wise degradation[4] of the fatty acid was carried out to determine the position of the radioactive label.

TABLE II

SYNTHESIS AND DEGRADATION OF BUTYRIC-4-C^{14} ACID

Compound or carbons	Specific radioactivity,[a] counts/min./mg. $BaCO_3$ Calcd.	Found
Glutamic-1,2-C_2^{14} acid	. . .	7.50
3-(Formyl-C^{14})-propionic acid	4.69[b]	. . .
Butyric-4-C^{14} acid	4.69	4.72
Carbon 1	0.0	0.05
Carbon 2	0.0	0.04
Carbon 3	0.0	0.24
Carbon 4	18.8	18.1

[a] See footnote for Table I. [b] Calculated from specific activity of glutamic-1,2-C_2^{14} acid.

The data of Tables I and II indicate that under the conditions of the Huang-Minlon modification[2] of the Wolff–Kishner reduction there occurred no detectable rearrangement of the carbon skeleton of pyruvic and 3-formylpropionic acids. It is believed that the appreciable radioactivity found for carbon 3 of butyric-4-C^{14} acid was probably not caused by the reduction or the degradation procedure, but may have been introduced during the synthesis of the labeled starting material.[5]

Experimental

Propionic-2-C^{14} Acid.—Carbonyl-labeled pyruvic acid (1.0 mmole) prepared by the method of Anker[6] was purified by partition chromatography. The aqueous solution of the sodium salt (0.85 mmole) obtained from the partition column was concentrated to a volume of 5 ml. in a 200-ml. flask. Redistilled diethylene glycol (25 ml.), 5 ml. of an 85% hydrazine solution and 1 g. of potassium hydroxide were added and the solution was refluxed for one hour. Water was then distilled off until the temperature reached 190°, and heating under reflux was continued for one hour. The reaction mixture was cooled, acidified with sulfuric acid and steam distilled. The steam distillate was concentrated and propionic acid was obtained in aqueous solution, as the sodium salt, by partition chromatography.[7] The chromatographic step was required in order to separate propionic acid from traces of acetic acid formed by thermal decomposition of the solvent. Propionic acid was identified by its position on the chromatogram, Duclaux distillation and preparation of the *p*-bromophenacyl ester, m.p. 59–60°; yield 73% of the theoretical based on sodium pyruvate.

Butyric-4-C^{14} Acid.—Because of its instability, 3-(formyl-C^{14})-propionic acid was prepared as needed by treating glutamic-1,2-C_2^{14} acid with an equimolecular amount of chloramine T at 50°.[8] It was found that this reagent converted glutamic acid quantitatively to 3-formylpropionic acid. The latter was not isolated from solution but was identified and weighed as the *p*-nitrophenylhydrazone, m.p. 178–180°, and the 2,4-dinitrophenylhydrazone, m.p. 198–200°. The aqueous solution of 3-(formyl-C^{14})-propionic acid was taken directly for the Wolff–Kishner reduction as described for propionic-2-C^{14} acid. Butyric-4-C^{14} acid was isolated by partition chromatography[7] and identified by its position on the chromatogram, Duclaux distillation and preparation of the *p*-bromophenacyl ester, m.p. 63–64.5°; yield 55% of theory based on glutamic acid.

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(6) H. S. Anker, *J. Biol. Chem.*, **176**, 1333 (1948).

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(8) H. D. Dakin, *Biochem. J.*, **11**, 79 (1917).

Preparation of Sodium Ferrate(VI)

BY LOUIS T. OCKERMAN AND JAMES M. SCHREYER

Numerous wet methods for the preparation of solutions of sodium ferrate, Na_2FeO_4, have been reported. Foster,[1] Thiesse,[2] Rosell,[3] and Grube and Gmelin[4] prepared such solutions by different oxidation methods, but were unable to isolate any solid Na_2FeO_4.

Wallace and Fleck[5] prepared crystalline Na_2FeO_4 by fusion of Na_2O_2 in an iron crucible. The crystals were described as probably being pure Na_2FeO_4, although no analysis was reported.

In view of the failure of previous investigators to prepare crystalline Na_2FeO_4 by wet methods, the authors made a further study of the problem.

