b.p. 115–116° (100 mm.).

Anal. Calcd. for $C_6H_6F_4O_4$: C, 33.04; H, 2.77; F, 34.84. Found: C, 33.1; H, 2.7; F, 34.2.

Dimethyl octafluorohexanedioate, dodecafluorooctanedioate, and hexadecafluorodecanedioate were similarly prepared (Table III).

2,2,3,3,4,4,5,5-Octafluoro-1,6-hexanediol.—Dimethyl octafluorohexanedioate (31.8 g.) was added slowly to lithium aluminum hydride (7.6 g.) in refluxing ethyl ether (600 ml.) under nitrogen. After refluxing for 16 hr. the mixture was held at 0–5° while ethyl acetate (40 ml.), sulfuric acid (75 ml., 33%), and water (100 ml.) were added. The aqueous phase was removed and washed with ether. The washings and the ether layer were combined, washed with water, dried, and distilled to give the diol (20.4 g., 78%), b.p. 135–136° (27 mm.). Recrystallization from carbon tetrachloride gave a product, m.p. 68.5–69°.

TABLE III

PROPERTIES OF THE PERFLUOROALKANEDIOIC ACID DIMETHYL ESTERS AND OF THE CORRESPONDING GLYCOLS

	$CH_3O_2C(CF_2CF_2)_{n-1}CO_2CH_3$		$HOCH_2(CF_2CF_2)_{n-1}CH_2OH$		
n[a]	B.p., °C. (mm.)	Yield, % (from methyl disulfide telomer)	M.p. °C.	B.p,, °C. (mm.)	Yield, % (from dimethyl ester)
2	115–116 (100)	80	81–82	...	72
3	121–123 (50)	83	69	135–136 (27)	78
4	126–127 (25)	76	...	...	..
5	144–146 (25)	64	...	...	..

[a] N.B., *n* refers to number of tetrafluoroethylene units in initial telomer. Note formulas in this table contain $n-1$ tetrafluoroethylene residues after acid hydrolysis.

Anal. Calcd. for $C_6H_6F_8O_2$: C, 27.49; H, 2.29; F, 58.00. Found: C, 27.2; H, 2.5; F, 57.1.

2,2,3,3-Tetrafluoro-1,4-butanediol.—Dimethyl tetrafluorosuccinate was reduced as in the previous experiment. The product (72%) was isolated by crystallization from carbon tetrachloride–ethyl acetate, m.p. 80.5–82°.

Anal. Calcd. for $C_4F_4H_6O_2$: C, 29.7; H, 3.7; F, 46.9. Found: C, 29.5; H, 3.8; F, 47.5.

Dodecafluorooctanediamide.—Dimethyl dodecafluorooctanedioate (51.8 g.) was dissolved in ethyl ether (518 ml.), and the solution saturated with anhydrous ammonia. The precipitate was filtered and recrystallized from ethanol to give the diamide (46.3 g., 97%), m.p. 241°.

Anal. Calcd. for $C_8H_4F_{12}N_2O_2$: C, 24.76; H, 1.04; F, 58.74; N, 7.22. Found: C, 24.7; H, 1.05; F, 59.0; N, 7.05.

Hexadecafluorodecanediamide.—Dimethyl hexadecafluorodecanedioate treated as in the previous experiment gave the diamide (90%), m.p. 245°.

Anal. Calcd. for $C_{10}H_4F_{16}N_2O_2$: C, 24.61; H, 0.83; F, 62.27; N, 5.74. Found: C, 24.7; H, 0.85; F, 62.0; N, 5.6.

Dodecafluorooctanedinitrile.—Dodecafluorooctanediamide (30 g.) was thoroughly mixed with phosphorus pentoxide (35 g.) and heated in a simple still. The volatile product was redistilled to give the dinitrile (26.5 g., 95%), b.p. 110°.

Anal. Calcd. for $C_8F_{12}N_2$: C, 27.29; F, 64.75; N, 7.96. Found: C, 27.3; F, 64.8; N, 8.0.

1H,10H-Eicosafluorodecane.—1,10-Bis(methylsulfonyl)eicosafluorodecane (80 g.) was boiled under reflux for 2 hr. with water (200 ml.) containing sodium hydroxide (100 g.). The low-melting product was distilled to give 1H,10H-eicosafluorodecane (94%), b.p. 153–155°, m.p. 42–43°.

Anal. Calcd. for $C_{10}H_2F_{20}$: C, 23.92; H, 0.4; F, 75.68. Found: C, 24.0; H, 0.5; F, 75.8.

The aqueous solution was neutralized (H_2SO_4), dried, and extracted with ethanol. Recrystallization of the extracted solids gave sodium methanesulfonate, identified by elemental analysis and its infrared spectrum.

