modified Eberstadt method recommended by Genung and Mallatt[11] for cellulose esters.

Acetylation.—The formates were dissolved in 10 volumes of anhydrous pyridine (stored over calcium hydride), an amount of freshly distilled acetic anhydride was added equivalent to twice the theoretical amount for the number of free hydroxyl groups in the formate, and the reaction mixture heated at 100° for 3.5 hours. The acetylated formates were isolated and analyzed in the same manner as the formic acid esters. The average degree of substitution of acetyl groups was calculated algebraically assuming no loss of formyl groups during acetylation.

Deformylation.—Five grams of acetylated formate was dissolved in 500 ml. of acetone. The solution was placed in a thermostat at 25 ± 0.10° and 50 ml. of an aqueous solution of redistilled piperidine (10% v./v.) added with mixing. For the rate studies, aliquots were removed periodically and 5 volumes of ice-water added. The resultant suspensions were titrated with standard hydrochloric acid using phenol red indicator, and the decrease in concentration of the base determined by comparison with a blank reaction mixture, identical except for the omission of the ester. When kinetic data were not sought, the reaction was allowed to proceed for 8 hours, whereupon the entire reaction mixture was filtered into 4–5 volumes of ice-water; the resultant precipitate was collected by suction, resuspended in water and dialyzed against deionized water. After dialysis the suspension was again filtered by suction. Drying of the filter cake in a vacuum oven resulted in products which were quite "horny," but which could be dissolved in pyridine for tritylation and tosylation. Light, finely divided diacetates were prepared by reprecipitation from pyridine solution into an excess of ethyl ether.

Tritylation.—The procedure of Malm, Tanghe, Laird and Smith[9c] was followed. Trityl contents were determined by quantitative recovery of the trityl ethers[9c] or by decomposition of the ether in sulfuric acid followed by precipitation and quantitative recovery of tritanol.[12]

Tosylation–Iodination.—The procedure of Gardner and Purves[9f] was used with slight modification. The acetates prepared by means of the deformylation reaction were dried and dissolved (overnight) in 10 parts of anhydrous pyridine. Eight to ten times the calculated theoretical amount of *p*-toluenesulfonyl chloride (recrystallized from carbon tetrachloride and stored over phosphorus pentoxide in the dark) was dissolved in the solution and the reaction mixture kept at 25° for 24 hours. The reaction products were isolated by precipitation into 80% methanol; the precipitates were washed free from chloride with the same solvent, the aqueous methanol replaced with anhydrous ether, and the products were dried in a vacuum oven. They were allowed to react with an equal weight of sodium iodide in 25 parts by volume of anhydrous diglyme (dimethyl ether of diethylene glycol) at 120° for 2 hours, and the iodo derivatives were obtained on pouring the reaction mixture into a large volume of water. These precipitates were purified by suspending in water, dialyzing the suspension against deionized water, filtering and drying. Sulfur and iodine were determined separately by the appropriate Carius method as described by Steyermark.[13]

(11) L. B. Genung and R. C. Mallatt, *Ind. Eng. Chem., Anal. Ed.*, **13**, 369 (1941).

(12) W. M. Hearon, G. D. Hiatt and C. R. Fordyce, THIS JOURNAL, **65**, 2449 (1943).

(13) A. Steyermark, "Quantitative Organic Microanalysis," The Blakiston Co., Philadelphia, Penna., 1951.

LAFAYETTE, IND.

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

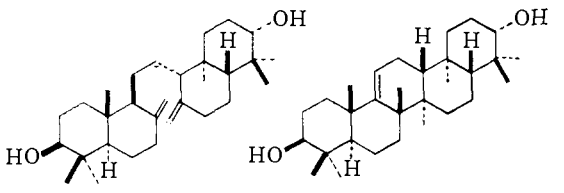
Syntheses in the Terpene Series. VII.[1] A Total Synthesis of the Dinoronocerane Carbon Skeleton

BY FRANZ SONDHEIMER AND DOV ELAD

RECEIVED FEBRUARY 27, 1959

The synthesis is described of a substance which is very probably the racemate of dinoronocerane (VIII).

