adenocarcinoma in mice and the testosterone propionate-resistant mammary fibroadenoma in rats[5] (see Table II).

TABLE II

TUMOR INHIBITION BY COMPOUND II

Compound	Dose, mg./kg.	% Tumor Inhibition[a] TP-Resistant[b] (Rats)	% Tumor Inhibition[a] C-3-H (Mice)
Prednisolone	15	0–20	100
Testosterone propionate	5	0–15	0
Compound II	15	72	96

[a] Results derived from multiple assays, using 8–20 animals/group. The steroids were administered subcutaneously in a CMC vehicle. [b] E. M. Glenn, S. L. Richardson, and B. J. Bowman, *Endocrinology*, **64**, 379 (1959).

EXPERIMENTAL[6]

17α-Acetoxy-9α-fluoro-11β-hydroxy-6α-methyl-1,4-pregnadiene-3,20-dione (II). A mixture of 5.0 g. of 9α-fluoro-11β,17α-dihydroxy-6α-methyl-1,4-pregnadiene-3,20-dione (I) in 625 ml. of glacial acetic acid, 125 ml. of acetic anhydride, and 2.0 g. of *p*-toluenesulfonic acid, monohydrate, was stirred vigorously at 26° until solution was completed (about 8 hr.). The reaction mixture was poured into a large volume of water containing 1 kg. of potassium bicarbonate. The product recovered by filtration, after drying, melted at 205–212° and constituted a quantitative yield. The crude product was recrystallized from ethyl acetate–Skellysolve B[7] to afford 2.5 g. (45.0% yield) of II, m.p. 225–228°, $[\alpha]_D$ + 49° (pyridine). The analytical sample, m.p. 230–232°, $[\alpha]_D$ + 50° (pyridine), was prepared by recrystallization from the same solvents.

Anal. Calcd. for $C_{24}H_{31}FO_5$: C, 68.89; H, 7.47; F, 4.54. Found: C, 68.90; H, 7.56; F, 4.7.

17α-Acetoxy-9α-fluoro-6α-methyl-1,4-pregnadiene-3,11,20-trione (III). To a solution of 1 g. of II in 50 ml. of acetone, 0.5 ml. of chromic acid solution[8] was added with stirring. After 5 min. the excess oxidizing agent was destroyed by the addition of a few drops of methanol. The reaction mixture was concentrated under vacuum and the product isolated by partition between methylene dichloride–water. The residue obtained from the methylene dichloride fraction when recrystallized from ethyl acetate–Skellysolve B weighed 300 mg. (30%) and melted at 273–275°. Recrystallization from the same solvents gave an analytical sample, m.p. 277–278.5°.

Anal. Calcd. for $C_{24}H_{29}FO_5$: C, 69.21; H, 7.07; F, 4.56. Found: C, 69.44; H, 7.36; F, 4.5.

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(5) Presented by E. M. Glenn, S. L. Richardson, B. J. Bowman, and S. C. Lyster at CCNSC Symposium titled, "Biologic Activities of Steroids in Relation to Cancer," Vergennes, Vt., Sept. 27–Oct. 2, 1959. (Abstracts of papers to be published.)

(6) The authors are indebted to G. E. VandenBerg of these laboratories for assistance in the preparation of these compounds.

(7) A saturated hydrocarbon fraction, b.p. 60–71°.

(8) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

The Preparation of 16-Methyl-Δ[16]-steroids Containing Ring C Substituents

SEYMOUR BERNSTEIN AND J. P. JOSEPH

Received March 9, 1960

Research in this laboratory on C^{14}-substituted steroids[1] has been extended to include methyl substituents. In view of the recent publications,[2] especially that by Slates and Wendler,[2g] on C^{16}-methyl steroids we wish to report here on our work in this area. This note describes the preparation of 16-methyl-Δ[16]-steroids which contain substituents in the C-ring, in particular, on 21-acetoxy-9α-fluoro-11β-hydroxy-16-methyl-4,16-pregnadiene-3,-20-dione (VII).

Following the procedure of Wettstein[3] 21-acetoxy-4,9(11),16-pregnatriene-3,20-dione[4] (Ia) on reaction with excess diazomethane gave 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4,9(11)-pregnadiene-3,20-dione (IIa).[5] A band attributable to —N=N—stretching[6] was observed at 1565 cm.$^{-1}$ in this and all the other pyrazolino-steroids herein prepared. Thermal decomposition of IIa readily afforded 21-acetoxy-16-methyl-4,9(11),16-pregnatriene-3,20-dione (IIIa).