1H,2H-Tetrafluoroethane, 1H,4H-octafluorobutane, 1H,6H-dodecafluorohexane, and 1H,8H-hexadecafluorooctane were prepared in a similar manner (Table II).

1H-4-(Methylsulfonyl)octafluorobutane.—1,4-Bis(methylsulfonyl)octafluorobutane (100 g.), sodium hydroxide (50 g.), and water (100 ml.) were boiled under reflux until most (~80%) of the sulfone had disappeared. The trapped volatile products and the separated organic phase were combined, washed, dried, and distilled to give 1H,4H-octafluorobutane (32 g., 56%), b.p. 39.5–40.5°, and 1H-4-(methylsulfonyl)octafluorobutane (10 g., 13%), b.p. 101° (40 mm.).

Anal. Calcd. for $C_5H_4F_8O_2S$: C, 21.44; H, 1.44; F, 54.24; S, 11.45. Found (for latter product): C, 21.6; H, 1.6; F, 56.3; S, 11.3.

Hydrolysis of 2H-Tetrafluoroethyl Phenyl Sulfone and of 2,2,3,3-Tetrafluorothiolane 1,1-Dioxide.—2H-Tetrafluoroethyl

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[8] Pressurized tetrafluoroethylene presents a severe explosion hazard unless stringent precautions are observed.

phenyl sulfone[9,10] (3 g.), sodium hydroxide (3 g.), and water (3 ml.) were boiled under reflux for 20 hr. The trapped volatile products contained 1.2 g., (90% yield) of 1,1,2,2-tetrafluoroethane, identified by mass spectroscopy.

2,2,3,3-Tetrafluorothiolane 1,1-dioxide[10] (6 g.), sodium hydroxide (4 g.), and water (9 ml.) were boiled under reflux for 6 hr. The solution was neutralized (H_2SO_4), dried, and extracted with ethanol. The extracted solids were recrystallized from ethanol to give sodium 3,3,4,4-tetrafluoro-1-butanesulfonate.

Anal. Calcd. for $C_4H_5F_4NaO_3S$: C, 20.7; H, 2.2; F, 32.7; Na, 9.9; S, 13.8. Found: C, 20.7; H, 2.3; F, 30.2; Na (ash), 9.7; S, 13.9.

Sodium 4-(Methylsulfonyl)octafluoro-1-butanesulfonate.—1,4-Bis(methylsulfonyl)octafluorobutane (50 g.), dissolved in concentrated sulfuric acid (300 g.), was heated to 190° and treated with chromium trioxide (70 g.) during 1 hr. The material was heated for a further 3 hr., cooled, diluted with water, neutralized (NaOH), dried, and extracted with ethanol. The extracted salts were crystallized twice from hot water to yield the sulfone-sulfonate.

Anal. Calcd. for $C_5H_3F_8NaO_5S_2$: C, 15.71; H, 0.79; F, 39.77; S, 16.78. Found: C, 15.5; H, 1.0; F, 38.0; S, 16.6.

Dipotassium Eicosafluoro-1,10-decanedisulfonate.—Potassium permanganate (30 g.), 1,10-bis(methylsulfonyl)eicosafluorodecane (15 g.), and water (200 ml.) were heated at 150° for 6 hr. in a 400-ml. bomb. The discharged product was boiled with ethanol under reflux to destroy excess oxidant, and the slurry was filtered hot. The residue was washed with hot water, and the combined aqueous solutions were treated with Dowex 50 resin (H^+ form) at 80° to pH 5. The solution was boiled for 5 min., filtered, and evaporated to leave the crystalline salt (13.1 g., 78%).

Anal. Calcd. for $C_{10}F_{20}K_2O_6S_2$: C, 16.3; F, 51.5; K, 10.6; S, 8.7. Found: C, 16.4; F, 51.8; K (ash), 10.3; S, 8.3.

The salts of tetrafluoro-1,2-ethane-, octafluoro-1,4-butane-, dodecafluoro-1,6-hexane-, and hexadecafluoro-1,8-octanedisulfonic acids were obtained similarly.

Dodecafluoro-1,6-hexanedisulfonyl Chloride.—Dry potassium dodecafluoro-1,6-hexanedisulfonate (100 g.) was powdered with phosphorus pentachloride–zinc chloride (270 g.)[5] and was heated vigorously in a simple still to 250° (50 mm.). Redistillation of the distillate gave the disulfonyl chloride (76 g., 82%), b.p. 138° (40 mm.).

Anal. Calcd. for $C_6Cl_2F_{12}O_4S_2$: C, 14.4; Cl, 14.2; F, 45.7; S, 12.8. Found: C, 14.1; H, <0.1; C, 14.5; F, 47.7; S, 12.6.

Acknowledgment.—The author wishes to thank Mr. Thomas E. Beukelman for n.m.r. (H^1 and F^{19}) studies and Dr. Robert K. Miller for infrared studies. Confirmatory structural proof for the described products by these two techniques was invaluable.

