pentachloride. A violent reaction took place. The resulting mixture was kept at room temperature for one hour. Water was then added (100 cc.), the two layers were separated, and the chloroform layer removed to the steam-bath. During the evaporation of the chloroform the chloride crystallized. It was filtered and dissolved in ether. The ether solution was washed with sodium hydroxide to remove acidic esters. The ether residue after one crystallization gave an almost pure chloride; yield 0.76 g.; m. p. 153°. The mother liquor was evaporated and the residue was distilled in high vacuum and recrystallized from methyl alcohol: yield 0.12 g.; total yield 0.88 g. (83%). Further repeated recrystallizations did not raise the melting point above 154° (uncorr.): $[\alpha]^{22}\text{D}$ +14.6° (19.2 mg. in 2 cc. of chloroform solution gave $\alpha^{22}\text{D}$ +0.14°. 1-dm. tube).

Summary.—A simple method is described for the preparation of dehydroandrosteryl chloride in good yield. The chloro ketone so prepared melts at 154° and has a specific rotation $[\alpha]^{22}\text{D}$ +14.6°.

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The Separation of the C_{17}-Epimers of Oestradiol by Digitonin

BY O. WINTERSTEINER

It has been shown by Schwenk and Hildebrandt[1] that two epimeric forms of oestradiol can be obtained by catalytic reduction of the 17-keto group of oestrone (theelin). The lower melting α-isomer (m. p. 178°, $[\alpha]\text{D}$ +81°), which occurs in follicular fluid[2] and in the urine of pregnant mares,[3] is the most potent oestrogenic compound known. The higher melting β-isomer (m. p. 223°, $[\alpha]\text{D}$ +54°), which is much less active physiologically, has only recently been prepared in pure form. Its properties will be described in more detail in a separate communication.[4] We have found recently that the two isomers can be separated conveniently by digitonin, whereby the laborious separation by fractional crystallization may be avoided. Only the lower-melting α-isomer forms a sparingly soluble digitonide, when treated with a solution of digitonin in 80% alcohol. The molecular compound deposits slowly in form of beautiful needles, which melt at about 265° after partial decomposition at 195°, and from which the diol can be regenerated easily by the usual methods. Also the 3-benzoate of the α-isomer yields a crystalline precipitate with digitonin, though more slowly than the free diol. Neither the high melting β-oestradiol nor its 3-benzoate precipitates with digitonin under identical conditions. These results show clearly that it is the configuration of the 17-carbon atom which determines the capacity to form insoluble digitonides of this type.

The digitonin reaction is also negative with oestriol (theelol), dihydroequilenin (δ-follicular hormone)[5] and 17-*trans*-testosterone.[6] Furthermore, no precipitate was obtained with a crude preparation of androstenediol-3-acetate, which according to the mode of its preparation should have contained some of the 17-*cis*-epimer. The melting point of dihydroequilenin, and that of its benzoate, its low specific rotation ($[\alpha]\text{D}$ −4.7°), its low physiological potency, and its failure to precipitate with digitonin would place this compound in the β-series of oestrogenic diols. On the other hand, if the same criteria be applied to 17-*trans*-testosterone, all the data except the negative digitonin reaction speak for its steric relationship to α-oestradiol. Caution is obviously necessary in interpreting the behavior of C_{17}-epimers toward digitonin as an indication of stereochemical relationships.

In the pregnane series, Butenandt and co-workers[7] have employed digitonin for the separation of C_{17}-epimers. *allo*-Pregnanedione, *allo*-pregnanol-3-one-20-3-acetate, and Δ^5-pregnenol-3-one-20, but not their C_{17}-epimers, termed *iso*-compounds by these workers, form insoluble digitonides.

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[1] Schwenk and Hildebrandt, *Naturwiss.*, **21**, 177 (1933).

[2] MacCorquodale, Thayer and Doisy, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1182 (1935); *J. Biol. Chem.*, **115**, 435 (1936).

[3] Wintersteiner, Schwenk and Whitman, *Proc. Soc. Exptl. Biol. Med.*, **32**, 1087 (1935).

[4] Whitman, Wintersteiner and Schwenk, forthcoming publication.