N-bromoacetamide-perchloric acid treatment of 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4,9(11)-bromohydrin IV. This was converted, without further purification, in refluxing methanolic potassium acetate directly into 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-9β,11β-epoxy-4-pregnane-3,20-dione(V).

(1) S. Bernstein, R. H. Lenhard, W. S. Allen, M. Heller, R. Littell, S. M. Stolar, L. I. Feldman, R. H. Blank, *J. Am. Chem. Soc.*, **78**, 5693 (1956), and subsequent papers.

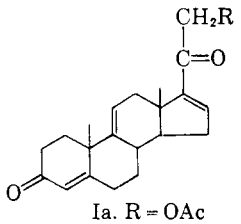
(2) (a) G. E. Arth, D. B. Johnston, J. Fried, W. W. Spooncer, D. R. Hoff, and L. H. Sarett, *J. Am. Chem. Soc.*, **80**, 3160 (1958). (b) G. E. Arth, J. Fried, D. B. Johnston, D. R. Hoff, L. H. Sarett, R. H. Silber, H. C. Stoerk, and C. A. Winter, *J. Am. Chem. Soc.*, **80**, 3161 (1958). (c) D. Taub, R. D. Hoffsommer, H. L. Slates, and N. L. Wendler, *J. Am. Chem. Soc.*, **80**, 4435 (1958). (d) E. P. Oliveto, R. Rausser, A. L. Nussbaum, W. Gebert, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4428 (1958). (e) E. P. Oliveto, R. Rausser, L. Weber, A. L. Nussbaum, W. Gebert, C. T. Coniglio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 4431 (1958). (f) E. P. Oliveto, R. Rausser, H. L. Herzog, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *J. Am. Chem. Soc.*, **80**, 6687 (1958). (g) H. L. Slates and N. L. Wendler, *J. Am. Chem. Soc.*, **81**, 5472 (1959).

(3) A. Wettstein, *Helv. Chim. Acta*, **27**, 1803 (1944).

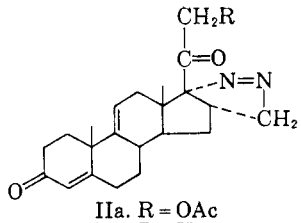
(4) W. S. Allen and S. Bernstein, *J. Am. Chem. Soc.*, **78**, 1909 (1956).

(5) This system of nomenclature for pyrazoline derivatives is according to that employed by G. P. Mueller and B. Riegel, *J. Am. Chem. Soc.*, **76**, 3686 (1954) for similar compounds.

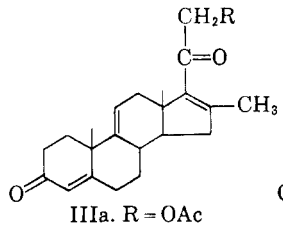
(6) R. N. Jones and C. Sandorfy, *Techniques of Organic Chemistry*, **9**, 545 (1956).



