mers have a molecular weight of about 1000, or 6 complete chemical units, there are therefore 6 different points in the chain where a new spiral direction may be introduced. On a purely statistical basis, therefore, there are 64 different configurations possible for the *cis* molecule. After a *cis* molecule is formed, the direction of the spiral cannot be changed because of steric hindrances. Therefore, it appears extremely unlikely that crystallization would take place in the all-*cis* polymer.

Crystallization was not observed by the X-ray diffraction technique for any of the *cis–trans* polymers. On the basis of the above analysis for all-*cis* molecules, and the irregularity introduced by the mixing of the *cis* and *trans* structures, crystallization would not be expected to occur.

The Infrared Spectra of Polymers.—The chemical evidence seems conclusive that the all-*cis* polymer and the all-*trans* polymer are completely *cis* and *trans*, respectively. Nevertheless, it seemed desirable to study the infrared spectra of these compounds not only to verify the deductions from chemical evidence but also to observe the spectra of such synthetic polymers. The spectra were obtained using a Beckman IR2 spectrophotometer. Those of the all-*cis* and all-*trans* polymers were obtained by point-by-point (sample-in, sample-out) measuring using a rock salt plate as standard and are shown in Fig. 4. The spectra of the pure diols were obtained in the same manner and are shown in Fig. 5. Those of the mixed polymers and monomers were obtained by recording and shown schematically in Fig. 6. The spectra of Figs. 4 and 5 are also included in this figure to facilitate comparison.

A comparison of the spectra of the mixed polymers with those of the all-*trans* and all-*cis* polymers shows many differences in the number of bands and intensities. These differences are large enough to show that, for example, there is no *cis*-diol–*trans* acid polymer or *trans* diol–*cis* acid polymer in the all-*cis* polymer. Thus if any isomerization occurred during the preparation of either the all-*cis* or all-*trans* polymer it must have happened in both the diol and the acid.

The question of whether or not both the diol and acid isomerized during the preparation of either the all-*cis* or all-*trans* polymer is more difficult to settle on the basis of the infrared spectra of the polymers. This is particularly true with respect to the presence of some all-*trans* polymer in the all-*cis* polymer. The C=C bands at 6.04 and 6.10 μ in the spectra of the all-*cis* polymer are sufficiently intense to make it improbable that there is much, if any, *cis* polymer in the all-*trans* polymer, especially since the band at 6.06 μ in the spectrum of the all-*trans* polymer is probably a harmonic of a lower lying band, as found by Rasmussen and Brattain[10] in the spectra of other *trans* compounds. Repeated experiments showed the 6.06 μ band to be real for this polymer and not due to water. The absence of it would be cause for concern as indicated above. The C=C bands at 6.04 and 6.10 μ, as well as the absence of any indication of a band at 12.25 μ in the all-*trans* polymer spectrum, seem sufficient to warrant the conclusion that the all-*trans* polymer is substantially, and probably completely, pure.

At first thought, it might seem that the well-established correlation rule of assigning the 10.34 μ band to a *trans* $\diagdown\mathrm{CH{=}CH}\diagup$ structure would unambiguously determine whether any *trans* polymer is present in the *cis* polymer. Unfortunately, both of the *cis* monomers used here have bands in their spectra at or near this wave length. A comparison of the spectra of the two polymers shows that, except for the 12.9 μ band in the all-*trans* polymer spectrum, it would be difficult, if not impossible, to detect a small amount (5%) of the *trans* polymer in the *cis* polymer in this manner. There is a weak band in the spectrum of the all-*cis* polymer which might indicate the presence of some all-*trans* polymer. If so, the amount must be small since, otherwise, the band at about 8.6 μ in the all-*cis* polymer spectrum would be broader than found, due to the shape of the 8.6 μ band in the all-*trans* spectrum. However, except for this band, the spectrum given can be regarded as the spectrum of an all-*cis* polymer of maleic acid and *cis*-2-butene-1,4-diol.

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[10] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

AKRON 17, OHIO

[CONTRIBUTION FROM HERCULES EXPERIMENT STATION, HERCULES POWDER CO.]

