the others since it is a stronger acid than the benzoylferrocenoic acid. A possible explanation of the greater strength of this acid could lie in hydrogen bonding of the carboxylate ion with the α-hydroxy group, stabilizing the ionized form, similar to the explanation advanced by Branch[7] for the large acid constant of salicylic acid.

EXPERIMENTAL

Acetyl- and benzoylferrocenoic acids were prepared by the methods previously described.[2]

Ethylferrocenoic acid was prepared by Clemmensen reduction of acetylferrocenoic acid according to the procedure described by Nesmeyanov.[8]

1-(α-Hydroxybenzyl)-1′-carbamylferrocene. To a warm solution of 8.4 g. (0.017 mole) of 1-benzoyl-1′-diphenylcarbamylferrocene[2] in 200 ml. of methanol containing 0.2 ml. of 50% sodium hydroxide was added 27 ml. of a 10% sodium borohydride solution made up in 10% aqueous sodium hydroxide. The reaction mixture was stirred at room temperature for 30 min. and at gentle reflux for 5 hr. On cooling, the product crystallized. A yield of 6.7 g. (79.5%) was obtained, m.p. 152–154°. The analytical sample was recrystallized from hexane and melted at 154.5–156°.

Anal. Calcd. for $C_{30}H_{25}NO_2Fe$: C, 73.93; H, 5.17. Found: C, 74.04; H, 5.14.

α-Hydroxybenzylferrocenoic acid. α-Hydroxybenzyldiphenylcarbamylferrocene (2.60 g.) was dissolved in a mixture of 25 ml. of benzene and 50 ml. of 10% ethanolic potassium hydroxide. The mixture was held at reflux for 2 hr. and was allowed to stand overnight at 50°. The solvent was removed and the residue was shaken with water (75 ml.) for 3 hr. The aqueous suspension was filtered, and the filtrate yielded upon acidification with hydrochloric acid 1.45 g. (81%) of crude α-hydroxybenzylferrocenoic acid. Recrystallization from benzene yielded a product melting at 129.5–130°.

Anal. Calcd. for $C_{18}H_{16}O_3Fe$: C, 64.31; H, 4.80. Found: C, 64.54; H, 4.95.

Benzylferrocenoic acid. A solution of 2.33 g. (0.00694 mole) of α-hydroxybenzylferrocenoic acid in 100 ml. of ethyl acetate containing 5 ml. of acetic acid was placed in an atmospheric hydrogenator over 0.7 g. of prereduced palladium oxide. The reduction required 850 min. for the calculated hydrogen uptake. After filtration, the solvent was removed with reduced pressure. The orange crude product, 2.05 g. (92%), melted at 148–151°. Recrystallization from cyclohexane yielded a product melting at 151–152.5° dec.

Acid constants. The acid constants were measured in 50 volume % ethanol in water, essentially according to the method described by Roberts.[9] Three or more determinations were made on each acid, and the mean deviations of the determinations are shown in Table I.

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[7] G. E. K. Branch and D. L. Yabroff, *J. Am. Chem. Soc.*, 2568 (1934).

[8] A. N. Nesmeyanov and O. A. Reutov, *Doklady Akad. Nauk., S.S.S.R.*, 120, 1267 (1958).

[9] J. D. Roberts, E. A. McElhill, and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).

Steroidal Cyclic Ketal. XXIII.[1] Some Reactions of the 3-Ethylenedioxy-Δ^5 Grouping in Steroids

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We wish to report here on some aspects of the chemistry of the 3-ethylenedioxy-Δ^5 grouping in the presence of a double bond at C-9,11 in the steroid molecule.

When 21-acetoxy-3,20-bisethylenedioxy-5,9(11)-pregnadien-17α-ol (I)[2] was treated with one equivalent of perbenzoic acid an epoxide was formed in 63% yield which was assigned the structure, 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)-pregnen-17α-ol (II). The structure II was established by its synthesis from 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxypregnane-11β,17α-diol (IIIb)[3] by selective dehydration of the 11β-hydroxyl group with phosphorus oxychloride in pyridine.[4,5] It would appear then that in a 5,9(11)-diene 3,20-bisethylene ketal the C-5,6-double bond is more reactive toward epoxidation than the 9,11-double bond, and moreover frontal attack is favored.[6]

When the 5,9(11)-diene bisketal I was treated with two equivalents of perbenzoic acid, a diepoxide IV separated in 74% yield. As the same product could be obtained by reaction of 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)-pregnen-17α-ol (II) with an additional equivalent of perbenzoic acid, the structure of IV was designated as 21-

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[1] Paper XXII, S. Bernstein, M. Heller, and W. S Allen, *J. Org. Chem.*, **26**, 1333 (1961).