(5) Wintersteiner, Schwenk, Hirschmann and Whitman, THIS JOURNAL, **58**, 2652 (1936).

(6) Ruzicka and Kägi, *Helv. Chim. Acta*, **19**, 842 (1936).

(7) Butenandt and Mamoli, *Ber.*, **68**, 1847 (1935); Butenandt and Fleischer, *ibid.*, **70**, 96 (1937).

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Reaction of Lanthanum Oxide with Ammonium Iodide

BY RALPH C. YOUNG AND JANE L. HASTINGS

By following the general method of Reed, Hopkins and Audrieth[1] for the preparation of the chlo-

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[1] Reed with Hopkins and Audrieth, THIS JOURNAL, **57**, 1159 (1935).

rides and the bromides of the rare earth metals it has been found possible to carry out the reaction between lanthanum oxide and ammonium iodide in such a manner that the final product contains about 90% of anhydrous lanthanum iodide.

The essential features of the procedure are as follows. One gram of ammonium iodide is poured into a Pyrex tube, 10 mm. in bore and 60 cm. long, closed at one end. There is then added a mixture of 1 g. of lanthanum oxide and 6 g. of ammonium iodide. The tube is inserted in an electric furnace to a distance of 22 cm., being slightly inclined downward at the outer open end, and is heated at 350°, with an occasional rotation, until no more water condenses in that part of the tube outside the furnace. Four hours are required for complete reaction, whereupon the excess ammonium iodide is removed by sublimation in a high vacuum at 250°. During the whole process the vapor from the ammonium iodide, passing over the product, protects it from reaction with oxygen which would otherwise occur even at low pressures. When no more ammonium iodide condenses outside the heated zone, the tube is sealed and quickly cooled to room temperature.

The product obtained by this method is nearly white with a very slight yellow tinge. Its hydration on exposure to air and the vigor of its reaction with water are indicative of the presence of anhydrous lanthanum iodide. On extraction with water 10% or less is insoluble. The atomic ratio of iodine to lanthanum in this insoluble residue varies from 0 to approximately 0.3. In the solution the ratio is 3, and, since no ammonium ion is present, it corresponds to the formula, LaI_3. Lanthanum iodide was also extracted from the raw product with 95% ethyl alcohol.

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COMMUNICATIONS TO THE EDITOR

INHIBITION OF THERMAL DECOMPOSITION OF *n*-BUTANE BY NITRIC OXIDE

Sir:

The recent work of Fletcher and Rollefson [THIS JOURNAL, **58**, 2129, 2135 (1936)] has shown that the acceleration of an organic vapor phase decomposition by ethylene oxide, and inhibition of the normal decomposition by nitric oxide give rather conclusive evidence that the decomposition proceeds via a chain mechanism.

We have previously shown [*ibid.*, **58**, 1317 (1936)] that ethylene oxide accelerates the decomposition of propane, *n*- and *i*-butane.

We now find that the decomposition of *n*-butane is strongly inhibited by small amounts of NO, as shown by the following table.

P_0 butane = 200 mm.: temp., 500 ± 1.0°: KCl-coated reaction bulb

P_0(NO), mm.	Init. rate, mm./min.	% Dec. at 120 min.	
		By ΔP	By anal.
0	1.0	26.5	31
20	0.05	7.1	13

The rates as measured by the analysis after 120 minutes indicate that the inhibition is somewhat less than would be concluded from the initial rates. However, the fact that the normal reaction falls off quite rapidly with time, while the inhibited reaction rate increases continuously, can in large part explain this discrepancy. Thus the actual inhibition must lie between a 20/1 ratio of normal to inhibited rate and a 3/1 ratio, as given by the runs to high percentage decomposition. Measurements over a wide range of P_0(NO) indicate a region of maximum inhibition at about 20 mm.

This result, together with the arguments advanced by Hinshelwood [Staveley and Hinshelwood, *Proc. Roy. Soc.* (London), **A154**, 335 (1936)] as to the possible causes of an observed inhibition, lead us to the conclusion that the decomposition of butane under these conditions is largely a chain reaction.

Further work is now in progress, attempting to correlate the two effects in a more quantitative