The triterpene alcohol α-onocerin (α-onoceradienediol) has been shown to possess the symmetrical structure I and to undergo an acid-cat-



I II

alyzed cyclization to the pentacyclic γ-onocerin (II).[2] The last-mentioned substance by contraction of ring E can be converted to compounds with the same carbon skeleton as the natural pentacyclic triterpenes of the hydroxyhopanone[3] and perhaps also the zeorin[4] type. We are interested in effecting total syntheses of triterpenes of the onocerin and hydroxyhopanone series since these represent an interesting class of natural products derivable from squalene by biogenetic paths not involving migration of methyl groups and also because the methods used for synthesizing these "symmetrical" compounds might be employed later for the more difficult synthesis of the pentacyclic triterpenes of the β-amyrin type.

Although α-onocerin itself has not yet been obtained by synthesis, three quite distinct synthetic approaches to closely related compounds were announced, in 1957, by Corey and Sauers,[5] by Romann, *et al.*,[6] as well as by ourselves.[7] Our own work, reported as a preliminary communication, resulted in a substance which is probably the racemate of dinoronocerane (VIII). The corresponding optically active compound had previously been obtained from α-onocerin.[2] This synthetic

(1) For part VI, see F. Sondheimer and D. Rosenthal, THIS JOURNAL, **80**, 3995 (1958).

(2) D. H. R. Barton and K. H. Overton, *J. Chem. Soc.*, 2639 (1955); see also K. Schaffner, R. Viterbo, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 174 (1956).

(3) W. J. Dunstan, H. Fazakerley, T. G. Halsall and E. R. H. Jones, *Croat. Chem. Acta*, **29**, 173 (1957); K. Schaffner, L. Caglioti, D. Arigoni, O. Jeger, H. Fazakerley, T. G. Halsall and E. R. H. Jones, *Proc. Chem. Soc.*, 353 (1957); K. Schaffner, L. Cagliotti, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **41**, 152 (1958).

(4) D. H. R. Barton, P. de Mayo and J. C. Orr, *J. Chem. Soc.*, 2239 (1958).

(5) E. J. Corey and R. R. Sauers, THIS JOURNAL, **79**, 3925 (1957).

(6) E. Romann, A. J. Frey, P. A. Stadler and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1900 (1957).

(7) D. Elad and F. Sondheimer, *Proc. Chem. Soc.*, 206 (1957).

substance contains six of the eight asymmetric centers and all but two of the carbon atoms of α-onocerin (I). We now describe this work in detail.

Our starting material was 1,1,10-trimethyl-*trans*-decal-5-one (III), obtainable in quantity from 2-methylcyclohexane-1,3-dione by a seven-step sequence.[8,9] The simplest method for obtaining the dinoronocerane carbon skeleton appeared to involve the condensation between the ketone III and acetylenedimagnesium bromide to yield the acetylene glycol V. However repeated attempts under various conditions and in different solvents failed to bring about the desired reaction; either the unchanged ketone III was recovered, or a substance, m.p. 70°, was obtained (when a very large excess of acetylenedimagnesium bromide was used), which was clearly the acetylenic carbinol IV as judged by its elemental composition and infrared spectrum. The same acetylenic carbinol IV was obtained more conveniently and in excellent yield by treatment of the ketone II with sodium acetylide in liquid ammonia, or alternatively with acetylene in *t*-butyl alcohol in the presence of potassium *t*-butoxide. These reactions all yielded only one isomer, undoubtedly the 5α-ethynylcarbinol IV in view of the presence of the axial 1β- and 10β-methyl groups in the ketone III shielding the β-side of the molecule.

A method for preparing acetylenic 1,4-glycols involves the interaction between an acetylenic carbinol of type IV with two equivalents of ethylmagnesium bromide and allowing the resulting complex to react with a carbonyl compound.[10] However no reaction occurred on attempted condensation between IV and III by this method under various conditions. The obtention of the acetylenic carbinol IV by the reaction of the ketone III with acetylenedimagnesium bromide and the non-reactivity of the dimagnesium bromide complex of IV is analogous to the behavior of the steroidal 17-ketone dehydroepiandrosterone[11] and may be due to the insolubility of the di-Grignard complex of IV in the solvent systems employed.

