and evaporated. There remained a semicrystalline residue weighing 14.6 g.

A small sample was chromatographed on aluminum oxide and gave after recrystallization from methanol colorless plates melting at 157–161°. $[\alpha]_D^{26}$ −40° ± 2°.

Anal. Calc'd for $C_{25}H_{38}O_4$: C, 74.59; H, 9.52. Found: C, 74.59; H, 9.47.

Infrared analysis indicated the absence of a ketone (no band from 1818–1538 cm.$^{-1}$).

3β-Hydroxypregn-5-en-20-one-20-ethylene ketal. Crude 3β-hydroxypregn-5-en-20-one-20-ethylene ketal acetate (10 g.) was saponified with 500 cc. of 5% methanolic sodium hydroxide at 26° during 4 hours which gave 8.1 g. of crude 3β-hydroxypregn-5-en-20-one-20-ethylene ketal. A sample was chromatographed on aluminum oxide and gave after recrystallization colorless prisms with the following constants: melting point, 163–166°; $[\alpha]_D^{26}$ −39° ± 2°. Infrared analysis indicated the absence of a ketone (no band from 1818–1538 cm.$^{-1}$) and the presence of a hydroxyl (band at 3650 cm.$^{-1}$).

Anal. Calc'd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07. Found: C, 76.97; H, 9.57.

Progesterone-20-ethylene ketal. A solution of 3.0 g. of aluminum isopropoxide in 30 cc. of toluene was added to a solution of 7.0 g. of crude 3β-hydroxypregn-5-en-20-one-20-ethylene ketal in 250 cc. of toluene and 55 cc. of cyclohexanone. The mixture was refluxed for 1 hour, steam-distilled, and taken up in benzene. The benzene layer was washed successively with water, ammonium chloride solution, and water again, and finally the benzene layer was dried and evaporated. The crude residue was purified by chromatography on aluminum oxide and gave after recrystallization from methanol 5.9 g. of pure progesterone-20-ethylene ketal (colorless prisms), melting at 189–191°; $[\alpha]_D^{26}$ +119° ± 2°.

Anal. Calc'd for $C_{23}H_{34}O_3$: C, 77.05; H, 9.56. Found: C, 77.32; H, 9.71.

The structure of this product was further established by its infrared analysis, indicating the presence of the conjugated ketone (band at 1681 cm.$^{-1}$) and the absence of a saturated ketone. An ultraviolet absorption spectrum showed a λ_{max}^{EtOH} 242 mμ (ε 16,800).

3β-Hydroxypregn-4-en-20-one-20-ethylene ketal. Progesterone-20-ethylene ketal (2 g.) was dissolved in 40 cc. of methanol and 1.0 g. of sodium borohydride was added in small portions with magnetic stirring over a period of four hours. The solution was stored overnight, water was added, the methanol was evaporated off *in vacuo*, and the mixture was filtered and recrystallized from methanol resulting in 1.8 g. of colorless prisms, melting from 157–175°. The infrared analysis indicated the presence of hydroxyl (band at 3700 cm.$^{-1}$) and the absence of a ketone (no band from 1818–1538 cm.$^{-1}$). The ultraviolet analysis showed no absorption from 225–270 mμ. An 800-mg. sample of the above mixture was carried through a digitonin separation and gave 609 mg. of the *beta*-fraction, which, after chromatography on aluminum oxide, crystallized in prisms from methanol, melting from 170–173°; $[\alpha]_D^{26}$ +71° ± 2°.

Anal. Calc'd for $C_{23}H_{36}O_3$: C, 76.62; H, 10.07. Found: C, 76.65; H, 9.98.

3β-Hydroxypregn-4-en-20-one. Crude 3β-hydroxypregn-4-en-20-one-20-ethylene ketal (300 mg.) was dissolved in 20 cc. of 0.08% ethanolic oxalic acid solution and allowed to stand for 16 hours at 25°. Then the mixture was neutralized with concentrated ammonia solution, the ethanol evaporated off *in vacuo*, and the resulting crystallizate was filtered off. After chromatography on aluminum oxide and recrystallization from methanol 230 mg. of colorless prisms, melting at 155–161° were obtained, $[\alpha]_D^{26}$ +135° ± 2°.

Anal. Calc'd for $C_{21}H_{32}O_2$: C, 79.70; H, 10.14. Found: C, 79.96; H, 9.98.

The structure of this product was further established by infrared analysis, indicating the presence of a hydroxyl (band at 3750 cm.$^{-1}$) and a ketone (band at 1705 cm.$^{-1}$). The ultraviolet analysis showed no absorption from 225–250 mμ (in ethanol).

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The Preparation and Properties of Some Fluorine-Containing Epoxides

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In an investigation directed toward the polymerization of fluorine-containing epoxides, six hitherto unreported fluorine-containing epoxides of the general formula $R_fCHCXYO$ (when X = H; Y = CH_3, C_2H_5; when X = CH_3; Y = CH_3; R_f = CF_3, *n*-C_3F_7) have been prepared. The procedure described by McBee, *et al.*[1,2] for the conversion of 1,1,1-trifluoroacetone to 3,3,3-trifluoro-1,2-epoxypropane was found to be satisfactory for the preparation of these new epoxides.