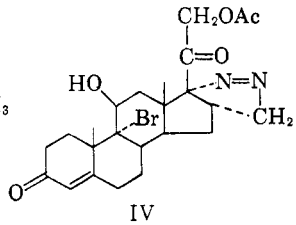
Ia. R = OAc
Ib. R = H



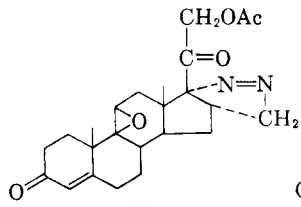
IIa. R = OAc
IIb. R = H



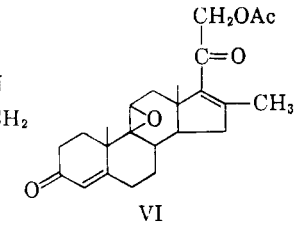
IIIa. R = OAc
IIIb. R = H



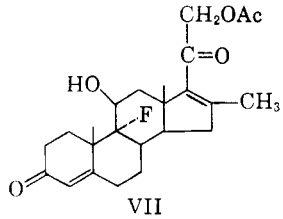
IV



V

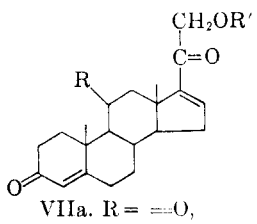


VI

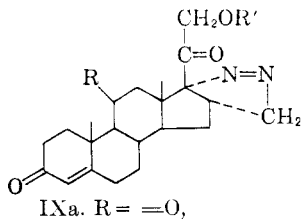


VII

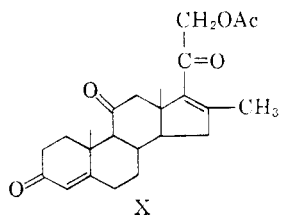
An attempt to treat the epoxide V with anhydrous hydrogen fluoride was unsuccessful as the pyrazoline ring was attacked by the reagent. Accordingly, thermal decomposition of V was accomplished first to give 21-acetoxy-9β,11β-epoxy-16-methyl-4,16-pregnadiene-3,20-dione (VI) as a gum which then on treatment with hydrogen fluoride gave, after chromatography, crystalline 21-acetoxy-9α-fluoro-11β-hydroxy-16-methyl-4,16-pregnadiene-3,20-dione(VII).



VIIa. R = =O, R' = Ac
VIIIb. R = OH(β), H; R' = H



IXa. R = =O, R' = Ac
IXb. R = OH(β), H; R' = H



X

By the same procedure[3] employed above, the pyrazoline derivatives (IXa) and (IXb) of 21 acetoxy-4,16- pregnadiene - 3,11,20 - trione[7] (VIIIa) and 11β,21-dihydroxy-4,16-pregnadiene - 3,20 - di - one[7] (VIIIb) were formed. The former was converted to 21-acetoxy-16-methyl-4,16-pregnadiene-3,11,20-trione (X) by pyrolysis. In a similar sequence (Ib$\rightarrow$IIb$\rightarrow$IIIb) 16-methyl-4,9(11),16-pregnatriene-3,20-dione(IIIb) was obtained from 4,9-(11),16-pregnatriene-3,20-dione[8](Ib).

EXPERIMENTAL

All melting points are uncorrected. The optical rotations are for chloroform solutions and were determined at 25°. The ultraviolet spectra were determined in ethanol unless otherwise noted; the infrared spectra were determined in a potassium bromide disk. The petroleum ether used boiled at 60–70° (Skellysolve B).

21-Acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4,9(11)-pregnadiene-3,20-dione (IIa). Forty grams of a 50% potassium hydroxide solution and 40 ml. of ether were cooled in a separatory funnel at 5°. To this 1.84 g. of *N*-methyl-*N*-nitroso-*N'*-nitroguanidine was added portionwise with gentle agitation until solution was complete, and then the mixture was allowed to remain for an additional 15 min. The two layers were separated, and the ether layer was dried over sodium hydroxide pellets for 0.5 hr. and carefully decanted into a dry flask. A solution of 184 mg. of 21-acetoxy-4,9(11),-16-pregnatriene-3,20 dione (Ia) in 20 ml. of methylene chloride was added to the ether solution and the mixture was allowed to remain at room temperature for 4 days (loosely stoppered flask). On spontaneous evaporation a mixture of solid and gum remained. One crystallization from acetone–petroleum ether gave 191 mg. of yellow crystals (IIa), m.p. 158–159° dec.

A sample was dissolved in methylene chloride and filtered through magnesium silicate and evaporated to give white crystals, IIa, m.p. 164–166° dec. Recrystallization did not alter the melting point; λ_{max} 237–238 mμ (ϵ 17,900); ν_{max} 1760, 1725, 1675, 1615, 1560, 1225, 1075 cm.$^{-1}$; $[\alpha]_D$ +64°.

Anal. Calcd. for $C_{24}H_{30}N_2O_4$ (410.50): C, 70.22; H, 7.37; N, 6.82. Found: C, 70.31; H, 7.49; N, 7.08.

21-Acetoxy-16-methyl-4,9(11),16-pregnatriene-3,20-dione (IIIa). Crude 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4,9-(11)-pregnadiene-3,20-dione (IIa) (206 mg.) was heated at 175° under reduced pressure (0.1 mm.) for 2 hr. A dark glass remained after cooling which was dissolved in acetone, and the solution was filtered through magnesium silicate and filter aid. The filtrate was evaporated *in vacuo* to give 203 mg. of a solid (IIIa), m.p. 133–139°. Three crystallizations from acetone–petroleum ether raised the melting point to 140–142.5°; λ_{max} 241 mμ (ϵ 22,600); ν_{max} 1755, 1675, 1640, 1605, 1226, 1080, 1035 cm.$^{-1}$; $[\alpha]_D$ +124°.