Experimental

Chlorine gas was passed into a solution containing 30 g. of solid NaOH per 75 ml. of water until the increase in weight amounted to 20 g. The temperature was maintained below 20° by means of an ice-bath. After the dissolution of 70 g. of solid NaOH, the solution was filtered. The beaker containing the solution was replaced in the ice-bath and 20 g. of ferric nitrate was added. The solution was cooled to 10–15° and saturated by adding solid NaOH. The solution was filtered through a fritted glass filter and the black mass was air dried by continued suction. A small volume of benzene was drawn through the mass on the filter, followed by 3 portions of 95% ethanol. Each portion was left in contact with the black mass for only a few minutes. The product was finally dried with a few milliliters of ethyl ether. A calcium chloride drying tube was attached to the mouth of the filter during the final drying operation.

The solid product obtained by the above procedure gave a purple color characteristic of the ferrate ion when added to water.

Although the sample appeared to be highly contaminated with hydrous ferric oxide, analysis by the chromite method[6] showed 41.38% Na_2FeO_4.

(1) W. Foster, *J. Chem. Soc.*, **35**, 123 (1879).

(2) Xavier Thiesse, *Compt. rend.*, **201**, 1135 (1935).

(3) C. A. O. Rosell, THIS JOURNAL, **17**, 760 (1895).

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Steroids. XXI.[1] Δ^7-Androstene-3β,17β-diol

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Steroids with an isolated double bond in the 7,8-position are of considerable importance[2,3] for biological experiments and synthetic purposes. Since no such representative is known in the androstane series, we have investigated two obvious synthetic routes as outlined below.

The first approach consisted of catalytic hydrogenation of $\Delta^{5,7}$-androstadiene-3β,17β-diol (IIa) to yield Δ^7-androstene-3β,17β-diol (IVa). The former substance has been prepared before by an

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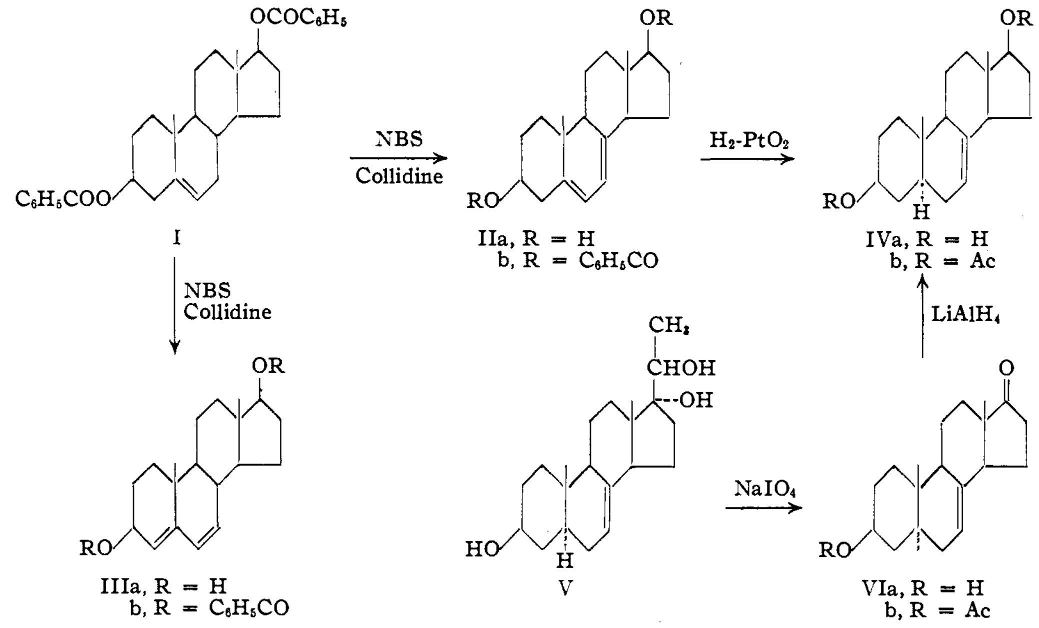
(2) G. Rosenkranz, J. Romo, E. Batres and C. Djerassi, *J. Org. Chem.*, **16**, 298 (1951),

(3) C. Djerassi, J. Romo and G. Rosenkranz, *ibid.*, **16**, 754 (1951).



application of the four-step Windaus synthesis[4] of $\Delta^{5,7}$-dien-3-ols, but a much better yield was realized by employing the Wohl–Ziegler bromination[5] of Δ^5-unsaturated steroidal alcohols[6] in the case of Δ^5-androstene-3β,17β-diol dibenzoate (I). The intermediate 7-bromo derivative was not isolated, but was dehydrobrominated directly with collidine. The resulting mixture of dienes was resolved by fractional crystallization yielding pure $\Delta^{5,7}$-androstadiene-3β,17β-diol (IIa) and its dibenzoate (IIb), identical with Butenandt's[4] compound, as well as the previously undescribed $\Delta^{4,6}$-isomer (III). Hydrogenation of II with platinum oxide in ethyl acetate solution led to the desired Δ^7-androstene-3β,17β-diol (IV).

