pound readily reduced potassium permanganate to manganous ion in sodium hydroxide solution. From the solution resulting from oxidation in acetone solution could be recovered benzenesulfonate as the *S*-benzylthiuronium derivative. Compound II gave no positive test for the presence of a sulfhydryl group.

The physical properties and analytical composition found for Compound II were suggestive of those listed for *N,N*-bis(benzenesulfonyl)hydroxylamine.[6] The latter, therefore, was synthesized, according to the directions of Koenigs,[6] through interaction of sodium benzenesulfinate and sodium nitrate in hydrochloric acid solution; white crystals were obtained, which melted, alone or in mixture with Compound II, at 115–118° (dec.). The infrared absorption spectra of both samples were identical.

Formation of N,N-bis(benzenesulfonyl)hydroxylamine by treatment with nitric acid of the reaction product of diphenylcadmium and benzenesulfonyl chloride. It was of interest to demonstrate that this hydroxylamine derivative can result from use of an arylcadmium reagent as well as from dialkylcadmiums. To a solution of 3.8 g. (0.02 mole) of benzenesulfonyl chloride in anhydrous ether was added 10 ml. of 2.0*N* diphenylcadmium solution (0.01 mole diphenylcadmium). The precipitated solid was removed, washed with ether, and dried before being mixed at 70° with 100 ml. of water, 7.5 ml. of concd. nitric acid, and 10 ml. of ethyl alcohol. The mixture was stirred for 5 min. before being chilled; seemingly, much of the original product had not dissolved. Next day, the mixture was filtered, the solid was triturated with hot 5% sodium hydroxide solution and filtered; the filtrate was acidified and the precipitated material was removed, dried, and recrystallized from chloroform. The melting point of this sample, alone or in admixture with the authentic hydroxylamine derivative, was 115–117°.

Identity of Compound III [N,N-bis(p-tolylsulfonyl)-hydroxylamine]. This substance closely resembled Compound II in physical and chemical properties, and in composition.

Anal. Calcd. for $C_{14}H_{15}NO_2S$: C, 49.35; H, 4.41; N, 4.08; O, 23.41; S, 18.76. Found: C, 49.53; H, 4.60; N, 3.61; O, 23.73; S, 18.56, analyses by Huffman Microchemical Laboratory.

The infrared absorption spectrum of this tolyl derivative was quite similar to that of the lower homolog of established structure; the former, therefore, is formulated as *N,N*-bis-(*p*-tolylsulfonyl)hydroxylamine.

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[CONTRIBUTION FROM THE SCHERING CORP. AND THE UNIVERSITY OF GLASGOW]

11-Oxygenated Steroids. XVIII. Wagner-Meerwein Rearrangement of Some 17α-Hydroxysteroids*

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The rearrangements of pregnane-3α,11β,17α,20β-tetrol 3,20-diacetate and 5-pregnene-3β,17α,20β-triol 3,20-diacetate by the action of *p*-toluenesulfonic acid in acetic acid–acetic anhydride solution, to 18-nor-17β-methyl-17-iso-12-pregnene-3α,11β,20β-triol 3,11,20-triacetate and 18-nor-17β-methyl-17-iso-5,12-pregnadiene-3β,20β-diol 3,20-diacetate, respectively are described. Under the same conditions, pregnane-3α,17α,20β-triol-11-one 3,20-diacetate affords the unrearranged 3,17,-20-triacetate. The mechanism is discussed.

Subsequent to the discoveries that the tertiary 17α-hydroxyl group[2] and the 11β-hydroxyl group[3] can be acetylated with acetic anhydride in the presence of an acid catalyst, we had occasion to investigate the possibility of acetylating pregnane-3α,-11β, 17α, 20β-tetrol 3,20-diacetate[4] (I) in an acetic anhydride–acetic acid-*p*-toluenesulfonic acid system at room temperature. We found that two products were produced, II and III, yields of the former averaging about 60% and those of the latter about 10%.

The structure of III was readily apparent. Infrared examination revealed the absence of hydroxyl groups and the presence of intense acetate absorptions. The empirical formula derived from carbon-hydrogen analyses was consistent with the presence of four acetate groups. Treatment of III with excess lithium aluminum hydride afforded the parent tetrol IV,[4] identical with an authentic sample, and acetylation of IV with acetic anhydride in pyridine regenerated I.