The Autoxidation and Chromic Anhydride Oxidation of the Lactone of "Hydroxytetrahydroabietic Acid"[1]

BY JAMES MINN, THOMAS F. SANDERSON AND LEE A. SUBLUSKEY

RECEIVED SEPTEMBER 6, 1955

The lactone of "hydroxytetrahydroabietic acid" in a molten state has been found to undergo non-catalytic and catalytic autoxidation with pure oxygen. In the products isolated—hydroperoxides, alcohols and ketones—the basic tricyclic ring structure of the original lactone was preserved; the oxidative attack was limited to the vicinity of the 7-isopropyl group. Similar results were also obtained with an anhydrous chromic anhydride oxidation of the lactone. The structures of the various products were established by interconversions with one another and by a conversion to the known pimanthrene.

Although considerable attention has been given to the autoxidation of relatively simple, saturated monocyclic and bicyclic hydrocarbons, such as substituted cyclopentanes and cyclohexanes, pinane and the decalins,[2] studies with larger polycyclic structures have not been reported. In this paper we describe the autoxidation of a tricyclic diterpenoid, the lactone of "hydroxytetrahydroabietic acid." This compound, m.p. 131–132°, whose structure recently has been shown to be 4aα-hydroxy-1β,4bβ-dimethyl-7ξ-isopropyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic lactone (I),[3] is the product which is so readily obtained from commercial, partially hydrogenated rosin[4] when treated with strong mineral acid.[5]

The lactone I, when stirred at a few degrees above its melting point in an atmosphere of oxygen with an ultraviolet light initiating source, was found to absorb oxygen readily, and in a few hours produced a reaction mixture which had an active oxygen content of 1.0%. By countercurrent distribution be-

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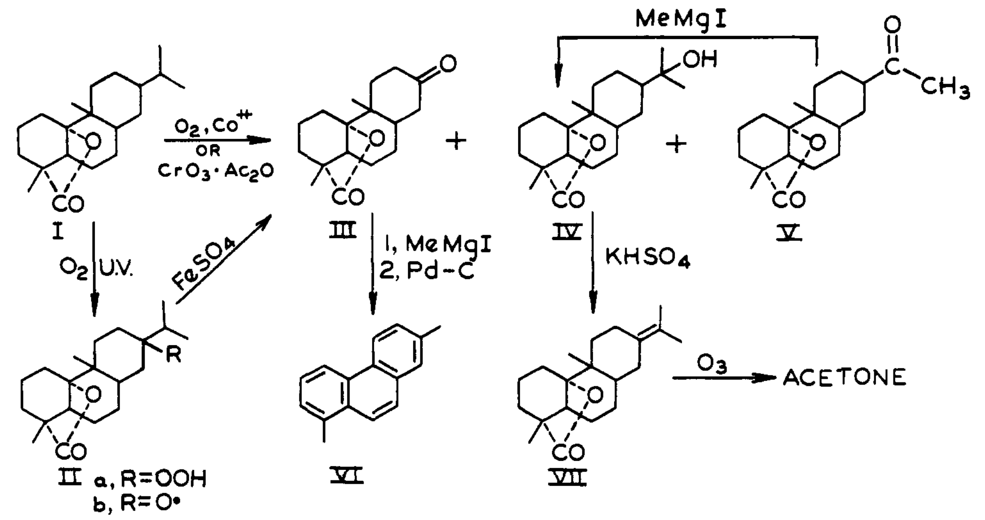
[1] Presented before the Division of Organic Chemistry, 128th Meeting, Am. Chem. Soc., Minneapolis, Minn., September 15, 1955.

[2] E. J. Gasson, E. G. E. Hawkins, A. F. Millidge and D. C. Quin, *J. Chem. Soc.*, 2798 (1950); K. I. Ivanov and V. K. Savinova, *Doklady Akad. Nauk. S.S.S.R.*, **59**, 493 (1948); R. Criegee and H. Dietrick, *Ann.*, **560**, 135 (1948); G. S. Fisher, L. A. Goldblatt, I. Kniel and A. D. Snyder, *Ind. Eng. Chem.*, **43**, 671 (1951); G. S. Fisher, J. S. Stinson and L. A. Goldblatt, THIS JOURNAL, **75**, 3675 (1953); G. Chavanne and E. Bode, *ibid.*, **52**, 1609 (1930).