The alternate synthesis of the diol IV involved periodic acid oxidation of Δ^7-allopregnene-3β,17α-20-triol (V)[7] followed by lithium aluminum hydride reduction of the resulting Δ^7-androsten-3β-ol-17-one (VI). The identity of the diol IV from both methods was established by a comparison of the physical constants and infrared spectra.

Experimental[8]

$\Delta^{5,7}$-Androstadiene-3β,17β-diol (II).—A mixture of 30 g. of Δ^5-androstene-3β,17β-diol dibenzoate (I),[9] 12.5 g. of N-bromosuccinimide and 600 cc. of dry carbon tetrachloride was refluxed for 4 minutes, two GE No. RSP2 photospot lamps serving as sources of illumination and heat. After adding 15 cc. of γ-collidine, the cooled solution was filtered and the filtrate was evaporated to dryness *in vacuo* at 25°. The semi-crystalline residue was dissolved in one liter of xylene, 50 cc. of collidine was added and the solution refluxed for one hour at which time the dehydrobromination was essentially completed as determined by the weight of the collidine hydrobromide formed. The collidine was removed by washing with dilute acid and water, the xylene was then distilled by passing steam through the solution for *ca.* one hour and the collected solid was recrystallized from methanol–chloroform yielding 16 g. of nearly colorless crystals with m.p. 182–190°.

The above mixture of benzoates was saponified in an atmosphere of nitrogen by refluxing with 450 cc. of ethanol and 22 g. of potassium hydroxide for one hour. The solution was poured with stirring into 3 liters of ice-cold water, the precipitate was filtered and recrystallized from acetone. The least soluble fraction after two recrystallizations afforded 3.2 g. (18%) of substantially pure **$\Delta^{5,7}$-androstadiene-3β,17β-diol** (IIa) with m.p. 196–207°, ultraviolet absorption maxima at 240 mμ (log ε 3.81), 270 mμ (log ε 4.03), 280 mμ (log ε 4.05) and 292 mμ (log ε 3.92). The small impurity of $\Delta^{4,6}$-isomer III was removed by further recrystallization from acetone and led to pure $\Delta^{5,7}$-androstadiene-3β,17β-diol (IIa) with m.p. 210–212°, $[\alpha]^{20}_D$ −158° (dioxane), ultraviolet absorption maxima at 270 mμ (log ε 4.11), 280 mμ (log ε 4.13) and 392 mμ (log ε 3.89); reported,[4] m.p. 212°. **The dibenzoate IIb** after recrystallization from chloroform–methanol exhibited m.p. 222–224.5°, $[\alpha]^{20}_D$ −33.5° (chloroform), −22° (dioxane); reported,[4] 217–218°.

$\Delta^{4,6}$-Androstadiene-3β,17β-diol (III).—The combined, crystalline mother liquors from the above acetone crystallizations were recrystallized several times from acetone-hexane, yielding 1.9 g. (11%) of fairly pure $\Delta^{4,6}$-dienediol IIIa with m.p. 178–185°, ultraviolet absorption maxima at 232 mμ (log ε 4.28), 240 mμ (log ε 4.33), 248 mμ (log ε 4.20), 270 mμ (log ε 3.40), 280 mμ (log ε 3.41) and 292 mμ (log ε 3.07). The analytical sample possessed the following constants: m.p. 194–196°, $[\alpha]^{20}_D$ −57°, ultraviolet absorption maxima at 232 mμ (log ε 4.34), 240 mμ (log ε 4.37) and 248 mμ (log ε 4,29).

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 78.77; H, 9.86.

$\Delta^{4,6}$-Androstadiene-3β,17β-diol dibenzoate (IIIb) was recrystallized from methanol–chloroform, whereupon it showed m.p. 202–203°, $[\alpha]^{20}_D$ −30.4° (chloroform), −37° (dioxane).

Anal. Calcd. for $C_{33}H_{36}O_4$: C, 79.79; H, 7.31. Found: C, 79.75; H, 7.50.

