maintain a positive pressure in the system, the breakoffsky Z was broken. At this point the initial reading of the volume of hydrogen was taken. When stirring was again resumed, the stream of hydrogen served to carry over into the reaction chamber any tritium gas remaining in U tube A. In this, as well as in the pilot runs, the progress of the reaction was followed by the decrease in the volume of hydrogen.

After hydrogenation was complete, the bulb K was lowered and tube C and bulb D were both cooled with liquid nitrogen. When all the solvent in A had distilled off, the system was sealed at H and the reaction flask B was removed. The product was isolated by redissolving in dry acetone and filtering through a thin bed of diatomaceous earth and decolorizing carbon. The flask and filtering medium were washed thoroughly with acetone (total volume about 20 ml.). Evaporation of the filtrate and washings in a low vacuum gave a yield of 594.6 mg. of crude product (116.2%). In all the reduction experiments made, the yield was in excess of 100%. Drying in a vacuum caused no loss in weight, while heating at 100° caused sublimation and loss of product.

When absolute ethanol was used as solvent, the excess weight was 23%. The yields of crude product obtained in pilot runs with acetone as solvent were 113.1, 119.0, 118.3, 119.5, 119.5%; with alcohol as solvent the yields were 123.5, 105.5, 123.5, 123.8%. A weighed amount of catalyst used in these experiments did not lose weight when extracted with either acetone or alcohol. The excess weight with either solvent corresponds closely to one mole of solvent.

The rates of hydrogen uptake in experiments with tritium and with hydrogen are shown in Fig. 2. Under identical experimental conditions there was an apparent increase in the rate of hydrogenation when tritium was present. Since this experiment could not be repeated due to the scarcity of tritium, this catalytic effect invites further investigation. The only explanation that we can offer for the increased rate of hydrogen uptake when tritium is present is that the high concn. of radioactivity, 500 mc., brings about an activation of reactants or some related phenomena. Alpha rays are known to bring about a dissociation of hydrogen (see Munde, *et al.*, *Bull. soc. chim. Belg.*, **56**, 386 (1947); Munde, *et al.*, *ibid.*, **57**, 88 (1948)).

Separation of Hexestrol and Isohexestrol.—The solubility data for pure hexestrol in benzene[7] in the temperature range 15–16° indicated that a ratio of 5 ml. of benzene per 100 mg. of hexestrol should give a 90% yield of product after recrystallization. The crude product was dissolved in 30 ml. of hot benzene. Crystals were allowed to form at room temperature and then at 6–8° (2 hr.). The mother liquor was filtered and transferred into a tared 40-ml. cone with a filter stick. The colorless crystals, dried in a vacuum, weighed 386.4 mg. (73.8%) and melted at 184–185°.

Evaporation of the mother liquor to dryness left 220.8 mg. of colorless residue which, recrystallized from 5 ml. of benzene and treated as above, gave 34.9 mg. (6.8%) of product melting at 160–164°. This is apparently a mixture of hexestrol and isohexestrol.

The second mother liquor was evaporated to a volume of 1.5 ml. and cooled to 6° for one hour. The mother liquor was removed as before and the colorless needles, washed with 0.5 ml. of benzene and dried, weighed 142.8 mg. (28%) and melted at 126–127°. The mother liquor from these crystals upon evaporation to dryness gave 30.2 mg. of crystals melting at 124–125°. These last two fractions correspond to isohexestrol.

Anal. Calcd. for $C_{18}H_{22}O_2$; C, 79.96; H, 8.20. Found: C, 80.00, 80.00; H, 8.12, 8.05.

The above method of separation gave, in five separate experiments: 72–77% yields of product melting at 183–185°; 5–7% of product melting at 175–180°; 26–27% of product melting at 126–128°; about 7% of product melting at 123–125°.

Other solvents tried (dioxane, dioxane–water, carbon tetrachloride) did not give as sharp a separation of hexestrol from isohexestrol.

Acknowledgment.—We wish to thank Dr. C. W. Sondern and the White Laboratories, Inc., for the dienestrol used in this investigation.