[3] L. A. Subluskey and T. F. Sanderson, *ibid.*, **76**, 3512 (1954).

[4] This material is derived from the *Pinus palustris* and similar conifers, and is produced by Hercules Powder Co. under the trade name of "Staybelite Resin."

[5] E. E. Fleck and S. Palkin, THIS JOURNAL, **61**, 1230 (1939); R. F. B. Cox (assigned to Hercules Powder Co.), U. S. Patent 2,355,782 (1944).



tween petroleum ether and aqueous methanol and a subsequent chromatographic separation through silica gel, it was possible to obtain a hydroperoxide concentrate that had an active oxygen content of 4.6% (or a $C_{20}H_{31}O_2{\cdot}OOH$ concentration of 48%). One of the hydroperoxides that was most certainly present in this concentrate was IIa, as evidenced by a ferrous sulfate reductive cleavage of the concentrate to yield the $C_{17}H_{24}O_3$ ketone III. Only a hydroperoxide of structure IIa would be expected to cleave the 7-isopropyl group and render a ketonic group at the 7-position, since reductive cleavages of this type involve the formation of an intermediate alkoxyl radical (*e.g.*, IIb)[6] followed by the fission of, in the case of a tertiary hydroperoxide, the nearest and weakest carbon–carbon bond.[7] Other products that were isolated during the concentration of the hydroperoxides were the $C_{20}H_{32}O_3$ hydroxy compound IV and the ketone III.

A more convenient method for obtaining the two oxygenated products, III and IV, was found by substituting a cobalt naphthenate catalyst for the ultraviolet light initiations in the autoxidation. The absorption of oxygen proceeded at about the same rate (7.5 mole % oxygen per hour), the maximum active oxygen content was less than 0.2%, and the hydroxy derivative IV and the ketone III were obtained in 27 and 12% yields, respectively, by chromatographing the total oxidate directly. While the other products of this catalytic autoxidation were oils and have yet to be completely separated and identified, acetone was also obtained and trace amounts of the $C_{19}H_{28}O_3$ methyl ketone V were isolated by chromatographing the ketonic fraction of a Girard's separation carried out on a portion of the original catalytic autoxidation product.

In an effort to determine whether the autoxidation products III, IV and V could also be obtained from a more conventional oxidation method, the lactone I was subjected to a chromic anhydride oxidation. In this case it was found that the anhydrous conditions provided by an acetic anhydride–acetic acid solvent were necessary, since acetic acid alone led almost exclusively to water-soluble oxidation products.[8] This result was probably due to the participation of by-product water which sufficiently increased the oxidizing power of the reagent to cause extensive degradation of the lactone molecule. After saponification of the acetoxy groups introduced in the chromic anhydride–acetic anhydride oxidation, a Girard's separation and chromatography gave the hydroxy derivative IV in a 29% yield, the ketone III in a 6.5% yield, and the methyl ketone V in a 12% yield.

The structures of the above oxidation products were established in the following manner. The ketone III was treated with methylmagnesium iodide and then dehydrogenated over palladium-on-carbon to give pimanthrene (VI) whose identity was confirmed by X-ray diffraction comparisons with authentic samples of the hydrocarbon and its trinitrobenzene and picric acid derivatives. By this the position of the ketonic carbonyl in III was definitely established. The hydroxy derivative IV was dehydrated by fusing with potassium hydrogen sulfate and subsequently ozonized to give acetone which was isolated as its 2,4-dinitrophenylhydrazone. Although no effort was made to isolate the other fragments from the ozonization, the presence of acetone in the cleavage products is indicative of the intermediate dehydrated structure VII and limits the position of the free hydroxyl group in IV to the vicinity of the 7-isopropyl group. Locating the exact position of this hydroxyl group was accomplished by converting the methyl ketone V to IV by careful reaction with methylmagnesium iodide followed by hydrolysis. Although proof of the structure of the methyl ketone V is inherent in the structure proof of IV, further confirmation was obtained from a positive iodoform test with V. Arguments for the structure of the hydroperoxide IIa which are based on the ferrous sulfate reductive cleavage mechanism were mentioned above.

