with charcoal and recrystallized four times from benzene. The final product was a white powder which melted at 105–105.5°. It did not depress the melting point of an authentic sample of di-n-octadecylphosphinic acid prepared from n-1-octadecene and hypophosphorous acid[2] (m.p. 105.3–106°), but did depress the melting point of the original di-n-octadecylphosphine oxide by 10°.

Anal. Calcd. for $(C_{18}H_{37})_2P(O)OH$: neut. equiv., 571. Found: neut. equiv., for the sample from the phosphine oxide 560, for the sample from hypophosphorous acid 583.

X-Ray diffraction patterns indicated that the two acid samples were essentially identical.

It was noted in taking the mixed melting point of di-n-

octadecylphosphine oxide with di-n-octadecylphosphinic acid that no depression was obtained unless the samples were very intimately mixed.

After normal mixing of the samples melting points of 105–106° were obtained, but when these melts were solidified and again heated they melted 10° lower.

Attempts to oxidize di-n-octadecylphosphine oxide with 30% hydrogen peroxide resulted in little or no reaction.

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PAULSBORO, NEW JERSEY

Perfluorinated Cyclic Ethers

BY ALBERT L. HENNE AND SIDNEY B. RICHTER

CF_2CF_2–O–CF_2CF_2 and $CF_2CF_2CF_2$–O–CF_2CF_2 were synthesized and found incapable of dissolving Lewis acids. The lack of basic properties already shown in perfluorinated open chain ethers is therefore not due to steric hindrance, and is attributed to electronegative induction.

Experimental Syntheses

Perfluorinated ethers do not dissolve in sulfuric acid, nor are they colored by ferric chloride, and this loss of basic character has been attributed to electronegative induction[1]; but since tetrahydrofuran is known to be more basic than open chain ethers,[2] the loss might have been caused by steric factors. Perfluorinated cyclic ethers were therefore prepared, in which the steric factor would be absent; they were found to be non-basic.

The syntheses follow. A perfluorinated dibasic ester $RO_2CCF_2(CF_2)CF_2CO_2R$ (formulated with one of its CF_2 groups in parentheses to denote either a succinate or a glutarate) was reduced to a diol $HOCH_2CF_2(CF_2)CF_2CH_2OH$ and the latter cyclized to an ether $(CF_2)CF_2CH_2$–O–CH_2CF_2. Chlorination yielded a perhalogenated cyclic ether $(CF_2)CF_2CCl_2$–O–CCl_2CF_2, which fluorination transformed into the desired perfluorinated cyclic ether $(CF_2)CF_2CF_2$–O–CF_2CF_2. Alternate routes, through a perfluorinated cyclic anhydride, failed. The last step of the sequence, halogen exchange, proved much easier with the smaller, five-membered ring which did not break than with the larger six-membered ring, where completion of the halogen exchange was almost prevented by decomposition. Resisted halogen exchange by the larger, fluorine-richer ring rather than weakness in ring size is regarded as the cause of the difference.

The resistance to solvolysis of the CF_2 groups next to the oxygen bridge was tested by heating cyclo-C_4F_8O with an alcohol solution of sodium alcoholate for a week at 100°, without effect. This behavior parallels that reported for "protected" CF_2 groups in open chain ethers.[1]

The infrared spectrum of cyclo-C_4F_8O is shown as Fig. 1, with the spectrum of the open chain C_4F_9–O–C_4F_9 for comparison.

Perfluorosuccinic Acid.—CF_2=CCl_2 was obtained by perchlorination[3] of commercial CF_3HCH_3 (quantitative) followed by zinc dechlorination (95% yield). Its dimerization[4] at 220° gave, in 24 hours, an 85% yield of cyclo-$CF_2CF_2CCl_2CCl_2$, quantitatively dechlorinated to cyclo-CF_2CF_2CCl–CCl, the oxidation[5] of which gave a 74% yield of diethyl perfluorosuccinate.

Perfluorosuccinic Anhydride.—This anhydride could not be obtained by heating the diacid with concentrated sulfuric acid at 140° for three hours; it was, however, obtained in 62% yield by heating a mixture of perfluorosuccinic acid (19 g. or 0.1 mole) with P_2O_5 (28.4 g. or 0.2 mole) to 185° in a Claisen flask, and the balance of the acid was recovered.

The anhydride CF_2CO–O–$COCF_2$, b.p. 54–55°, $n^{20}D$ 1.3240, d^{20}_4 1.6209, MR 21.30, ARF 1.40, had properties which agreed with those shown in a recent patent.[6] Attempts to transform it to CF_2CCl_2–O–CCl_2CF_2 with PCl_5 failed, and attempts to reduce it to a lactone CF_2CO–O–CH_2CF_2 gave only the diol described hereunder.

