depend on approximately the first power of acid concentration, there are numerous instances of other acid-catalyzed reactions in which the dependence has been found to be complex.[12]

Except for one instance which appears anomalous, the data in Tables IIIa and IIIb indicate no significant change in velocity caused by variation of chain length. This constitutes further support for the earlier assumption that degradation of the chain during the reaction is without appreciable effect in so far as the kinetics of alcoholysis are concerned. According to equation (2), the rate of appearance of polyvinyl alcohol divided by the initial concentration of polymer (x_0) at any given value of x should be a constant. Tables IVa and IVb show that this condition is approached in dilute solutions. With increasing polymer concentration, there is a well-defined downward drift of the values of K. Since an over-all change in concentration of eightfold causes only about a 25% change in the relative rate of alcoholysis, it may be concluded that the deviations in more concentrated solutions of the polymer are due to secondary causes.

From Fig. 5 it is seen that the data conform to the Arrhenius equation. It thus appears likely that all of the rate constants K_n appearing in the scheme represented by equation (3) have approximately the same dependence on temperature.

Summary

1. The alcoholysis of polyvinyl acetate in absolute methanol has been studied, using both hydrogen chloride and sodium hydroxide as catalysts.

2. The reaction possesses apparent autocatalytic characteristics, which may be due either to an autocatalytic or to a stepwise nature.

3. The reaction rate is dependent on the first power of the concentration of the basic catalyst, and on the 1.22 power of the concentration of the acidic catalyst.

4. The reaction rate is further dependent upon approximately the first power of the polymer concentration, independent of the molecular weight of the polymer, and responds to temperature changes according to the Arrhenius equation.

5. A qualitative explanation of these relationships is suggested.

ROCHESTER, N. Y. RECEIVED JULY 30, 1941

[12] See, *e. g.*, H. Dawson and F. Powis, *J. Chem. Soc.*, **103**, II, 2135 (1913).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Oxidation Products of $\Delta^{9,10}$-Octalin

BY WILLIAM P. CAMPBELL AND G. CHRIS HARRIS

This work was initiated for the purpose of finding a suitable method of preparing the octalone-1 which has been designated by Hückel and Naab[1] as the $\Delta^{9,10}$-isomer. In addition it was planned to prepare intermediates such as $\Delta^{9,10}$-octalol-1 which, along with the known 9,10-dihydroxydecalin, may be converted by dehydration into different isomeric hexahydronaphthalenes. The latter are of interest as model compounds for the many natural products which contain this diene system.

For the preparation of $\Delta^{9,10}$-octalin the method of Linstead *et al.*[2,3] was followed although certain modifications which appear to be essential were made. The method consists of the dehydration of β-decalol and isomerization of the resulting octalin by means of phosphoric acid and phosphoric anhydride. The yield of $\Delta^{9,10}$-octalin from β-decalol was 78%. Although we have obtained the known blue nitroso chloride derivative[3c] of $\Delta^{9,10}$-octalin from our product, the possibility that small amounts of isomers are present[2] is by no means excluded.

The desired octalone-1 has been obtained by the action of nitrous acid on 9-amino-$\Delta^{4,10}$-octalin and by the chromic acid oxidation of $\Delta^{9,10}$-octalin.[1] More recently it has been made by cyclization of γ-(Δ^1-cyclohexenyl)-butyric acid.[4] We have obtained the same substance in 45% over-all yield by the following series of reactions. The oxidation of $\Delta^{9,10}$-octalin with selenium dioxide in the presence of acetic anhydride at 5° gave the acetate of $\Delta^{9,10}$-octalol-1 (II) in 65% yield. Hydroly-

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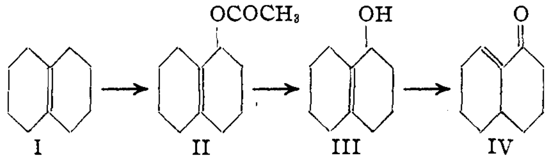
[1] Hückel and Naab, *Ann.*, **502**, 136 (1933).

[2] Linstead, Wang, Williams and Errington, *J. Chem. Soc.*, 1136 (1937).

