Ethyl β-(Bromomethyl)-cinnamate (A).—A solution of 36 g. (0.19 mole) of ethyl β-methylcinnamate, 36 g. (0.20 mole) of N-bromosuccinimide, and 10 cc. of carbon tetrachloride was heated on an oil-bath at 95-105° for forty-eight hours. At the conclusion of the heating period, the reaction mixture was diluted with carbon tetrachloride, chilled, and filtered to remove succinimide. The filtrate was shaken with water, dried over anhydrous magnesium sulfate, then fractionated through an 8-in. Vigreux column. There was thus obtained a 23-g. fraction boiling at 120-145° (1-5 mm.). Refractionation of this material gave 20 g. of an oil, boiling at 131-141° (1 mm.). A second refractionation gave an analytical sample boiling at 134-136° (1 mm.); n^{20}D 1.5773.

Anal. Calcd. for $C_{12}H_{13}BrO_2$: C, 53.54; H, 4.87; Br, 29.70. Found: C, 53.17; H, 4.63; Br, 29.86.

(B).—A solution of 146 g. (0.77 mole) of ethyl β-methylcinnamate, 68.5 g. (0.39 mole) of N-bromosuccinimide, and 9.2 g. (0.04 mole) of benzoyl peroxide in 115 cc. of carbon tetrachloride was heated under reflux in an oil-bath for seven and three-fourths hours. The reaction mixture was chilled and the succinimide crystals removed on a filter, then washed once with hot carbon tetrachloride. The washings were chilled, filtered, and combined with the initial filtrate. This solution was washed thoroughly with saturated, aqueous sodium carbonate, separated, and dried over anhydrous magnesium sulfate. Fractionation under reduced pressure through a 6-in. Vigreux column gave 51 g. of an oil boiling at 142-154° (4-5 mm.), a yield of 50% of theoretical. Refractionation of this material gave 48 g. of a pale yellow oil boiling at 123-127° (0.4 mm.), indicating that the initial cut was essentially homogeneous. The refractive index at 20° of refractionated material boiling at 134-136° (1 mm.), was 1.5770.

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Hydrodiethylstilbestrol Compounds. V. Reinvestigation of the Racemic Octahydro Compounds

BY HERBERT E. UNGNADE AND PAUL W. TUCKER[1,2,3]

A mixture of racemic octahydrodiethylstilbestrol compounds has been prepared by partial hydrogenation of diethylstilbestrol with Raney nickel catalyst.[4] The mixture consisted mainly of two crystalline substances (I) and (II) melting at 147-148° and 47-50°. There is some question about the identity of these substances since a third octahydro compound (III), m. p. 144-145°[4,5] has also been isolated in traces from the same reaction mixture. While this compound is not identical with the two known *meso* compounds,[6,7] it has not been possible to assign it definitely to either series since the hydrogenation of diethylstilbestrol yields traces of *meso* compounds along with the racemic isomers.[4] For this reason the racemic octahydro compounds have now been prepared from authentic *dl*-hexestrol monomethyl ether (IV) according to the method of Wilds and McCormack.[7,8]

A separation of the octahydro compounds can be effected by extraction of the mixture first with 5% aqueous potassium hydroxide solution and then with Claisen alkali.[7] The material obtained from the aqueous alkali extract can be crystallized and affords (III), m. p. 141-142°. The Claisen alkali extract yields a mixture of isomers, m. p. 47-50°, which cannot be separated by crystallization or sublimation similar to the "mixture I" of Ludutsky.[4,9] Chromatographic adsorption of the mixture, however, permits a direct separation to give (I), m. p. 146-147°, and (II), m. p. 47-50°.

It has thus been shown that (I), (II) and (III) belong to the racemic series. Compounds (I) and (III) are regarded as pure *trans*- and *cis*-isomers, (II) probably represents a mixture of these alcohols.[10]

Experimental[11]

***dl*-Hexestrol Monomethyl Ether (IV).**—*dl*-Hexestrol (41.87 g.) was methylated according to the procedure of Bretschneider.[12] The separation of the methylation products was analogous to the separation of the *meso*-isomers.[7] The monomethyl ether was extracted with benzene. The extract was washed until neutral and dried by distillation. The dry product (16.31 g.) crystallized on standing. It melted at 78-79° (from Skellysolve B).

