The picrate crystallized from ethanol in orange-red, flat rods of m. p. 127–128°.

Anal. Calcd. for $C_{28}H_{19}O_8N_3$: C, 64.0; H, 3.6. Found: C, 64.4; H, 3.9.

2,3-Diphenyl-1,4-naphthoquinone (III).—The naphthol II (2 g.) was dissolved in acetic acid (50 cc.) and, after addition of potassium dichromate (2 g.) in acetic acid (30 cc.), heated to boiling for two minutes. Upon pouring onto ice, a yellow precipitate (1.7 g.) was obtained. It crystallized from ethanol in yellow prisms of m. p. 135–136°. An additional recrystallization from acetic acid raised the m. p. to 140–141°, as reported in the literature.[6] The yield of pure product was 1.2 g. (60%).

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.1; H, 4.5. Found: C, 85.2; H, 4.7.

DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE RECEIVED APRIL 17, 1946

The Resistance to Hydrogenation of β-Stenols in Ethyl Acetate with Adams Platinum Oxide Catalyst

BY SEYMOUR BERNSTEIN AND LOUIS DORFMAN

It is known that dehydroergostenol on hydrogenation with either platinum oxide in glacial acetic acid[1] or with palladium in ethyl acetate[2] affords α-ergostenol and not δ-ergostenol since the unhydrogenated double bond migrates to the α-position. It was therefore surprising to find that dehydroergostenol was not hydrogenated with platinum oxide catalyst in ethyl acetate and the starting material was recovered unchanged. Likewise β-ergostenol could not be hydrogenated under these conditions.

This hitherto unsuspected fact that β-stenols are resistant to hydrogenation with platinum oxide in ethyl acetate should prove useful in future synthetic and structural work in the steroid field, *e. g.*, in the cardiac aglucons.

LEDERLE LABORATORIES, INC.
PEARL RIVER, NEW YORK RECEIVED[3] APRIL 22, 1946

(1) Morrison and Simpson, *J. Chem. Soc.*, 1710 (1932).
(2) Windaus and Lüttringhaus, *Ann.*, **481**, 119 (1930).
(3) Original manuscript received September 19, 1945.

Some Substituted Acetophenones[1]

BY E. CAMPAIGNE AND WM. BRADLEY REID, JR.

Ortho- and *meta*-methyl- and *ortho-* and *meta*-phenylacetophenones, required in another investigation, were prepared from acetic anhydride by the low temperature Grignard procedure of Newman and Booth.[2] The required Grignard reagent and yield of the corresponding methyl ketones were as follows: *o*-tolylmagnesium bromide, 48.2%; *m*-tolylmagnesium bromide, 46.4%; *o*-xenylmagnesium iodide, 61.8%; *m*-xenylmagnesium iodide, 26.8%.

The biphenyl compounds, being new, were characterized by means of their crystalline semicarbazones and 2,4-dinitrophenylhydrazones.

Experimental

***o*-Phenylacetophenone.**—2-Iodobiphenyl was produced in 82.7% yield by the toluene extraction of a mixture obtained by treating a diazotized solution of 2-aminobiphenyl (Monsanto Chemical Company) with excess potassium iodide solution. The 2-iodobiphenyl was converted to the Grignard reagent and treated with acetic anhydride, yielding *o*-phenylacetophenone as a yellow oil, b. p. 104–105° at 1 mm. This oil yielded a semicarbazone in white plates, melting at 197°.

Anal.[3] Calcd. for $C_{15}H_{15}N_3O$: N, 16.59. Found: N, 16.67.

A 2,4-dinitrophenylhydrazone was also prepared, and obtained in light orange plates, melting at 169–170°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: N, 14.88. Found: N, 14.83.

3-Iodobiphenyl.—Using the method of Elks, Haworth and Hey,[4] *m*-nitroaniline was converted to 3-nitrobiphenyl in 43% yield. This nitro-compound, which melted at 59–61°, was reduced to the amine by hydrogenation over Adams platinum oxide catalyst in portions in 98.5% yield. The 3-aminobiphenyl, after distillation at 177–178° at 18 mm. pressure, solidified to a white solid melting at 31–31.5°. A solution of 53 g. (0.314 mole) of 3-aminobiphenyl in 500 ml. of 1.3 *M* sulfuric acid was diazotized with a solution of 22.5 g. (0.326 mole) of sodium nitrite in 50 ml. of water. The solid yellow diazo salt that formed was stirred vigorously in 500 ml. of toluene while a solution of 100.5 g. (0.628 mole) of potassium iodide in 250 ml. of water was added over a period of thirty minutes. The temperature of the reaction was maintained at +5° during the addition. The resulting red complex slowly decomposed at room temperature, and the black toluene layer that separated after several hours was dried and distilled at reduced pressure. The fraction which boiled at 145–155° at less than 1 mm. was redistilled at this pressure, and 3-iodobiphenyl was collected as a yellow oil, boiling at 149–152°. The yield was 42 g. or 48% of theoretical.

