Solutions of neo-β-carotene U and "carotenoid X" were mixed and subjected to chromatographic analysis on calcium hydroxide. There was no separation of bands, showing that the two pigments were identical. By a similar experiment neo-β-carotene B and "neo-β-carotene" from alfalfa were found to be identical.

Direct comparisons of the absorption of light by the preparations were made by means of a quartz spectrograph. In petroleum naphtha (Skellysolve F) solutions, photographed at different settings of the photometer, "carotenoid X" and neo-β-carotene U both had absorption maxima at 468 and 443 mμ; "neo-β-carotene" from alfalfa and neo-β-carotene B likewise had the same absorption curve with maxima at 473 and 446 mμ.

The pigments were also compared by dissolving approximately equal quantities in hexane, treating with iodine and analyzing the product by chromatographic separation on calcium hydroxide. The colorimetric ratio of the pigments formed from neo-β-carotene U was, unknown pigment: neo-β-carotene U: β-carotene: neo-β-carotene B: neo-β-carotene E = 2:22:42:29:5 and from "carotenoid X" of alfalfa = 3:23:46:24:4. For neo-β-carotene B the ratio was, 2:25:45:28:0 and for neo-β-carotene from alfalfa 1:22:43:34:0. The ratios of stereoisomers produced by this treatment were nearly the same in the two comparisons, another evidence of the identity of the carotenes compared from alfalfa. The same carotenes have been found in the chromatographic analysis of other plants (spinach, collards, grasses, etc.).

DIVISION OF CHEMISTRY
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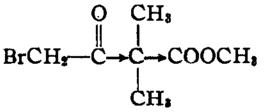
RECEIVED NOVEMBER 22, 1943

The Action of Sodium Cyanide on Methyl γ-Bromo-α,α-dimethylacetoacetate

BY C. F. KOELSCH

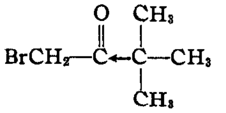
The reaction of sodium cyanide with an α-halogenated ketone usually leads to the formation of a β-ketonitrile; for example, bromopinacolone yields pivaloylacetonitrile.[1] A few α-haloketones, however, furnish α,β-oxidonitriles; for example, desyl chloride yields α,β-epoxy-α,β-diphenylpropionitrile.[2]

On the basis of the polarizations indicated in formulas I and II, it was anticipated that methyl γ-bromo-α,α-dimethylacetoacetate (I) might not parallel bromopinacolone (II) in its behavior toward sodium cyanide, but might suffer attack at its carbonyl group, leading to an oxide (IV).



$$BrCH_2—\overset{\overset{O}{\|}}{C}\rightarrow\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}\rightarrow COOCH_3$$

I



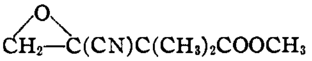
$$BrCH_2—\overset{\overset{O}{\|}}{C}\leftarrow\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_3$$

II

The reaction had been studied long ago[3,4,5] and the product had been assigned structure III. But a survey of the old data indicated that the properties of the product were more in accord with structure IV.

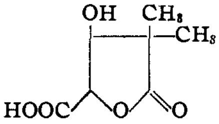
$CNCH_2COC(CH_3)_2COOCH_3$

III

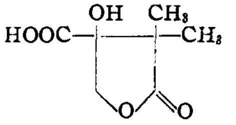


IV

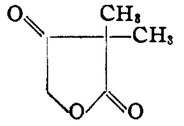
In the present work it was demonstrated that IV is correct. This was done by showing that the hydrolysis product of the nitrile, previously considered to be formed through hydration of the enol of III and formulated as V, actually is VI. The hydrolysis product was identical with the acid obtained by adding hydrogen cyanide to VII and hydrolyzing the resulting cyanohydrin, procedures which can lead only to VI.



V



VI



VII

2,4-Diketo-3,3-dimethyltetrahydrofuran[6] (VII), b. p. 200–210° (740 mm.) or 103–107° (16 mm.), was obtained in 86% yield when 25 g. of methyl γ-acetoxy-β-keto-α,α-dimethylbutyrate[7] was boiled for two hours with 5 g. of 10 molar alcoholic hydrogen chloride (contrary to the statement of Conrad and Gast,[6] the acetoxy ester was unchanged after it had been kept for three months; it also was unaffected when it was heated with potassium carbonate). When 1.3 g. of VII was shaken for fifteen minutes with a solution of 0.6 g. of sodium cyanide and 0.8 ml. of hydrochloric acid in 4 ml. of water, it furnished an oily cyanohydrin. This was removed with ether and boiled for one hour with 6 ml. of 20% hydrochloric acid; when the solution was cooled, it deposited 0.5 g. of VI, colorless prisms from water, m. p. 213–217° alone or mixed with the compound obtained from I by the procedure of Lawrence.[3] When it was boiled with methanol and sulfuric acid, VI gave a methyl ester that melted at 104–105° alone or mixed with Lawrence's ester.

Recognition of the correct structure (IV) for the nitrile previously considered to be III necessitates changes in the structures of substances derived from this compound. Simple esters, etc., need not be specifically mentioned here, but the following revisions must be pointed out. "3-Acetoxy-4,4-dimethyl-5-ketotetrahydro-furoic acid"[4] is actually 3-acetoxy-4,4-dimethyl-5-ketotetrahydrofuran-3-carboxylic acid; "4,4-dimethyl-5-ketotetrahydrofuroic acid"[4,5] is actually 4,4-dimethyl-5-ketotetrahydrofuran-3-carboxylic acid; "ethyl α′-chloro-β-hydroxy-α,α-dimethylglutarate"[3] is actually ethyl α-chloromethyl-α-hydroxy-β,β-dimethylsuccinate; "α,α-dimethyl glutaconic acid"[5] is actually[8] α,α-dimethylitaconic acid. Some doubt now attaches to the structures formerly assigned[3] to homologs of III and V, *viz.*, ethyl γ-cyano-β-keto-α-ethyl-α-

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[1] Widman and Wahlberg, *Ber.*, **44**, 2065 (1911).

[2] Kohler and Brown, THIS JOURNAL, **55**, 4299 (1933). Other examples may be found in the work of Justoni [*Gazz. chim. ital.*, **71**, 41 (1941), *Chem. Abs.*, **36**, 1016 (1942)] and of Delbaere [*Bull. soc. chim. Belg.*, **51**, 1 (1942), *Chem. Abs.*, **37**, 5018 (1943)].

[3] Lawrence, *J. Chem. Soc.*, **75**, 417 (1899).

[4] Conrad and Gast, *Ber.*, **32**, 137 (1899).

[5] Conrad, *ibid.*, **33**, 1920 (1900).

[6] Conrad and Gast, *ibid.*, **31**, 2728 (1898).

[7] Conrad and Kreichgauer, *ibid.*, **30**, 857 (1897).

[8] *Cf.* Perkin, *J. Chem. Soc.*, **81**, 249 (1902).

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
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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).

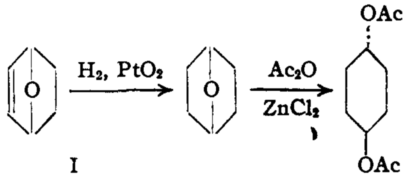
[11] Fogg and Hess, THIS JOURNAL, **58**, 1751 (1936).

NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS RECEIVED SEPTEMBER 20, 1943

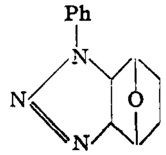
3,6-Epoxycyclohexene from Furan and Ethylene[1]

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).