Summary.—1. The estrogen "hexestrol" (*meso*-3,4-di-(4-hydroxyphenyl)-hexane) has been prepared labeled with tritium.

2. Both *meso* and racemic hexestrol are obtained by the hydrogenation of "dienestrol" (3,4-di-(4-hydroxyphenyl)-2,4-hexadiene) with palladium-on-carbon catalyst.

3. The presence of 500 mc. of tritium exerted a significant influence upon the rate of uptake of hydrogen.

4. The hexestrol labeled with tritium contained approximately 1 mc. of radioactivity per milligram.

LOS ALAMOS, NEW MEXICO RECEIVED MAY 5, 1950

The Magnetic Susceptibility of Iodine Dioxide

BY W. K. WILMARTH AND S. S. DHARMATTI

The "dioxides" of chlorine, bromine and iodine have all been known for many years but only in the case of chlorine is the degree of polymerization known, and even here only dilute solutions have been studied.[1] Iodine dioxide, the more easily prepared of the latter two members, is a non-hygroscopic relatively stable compound at room temperature. It either reacts with or is insoluble in all common solvents, so measurements can only be made on the pure solid. Magnetic susceptibility measurements, described below, show that the compound is diamagnetic and hence the molecule must contain an even number of IO_2 units. It would appear that transition in bond type must occur either in solid chlorine dioxide or at bromine dioxide. We are at present engaged in preparing bromine dioxide in quantities sufficient for both magnetic susceptibility measurements and clarification of its general chemistry.

Experimental

Iodine dioxide was prepared as described by M. M. P. Muir.[2] The initial yellow solid was decomposed by exposure to moist air and the iodine dioxide separated from iodine by washing with water, alcohol and ether. The analysis, after several such washings, was obtained by adding excess iodide to a known quantity of iodine dioxide and titrating with standard thiosulfate. *Anal.* Found: I, 79.86; calcd.: I, 78.8.

Magnetic Susceptibility of $(IO_2)_x$.—A specimen was carefully packed in the conventional glass tube and measured in the solid state using the Gouy technique. A gram susceptibility of -0.239×10^{-6} was obtained, corresponding to a molal susceptibility of -76.0×10^{-6} using

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(7) Cheymol and Carayon-Gentil, *Bull. Soc. Chim. Biol.*, **28**, 136 (1946) (*C. A.*, **41**, 3518e (1947)).

(1) N. W. Taylor, THIS JOURNAL, **48**, 854 (1926).

(2) M. M. P. Muir, *J. Chem. Soc.*, **95**, 656 (1909).

the molecular weight of the dimeric formula. The substance is clearly diamagnetic and hence the monomeric IO_2 unit does not occur in the solid state.

In principle one could further elucidate the detailed molecular structure by either a theoretical calculation of the expected magnetic susceptibility for each of the various models or through a comparison with the appropriate experimental values. Actually neither method is sufficiently refined to distinguish between the various structural possibilities. Using the method of Angus[3] one can sum the appropriate values of +4 iodine and −2 oxygen to obtain a value of -96.52×10^{-6} for I_2O_4. Alternately, assuming a structure of (IO^+) (IO_3^-) and using Angus' values of +3 and +5 iodine, one calculates -97.10×10^{-6}. These discrepancies are not unexpected and indeed are no larger than might be anticipated for such a calculation. Summation of Pascal's[4] experimental values leads to -107.64×10^{-6}; here again one might expect too large a value since Pascal's value for iodine is applicable to a single bonded covalent iodide atom. An experimental value[5] of IO_3^- of -51.4×10^{-6} would lead, on the assumption of the iodyl iodate model, to an experimental value of -24.88×10^{-6} for the iodyl ion.

Acknowledgment.—We are indebted to the Office of Naval Research for financial support of this work.

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[3] Angus, *Proc. Roy. Soc. (London)*, **A136**, 569 (1932).

[4] Selwood, "Magnetochemistry," Interscience Publishers Inc., New York, N. Y., 1943, p. 52.

[5] V. C. G. Trew, *Trans. Faraday Soc.*, **37**, 476 (1941).

