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2. Katsumi Tanabe, Rinji Takasaki, and Ryozo Hayashi: Steroid Series. IV.[1) Ozonization of Cyclic 3-(Ethylene Acetal) of Δ^4-3-oxosteroids.

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As described in a previous paper[1) of this series, it appears generally difficult to prepare a normal ozonide of cholesterol and cholesterol acetate under usual conditions, whereas Dauben and Fonken[2) described a high yield isolation of 5-oxo-5,6-secocholestane-6-carboxylic acid by usual ozonization of cholest-5-ene, followed by oxidation of the product with hydrogen peroxide. It would thus indicate that some substituent at C-3 position of Δ^5-steroid exerts a remarkable effect on the mode of ozonolysis reaction.

In this connection it seems of interest to investigate the ozonolysis of double bond at C-5 position in steroid bearing ethylene acetal group at C-3 position. In this paper will be described observations on the action of ozone on cyclic-3-ethylene acetals of cholest-4-en-3-one, pregn-4-ene-3,20-dione, and androst-4-ene-3,17-dione.

Cyclic-3-ethylene acetal of cholest-4-en-3-one[3) (Ia) in dichloromethane was treated with ozonized air under chilling with dry ice-acetone mixture until the solution had turned light blue, absorbing about one molar equivalent of ozone. Reduction of the product with zinc dust and acetic acid afforded a vitreous substance, which was chromatographed on acid-washed alumina. The first fraction eluted with benzene gave 5,6β-epoxy-5β-cholestan-3-one 3-(ethylene acetal)(IIa) of m.p. 126~127°, $[\alpha]_D$ +12.5°, in 53.5% yield. The identity was confirmed with an authentic sample prepared by the method of Petrow, *et al.*[4) by a mixed melting point determination and infrared comparison.

The second fraction eluted with the same solvent furnished a syrupy material in 32.8% yield, which, although it failed to crystallize, showed absorption bands at 3520(OH), 2730, 1725(CHO), and 1110(acetal) cm^{-1}, and gave a semicarbazone of m.p. 224.5°(decomp.), corresponding to $C_{30}H_{51}O_4N_3$. This substance, as will be shown in a succeeding paper,[5) was converted into 3-oxo-5-hydroxy-B-nor-5β-cholestane-6β-carboxylic acid (V) on oxidation with chromium trioxide in acetic acid, whose structure was then rigorously established. From these observations the structure, 5-hydroxy-6β-formyl-B-nor-5β-cholestan-3-one 3-(ethylene acetal)(IIIa) was assigned to this substance. The more stable quasi-equatorial β-configuration assigned to C-6 was made from the mode of its preparation involving an aldol condensation of a probable intermediate, 5-oxo-5,6-secocholestan-6-al 3-(ethylene acetal)[1) (VI).

Pregn-4-ene-3,20-dione bis(ethylene acetal)[6) (Ib) was ozonized in a similar fashion followed by reduction of the resulting product with zinc dust and acetic acid. The ozonolysis reaction mixture, on chromatography over acid-washed alumina, afforded 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal)(IIb) of m.p. 158.5~160°, $[\alpha]_D$ +68°, from benzene eluate in 55.5% yield, and the fraction eluted with a mixture of benzene-ether (1:1) gave 5-hydroxy-6β-formyl-B-nor-5β-pregnane-3,20-dione 3-(ethylene acetal)(IIIb), m.p. 144° (decomp.), $[\alpha]_D$ +52.2°, in 31.5% yield. The structure (IIIb) was indicated by its composition and infrared absorption bands at 3536(OH), 2730, 1725(CHO), 1710(20-CO), and 1107

