The final product was obtained in two fractions: (a) The first distils at 100–103° (10^{-3} mm.), $n^{26}D$ 1.5640, showing an absorption maximum at 312 mμ and a molecular coefficient of extinction of 27,450. *Anal.* Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74. Found: C, 83.74; H, 10.59. (b) The second distils at 110–115° (10^{-3} mm.), $n^{26}D$ 1.5771, showing an absorption maximum at 315 mμ and a molecular coefficient of extinction of 33,750. *Anal.* Calcd. for $C_{21}H_{32}O$: C, 83.94; H, 10.74. Found: C, 83.79; H, 10.69.

Figure 1 shows the similarity in shape of the absorption curves of products V to that of Vitamin A alcohol. The slight displacement of the maxima and the lower maximum intensities of absorption may indicate stereoisomeric variations from the natural product. Biological assays are at present in progress.

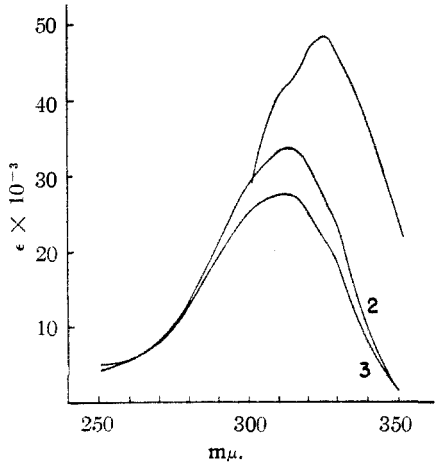

Fig. 1.—Curve 1, vitamin A, alcohol; curve 2, product V (b); curve 3, product V (a); solvent, isopropanol.

When the crude acetylenic compound III[4] was hydrogenated in the presence of a poisoned palladium catalyst only the theoretical quantity of hydrogen for the semihydrogenation of one acetylenic bond was absorbed. The resulting divinyl carbinol, IV, distilled at 113–115° (10^{-3} mm.), $n^{26}D$ 1.5099 and, as would be expected theoretically, showed no significant absorption in the ultraviolet.

Anal. Calcd. for $C_{21}H_{34}O_2$: C, 79.19; H, 10.76. Found: C, 79.37; H, 10.63. The yield of IV from I was 84%.

The rearrangement and simultaneous dehydration of the divinyl carbinol IV to products V (a) and V (b) was accomplished in glacial acetic acid with a trace of *p*-toluenesulfonic acid at room temperature. The total yield of (a) and (b) from IV was 77%.

Work is at present in progress toward the synthesis of the corresponding acetate of V by similar methods in which the acetoxy analog of II[3] is condensed with I. In addition to the magnesium derivative of I, the zinc derivative is being investigated in view of its inertness toward esters.

(4) The crude acetylenic compound III split out water spontaneously on distillation at 10^{-3} mm., and the redistilled product boiled at 112–114° (10^{-4} mm.), $n^{26}D$ 1.5715. *Anal.* Calcd. for $C_{21}H_{36}O$: C, 84.51; H, 10.13. Found: C, 84.10; H, 10.28.

ORTHO RESEARCH FOUNDATION
ORGANIC CHEMISTRY DIVISION
LINDEN, NEW JERSEY WILLIAM OROSHNIK

RECEIVED AUGUST 17, 1945

REACTIONS OF VANILLIN

Sir:

In a search for a simple process for converting vanillin directly into vanillic acid, it was found that silver oxide and excess alkali in aqueous solution effected this transformation. Unlike other alkaline silver oxide oxidations of aldehydes which require one mole of oxide to one mole of aldehyde, this oxidation took place with only one-half mole of silver oxide according to the equation

$$2\ RCHO + Ag_2O + 2\ NaOH \xrightarrow{NaOH} 2\ RCOONa + 2\ Ag + H_2O + H_2$$

This unexpected discovery led to the assumption of a Cannizzaro mechanism for the reaction and this hypothesis was confirmed by experiments employing less than one-half mole of silver oxide in which vanillyl alcohol (in the form of its dimer) was recovered in the calculated amount, depending upon the amount of silver oxide used. Thus, a mixture of 1.0 mole of vanillin, 0.25 mole of freshly prepared silver oxide, 4.0 moles of sodium hydroxide and 1000 g. of water was heated to boiling for one hour and filtered. Acidification of the filtrate with carbon dioxide yielded 34.2 g. (corresponding to 0.24 mole of vanillyl alcohol) 4,4′-dihydroxy-3,3′-dimethoxydiphenylmethane, m. p. 108–109° (from water or ligroin) (*Anal.* Calcd. for $C_{15}H_{16}O_4$: C, 69.20; H, 6.20; CH_3O, 23.85. Found: C, 68.99; H, 6.23; CH_3O, 23.69). The carbonated filtrate yielded 119.6 g. (0.71 mole) of vanillic acid, m. p. 209–210°. It was further found that the active silver metal produced in the above reaction would catalyze a Cannizzaro reaction of vanillin to give equivalent amounts of vanillic acid and polymerized vanillyl alcohol. In the presence of alkali alone vanillin does not undergo a Cannizzaro reaction.[1-4]

In addition to vanillin, other ortho- and para-hydroxy- and amino-substituted benzaldehydes, ordinarily inert in the presence of strong alkali, easily underwent the Cannizzaro reaction in the presence of active silver to yield the derived acid and unpolymerized alcohol. Active silver also catalyzed the crossed Cannizzaro reaction of these aldehydes with formaldehyde to give substantially quantitative yields of unpolymerized alcohols, even in the case of vanillin.

