methyl-(and α,α-diethyl)-butyrate, and 3-hydroxy-4-ethyl-4-methyl- (and 4,4-diethyl)-5-ketotetrahydrofuroic acid, but circumstances will not permit a continuation of the present study to include these substances.

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA RECEIVED NOVEMBER 5, 1943

Observations on the Rare Earths. L.[1] The Separation of Erbium from Yttrium by Fractional Precipitation of the Ferrocyanides[2]

BY THERALD MOELLER AND H. E. KREMERS

Yttrium and erbium oxide mixtures which accumulate during bromate fractionations of the yttrium earths are usually further separated by basicity methods, although the very favorable solubility difference between the ferrocyanides of these elements[3,4] renders ferrocyanide fractionation more rapid. In spite of the gelatinous nature of the precipitates, comparatively pure yttrium material has been prepared by this procedure,[5,6,7,8] and Prandtl,[9] using large quantities of nitric acid to promote crystallinity, has obtained erbium oxide of high purity. The lack of specificity in Prandtl's directions suggested a further study of the problem, and the resulting modified procedure gives consistently reproducible results, is rapid, and is free from undesirable oxidation of the ferrocyanide.

Experimental

Ferrocyanide Precipitation.—Erbium–yttrium chloride solutions were prepared in 3 *N* hydrochloric acid to contain 2% rare earth oxide and 10% ammonium chloride. To these solutions at room temperature, sufficient 20% potassium ferrocyanide solution (calculated as the trihydrate) to precipitate about one-half the rare earth material was added slowly with constant stirring. Experimentally, about 15 ml. precipitated the equivalent of 1 g. of rare earth oxide from material analyzing 85–100% Er_2O_3 and 20 ml. for lower erbium concentrations. Slow precipitation began only after complete addition of the ferrocyanide. After several hours, the precipitates were removed by suction filtration on qualitative paper.

Recovery of Rare Earth Materials.—Part of the iron was removed from the precipitates by boiling the solids with 50% sodium hydroxide, diluting, and filtering. After ignition of these hydroxides, the remainder of the iron was removed by oxalate precipitation of the rare earths from chloride solutions. The ferrocyanide mother liquors gave iron-free oxides after two precipitations with oxalic acid.

Fractionation of Erbium–Yttrium Mixtures.—Erbium–yttrium mixtures showing no absorption lines for holmium or thulium were fractionated by the above procedure. Each fractionation was followed by means of spectrophotometric analyses (based upon the 489 and 653 mμ erbium absorption bands)[10] of oxides recovered from both precipitates and mother liquors. Oxides of approximately the same composition were combined and refractionated.

The fractionation of 43 g. of a mixture (ER-18) containing 57% Er_2O_3 gave 4.8 g. of 89% Er_2O_3, 2.1 g. of 86% Er_2O_3, 5.9 g. of 80% Er_2O_3, 6.8 g. of 62% Er_2O_3, 6.7 g. of 38% Er_2O_3, and 15 g. of an oxide mixture low in erbium after twenty-eight fractional precipitations (five series with five or six fractions in each).

A series of fractions (ER-34) obtained from a urea separation[11] and a previous ferrocyanide fractionation and consisting of (1) 6.9 g. of 87% Er_2O_3, (2) 5.9 g. of 80% Er_2O_3, (3) 13.8 g. of 59% Er_2O_3, (4) 20.3 g. of 27% Er_2O_3, and (5) 45 g. of 17% Er_2O_3 yielded ultimately 3.14 g. of 98.5% Er_2O_3 (two precipitations of fraction (1)); 1.3 g. of 94% Er_2O_3, 2.35 g. of 93% Er_2O_3 and 2.8 g. of 80% Er_2O_3 (four precipitations of fractions (2), (3), and (4), respectively); and 5.6 g. of 48% Er_2O_3 (three precipitations of fraction (5)). In addition, 5.0 g. of 65% Er_2O_3, 17.6 g. of 44% Er_2O_3, and 9.5 g. of 27% Er_2O_3 were recovered from the final mother liquors.

Success of the ferrocyanide procedure is dependent upon the complete removal of iron, since even traces of iron yield gelatinous blue precipitates which nullify the effects of crystallinity in the rare earth ferrocyanides. Although some unavoidable loss is inherent in the oxalate precipitations, the speed and efficiency of the method recommend it.

