ley of the Department of Zoology, have indicated androgenic activity for the diketone II at a total dose of 2.5 mg. (26 to 83% increase in comb weight over the controls). A total dose of 0.012 mg. of testosterone propionate resulted in 40% increase. The keto alcohol I has given inconclusive results. Further investigation of physiological effects in other species awaits the preparation of additional material.

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RECEIVED JULY 20, 1949

SYNTHESIS OF VITAMIN A

Sir:

The appearance of an article by Schwarzkopf and collaborators¹ on the synthesis of vitamin A by the reduction of vitamin A esters with lithium aluminum hydride prompts us to record experimental work carried out in these laboratories.

Ethyl β -ionylidene acetate² was reduced with lithium aluminum hydride in 85% yield to β -ionylidene ethyl alcohol following the method of Milas and Harrington³ [b. p. 112–114° at 0.4 mm.; $\lambda_{\max}^{\text{isoŏctane}}$ 2840 Å., $E_{1\text{ cm.}}^{1\%}$ 1205]; trityl ether (m. p. 132–134°) anal. Found: C, 88.13; H, 8.47; $\lambda_{\max}^{\text{isoŏctane}}$ 2850 Å., $E_{1\text{ cm.}}^{1\%}$ 733.

Oxidation of β -ionylidene ethyl alcohol with manganese dioxide by the method used to convert vitamin A to the aldehyde⁴ produced a mixture of two stereoisomeric β -ionylideneacetaldehydes in 60% yield separable by chromatography into essentially equal amounts of nor- β -ionylideneacetaldehyde⁵ [b. p. 90-95° at 10^{-2} mm.; n^{25} D

- (1) Schwartzkopf, Cahnmann, Lewis, Swindinsky and Wuest, Helv. Chim. Acta, 32, 443 (1949).
 - (2) Karrer, Salomon, Morf and Walker, ibid., 15, 878 (1932).
 - (3) Milas and Harrington, This Journal, 69, 2247 (1947).
 - (4) Ball, Goodwin and Morton, Biochem. J., 42, 516 (1948).
- (5) The names nor and $iso-\beta$ -ionylideneacetaldehyde denote stereochemical relationships to β -carotene. The nor (normal) aldehyde is obtainable from β -carotene by oxidation—Wendler, Rosenblum and Tishler, This JOURNAL, in press.

1.5780; $\lambda_{\text{max}}^{\text{isooctane}}$ 2650 Å., $E_{1 \text{ cm.}}^{1\%}$ 567 and 3150 Å., E¹% 760, anal. Calcd. for C₁₅H₂₂O: C, 82.57; H 10.09. Found: C, 82.14; H, 10.36. Semicarbaλ_{max}. 3230 Å., m. p. 195-196°; $E_{1 \text{ cm.}}^{1\%}$ 1330; anal. Found: C, 69.56; H, 8.82; N, 15.29]⁶ and *iso-β*-ionylidene acetaldehyde⁵ [b. p. 80–85° at 10^{-2} mm.; n^{25} D 1.5780; $\lambda_{\text{max}}^{\text{1sooctane}}$ 3180 Å., $E_{1\text{cm}}^{1\%}$ 904. Anal. Found: C,82.14; H, 10.33. Semicarbazone: m. p. 175-176°, $\lambda_{\text{max. 3175}}^{\text{chloroform}} E_{1\text{ cm.}}^{1\%}$ 1000. Anal. Found: C, 70.16; H, 9.07; N, 15.03]. nor-β-Ionylideneacetaldehyde was condensed with acetone in the presence of aluminum tbutoxide whereby the previously described C₁₈ketone was obtained in 80-85% yield; $\lambda_{\text{max}}^{\text{isooctane}}$ 3360 Å.; semicarbazone: m. p. 186-188°; $\lambda_{\text{max}}^{\text{chloroform}}$ 3490 Å., $E_{1\text{ cm}}^{1\%}$ 1680. The C_{18} -ketone was constant by the $E_{18}^{1\%}$ verted by the Reformatsky reaction to the C20hydroxyester which was dehydrated by iodine to vitamin A ester and the latter saponified to vitamin A acid, m. p. 179-180°; λ_{max}. 3500 Å., $E_{1 \text{ cm.}}^{1\%}$ 1415. From *iso-\beta-*ionylideneacetaldehyde there was obtained a more difficultly characterizable C₁₈-ketone exhibiting a broad band at 3340-3370 Å, indicating a mixture of the nor and iso forms. This ketone afforded vitamin A acid in the same yield as that obtained from the nor series

(6) The β-ionylidenealdehydes semicarbazones prepared by Kuhn and Morris, Ber., 70, 853 (1937), and by van Dorp and Arens, Rec. trav. chim., 67, 459 (1948), apparently have the nor configuration.

(25%); m. p. 180.5-181.5°; $\lambda_{max.}^{ethanol}$ 3530 Å.,

 $E_{1 \text{ cm.}}^{1\%}$ 1510; mixed m. p. with acid from nor series,

180-181°. Both vitamin A acids on reduction

with lithium aluminum hydride gave vitamin A

exhibiting a single, well-defined maximum at

3260 Å., $E_{1 \text{ cm.}}^{1\%}$ 1330 (80% yield) as measured in

(7) Arens and van Dorp, Rec. trav. chim., 65, 338 (1946); Heilbron, Jones and O'Sullivan, J. Chem. Soc., 866 (1946); Karrer, Jucker and Schick, Helv. Chim. Acta, 29, 704 (1946).

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isoöctane.

N. L. WENDLER H. L. SLATES M. TISHLER

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NEW BOOKS

Oxidation-Reduction Potentials in Bacteriology and Biochemistry. By L. F. Hewitt, Ph.D., B.Sc., F.R.I. C., Acting Director, Serum Research Institute, Carshalton, Surrey. Fifth Edition. Published by the London County Council, 1948, and may be purchased, either directly or through any Bookseller, from Staples, Ltd., 14, Great Smith Street, Victoria Street, Westminster, S.W.1. 130 pp. 17 × 25 cm. Price, 4s. 6d. By post, 4s. 10d.

The last previous edition of this small monograph was published in 1936. The present fifth edition follows the pattern of earlier ones. The first chapter contains a brief

outline of the theory of oxidation-reduction reactions and the mathematical expressions relating oxidation-reduction potentials to the components of the reactions. The second chapter describes the methods for measuring oxidation-reduction potentials and gives tables of oxidation-reduction indicators. The third chapter deals with oxidation-reduction systems of biological interest. In the fourth chapter, the bacteriological applications of oxidation-reduction studies are described. This fourth chapter is the most important in the monograph, since it constitutes the best review of the work in this particular field—a field to which the author himself has made many contributions. The monograph concludes with two short