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[9] D. C. England, L. R. Melby, M. A. Dietrich, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, **82**, 5116 (1960).

[10] C. G. Krespan, *J. Org. Chem.*, **27**, 3588 (1962).

A Novel Method for the Preparation of Bicyclooctane Systems. III.[1,2] Cyclization of Vinylcyclohexenes

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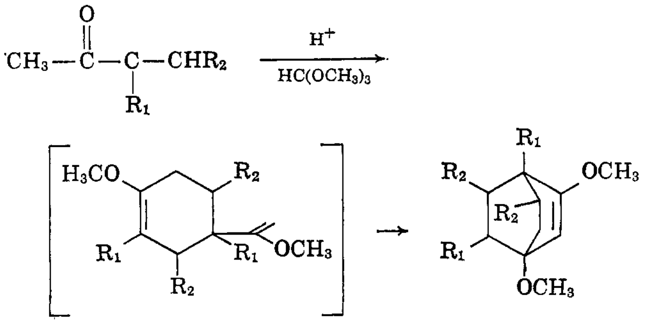
An acid-catalyzed cyclization of variously substituted 4-vinyl-1-cyclohexenes leading to bicyclooctene systems was studied. The presence of substituents such as phenyl and methoxyl groups at C-1 of vinylcyclohexenes favors the acid-catalyzed ring-closure reaction, whereas electron-attracting groups such as carbonyl, carboxyl, and cyano at C-1 resist cyclization. Mechanism of the cyclization of 1-phenyl-4-vinyl-1-cyclohexenes (**10** and **31**) might involve, in part, the anchimeric effect of a junction-forming second double bond.

Reaction of α,β-unsaturated ketones with trimethyl orthoformate in the presence of an acid catalyst affords bicyclo[2.2.2]octane systems, and the mechanism of the reaction involves the acid-catalyzed cyclization of vinylcyclohexenes derived by a condensation of enol ethers of α,β-unsaturated ketones.[1,2] It was also described in a recent paper[2a] that cyclization of 4-substituted 1-methoxy-4-(1-methoxyvinyl)-1-cyclohexenes leads to 1-substituted 2,4-dimethoxybicyclo[2.2.2]oct-2-enes and of 1,4-diphenyl-4-vinyl-1-cyclohexene (**31**) to 1,4-diphenylbicyclo[3.2.1]oct-3-ene (**14**).



Ipatieff and his colleagues[3] obtained 2,6-dimethylbicyclo[3.2.1]oct-2-ene among other products when limonene was passed over silicophosphoric acid catalyst at 210°. Wenkert[4,5] has reported transformation of the 3-vinyl-1-cyclohexene structure in the tricarbocyclic diterpene, rimurene, into the bicyclo[3.2.1]oct-6-ene system (isophyllocaladene) by treatment with formic acid. Patent literature[6] has described cyclization of 4-vinyl-1-cyclohexene with tris[2-(3-cyclohexen-1-yl)ethyl]aluminum leading to bicyclo[3.2.1]oct-2-ene.

We report herein cyclization and attempted cyclization of variously substituted vinylcyclohexenes, and discuss the effects of substituents on the cyclization. The mechanism of the reaction is also discussed.

Cyclization of 4-Methyl-1-methoxy-4-vinyl-1-cyclohexene (6).—The hitherto unknown 4-methyl-1-methoxy-4-vinyl-1-cyclohexene (**6**) was prepared from 4-acetyl-4-methyl-1-cyclohexanone (**1**).[7] Reaction of **1** with excess morpholine in boiling benzene afforded

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[1] K. Morita, G. Somp, and E. V. Jensen, *J. Am. Chem. Soc.*, **84**, 3779 (1962).

[2] (a) K. Morita, M. Nishimura, and Z. Suzuki, *J. Org. Chem.*, **30**, 533 (1965); (b) K. Morita and Z. Suzuki, *Tetrahedron Letters*, **No. 6**, 203 (1964).

[3] V. N. Ipatieff, J. E. Germaine, W. W. Thompson, and H. Pines, *J. Org. Chem.*, **17**, 272 (1952).

[4] E. Wenkert, *Chem. Ind.* (London), 282 (1955).

[5] *Cf.* (a) A. J. Birch, R. W. Richards, H. Smith, A. Harris, and W. B. Whalley, *Tetrahedron*, **7**, 241 (1959); (b) G. Büchi, E. Koller, and C. W. Perry, *J. Am. Chem. Soc.*, **86**, 5646 (1964).

[6] Schering A. G., French Patent, 1,351,716 ((1964); *Chem. Abstr.*, **60**, 13164*f* (1964).

[7] J. Colonge and R. Vuillemet, *Bull. soc. chim. France*, 2235 (1961)