Tetrafluorobutanediol $HOCH_2CF_2CF_2CH_2OH$.—Diethyl perfluorosuccinate (102 g. or 0.414 mole) was reduced with $LiAlH_4$ (17.3 g. or 0.45 mole) in dry ether to give $HOCH_2$–$CF_2CF_2CH_2OH$ (57.6 g. or 0.355 mole) in 86% yield. This diol, b.p. 110–112° at 13 mm., melted at 80–80.6° after recrystallization from benzene, agreeing with McBee's description.[7] Its first and second ionization constants were determined by Glasstone's method[8] as 1.2×10^{-11} and 4.1×10^{-12}, the correct order of magnitude.[7,9]

Cyclization.—A mixture of the glycol (81 g. or 0.5 mole) and concentrated sulfuric acid (10 g. or 0.1 mole) was kept in an oil-bath at 185°. The cyclic ether which distilled over was dried with Drierite and redistilled, to give CF_2CH_2–O–CH_2CF_2 (71 g. or 0.49 mole), b.p. 68° in 97% yield.

(1) A. L. Henne and M. A. Smook, THIS JOURNAL, 72, 4378 (1950).

(2) H. C. Brown and R. M. Adams, *ibid.*, 64, 2551 (1942).

(3) E. T. McBee, A. L. Henne, H. B. Hass and N. H. Elmore, *ibid.*, 62, 3340 (1940).

(4) A. L. Henne and R. P. Ruh, *ibid.*, 69, 279 (1947).

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

(6) J. J. Padbury and E. L. Kropa, U. S. Patent 2,502,478 (1950).

(7) E. T. McBee, W. F. Marzluff and O. R. Pierce, THIS JOURNAL, 74, 444 (1952).

(8) S. Glasstone, *J. Chem. Soc.*, 1821 (1935).

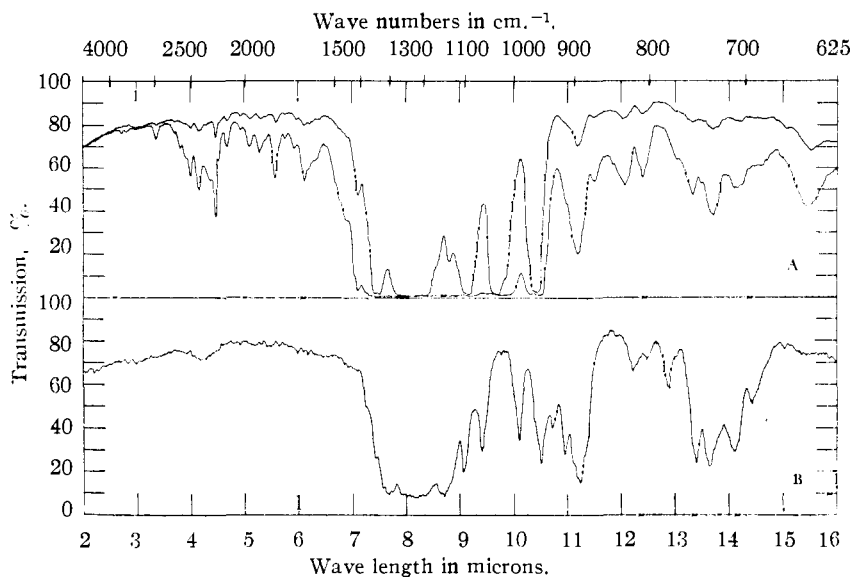(9) A. L. Henne and R. L. Pelley, THIS JOURNAL, 74, 1426 (1952).

Fig. 1.—Infrared spectra of: A, cyclo-C_4F_8O, top line, gas at 50 mm.; lower line, gas at 300 mm.; B, C_4F_9-O-C_4F_9 liquid.

Chlorination of the Cyclic Ether.—The cyclic ether (87 g. or 0.58 mole) was placed in a quartz flask illuminated with a General Electric "Sun Lamp." Chlorine was bubbled through for two days. An ice-cooled trap attached to the reflux condenser caught entrained material, which was returned from time to time. The perhalogenated cyclic ether

CF_2CCl_2-O-CCl_2CF_2 (128 g. or 0.45 mole), b.p. 131-132°, was obtained in 78% yield.

benzene, the diol melted at 78.2-78.8°, agreeing with Mc-Bee.[7]

Cyclization.—The diol (126.5 g. or 0.597 mole) mixed with concentrated H_2SO_4 (215.6 g. or 2.2 moles) had to be heated to 250° to cause distillation of a milky liquid; this was dried with Drierite, and distilled from P_2O_5 to yield the

cyclic ether $CF_2CF_2CH_2$-O-CH_2CF_2, b.p. 98-100° (100 g. or 0.514 mole), in 86% yield.

