present in large amount, as it is in hair. When a chromatogram was run on a mixture of the hair basic amino acid fraction and known synthetic hydroxylysine, the hydroxylysine spot was observed to be in a position slightly different from that of any of the spots on the chromatogram of the hair basic amino acid alone, and to have a color distinct from the colors of the spots near it. Thus, it seems unlikely that hydroxylysine is present in human hair, at least in amount large enough to be readily detected by this method.

Chromatograms on the basic amino acid fraction of wool showed two spots close to the position occupied by hydroxylysine and having the same color as that exhibited by hydroxylysine. When a two-dimensional chromatogram was run on a mixture of the wool basic amino acids and known hydroxylysine, the hydroxylysine spot covered both of the spots observed on the chromatogram of the wool basic amino acids alone. In view of the report by Middlebrook[4] that hydroxylysine is present in wool, it seems quite possible that one of these spots might be hydroxylysine.

Experimental.—The proteins were hydrolyzed under nitrogen for 20 to 24 hours with 6 *N* hydrochloric acid. Excess hydrochloric acid was removed by treating the hydrolyzate with Amberlite IR-4B to *p*H 3.5. After removal of aromatic amino acids by the method of Partridge,[5] basic amino acids were adsorbed on a column of Amberlite IRC-50 buffered at *p*H 7.0. They were eluted from the column with 1 *N* hydrochloric acid, the eluate evaporated just to dryness, and taken up in water. The basic amino acids were separated from sodium chloride and other salts by precipitation with phosphotungstic acid, the phosphotungstates decomposed with 2 *N* hydrochloric acid, and phosphotungstic acid extracted with a mixture of amyl alcohol, ether and ethyl alcohol. The aqueous layer was then evaporated to dryness and taken up in a small amount of water for chromatography. The chromatographic solvents were an 80% solution of Merck and Co., Inc., reagent grade phenol in water, and Eastman Kodak Co. symmetrical collidine saturated with water. Ninhydrin, 0.25% in water-saturated *n*-butanol, was used as the color-developing agent.

---

[4] W. R. Middlebrook, *Nature*, **164**, 321 (1949).

[5] S. M. Partridge, *Biochem. J.*, **45**, 459 (1949).

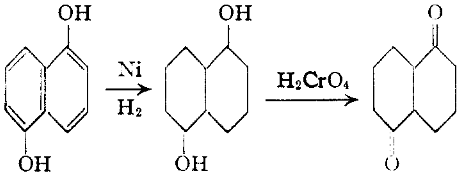
NOYES CHEMICAL LABORATORY
UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

RECEIVED JULY 31, 1951

Decalin-1,5-dione

BY WILLIAM S. JOHNSON, C. DAVID GUTSCHE[1] AND D. K. BANERJEE[2]

Decalin-1,5-dione (III) is an intermediate in the total synthesis of estrone,[3] and has potential uses in other steroid syntheses.[4] It was prepared by Hudson and Robinson[5] by the hydrogenation of 1,5-dihydroxynaphthalene (I) over Raney nickel to decalin-1,5-diol (II), followed by chromic acid oxidation. Their procedure, however, was unsatisfactory because the diol could be obtained in only 5-8% yield, the chief product being α-decalols produced by hydrogenolysis.



I II III

In the present work the hydrogenation step was carried out over W-7 Raney nickel catalyst with added sodium hydroxide to avoid hydrogenolysis[6] and the mixture of stereoisomeric diols (II) was produced in over 70% yield. There are five diastereoisomeric forms of the diol II possible and two of these have been described previously: Campbell and Harris[7] synthesized an isomer, m.p. 178–178.5°, by catalytic reduction of an octalin-1,5-diol obtained by selenium dioxide oxidation of Δ^9-octalin. Hudson and Robinson[5] isolated what appeared to be a pure isomer, m.p. 159–161°, by repeated recrystallization of the mixture of diols II produced on catalytic hydrogenation. In our work a small amount of a new isomer melting at 210–211° was isolated from one of the hydrogenation runs.

Oxidation of the mixture of diols II with chromic anhydride in acetic acid gave a mixture of *cis*- and *trans*-decalin-1,5-dione in 60% yield.[5] In the present work a modified procedure was developed in which the oxidation was carried out with sodium dichromate and sulfuric acid in the presence of dilute acetic acid and benzene. Starting with the crude mixture of diols II, the mixture of diones III was obtained in over 70% yield. This mixture can be used directly for certain synthetic purposes,[3,4] or may be easily fractionated into fairly pure *cis* (m.p. 79–80° pure) and *trans* (m.p. 166–167° pure) isomers. The *cis* isomer has not been previously isolated. Since the *cis* is easily isomerized to the *trans* form,[5] the crude ketone mixture can be converted essentially entirely over to the latter by heating with acid.