The structure of II was considerably more complex. From the infrared absorption spectrum it was possible to decide that there was no hydroxyl present, that there were probably three acetate groups, and possibly a trisubstituted unsaturation. Carbon-hydrogen analyses were in reasonable accord with the formula $C_{27}H_{40}O_6$, which corresponded to three

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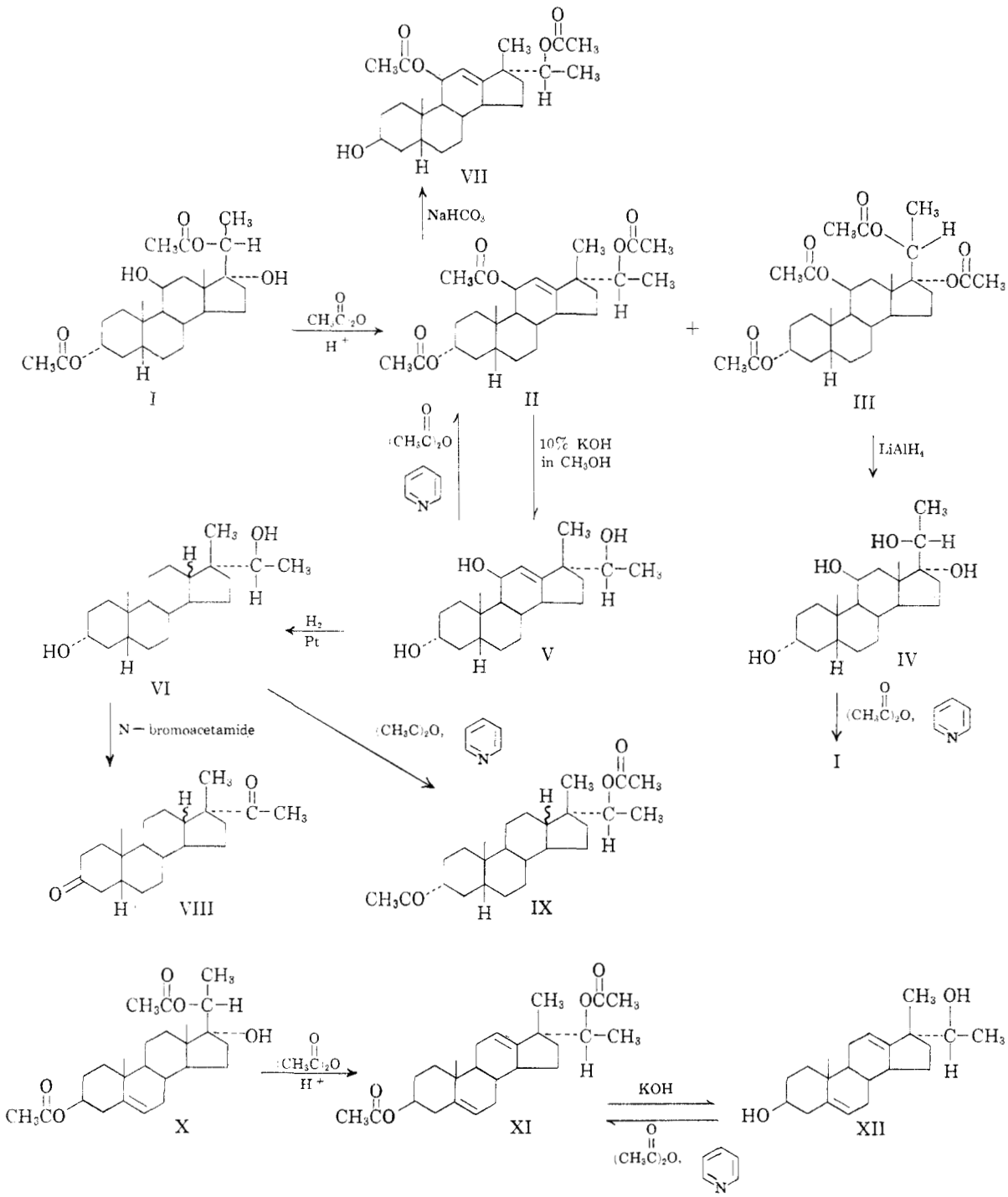