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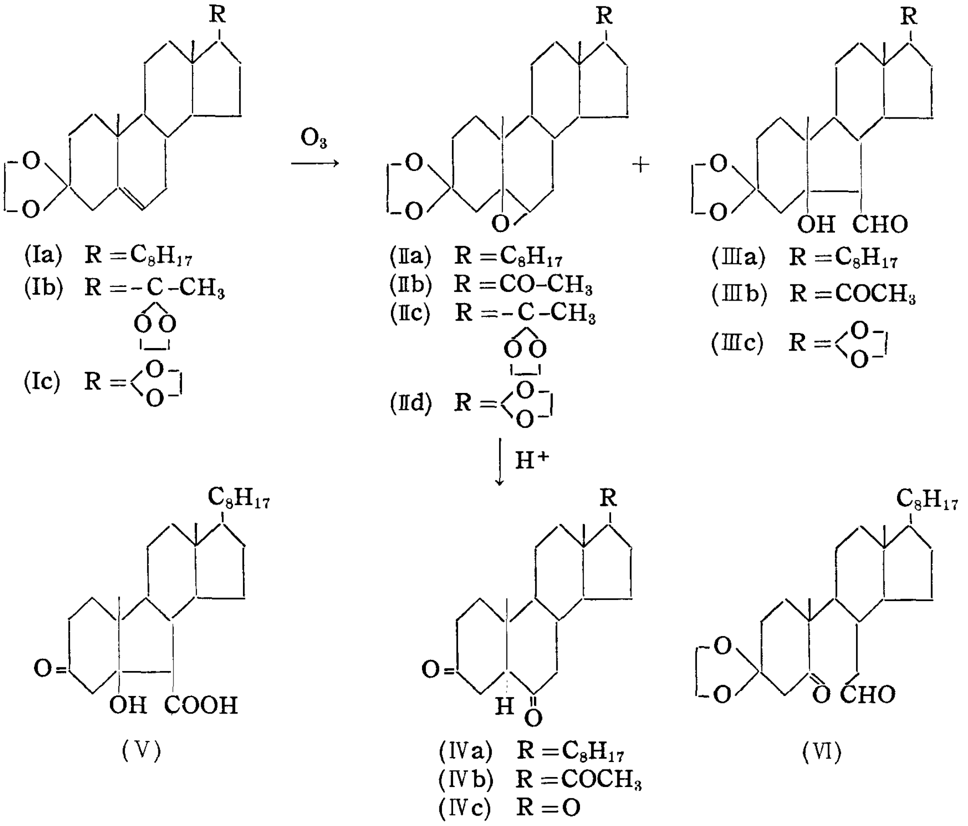
1) Part III: This Bulletin **9**, 1 (1961).
2) W.G. Dauben, G.J. Fonken: J. Am. Chem. Soc., **78**, 4736 (1956).
3) U.S. Pat. 2,378,918.
4) G. Cooley, B. Ellis, D.N. Kirk, P.V. Petrow: J. Chem. Soc., **1957**, 4112.
5) Part V: This Bulletin, **9**, 12 (1961).
6) H.J. Dauben, J.R.B. Löken, H.J. Ringold: J. Am. Chem. Soc., **76**, 1359 (1954).



(Ia) $R=C_8H_{17}$
(Ib) $R=-C-CH_3$
(Ic) $R=$
(IIa) $R=C_8H_{17}$
(IIb) $R=CO-CH_3$
(IIc) $R=-C-CH_3$
(IId) $R=$
(IIIa) $R=C_8H_{17}$
(IIIb) $R=COCH_3$
(IIIc) $R=$
(V)
(IVa) $R=C_8H_{17}$
(IVb) $R=COCH_3$
(IVc) $R=O$
(VI)

(acetal) cm^{-1}. Both (IIb) and (IIIb) showed a dark-violet coloration to Adachi's methyl ketone test,$^{7)}$ indicating that partial hydrolysis of one of the two acetal groups had occurred at C-20 position.

When the ozonized mixture of (Ib) was reduced with zinc dust and water instead of acetic acid, 5,6β-epoxy-5β-pregnane-3,20-dione bis(ethylene acetal) (IIc) of m.p. 165.5~166°, with $[\alpha]_D$ $+12.8°$, in addition to 22% yield of β-epoxide 3-(ethylene acetal) (IIb), was also separated in 27.3% yield by chromatography over acid-washed alumina.

In order to confirm the structure of the 5β,6β-epoxides obtained as above, epoxidation of (Ib) with monoperphthalic acid was conducted and the product was separated over alumina. The first fraction eluted with benzene gave 5,6β-epoxy-5β-pregnane-3,20-dione bis(ethylene acetal) (IIc), m.p. 166~167°, $[\alpha]_D$ $+11.8°$,[*2] in 31% yield, and the second fraction eluted with the same solvent afforded 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb), m.p. 158.5~160°, $[\alpha]_D$ $+67°$, in 1.83% yield. Finally, 5,6α-epoxy-5α-pregnane-3,20-dione bis(ethylene acetal) (VII) of m.p. 181~182°, $[\alpha]_D$ $-53°$,[*3] was isolated in 36.8% yield from the eluate with a mixture of benzene-ether (1:1).