[3] Other methods for the preparation of $\Delta^{9,10}$-octalin: (a) Nametkin and Gaglow, *Ber.*, **62**, 1570 (1929); (b) Durland and Adkins, THIS JOURNAL, **61**, 429 (1939); (c) Hückel, Danneel, Schwartz and Gercke, *Ann.*, **474**, 121 (1929).

[4] Nenitzescu and Przemetzky, *Ber.*, **74**, 676 (1941).

sis of this product followed by an Oppenauer[5] oxidation of the alcohol (III) gave the octalone. The identity of this product with that previously reported was established by conversion to the oxime and semicarbazone.



The double bond in this octalone had been placed[1] at 9,10 because of the formation from $\Delta^{9,10}$-octalin (I) and because rearrangement to another position was considered unlikely. We have obtained evidence based on the ultraviolet absorption spectrum of our sample, which shows the substance to be $\Delta^{8,9}$-octalone-1 (IV). The curve (Fig. 1, curve 2) shows a maximum at 243 mμ (log E = 4.0) characteristic of an α,β-unsaturated ketone and one at 305 mμ (log E = 1.8) which is due to the carbonyl group. The former falls within the range (234 to 244 mμ) which was recently shown by Woodward[6] to be characteristic of α,β-unsaturated ketones having one hydrogen on the doubly-bound carbon atoms. The only octalone-1 which meets this requirement is the $\Delta^{8,9}$-derivative (IV).[6a]

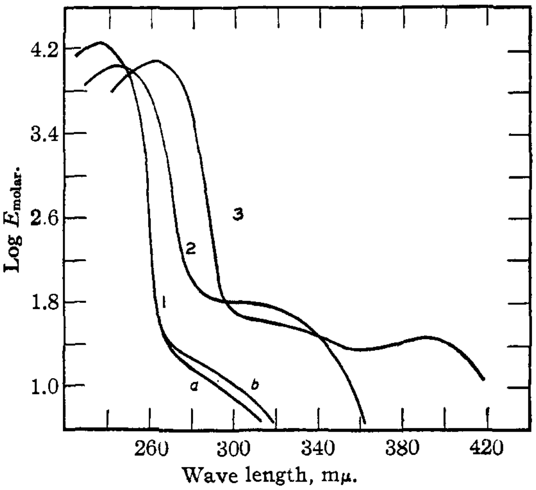
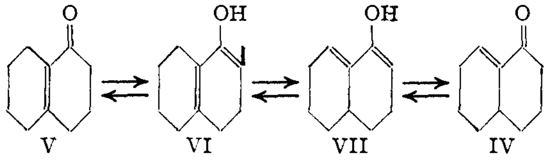
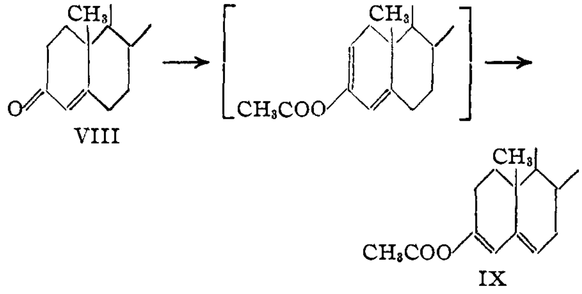


Fig. 1.—Absorption spectra: 1a and b, 1,2,3,5,6,7-hexahydronaphthalenediol-1,5 diacetate and the diol, respectively; 2, $\Delta^{8,9}$-octalone-1; 3, $\Delta^{9,10}$-octalindione-1,5.

A rearrangement of $\Delta^{9,10}$-octalone-1 (V) to the $\Delta^{8,9}$-isomer might be expected if one assumes that enolization of the $\Delta^{9,10}$-compound occurs to an appreciable extent. The enol form (VI) possesses an unstable arrangement of the double bonds and would be expected to isomerize to the more stable distributed form (VII) quite readily. An analogy for this kind of shift is found in the conversion of cholestenone (VIII) into the enol acetate (IX).[7] Although hydrolysis, in this case, would regenerate the original ketone because the double bond would return to a position of conjugation with the carbonyl,[8] a shift of this kind would not be expected to occur in the octalone where conjugation is attained without rearrangement.