[2] S. Bernstein, R. Littell, and J. H. Williams, *J. Am. Chem. Soc.*, **75**, 4830 (1953).

[3] S. Bernstein and R. H. Lenhard, *J. Am. Chem. Soc.*, **77**, 2233 (1955).

[4] R. Littell and S. Bernstein, *J. Am. Chem. Soc.*, **78**, 984 (1956).

[5] In this connection, the 11β-hydroxyl group in the 5α,-6α-epimer of III has been shown to be stable to dehydration conditions with phosphorus oxychloride. However, this dehydration can be effected with thionyl chloride but with simultaneous elimination of the 17α-hydroxyl group. See, S. Bernstein, M. Heller, F. J. McEvoy, and S. M. Stolar, *J. Org. Chem.*, **26**, 505 (1961).

[6] This observation is of interest in view of the finding (ref. 3) that when the bisethylene ketal (Va) of hydrocortisone was treated with perbenzoic acid, an excellent separation (*ca*, 60% yield) of the 5α,6α-epoxide occurred. The 5β,6β-epoxide IIIa has now been isolated from the mother liquor by chromatography; *m.p.* 193–196°; $[\alpha]_D^{25}$ +5° (pyridine); ν_{max} 3495, 1110, and 1036 cm.$^{-1}$ *Anal.* Calcd for $C_{25}H_{38}O_8$ (466.55): C, 64.36; H, 8.21. Found: C, 64.15; H, 8.50.

Also epoxidation of the 3-ethylenedioxy-Δ^5 grouping in a number of steroids unsubstituted in Ring C has given a mixture of α- and β-epoxides in which the α-epimer is apparently the major product; see, *e.g.* A. Bowers, L. C. Ibáñez, and H. J. Ringold, *Tetrahedron*, **7**, 138 (1959).

acetoxy - 3,20 - bisethylenedioxy - 5β,6β;9α,11α-diepoxypregnan-17α-ol.[7]

In view of a previous report[8] that a 3-ethylene ketal grouping has an important influence on the stereochemistry of osmylation of a 5,6-double bond, a study of the hydroxylation of the 5,9(11)-diene bisketal I was made. When the latter reacted with osmic acid (11% excess for two double bonds) in benzene, a 70% yield of 21-acetoxy-3,20-bisethylenedioxy-9(11)pregnene-5β,6β,17α-triol (Va) was obtained. Unlike the peroxidation reaction the osmic acid attacked only the C-5,6-double bond,[9] but, in an analogous manner, frontal attack at the C-5,6 position was favored.

The structure of Va was established by acetylation to give the 6β,21-diacetate Vb and also by hydrolysis with aqueous acetic acid[10] to give 21 - acetoxy - 20 - ethylenedioxy - 6β,17α - dihydroxy - 4,9 (11) - pregnadien - 3 - one (VI). The hyposchromic shift in the ultraviolet absorption spectrum of VI (λ_{max} 235 mμ) compared to that of the corresponding 6-deoxy compound (λ_{max} 239 mμ) indicated the 6-hydroxyl group to be attached in the 6β(axial)-configuration.[11,12] It is known that when a 3β-hydroxy (or 3β-acetoxy)-5β,6β-epoxide is treated with lithium aluminum hydride the epoxide is opened to give mainly a 6β-hydroxy compound along with a small amount of the 5β-hydroxy isomer.[13] However, when 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)pregnen-17α-ol (II) was heated under reflux with a large excess of lithium aluminum hydride in tetrahydrofuran followed by acetylation of the product, the starting material was recovered in 76% yield. Attempted reduction of the 5β,6β; 9α,11α-diepoxy bisketal IV likewise returned starting material after acetylation, albeit in only 20% yield.[14] Under the same conditions the 5β,6β-epoxide (IIIb) of hydrocortisone acetate bisethylene ketal was recovered unchanged in 72% yield.[15] These results suggest that the stability of the 5β,6β-epoxide is related to the presence of the C-3-ketal group which may be due to the 1,3-diaxial interaction of the 3α-group (of the ketal) and of the entering hydride reagent in the transition state.[16] However, application of such steric considerations to explain generally the course of the peroxidation and osmylation reactions on the 5,9(11)-diene bisketal I, hydrocortisone bisketal Va,b, and other Δ^5-ketals (in which Ring C is saturated and unsubstituted) becomes difficult because of the divergent findings. However, it is apparent that a C-9,11-double bond exerts a decisive influence favoring frontal attack on a Δ^5-3-ketal grouping in the reactions described.