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(6) M. S. Kharasch, F. S. Arimoto and W. Nudenberg, *J. Org. Chem.*, **16**, 1556 (1951).

(7) P. George and A. D. Walsh, *Trans. Faraday Soc.*, **42**, 94 (1946); M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **15**, 763 (1950).

(8) The authors wish to thank Theodore N. Goreau for his participation in this particular phase of the work.

Experimental[9]

Autoxidation of 4aα-Hydroxy-1β,4bβ-dimethyl-7ξ-isopropyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic Lactone (I). A. Non-catalytic Method.—This autoxidation was carried out at 133–134° by bubbling a stream of oxygen through 30.4 g. of the molten lactone I; during the first 2.5 hr. the reaction was irradiated with an ultraviolet light.[10] At the end of 11 hr. the hydroperoxide content was 10.5%[11] which corresponds to a 1.0% active oxygen content; weight of total oxidate, 32.3 g.

B. **Catalytic Method.**—A 60.8-g. (0.2 mole) sample of the lactone I together with 60 drops of a cobalt naphthenate catalyst solution[12] was stirred in a circulating atmosphere of oxygen at 139° for 10 hr. By means of a gas buret attached to the reaction vessel, it was determined that a total of 6.02 g. (0.19 mole) of oxygen had been absorbed by the molten reaction mixture during its oxidation. The total weight of the oxidate was 62.8 g. By employing a Dry Ice trap in the oxygen circulating system, the volatile materials were collected. From this 0.45 g. of the 2,4-dinitrophenylhydrazone derivative of acetone[13] was obtained, m.p. 124.5–125.5°.

A 50-g. portion of the main oxidate was then dissolved in benzene and chromatographed through a column of ethyl acetate-washed alumina. After eluting with benzene and obtaining 35.2 g. of unreacted lactone, four principal fractions were obtained by further elution with benzene, benzene–methylene chloride (1:1), methylene chloride and ether–methanol (1:1), respectively. Fraction 1 (2.33 g.) was an oil which formed a 2,4-dinitrophenylhydrazone and gave a negative iodoform test; fraction 2 (4.78 g.) was crystalline, and failed to precipitate a 2,4-dinitrophenylhydrazone; fraction 3 (0.68 g.) was an oil and formed a 2,4-dinitrophenylhydrazone; and fraction 4 (0.91 g.) was an oil which formed a 2,4-dinitrophenylhydrazone and gave a positive iodoform test. Further purification of Fractions 1 and 2 yielded III and IV (see below); fractions 3 and 4, on the other hand, proved too complicated for convenient resolution.

4aα-Hydroxy-7-oxo-1β,4bβ-dimethyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic Lactone (III).—This compound was isolated from the above Fraction 1, *via* its semicarbazone or by direct crystallization from ether. Recrystallization from ethyl acetate gave the pure compound, m.p. 146.5–148°, $[\alpha]^{25}_{D}$ −3.6° (in chloroform), yield 1.91 g. (12%).

Anal. Calcd. for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.80; H, 8.74.

This compound was also obtained in a 14% yield by carrying out a Girard's separation directly on the crude catalytic autoxidation products and then purifying by chromatography.

The 2,4-dinitrophenylhydrazone derivative of this compound melted at 231–233°.

Anal. Calcd. for $C_{23}H_{28}O_6N_4$: C, 60.51; H, 6.18; N, 12.27. Found: C, 60.57; H, 6.26; N, 12.34.

4aα,14-Dihydroxy-7ξ-isopropyl-1β,4bβ-dimethyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic 4aα-Lactone (IV).—Recrystallization of the above fraction 2 from acetone gave this compound in a 27% yield (4.2 g.), m.p. 180.5–181.5°, $[\alpha]^{25}_{D}$ −7.5° (in chloroform).

Anal. Calcd. for $C_{20}H_{32}O_3$: C, 74.95; H, 10.06; mol. wt., 320. Found: C, 74.93; H, 10.26; mol. wt., 317.

This compound was also isolated in 22% yield by chromatographing (alumina) the non-ketonic fraction from a Girard separation of the crude catalytic autoxidation products.

