of hot methanol and treated with 10 ml. of 3N sulfuric acid at room temperature for 20 hr. Slow addition of 190 ml. of water, and cooling, precipitated the crude product, which was recovered by filtration, washed with water, and dried. One recrystallization from acetone–Skellysolve B afforded 6.75 g. of Va, m.p. 162–165.5°. A sample for analysis was repeatedly recrystallized from the same solvents to m.p. 171–173°, $[\alpha]_D$ + 106° (acetone), $\gamma_{\max}^{\text{Nujol}}$ 3420 (OH), 1715, 1687 (C═O).

Anal. Calcd. for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89. Found: C, 76.58; H, 9.98.

Another experiment, carried out as described above, was worked up by extraction with methylene chloride, following dilution of the acid hydrolysis mixture with water. The crude material thus obtained was chromatographed over 350 g. of Florisil. Elution with 5% acetone–methylene chloride afforded about 2.5 g. of crude oil, recrystallized from acetone–Skellysolve B to give 1.18 g. of *11β-hydroxy-11-methyl-5β-pregnane-3,20-dione 3-ethylene acetal* (IV), m.p. 139–142°, $\gamma_{\max}^{\text{Nujol}}$ 3420 (OH), 1682 (C═O), 1100, 1087, 1048 (C—O).

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81. Found: C, 73.62; H, 10.33

Hydrolysis of 100 mg. of IV in 5 ml. of methanol containing 5 ml. of 0.1N sulfuric acid at room temperature overnight afforded, following addition of 4 ml of water, 85 mg. of the dione Va, m.p. 167–168°.

3α,11β-Dihydroxy-11-methyl-5β-pregnan-20-one (VIIIa). *A. By selective reduction*[4] *of* Va. To a solution of 1.9 g. of Va in 10 ml. of purified[6] dioxane, cooled in an ice bath, was added 62 mg. of sodium borohydride in 1 ml. of 0.1N sodium hydroxide. The mixture was stirred for 2 min. with cooling, and then diluted slowly (5 min.) with 12 ml. of water, followed by 0.65 ml. of concentrated hydrochloric acid. Further dilution with water and extraction with methylene chloride gave a crude product that was chromatographed over Florisil. Elution with, at first 2% acetone–methylene chloride, and finally, 25% acetone–methylene chloride gave crude VIIIa, recrystallized first from acetone–Skellysolve B and then from ethyl acetate to give 0.93 g. of pure VIIIa, m.p. 181–183°, identical to VIIIa prepared as described below.

B. From 3α-hydroxy-5β-pregnane-11,20-dione (VI). 3α-Hydroxy-5β-pregnane-11,20-dione (VI) was converted to the 20-ethylene acetal (VII),[2] m.p. 139–141°, $[\alpha]_D$ + 55° (acetone).

A solution of 13.6 g. of VII in 150 ml. of benzene and 100 ml. of ether was treated with 144 ml. of M ethereal methyllithium at room temperature overnight. The reaction mixture was washed several times with water, the organic phase dried over sodium sulfate, and evaporated to dryness. Attempts to crystallize the resultant glass were unsuccessful, both before and after chromatography over Florisil (the major product was eluted with 5–10% acetone–Skellysolve B, and amounted to about 13 g.), so it was dissolved in 200 ml. of methanol and treated with 10 ml. of 3N sulfuric acid at room temperature for 28 hr. Addition of 200 ml. of water, and prolonged cooling at about 5° afforded 6.74 g. of crude crystals, m.p. 149–168°, consisting largely of VIIIa. A sample for analysis was recrystallized repeatedly from acetone–Skellysolve B to m.p. 184–186°, $[\alpha]_D$ + 111° (acetone), $\gamma_{\max}^{\text{Nujol}}$ 3540, 3440 (OH), 1687 (C═O).

Anal. Calcd. for $C_{22}H_{36}O_3$: C, 75.81; H, 10 41. Found: C, 75.43; H, 10.25.

The *3-acetate* (VIIIb), prepared by treatment of 200 mg. of VIIIa with 2 ml. of pyridine and 2 ml. of acetic anhydride at room temperature overnight, was obtained in 93% yield, m.p. 169–171.5°. Recrystallization from acetone–Skellysolve B afforded an analytical sample, m.p. 171–172.5°, $[\alpha]_D$ + 112° (acetone), $\gamma_{\max}^{\text{Nujol}}$ 3440 (OH), 1725, 1240 (CH_3CO_2), 1684 (C═O).