acetate groups being present and to the loss of one hydroxyl (or acetate) with the concomittant formation of a double bond. *All of the acetate groups could be removed by solvolysis with 10% alcoholic potassium hydroxide*, an unsaturated triol (V) resulting thereby. *Acetylation of V with acetic anhydride in pyridine solution at room temperature regenerated II*. From the preceding two observations, it was apparent that disturbances affecting positions 11 and 17 had occurred. This follows from the fact that in I, IV, and all known, similarly hydroxylated pregnanes and pregnenes, the 11β- and 17α-hydroxyl groups resist acetylation in this medium at room temperature, and the 11β- acetate resists hydrolysis by the technique described. Incidentally, it was observed that only one acetate group was removed by hydrolysis of II with sodium bicarbonate, and this was presumed to lead to VII.

Hydrogenation of V in acetic acid solution with Adams' platinum catalyst resulted in the loss of *still another hydroxyl group* as well as saturation of the double bond, the empirical formula of VI corresponding to $C_{21}H_{36}O_2$. The loss of the hydroxyl group was best rationalized by assuming that it was

in a position to be activated toward hydrogenolysis by being allylic to the unsaturation. The presence of only two hydroxyl groups in VI was further illustrated by the formation of an hydroxyl-free diacetate (IX) with acetic anhydride in pyridine and by oxidation to a diketone (VIII) with *N*-bromoacetamide. All of the facts gathered to this point were consistent with the hypothesis that a Wagner-Meerwein type rearrangement, as well as acetylation, occurred when I was treated with the indicated medium. Acid-promoted loss of the 17-hydroxyl group was followed by migration of the methyl group from 13β to 17β and finally by loss of a proton from 12 with resultant formation of a double bond. It was now reasonable to expect that the altered stereochemistry of ring C might reduce hindrance at 11 sufficiently to permit ready hydrolysis of an 11β-acetate and ready reesterification by a mild acetylating medium.[4a] Furthermore, loss of the 11β-hydroxyl group under strong hydrogenating conditions was properly accommodated.

A rearrangement of a similar type has been proposed by Heusler and Wettstein[5] to describe the reaction of 16α, 17α-oxidopregnenolone 3-acetate with formic acid–sulfuric acid. These authors propose that the product which results bears a double bond at 13, but this is not proved. We suggest that the location of this double bond is in doubt, and that 12 is a more likely possibility in the light of our results.

Since migration of a double bond from 13 to 12 might conceivably occur on the platinum employed as a hydrogenation catalyst, it was desirable to test further the assignment of the double bond to 12 in V (and II). It has been reported that nuclear magnetic resonance (NMR) spectra of compounds containing hydrogen atoms attached to carbon bearing a double bond contain a band peculiar to this structure.[6] Since the assignment of the double bond to 12 leads to one such grouping and assignment to 13 affords none, it was hoped that NMR measurement would provide an unequivocal answer. With this end in view we invoked the kind offices of Dr. James N. Shoolery of the Varian Associates, and his measurements of the NMR spectrum of II showed clearly that the double bond is at 12, in accord with the evidence from hydrogenation.

Pregnane-3α, 17α, 20β-triol-11-one 3,20-diacetate had been selected as a substrate for rearrangement in the hope that the reaction would follow the path described for I, and the product, which resulted might then possess a conjugated carbonyl system in ring C, whose presence could be substantiated readily by ultraviolet and infrared measurements. However, no rearrangement was observed under essentially the conditions employed previously with I. Instead, pregnane-3α, 17α, 20β-triol-11-one 3, 17, 20-triacetate was the only product isolated. Its structure was confirmed by hydrolysis with alkali to the triol and reacetylation with acetic anhydride in pyridine solution to the starting material. The failure of the 11-carbonyl compound to rearrange is not peculiar to this series. Beyler and Hoffman[7] observed that 16α, 17α-oxidopregnane-3α-ol-11,20-dione, an analog of the compound studied by Heusler and Wettstein,[5] did not undergo Wagner-Meerwein rearrangement in formic acid–sulfuric acid, but instead gave normal solvolysis of the epoxide.

On the other hand, 5-pregnene-3β, 17α, 20β-triol 3,20-diacetate (X) afforded rearrangement in the anticipated fashion under the conditions described previously. The structure of the resulting product (XI) was inferrred from analytical data, the ready solvolysis with alkali of the two acetate groups, reacetylation of XII with acetic anhydride in pyridine to XI, and by analogy with the structure of II.