Concentration of Hydroperoxides.—A 29.2-g. sample of the oxidate obtained from the non-catalytic method of autoxidation was distributed countercurrently through six stages between petroleum ether and 85% aqueous methanol. For this, six one-liter separatory funnels were used, each containing 400-cc. amounts of the two solvents. The hydroperoxide-enriched fraction contained 9.33 g. of a product analyzing for 23.1% hydroperoxides.[11] This fraction was further concentrated by chromatographing through a silica gel–Celite (2:1) column with methylene chloride. Elution with methylene chloride–ether (4:1) gave 1.8 g. of a yellow oil concentrate which analyzed for 48.3% hydroperoxides.[11] This concentrate did not form a precipitate when treated with a 2,4-dinitrophenylhydrazine hydrochloride reagent solution. The presence of at least two other hydroperoxide concentrates was indicated by peaks which occurred during further elution of the chromatographic column. Along with these hydroperoxide peaks, 1.65 g. of the ketone III and 1.51 g. of the hydroxy derivative IV were also obtained.

Ferrous Sulfate Reduction of the Hydroperoxide Concentrate.—A 1.35-g. sample of the above 48.3% hydroperoxide concentrate dissolved in 50 cc. of methanol was added slowly to a solution of 2.78 g. of ferrous sulfate heptahydrate, 25 cc. of methanol and 25 cc. of water. After stirring for 2 hr. at 50–60°, the resulting dark brown reaction mixture was poured in 300 cc. of water which in turn was extracted with methylene chloride to yield 1.22 g. of a yellow oil.

This yellow oil was then treated with a 2,4-dinitrophenylhydrazine hydrochloride solution, and the precipitated 2,4-dinitrophenylhydrazone product (400 mg.) was collected and chromatographed through a silica gel–Celite (2:1) column with methylene chloride to give 300 mg. of the 2,4-dinitrophenylhydrazone of **4aα-hydroxy-7-oxo-1β,-4bβ-dimethyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic lactone (III)**,[13] m.p. 229–231°.

Anal. Calcd. for $C_{23}H_{28}O_6N_4$: C, 60.51; H, 6.18; N, 12.27. Found: C, 60.95; H, 6.30; N, 12.47.

Chromic Anhydride Oxidation of I.—To a solution consisting of 30.4 g. (0.1 mole) of I, 500 cc. of acetic acid and 450 cc. of acetic anhydride, 33.3 g. (0.33 mole) of chromic anhydride was added slowly with stirring over a period of 7 hr. Stirring was continued at room temperature overnight. The dark green reaction solution was then poured into 8 l. of ice-water containing 100 g. of sodium acetate and stirring was continued for another 3 hr. The product was extracted with ether and, after washing and drying, evaporation yielded 23.0 g. of crude oxidate.

A Girard separation of this oxidate gave 12.4 g. of non-ketonic material and 8.74 g. of ketonic material. A chromatographic separation of the latter on a basic alumina column eluting first with benzene and then with methylene chloride gave two crystalline products. Recrystallization of the first from isoöctane gave pure **4aα-hydroxy-7ξ-acetyl-1β,4bβ-dimethyl-8aα,10aβ-perhydrophenanthrene-1α-carboxylic lactone (V)**, m.p. 138–139°, $[\alpha]^{25}_{D}$ −22.6° (in chloroform), yield 3.75 g. (12%). This compound gave a positive iodoform test.

Anal. Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 74.94; H, 9.46.

The 2,4-dinitrophenylhydrazone derivative of V melted at 231–235°.

Anal. Calcd. for $C_{25}H_{32}O_6N_4$: C, 61.96; H, 6.65; N, 11.56. Found: C, 61.95; H, 6.85; N, 11.60.

Recrystallization of the second product from the above chromatographic separation from isopropyl ether gave 1.80 g. (6.5% yield) of a pure $C_{17}H_{24}O_3$ compound, m.p. 150–152°, which proved, by mixture melting point and infrared spectra comparisons, to be the same keto lactone III that was isolated from the autoxidation experiments.

Partial alkaline hydrolysis of the non-ketonic fraction from the Girard separation of the chromic anhydride oxidate followed by recrystallization from acetone gave 9.3 g. (29% yield) of IV, the identification of which was confirmed by a mixture melting point and an X-ray diffraction pattern comparison with a sample obtained from the autoxidation experiments.