The double bonds in the octalol-1 (III) and the acetate (II) are very probably in the 9,10 position. The compounds are formed from $\Delta^{9,10}$-octalin and no reason for postulating a shift of the double bond is apparent. In addition, further oxidation of the acetate by selenium dioxide takes place in the 5-position, as would be expected if the double bond is at 9,10. While this evidence is not conclusive, it strongly indicates a 9,10 double bond.

The $\Delta^{8,9}$-octalone-1 possesses an asymmetric carbon atom at C_{10} and might be capable of resolu-

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[5] Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).

[6] Woodward, THIS JOURNAL, **63**, 1123 (1941).

[6a] In a recent private communication, Dr. R. B. Woodward has told us about some new work on the relationship of ultraviolet absorption spectra to structure, which will appear in THE JOURNAL at an early date. It was pointed out that all of the α,β,β-trisubstituted α,β-unsaturated ketones ($\Delta^{9,10}$-octalone-1 type) for which ultraviolet absorption curves have been determined, possess an exocyclic carbon–carbon double bond, whereas $\Delta^{9,10}$-octalone possesses no such bond. This variation in structure may place the most probable maximum for $\Delta^{9,10}$-octalone at about 247 mμ. This work renders the value obtained for our ketone, 243 mμ, inconclusive and further evidence is necessary before a definite decision between the 8,9 and 9,10 positions of the double bond can be made. Unfortunately, no other ketone of the $\Delta^{9,10}$-octalone type is available for comparison. We feel, however, that the rearrangement of the double bond from 9,10 to 8,9 through the enol form as shown above is highly probable.

[7] Westphal, *Ber.*, **70**, 2128 (1937); Inhoffen, *ibid.*, **69**, 2141 (1936).

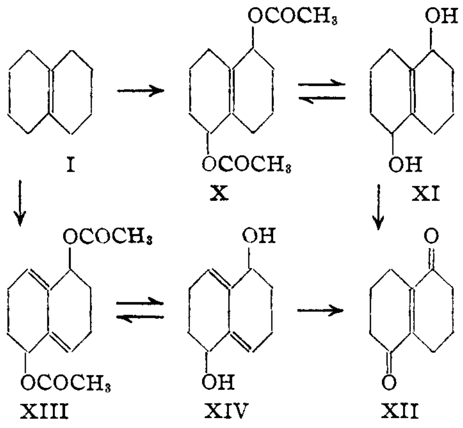
[8] Strain in Gilman's "Organic Chemistry," John Wiley and Sons, New York, N. Y., 1938, p. 1279.

tion. An unsuccessful attempt to accomplish this was made using the condensation product with *l*-menthyl N-aminocarbamate.[9] It is possible that the failure to obtain evidence of optical activity is the result of easy racemization by way of the equilibrium system postulated for the rearrangement of $\Delta^{9,10}$-octalone-1 to the $\Delta^{8,9}$-isomer.

The octalone was heated with dimethylbutadiene at 100° for nearly fifty hours, and 90% of the starting material was recovered from the reaction mixture as the oxime.

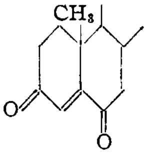
At higher temperatures the oxidation of $\Delta^{9,10}$-octalin by selenium dioxide gives progressively lower yields of the octalol acetate and from the higher boiling fraction of these reaction mixtures two different solid diacetates have been isolated in low yields.

