A sample of this material recrystallized from ethanol gave orange prisms which also contained a mole of solvent.

Anal. Calcd. for $C_{13}H_{13}N_5O_2 \cdot C_2H_5OH$ (317): C, 56.8; H, 6.0; N, 22.1. Found: C, 56.6; H, 6.2; N, 22.6.

2-Amino-3-methyl-7-phenyl-4(3*H*)-pteridinone (IVb).—A mixture of 8.0 g. (42 mmoles) of 2,5,6-triamino-3-methyl-4(3*H*)-pyrimidinone hydrochloride[6] and 13.6 g. (165 mmoles) of sodium acetate was slurried in 160 ml. of water and quickly mixed with a warm (35°) solution of 7.0 g. (45 mmoles) of phenylglyoxal hydrate in 120 ml. of ethanol. After several hours at room temperature the product was collected; yield 11.6 g. (97%).

A solution of this anil in 450 ml. of 2-methoxyethanol was heated to reflux for 5.5 hr. using a take-off intermittently to remove water (about 150 ml. of fresh 2-methoxyethanol was added during this period while a total of 300 ml. of distillate was collected). The reaction solution was evaporated to a small volume and slurried with warm water to give a volume of about 450 ml. This was cooled well and the product was collected; yield 10 g. (98%). This material was chromatographically pure and contained none of the 6-phenyl isomer. It was recrystallized from 450 ml. of acetic acid. The product was collected, air-dried and then dried in an oven at 100° for 4 hr.; yield 6.7 g. (63%); m.p. 352–355°; R_f 0.6 [isopropyl alcohol–1.0 *N* NH_4OH (7:3)] (blue); $\lambda_{max}^{pH\ 7.0}$ 236 mμ (ε 21,800), 277 mμ (ε 18,400), 369 mμ (ε 11,900); $\lambda_{max}^{0.1\ N\ HCl}$ 225 mμ (ε 24,800), 260–280 (sh) (ε 6,600), 347 mμ (ε 21,000); the spectrum in 0.1 *N* sodium hydroxide was essentially the same as at pH 7.0. The spectrum in 0.1 *N* hydrochloric acid is almost superimposable on the spectrum of 2-amino-4-hydroxy-7-phenylpteridine (IVa).

Anal. Calcd. for $C_{13}H_{11}N_5O$ (253): C, 61.6; H, 4.4; N, 27.7. Found: C, 61.4; H, 4.4; N, 27.9.

2-Methylamino-4-hydroxy-7-phenylpteridine.—2-Amino-3-methyl-7-phenyl-4(3*H*)-pteridinone (200 mg., 0.8 mmole) (IVb) was suspended in a solution of 10 ml. of 2-methoxyethanol and 15 ml. of 1.0 *N* sodium hydroxide and heated on a steam bath for 1.5 hr. The hot solution was acidified with 1.5 ml. of acetic acid and cooled; yield 125 mg. This was recrystallized from 15 ml. of dimethylformamide; yield 85 mg.; R_f 0.5 [isopropyl alcohol–1.0 *N* ammonium hydroxide (7:3)] (blue); $\lambda_{max}^{0.1\ N\ NaOH}$ 238 mμ (ε 20,500), 270 mμ (ε 25,300), 388 mμ (ε 12,900); $\lambda_{max}^{pH\ 7.0}$ 239 mμ (ε 21,500), 281 mμ (ε 20,800), 369 mμ (ε 13,100); $\lambda_{max}^{0.1\ N\ HCl}$ 230 mμ (ε 28,200), 349 mμ (ε 22,000).

Anal. Calcd. for $C_{13}H_{11}N_5O$ (253): C, 61.6; H, 4.4; N, 27.7. Found: C, 61.9; H, 4.0; N, 27.5.

2-Amino-3-methyl-6-phenyl-4(3*H*)-pteridinone (VIIb) and Its Isomer IVb.—A solution of 10.2 g. (53.0 mmoles) of 2,5,6-triamino-3-methyl-4(3*H*)-pyrimidinone·hydrochloride[6] in 270 ml. of water was mixed with a solution of 12.0 g. (58.0 mmoles) of phenylglyoxal diethyl acetal in 75 ml. of water and heated to reflux for 8 hr. This was cooled overnight, the product was collected, and washed with water and ether and dried; yield 12.4 g. (92%). (Paper chromatography showed this to be a mixture of the isomeric 6-phenyl VIIb and 7-phenyl IVb derivatives).