DEPT. OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIF.
RECEIVED MAY 31, 1950

NEW COMPOUND

Some Derivatives of *o*-Cresol

Some derivatives of *o*-cresol were prepared as reference compounds in other work.

1-(*o*-Toloxy)-3-chloro-2-propanone.—A 16.8-g. (0.091 mole) sample of freshly distilled *o*-toloxyacetyl chloride was converted to the diazoketone essentially according to the procedure of Newman and Beal.[1] The diazoketone, in solution in 650 ml. of ether, was not isolated but decomposed by passing dry hydrogen chloride into the solution until the evolution of nitrogen ceased. After washing with 150 ml. of cold water and two 50-ml. portions of 5% sodium carbonate, the ether solution was dried with sodium sulfate and evaporated to a red oil; yield 16.3 g. (90%). Distillation at 0.2 mm. gave 2.4-g. forerun boiling below 87° and 10.3 g. (57%) of chloroketone distilling between 87–92°. Two recrystallizations from petroleum ether gave colorless needles, m. p. 50°. The compound recrystallized immediately after melting and remelted at 54°.

Anal.[2] Calcd. for $C_{10}H_{11}O_2Cl$: C, 60.46; H, 5.58. Found: C, 60.61; H, 5.71.

β-(2-Methyl-4-nitrophenoxy)-lactic Acid.—Ten grams of β-chlorolactic acid, 24.6 g. of 2-methyl-4-nitrophenol and 85 ml. of 12% sodium hydroxide were heated two hours on the steam-bath. The cooled aqueous solution was acidified to congo red and extracted with ether. The substituted lactic acid separated on acidification of a potassium bicarbonate extract of the ether solution. Recrystallization from hot water, after treatment with Darco G-60 gave 3.27 g. (17%) of a pale yellow powder, contaminated by a few bright yellow needles which were separated manually. The major product melted at 111° after recrystallization from water.

Anal. Calcd. for $C_{10}H_{11}O_6N$: C, 49.79; H, 4.60. Found: C, 49.51; H, 4.48.

The minor product, m. p. 85°, after recrystallization from water, was not further characterized.

***o*-Toloxyacetylglycine.**—Five ml. of *o*-toloxyacetyl chloride (b. p. 108–109° (8 mm.)) was added with stirring and cooling to 13.3 g. of glycine homogenized with 13 ml. of 20% sodium hydroxide. When the reaction had subsided, alternate additions of 13 ml. of sodium hydroxide and 5 ml. of the acid chloride were made until a total of 32.7 g. of the acid chloride and 76 ml. of sodium hydroxide had been added. After standing an hour and a half, the reactants were poured into chipped ice, acidified to congo red with dilute hydrochloric acid and filtered. The crude product weighing 36.5 g., m. p. 185–186°, was recrystallized from 450 ml. of ethanol; yield 28.5 g., 70%, m. p. 190–190.5°, raised to 191–191.5° by two further recrystallizations from ethanol.

Anal. Calcd. for $C_{11}H_{13}O_4N$: C, 59.19; H, 5.87. Found: C, 59.23; H, 5.89.

Ethyl β-(*o*-Toloxy)-lactate.—Nine grams of β-(*o*-toloxy)-lactic acid[3] was converted to the ester by refluxing 3 hours with 30 ml. of absolute ethanol containing 5% hydrochloric acid. Distillation of the residue after removal of hydrochloric acid and excess alcohol gave 6.45 g. (67%) of the ester, b. p. 99–102° (0.2 mm.).

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.23; H, 7.38.

DIVISION OF PHARMACOLOGY AND TOXICOLOGY
UNIVERSITY OF ROCHESTER
SCHOOL OF MEDICINE AND DENTISTRY
ROCHESTER 20, NEW YORK RICHARD F. RILEY[4,5]
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[1] Newman and Beal, THIS JOURNAL, **71**, 1506 (1949).

[2] Microanalyses by C. W. Beazley, Skokie, Illinois.

[3] Riley, THIS JOURNAL, **72**, 5712 (1950).

[4] Aided by a grant from The National Foundation for Infantile Paralysis, Inc.

[5] University of California Atomic Energy Project, Post Office Box 31, Beverly Hills, Calif.