Anal. Calcd. for $C_{24}H_{30}O_4$ (382.48): C, 75.36; H, 7.91. Found: C, 75.55; H, 8.16.

21-Acetoxy-9α-bromo-11β-hydroxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,20-dione (IV). A solution of 90 mg. of 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4,9(11)-pregnadiene-3,20-dione (IIa) in 5 ml. of peroxide-free dioxane and 1 ml. of water was cooled to 15°. There was then added 42

(7) W. S. Allen and S. Bernstein, *J. Am. Chem. Soc.*, **77**, 1028 (1955).

(8) S. A. Szpilfogel and V. Gerris, *Rec. trav. chim.*, **74**, 1462 (1955), and S. Bernstein, J. J. Brown, L. I. Feldman, and N. E. Rigler, *J. Am. Chem. Soc.*, **81**, 4596 (1959).

mg. of *N*-bromoacetamide and 0.20 ml. of 10% perchloric acid. After 15 min. at 15–20°, the reaction was quenched with saturated sodium sulfite and extracted with methylene chloride. The methylene chloride solution was washed with water, dried over magnesium sulfate, and evaporated *in vacuo* at room temperature. The resulting white solid (110 mg.) was recrystallized twice from acetone–petroleum ether to give 23 mg. of crystals, IV, m.p. 172.5–174° dec.; $\lambda_{max}^{methanol}$ 242 mμ (ε 17,700); ν_{max} 3450, 1760, 1738, 1650, 1552, 1235, 1085, 1040 cm.$^{-1}$; $[\alpha]_D$ +252°.

Anal. Calcd. for $C_{24}H_{31}BrN_2O_5$ (507.43): C, 56.80; H, 6.16; Br, 15.75; N, 5.52. Found: C, 56.48; H, 6.32; Br, 15.97; N, 5.83.

21-Acetoxy-16α,17α-[3,1-(1-pyrazolino)]-9β,11β-epoxy-4-pregnene-3,20-dione (V). Crude 21-acetoxy-9α-bromo-11β-hydroxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,20-dione (IV, 2.8 g.) was dissolved in 225 ml. of refluxing methanol containing 6 g. of dry potassium acetate. After 3 hr. the solution was cooled and evaporated *in vacuo*. After trituration of the residue with cold water the product, V, was collected by filtration, dissolved in methylene chloride, dried over magnesium sulfate, and filtered through magnesium silicate. Evaporation of the methylene chloride provided a gum which crystallized from acetone–petroleum ether to give 1.0 g. of crystalline epoxide V, m.p. 163–166° dec. A 100-mg. portion was recrystallized twice from acetone–petroleum ether to give 30 mg., m.p. 173–175° dec.; λ_{max} 241 mμ (ε 16,000); ν_{max} 1765, 1740, 1675, 1634, 1560, 1230, 1085 cm.$^{-1}$; $[\alpha]_D$ +13°.

Anal. Calcd. for $C_{24}H_{30}N_2O_5$ (426.50): C, 67.58; H, 7.09; N, 6.57. Found: C, 67.51; H, 7.28; N, 6.42.

21-Acetoxy-9β, 11β-epoxy-16-methyl-4, 16-pregnadiene-3, 20-dione (VI). 21-Acetoxy-16α,17α-[3,1-(1-pyrazolino)]-9β,-11β-epoxy-4-pregnene-3,20-dione (V) (200 mg.) was heated under reduced pressure (0.5 mm.) in an oil bath (temperature 140–170°). After gas evolution was complete, the cooled mass was dissolved in methylene chloride and filtered through magnesium silicate. The filtrate was evaporated *in vacuo* to give 119 mg. of VI was a yellow gum; λ_{max} 244 mμ (ε 21,500); ν_{max} 1755, 1680, 1625, 1230, 1075 cm.$^{-1}$