After some experimentation, it was found that the desired condensation could be carried out successfully by allowing the acetylenic carbinol IV to react with an excess of sodamide in liquid ammonia and then adding the ketone III. A reaction of this type would be expected to yield not only the racemic glycol V but also the *meso*-glycol VI, attack of the ketone III again undoubtedly occurring from the side opposite to the axial 1- and 10-methyl groups. Indeed two different glycols, m.p. 210° and 190°, could be isolated, the latter in predominant amount. These were not polymorphic forms, as each could be crystallized unchanged in the presence of a seed of the other. The substances gave a mutual depression in melting point on admixture, despite the fact that their infrared spectra (which showed the absence both of a carbonyl and of a free ethynyl group) were almost superimposable.

It has previously been pointed out[12] that with very few exceptions a centrosymmetrical *meso* compound has a higher melting point than the corresponding racemic diastereomer. Among the twenty pairs examined in which the two asymmetric centers were separated by two carbon atoms, not a single *meso* form was found that exhibited a lower melting point than the racemic isomer. For this reason we are assigning with a fair degree of certainty the racemic structure V to the glycol with m.p. 190° and the *meso* structure VI to the glycol with m.p. 210°.

Only the racemic glycol V (m.p. 190°), formed in greater amount, is of use for the present synthesis. The excess tertiary hydroxyl groups were removed through dehydration with potassium hydrogen sulfate at 170°, whereby the corresponding dienyne VII, m.p. 130°, was smoothly produced. This hydrocarbon showed ultraviolet maxima (in isoöctane) at 265 mμ (ε 17,400) and 279 mμ (ε 13,000), in good agreement with those shown by a sample of dicyclohexenyl-acetylene (IX) [λ_{max}^{EtOH} 262.5 mμ (ε 17,500) and 276 mμ (ε 12,800)][13] containing the same chromophoric system. The corresponding dehydration of the *meso*-glycol VI (m.p. 210°) proceeded less smoothly and yielded a mixture of products which was not investigated further.

Finally the racemic dienyne VII was fully hydrogenated in dioxane–acetic acid over a platinum catalyst, a reaction which led to a saturated hydrocarbon with m.p. 185°. The α-side of the dienyne VII is considerably less hindered than the β-side, in view of the presence of the axial 1β- and 10β-methyl groups in both halves of the molecule, and absorption of hydrogen would therefore be expected to occur from the α-side. For this reason the saturated hydrocarbon is assigned the structure VIII, which is the racemate of dinoronocerane. The corresponding optically active compound (m.p. 119°, $[\alpha]_D$ + 62°) had been obtained[2] from α-onocerin (I) and a sample was kindly provided by Professor D. H. R. Barton. As expected, the infrared spectra of the synthetic and natural hydrocarbons determined in chloroform as well as in carbon disulfide solution were found to be completely identical. Our structural assignment would therefore appear to be correct.

It must be pointed out, however, that the infrared spectra of saturated hydrocarbons such as VIII measured in solution usually show little fine structure unless the solutions be very concentrated.

(8) F. Sondheimer and D. Elad, *Bull. Research Council Israel*, **5A**, 269 (1956); THIS JOURNAL, **79**, 5542 (1957).

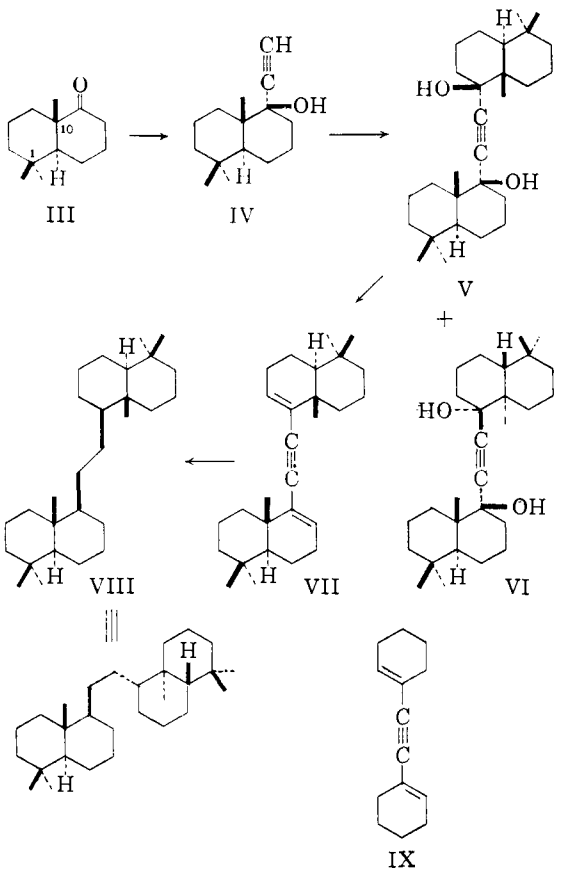
(9) J. D. Cocker and T. G. Halsall, *Chemistry & Industry*, 1275 (1956); *J. Chem. Soc.*, 3441 (1957).