Δ^7-Androsten-3β-ol-17-one (VI).—A solution of 0.4 g. of Δ^7-allopregnene-3β,17α,20-triol (V)[7] in 25 cc. of methanol was allowed to stand at room temperature for 20 hours with 0.44 g. of sodium metaperiodate in 6 cc. of water. The solid,

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[4] A. Butenandt, E. Hausmann and J. Paland, *Ber.*, **71**, 1316 (1938).

[5] C. Djerassi, *Chem. Revs.*, **43**, 271 (1948).

[6] See G. Rosenkranz, J. Romo and J. Berlin, *J. Org. Chem.*, **16**, 290 (1951) for a summary of the most recent references in the steroid field.

[7] J. Pataki, G. Rosenkranz and C. Djerassi, THIS JOURNAL, **73**, 4055, (1951). The starting material in this synthesis was $\Delta^{7,16}$-allopregnadien-3β-ol-20-one (ref. 3).

[8] Melting points are uncorrected. Unless indicated otherwise, rotations were determined in chloroform, ultraviolet absorption spectra in 95% ethanol and infrared spectra in carbon disulfide solution. Thanks are due to Srta. Paquita Revaque and staff for these measurements and to the Srtas. Amparo Barba and Rachel Cervera for the microanalyses.

[9] D. H. R. Barton and J. D. Cox, *J. Chem. Soc.*, 783 (1948).

which had precipitated, was collected and proved to be pure starting material (0.22 g.). Dilution of the filtrate with water and recrystallization of the precipitate from ether-hexane afforded 0.1 g. of colorless crystals of the ketone VIa with m.p. 153–155°, $[\alpha]^{20}\text{D}$ +33°, infrared carbonyl band at 1742 cm.$^{-1}$ typical of 17-ketosteroids.[10]

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.78. Found: C, 78.89; H, 9.79.

Δ^7-**Androsten-3**β**-ol-17-one 3-acetate** (VIb), recrystallized from dilute methanol, had m.p. 140–141°, $[\alpha]^{20}\text{D}$ +31.3°.

Anal. Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.47; H, 9.35.

Δ^7-**Androstene-3**β**,17**β**-diol (IV) (a) By Catalytic Hydrogenation of** $\Delta^{5,7}$**-Androstadiene-3**β**,17**β**-diol (IIa).**—A solution of 0.5 g. of the dienediol IIa in 80 cc. of ethyl acetate was shaken in an atmosphere of hydrogen at room temperature and atmospheric pressure with 50 mg. of platinum oxide catalyst for three hours at which time the hydrogen uptake corresponded to approximately one mole. Filtration of the catalyst, evaporation of the solvent to dryness and recrystallization from hexane–acetone yielded 0.38 g. of colorless crystals with m.p. 181–183°, $[\alpha]^{20}\text{D}$ −23° and no selective absorption in the ultraviolet. The infrared spectrum was identical with that of a specimen prepared according to procedure (b).

Anal. Calcd. for $C_{19}H_{30}O_2$: C, 78.57; H, 10.41. Found: C, 78.22; H, 10.76.

(b) **By Lithium Aluminum Hydride Reduction of** Δ^7-**Androsten-3**β**-ol-17-one (VIa).**—The reaction was carried out in the usual manner with 3.0 g. of the ketone VIa, 60 cc. of tetrahydrofuran and 2.5 g. of lithium aluminum hydride. The diol IVa was obtained in 80% yield and possessed the same physical constants and infrared spectrum as the sample described under (a).

The diacetate IVb (ether–pentane) exhibited m.p. 119–121°, $[\alpha]^{20}\text{D}$ −28.8°.

Anal. Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.81; H, 9.06.

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[10] R. N. Jones, P. Humphries and K. Dobriner, THIS JOURNAL, **72**, 956 (1950).

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The Dipole Moments of Some Boron Trifluoride Etherates

BY ROBERT C. OSTHOFF,[1] CHARLES A. BROWN AND JANET A. HAWKINS

Since there appeared to be considerable doubt as to the magnitude of the dipole moment of $F_3BO(CH_2CH_3)_2$,[2] measurements of the electric moment of this compound were repeated. Further, it was of interest to establish the dipole moment of a higher etherate of boron trifluoride. The compound formed by boron trifluoride and tetrahydrofuran appeared to be one of the more stable etherates of boron trifluoride,[3] and its dipole moment has also been determined.