From the observations reported here, one can propose that stereochemical and/or electronic effects are present which control events occurring at a point two carbon atoms removed from the site of variable substitution.[7a] On the one hand, hydroxyl and hydrogen substituents axial at 11 promote or do not interfere with migration of the axial 13β-methyl group, while 11-carbonyl inhibits or does not promote rearrangement. The forces influencing the reaction might be considered as (*a*) the positive push towards 17 provided by steric repulsion between an axial substituent at 11 and the angular methyl group or (*b*) the inhibiting, electron-withdrawing, inductive effect of the 11-carbonyl which reduces electron availability at the 13-methyl with resultant decreased tendency toward migration to a positive center at 17.

Since the completion of these experiments, preliminary reports have appeared[8,9] which describe a closely related Wagner-Meerwein rearrangement in which 17α, 21-oxido-4-pregnen-11β-ol-3,20-dione rearranges into 13α, 21-oxido-17β-methyl-18-nor-17-iso-4-pregnen-11β-ol-3,20-dione upon acid treatment.

(4a) It is possible that inversion may have occurred at 11 under the strongly acid conditions of the rearrangement and hence it is not permissible to rule out the α-configuration for the 11-acetate.

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EXPERIMENTAL[10]

Pregnane-3α,11β,17α,20β-tetrol 3,20-diacetate (I). A solution of 2.00 g. of pregnane-3α,11β,17α,20β-tetrol[4] in 15 ml. of acetic anhydride and 50 ml. of pyridine was allowed to stand at room temperature overnight. The solution was diluted with water and the precipitate which formed following the completion of hydrolysis of the acetic anhydride was removed by filtration. The dried solid was taken up in xylene, boiled to remove traces of water, and concentrated to dryness *in vacuo*. The resulting oil was crystallized from xylene from which there resulted 2.07 g. of I, m.p. 181–184°. Recrystallization from ether-hexane raised the m.p. to 184–185°, λ_{max}^{Nujol} 2.82 μ (OH), 5.76 μ (acetate carbonyl) and 8.10 μ (C—O—C of acetate), $[\alpha]_D^{25}$ +70° ($CHCl_3$).

Anal. Calcd. for $C_{25}H_{40}O_6$: C, 68.77; H, 9.24. Found: C, 68.58; H, 9.43.

Solvolysis of I with 10% alcoholic potassium hydroxide. A solution of 400 mg. of I in 10 ml. of 10% methanolic potassium hydroxide was refluxed for 3 hr. Crystallization of the product began after 5 min. of reflux. The reaction mixture was cooled to room temperature and diluted with water. Filtration of the resulting precipitate afforded 260 mg. of pregnane-3α,11β,17α,20β-tetrol, m.p. 278–282°, identical in all respects with that from which I was prepared.

Acetylation of I to yield II and III. To a solution of 15.15 g. of I in 134 ml. of glacial acetic acid was added 134 ml. of acetic anhydride and 2.05 g. of *p*-toluenesulfonic acid. The reaction mixture was maintained at 25° overnight and was then diluted with water. Following hydrolysis of the unreacted acetic anhydride, the reaction mixture was extracted with methylene chloride and the extracts were washed to neutrality with water. The dried extracts were concentrated and crystallized from aqueous methanol. There resulted 14.63 g., m.p. 109–122°. Chromatography of this solid on 120 g. of Florisil, prepared with hexane, and elution with mixtures of-hexane and ether afforded a series of crystalline fractions. From 1% and 5% ether-in-hexane there resulted 9.60 g. of crystals, m.p. 116–124.5°. Recrystallization of these from aqueous methanol gave 8.63 g. of II, as needles, m.p. 122–124°. Additional recrystallization raised the m.p. to 124–125°, $[\alpha]_D^{25}$ +83° ($CHCl_3$), λ_{max}^{Nujol} 5.79 μ (acetate carbonyl) and 8.00 μ (C—O—C of acetate).

Anal. Calcd. for $C_{27}H_{40}O_6$: C, 70.40; H, 8.74. Found: C, 70.18; H, 9.12.