21-Acetoxy-9α-fluoro-11β-hydroxy-16-methyl-4,16-pregnadiene-3,20-dione (VII). A solution of 1.9 g. of 21-acetoxy-9β,11β-epoxy-16-methyl-4,16-pregnadiene-3,20-dione (VI) in 12.6 ml. of methylene chloride was cooled to −60° and added to a previously cooled (−60°) solution of 7 ml. of tetrahydrofuran, 2.5 ml. of methylene chloride, and 3.5 ml. of anhydrous hydrogen fluoride in a polyethylene flask. After 3.5 hr. at −5° the deep red solution was poured carefully into excess sodium bicarbonate solution. The methylene chloride layer was separated and washed with water until neutral, dried over magnesium sulfate, and evaporated *in vacuo* to give a glass (1.9 g.). A solution of this glass in benzene was added to a column of 100 g. of silica gel (>200 mesh) and was chromatographed successively with benzene, benzene-ether solution, and absolute ether. Elution with absolute ether afforded 1.2 g. of VII as white crystals, m.p. 175–179°. After two recrystallizations from acetone–petroleum ether the melting point was raised to 182–184°; $\lambda_{max}^{methanol}$ 241 mμ (ε 23,000); ν_{max} 3450, 1748, 1665, 1635, 1590, 1225, 1073, 1040 cm.$^{-1}$; $[\alpha]_D$ +119°.

Anal. Calcd. for $C_{24}H_{31}FO_5$ (418.48): C, 68.88; H, 7.47; F, 4.54. Found: C, 68.56; H, 7.63; F, 4.35.

21-Acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,11,20-trione (IXa). Twenty grams of a 50% potassium hydroxide solution and 200 ml. of methylene chloride were cooled in a separatory funnel immersed in an ice bath. To this was added portionwise 20 g. of nitrosomethylurea with gentle agitation until solution was complete, and then allowed to remain for an additional 15 min. The two layers were separated and the methylene chloride solution was dried over sodium hydroxide pellets for 0.5 hr. and carefully decanted into a dry flask. A solution of 2.8 g. of 21-acetoxy-4,16-pregnadiene-3,11,20-trione (VIIIa) in 28 ml. of methylene chloride was added to the diazomethane solution and then allowed to remain at room temperature for 18 hr. in a loosely stoppered flask. The methylene chloride was evaporated under a stream of air, and the resulting solid was crystallized from acetone–petroleum ether to give 2.2 g. of 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,11,20-trione (IXa), m.p. 182–183° dec. The melting point did not change on further recrystallization; λ_{max} 236 mμ (ε 16,600); ν_{max} 1765, 1740, 1715, 1685, 1625, 1555, 1235, 1220 cm.$^{-1}$; $[\alpha]_D$ +184°.

Anal. Calcd. for $C_{24}H_{30}N_2O_5$ (426.50): C, 67.58; H, 7.09; N, 6.57. Found: C, 67.10, 67.41; H, 7.30, 7.24; N, 6.86.

21-Acetoxy-16-methyl-4,16-pregnadiene-3,11,20-trione (X). In an oil bath at 180–185°, 300 mg. of 21-acetoxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnen-3,11,20-trione (IXa) was heated until gas evolution ceased. The resulting glass was cooled and dissolved in methylene chloride. After filtration through filter aid, the methylene chloride was removed *in vacuo*, and the residue crystallized from acetone–petroleum ether to give 203 mg. of 21-acetoxy-16-methyl-4,16-pregnadiene-3,11,20-trione (X), m.p. 168–172°. Two further recrystallizations of a sample raised the melting point to 174–176°; λ_{max} 240 mμ (ε 23,500); ν_{max} 1755, 1705, 1675, 1615, 1380, 1225, 1075 cm.$^{-1}$; $[\alpha]_D$ +178°.

Anal. Calcd. for $C_{24}H_{30}O_5$ (398.48): C, 72.33; H, 7.59. Found: C, 72.14; H, 7.80.

11β,21-Dihydroxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,20-dione (IXb). To a dry diazomethane solution prepared as described previously from 3.3 g. of nitrosomethylurea, a solution of 500 mg. of 21-acetoxy-11β-hydroxy-4,16-pregnadiene-3,20-dione (VIIIb) in 2 ml. of methylene chloride was added. After 18 hr. the methylene chloride and excess diazomethane were removed by evaporation in an air stream, and the residue was crystallized from acetone–petroleum ether to give 460 mg. of 11β,21-dihydroxy-16α,17α-[3,1-(1-pyrazolino)]-4-pregnene-3,20-dione (IXb), m.p. 156–159° dec. Recrystallization from the same solvents raised the melting point to 165–167° dec.; λ_{max} 239 mμ (ε 15,700), 280 mμ (ε 280); ν_{max} 3450, 1725, 1675, 1635, 1555, 1100, 1045 cm.$^{-1}$; $[\alpha]_D$ +173°.