EXPERIMENTAL

Melting points. All melting points are uncorrected. *Petroleum ether.* The fraction used had a b.p. 60–70°. *Absorption spectra.* The ultraviolet absorption spectra were determined in methanol unless otherwise specified. The infrared absorption spectra were carried out in pressed potassium bromide. *Rotations.* All optical rotations were determined in chloroform unless otherwise specified.

21-Acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)-pregnen-17α-ol (II). *A.* To a solution of 1.22 g. (2.57 mmoles) of 21-acetoxy-3,20-bisethylenedioxy-5,9(11)-pregnadien-17α-ol (I) in 15 ml. of chloroform was added 365 mg. (2.65 mmoles) of perbenzoic acid in 25 ml. of benzene and the mixture was allowed to stand at room temperature for 7 days. The reaction mixture was diluted with chloroform, and the extract was washed twice with saturated potassium carbonate solution, twice with water, dried, and evaporated. Crystallization of the residue from acetone–petroleum ether gave 800 mg. of white crystals, m.p. 198–200°. Three further crystallizations from acetone–petroleum ether gave 570 mg. of the pure 5β,6β-epoxide II, m.p. 203–206°; $[\alpha]^{25}_{D}$ − 9°; ν_{max} 3520 and 1746 cm.$^{-1}$

Anal. Calcd. for $C_{27}H_{38}O_8$ (490.57): C, 66.10; H, 7.81. Found: C, 65.96; H, 8.03.

B. To a cooled solution of 400 mg. of 21-acetoxy-3,20-bisethylenedioxy - 5β,6β - epoxypregnane - 11β,17α - diol (IIIb) in 4 ml. of pyridine was added 0.4 ml. of phosphorus oxychloride. The solution was allowed to stand at −15° for 16 hr. and then at +5° for 24 hr. when it was poured into ice water to give 360 mg. of white crystals, m.p. 193–196°. Three crystallizations from acetone–petroleum ether gave pure 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9-(11)-pregnen-17α-ol (II), m.p. 197–199°; $[\alpha]^{25}_{D}$ + 6°. Infrared spectral analysis and admixture melting point determination indicated this product to be identical with the sample prepared in *A* above.

Anal. Found: C, 66.00; H, 8.00.

21-Acetoxy-3,20-bisethylenedioxy-5β,6β;9α,11α-diepoxypregnan-17α-ol (IV). *A.* A solution of 1.05 g. of 21-acetoxy-3,20-bisethylenedioxy-5,9(11)-pregnadien-17α-ol (I) and 870 mg. of perbenzoic acid in 5 ml. of chloroform and 30 ml. of

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[7] Epoxidation of a 9,11-double bond has been shown to proceed by rear-attack, see *e.g.*, L. F. Fieser and S. Rajogopalan, *J. Am. Chem. Soc.*, **73**, 118 (1951). The same steric course has been assumed for the epoxidation of the C-9,11-double bond in I.

[8] S. Bernstein, W. S. Allen, C. E. Linden, and J. Clemente, *J. Am. Chem. Soc.*, **77**, 6612 (1955), found that hydroxylation of the bis-ethylene ketal of progesterone with osmium tetroxide gave the 5β,6β-diol in 49% yield. The epimeric α-diol could not be isolated.

[9] The 9,11-double bond of 21-acetoxy-3,20-bisethylenedioxy-9(11)-pregnene-5α,17α-diol has been hydroxylated with osmic acid under forcing conditions to give the 9α,11α-diol in low yield (ref. 4).

[10] R. Antonucci, S. Bernstein, M. Heller, R. H. Lenhard, R. Littell, and J. H. Williams, *J. Org. Chem.*, **18,** 70 (1953).