From 10% and 20% ether-in-hexane and 100% ether, there resulted 2.64 g. of solid melting about 115°, resolidifying, and remelting as high as 165°. Recrystallization from heptane afforded 1.62 g. of III, m.p. 170–179°. A portion of this solid was rechromatographed over Florisil in the way described previously and the 20% ether-in-hexane fractions were combined and crystallized from heptane giving III, m.p. 177–179°, $[\alpha]_D^{25}$ +56° ($CHCl_3$), λ_{max}^{Nujol} 5.76 and 5.79 μ (acetate carbonyls), 8.02 and 8.14 μ (C—O—C of acetate).

Anal. Calcd. for $C_{29}H_{44}O_8$: C, 66.90; H, 8.52. Found: C. 66.70; H, 8.30.

Partial hydrolysis of II. A solution of 460 mg. of II in 17 ml. of methanol to which had been added a solution of 250 mg. of sodium bicarbonate in 3 ml. of water was refluxed for 2 hr. Water was added to the cooled solution and the resulting precipitate was removed by filtration. There was isolated 350 mg. of fine needles of VII, m.p. 81.5–86°. Recrystallization from aqueous methanol afforded VII, m.p. 85–88°, $[\alpha]_D^{25}$ +59° ($CHCl_3$), $\lambda_{max}^{CS_2}$ 2.94 μ (OH), 5.77 μ (acetate carbonyl), 8.06 μ (C—O—C of acetate). Integration of the acetate carbonyl band showed that two acetate groups were present.

Anal. Calcd. for $C_{25}H_{38}O_5.H_2O$: C, 68.77; H, 9.24. Found: C, 68.81; H, 9.75.

Acetylation of VII with acetic anhydride in pyridine regenerated II.

Solvolysis of II. A solution of 5.00 g. of II in 250 ml. of methanol containing 25 g. of potassium hydroxide was refluxed for 3 hr. The reaction mixture was cooled to 5°. and neutralized with 4*N* hydrochloric acid. The precipitated potassium chloride was removed by filtration, and the filtrate was concentrated with gradual addition of water. Long needles of V precipitated and were recovered by filtration. There resulted 3.48 g. of V, m.p. 158–160°, $[\alpha]_D^{25}$ +14° (dioxane), λ_{max}^{Nujol} 3.06 μ (OH).

Ana.. Calcd. for $C_{21}H_{34}O_3.H_2O$: C, 71.55; H, 10.30. Found: C, 71.83; H, 10.03.

Acetylation of V to give II. A solution of 200 mg. of V in 4 ml. of pyridine and 2 ml. of acetic anhydride was allowed to stand overnight at room temperature. The solution was diluted with water and extracted with methylene chloride. The extracts were washed with water, dried, and concentrated. The residue was recrystallized from methanol-water. There resulted 190 mg. of II, m.p. 123–124°, which did not depress the melting point of the product (II) of acid catalyzed acetylation of I. Infrared spectra of the two samples were identical.

Reduction of V to VI. A solution of 1.5 g. of V in 100 ml. of glacial acetic acid containing 1.5 g. of Adams platinum oxide catalyst was shaken under 1 atm. of hydrogen at room temperature until hydrogen uptake ceased (usually 24 hr.). The catalyst was removed by filtration and the filtrate *in vacuo* to a residue. A solution of the residue in methylene chloride was washed with water, dried, and concentrated with gradual addition of hexane. There precipitated then a total of 800 mg. of VI, m.p. 177–181°. Further purification by chromatography over Florisil raised the m.p. to 185–187°, $[\alpha]_D^{25}$ +1.3° (dioxane), λ_{max}^{Nujol} 3.10 μ (OH). Quantitative estimation of hydroxyl by integration indicated that two hydroxyl groups were present.

Anal. Calcd. for $C_{21}H_{36}O_2$: C, 78.67; H, 11.32. Found: C, 78.56; H, 11.27.

Acetylation of VI to IX. A solution of 200 mg. of VI in 4 ml. of pyridine was treated with 2 ml. of acetic anhydride overnight at room temperature. The reaction mixture was hydrolyzed and extracted as before, and the total residue was chromatographed on Florisil. Elution with hexane afforded 130 mg. of IX, crystallized from aqueous methanol, m.p. 74–76°. Two additional crystallizations from aqueous acetone gave IX, m.p. 78–80°, $[\alpha]_D^{25}$ +26° (dioxane), λ_{max}^{Nujo} 5.76 μ (acetate carbonyl) and 8.06 μ (C—O—C of acetate). Integration of the carbonyl band indicated that two acetate groups were present.