To the first of these, obtained by oxidation at 30°, the structure of $\Delta^{9,10}$-octalindiol-1,5 diacetate (X) is assigned. The evidence for this structure is based on the following reactions. Hydrolysis of the diacetate yielded the corresponding diol (XI) which was converted to the unsaturated diketone (XII) by an Oppenauer oxidation. Dehydrogenation of the diketone with palladium–charcoal gave 1,5-dihydroxynaphthalene which was isolated as the diacetate and identified by comparison with a known sample. Thus the oxygen atoms in this series of compounds are shown to be at the 1- and 5-positions. The double bond in the diol and diacetate is placed at 9,10 for the reasons outlined above in connection with $\Delta^{9,10}$-octalol-1. Perhaps the most convincing argument for the 9,10 double bond is its formation by selenium dioxide oxidation which is known to occur at methylene groups activated by a double bond. Thus, only $\Delta^{9,10}$-octalin could be attacked at the 1- and 5-positions. However, the possibility that rearrangement occurs during or after the oxidation must be considered although it does not seem likely.



On catalytic hydrogenation in acetic acid solution, the diacetate of $\Delta^{9,10}$-octalindiol-1,5 (XI) absorbed one mole of hydrogen rapidly and a second mole more slowly. It was thought that this absorption might be accounted for by saturation of the double bond and hydrogenolysis of one of the acetoxy groups. The reaction product, however, was not homogeneous and the only product isolated was a small amount of 1,5-dihydroxydecalin.

The $\Delta^{9,10}$-octalindione-1,5 (XII) was characterized by the formation of a dioxime and by the dehydrogenation to 1,5-dihydroxynaphthalene. The double bond is placed at 9,10 because the ultraviolet absorption spectrum[10] ($\lambda_{\max.}$ = 263 mμ, log E = 4.1) (Fig. 1, curve 3) requires conjugation and, in addition, definitely eliminates the other possible structures with double bonds at 8,9 or at 2,3. The latter structures should give curves similar to that of $\Delta^{8,9}$-octalone-1. Although absorption curves for strictly analogous compounds are not available, those of several steroids containing the Δ^{4}-cholestendione-3,6[11] structure (XV) are pertinent. These curves show a maximum at 252 mμ and by analogy with the work of Woodward[6] a shift to longer wave lengths of 14 mμ for the $\Delta^{9,10}$-octalindione is not unreasonable.



XV

The second diacetate was obtained by the oxidation of $\Delta^{9,10}$-octalin at 120°. Analysis of the compound and the hydrolysis product proved that the molecule contained two atoms of hydrogen less than the $\Delta^{9,10}$-octalindiol-1,5. Thus an unsaturated keto-alcohol, a saturated diketone, or a diene-diol was indicated. The oxygen atoms were shown to be at 1 and 5 by oxidation by the Op-

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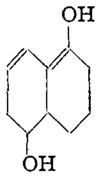
(9) Woodward, Kohman and Harris, THIS JOURNAL, **63**, 120 (1941).

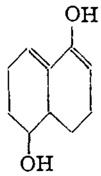
(10) Because of the lack of spectra of similar compounds for comparison, the interpretation of that portion of the curve at longer wave lengths is uncertain, but the slight inflection at 3200 mμ (log E = 1.6) and the maximum at 392 mμ (log E = 1.5) are of the correct order of intensity for carbonyl absorption.

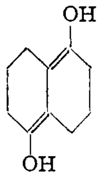
(11) Butenandt and Riegel, *Ber.*, **69**, 1163 (1936).

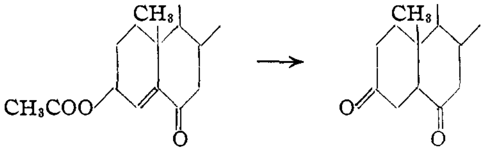
penauer method to the $\Delta^{9,10}$-octalindione (XII). Formulas which contain carbonyl groups were eliminated from consideration since the hydrolysis product failed to form an oxime under conditions more vigorous than those used to form similar derivatives of $\Delta^{8,9}$-octalone-1 and $\Delta^{9,10}$-octalindione-1,5.