[11] C. P. Balant and M. Ehrenstein, *J. Org. Chem.*, **17,** 1587 (1952).

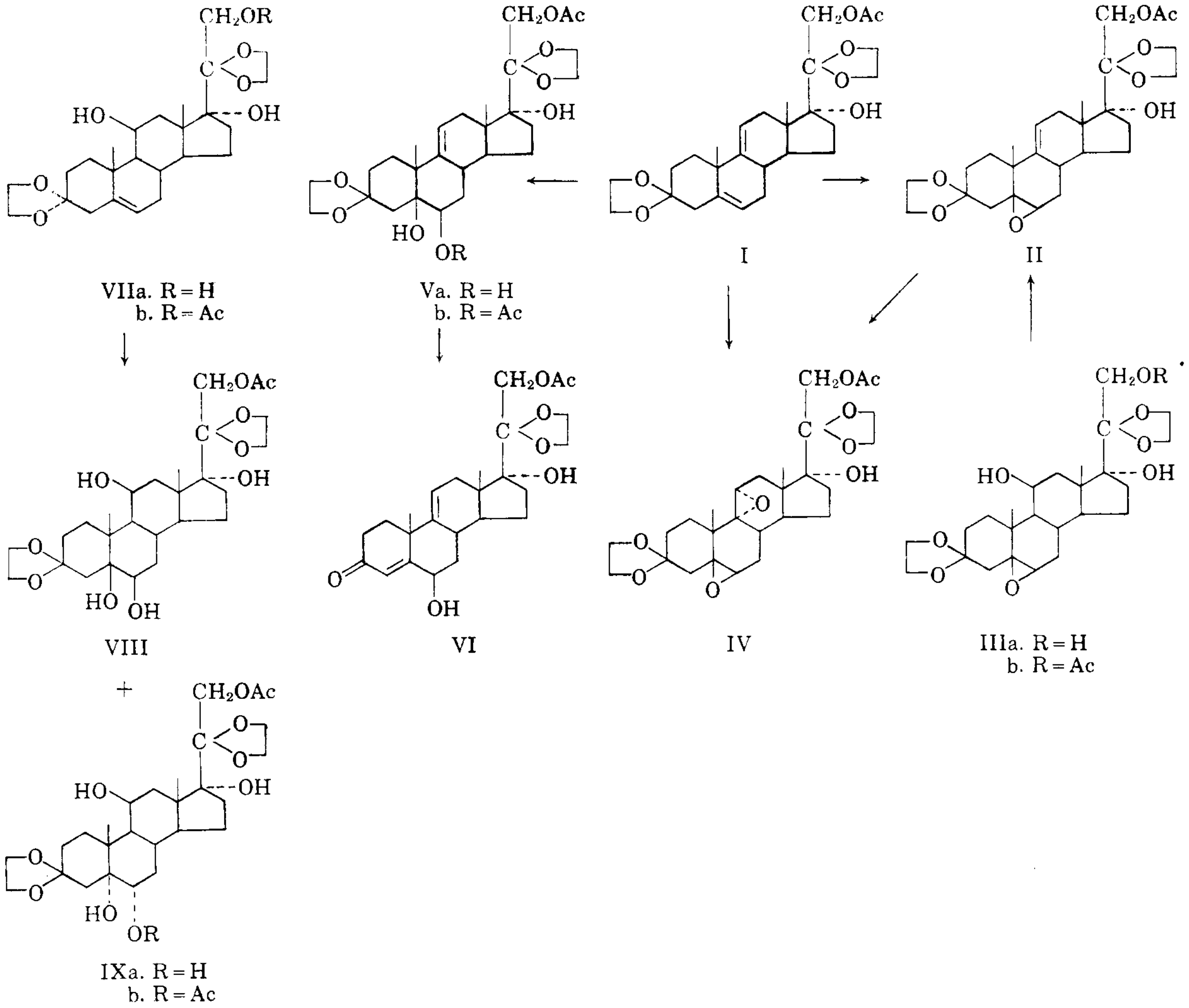
[12] S. Bernstein and R. Littell, *J. Org. Chem.*, **25,** 313 (1960).

[13] P. A. Plattner, H. Heusser, and M. Feurer, *Helv. Chim. Acta*, **32,** 587 (1949).