Anal. Calcd. for $C_{25}H_{40}O_4$: C, 74.21; H, 9.97. Found: C, 74.56; H, 10.06.

Oxidation of VI to VIII. A solution of 340 mg. of VI in 50 ml. of acetone and 10 ml. of water was treated with 840 mg. of N-bromoacetamide at room temperature and the reaction mixture was placed in the icebox. After 3 hr., the reaction mixture was diluted with aqueous sodium sulfite until the red-orange color disappeared. It was then diluted with water and extracted with methylene chloride. The extracts were washed with water, dried, and concentrated, and the residue was crystallized from aqueous methanol. There resulted 250 mg. of VIII, m.p. 80–83° which, on further recrystallization, melted at 82–83°, $[\alpha]_D^{25}$ −4.3° (dioxane), λ_{max}^{Nujol} 5.87 μ (carbonyl).

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.62; H, 10.21.

Lithium aluminum hydride reduction of III to IV. A solution of 85 mg. of III in 100 ml. of tetrahydrofuran was refluxed overnight with 200 mg. of lithium aluminum hydride. A few drops of acetone were added to destroy the excess reagent and then water was added. The precipitated solids were removed by filtration, washed thoroughly with ether, and the filtrate was extracted with ether. The com-

(10) All melting points are corrected. Analyses and optical data were obtained by the Physical Chemistry Department of Schering Corp. and by Galbraith Laboratories, Knoxville, Tenn. Dr. Jo-Yun Chen, Miss Cecilia Vitiello, and Messrs. Milton Yudis and Edward Townley interpreted the infrared spectra.

bined extracts were washed with water, dried, concentrated, and crystallized from methylene chloride–hexane. There resulted 40 mg. of IV, m.p. 278–282°, with an infrared spectrum identical with that of an authentic sample.[4]

Acetylation of IV with acetic anhydride in pyridine according to the procedure noted earlier gave I.

Preparation of 5-pregnene-3β,17α,20β-triol. A solution of 10 g. of 17α-hydroxypregnenolone 3-acetate in 1500 ml. of methanol was treated with a solution of 10 g. of sodium borohydride in 100 ml. of water. External cooling was applied and the reducing agent was added gradually to reduce the vigor of the reaction. The reaction mixture was allowed to stand overnight at room temperature and was then concentrated to 600 ml. on the steam bath. About 200 ml. of water was added to induce crystallization. The resulting solid weighed 10.4 g. and did not melt below 280°. From the weight and melting point it was surmised that the product was present as a borate ester of some kind. The solid was boiled with 400 ml. of water for 3 hr. and allowed to stand overnight. It was then removed by filtration and recrystallized from methanol-water. There resulted 7.0 g. of 5-pregnene-3β,17α,20β-triol, m.p. 217–223°. A sample recrystallized for analysis, melted at 220–223°, $[\alpha]_D^{25}$ −108° ($CHCl_3$), λ_{max}^{Nujol} 3.2 μ (OH). The analytical sample was dried *in vacuo* at 110°C. for 24 hr.

Anal. Calcd. for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.56; H, 10.29.

5-Pregnene-3β,17α,20β-triol 3,20-diacetate (X). Acetylation of 5-pregnene-3β,17α,20β-triol with acetic anhydride in pyridine solution according to procedures given previously afforded the 3,20-diacetate. Recrystallization from methylene chloride–hexane gave the desired product, m.p. 155–157°, $[\alpha]_D^{25}$ −33° ($CHCl_3$).

Anal. Calcd. for $C_{25}H_{38}O_5$: C, 71.74; H, 9.15. Found: C, 71.73; H, 9.09.