The ultraviolet absorption curves of the diacetate and the hydrolysis product are nearly identical. They have a maximum at 238 mμ (log E = 4.2), and show no indication of the carbonyl absorption at longer wave lengths (Fig. 1, Curves 1a and 1b). This latter observation provides confirmatory evidence of the absence of ketone functions in the molecule. With this established the maximum at 238 mμ may be considered as representative of a conjugated diene in which the double bonds are distributed between the two rings.[12] The only compounds which meet these requirements are 1,2,3,5,6,7-hexahydronaphthalenediol-1,5 (XIV) and the corresponding diacetate (XIII). The other formulas which can be considered are XVI to XVIII and all of them suffer from the necessity of postulating stable enol forms. Even if this possibility is admitted formulas XVI and XVII are eliminated because of their similarity to $\Delta^{8,9}$-octalone-1 whereas the substance under consideration differs markedly from the octalone both in its absorption spectrum and its reaction with hydroxylamine. The possibility of enolization may be greatest for XVIII since the enol form is completely conjugated. However, it seems extremely unlikely that a substance of this structure would fail to form a carbonyl derivative. This view is substantiated by the observation that many compounds containing the analogous cholestanedione-3,6 structure (XX) form carbonyl derivatives with both functional groups. To extend the analogy to similarly constituted sterol derivatives it should be pointed out that the hexahydronaphthalenediol might be expected to undergo a rearrangement to decalindione-1,5 on treatment with alkali. A similar reaction has been observed in the conversion of 6-keto-3-acetoxy-Δ^4-cholestene (XIX) to cholestanedione-3,6 (XX) by refluxing with methanol containing 4% of potassium hydroxide,[13] although 1% alkali at room temperature brings about the hydrolysis without rearrangement. In regard to this possibility we can report only that rearrangement did not occur on refluxing with 2% alkali in ethanol. The action of alkali at higher temperatures was not investigated.


XVI


XVII


XVIII



XIX XX

The oxidation of $\Delta^{9,10}$-octalin with selenium dioxide at an intermediate temperature gave a solid diacetate mixture which melted over a three degree range. A separation of the components of this mixture was accomplished by fractional crystallization of the hydrolysis product. Both $\Delta^{9,10}$-octalindiol-1,5 and the hexahydronaphthalenediol were obtained, and their identity was confirmed by conversion to the corresponding diacetates.

Finally the question arises regarding the mechanism by which the hexahydronaphthalenediol-1,5 is formed from $\Delta^{9,10}$-octalin and that by which $\Delta^{9,10}$-octalindione-1,5 is produced from the diol. In both reactions it is necessary to postulate a rearrangement of double bonds in order to obtain the desired product. It is an easy matter to work out plausible schemes for each reaction, but these are of little value since, at present, we have no experimental evidence which will aid in deciding between them.

Acknowledgment.—We wish to express our thanks and appreciation to Dr. R. Norman Jones for determining the ultraviolet absorption spectra reported in this paper and for his aid in interpreting them.

Experimental Part[14]

The Preparation of $\Delta^{9,10}$-Octalin.—The mixed β-decalols used in this preparation were obtained by the hydrogenation of redistilled β-naphthol with Raney nickel at 150–170° and 2000 lb. pressure. The decalol fraction boiling at 155–163° at 53 mm. was obtained in 77% yield.

To a well-stirred solution of 167.3 g. of phosphorus pent-

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[12] Fieser and Campbell, THIS JOURNAL, **60**, 159 (1938); Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940).

[13] Heilbron, Jones and Spring, *J. Chem. Soc.*, 801 (1937). See also Butenandt and Schramm, *Ber.*, **69**, 2289 (1936).

[14] All melting points are corrected. Analyses by Miss Eleanor Werble.

oxide in 1673 g. of 85% phosphoric acid was added 167.3 g. of mixed β-decalols. The temperature of the mixture was raised to 150° for ten minutes. Then, while this temperature was maintained, a slight vacuum was applied to the system and the octalin was caused to distil with steam by the dropwise addition of water. This was continued until no more octalin was obtained. The product was taken up in ether, dried and, after removal of the solvent, was distilled over sodium; yield, 131 g. (87%); b. p. 189–191°.

This product was heated with stirring with 44 g. of phosphorus pentoxide at 140° for three hours. The flask was cooled and ice was added to react with the phosphorus pentoxide. The octalin was taken up in ether and after washing and drying the solvent was removed. Distillation of the residue gave 115 g. of the octalin, b. p. 190–192°. The over-all yield from the decalol was 78%.