TABLE I

PHYSICAL PROPERTIES OF THE CYCLIC ETHERS

	B.p. °C.	Mm.	$n^{20}D$	d^{20}_4	MR	AR_F	Analyses, % Calcd.	Found
CF_2CH_2—O—CH_2CF_2	68	743	1.3244	1.4305	20.22	1.12	F, 52.78	F, 51.58
CF_2CCl_2—O—CCl_2CF_2	131-132	742	1.4120	1.7382	40.32	1.28	Cl, 50.35	Cl, 49.1
CF_2CF_2—O—CF_2CF_2	0.8-1.2	733		(molecular weight calcd. 216, found 221)				
$CF_2CF_2CH_2$—O—CH_2CF_2	98-100	742	1.3250	1.5588	25.04	1.15	F, 58.15	F, 56.65
$CF_2CF_2CCl_2$—O—CCl_2CF_2	159	737	1.4008	1.7662	45.67	1.34	Cl, 42.77	Cl, 41.93
$CF_2CF_2CF_2$—O—CF_2CF_2	26	742					C, 22.6	C, 22.9

Fluorination to Perfluorinated Cyclic Ether.—CF_2CCl_2-O-CCl_2CF_2 (59 g. or 0.209 mole) and SbF_3Cl_2 (136 g. or 0.544 mole) were heated at 155 °for 24 hours in a steel bomb. The pressure rose to 230 p.s.i. and dropped to 50 p.s.i. on cooling to room temperature. This pressure was released into a Dry Ice trap which collected raw CF_2CF_2-O-CF_2CF_2 (30.3 g. or 0.14 mole) in 67.2% yield. This compound was purified by passage through two 10% HCl bubblers to remove traces of antimony salts, concentrated H_2SO_4 to remove unsaturated impurities and finally distilled from P_2O_5. The purified material was compared to an analyzed sample prepared by perfluorination of tetrahydrofuran by Minnesota Mining and Manufacturing Company and found identical in physical properties and infrared spectrum.

Perfluoroglutaric Ester.—Oxidation of $CF_2CF_2CF_2CCl$=CCl with basic permanganate[6] to perfluoroglutaric acid followed by immediate esterification of the aqueous acid[7] gave diethyl perfluoroglutarate, b.p. 75-81° at 3-4 mm., $n^{26}D$ 1.3585, in 81% over-all yield.

Reduction to Diol $HOCH_2CF_2CF_2CF_2CH_2OH$.—This was done as above, in 87.2% yield. After recrystallization from

Chlorination to $CF_2CF_2CCl_2$-O-CCl_2CF_2 was performed as above, in 89% yield.

TABLE II

SOLUBILITY TESTS

	(A)	(B)	(C)	(D)
CF_2CH_2—O—CH_2CF_2	s	s	s	s
CF_2CCl_2—O—CCl_2CF_2	s	s	i	i
CF_2CF_2—O—CF_2CF_2	s^a	i	i	i
$CF_2CF_2CH_2$—O—CH_2CF_2	s	s	s	s
$CF_2CF_2CCl_2$—O—CCl_2CF_2	s	s	i	i
$CF_2CF_2CF_2$—O—CF_2CF_2				i

[a] Soluble in ether between 0 and −15°, insoluble below −15°. s denotes solution or complex formation, and i lack of either with ether (A), 95% ethanol (B), concd. H_2SO_4 (C) and $FeCl_3$ (D).

Fluorination.—The passage from cyclo-$C_5F_6Cl_4O$ to cyclo-$C_5F_{10}O$ proved considerably more difficult than for the smaller ring. When the fluorination was vigorous, the ring broke; for less rigorous conditions, only part fluorination occurred. A two-step procedure finally succeeded. Cyclo-$C_5F_6Cl_4O$ (100 g. or 0.3 mole) was mixed with SbF_3Cl_2 (100 g. or 0.4 mole) and heated to 125° for seven hours in a 450-ml. steel bomb, with shaking. The pressure rose to 75 p.s.i. The temperature was raised to 160° for 16 hours, which brought the pressure up to 230 p.s.i. After cooling, a light fraction (41 g.), b.p. 52–95°, was collected by distillation, which was a mixture of cyclo-C_5F_9ClO and cyclo-$C_5F_8Cl_2O$. This mixture (78.5 g.) and SbF_3Cl_2 (46 g. or 0.184 mole) were shaken at 160° for five hours in a bomb. The pressure rose to 320 p.s.i. After cooling, repeated distillation of the crude gave about 3 g. of a material, b.p. 26°,

which was regarded as the desired $\overline{CF_2CF_2-O-CF_2CF_2CF_2}$ on the basis of its boiling point and a carbon analysis, and about 10 g. of cyclo-C_5F_9ClO, b.p. 48–49°, which broke down when subjected to refluorination. Repetition of this last fluorination with antimony salts under a variety of conditions always led to extensive decomposition.