Acknowledgment.—The authors wish to express their appreciation to Dr. C. J. Rodden of the National Bureau of Standards for the analysis of an erbium oxide sample used in the calibration of our spectrophotometer.

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(1) For the preceding communication in this series see Kleinberg, Taebel and Audrieth, *Ind. Eng. Chem., Anal. Ed.*, **11**, 368 (1939).

(2) Presented before the Division of Physical and Inorganic Chemistry at the 106th meeting of the American Chemical Society at Pittsburgh, Pa., September 6, 1943.

(3) Rowland, *Chem. News*, **70**, 68 (1894).

(4) Prandtl and Mohr, *Z. anorg. allgem. Chem.*, **236**, 243 (1938).

(5) Bettendorf, *Ann.*, **352**, 88 (1907).

(6) Meyer and Wuorinen, *Z. anorg. Chem.*, **80**, 7 (1913).

(7) Prandtl, *Z. anorg. allgem. Chem.*, **143**, 277 (1925).

(8) Canneri, *Atti accad. Lincei*, **8**, 164 (1928).

(9) Prandtl, *Z. anorg. allgem. Chem.*, **198**, 157 (1931).

(10) Rodden, *J. Research Natl. Bur. Standards*, **28**, 265 (1942).

(11) Fogg and Hess, THIS JOURNAL, **58**, 1751 (1936).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
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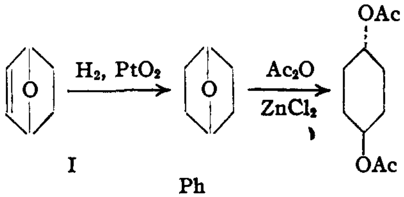
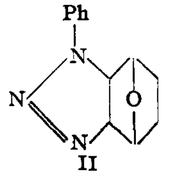
3,6-Epoxycyclohexene from Furan and Ethylene[1]

BY WALTER NUDENBERG AND LEWIS W. BUTZ

3,6-Epoxycyclohexene (I) has now been prepared by the procedure and with the apparatus previously employed in similar preparations.[2] It has been characterized as indicated below.



I



II

Into a mixture of 30–35 g. of furan and a few crystals of hydroquinone ethylene was introduced in two or three portions with intermittent shaking up to an initial pressure of 1100–1200 lb. per sq. in. at room temperature. The bomb was heated to 155° and kept at 150–155°, the pressure dropping and ultimately becoming constant after six-

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(1) Not subject to copyright. This work was supported by an allotment from the Special Research Fund (Bankhead–Jones Act of June 29, 1935).

(2) Joshel and Butz, THIS JOURNAL, **63**, 3350 (1941).

teen hours. After cooling the bomb, the gas was allowed to escape through a trap cooled by solid carbon dioxide, and the deposited furan was returned to the reaction mixture. The whole was distilled in three fractions: the first, of unreacted furan, 14–16 g.; the second, b. p. 40–118°, chiefly furan, 1.5 g., the third, a colorless liquid, b. p. 118–122°, 1.2–1.5 g. This last was 3,6-epoxycyclohexene, b. p. 118–119°, n^{20}_{D} 1.4629; yield, 5–8% on the furan consumed.

The triazoline derivative, formula II,[3] was prepared by mixing a few drops of phenyl azide with a similar quantity of epoxycyclohexene and allowing the resulting yellow solution to crystallize in the ice box overnight. Repeated crystallization from ethyl acetate gave fine white needles, m. p. 166–167° (cor.) (after drying over phosphorus pentoxide).

Anal.[4] Calcd. for $C_{12}H_{13}ON_3$: C, 67.0; H, 6.1; N, 19.5. Found: C, 67.1; H, 6.1; N, 19.5.

The epoxycyclohexene (4.5 g.) in 12 ml. of methanol was hydrogenated using 50 mg. of Adams catalyst. Distillation of the residue remaining after removal of the catalyst and methanol gave a fraction b. p. 110–120°. This material was refluxed, without further purification, with acetic anhydride and several crystals of zinc chloride for two hours. The excess acetic anhydride was distilled off and the remaining brown oil poured into hot water. Crystallization did not occur. The oil was extracted with ether, the solution dried and the ether evaporated. The residual oil on standing deposited crystals, m. p. 102–103.6°, from aqueous ethanol. A mixture with authentic ester,[5] m. p. 102–104°, also melted at 102–103.6°.