(1) Lock, *Ber.*, **62**, 1181 (1929).
(2) Raikow and Raschtanow, *Oesterr. Chem. Ztg.*, **5**, 169 (1902).
(3) Tomlinson and Hibbert, THIS JOURNAL, **58**, 349 (1936).
(4) Geissman, Chapter 2 in Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 104–107

Oxidations of vanillin have also been obtained with mercuric and auric oxides but, in these cases, the Cannizzaro reaction was inoperative.

The experimental details and theoretical considerations of these investigations will appear in a forthcoming series of papers.

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN IRWIN A. PEARL

RECEIVED AUGUST 17, 1945

NEW BOOKS

Physico-Chemical Methods. By JOSEPH REILLY, Boyle Medallist, Royal Dublin Society, Professor of Chemistry, University College, Cork, and William Norman Rae, Professor of Chemistry and Physics, Royal College of Surgeons in Ireland. Volume I and Volume II. Fourth edition. D. Van Nostrand Company, Inc., 250 Fourth Avenue, New York, N. Y., 1944. Volume I: ix + 610 pp. Volume II: vii + 585 pp. Illustrated. 16 × 24.5 cm. Price, $17.50.

According to the authors, "No drastic alterations have been made in the present edition." Nevertheless considerable new material has been added to the comprehensive treatment of the previous edition. Some twenty-five new pages deal with surface area, thermopiles, the tensile strength of liquids, microfractionation, micro diffusion, the ultracentrifuge and artificial radioactivity. There are numerous other interesting additions of less significance.

The purpose of the authors, as stated in the first edition, is to describe laboratory procedures at a much more advanced level than is possible in a manual for undergraduate students and thus make it unnecessary for an investigator to go to sources which are often not readily accessible. This objective has been only partially realized. While it is possible in the case of many procedures to give complete instructions, more complicated apparatus, such as the ultracentrifuge, can only be properly constructed by reference to the original literature. In the discussion of these topics the work becomes more of a commentary, with references, than a laboratory directive. As such it will serve as a convenient starting point for one beginning a search of the literature.

Apparently most of the fourth edition is printed from the plates of the third edition. New materials have been introduced by the expedient of eliminating cuts in some places and using a decimal system of paging (*i. e.*, 18.1, 18.2, etc.) in other places. Chapter XIII has been omitted entirely for no obvious reason. This chapter entitled "Molecular Properties" in the third edition included the sub-titles of solubility, molecular weights, molecular weights—micro methods, partition coefficients, rates of reaction, mass action and stability of explosives.

The paper and binding are not up to the excellent standard of the third edition. While apparently less durable they are probably satisfactory except for the hardest usage.

H. E. BENT

Ultracentrifugal Studies on Serum and Serum Fractions. By KAI O. PEDERSEN. To be obtained through Almquist and Wiksells AB, Upsala, Sweden, 1945. 178 pp. 16 5 × 24 cm. Price, 10 Swedish crowns (about $2.50).

This thesis of Pedersen's has been long awaited by all who had seen preliminary reports of his work on the serum proteins in "The Ultracentrifuge" by Svedberg and Pedersen. A great deal of valuable information for anyone interested in the serum proteins in general, or their ultracentrifugal behavior in particular, is contained in this volume.

The outstanding contributions reported here are undoubtedly his elucidation of the behavior of the so-called "X-protein" of human serum or plasma, first described by McFarlane in 1935, and the description of a new serum globulin of low molecular weight (*ca.* 50,000) called "fetuin."

The X-protein of human serum is found to have a sedimentation behavior in the ultracentrifuge highly dependent upon the density of the centrifuged solution. From studies of the dependence of sedimentation constant upon density, the specific volume of this component is calculated to be 0.969, a value remarkably large for a protein molecule. Certain serum fractions prepared by high-speed centrifugation or electrophoresis are shown to have sedimentation properties similar to those of this labile component of human serum. These fractions were found to be rich in β-globulin and lipid. Pedersen says that to date he has observed no components showing this "density effect" in sera other than human.

The low molecular weight globulin fetuin was first observed in serum from newly born calves. It has also been found in large quantities in the serum from the foal and from sheep foetus. Pedersen points out that these cases where fetuin is found represent animals where the antibodies do not appear in the serum of the newborn until it has received colostrum, whereas in rodents and man the antibodies are known to be transferred from the mother to the foetus.

A large part of this thesis describes ultracentrifuge studies of various fractions of serum obtained by ammonium sulfate precipitation, and of various "delipidated" sera. These experiments were made with the serum or plasma of the adult cow, calf, calf foetus, adult and foetal rabbit, foal, sheep foetus, normal adult human, pathological adult human, and human umbilical cord. This very ambitious program is well described in a series of about forty tables. Unfortunately, there is not much supplementary chemical or electrophoretic work upon these fractions, but this deficiency is very understandable when it is remembered that this large mass of data was obtained in connection with experiments primarily concerned with ultracentrifugal studies.

Some of the other conclusions of the author are of considerable interest. Observations concerning the isohemagglutinins of human serum are presented, but unfortunately there are few data presented in the form of quantitative immunological assay of the materials used. Several γ-globulin fractions were prepared and studied, and gave molecular weights from 153,000 for human γ-globulin, to 192,000 for a γ-globulin fraction from cow serum. Serum albumin from human and from cow foetus serum were also rather intensively investigated, as were several high molecular weight globulins obtained from pathological human serum.

This valuable contribution to protein and ultracentri-