Solubilities.—The solubility tests confirm the expected lack of basic properties. They are listed in Table II. In doubtful cases, where the formation of a complex with ferric chloride could not be readily observed, calcium hydride was added[10] as this reagent evolves hydrogen and forms an easily detected complex.

(10) Reich and Serpek, *Helv. Chim. Acta*, **3**, 138 (1920).

Columbus, Ohio

The Chemistry of the Perfluoro Acids and Their Derivatives. III. The Perfluoro Aldehydes[1]

By Donald R. Husted and Arthur H. Ahlbrecht

Perfluoro aldehydes and the corresponding aldehydrols have been prepared by a new synthetic method, namely, lithium aluminum hydride reduction of the perfluoro acid. The Rosenmund reaction has also been used to prepare perfluoro aldehydes from the corresponding perfluoro acid chlorides. The chemistry of the perfluoro aldehydes has been studied and 2,4-dinitrophenylhydrazones and diacyl derivatives prepared.

A number of fully fluorinated aldehydes have been prepared and this paper presents data on the first three members of the series: perfluoroacetaldehyde, perfluoropropionaldehyde and perfluorobutyraldehyde. These perfluoro aldehydes were obtained by the lithium aluminum hydride reduction of the corresponding perfluoro acids. The reduction product was a mixture composed mainly of the expected primary alcohol[3] and the aldehydrol from which the free aldehyde was obtained by dehydration. The alcohol (except in the case of 1,1-dihydroperfluorobutanol as noted below) was easily removed from the reaction product by distillation and the residue, consisting mainly of the aldehydrol, was treated with hot concentrated sulfuric acid or phosphorus pentoxide to liberate the aldehyde. The perfluoro aldehydes studied are low boiling liquids which distil readily from the reaction mixture.

Since the boiling points of 1,1-dihydroperfluorobutanol, $C_3F_7CH_2OH$, and the corresponding aldehydrol, $C_3F_7CH(OH)_2$, differ by only about one degree, the mixture of these two compounds was not conveniently separated by fractional distillation, but was treated directly with concentrated sulfuric acid. The perfluorobutyraldehyde distilled readily as the low boiling fraction and the 1,1-dihydroperfluorobutanol was recovered as the higher boiling fraction.

(1) Combination of two papers, one presented before the Fluorine Symposium at the 116th Meeting (Sept., 1949), Abstracts, p. 10K, paper #17, of the American Chemical Society, Atlantic City, New Jersey, and one before the 118th meeting at Chicago, Illinois. Paper I, "The Chemistry of Perfluorobutyric Acid" and II, "The Chemistry of Derivatives of Perfluorobutyric Acid" which were given at Atlantic City are in preparation for publication.

(2) Received originally October 20, 1950. The manuscript in its present form was received June 4, 1952.

(3) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, This Journal, **69**, 1199 (1947).

The perfluoroaldehydes react rapidly with water to form relatively stable solid hydrates, which may account for Swarts'[4] failure to obtain the aldehyde by dichromate oxidation of 1,1-dihydroperfluoroethanol in water solution. The aldehyde, if formed, would immediately react with water and the nonvolatile hydrate would be further oxidized to the corresponding perfluoro acid. The substitution of concentrated sulfuric acid for dilute sulfuric acid in the oxidation of 1,1-dihydroperfluorobutanol resulted in the formation of small amounts of perfluorobutyraldehyde.

Further evidence that anhydrous methods of reduction are to be preferred is the high yield obtained from the Rosenmund reduction of the perfluoro acid chloride with poisoned palladium catalyst.

The perfluoro aldehydes have also been obtained by the lithium aluminum hydride reduction of perfluoro acid amides. They were isolated in the form of the hydrate after the addition of water. A substantial amount of the 1,1-dihydroperfluoroamine was also formed in this reduction.[5]

The preparation of perfluoroacetaldehyde, recently reported by Henne[6] and by Shechter[7] has also been accomplished by reduction of the corresponding nitrile and by the oxidative nitration of 1,1,1-trifluoropropane.

The structure assignment of these compounds is based on a variety of chemical and physical evidence. The aldehydes give a positive test with Schiff's fuchsin aldehyde reagent. The aldehydrols

(4) F. Swarts, *Bull. soc. chim. Belg.*, **43**, 476 (1934).

(5) (a) A. Uffer and E. Schlitter, *Helv. Chim. Acta*, **31**, 1397 (1948); (b) L. Friedman, Atlantic City, N. J., A.C.S. Meeting, September 19, 1949, Organic Division, Section A, Paper No. 6, page 5M.

(6) A. L. Henne, R. L. Pelly and R. M. Alm, This Journal, **72**, 3370 (1950).

(7) H. Shechter and F. Conrad, *ibid.*, **72**, 3371 (1950).