Pimanthrene from III.—One gram of the 7-ketolactone III was allowed to react with an excess of methylmagnesium iodide in ether solution stirred at room temperature. After decomposition of the reaction complex with a 25% ammo-

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(9) All melting points are uncorrected. Microanalyses by V. A. Aluise and N. A. Walker and X-ray diffraction comparisons by W. E. Fox, all of the Experiment Station, Hercules Powder Co. All rotations were observed in a 1-dm. polarimeter tube at 1% concentrations in the solvent indicated.

(10) For an ultraviolet light source a Hanovia Inspectolite (Hanovia Chemical and Manufacturing Co., Newark 5, N. J.) emitting at 3660 Å. was used.

(11) Calculated as $C_{20}H_{31}O_2{\cdot}OOH$ and determined iodometrically (sodium iodide in isopropyl alcohol–acetic acid), C. D. Wagner, R. H. Smith and E. D. Peters, *Ind. Eng. Chem., Anal. Ed.*, **19**, 976 (1947).

(12) "Nuodex Cobalt 6%," a commercial resin dryer which is 6% cobalt metal and is prepared and sold by Nuodex Products Co., Inc., Elizabeth, N. J.

(13) Identified by an X-ray diffraction comparison with an authentic sample.

nium chloride solution, the product (1.16 g.) was isolated by ether extraction and then dehydrogenated by treating with an equal amount of 5% palladium-on-carbon at 300–325° for 8 hr. The dehydrogenated product was isolated by an ether extraction and then chromatographed through a silica gel column with hexane to give 273 mg. of pure pimanthrene, m.p. 84–85° (lit.[14] m.p. 86°). The trinitrobenzene derivative was prepared, m.p. 160–160.5° (lit.[15] m.p. 161–162°); and the picric acid derivative was also prepared, m.p. 130–131° (lit. m.p. 132°).[16] Melting points of mixtures of these derivatives with authentic samples were not depressed below their individual melting points. X-Ray diffraction patterns of the hydrocarbon and its derivatives were identical to those of authentic samples. The authentic sample of pimanthrene was obtained from the dehydrogenation of dihydrodextropimaric acid (m.p. 241–243°, $[\alpha]_D$ +19.2°).[17]

Dehydration and Ozonization of IV.—A 3.2-g. sample of the hydroxy lactone IV was fused with potassium hydrogen sulfate for 30 min. at 190°. Extraction with methylene chloride yielded an oil which crystallized upon standing, m.p. 80–85°. This was dissolved in methylene chloride and then treated with an excess of ozone at −70° for 12 min. The ozonide was decomposed with zinc and acetic acid at 50°, the evolved gases aided by a nitrogen sparge being passed through a 2,4-dinitrophenylhydrazine hydrochloride solution. The resulting orange precipitate was purified by chromatography, m.p. 124–125°, and identified as the 2,4-dinitrophenylhydrazone of acetone.[13] No evidence for the corresponding formaldehyde derivative was obtained.

Conversion of V to IV.—A 500-mg. sample of the 7-acetyl compound V was stirred at room temperature for 18 hr. with a Grignard solution prepared from 160 mg. of magnesium, 940 mg. of methyl iodide and 25 cc. of ether. After isolation, the product (470 mg.) was twice recrystallized from acetone to give 90 mg. of a material which melted at 178–179°. An X-ray diffraction pattern comparison showed this to be identical to the 14-hydroxy compound IV obtained by the catalytic autoxidation of the original lactone I.

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[14] R. D. Haworth, B. M. Letsky and C. R. Mavin, *J. Chem Soc.*, 1789 (1932).

[15] L. C. Craig and W. A. Jacobs, *J. Biol. Chem.*, **152**, 648 (1944).

[16] W. A. Jacobs and C. F. Huebner, *ibid.*, **170**, 200 (1947).