(10) *Cf.* J. Cymerman, I. M. Heilbron, A. W. Johnson and E. R. H. Jones, *ibid.*, 141 (1944), and references cited there.

(11) F. Sondheimer, O. Mancera, H. Flores and G. Rosenkranz, THIS JOURNAL, **78**, 1742 (1956).

(12) R. Stern, Abstracts of Papers, 131st Meeting of the American Chemical Society, Miami, Fla., April, 1957, p. 5-O; R. Stern, J. English and H. G. Cassidy, THIS JOURNAL, **79**, 5797 (1957).

(13) These values were determined in our laboratories by Dr. M. S. Gibson for a chromatographically pure sample of IX. Considerably lower intensity figures [λ_{max}^{EtOH} 262.5 mμ (ε, 12,500) and 275.5 mμ (ε, 9000)] had previously been reported by H. Bastron, R. E. Davis and L. W. Butz (*ibid.*, **65**, 973 (1943)) for dicyclohexenylacetylene as prepared by P. S. Pinkney, G. A. Nesty, R. H. Wiley and C. S. Marvel (*ibid.*, **58**, 972 (1936)) by dehydration of the corresponding di-tertiary glycol with 40% sulfuric acid and simple distillation of the product. Repetition of this experiment in our hands yielded a quite impure sample of the dienyne IX, the main contaminant being ketonic in nature.



Unfortunately the racemic hydrocarbon VIII was not too soluble in most solvents suitable for infrared measurements and for this reason also an attempt kindly made through the courtesy of Prof. H. H. Günthard to determine the infrared spectrum of VIII at very low temperatures (when additional fine structure would be expected to appear) was unsuccessful. The possibility therefore that the synthetic compound belongs to the *meso* series or differs otherwise stereochemically from natural dinoronocerane cannot be excluded with certainty. Nevertheless our work indicates that the present route can lead to compounds with the onocerin type of carbon skeleton and this approach is being investigated further.

Acknowledgment.—We would like to thank Professor D. H. R. Barton, Royal College of Science, London, for a gift of natural dinoronocerane.

Experimental[14]

1,1,10β-Trimethyl-5α-ethynyl-*trans*-decal-5β-ol (IV) from 1,1,10-Trimethyl-*trans*-decal-5-one (III). (a) By Reaction with Sodium Acetylide in Liquid Ammonia.—A solution of sodium acetylide in liquid ammonia was prepared from 3.5 g. of sodium in *ca.* 300 cc. of ammonia by conversion to sodamide through addition of a little ferric nitrate, followed by passage of purified acetylene for 30 minutes, the whole being stirred and cooled in a Dry Ice–acetone-bath. 1,1,10-Trimethyl-*trans*-decal-5-one (III)[8,9] (1.5 g.) dissolved in 30 cc. of dry ether was then added during 10 minutes and the mixture was stirred with cooling for 4 hr. Ammonium chloride (20 g.) was then added, the ammonia was allowed to evaporate and water and ether were added to the residue. The ether layer was washed with dilute hydrochloric acid, sodium bicarbonate solution and water and was then dried and evaporated. The crystalline residue was chromatographed on 75 g. of alumina, when benzene–ether (1:1) eluted 1.35 g. (79%) of the acetylenic carbinol IV with m.p. 62–65°. Crystallization from pentane yielded the analytical sample, m.p. 69–70°, λ_{max} 3.02 μ (acetylenic hydrogen), no bands in the 5.5–6.5 μ region.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.98; H, 11.00.