[14] The stability of a 9α,11α-epoxide in certain structures to lithium aluminum hydride has been noted; see, L. F. Fieser and S. Rajogopalan, *J. Am. Chem. Soc.*, **73,** 118 (1951); and A. S. Hallsworth and H. B. Henbest, *J. Chem. Soc.*, 1604 (1957).

[15] The possibility that this 5β,6β-epoxide may be stable to lithium aluminum hydride has been suggested by Bernstein and Lenhard.[3]

[16] This type of steric effect has been utilized to explain the C-5-methylation of a 6-keto-3-ethylenedioxy derivative to yield a 5β-methyl compound; J. H. Fried, G. E. Arth, and L. H. Sarett, *J. Am. Chem. Soc.*, **82,** 1684 (1960); and J. H. Fried, A. N. Nutile, and G. E. Arth, *J. Am. Chem. Soc.*, **82,** 5704 (1960).



ethyl acetate was allowed to stand at room temperature for 72 hr. Crystals separated during the course of the reaction. The mixture was cooled and product was collected by filtration to give 830 mg. (74%), m.p. 232–237°. Two crystallizations of a 200-mg. portion from chloroform-methanol gave 105 mg. of the pure diepoxide IV, m.p. 236–237°; $[\alpha]_D^{24}$ − 16°; ν_{max} 3540 and 1752 cm.$^{-1}$

Anal. Calcd. for $C_{27}H_{38}O_9$ (506.57): C, 64.01; H, 7.56. Found: C, 63.93; H, 7.78.

B. A solution of 170 mg. of 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)-pregnen-17α-ol (II) in 15 ml. of ethylacetate containing 61 mg. of perbenzoic acid was allowed to stand at room temperature for 3.5 days. The product was extracted with ethyl acetate and the extract was washed with sodium carbonate and sodium chloride solutions. After being dried, the extract was evaporated and crystallized from ether to give 135 mg. of white crystals, m.p. 234–237°. Two further crystallizations from acetone–petroleum ether gave 80 mg. of IV, m.p. 238–240°; $[\alpha]_D^{25}$ − 14°. Infrared spectral analysis showed the product to be identical with the diepoxide prepared in *A* above.

21-Acetoxy-3,20-bisethylenedioxy-9(11)-pregnene-5β,6β,17α-triol (Va). A solution of 830 mg. (1.74 mmoles) of 21-acetoxy - 3,20 - bisethylenedioxy - 5,9(11) - pregnadien-17α-ol (I) and 1.00 g. (3.92 mmoles) of osmic acid in 20 ml. of benzene and 1.0 ml. of pyridine was allowed to stand at room temperature for 90 hr. with occasional stirring. After the addition of 69 ml. of water, 46 ml. of methanol, and 7.15 g. each of sodium sulfite and potassium bicarbonate, the mixture was stirred for an additional 5 hr. The inorganic precipitate was collected by filtration and washed with chloroform. The combined filtrates were washed with saturated saline, dried, and evaporated. The crude residue was twice crystallized from acetone–petroleum ether to give 610 mg. (70%) of a white solid, m.p. 176–178°. Four further crystallizations from the same solvent pair gave pure XIa, m.p. 182–183°; λ_{max} none; $[\alpha]_D^{25}$ + 20°; ν_{max} 3520, 1752, 1725, 1650, and 1230 cm.$^{-1}$

Anal. Calcd. for $C_{27}H_{40}O_9$ (508.59): C, 63.76; H, 7.93. Found: C, 63.80; H, 8.20.

6β,21-Diacetoxy-3,20-bisethylenedioxy-9(11)-pregnene-5β,-17α-diol (Vb). A solution of 240 mg. of 21-acetoxy-3,20-bisethylenedioxy-9(11)-pregnene-5β,6β,17α-triol (Va) in 3 ml. of pyridine and 1 ml. of acetic anhydride was allowed to stand at room temperature for 18 hr. The solvents were evaporated, and the oily residue was crystallized from acetone–petroleum ether to give 220 mg. of white powder, m.p. 165–185°. Two further crystallizations from the same solvent pair gave the pure diacetate Vb, m.p. 206–208°; $[\alpha]_D^{25}$ − 7°; ν_{max} 3520, 1746, and 1245 cm.$^{-1}$

Anal. Calcd. for $C_{29}H_{42}O_{10}$ (550.65): C, 63.25; H, 7.69; Ac, 15.6. Found: C, 63.45; H, 7.88; Ac, 15.1.