Anal. Calcd. for $C_{22}H_{30}N_2O_4$ (386.48): C, 68.37; H, 7.82; N, 7.25. Found: C, 68.48; H, 8.16; N, 7.31.

16α,17α-[3,1-(1-Pyrazolino)]-4,9(11)-pregnadiene-3,20-dione (IIb). A solution of 155 mg. of 4,9(11),16-pregnatriene-3,20-dione (Ib) in 20 ml. of methylene chloride was added to a dry solution of diazomethane in ether (25 moles diazomethane per mole steroid). After 4 days at room temperature, evaporation in a stream of air gave a tacky solid which was dissolved in methylene chloride, the solution passed through magnesium silicate, and evaporated to give 89 mg. of crystalline product (IIb), m.p. 170–171° dec. Recrystallization from ether did not change the melting point; λ_{max} 237 mμ (ε 19,700); ν_{max} 1710, 1665, 1615, 1550 cm.$^{-1}$; $[\alpha]_D$ +138°.

Anal. Calcd. for $C_{22}H_{28}N_2O_2$ (352.46): C, 74.96; H, 8.01; N, 7.95. Found: C, 74.96; H, 8.22; N, 8.05.

16-Methyl-4,9(11),16-pregnatriene-3,20-dione (IIIb). The pyrazoline derivative IIb (100 mg.) was heated at atmospheric pressure in an oil bath at 170–180° until gas evolution was complete. The remaining gum was dissolved in methylene chloride and the solution was filtered through magnesium silicate. The filtrate was evaporated leaving a gum which gave 75 mg. of crystals, m.p. 135–138°, on trituration with ether. Two further recrystallizations from petroleum ether gave 15 mg. of IIIb, m.p. 142–144°; $\lambda_{max}^{methanol}$ 241 mμ (ε 22,900); ν_{max} 1668, 1645, 1610 cm.$^{-1}$; $]\alpha]_D$ +139°.

Anal. Calcd. for $C_{22}H_{28}O_2$ (324.44): C, 81.44; H, 8.70. Found: C, 81.58; H, 9.07.

Acknowledgment. We wish to thank Louis M. Brancone and associates for the analyses, and William Fulmor and associates for the infrared and

ultraviolet absorption spectra and optical rotation data.

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An Unexpected Reaction of 3,5-Di-*O*-benzoyl-2-deoxy-D-ribose