(b) **By Reaction with Acetylene and Potassium *t*-Butoxide.**—A solution of 0.3 g. of the ketone III in 5 cc. of dry *t*-butyl alcohol was added to a solution of 0.2 g. of potassium in 7 cc. of *t*-butyl alcohol. A slow stream of dry, purified acetylene was then passed through the mixture at room temperature with stirring for 16 hr. Water and ether were added, the organic layer was washed with dilute hydrochloric acid, sodium bicarbonate solution and water. The dried extract was evaporated and the residue was chromatographed on 15 g. of alumina. This procedure yielded 0.23 g. (68%) of the acetylenic carbinol IV, identical with that prepared by method a.

(c) **By Reaction with Acetylenedimagnesium Iodide.**—A solution of ethylmagnesium iodide in 100 cc. of ether was prepared from 4 g. of magnesium and 30 cc. of ethyl iodide. Benzene was then added at the same time as ether was distilled off and the volume was made up to 200 cc. with benzene. Acetylene was then passed through the stirred solution for 4 hr., with ice-cooling. A solution of the ketone III (1 g.) in benzene (30 cc.) was added and the mixture was stirred at room temperature for 16 hr. and then for 2 hr. at 60–70°. Isolation in the usual way yielded 1.2 g. of material which after chromatography on 60 g. of alumina yielded 0.75 g. of the acetylenic carbinol IV, identical with that prepared by method a.

Di-5α-(1,1,10β-trimethyl-*trans*-decal-5β-ol)-acetylene (Racemic Glycol) (V) and the Corresponding *meso*-Glycol VI.—A suspension of sodamide in liquid ammonia was prepared by the addition of 0.53 g. of sodium to *ca.* 60 cc. of ammonia, followed by a small amount of ferric nitrate, the mixture being stirred and cooled with Dry Ice–acetone. A solution of 1.35 g. of the acetylenic carbinol IV in 40 cc. of dry ether was then added during 10 minutes and the cooled mixture was stirred for 45 minutes before a solution of 1.2 g. of the ketone III in 25 cc. of ether was added. Stirring and cooling was continued for 4 hr. and 5 g. of ammonium chloride was then added. The ammonia was allowed to evaporate and the product was isolated with ether in the usual way. The total residue (2.25 g.) was chromatographed on 110 g. of alumina. Petroleum ether–benzene (5:1) eluted 0.13 g. of the unchanged ketone III, while benzene–ether (1:1) eluted 0.91 g. of the unchanged acetylenic carbinol IV. Chloroform eluted 0.71 g. of a mixture of the glycols V and VI which was partially solid. Crystallization of this mixture from pentane yielded 0.15 g. of one isomer with m.p. 205–208°. Further crystallization of this product from pentane yielded the analytical sample m.p. 209–210°. The infrared spectrum showed a hydroxyl band, but no band at *ca.* 3.02 (acetylenic hydrogen) or 5.8 μ (saturated ketone).

Anal. Calcd. for $C_{28}H_{46}O_2$: C, 81.10; H, 11.18. Found: C, 80.92; H, 11.37.

The concentrated mother liquors on crystallization from pentane produced 0.41 g. of the other isomer with m.p. 184–186°. Further crystallization led to the analytical sample, m.p. 189–190°, depressed to 164–168° on admixture with the higher melting isomer. The infrared spectrum of the lower melting isomer was practically identical with that of the higher melting one.

Anal. Calcd. for $C_{28}H_{46}O_2$: C, 81.10; H, 11.18. Found: C, 81.03; H, 10.95.