21-Acetoxy-20-ethylenedioxy-6β,17α-dihydroxy-4,9(11)-pregnadien-3-one (VI). A solution of 150 mg. of 21-acetoxy-3,20 - bisethylenedioxy - 9(11) - pregnene - 5β,6β,17α-triol (Va) in 1.5 ml. of acetic acid and 0.75 ml. of water was heated at 100° for 45 min. The mixture was cooled and diluted with water to give 50 mg. of a white solid, m.p. 217–220°. The product was crystallized three times from acetone–petroleum ether to give pure VI, m.p. 224–226°; $\lambda_{max}^{Abs.\ alc.}$ 235 mμ (ε 13,500); ν_{max} 3600, 3450, 1740, 1685, and 1240 cm.$^{-1}$

Anal. Calcd. for $C_{25}H_{34}O_7$ (446.52): C, 67.24; H, 7.68. Found: C, 67.65; H, 7.50.

21-Acetoxy-3,20-bisethylenedioxypregnane-5β,6β,11β,17α-tetrol (VIII) *and 21-acetoxy-3,20-bisethylenedioxypregnane-5α,6α,11β,17α-tetrol* (IXa). A solution of 2.33 g. of 21-acetoxy-3,20-bisethylenedioxy-5-pregnene-11β,17α-diol (VIIb) and 1.5 g. of osmic acid in 60 ml. of benzene and 1.5 ml. of pyridine was allowed to stand at room temperature for 5 days with occasional stirring. After the addition of 100 ml. of water, 70 ml. of methanol, and 10.8 g. each of sodium sulfite and potassium bicarbonate, the mixture was stirred for an additional 7 hr. The inorganic precipitate was collected by filtration and washed with chloroform. The combined filtrates were washed with saturated saline, dried, and evaporated. The resulting glass was chromatographed on 130 of silica gel. The fractions eluted with 20–40% acetone in ether gave, after crystallizations from acetone-ether, 700 mg. of a white powder, m.p. 178–184°. Four crystallizations of a small portion from acetone-ether gave the pure 5β,6β-diol VIII, m.p. 194–195°; $[\alpha]^{25}_{D} + 34°$; ν_{max} 3520, 1750, and 1250 cm.$^{-1}$

Anal. Calcd. for $C_{27}H_{42}O_{10}$ (526.61): C, 61.58; H, 8.04. Found: C, 61.80; H, 8.26.

The fractions eluted with 80% acetone in ether gave, after crystallization from acetone–petroleum ether, 450 mg. of crystals, m.p. 231–234°. Two further crystallizations of a small portion from acetone–petroleum ether gave the pure 5α,6α-diol IXa, m.p. 236–237°; $[\alpha]^{25}_{D} + 9°$; ν_{max} 3520, 1750 and 1240 cm.$^{-1}$

Anal. Found: C, 61.53; H, 8.40.

6α,21-Diacetoxy-3,20-bisethylenedioxypregnane-5α,11β,17α-triol (IXb). A solution of 200 mg. of 21-acetoxy-3,20-bisethylenedioxypregnane-5α,6α,11β,17α-tetrol (IXa) in 1.5 ml. of acetic anhydride and 4 ml. of pyridine was allowed to stand at room temperature for 18 hr., when it was poured into water. The resulting precipitate was collected by filtration to give 165 mg., m.p. 234–236°. Four crystallizations from acetone–petroleum ether gave the pure diacetate IXb, m.p. 231–232°; $[\alpha]^{25}_{D} + 5°$; ν_{max} 3450, 1740, and 1250 cm.$^{-1}$

Anal. Calcd. for $C_{29}H_{44}O_{11}$ (568.64): C, 61.25; H, 7.80; Ac, 15.13. Found: C, 60.96; H, 7.93; Ac, 15.48.