The alkyl perfluoroalkyl ketones were most conveniently prepared using the method described by Dishart and Levine[3] in which one mole of perfluorocarboxylic acid was treated with three moles of alkyl Grignard reagent. By this procedure, the ketones were prepared in 40–60% yields accompanied by considerable amounts of the corresponding secondary alcohols. It was found, however, that the alkyl perfluoroalkyl ketones could also be prepared in similar yields by the reaction of 1.1 moles of the alkyl Grignard reagent with one mole of the lithium salt of the perfluorocarboxylic acid using the reverse addition technique. Using this procedure no secondary alcohols were isolated; however, perfluorocarboxylic acid-diethyl ether complexes[4] were obtained accounting for 20 to 35% of the perfluorocarboxylic acid. Other workers[5] have also shown that *n*-butyl trifluoromethyl ketone can be prepared in a 61% yield by treating lithium trifluoroacetate with *n*-butyllithium.

Bromination of the alkyl perfluoroalkyl ketones in concentrated sulfuric acid resulted in each case in a single monobromo derivative. These monobromoketones were shown to be the α-bromo derivatives by their subsequent conversion to substituted 1,2-epoxides.

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TABLE I

PHYSICAL PROPERTIES OF NEW COMPOUNDS

Compound	Yield, %	B.P., °C.	Mm.	n_D^{20}	d_4^{20}	AR_F	Analysis[a] Carbon Calc'd	Carbon Found	Hydrogen Calc'd	Hydrogen Found	Fluorine Calc'd	Fluorine Found
$C_3F_7COCHBrCH_3$	60	57	85	1.3491	1.686	1.25	23.62	23.74	1.38	1.38	43.60	43.60
$C_3F_7COCHBrC_2H_5$	72	52	31	1.3594	1.627	1.23	26.35	26.37	1.89	1.96	41.69	41.76
$C_3H_7COCBr(CH_3)_2$	66	62.1	61	1.3628	1.631	1.26	26.35	26.36	1.89	2.03	41.69	41.83
$CF_3COCHBrCH_3$	82	93	748	1.3805	1.640	1.25	23.41	23.40	1.95	2.04	27.80	27.89
$CF_3COCHBrC_2H_5$	83	61	124	1.3905	1.554	1.25	27.42	27.47	2.73	2.86	26.03	25.87
$CF_3COCBr(CH_3)_2$	63	57.5	135	1.3920	1.547	1.31	27.42	27.41	2.73	2.80	26.03	26.00
$C_3F_7CH(OH)CHBrCH_3$	56	85	81	1.3709	1.748	1.16	23.45	23.37	1.95	2.01	43.32	43.35
$C_3F_7CH(OH)CHBrC_2H_5$	65	75.0–75.8	32	1.3770	1.674	1.14	26.16	26.16	2.49	2.30	41.43	41.52
$C_3F_7CH(OH)CBr(CH_3)_2$	54	83.9	62	1.3798	1.664	1.17	26.16	25.70	2.49	2.47	41.43	41.56
$CF_3CH(OH)CHBrCH_3$	78.5	65.5	63	1.4080	1.697	1.15	23.19	23.23	2.90	2.90	27.54	27.72
$CF_3CH(OH)CHBrC_2H_5$	34	94.0–94.5	116	1.4148	1.602	1.08	27.17	27.15	3.65	3.75	25.79	25.69
$CF_3CH(OH)CBr(CH_3)_2$	42	67.5	47	1.4159	1.591	1.18	27.17	27.20	3.65	3.66	25.79	25.86
$C_3F_7\overline{CHCHO}(CH_3)$	76	93.5	748	1.3091	1.424	1.26	31.86	31.86	2.21	2.25	58.84	58.93
$C_3F_7\overline{CHCHO}(C_2H_5)$	83	110.5–111	749	1.3218	1.358	1.28	35.00	35.01	2.92	3.02	55.42	55.42
$C_3F_7\overline{CHCHO}(CH_3)_2$	85	102.5–103	747	1.3187	1.351	1.26	35.00	35.03	2.92	2.95	55.42	55.59
$CF_3\overline{CHCHO}(CH_3)$	90	58.5–59.0	747	1.3167	1.207	1.12	38.10	38.10	3.97	3.91	45.24	45.34
$CF_3\overline{CHCHO}(C_2H_5)$	83	78.8–79	745	1.3340	1.146	1.23	42.86	42.80	5.00	4.87	40.71	40.83
$CF_3\overline{CHCO}(CH_3)_2$	84	71.3–71.9	747	1.3292	1.125	1.26	42.86	43.03	5.00	5.05	40.71	40.64
$C_3H_7CH(OH)CH(OH)C_2H_5$		88[b]					32.55	32.59	3.49	3.91	51.55	52.60

[a] Analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodside, New Jersey. [b] Uncorrected melting point.