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.44; H, 8.72.[13]

***cis* and *trans*-*dl*-*r*-3-(*p*-Hydroxyphenyl)-4-(4-hydroxycyclohexyl)-hexane.**—*dl*-Hexestrol monomethyl ether (16.31 g.), dissolved in 100 cc. of purified dioxane was reduced at 250° and 440 atm. of hydrogen with 4.5 g. of copper-chromium oxide catalyst as described by Wilds and McCormack.[7] The clear glassy product (15.39 g.) was refluxed for eight hours with 100 cc. of sodium methoxide solution containing 5 g. of sodium. Most of the methanol was distilled off. The residue was diluted with water and extracted with benzene. The benzene solution was washed and distilled. The residual product weighed 15.39 g. Part of the product (8.0 g.) was demethylated with methylmagnesium iodide according to Wilds and McCormack.[7] The ether solution obtained after decomposition of the Grignard reaction mixture was washed with four portions of 5% aqueous potassium hydroxide solution. Regeneration of the phenolic material from the washings yielded 1.50 g. of dark glassy material. The main product was extracted from the ether solution with Claisen alkali. It consisted of 3.91 g. of yellow glassy solid which melted

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[1] George Breon Fellow, 1946-1948.

[2] In part from the Ph.D. thesis of P. W. Tucker (1948).

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[4] Ungnade and Ludutsky, THIS JOURNAL, 69, 2629 (1947).

[5] Hoehn and Ungnade, *ibid.*, 67, 1617 (1945).

[6] Ungnade and Tucker, *ibid.*, 70, 4132 (1948).

[7] Wilds and McCormack, *ibid.*, 70, 884, 4127 (1948).

[8] The authors are indebted to Dr. A. L. Wilds for advance information on his procedures.

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[10] The present evidence does not permit to state with certainty which of the pure isomers is *cis* or *trans*.[7] The low melting mixtures (II) have been characterized previously by analyses, spectra and perhydrogenation.[4] The low melting points of (II) as compared to mixtures of the pure isomers are probably accounted for by polymorphism which has also been observed with other mixtures in this series. The glassy melts are very difficult to resolidify.

[11] All temperatures uncorrected.

[12] Bretschneider, Bretschneider and Ajtai, *Ber.*, 74, 583 (1941).

[13] Semi-microanalysis by Karl Zilch.

at 47–50° after crystallization from benzene–petroleum ether mixture.

A separation of this mixture of isomers was effected by adsorption of the material (2.0 g.) on alumina from its benzene solution. The benzene eluates of the "flowing chromatogram" (0.55 g.) melted at 146–147° after crystallization from the same solvent. When mixed with the "*trans*"-isomer of Ludutsky[4,9] (m. p. 147–148°) the compound melted at 145.7–146.7°. The subsequent ether eluate (0.81 g.) from the same chromatogram could be crystallized from benzene–petroleum ether mixture and melted at 47–50°.[14] Vacuum sublimation of this material gave a crystalline sublimate, m. p. 43–46°. The residue melted at 58–61°.

The product obtained from the aqueous alkali (1.50 g.) was crystallized from Skellysolve B. The first crop of crystals, m. p. 110–120°, weighed 150 mg. Three crystallizations from benzene–ligroin raised the melting point to 141–142°. The mixture with the octahydro compound of Hoehn[5] (m. p. 144–145°) melted at 141–142°.

Ultraviolet Absorption Spectra.—The ultraviolet absorption spectra of the compounds were determined in 95% alcohol in approximately 0.0002 molar solution with a Beckman spectrophotometer.[15] The results are given in Table I.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF THE RACEMIC COMPOUNDS

	ελmax.		ελmin.
Compound	225 mμ	280 mμ	250 mμ
I	3.803	3.205	2.023
II	3.868	3.232	2.281
III	...[a]	3.274	2.286
V[b]	4.119	3.477	2.441

[a] Not determined. [b] Racemic hexestrol.