Laubengayer and Finlay[2] have measured the dipole moments of $F_3BO(CH_3)_2$, $F_3BO(CH_3)(CH_2CH_3)$ and $F_3BO(CH_2CH_3)_2$. However, these authors state that in the case of the diethyl etherate of boron trifluoride the three values of the molar orientation polarization, P_2, obtained were such as to prohibit an extrapolation to infinite dilution. The value of $P_{2\infty}$ that was used by Laubengayer and Finlay in the evaluation of the dipole moment was merely the arithmetic mean of the three values.

Experimental

Benzene.—Merck and Co., Inc., reagent grade benzene was dried over phosphorus pentoxide and distilled through a 150-cm. packed column; b.p. 80.0°, $n^{25}\text{D}$ 1.49821.

$F_3BO(CH_2CH_3)_2$.—Baker and Adamson technical boron trifluoride-diethyl etherate complex was fractionated *in vacuo;* vapor pressure at 20.0°, 2.2 mm.

Tetrahydrofuran.—du Pont "Stabilized" tetrahydrofuran was dried over calcium hydride and distilled from lithium aluminum hydride. The fraction boiling at 65–66° at 763 mm. was collected; $n^{25}\text{D}$ 1.4044.

$F_3BO(CH_2)_4$.—Matheson tank boron trifluoride was passed into the tetrahydrofuran at room temperature until the boron trifluoride was present in excess. The excess boron trifluoride was removed *in vacuo* at room temperature, and the reaction mixture was then fractionated. The fraction boiling at 69.0° and 4 mm. was collected; vapor pressure at 79.0°, 7.2 mm.

Apparatus and Methods.—Electric moments were measured in benzene solution at 25.00° using a modified heterodyne beat apparatus which will be described in a later communication.[4] The measurements were made at 100 kilocycles. The dipole moments were calculated according to the method described by Smyth.[5] The molar refraction, $R^{25}\text{D}$, of $F_3BO(CH_2CH_3)_2$ employed, was the value of 26.63 previously reported.[2] The molar refraction of $F_3BO(CH_2)_4$ was evaluated by means of a Pulfrich refractometer. In this manner the molar refraction was observed to be 28.504 cm.^{3}.

The benzene solutions that were subjected to measurements were clear and handled in the absence of air. The dielectric constant of benzene was taken as 2.273.[6]

The observed data are summarized in Table I.

TABLE I

Mole fraction, c_2	Dielectric constant, ϵ	Density, d	Total molar orientation polarization of solute, P_2
	$F_3BO(CH_2CH_3)_2$		
0.014260	2.833	0.87820	544.7
.008138	2.586	.87687	557.4
.004124	2.440	.87541	582.1
.002297	2.363	.87354	568.2
	$P_{2\infty} = 530.1$, $\mu = 4.96 \pm 0.14\ D$		
	$F_3BO(CH_2)_4$		
0.020390	3.169	0.88132	568.4
.010615	2.726	.87640	579.2
.006921	2.554	.87562	585.2
.003416	2.426	.87381	621.9
	$P_{2\infty} = 688.5$, $\mu = 5.68 \pm 0.17\ D$		

The observed dipole moment of $F_3BO(CH_2CH_3)_2$ of 4.96 ± 0.14 *D* was well within the experimental error of the value reported by Laubengayer and Finlay of 4.92 ± 0.38 *D*.

If one assumes that the dipole moment of 1.68 *D*[7] for the tetrahydrofuran molecule remains essentially unaltered in the addition compound, the electric moment of 5.68 *D* for $F_3BO(CH_2)_4$ gives a calculated bond moment for the B–O bond of 2.50 *D*. This value indicates a more equal sharing of the electron pair of the ether oxygen than was found in the case of $F_3BO(CH_2CH_3)_2$. This greater sharing of the donated electron pair accounts for the greater stability of the tetrahydrofuran complex. This stability increase has also been accounted for on the basis of steric concepts by Brown and Adams.[3]

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[2] A. W. Laubengayer and G. R. Finlay, THIS JOURNAL, **65**, 884 (1943).

[3] H. C. Brown and R. M. Adams, *ibid.*, **64**, 2557 (1942).

[4] C. A. Brown and R. C. Osthoff, paper to be submitted shortly.

[5] C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Reinhold Publ. Corp., New York, N. Y., 1931, Chapter I.

[6] J. Hadanard, *Compt. rend.*, **204**, 1234 (1937).

[7] H. de Vries Robles, *Rec. trav. chim.*, **58**, 111 (1939).