This material was suspended in a solution of 250 ml. of dimethylformamide (DMF) and 6.2 ml. of concentrated hydrochloric acid, which was heated to boiling for several minutes and filtered hot; yield 5.5 g. (fraction A). (Paper chromatography showed this product to be the 6-phenyl derivative VIIb contaminated with a small amount of 2-amino-4-hydroxy-6-phenylpteridine but verv little of the 7-phenyl isomer.) Fraction A was probably sufficiently pure for most purposes. However, it was purified further as follows. It was suspended in 900 ml. of dimethylformamide and 24 ml. of concentrated hydrochloric acid, heated to boiling, and filtered; yield 2.5 g. (fraction B). The filtrate was cooled, diluted with 600 ml. of water, and cooled some more; yield 2.4 g. (fraction C). Fraction B was dissolved in a solution of 600 ml. of dimethylformamide and 18 ml. of concentrated hydrochloric acid which was then cooled and diluted with 300 ml. of water; yield 2.2 g. (fraction D).

Fractions C and D were combined, added to a hot solution of sodium acetate, mixed well, and cooled; yield 4.1 g. (30%) of the 6-phenyl isomer.

For analyses a small sample was recrystallized from a dimethylformamide–hydrochloric acid solution and then freed of hydrochloric acid by slurrying in a sodium acetate solution just as described above; m.p. 355–358°; R_f 0.5 [isopropyl alcohol–1.0 *N* NH_4OH (7:3)] (blue); $\lambda_{max}^{pH\ 7.0}$ 296 mμ (ε 23,800), 375 mμ (ε 8,500); $\lambda_{max}^{0.1\ N\ HCl}$ 278 mμ (ε 19,700), 352 mμ (ε 9,400). The spectrum of this compound in 0.1 *N* hydrochloric acid is almost superimposable on the spectrum of 2-amino-4-hydroxy-6-phenylpteridine (VIIa).

Anal. Calcd. for $C_{13}H_{11}N_5O$ (253): C, 61.6; H, 4.4; N, 27.7. Found: C, 61.6; H, 4.4; N, 28.1.

The filtrate from fraction A was warmed, diluted with 375 ml. of water, adjusted to pH 5.5 with sodium acetate, and cooled; yield 4.7 g. This was recrystallized from 180 ml. of acetic acid and a second time from 80 ml. of acetic acid using charcoal to clarify the solution each time. The product was dried in an oven at 100°; yield 2.2 g.; m.p. 346–349°. Chromatography indicated that this was fairly pure 7-phenyl isomer IVb.

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Synthesis of 5-Amino-5-deoxy Derivatives of L-Idose[1]

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Synthesis of suitably substituted C-5 hydroxyls of aldopentoses and aldohexoses offers a direct route for the introduction of selected hetero atoms into pyranose rings. Preparation of a thiapyranose and thiapyranosides, obtained through the placement of a mercapto group on carbon 5 of several pentoses and hexoses, has been reported recently.[2–5]

This work describes the synthesis of 5-amino-5-deoxy derivatives of L-idose from new derivatives of D-glucose.

3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (I) is hydrolyzed selectively to remove the 5,6-*O*-isopropylidene group. Subsequent tritylation of compound I gives crystalline 3-*O*-benzyl-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-glucofuranose (II) in 94% yield. Tosylation of compound II then affords crystalline 3-*O*-benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (III) in 95% yield. A heterogeneous solution, observed in a conventional hydrazinolysis[6] of compound III, markedly diminishes the yield of 3-*O*-benzyl-5-deoxy-5-hydrazino-1,2-*O*-isopropylidene-6-*O*-triphenyl-β-L-idofuranose (IV). However, when compound III is dissolved in absolute 1-butanol with anhydrous hydrazine, a homogeneous solution is maintained and the reaction gives a smooth SN2 displacement of the 5-*O*-tosyloxy group with the formation of crystalline compound IV in 75% yield. Thus, hydrazinolysis of compound III is more seriously inhibited by solution heterogeneity, than by molecular steric effects. An L-idose configuration is assigned to compound IV, since experimental evidence presented by previous in-