Recently, Bowers, *et al.*$^{8)}$ reported the same epoxidation reaction of (Ib) and described essentially the same results except that they isolated 5,6α-epoxy-5α-pregnane-3,20-dione 3-(ethylene acetal) of m.p. 197~199°, $[\alpha]_D$ $+11°$, instead of 5β,6β-epoxide 3-(ethylene acetal) (IIb) isolated in the present experiment.

The samples of (IIb) and (IIc) obtained on oxidation with ozone were identical in all respects with those prepared by peracid oxidation.

On similar treatment of androst-5-ene-3,17-dione bis(ethylene acetal)$^{9)}$ (Ic) with ozone

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[*2] Reported$^{8)}$ m.p. 161~163°, $[\alpha]_D$ ±0°.
[*3] Reported$^{8)}$ m.p. 183~185°, $[\alpha]_D$ $-50°$.
7) J. Adachi : Nippon Kagaku Zasshi, **71**, 566 (1950).
8) A. Bowers, L.C. Ibanez, H.J. Ringold : Tetrahedron, **7**, 138 (1959).
9) H.L. Herzog, M.A. Jevnik, M.E. Tully, E.B. Hershberg : J. Am. Chem. Soc., **75**, 4425 (1953).

followed by zinc dust reduction, it gave 5,6β-epoxy-5β-androstane-3,17-dione bis(ethylene acetal) (IId), m.p. 137~138°, [α]$_D$ −8.1°, and 5-hydroxy-6β-formyl-B-nor-5β-androstane-3,17-dione bis(ethylene acetal) (IIIc) of m.p. 99~102°, with [α]$_D$ +6.6°, in 40.3% and 29.1% yield, respectively. The structure assigned to (IId) was based on its analytical values, infrared absorption (no carbonyl band but a broad band at 1110 cm^{-1} attributable to acetal groups), and analogy with the cholestane and pregnane series. The infrared spectrum of (IIIc) exhibited absorption bands at 3520 (OH), 2730, 1725 (CHO), and 1112 (acetal) cm^{-1}, and its composition ($C_{21}H_{34}O_6$) and the mode of its preparation analogous to the other series were the bases on which the structure of (IIIc) was assigned.

Treatment of 5,6β-epoxysteroid 3-(ethylene acetal) with acid was found to result in the formation of 3,6-dioxosteroid with 5α-hydrogen. Thus, (IIa) was converted to 5α-cholestane-3,6-dione (IVa) by treatment with methanolic sulfuric acid or with boron trifluoride-diethyl ether in benzene. Conversion of (IIb) and (IIc) into 5α-pregnane-3,6,20-trione (IVb), and (IId) into 5α-androstane-3,6,17-trione (IVc) could be effected in a similar manner.

Formation of 5β,6β-epoxide of cholesterol acetate on ozonization was described also in the preceding paper[1] and this appears to be the first example of a direct formation of epoxide by the action of ozone on steroidal double bond. Such a reaction, however, is not without example in cases where the double bonds are sterically hindered on one side.[10] Several similar epoxidation reactions with ozone can also be found in the triterpene series.[11]

Experimental[*4]

Ozonization of Cholest-5-en-3-one 3-(ethylene acetal) (Ia)—A solution of 7.7 g. of cholest-5-en-3-one 3-(ethylene acetal) (Ia) in 800 cc. of CH_2Cl_2 was ozonized by passing a stream of ozonized air (0.6 mmole of O_3/min.) at about −50° by chilling with dry ice-Me_2CO mixture until the solution turned pale blue (requiring ca. 48 min.). Zn dust (15 g.) and AcOH (60 cc.) were added to the reaction mixture and the solution was stirred for 3 hr. at room temperature. After filtration of inorganic substance, the filtrate was washed with H_2O and 2% $NaHCO_3$ solution, and dried over Na_2SO_4. Evaporation of the solvent at a reduced pressure gave a colorless syrup which was chromatographed on acid-washed alumina (240 g.). Elution with benzene afforded 4.33 g. of a colorless solid of m.p. 125~127° (53.5%), which was recrystallized from benzene-MeOH to give 5,6β-epoxy-5β-cholestan-3-one 3-(ethylene acetal) (IIa) as white needles, m.p. 126~127°, $[\alpha]_D^{28}$ +12.5° (c=1.12). *Anal.* Calcd. for $C_{29}H_{48}O_3$: C, 78.32; H, 10.88; O, 10.79. Found: C, 78.29; H, 10.51; O, 10.50. IR ν_{max}^{KBr} cm^{-1}: 1098 (acetal). This showed no depression of m.p. on admixture with an authentic sample prepared by the method of Petrow, *et al.*[4] and infrared spectra of the two compounds agreed completely.