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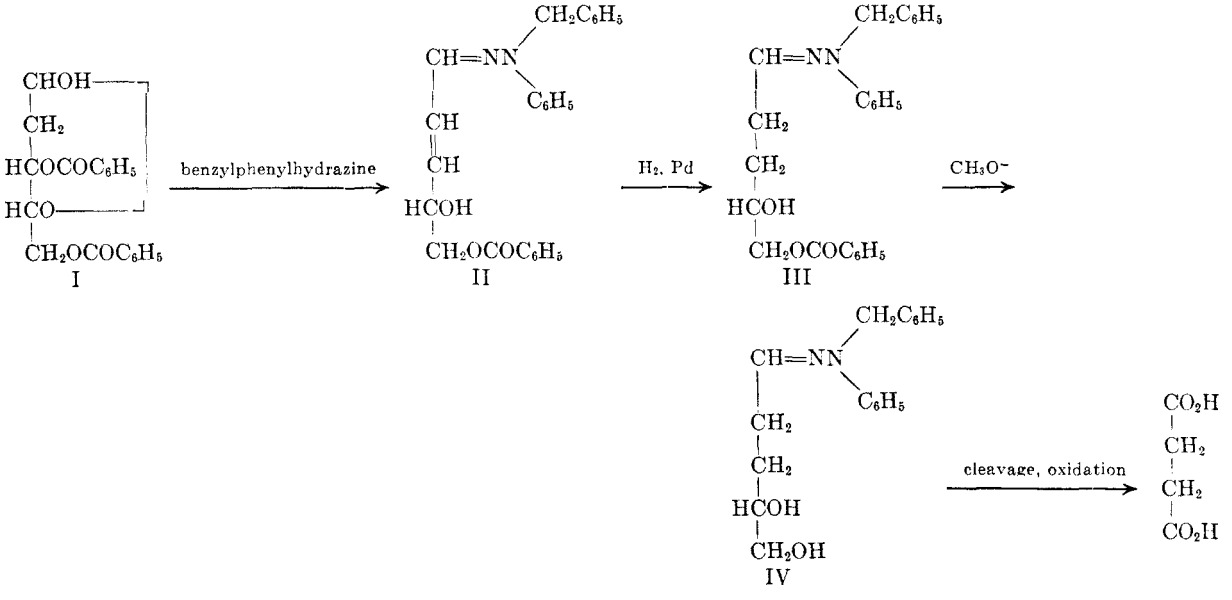
Relative to a synthetic program in the 2-deoxy-D-ribose series, we have prepared crude, amorphous 3,5-di-*O*-benzoyl-2-deoxy-D-ribose. An attempt was made to characterize this substance by converting it in the usual manner to a benzylphenylhydrazone. A crystalline hydrazone was indeed obtained, but its analysis revealed that loss of benzoic acid had accompanied the reaction. The product was shown to be 5-*O*-benzoyl-D-*glycero*-4,5-dihydroxy-2-pentenal benzylphenylhydrazone by reduction of the double bond, cleavage of substituents, and oxidation to succinic acid.



The unsaturated hydrazone was obtained readily in the presence of 1-benzyl-1-phenylhydrazine in aqueous ethanol, and somewhat more slowly with the hydrazine and acetic acid in aqueous ethanol. This unexpected, facile β-elimination of an ester group may be related to certain difficulties we have encountered in attempting to apply routine reaction conditions for syntheses based on 2-deoxy-D-ribose.

Acetylation of 3,5-di-*O*-benzoyl-2-deoxy-D-ribose in pyridine proceeded normally to give a crystalline monoacetate. This product conceivably could be either 4-*O*-acetyl-3,5-di-*O*-benzoyl-*aldehydo*-2-deoxy-D-ribose or the isomeric 1-*O*-acetyl-3,5-di-*O*-benzoyl-2-deoxy-D-ribose. Since the substance shows no mutarotation in USP chloroform, which contains ethanol, it has been assigned the latter structure.

EXPERIMENTAL

Methyl 3,5-di-O-benzoyl-2-deoxy-α,β-D-ribofuranosides. Three grams of 2-deoxy-D-ribose[1] in 60 ml. of absolute methanol was treated with 4.5 ml. of 0.14*N* hydrogen chloride in methanol and the resulting glycosidation was followed polarimetrically.[2] After 15 min., when a maximum positive specific rotation of +39.6° based on starting sugar had been reached, the solution was passed through a column containing 10 ml. of Duolite A-4 resin (wet with methanol) onto 2 ml. of pyridine. The solution was concentrated to dryness at reduced pressure and the resulting sirup was dried in high vacuum over phosphorus pentoxide. The dried sirup was dissolved in 33 ml. of dry pyridine and treated at 0° with 10.5 ml. of benzoyl chloride. After 1 day at room temperature, several drops of water were added and the solution was concentrated to a thin sirup in a stream of dry air. The residue was taken up in chloroform and washed successively with cold 3% sulfuric acid, water, saturated sodium bicarbonate solution, and water. After drying over sodium sulfate, the solution was concentrated at reduced pressure to a sirup (8.4 g.).

Fractional distillation of products prepared similarly gave about 70% of distillate, b.p. 135–138° (vapor temp.) at 10^{-4} mm., n_D^{25} 1.5456 to 1.5459, $[\alpha]_D^{33}$ +41° to +43° (*c* 1.5 in chloroform) and methoxyl content 8.47% to 8.65% (theory 8.71%). Qualitative paper chromatography, and the hydrolysis experiment described below, indicated such

(1) J. C. Sowden, *J. Am. Chem. Soc.*, **76**, 3541 (1954).
(2) R. E. Deriaz, W. G. Overend, M. Stacey, and L. F. Wiggins, *J. Chem. Soc.*, 2836 (1949).