The blue **nitroso chloride**,[3c] m. p. 92.5°, was obtained in 50% yield by treating the octalin (1 g.) with ethyl nitrite (2 g.) and concentrated sulfuric acid (1.5 cc.) at −70°.

$\Delta^{9,10}$-Octalol-1 Acetate.—To a stirred solution of 27.2 g. (0.2 mole) of $\Delta^{9,10}$-octalin in 400 g. of acetic anhydride at 0° was added a solution of 11.1 g. (0.1 mole) of selenium dioxide in 28.2 g. of water. The rate of addition was controlled so that the temperature did not rise above 5° and the mixture was stirred at this temperature for eighteen hours. The mixture was filtered with suction through a layer of Norit and, after removal of the solvent in vacuum, the residual oil was distilled rapidly at reduced pressure to separate it from the dissolved selenium. Redistillation gave 24.6 g. (65%) of the acetate b. p. 125–127° at 10 mm.

Anal. Calcd. for $C_{12}H_{18}O_2$: sapon. equiv., 194. Found: sapon. equiv., 193.

$\Delta^{8,9}$-Octalone-1.—The above acetate (8 g.) was hydrolyzed by refluxing for two hours with 250 cc. of 2% sodium ethylate in ethanol. After removal of the solvent in vacuum and the addition of water, the product was taken up in ether and dried. Removal of the ether gave 6 g. (94%) of **$\Delta^{9,10}$-octalol-1.**

An Oppenauer[5] oxidation of the octalol was carried out by treating a solution of the above product in 110 cc. of acetone and 150 cc. of benzene with a hot solution of 19.3 g. of aluminum *t*-butylate in 75 cc. of benzene at 75–80° for eight hours. After the addition of dilute sulfuric acid, the benzene layer was separated and the aqueous layer was extracted with benzene. The combined benzene extracts were washed and the solvent was removed in vacuum. Distillation of the product gave 4.5 g. (73%) of slightly yellow, oily octalone, b. p. 127–128° at 10 mm.

The identity of this product with that reported in the literature[1] was established by the preparation of the oxime, m. p. 146–147° (lit. 148°), in 91% yield and the semicarbazone, m. p. 241–242° (lit. 243°), in 95% yield.

$\Delta^{8,9}$-Octalone-1 *l*-Menthylhydrazone.[9]—For this work, octalone which was purified as the oxime was used. Hydrolysis of the oxime was accomplished by the method of Ruzicka, *et al.*,[15] in 92% yield. The octalone (10.6 g.) and *l*-menthyl N-aminocarbamate (15.1 g.) were dissolved in the minimum amount of 95% ethanol containing 2 g. of sodium acetate and 1 g. of acetic acid per 100 cc. After refluxing for two hours, the addition of two drops of water and cooling resulted in the separation of 18 g. (75%) of crystalline product; m. p. 166.5–167°; $[\alpha]^{25}_D$ −203° (3.3% in chloroform).

Fractional crystallization of 14.7 g. of this material from 95% ethanol gave eight crops of crystals totaling 14.5 g. The melting points and rotations of these crops were the same as reported above within a few tenths of a degree. In this run as in several others no evidence of resolution by this reagent was apparent.

$\Delta^{9,10}$-Octalindiol-1,5 Diacetate.—This selenium dioxide oxidation was run in the manner described above using 13.6 g. (0.1 mole) of octalin in 200 g. of acetic anhydride and 11.1 g. (0.1 mole) of selenium dioxide in 28.2 g. of water. The reaction was run at 25–30° for eighteen hours. Distillation of the product gave 6.7 g. (35%) of $\Delta^{9,10}$-octalol-1 acetate and 8.5 g. of a thick oil boiling at 145–148° at 2 mm. A colorless crystalline solid separated from a hexane solution of this oil which on recrystallization from ether–hexane gave 3.1 g. (12.5%) of the pure diacetate, m. p. 122–123°.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99; mol. wt., 252. Found: C, 66.56; H, 8.11; mol. wt., 264 (Rast), 258 (sapon. equiv.).