[17] T. Hasselstrom and B. L. Hampton, THIS JOURNAL, **61**, 967 (1939).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

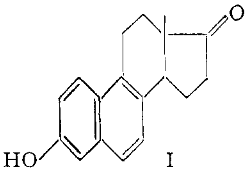
The Hydrogenation of Equilenin to an Isoestradiol

BY WILLIAM G. DAUBEN AND LEO AHRAMJIAN

RECEIVED JUNE 27, 1955

When equilenin is hydrogenated over Raney nickel in alkaline solution a mixture consisting of 20% of an isoestradiol and 50% of $\Delta^{5,7,9}$-estratriene-3β,17β-diol is formed. Under acidic conditions, no phenolic product is obtained. This formation of an estradiol isomer represents the first conversion of equilenin to an estradiol-type of structure by catalytic hydrogenation. The stereochemistry of the products and the effect of *p*H on the course of hydrogenation is discussed.

Since the isolation and determination of the structure of the estrogens,[1] many investigators have tried to convert the relatively inactive compound equilenin (I) to the naturally occurring hormone 17β-estradiol (II). In hydrogenation studies, for example, it has been found that the reaction over a platinum catalyst in acidic solution proceeds by either reducing the phenolic ring A to yield $\Delta^{5,7,9}$-estratriene-3β,17β-diol (III)[2] or by reducing the phenolic ring with concomitant hydrogenolysis to form $\Delta^{5,7,9}$-estratriene-17β-ol (IV).[2–4]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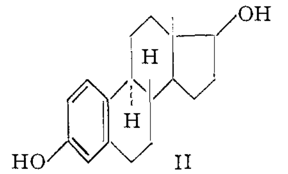
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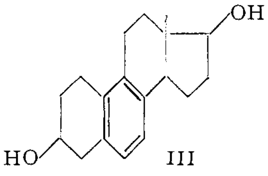
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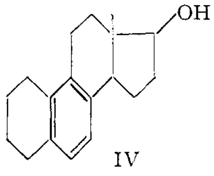
IV

With a chemical reducing agent, the reduction of the isomeric 17-dihydroequilenins by sodium and amyl alcohol has yielded the four isomeric $\Delta^{5,7,9}$-estratriene-3,17-diols (III).[2,5–8] In addition, Marker[5] has reported that besides these neutral products, a small yield of the phenolic 17β-estradiol (II) can be isolated (from 1.0 g. of the 17β-dihydroequilenin, 194 mg. of crude phenolic material was received which was converted into 41 mg. of the 3-monobenzoate). This same reduction was studied by Ruzicka, Müller and Morgeli,[2] however, and in their hands no pure phenolic material was obtained. In a similar vein, Marker and his colleagues[9] also reported a reduction of dehydroergosterol to a ring A phenolic material and this again was not able to be repeated by Windaus and Deppe.[10]

During the past decade, the importance of the acidity and the basicity of the media in a catalytic hydrogenation over Raney nickel of a phenol has been established[11–15] as being an important factor

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[1] L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 306.

[2] L. Ruzicka, P. Müller and E. Morgeli, *Helv. Chim. Acta*, **21**, 1394 (1938).

[3] R. E. Marker, O. Kamm, T. S. Oakwood and F. H. Tendick, THIS JOURNAL, **59**, 769 (1937).

[4] W. E. Bachmann, A. S. Dreiding and E. F. M. Stephenson, *ibid.*, **73**, 2765 (1951).

[5] R. E. Marker, *ibid.*, **60**, 1897 (1938).

[6] R. E. Marker, E. Rohrmann, E. L. Little and F. H. Tendick, *ibid.*, **60**, 2440 (1938).

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[8] R. D. H. Heard and M. M. Hoffman, *J. Biol. Chem.*, **138**, 651 (1941).

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[10] A. Windaus and M. Deppe, *Ber.*, **70**, 76 (1937).

[11] H. E. Ungnade and A. D. McLaren, THIS JOURNAL, **66**, 1181 (1944); H. E. Ungnade and F. V. Morriss, *ibid.*, **70**, 1898 (1948); **72**, 2112 (1950).

[12] G. Stork, *ibid.*, **69**, 576 (1947).

[13] W. G. Dauben and R. E. Adams, *ibid.*, **70**, 1759 (1948).

[14] L. F. Fieser and M. Leffler, *ibid.*, **70**, 3196 (1948).

[15] W. G. Dauben, C. F. Hiskey and A. H. Markhart, Jr., *ibid.*, **73**, 1393 (1951).