Di-5-(1,1,10β-trimethyl-Δ⁵-*trans*-octalin)-acetylene (VII).—An intimate mixture of 340 mg. of the glycol V (m.p. 189–190°) and 390 mg. of freshly fused potassium hydrogen sulfate was heated in an oil-bath at 170–180° in a vacuum (*ca.* 25 mm.) for 12 minutes, by which time the evolution of gas had ceased. Water and benzene were added to the cooled mixture, the organic layer was washed with sodium

(14) Melting points are uncorrected. All chromatograms were made with Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.). Ultraviolet spectra were measured on a Unicam model S.P. 500 spectrophotometer and infrared spectra in chloroform solution (unless specified otherwise) on a Baird double-beam recording spectrophotometer. Analyses were carried out in our microanalytical laboratory under the direction of Mr. Erich Meier.

bicarbonate solution and water and was then dried and evaporated. Crystallization of the residue from methanol yielded 213 mg. (69%) of the dienyne VII with m.p. 124–126°. The analytical sample showed m.p. 128–130°, $\lambda_{max}^{isooctane}$ 265 and 279 mμ (ε 17,400 and 13,000, respectively), no hydroxyl band in the infrared.

Anal. Calcd. for $C_{28}H_{42}$: C, 88.82; H, 11.18. Found: C, 88.70; H, 11.01.

Dehydration of the higher melting glycol (m.p. 209–210°) with potassium hydrogen sulfate under the above described conditions yielded a non-crystalline residue, $\lambda_{max}^{isooctane}$ 240 mμ (ε 7,100). Chromatography of this material on alumina showed it to be a complex mixture and no pure substance could be isolated.

sym-**Di-5β-(1,1,10β-trimethyl-*trans*-decalin)-ethane (Racemic Dinoronocerane) (VIII).**—A solution of 226 mg. of the dienyne VII in 20 cc. of dioxane and 25 cc. of glacial acetic acid was shaken in hydrogen over 300 mg. of a pre-reduced platinum catalyst at room temperature and atmospheric pressure overnight. The catalyst was then removed and the solvents were evaporated. The crystalline residue, which gave a negative unsaturation test with tetranitromethane, was dissolved in hexane and passed through a column containing 15 g. of alumina. The solvent was again evaporated and the resulting material on crystallization from chloroform–methanol yielded the saturated racemic hydrocarbon VIII with m.p. 184–185°.

Anal. Calcd. for $C_{28}H_{50}$: C, 86.97; H, 13.03. Found: C, 86.84; H, 12.83.

The synthetic compound in chloroform solution showed infrared bands at 3.42, 6.86, 6.94, 7.24, 7.35, 7.46, 7.63, 7.86, 10.28 and 10.53 μ. A sample of the natural optically active dinoronocerane (m.p. 118–119°, $[\alpha]_D$ +62°)[2] showed a completely superimposable spectrum in this solvent. Similarly identical spectra were obtained in carbon disulfide solution.

REHOVOTH, ISRAEL

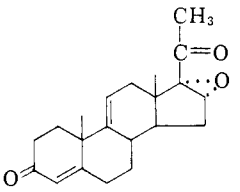
COMMUNICATIONS TO THE EDITOR

17α-ACETOXY-9-HALO-11-OXYGENATED-PROGESTERONES. A NEW CLASS OF ORALLY ACTIVE PROGESTINS

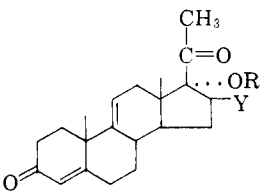
Sir:

The demonstrated clinical utility of 17α-ethynyl-17β-hydroxy-4-estren-3-one (Norlutin)[1] and 17-α-ethynyl-17β-hydroxy-5(10)-estren-3-one (Enovid)[1] has intensified the search for more potent, orally active progestins. Our recent discovery of the high oral progestational activity of 21-fluoro-17α-acyloxyprogesterones[2] has prompted us to prepare other fluorinated 17α-acyloxyprogesterones.