Reduction of the α-bromoketones with an ethereal slurry of lithium aluminum hydride yielded the corresponding bromoalcohols as the main product. Although no products from side reactions were isolated, the aqueous layer, from hydrolysis of the reaction mixture, showed the presence of bromide ion indicating some replacement of the bromine did occur.

The epoxides were obtained in good yields by treating the bromoalcohols with hot 50 percent aqueous sodium hydroxide. The substituted 1-heptafluoropropyl-1,2-epoxides were converted to the *vicinal* diols as was evidenced by a positive periodic acid test. It was thus assumed that the substituted trifluoromethyl epoxides were also 1,2-epoxides.

The physical properties, analysis, and yields of the new compounds prepared are reported in Table I.

The infrared spectra of the epoxides were compared with that of the corresponding bromoalcohols and bromoketones. In the trifluoromethyl epoxide series new bands appeared at 7.95 mμ, 11.2–11.4 mμ, and 12.6 mμ. The latter band was displaced to 12.1–12.25 mμ in the heptafluoropropyl epoxide series but no new band appeared in the 11.2 region. A new band was present as a shoulder in C_3F_7-$\overset{\frown}{CHCO}(CH_3)_2$, the carbon-fluorine absorption masked out this region in the other two epoxides. Spectra were determined in the liquid state.

EXPERIMENTAL

Alkyl perfluoroalkyl ketones. A. From perfluorocarboxylic acids. The ketones were prepared by the general procedure described by Dishart and Levine.[3] To three moles of alkyl Grignard reagent in one liter of ether cooled in an ice-bath was added dropwise with stirring one mole of perfluorocarboxylic acid in an equal volume of ether. After stirring overnight, the reaction mixture was hydrolyzed by pouring into ice-concentrated hydrochloric acid. The ether layer was separated and the water layer was extracted with three-100 ml. portions of ether. The combined ether layers were dried over Drierite and distilled to remove the ether; the residual liquid then was dried over phosphoric anhydride and fractionally distilled at atmospheric pressure through an efficient column.

B. Lithium salt of perfluorocarboxylic acid method. The lithium salt of perfluorobutyric acid was prepared by slowly adding one mole of the acid to one-half mole of lithium carbonate in 20 ml. of water. After evaporation of the water, the salt was dried thoroughly in a vacuum oven at 80–100°.

One mole of lithium perfluorobutyrate was dissolved in one liter of dry ether and cooled in an ice-bath. To this vigorously stirred solution was added dropwise 1.10 moles of previously prepared ethylmagnesium bromide in 400 ml. of ether over a period of two hours. The reaction mixture was stirred for an additional two hours at room temperature, then cooled in an ice-bath, and finally was hydrolyzed by the dropwise addition of 200 ml. of 20% sulfuric acid. The ether layer was separated and the water layer was extracted with three-100 ml. portions of ether. The combined ether layers were dried over Drierite and the ether was removed by distillation. The residual liquid was dried with phosphorus pentoxide and rectified to give 105 g. (44% yield) of ethyl heptafluoropropyl ketone, b.p. 82–83°, n_D^{20} 1.3030 and 70 g. of 2 $C_3F_7CO_2H.Et_2O$, b.p. 129°.

1,2-Epoxides. The perfluoroalkyl alkyl ketones were converted to the 1,2-epoxides using the procedure of McBee and Burton.[1,2] Bromination of the ketones in concentrated sulfuric acid yielded the α-bromo derivatives which upon reduction with an ethereal slurry of lithium aluminum hydride gave the α-bromoalcohols. Epoxidation of the bromoalcohols was accomplished with 50% aqueous sodium hydroxide. The yields of these reactions are reported in Table I.

Hydrolysis of 1,2-epoxides. 1,1,1,2,2,3,3-Heptafluoro-4,5-epoxyheptane (2 g.) was heated in a sealed tube with 6 ml. of 20% sulfuric acid at 105° for 60 hours. Upon cooling, a white solid was obtained which was recrystallized from benzene to yield 1,1,1,2,2,3,3,-heptafluoro-4,5-heptanediol, m.p. 88°. The diol gave a positive periodic acid test.[6]

Similar treatment of 1,1,1,2,2,3,3-heptafluoro-4,5-epoxyhexane and 1,1,1,2,2,3,3-heptafluoro-5-methyl-4,5-epoxyhexane gave oils which were the corresponding glycols; each of which gave a positive periodic acid test.

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Synthesis and Biological Activity of Some 6-(Substituted)thiopurines

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The effect of 6-(2-furfuryl)aminopurine (Kinetin) on cell division in tobacco wound callus tissue[2–4] as well as the effects of a series of 6-(substituted)aminopurines upon development in mosses[5,6] and more recently, the use of 6-(substituted)amino- and -thio-purines upon the inhibition of tentacle regeneration in hydra[7,8] have been reported. These results suggest a widespread importance of 6-(sub-

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