Acid catalyzed acetylation and rearrangement of X to XI. To a solution of 0.84 g. of diacetate in 4 ml. of acetic acid and 4 ml. of acetic anhydride was added 0.12 g. of *p*-toluenesulfonic acid. The reaction mixture was allowed to stand overnight at room temperature, whereupon 50 ml. of ice water was added. The resulting gray solid was removed by filtration, washed with water, dried (yield 0.78 g., m.p. 110–116°), and chromatographed over Florisil (0.68 g. chromatographed on 10 g. of Florisil). The desired product was eluted with 5% ether-in-hexane. A total of 0.40 g., m.p. 123–130° was collected in eight fractions. Recrystallization, effected from acetone-water, gave 0.26 g. of rearranged product XI, m.p. 131–132°, $[\alpha]_D^{25}$ −64° ($CHCl_3$), λ_{max}^{Nujol} 5.75 μ (acerate carbonyl) and 8.10 μ (C—O—C of acetate).

Anal. Calcd. for $C_{25}H_{36}O_4.C_3H_6O$: C, 73.32; H, 9.23. Found: C, 73.61; H, 9.52.

Solvolysis of XI to XII. A solution containing 0.40 g. of rearranged diacetate from the preceding experiment in 10 ml. of 10% methanolic potassium hydroxide was refluxed for 3 hr. The solution was diluted with water and neutralized with 4*N* hydrochloric acid. The resulting precipitate was removed by filtration and recrystallized from methanol-water. There resulted 0.27 g. of XII, m.p. 139–140°. Further recrystallization did not alter the m.p., $[\alpha]_D^{25}$ −213° ($CHCl_3$), λ_{max}^{Nujol} 3.02 μ (OH).

Anal. Calcd. for $C_{21}H_{32}O_2$: C, 79.70; H, 10.19. Found: C, 79.80; H, 10.36.

Acetylation of XII to XI. Acetylation of the product of the previous experiment in the usual way afforded the previously described diacetate XI, m.p. 128–130° in quantitative yield. The infrared spectrum matched that of a sample obtained from acid-catalyzed acetylation of X.

Pregnane-3α,17α,20β-triol-11-one. This compound was prepared according to Oliveto and Hershberg[11] with the exception that the reaction was stopped after 15 min. at room temperature. From 1 g. of pregnane-3α,17α-diol-11,20-dione with 100 ml. of *t*-butyl alcohol, 1 g. of sodium borohydride, and 25 ml. of water there resulted 0.53 g. of triolone, m.p. 219–222°.

Pregnane-3α,17α,20β-triol-11-one 3,20-diacetate. This compound was prepared by acetylation in the usual way with acetic anhydride in pyridine.[11] The constants were in agreement with the published values.

Pregnane-3α,17α,20β-triol-11-one 3,17,20-triacetate. A suspension of 0.15 g. of the 3,20-diacetate, described previously, in 1.4 ml. of acetic acid and 1.4 ml. of acetic anhydride containing 0.02 g. of *p*-toluenesulfonic acid was allowed to stand overnight at room temperature. All the starting material had dissolved in this interval. Twenty-five ml. of ice water was added and the oily precipitate was extracted with methylene chloride. The extracts were washed to neutrality with water, dried, and concentrated. The residue, upon crystallization from ether-hexane, gave 0.08 g. of large, rectangular prisms, m.p. 99–105° dec., $[\alpha]_D^{25}$ +50° (dioxane), λ_{max}^{Nujol} 5.72 and 5.79 μ (acetate carbonyl), 5.85 μ (11-carbonyl) and 8.08 μ (C—O—C of acetate).

Anal. Calcd. for $C_{27}H_{40}O_7$: C, 68.04; H, 8.46. Found: C, 67.65; H, 8.87.

This steroid was the only crystalline product isolated and identified though the quantities of catalyst and solvents were increased separately, and together, as much as fourfold, and crystallization mother liquors were chromatographed.

Alkaline hydrolysis of pregnane-3α,17α,20β-triol-11-one 3,17,20-triacetate. A solution of 0.40 g. of triacetate in 10 ml. of 10% methanolic potassium hydroxide was refluxed for 3 hr. The reaction mixture was diluted with water, neutralized with 4*N* hydrochloric acid and extracted with methylene chloride. The extracts were washed with water, dried, concentrated, and the residue was crystallized from acetone-hexane. There resulted 0.14 g. of pregnane-3α,17α,-20β-triol-11-one, m.p. 213–217°, whose infrared spectrum was identical with that of an authentic sample.[11]

Acetylation of the triolone from this experiment with acetic anhydride in pyridine solution in the usual way afforded pregnane-3α,17α,20β-triol-11-one 3,20-diacetate, identical in infrared spectrum and melting point with an authentic sample.

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