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(14) The unusual behavior on adsorption is perhaps explained by the formation of a complex compound between the isomers. This would also explain the reported difficulties in separation.[4]

(15) Absorption spectra by Dr. E. E. Pickett, University of Missouri.

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The Half-Life of Protactinium (Pa^{231})

BY Q. VAN WINKLE,[1a] R. G. LARSON[1b] AND LEONARD I. KATZIN

The half-life of protactinium (Pa^{231}), the parent of actinium in the actino–uranium decay series, has been determined by a number of investigators. Values have been reported which range from 12,500 years to 32,000 years.[2,3,4] In view of the indirect methods used in the determinations, and their wide scatter, a redetermination of the protactinium half-life value has been made through direct determination of the specific activity with the aid of modern methods for counting alpha particles. A value of 34,300 ± 300 years has been found using the formula Pa_2O_5 for the ignited oxide of protactinium.

Experimental

Two samples of protactinium oxide were used in the half-life determinations. One was taken from material which had been isolated and purified by Larson, Katzin and Hausman,[5] and the second was taken from a preparation which had been isolated and purified by Thompson, Van Winkle and Malm.[6] These samples were given an additional purification by precipitating protactinium as the hydrated oxide from 0.5–1.0 *N* nitric acid either by heating on a boiling water-bath for five minutes (sample 1), or through precipitation with hydrogen peroxide added to 3% concentration (sample 2).

Samples of hydrated oxide were slurried into platinum crucibles using 1 *N* nitric acid, then dried and ignited to constant weight in a muffle furnace at 700–800°. Weighings were made on a semimicro balance with a sensitivity of 0.15 scale divisions per 10 micrograms. After ignition to constant weight, the oxide was made soluble by adding concentrated hydrofluoric acid and evaporating to dryness. The dried material was dissolved in 6 *N* hydrochloric acid solution (sample 1) or 1 *N* nitric acid (sample 2) and made up to volume. Aliquots of these two solutions were evaporated on platinum counting discs for determination of the alpha emission rate. Results are based on four aliquots of sample 1 and six aliquots of sample 2.

Aliquots from both sample solutions were analyzed spectrographically for impurities in the protactinium. We wish to thank Dr. Frank Tomkins for performing these analyses.

Determination of alpha particle emission rate was made with a counter having a mixture of argon and carbon dioxide at atmospheric pressure flowing through the chamber. The counter has been described by Jaffey.[7] Its effective counting yield is 51.7% and its coincidence loss has been estimated as 1.26% per 100,000 counts per minute.

Results

The data obtained have been summarized in Table I. The values appearing in line 3 for the weight of oxide were obtained by correcting the weight in line 2 for the impurities revealed by the spectrographic analysis. The corrections were made on the basis of the corresponding oxides. Sample 1 contained 1.5% iron, 0.15% calcium and 0.035% magnesium by weight. Impurities in sample 2 were less than the minimum detectable

TABLE I

Sample	1	2
Atm. ignited oxide, mg.	0.72	2.86
Cor. wt. oxide, mg.	0.705	2.86
Solution volume, ml.	5.00	49.63
Aliquot, μl.	25.0	50.35
Av. counting rate (cor.) of aliquot (51.7% counting yield)	153,500	128,100
Specific activity (counts/min./g. Pa)	5.11×10^{10}	5.18×10^{10}
Half-life, years	34,700	34,300

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(2) O. Hahn, *et al.*, *Ber. Berlin. Akad.*, 278 (1927); *Naturwiss.*, **16**, 454 (1928); *Z. angew. Chem.*, **42**, 926 (1929); *Naturwiss.*, **20**, 505 (1932); **15**, 803 (1927).

(3) J. H. Mennie, *Phil. Mag.*, [6] **46**, 684 (1923).

(4) A. von Grosse, *Ber.*, **61**, 243 (1928); *Naturwiss.*, **20**, 505 (1932).

(5) R. Larson, L. I. Katzin and E. Hausman, Plutonium Project Record, Vol. 17B, no. 6.3.

(6) R. C. Thompson, Q. Van Winkle and J. G. Malm, Plutonium Project Record, Vol. 17B, no. 6.4.

(7) A. H. Jaffey, Plutonium Project Record, Vol. 14A, Chapter 17.