Hydrolysis of the oily product remaining in the hexane solution with alcoholic alkali gave 4.2 g. (from 13.3 g. of oil) of solid, m. p. 157–168° from ethanol–ethyl acetate. Reacetylation of this material gave an oily product. Oxidation of the solid by the Oppenauer method gave $\Delta^{9,10}$-octalindione-1,5 (see below) in 10% yield.

The same diacetate, m. p. 122–123°, was obtained by oxidation of $\Delta^{9,10}$-octalol-1 acetate in a similar manner with selenium dioxide. The yield was 16%.

$\Delta^{9,10}$-Octalindiol-1,5.—Hydrolysis of 0.27 g. of the above diacetate as previously described gave 0.16 g. (94%) of the diol, m. p. 169–182°. When a sample of this product was immersed in the bath at 220° it melted apparently with the evolution of a gas. On cooling it resolidified and remelted at 189–192°. Recrystallization from ethanol–ethyl acetate gave 0.14 g. of the diol melting at 195.5–197°.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.40; H, 9.59. Found: C, 71.59; H, 9.51.

Acetylation of this product with acetic anhydride and pyridine gave the diacetate m. p. 122–123° from ether–hexane in quantitative yield. The melting point, mixed with the above diacetate, was the same.

$\Delta^{9,10}$-Octalindione-1,5.—The oxidation of 5.6 g. of the octalindiol-1,5 by the Oppenauer reaction as described above gave a dark brown oil. On distillation at 2 mm. a low-boiling oil was obtained followed by the diketone which crystallized in the receiver. Recrystallization from ether–hexane gave 1.5 g. (30%) of pale yellow crystals, m. p. 113–114°.

Anal. Calcd. for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 72.92; H, 7.10.

The **dioxime** was obtained by the action of hydroxylamine in dilute aqueous alcoholic alkali. It did not melt below 285°.

Anal. Calcd. for $C_{10}H_{14}O_2N_2$: N, 14.43. Found: N, 14.85.

Naphthalenediol-1,5 Diacetate from $\Delta^{9,10}$-Octalindione-1,5.—A mixture of 0.3 g. of the diketone and 0.1 g. of palladium–charcoal was heated at 330° for one-half hour

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(15) Ruzicka, Seidel and Schinz, *Helv. Chim. Acta*, **16**, 1143 (1933).

when 86 cc. (95%) of hydrogen was evolved. An ether solution of the product was filtered to remove the catalyst and evaporated. After heating the residue under water-pump vacuum on the steam-bath for one hour, acetic anhydride and one drop of concentrated sulfuric acid were added. The solution was poured into ice and water after one-half hour and the product was extracted with ether. Crystallization from ether–hexane gave a few mg. of the diacetate of naphthalenediol-1,5, m. p. 160–161°. A mixed melting point with a synthetic sample gave no depression.

The Diacetate of 1,2,3,5,6,7-Hexahydronaphthalenediol-1,5.—The oxidation of 13.6 g. of $\Delta^{9,10}$-octalin by molar quantities of selenium dioxide was carried out as previously described except that the temperature was maintained at 120–124°. After the removal of some monoacetate, 8 g. of an oil boiling at 146–149° at 2 mm. was obtained. By treating with hexane as before 3.2 g. of crystalline solid m. p. 120–128.5° separated. Crystallization from ether–hexane gave 0.62 g. of pure diacetate, m. p. 139–140°.

Anal. Calcd. for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25; mol. wt., 250. Found: C, 67.20, 67.25; H, 7.21, 7.38; mol. wt. (by sapon. equiv.), 253.

From the mother liquors 2.2 g. of product, m. p. 101–109°, was obtained. This is similar to the mixture m. p. 108–111° described below.

1,2,3,5,6,7-Hexahydronaphthalenediol-1,5.—Hydrolysis of 0.62 g. of the above diacetate was carried out as previously described, yielding 0.21 g. (50%) of product m. p. 155.5–156.5°.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.30; H, 8.61.