Anal. Calcd. for $C_{12}H_9I$: I, 45.42. Found: I, 45.69.

***m*-Phenylacetophenone.**—The Grignard reagent was prepared from 3-iodobiphenyl and converted to *m*-phenylacetophenone by treatment with acetic anhydride. The ketone was obtained as a light yellow oil boiling at 148–151° at less than 1 mm. pressure. It readily formed a semicarbazone which was obtained as white plates, melting at 222–223°.

Anal. Calcd. for $C_{15}H_{15}N_3O$: N, 16.59. Found: N, 16.47.

The 2,4-dinitrophenylhydrazone was also obtained as orange needles, m. p. 191–192°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: N, 14.88. Found: N, 14.68.

(3) All analyses are by Mrs. W. B. Reid, Jr., of this Laboratory.
(4) Elks, Haworth and Hey, *J. Chem. Soc.*, 1285 (1940).

DEPARTMENT OF CHEMISTRY
INDIANA UNIVERSITY
BLOOMINGTON, INDIANA RECEIVED APRIL 26, 1946

A Simple Purification Procedure for DDT[1]

BY KATHRYN H. COOK AND WALTER A. COOK

A survey of the literature on the new insecticide popularly known as DDT, discloses the fact

(1) Abstracted from a part of the thesis submitted by Wm. Bradley Reid, Jr., to the faculty of the Graduate School in partial fulfillment of the requirements for the Degree, Doctor of Philosophy, in the Department of Chemistry, Indiana University.
(2) Newman and Booth, THIS JOURNAL, **67**, 154 (1945).

(1) Presented before the Division of Organic Chemistry at the Atlantic City Meeting of the American Chemical Society, April 11, 1946.

that the purification of this substance is not as readily accomplished as would be expected. That this is obviously the case, can be concluded from the recent studies on the chemical composition of technical DDT by Haller, Bartlett, Drake, Newman and associates, and reported melting point data by these and other investigators,[2] which values range from 105 to 109°. Moreover the fact that three grades of DDT are recognized by the War Production Board and the armed forces of this country is a further suggestion of difficulties involved in its purification. The writers have found that a simple extraction or washing process of technical or laboratory prepared DDT specimens will provide a grade of purity at least equal to the minimum limit prescribed for aerosol quality (m. p. 103°) and, in most instances a value of 105° or better. The details of the experimental purification procedure of a technical DDT specimen procured from a well-known supply distributor are given as follows.

One hundred grams of the technical product which melted at 60° is treated with 50 ml. of 95% ethyl alcohol to form a thick paste and then diluted with 300 ml. of water. This mixture is filtered on a Buchner, transferred to a 600 ml. beaker and treated with 250 ml. of 95% ethyl alcohol. After chilling in an ice–salt brine it was filtered and washed with an additional 100-ml. portion of cold alcohol. The alcohol extracted product is treated similarly with (30–60°) petroleum ether and after filtration, washing and drying, 65 g. of partially purified DDT m. p. (block value) 106–107° is obtained. The latter fraction on recrystallization from 800 ml. hot 95% ethanol gave 60 g. of product, m. p. 109.5–110° (cor.). This upon two additional and alternate petroleum ether extractions, and alcohol recrystallizations under conditions as described above, yielded 46 g. pure product m. p. 110–110.5° (cor.) in a Roth apparatus. Further purification attempts did not change this value. Needless to say in ordinary purification work, the products from the previous steps were not completely dried inasmuch as the efficiency of subsequent extractions is believed to be lowered due to decreased wetting effect of the solvent; furthermore less time is required in the purification process. Thus, the technical specimen referred to above contains approximately 67% DDT, and approximately 70% of the actual DDT is recovered. Cautious evaporation of the several extraction filtrates to remove the last traces of solvent reveals evidence in the residues of progressively decreasing quantities of contaminants together with some pure DDT.

Laboratory specimens prepared by a modification of the chlorosulfonic acid condensation,[3] and similarly purified as previously described, melted at 110–110.5° (cor.). Mixed melting point of the laboratory purified product and that isolated from technical DDT, showed no depression.