Further elution with the same solvent gave a pale yellow syrupy substance of 5-hydroxy-6β-formyl-5β-cholestan-3-one 3-(ethylene acetal) (IIIa) which failed to crystallize. Yield, 2.7 g. (32.8%). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3520 (OH), 2730, 1725 (CHO), 1110 (acetal).

Semicarbazone: Needles (from EtOH), m.p. 224.5° (decomp.). *Anal.* Calcd. for $C_{30}H_{51}O_4N_3$: C, 69.63; H, 9.86; N, 8.12. Found: C, 69.81; H, 9.82; N, 8.11.

5α-Cholestane-3,6-dione (IVa)—(i) A solution of 300 mg. of 5,6β-epoxy-5β-cholestan-3-one 3-(ethylene acetal) (IIa) in 70 cc. of MeOH and 4 cc. of 8% (v/v) H_2SO_4 was refluxed for 1 hr., diluted with H_2O, and extracted with Et_2O. The extract was washed with H_2O and dried. Evaporation of the solvent gave a crystalline material, which was recrystallized from benzene-petr. ether to yield 260 mg. of 5α-cholestane-3,6-dione (IVa), m.p. 168.5~170°, $[\alpha]_D^{23}$ +3.7° (c=1.2). *Anal.* Calcd. for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.60; H, 11.39. IR ν_{max}^{KBr} cm^{-1}: 1712 (six-membered ring ketone).

This proved identical by mixed m.p. determination and infrared spectra with the sample prepared by the method of Ross.[12]

[*4] All m.p.s are uncorrected. Rotations were measured in $CHCl_3$.

10) P.S. Bailey: Chem. Revs., **58**, 945 (1958).

11) *a*) L. Ruzicka, O. Jeger, J. Redel, E. Volli: Helv. Chim. Acta, **28**, 199 (1945); *b*) D.H.R. Barton, C.J.W. Brooks: J. Chem. Soc., **1951**, 257; *c*) D.H.R. Barton, E. Seoane: *Ibid.*, **1956**, 4150; *d*) D.H.R. Barton, P. DeMayo, J.C. Orr: *Ibid.*, **1958**, 2239.

12) W.C.J. Ross: J. Chem. Soc., **1946**, 737.

(ii) A solution of 500 mg. of (IIa) in 12 cc. of benzene and 0.5 cc. of BF_3-Et_2O was kept at room temperature for 5 hr. The mixture was diluted with H_2O and extracted with Et_2O. The extract was washed with 5% $NaHCO_3$ solution and H_2O, and dried. Evaporation of the solvent afforded a brownish residue, which was crystallized from petr. ether (b.p. 60~80°) to give 112 mg. of solid with m.p. 163~168°. Recrystallization from the same solvent gave colorless plates of m.p. 170~171°, which showed no depression on admixture with the authentic sample of 5α-cholestane-3,6-dione (IVa).

Ozonization of Pregn-4-ene-3,20-dione Bis(ethylene acetal) (**Ib**)—(i) Ozonized air (0.6 mmole of O_3/min.) was passed through a solution of 5.0 g. of pregn-4-ene-3,20-dione bis(ethylene acetal) (Ib) in 500 cc. of CH_2Cl_2 for 30 min. at about −50°. To the solution was added 10 g. of Zn dust and 40 cc. of AcOH, and the mixture was stirred for 2 hr. at room temperature. After filtration of inorganic material, the filtrate was washed with H_2O and 2% $NaHCO_3$ solution, and dried. After treatment as described above, a colorless syrup was obtained, which was chromatographed on 250 g. of acid-washed alumina. Elution with benzene afforded 2.58 g. (55.5%) of 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb), m.p. 156~158°, raised by recrystallization from benzene-petr. ether to 158.5~160°, $[\alpha]^{23}_{D}$ +68° (c=1.0), undepressed on admixture with the authentic sample prepared as described below. The infrared spectra of the two compounds were identical. *Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15; O, 17.09. Found: C, 73.30; H, 9.11; O, 16.86. IR ν^{KBr}_{max} cm^{-1}: 1710 (20-CO), 1102 (acetal).