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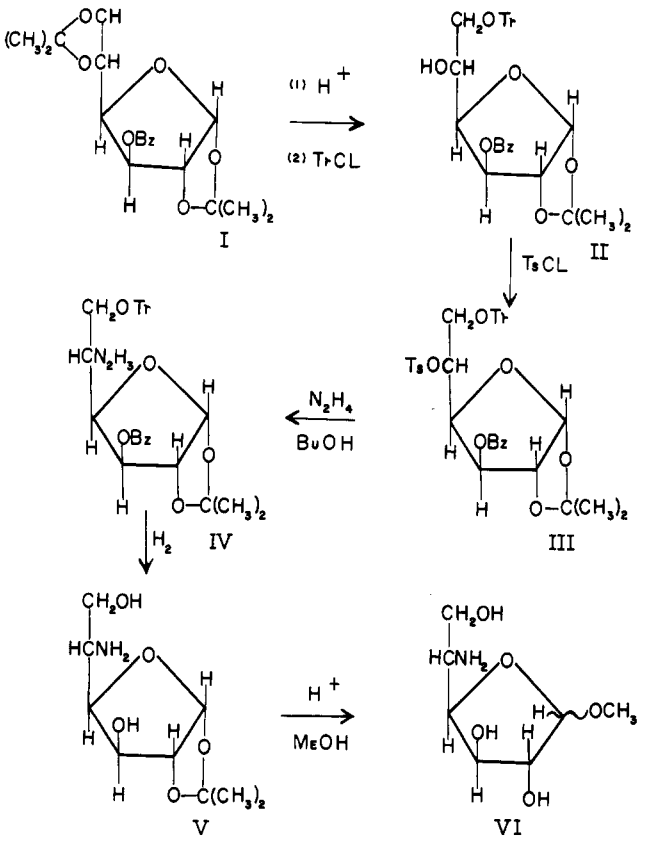

vestigators[7-9] shows that hydrazine displaces, with inversion, tosyloxy groups located on asymmetric carbon atoms.

Although hydrogenolysis of benzyl and trityl groups with Raney nickel has been demonstrated,[10] compound IV was not completely freed of these groups. Therefore, the resulting sirup was further reduced with palladium on carbon to produce crystalline 5-amino-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (V).

Methanolysis of compound V furnishes methyl 5-amino-5-deoxy-α,β-L-idofuranoside (VI). The observation, that compound VI consumes two moles of periodate with the release of one mole of formaldehyde, shows the presence of a furanose ring structure, and suggests that under the conditions employed for methyl glycoside formation, the five-membered oxygen-containing ring is preferred to a six-membered nitrogen-containing ring.

Experimental

Analytical Methods.—Chromatographic identification and purification of sugar derivatives were performed at 25° on Whatman no. 1 and 3 MM filter papers, which were developed in irrigants (A) ethyl acetate–pyridine–water (10:4:3 v./v.) and (B) 1-butanol–ethanol–water (40:11:19 v./v.). Spray indicators employed were (C) permanganate–periodate and (D) ninhydrin. A calibrated Fisher-Johns apparatus was used for melting point determinations.

3-*O*-Benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (I).—1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose (180 g.) was added in small portions to a stirred solution of 38 g. of sodium sand in 600 ml. of diethyl ether. The reaction mixture, after stirring for 24 hr. at 25°, was rapidly filtered and concentrated to a sirup to which was added 85 ml. of freshly distilled benzyl chloride. Benzylation was accomplished by stirring the reaction mixture for 8 hr. at 60°. The product was dissolved in 600 ml. of petroleum ether, washed five times with 200-ml. portions of water, and dried over anhydrous magnesium sulfate. After filtration and evaporation to a thick yellow sirup, distillation gave pure sirupy 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (I); yield, 155 g. (64%); b.p. 160–165°, $[\alpha]^{25}D$ −26.2 (*c* 1.60 in ethanol).

3-*O*-Benzyl-1,2-*O*-isopropylidene-6-*O*-triphenylmethyl-α-D-glucofuranose (II).—Selective hydrolysis of 128 g. of compound I, in 500 ml. of 60% aqueous acetic acid at 35° for 5 hr., removed the 5,6-*O*-isopropylidene group. The hydrolyzate was concentrated under reduced pressure to a sirup. This sirup was dissolved in chloroform, washed sequentially with dilute sodium bicarbonate solution and water, and was dried over anhydrous magnesium sulfate. After filtration and evaporation 107 g. (95%) of the sirupy product, namely, 3-*O*-benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose, $[\alpha]^{25}D$ −48.4° (*c* 2.50 in chloroform), was dissolved in 600 ml. of dry pyridine to which was added 110 g. of trityl chloride (chlorotriphenylmethane). The reaction mixture was maintained at 25° for 3 days, then cooled to 5°. Water was added until a constant turbidity of the solution was obtained. After 2 hr. the turbid solution was poured into 4 l. of ice–water and stirred until the gummy derivative had settled. The aqueous phase was poured off and replenished with fresh ice–water. After several successive washings the product was dissolved in 600 ml. of chloroform, washed with 10% aqueous acetic acid, neutralized with sodium bicarbonate solution, and finally washed with water. The chloroform phase was dried over anhydrous magnesium sulfate. Compound II crystallized from a chilled benzene and ethanol mixture; yield, 188 g. [over-all yield from I, 94%; m.p. 116°, $[\alpha]^{25}D$ −36.0 (*c* 2.97 in chloroform)].