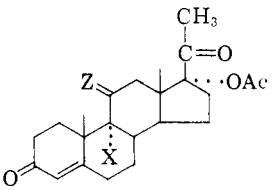
Treatment of 16,17α-epoxy-4,9(11)-pregnadiene-3,20-dione (I),[3] m.p. 181–182°; $[\alpha]_D$ +190° ($CHCl_3$); $\lambda_{max.}^{methanol}$ 239 mμ, ε = 16,900; (found: C, 77.31; H, 7.77); with hydriodic acid[4] in acetic acid gave in excellent yield 16β-iodo-17α-hydroxy-4,9(11)-pregnadiene-3,20-dione (II); m.p. 161–163° dec.; $[\alpha]_D$ +78.2 ($CHCl_3$); $\lambda_{max.}^{methanol}$ 238.5 mμ, ε = 17,800; (found: C, 55.78; H, 5.97; I, 27.78). The 16-iodine was removed readily with Raney nickel,[4] and the resulting 17α-hydroxy-4,9(11)-pregnadiene-3,20-dione (III),[5] was acetylated with acetic anhydride and *p*-toluenesulfonic acid to give 17α-acetoxy-4,9(11)-pregnadiene-3,20-dione (IV); m.p. 243–246°; $[\alpha]_D$ +53.1 °($CHCl_3$); $\lambda_{max.}^{methanol}$ 239 mμ, ε = 18,150; (found: C, 74.42; H, 8.24). This $\Delta^{9,11}$-steroid was converted in the conventional manner[5] to 9α-bromo-11β-hydroxy-17α-acetoxyprogesterone (V); m.p. 133–138° dec.; $\lambda_{max.}^{methanol}$ 242.5 mμ, ε = 15,900; $[\alpha]_D$ +100° ($CHCl_3$); (found: C, 58.77; H, 6.59). In order to prepare the 9α-fluoro-derivatives, 9,11β-epoxy-17α-acetoxyprogesterone (VI); m.p. 229–232.5°; $\lambda_{max.}^{methanol}$ 243.5 mμ; ε = 15,100; $[\alpha]_D$ −49.5° ($CHCl_3$); (found: C, 71.28; H, 7.58); was obtained from V by treatment with sodium carbonate

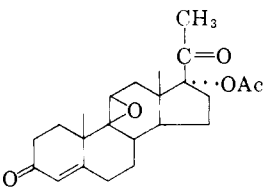


I



II, R = H; Y = I
III, R = H; Y = H
IV, R = Ac; Y = H





V, X = Br, Z = α-H, β-OH
VII, X = F, Z = α-H, β-OH
VIII, X = F, Z = α-H, β-OAC
IX, X = F, Z = O =

VI

in aqueous tetrahydrofuran. The opening of the oxide ring in VI with hydrogen fluoride in tetrahydrofuran[6] yielded the desired 9α-fluoro-11β-hydroxy-17α-acetoxyprogesterone (VII); m.p. 266–269°; $[\alpha]_D$ +77.6° ($CHCl_3$); $\lambda_{max.}^{methanol}$ 238 mμ, ε = 17,500; (found: C, 67.74; H, 7.60). Compound VII was acetylated with acetic anhydride, *p*-toluenesulfonic acid[7] to 9α-fluoro-11β,17α-diacetoxyprogesterone (VIII); m.p. 277–282°; $[\alpha]_D$ +94.8° ($CHCl_3$); $\lambda_{max.}^{methanol}$ 236.5 mμ, ε = 17,400;

(1) O. v. St. Whitelock, Editor in Chief, "New Steroid Compounds with Progestational Activity," *Ann. N. Y. Acad. Sci.*, **71**, 479–806 (1958).

(2) C. G. Bergstrom, P. B. Sollman, R. T. Nicholson and R. M. Dodson, unpublished data.

(3) R. M. Dodson and C. G. Bergstrom, U. S. Patent 2,705,711, April 5, 1955.

(4) S. P. Barton, B. Ellis and V. Petrow, *J. Chem. Soc.*, 478 (1959).

(5) J. Fried, J. F. Herz, E. F. Sabo, A. Borman, F. M. Singer and P. Numerof, THIS JOURNAL, **77**, 1068 (1955).

(6) R. F. Hirschmann, R. Miller, J. Wood and R. E. Jones, *ibid.*, **78**, 4956 (1956).

(7) R. B. Turner, *ibid.*, **75**, 3489 (1953). Note the low progestational activity of similar compounds devoid of the 9α-fluorine. E. P. Oliveto, R. Rausser, C. Gerold, E. B. Hershberg, M. Eisler, R. Neri and P. L. Perlman, *J. Org. Chem.*, **23**, 121 (1958).