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81. Found: C, 73.50; H, 9.61.

11β,20ξ-Dihydroxy-11-methyl-5β-pregnan-3-one (IXa) was obtained by treatment of 500 mg. of the monoketal IV with 122 mg. of sodium borohydride in 10 ml. of methanol at room temperature overnight, followed by hydrolysis of the ketal by addition of 2 ml. of 3N sulfuric acid in 5 ml. of methanol. After a 4 hr. hydrolysis, dilution with water and extraction with methylene chloride and eventual evaporation of the solvent gave an oil (IXa) that failed to crystallize even after Florisil chromatography (elution with 10% acetone–Skellysolve B).

Acetylation of the oily IXa with acetic anhydride–pyridine at room temperature gave, after two recrystallizations from acetone–Skellysolve B, the 20ξ-acetate, m.p. 167–169°, $[\alpha]_D$ + 42° (acetone), $\gamma_{\max}^{\text{Nujol}}$ 3500 (OH), 1707 (C═O), 1262 (acetate C—O), not identical with VIIIb.

Anal. Calcd. for $C_{24}H_{38}O_4$: C, 73.80; H, 9.81 Found: C, 73.82; H, 9.77.

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2-Fluoro- and 2,2-Difluoroethylnitroguanidine

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The preparation of 2,2,2-trifluoroethylnitroguanidine has been reported.[1] 2-Fluoro- and 2,2-difluoroethylnitroguanidine have now been prepared in a similar manner by the reaction of the respective fluoroethylamines with 1-nitro-2-methyl-2-thiopseudourea. Efforts to nitrate the fluoroalkylnitroguanidines to dinitroguanidine by methods similar to those of McKay and Milks[2] and Meen and Wright[3] were not successful. The nitrate salts of the original fluoroalkylamines were isolated indicating that decomposition had occurred. 2-Fluoroethylnitroguanidine was cyclized to the tetrahydrofluoride salt of 2-imino-1,3-diazacyclopentane. The free base of this compound was identified as the picrate. A comparable cyclization procedure applied to the other fluoroalkylnitroguandiines gave negative results. The nitrate and picrate salts of 2-fluoro- and 2,2-difluoroethylguanidine were prepared from the corresponding fluoroethylnitroguanidines.

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EXPERIMENTAL[4]

2-Fluoroethylnitroguanidine. To 4.0 g. (0.0296 mole) of 1-nitro-2-methyl-2-thiopseudourea was added 8.7 g. (0.1382 mole) of 2-fluoroethylamine.[5] An immediate reaction took place which was controlled by cooling with ice. The reaction was maintained at 35–40° for 50 min., cooled to room temperature, 50 ml. of ether added, and the solid was removed by filtration. The precipitate was washed on the filter with three 25-ml. portions of ether. Crystallization from ethanol gave a product which melted at 145–145.5°. The yield based on 1-nitro-2-methyl-2-thiopseudourea was 77.2%.

Anal. Calcd. for $C_3H_7FN_4O_2$: C, 24.00; H, 4.70; N, 37.32. Found: C, 24.40; H, 4.86; N, 36.94.

2-Fluoroethylguanidine picrate. The picrate was prepared by the hydrogenolysis procedure used for the preparation of 2,2,2-trifluoroethylguanidine picrate[1] and melted at 189–191°.

Anal. Calcd. for $C_9H_{11}FN_6O_7$: C, 32.34; H, 3.32; N, 25.15. Found: C, 32.46; H, 3.26; N, 24.70.

2-Fluoroethylguanidine nitrate. This salt was prepared by the method used to prepare 2,2,2-trifluoroethylguanidine nitrate[1] and melted at 104–105°.

Anal. Calcd. for $C_3H_9FN_4O_3$: C, 21.43; H, 5.40; N, 33.33. Found: C, 21.21; H, 5.26; N, 33.13.

2-Imino-1,3-diazacyclopentane tetrahydrofluoride. 2-Fluoroethylnitroguanidine (1.0 g., 0.066 mole) was dissolved in 50 ml. of 1-hexanol and heated at the reflux temperature (157°) for 6 hr. At the end of that time some crystalline material deposited on the side of the flask.