Attempted reduction of 5β,6β-epoxides with lithium aluminum hydride. A. To a solution of 250 mg. of 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxy-9(11)-pregnen-17α-ol (II) in 20 ml. of tetrahydrofuran was added 500 mg. of lithium aluminum hydride and the mixture was heated under reflux for 3 hr. The mixture was cooled, water was added, and the resulting precipitate was separated by filtration and washed several times with chloroform. The combined filtrates were washed with water, dried, and evaporated. The crude glass so obtained was treated with 2 ml. of acetic anhydride in 5 ml. of pyridine at room temperature for 60 hr. Evaporation of the solvents followed by crystallization of the residue from acetone–petroleum ether gave 190 mg. (76%) of starting material II, m.p. 200–204°. Infrared spectral analysis showed the product to be identical with the starting material.

B. A solution of 250 mg. of 21-acetoxy-3,20-bisethylenedioxy-5β,6β,9α,11α-diepoxypregnan-17α-ol (IV) in 20 ml. of tetrahydrofuran containing 500 mg. of lithium aluminum hydride was heated under reflux for 8 hr. and allowed to stand at room temperature overnight. The crude product, isolated as described in *B* above, was treated with 1 ml. of acetic anhydride in 3 ml. of pyridine at room temperature overnight. After the addition of methanol the reaction mixture was concentrated, ether was added, and 50 mg. (20%) of crystals, m.p. 230–232°, was obtained. Admixture melting point with IV gave no depression. A crystallization from chloroform-ether gave 28 mg. of material, m.p. 235–236° whose infrared spectrum was identical with that of IV.

C. To a solution of 250 mg. of 21-acetoxy-3,20-bisethylenedioxy-5β,6β-epoxypregnane-11β,17α-diol (IIIb) in 35 ml. of tetrahydrofuran was added 750 mg. of lithium aluminum hydride. The mixture was refluxed for 4 hr., then was allowed to stand at room temperature overnight. After cautious addition of water to decompose excess reagent the residue was filtered, and the filtrate was evaporated to give 205 mg. of a low melting solid. The crude residue was treated with 0.8 ml. of acetic anhydride in 4 ml. of pyridine for 20 hr. at room temperature. The mixture was extracted with ethyl acetate, and the extract was washed with dilute sodium bicarbonate solution and dried. Evaporation gave 180 mg. (72%) of crystalline product, m.p. 194–198°. Crystallization from acetone–petroleum ether gave pure IIIb, m.p. 204–205°, $[\alpha]^{25}_{D} + 21°$. Infrared spectral analysis showed the product to be identical with an authentic sample[3] of starting material.

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Hammett Sigma Constants for *m*- and *p*-Benzoyl Groups[1a]

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During the course of a recent investigation,[1b] the Hammett sigma constants for *m*- and *p*-benzoyl groups were required. Values of these constants based upon ionization constant data[2] were not available. Furthermore, as the benzoyl group is often easily introduced into molecules and in certain situations might be a more convenient (*e.g.*, less reactive) substituent than some of the other carbonyl functions, we considered that a knowledge of the σ constants for the benzoyl group might be of value in substituent effect studies. The isomeric *m*- and *p*-benzoylbenzoic acids were therefore prepared, and their ionization constants were determined and compared with those of five other acids having substituents with well established σ values.

EXPERIMENTAL

p-Methylbenzophenone. A mixture of 15 g. of anhydrous aluminum chloride, 80 cc. of carbon disulfide and 14.1 g. of benzoyl chloride was refluxed until homogeneous. Then 10.0 g. of dry toluene was added. After refluxing for 30 min., the solvent was distilled. The mixture obtained by stirring this residue into ice and concd. hydrochloric acid was extracted with ether. The ether solution was washed with 10% hydrochloric acid and water and dried over calcium chloride. Distillation of the residue obtained by evaporation of the ether solution gave 14.2 g. (72%) of *p*-methylbenzophenone as a colorless oil, b.p. 140–145° at 6.5 mm. (reported[3] b.p. 327–328°) which solidified on standing. It was crystallized from petroleum ether (b.p. 30–65°) to obtain 10.5 g. (53%)

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(1) (a) This research was sponsored by a Frederick Gardner Cottrell grant from the Research Corporation. (b) W. N. White, D. Gwynn, R. Schlitt, C. Girard, and W. Fife, *J. Am. Chem. Soc.*, **80**, 3271 (1958).

(2) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

(3) K. v. Auwers and P. Strodter, *Ber.*, **59**, 533 (1926).