In order to establish further that the compound with m. p. 110–110.5° was pure DDT and not DDD[4] (1,1-di-*p*-chlorophenyl-2,2-dichloroethane), which melts also at 110.5–111°, a mixed melting point determination of both substances showed a marked depression. Additional evidence for the identification of our product (m. p. 110–110.5° cor.) as DDT is given in the following.

Anal.[5] Calcd. for $C_{14}H_9Cl_5$: C, 47.43; H, 2.56; Cl, 50.01. Found: C, 47.06; H, 2.76; Cl, 49.93.

A dinitro derivative[2] of our product melted at 148–148.5° (cor.). This value is in agreement with that reported by Haller and associates, and higher than the 143° value reported by Zeidler. In ordinary recrystallization operations in which large quantities of partially purified DDT are involved acetone is superior to alcohol inasmuch as less acetone is required and the contaminants are more soluble. For example, with 354.5 g. (1 mole) of partially purified DDT (m. p. 105–107°) dissolved in 1600 ml. acetone at room temperature, filtered and on slow addition of 400 ml. water with stirring, a product was obtained which upon drying weighed 335 g. (94.7% recovery); m. p. 109.5–110° (cor.). With alcohol in place of acetone as the solvent, at least two recrystallizations each with a solvent-volume, solute-weight ratio of approximately 10 to 1 were found necessary to achieve the same degree of purity. It should be noted, further, that the above described purification procedure is not intended to cover commercial dusting powders or artificially blended spray preparations containing DDT as one of the ingredients. Moreover, as a future primary reference standard for entomological and pharmacological studies, the product which melts at 110–110.5° (cor.) is recommended for acceptance.

(2) Haller, Bartlett, Drake, Newman and co-workers, THIS JOURNAL, **67**, 1591 (1945); Gooden, *ibid.*, **67**, 1617 (1945); Zeidler, *Ber.*, **7**, 1180 (1874); Bailes, *J. Chem. Ed.*, **22**, 122 (1945), and Gunther, *ibid.*, **22**, 238 (1945). The latter states that one to two recrystallizations from excess ethanol or isopropanol usually yields a m. p. of 105° and to secure a very pure product it is usually necessary to decolorize the material at least once with charcoal, followed by four or five recrystallizations.

(3) Rueggeberg and Torrans, *Ind. Eng. Chem.*, **38**, 211 (1946).

(4) Sample kindly supplied by Dr. William A. Mosher of Pennsylvania State College.

(5) Duplicate analyses were made and the average values for C, H and Cl reported here. Microanalyses by Dr. Carl Tiedcke.

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RECEIVED NOVEMBER 23, 1945

Specificity of the Action of Urease

BY CLARA L. DEASY

Urease catalyzes the hydrolysis of urea, but the enzyme has been shown to be without effect on a number of derivatives of urea.[1] This study was made to determine whether urease can catalyze the hydrolysis of guanylurea, or whether the action of urease on urea can be inhibited by guanylurea.

Experimental.—Guanylurea was used in the form of the commercially available sulfate,[2] which was recrystallized after treatment with bone charcoal. The urease solution was prepared according to the Folin–Wu method,[3] except that the concentration of the solution was increased by using five times the amount of jack bean meal.

The urea was used in 3% solution (30 mg./ml.); 5 ml. of water and 1 ml. of urease solution were added in each determination. The mixtures were incubated for fifteen minutes at 45–50°. Analysis of extent of hydrolysis was made according to the method of Marshall,[4] by titration with standard hydrochloric acid (0.09306 *N*) with methyl orange as indicator. Blanks were run on the urease, urea, guanylurea sulfate and guanylurea sulfate + urea, each incubated for fifteen minutes at 45–50° with 5 ml. of water. The necessary blanks were subtracted from the volume of standard hydrochloric acid used in each determination to give the corrected volume (Column 4, Table I). Each experiment is an average value of 4 determinations.

In experiment 1 the blanks for guanylurea sulfate and for urease exceeded by 0.03 ml. the volume of standard hydro-

(1) See, for example, Armstrong and Horton, *Proc. Roy. Soc.* (London), **B85**, 109 (1912); Cajori, *Proc. Soc. Exptl. Biol. Med.*, **30**, 184 (1932); Bonnet and Razafimahery, *Enzymologia*, **1**, 55 (1936).

(2) Supplied through the courtesy of American Cyanamide and Chemical Corp.

(3) Peters and Van Slyke, "Quantitative Clinical Chemistry," Vol. II, Williams and Wilkins Co., Baltimore, Md., 1932, p. 545.

(4) Marshall, *J. Biol. Chem.*, **14**, 283 (1913).