Further elution with benzene-Et_2O (1:1) afforded 1.54 g. (31.5%) of 5-hydroxy-6β-formyl-B-nor-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIIb) with m.p. 143° (decomp.). After one recrystallization from benzene-petr. ether it melted at 144° (decomp.), $[\alpha]^{24}_{D}$ +52.2° (c=1.11). *Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found: C, 71.28; H, 8.92. IR ν^{KBr}_{max} cm^{-1}: 3536 (OH), 2730, 1725 (CHO), 1710 (20-CO), 1107 (acetal).

(ii) An ozonized reaction mixture (2 g.) of pregn-4-ene-3,20-dione bis(ethylene acetal) (Ib), prepared as described above, was reduced with 500 mg. of Zn dust and 10 cc. of H_2O at room temperature for 3 hr. After treatment as usual, the resulting colorless syrup was chromatographed on acid-washed alumina. Elution with benzene gave 576 mg. (27.3%) of 5,6β-epoxy-5β-pregnane-3,20-dione bis(ethylene acetal) (IIc), m.p. 164~165°, which was recrystallized from benzene-petr. ether to form needles of m.p. 165.5~166°, $[\alpha]^{26}_{D}$ +12.8° (c=1.14). *Anal.* Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found: C, 71.45; H, 8.98. IR ν^{Nujol}_{max} cm^{-1}: 1095 (acetal).

Further elution with the same solvent afforded 392 mg. (22%) of 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb) which, after one recrystallization from benzene-petr. ether, melted at 158.5~160°. The identity with an authentic sample was confirmed by mixed m.p. determination and infrared spectra.

5α-Pregnane-3,6,20-trione (**IVb**)—(i) To a solution of 300 mg. of 5,6β-epoxy-5β-pregnane-3,20-dione bis(ethylene acetal) (IIc) in 70 cc. of MeOH, 4 cc. of 8% (v/v) H_2SO_4 solution was added. The mixture was refluxed for 1 hr., poured into H_2O, and extracted with CH_2Cl_2. The extract was washed with 2% $NaHCO_3$ solution and H_2O, and dried. The solvent was evaporated under a reduced pressure leaving a syrupy substance, which crystallized from benzene-petr. ether to 5α-pregnane-3,6,20-trione (IVb) as needles of m.p. 233~234°, $[\alpha]^{24}_{D}$ +69° (c=1.13) (reported m.p. 231~233° with $[\alpha]_D$ +65° (dioxane)[13]; m.p. 232~233° with $[\alpha]_D$ +61.0° ($CHCl_3$)[14]) *Anal.* Calcd. for $C_{21}H_{30}O_3$: C, 76.32; H, 9.15. Found: C, 76.89; H, 9.32. IR ν^{Nujol}_{max} cm^{-1}: 1712 (six-membered ring ketone).

(ii) A mixture of 300 mg. of 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb) and 4 cc. of 8% (v/v) H_2SO_4 solution in 70 cc. of MeOH was refluxed and 5α-pregnane-3,6,20-trione thus obtained showed m.p. 233.5~234.5° on recrystallization from Me_2CO, and without showing depression of m.p. on admixture with the sample obtained as above.

(iii) A solution of 500 mg. of 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb) in 10 cc. of AcOH was refluxed for 1 hr. After dilution with H_2O, the mixtue was extracted with Et_2O, the extract was washed with 2% $NaHCO_3$ solution and H_2O, and dried. Evaporation of the solvent gave a syrup, which crystallized from MeOH to needles of m.p. 215~225°; yield, 280 mg. Recrystallization from the same solvent gave 5α-pregnane-3,6,20-trione (IVb) of m.p. 233~234°, which was identified with the above-obtained sample.

Ozonization of Androst-5-ene-3,17-dione Bis(ethylene acetal) (**Ic**)—A solution of 9 g. of androst-5-ene-3,17-dione bis(ethylene acetal) (Ic) in 900 cc. of CH_2Cl_2 was treated with ozonized air at about −50° as in preceding experiments. Ten grams of Zn dust and 74 cc. of AcOH were added to the mixture and the solution was stirred for 3 hr. at room temperature. After treatment as described above, 9.5 g. of a colorless syrup was obtained, which was chromatographed over 450 g. of acid-washed alumina. The first eluate with benzene afforded 3.68 g. (40.3%) of crystalline material melting at 135.5~137.5°. Recrystallization from petr. ether gave 5,6β-epoxy-5β-androstane-3,17-dione bis(ethylene acetal) (IId) of m.p. 137~138°, $[\alpha]^{27}_{D}$ −8.1°. *Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found: C,

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13) F. Sondheimer, G. Rosenkranz, C. Amendolla: J. Chem. Soc., **1954**, 1226.