After standing overnight at room temperature, the brown crystalline material was removed, dissolved in hot water, and treated with Norit to remove the color. The Norit was removed, the aqueous solution evaporated to dryness and the residue crystallized from a mixture of ethanol and water. The purified material weighed 0.174 g. An elemental analysis indicated approximately 3.6 molecules of hydrogen fluoride for each molecule of imino compound. After dissolving in 40% aqueous hydrogen fluoride, allowing to stand overnight at room temperature, evaporating to dryness, and crystallizing from an ethanol-water solution, the elemental analysis corresponded to the tetrahydrofluoride salt of 2-imino-1,3-diazacyclopentane and melted at 227–231° dec.

Anal. Calcd. for $C_3H_{11}F_4N_3$: C, 21.82; H, 6.72; N, 25.45. Found: C, 21.37; H, 5.75; N, 25.10.

This compound was converted to the picrate which melted at 221–223°. A mixed melting point with an authentic sample of 2-imino-1,3-diazacyclopentane picrate was not depressed. This picrate also gave the correct elemental analysis.

N-(2,2-Difluoroethyl)-phthalimide. This compound was prepared by a modification of the method of Childs and coworkers.[5] 1,1-Difluoro-2-bromoethane, 6.05 g. (0.0417 mole, 10% excess), 6.966 g. (0.0376 mole) potassium phthalimide and 5 ml of dimethylformamide were placed in a 22-ml. Parr bomb. The bomb was attached to a horizontal stirring shaft in such a manner that it would rotate end over end inside a furnace. The bomb was rotated and heated at 210° for 8 hr. After cooling, the contents of the bomb were removed, poured into water, and filtered. The precipitate was washed with water, dissolved in hot ethanol, and treated with decolorizing carbon. The carbon was removed and the product crystallized from the ethanol solution. After recrystallization from ethanol the product weighed 3.73 g. (47%) and melted at 116.5–117.5°.

Anal. Calcd. for $C_{10}H_7F_2NO_2$: C, 56.87; H, 3.34; N, 6.63. Found: C, 56.91; H, 3.02; N, 6.56.

2,2-Difluoroethylnitroguanidine. 2,2-Difluoroethylamine (1.897 g., 0.0234 mole), prepared from *N*-(2,2-difluoroethyl)-phthalimide by the method of Childs and co-workers[5] was placed in a 50-ml. flask fitted with a Teflon-coated magnetic stirrer and a reflux condenser. To this was added at once 1.458 g. (0.0108 mole) of 1-nitro-2-methyl-2-thiopseudourea. The flask was then placed in a water bath at 50° and the contents stirred. The reaction was allowed to proceed without heating until at the end of 20 min. the temperature of the bath was 34°. Ethyl ether (10 ml.) was then added through the condenser and the reaction heated at the reflux temperature of the ether for an additional 20 min. The reaction mixture was then cooled, filtered, and the precipitate washed with ether. The product weighed 1.66 g. (91%) and after two crystallizations from ethanol melted at 162.5–163.5°.

Anal. Calcd. for $C_3H_6F_2N_4O_2$: C, 21.43; H, 3.60; N, 33.33. Found: C, 21.66; H, 3.84; N, 33.00.

2,2-Difluoroethylguanidine picrate. The picrate was prepared by the hydrogenolysis procedure used to prepare 2,2,2-trifluoroethylguanidine picrate[1] and melted at 197–198°.

Anal. Calcd. for $C_9H_{10}F_2N_6O_7$: C, 30.69; H, 2.86; N, 23.86. Found: C, 30.88; H, 3.03; N, 23.82.

2,2-Difluoroethylguanidine nitrate. The nitrate salt was prepared from the picrate by the method used to prepare 2,2,2-trifluoroethylguanidine nitrate[1] and melted at 93.0–94.5°.

Anal. Calcd. for $C_3H_8F_2N_4O_3$: C, 19.36; H, 4.33; N, 30.10. Found: C, 19.24; H, 4.45; N, 29.51.

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[4] All melting points were measured on a Kofler micro hot stage.

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Carbonyl Stretching Frequencies of Some Oxalate Esters

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Only a few references indicate the position of the carbonyl stretching frequencies of oxalate esters. Hampton and Newell reported only a single peak for di-*n*-butyl oxalate,[1] at 1746 cm.$^{-1}$ This information led Bellamy to conclude that interaction between adjacent carbonyl groups was small.[2] Miyazawa and Kurantani[3] also reported only a single C═O stretching frequency for dimethyl oxalate, 1730 cm.$^{-1}$ More recently Bender observed two carbonyl stretching frequencies in a spectrum of diethyl oxalate.[4] Our findings also show two carbonyl stretching frequencies in oxalate esters.

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