and was gently agitated for 12 hr. at 60°. After filtration, this solution was evaporated to dryness and 8.83 g. of a clear sirupy product was obtained. Hydrogenolysis quantitatively converted the C-5 substituent of compound IV to the 5-amino-5-deoxy group, as evidenced by negative tests[11,12] for the presence of hydrazino group activity. Since complete removal of the C-3 and C-6 substituents had not occurred, further reduction was employed. A 5-g. portion of the sirup, obtained from the Raney nickel reduction, was dissolved in 100 ml. of absolute ethanol containing 15 g. of 5% palladium on carbon. The mixture was subjected to 50 p.s.i. of hydrogen in a hydrogenation apparatus and shaken at 25° for 4 days. Filtration and evaporation of the product gave a sirup which was taken up in chloroform and extracted three successive times with water. The combined water extracts were evaporated under reduced pressure to a sirup which crystallized spontaneously from a methanol–chloroform mixture to produce compound V; yield, 517 mg; m.p. 178°, R_f 0.68 in irrigant A and 0.60 in irrigant B, $[\alpha]^{25}D$ -3.0 (*c* 0.89 in methanol).

Anal. Calcd. for $C_9H_{17}NO_5$ (219.23): C, 49.30; H, 7.81; N, 6.39. Found: C, 49.58; H, 7.78; N, 6.25.

Methanolysis of V.—A 400-mg. portion of compound V was treated with 50 ml. of 0.8 *N* methanolic hydrogen chloride at 25°, until constant optical rotation was maintained (37 hr.). The hydrolyzate was neutralized with silver carbonate, filtered, and concentrated under reduced pressure to a thin sirup. The sirup was dissolved in 30 ml. of water, treated with hydrogen sulfide to remove excess silver ions, filtered, concentrated to 20 ml., then placed on a column of Amberlite IR-400 (OH^-). The column was eluted successively with water and a dilute ammonium hydroxide solution. The effluent, containing amino sugar VI as the free base, was concentrated under reduced pressure to a sirup (235 mg.); $[\alpha]^{25}D$ + 20.5 (*c* 0.73 in methanol). Compound VI, after chromatography on paper, revealed R_f values of 0.34 in irrigant A and 0.43 in irrigant B when developed with spray indicators C or D. A positive 5-nitrosalicylaldehyde[13] test and nitrous acid test indicated that product VI contained a primary amino group. Periodate oxidation showed that two moles of oxidant were consumed, and one mole of formaldehyde was produced per mole of methyl glycoside. Oxidant consumption was determined by a method specific for amino sugars[14] and formaldehyde by the chromotropic acid procedure.[15,16] After destruction of excess periodate with ethylene glycol, an aliquot of periodate oxidized VI was adjusted to pH 2.0 with potassium hydrogen sulfate and steam distilled.[17,18] No formic acid was detected in the distillate. Nitrogen content of compound VI was determined by micro-Kjeldahl analysis.

Anal. Calcd. for $C_7H_{15}NO_5$ (193.20): OCH_3, 16.06; N, 7.25. Found: OCH_3, 15.93; N, 7.21.

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The Chemistry of Perfluoro Ethers. IV. The Structure of the Monocyclic Diether $C_8F_{16}O_2$

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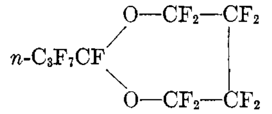
The reaction of aluminum chloride with perfluoroethers, resulting in replacement of all α fluorine atoms by chlorine,[1–3] is valuable for the proof of structure of these exceedingly unreactive materials. In the present instance the reaction is extended to characterize a monocyclic diether, $C_8F_{16}O_2$.[4]

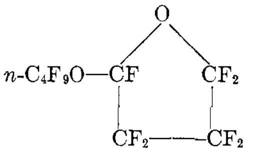
The products of the reaction with aluminum chloride were identified as *n*-perfluorobutyryl chloride[2] (in small amounts), 1,1,1-trichloroperfluorobutane[2] and 4,4,4-trichlorotetrafluorobutyryl chloride.[3] No higher homologs[3] of the latter, nor any α,α,α′-trichloroperfluoroethers, were found; considerable amounts of decomposition products, notably hexachloroethane, were present as is usual in these reactions.[1–3] While the first two materials might arise from perfluorodibutyl ether, the elemental analysis, phsyical properties and infrared spectrum of $C_8F_{16}O_2$ indicate that it contains little or no $(n\text{-}C_4F_9)_2O$; one may, therefore, conclude that the $n\text{-}C_3F_7CFO_2$ or the $n\text{-}C_4F_9O$ group is present in the diether, and that it yields mainly $n\text{-}C_3F_7CCl_3$ upon cleavage. The third product had previously been obtained by reaction of aluminum chloride with perfluorotetrahydrofuran,[3] and its formation indicates the presence of a similar grouping in the compound $C_8F_{16}O_2$.

Only two structures, I and II, are consistent with the foregoing facts. Each of these has five α-fluorines, corresponding to the five chlorine atoms found in the major products which also retain the two oxygen atoms. The less likely structure I contains a seven-membered ring, and theoretically might be excluded by the n.m.r. spectrum; however, owing to the accidental spectral equivalence of certain fluorines, an absolute proof cannot at present be given. The cyclic diether $C_8F_{16}O_2$ thus may be either I or II. This is believed to be the first reported example of a perfluorinated acetal structure.

I



II



Experimental

Physical properties of the diether have been reported.[4] By the elementary analysis and the absence of infrared absorptions for the C═C or C═O groups it is shown to be a monocyclic diether.

Anal. Calcd. for $C_8F_{16}O_2$: C, 22.24; F, 70.36. Found: C, 22.3; F, 70.8.

The diether, 20.0 g. (0.046 mole), and aluminum chloride, 18.0 g. (0.135 mole), were heated together at 200° for 14 hr. in a rocking autoclave of 43-ml. volume. The reaction mixture was worked up as previously described,[2] products being separated by distillation. Unchanged $C_8F_{16}O_2$ amounted to *ca.* 3 g. A relatively poor yield of $n\text{-}C_3F_7COCl$, *ca.* 1 g., was obtained in the fractions boiling slightly above room temperature; it was identified beyond question by infrared spectroscopy.[2] The major products were $n\text{-}C_3F_7CCl_3$,[2] b.p. 89–94°, 6.0 g., also readily identified by infrared spectroscopy,[2] and $CCl_3CF_2CF_2COCl$,[2] b.p. 145–153°, 3.4 g., characterized not only by infrared analysis but also by conversion to the amide, m.p. 126–127°, m.m.p. with authentic 4,4,4-trichlorotetrafluorobutyramide,[3] 126–127°.

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