Reacetylation of a sample of this product with acetic anhydride and pyridine gave the original diacetate, m. p. 139–140° in 94% yield. A mixed melting point determination confirmed the identity of the substance.

Oxidation of 0.1 g. of the hexahydronaphthalenediol by the Oppenauer reagent gave 0.04 g. (41%) of $\Delta^{9,10}$-octalindione-1,5, m. p. 113.5–115°, identified by mixed melting point.

The Attempted Reaction of 1,2,3,5,6,7-Hexahydronaphthalenediol-1,5 with Hydroxylamine.—After hydrolysis of 0.2 g. of the hexahydronaphthalenediol diacetate by refluxing with alcoholic alkali, the solvent was removed in vacuum. The residue was dissolved in 5 cc. of water and a few drops of ethanol and neutralized. This solution was heated for forty-five minutes on the steam-bath with 0.5 g. of hydroxylamine hydrochloride and 2 cc. of 10% sodium hydroxide solution. The solvent was removed in vacuum, 2 cc. of water was added, and the solid which remained undissolved was collected and crystallized from ethyl acetate. The product, m. p. 155–156°, was identified as the hexahydronaphthalenediol by a mixed melting point. The yield (50 mg.) was nearly equal to that obtained above on hydrolysis of the acetate.

The Selenium Dioxide Oxidation of $\Delta^{9,10}$-Octalin at 70°.—This reaction was carried out as previously described using 0.1 mole each of octalin and the oxidizing agent. On distillation, 3.3 g. (17%) of the monoacetate and 8.9 g. of oil, b. p. 145–148° at 2 mm., were obtained. From the oil, by use of hexane, 3.3 g. (13%) of a solid m. p. 108–111° was obtained. Further crystallization from ether–hexane did not raise the melting point. Analysis of this material gave values for carbon (67.39) and hydrogen (7.24) which are intermediate between those for the diacetates of $\Delta^{9,10}$-octalindiol-1,5 and the hexahydronaphthalenediol. The molecular weight from saponification equivalent (256) checked with either of these compounds.

Hydrolysis of 4.1 g. of this product as described above gave 2.2 g. (80%) of solid m. p. 174–183°, which on crystallization from ethanol–ethyl acetate gave three crops of crystals as follows: first 0.75 g., m. p. 190–197°; second 0.5 g., m. p. 147–153°; third 0.15 g., m. p. 143–146.5°. On recrystallization, the first crop yielded 0.26 g. of $\Delta^{9,10}$-octalindiol-1,5 (m. p. 196–197°) and the second crop, 0.15 g. of the hexahydronaphthalenediol (m. p. 155–156.5°). Acetylation of each of these diols with acetic anhydride and pyridine gave the corresponding diacetates. The identity of these substances was established by determining the melting points of mixtures with the appropriate diols and diacetates prepared above.

Decalindiol-1,5.—A solution of 1.0 g. of the diacetate of $\Delta^{9,10}$-octalindiol-1,5 in 25 cc. of acetic acid was shaken with hydrogen and 0.1 g. of Adams catalyst. One mole of hydrogen was absorbed in fifteen minutes and a second in two hours. After removal of the catalyst the solvent was evaporated in vacuum. After washing and drying in ether solution the product was hydrolyzed as before. Crystallization from ether–petroleum ether gave 0.1 g. (16%) of the diol, m. p. 177.5–178°. Recrystallization gave pure material melting at 178–178.5°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.56; H, 10.63. Found: C, 70.60; H, 10.30.

Summary

The oxidation of $\Delta^{9,10}$-octalin by selenium dioxide at various temperatures has been studied. The acetate of $\Delta^{9,10}$-octalol-1 was obtained in good yield and this substance was converted to $\Delta^{8,9}$-octalone-1. The structure assigned to the latter compound is at variance with that reported in the literature and is based on the ultraviolet absorption spectrum.

Among other oxidation products obtained in this work are $\Delta^{9,10}$-octadiol-1,5 and the corresponding unsaturated diketone as well as 1,2,3,5,6,7-hexahydronaphthalenediol-1,5. The evidence upon which these structures are based is presented.

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RECEIVED JULY 24, 1941