14) C.P. Balant, M.E. Ehrenstein: J. Org. Chem., **17**, 1587 (1952).

70.92; H, 8.94. IR ν_{max}^{KBr} cm^{-1} : 1110 (acetal).

The eluate with benzene-Et$_2$O (1:1) after evaporation of the solvent gave 2.74 g. (29.1%) of 5-hydroxy-6β-formyl-B-nor-5β-androstane-3,17-dione bis(ethylene acetal) (IIIc) of m.p. 77~80° (decomp.). Recrystallization from benzene-petr. ether gave plates with m.p. 99~102° (decomp.), $[\alpha]_D^{27}$ +6.6° (c=1.22). *Anal.* Calcd. for $C_{21}H_{34}O_6$: C, 70.40; H, 8.75. Found : C, 70.30; H, 8.41. IR ν_{max}^{KBr} cm^{-1} : 3520 (OH), 2730, 1725 (CHO), 1112 (acetal).

5α-Androstane-3,6,17-trione (IVc)—A solution of 300 mg. of 5,6β-epoxy-5β-androstane-3,17-dione bis(ethylene acetal) (IId) in 70 cc. of MeOH and 4 cc. of 8% (v/v) H_2SO_4 solution was refluxed for 1 hr. After dilution with H_2O, the solution was extracted with Et$_2$O, the extract was washed with 2% NaHCO$_3$ solution and H_2O, and dried. Removal of the solvent gave a colorless syrup, which was chromatographed on 10 g. of alumina. Elution with benzene, after removal of the solvent followed by recrystallization of the product from Me$_2$CO, afforded 62 mg. of 5α-androstane-3,6,17-trione (IVc), m.p. 191~193°, $[\alpha]_D^{24}$ +67° (c=0.75) (reported m.p. 192~193° with $[\alpha]_D^{20}$ +72° (CHCl$_3$)13) and m.p. 191.5~192.5° with $[\alpha]_D^{28}$ +71.0° (CHCl$_3$)14)). *Anal.* Calcd. for $C_{19}H_{26}O_3$: C, 75.46; H, 8.67. Found : C, 75.74; H, 8.31. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1740 (17-CO), 1715 (3,6-CO).

Peracid Oxidation of Pregn-4-ene-3,20-dione Bis(ethylene acetal) (Ib)—A mixture of 5.0 g. of pregn-4-ene-3,20-dione bis(ethylene acetal) (Ib) in 50 cc. of benzene and 4.5 g. of monoperphthalic acid in 100 cc. of Et$_2$O was allowed to stand for 3 days at room temperature. The solution was then washed with 5% KOH solution and H_2O, and dried. Evaporation of the solvent afforded 4.93 g. of a syrup, which was chromatographed on 150 g. of alumina. Elution with benzene afforded 1.61 g. (31%) of 5,6β-epoxy-5β-pregnane-3,20-dione bis(ethylene acetal) (IIc) as needles melting at 166~167° after recrystallization from petr. ether (b.p. 60~80°). $[\alpha]_D^{24}$ +11.8°. *Anal.* Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found : C, 71.98; H, 9.00.

Further elution with benzene afforded 85 mg. (1.83%) of 5,6β-epoxy-5β-pregnane-3,20-dione 3-(ethylene acetal) (IIb) as rhombics melting at 158.5~160° after recrystallization from benzene-petr. ether, $[\alpha]_D^{24}$ +67°. *Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found : C, 73.51; H, 9.03.

Elution with benzene-Et$_2$O (1:1) gave 1.9 g. (36.8%) of 5,6α-epoxy-5α-pregnane-3,20-dione bis(ethylene acetal) as needles melting at 181~182° after recrystallization from petr. ether (b.p. 60~80°). $[\alpha]_D^{24}$ −53° (c=1.24). *Anal.* Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found : C, 71.62; H, 9.10. IR ν_{max}^{Nujol} cm^{-1} : 1095 (acetal).

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Summary

By the action of ozone on cyclic ethylene acetals of cholest-4-en-3-one, pregn-4-ene-3,20-dione, and androst-4-ene-3,17-dione, the corresponding 5β,6β-epoxides and 5β-hydroxy-6β-formyl-B-norsteroids with 3-(ethylene acetal) were obtained.

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