Anal. Calcd. for $C_{35}H_{36}O_6$ (552.64): C, 76.06; H, 6.56. Found: C, 76.06; H, 6.74.

3-*O*-Benzyl-1,2-*O*-isopropylidene-5-*O*-*p*-tolylsulfonyl-6-*O*-triphenylmethyl-α-D-glucofuranose (III).—Tosylation was performed by the addition of 165 g. of compound II to 280 ml. of dry pyridine, to which was added 240 ml. of alcohol free chloroform, containing 165 g. of tosyl chloride (*p*-toluenesulfonyl chloride). After 3 days at 37°, the reaction mixture was cooled to 0° and 10 ml. of water were added in order to hydrolyze excess tosyl chloride. Within 0.5 hr. the solution was poured into 3 l. of water and 600 ml. of chloroform was then added. The water layer was drawn off, extracted twice with chloroform, and the combined washings and chloroform phase were washed free of pyridine with several portions of chilled 10% aqueous acetic acid. Upon neutralization with sodium bicarbonate solution, the chloroform phase was washed free of salts and dried over anhydrous magnesium sulfate. After filtration and evaporation, a light yellow sirup was obtained. Complete crystallization of this sirup from a chilled benzene and ethanol mixture gave compound III; yield, 200 g. (95%); m.p. 133–134°, $[\alpha]^{25}D$ −13.8° (*c* 7.48 in chloroform).

Anal. Calcd. for $C_{42}H_{42}O_8S$ (706.81): C, 71.36; H, 5.99; S, 4.53. Found: C, 71.30; H, 5.79; S, 4.54.

3-*O*-Benzyl-5-deoxy-5-hydrazino-1,2-*O*-isopropylidene-β-L-idofuranose (IV).—A 33-g. portion of compound III was added to a stirred solution of 200 ml. of absolute 1-butanol and was dissolved by raising the temperature to 95°. A homogeneous solution was still observed after 210 ml. of anhydrous hydrazine was added. The solution was gently refluxed at 117–119°. After 24 hr. the solution was cooled to 25° and extracted five successive times with fresh 75-ml. portions of diethyl ether. The combined ether extracts were washed four successive times with 50-ml. portions of 50% potassium hydroxide solution, three successive times with 75-ml. portions of ice-cold water, and were dried over anhydrous potassium carbonate. This solution was filtered and evaporated under reduced pressure at less than 40° to approximately 100 ml. The hydrazino derivative crystallized when the solution was cooled to 5°. Crystalline compound IV was filtered and triturated with chilled ether; yield, 20 g. (75%); m.p. 126–127°, $[\alpha]^{25}D$ −18.3 (*c* 2.00 in benzene).

Anal. Calcd. for $C_{35}H_{38}N_2O_5$ (566.67): C, 74.18; H, 6.76; N, 4.94. Found: C, 74.30; H, 6.40; N, 4.67.

5-Amino-5-deoxy-1,2-*O*-isopropylidene-β-L-idofuranose (V).—Compound IV (10 g.) was dissolved in 100 ml. of absolute ethanol containing 30 g. of freshly prepared Raney nickel. This mixture was subjected to 1700 p.s.i. of hydrogen in a Paar bomb

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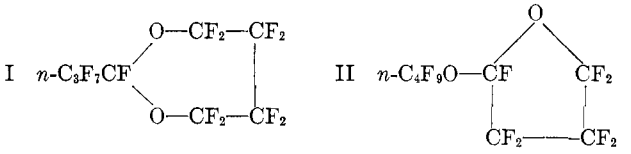
The reaction of aluminum chloride with perfluoroethers, resulting in replacement of all α fluorine atoms by chlorine,[1-3] is valuable for the proof of structure of these exceedingly unreactive materials. In the present instance the reaction is extended to characterize a monocyclic diether, $C_8F_{16}O_2$.[4]

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.

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°.

Acknowledgment.—The author thanks Dr. T. J. Brice of these laboratories for the pure sample of $C_8F_{16}O_2$[4] and is indebted to Drs. W. E. Keiser and J. J. McBrady for infrared spectroscopy, and to Mr. J. D. Keating for assistance with the autoclave reaction.

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