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(3) Alder and Stein, *Ann.*, **501**, 1 (1935).

(4) Analysis by Dr. T. S. Ma, University of Chicago.

(5) Baeyer, *Ann.*, **278**, 93 (1894). The *trans*-quinitol diacetate was kindly furnished by Mr. A. M. Gaddis, who prepared it from hydroquinone.

BUREAU OF ANIMAL INDUSTRY
AGRICULTURAL RESEARCH ADMINISTRATION
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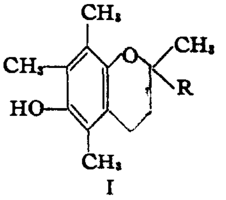
Coupling of Gamma Tocopherol and Failure of β-Tocopherol to Couple with Diazonium Salts

BY MARY LOUISE QUAIFE

Inspection of the structural formulas of α-tocopherol (I), β-tocopherol (II), and γ-tocopherol (III) suggests that both II and III are capable of coupling with diazonium salts.[1] We have found that γ-tocopherol couples readily, but the beta isomer, surprisingly, does not. Consequently, III can be determined in the presence of I and II. This note describes the reaction upon which the procedure is based and also experiments showing the failure of β-tocopherol to couple.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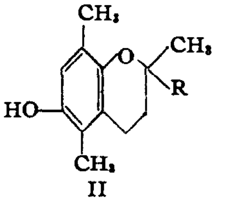
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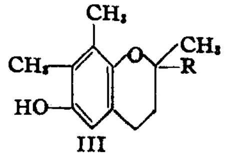
III

R = $C_{16}H_{33}$

γ-Tocopherol is determined by photometric estimation of the red dye produced by its reaction with diazotized *p*-nitroaniline in aqueous alcohol solution at *p*H of about 6. The dye, extracted with Skellysolve H, gives a stable color with absorption maxima at 530 mμ and 380 mμ. Over the range of quantity of γ-tocopherol employed in the analysis (0.2 to 0.5 mg.) absorption at either wave length is proportional to concentration. It is measured at 520 mμ for convenience. The method has been applied to estimation of γ-tocopherol content of tocopherol concentrates with results as shown in Table I. Total tocopherols were determined by the method of Emmerie and Engel.[2]

TABLE I

γ-TOCOPHEROL CONTENT OF VEGOL (CONCENTRATE OF NATURAL MIXED TOCOPHEROLS) FRACTIONS (DUPLICATE ANALYSES)

Sample	γ-Tocopherol, %	% total tocopherols	Ratio of γ- to total tocopherol; % γ-
Vegol (C)	2.8	4.3	65
	3.1	4.5	69
Vegol (I)	16.3	26.3	62
	17.8	26.7	67
Vegol (II)	21.4	42.0	51
	19.7	42.3	47
Vegol (III)	9.0	40.2	22
	9.5	40.2	24

When the procedure was applied to natural β-tocopherol, it required 12 mg. to give absorption at 520 mμ, equivalent to that given by only 0.05 mg. of γ-tocopherol. Since in this case the *p*H was about 6, the ability of β-tocopherol to couple with benzenediazonium chloride was tested over a *p*H range of 4.5 to 11. The test procedure was similar to that used in the analytical method except for increased amounts of β-tocopherol. Control series were run using equal amounts of γ-tocopherol as well as aqueous alcohol blanks. The resultant Skellysolve extracts of the reaction mixtures of the tocopherols (0.4 mg./cc.) and of the blank had colors as shown in Table II.

TABLE II

COLORS OF COUPLING PRODUCTS OF TOCOPHEROLS AND BENZENEDIAZONIUM CHLORIDE

*p*H	Blank	β-Tocopherol	γ-Tocopherol
4.5	Colorless	Colorless	Colorless
9.0	Light yellow	Light yellow	Deep orange
11.0	Light yellow	Light yellow	Deep orange

Absorption spectra over the range of 310 to 620 mμ of the reaction products at *p*H 9 show no difference in absorption between the Skellysolve extracts of the β-tocopherol reaction mixture and the blank. The γ-tocopherol azo dye formed at *p*H 9 had a density of 1.7 at 475 mμ, the peak of absorption.

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(1) Scudi and Buhs, *J. Biol. Chem.*, **146**, 6 (1942).

(2) Emmerie and Engel, *Rec. trav. chim.*, **57**, 1351 (1938).