Experimental[8]

Purification of 1,5-Dihydroxynaphthalene.—A solution of 600 g. of crude 1,5-dihydroxynaphthalene (Eastman Kodak Co., technical grade) in 3 l. of alcohol was boiled with 120 g. of Norit for 5 minutes, and filtered while hot. The insoluble tar and Norit remaining in the funnel were washed several times with boiling alcohol. The combined filtrates were again boiled with another 120 g. of Norit and 12 teaspoonfuls of Raney nickel, and filtered while hot. This filtrate was treated a third time with 60 g. of Norit and filtered yielding a straw-colored filtrate. Upon cooling to room temperature 234 g. of the diol crystallized. This material was separated by filtration. About 60 g. of Norit was added to the filtrate which was then concentrated by distilling off about 1 l. of the solvent (a rubber-sealed stirrer was employed to prevent bumping), filtered and chilled in the refrigerator. A second crop amounting to 108 g. was thus obtained. By repeating the concentration (Norit) and crystallization three times a total of 424 g. (71% recovery) of material suitable for hydrogenation was obtained.

---

[1] Wisconsin Alumni Research Foundation Postdoctoral Fellow, 1947. Washington University, St. Louis, Missouri.

[2] Watumull Foundation Fellow; W. A. R. F. Postdoctorate Fellow, 1948-1949. College of Engineering and Technology, Bengal, India.

[3] W. S. Johnson, D. K. Banerjee, W. P. Schneider and C. D. Gutsche, THIS JOURNAL, **72**, 1426 (1950).

[4] See for example, W. S. Johnson, J. Szmuszkovicz and M. Miller, *ibid.*, **72**, 3726 (1950).

[5] B. J. F. Hudson and R. Robinson, *J. Chem. Soc.*, 691 (1942).

[6] *Cf.* H. E. Ungnade and A. D. McLaren, *ibid.*, **66**, 118 (1944) and H. E. Ungnade and D. V. Nightingale, *ibid.*, **66**, 1218 (1944).

[7] W. P. Campbell and G. C. Harris, *ibid.*, **63**, 2721 (1941).

[8] Unless otherwise specified all melting points are corrected for stem exposure.

Decalin-1,5-diol.[9]—In a typical run a 1350-ml. hydrogenation bomb was charged with 300 g. of purified 1,5-dihydroxynaphthalene, 1 g. of reagent grade sodium hydroxide pellets, 19 teaspoonfuls of W-7 Raney nickel catalyst[10] and 450 ml. of absolute alcohol. The bomb was closed and filled with hydrogen directly from a hydrogen cylinder having a pressure of at least 1400 p.s.i. (otherwise it was necessary to employ a booster pump to increase the pressure in the bomb). The shaker was started and the bomb heated to 100° over a period of 1.5 hours. The reaction proceeded rapidly and additional hydrogen was introduced from the cylinder as required. After about three hours the uptake of hydrogen had ceased, the bomb was cooled to room temperature, opened and alcohol was added to the suspension with warming until the precipitated diol dissolved. The solution was filtered and the catalyst washed thoroughly with hot alcohol by decantation. The alcohol was removed from the combined filtrates by distillation, finally at reduced pressure. The semi-crystalline residue was treated with 250–300 ml. of 10% potassium hydroxide solution and 200–300 ml. of benzene, and the whole was shaken vigorously until solid diol separated. After standing for about 20 minutes with occasional shaking, the diol was collected by filtration and washed twice with water, then with ether. The dried almost colorless crystalline mixture of isomeric decalin-1,5-diols amounted to 220 g. (69% yield). The m.p. of such specimens was usually about 140–150°.

Further material was obtained as follows: filtrates and washings from a series of five reductions carried out as described above were combined. The aqueous layer was separated, and extracted with chloroform in a continuous extractor for about 24 hours. The chloroform solution was washed once with water, dried over anhydrous sodium sulfate and evaporated. Upon trituration of the gummy residue with benzene 142 g. of diol crystallized. The benzene-ether from the combined residues was washed with water, dried over anhydrous sodium sulfate and evaporated. The residue was distilled at reduced pressure, and the fraction boiling at 168–187° (23 mm.) was triturated with benzene, giving an additional 30 g. of diol. The total yield from 1700 g. of 1,5-dihydroxynaphthalene was 1304 g. or 72%.

In a preliminary reduction experiment carried out in this Laboratory by H. Billica and V. Soukup a small amount of high melting material was isolated by ether extraction and crystallization. After recrystallization from ethyl acetate it was obtained as colorless needles, m.p. 210–211°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found[11]: C, 70.14; H, 10.66.

Decalin-1,5-dione.—A suspension of 50.00 g. of decalin-1,5-diol in 700 ml. of benzene was cooled to 6° (ice-bath), and to this was added dropwise with stirring a cold solution of 70 g. of sodium dichromate in 52.5 ml. of glacial acetic acid, 95 ml. of concentrated sulfuric acid and 310 ml. of water. During the addition which required about 4 hours the temperature of the reaction mixture was not allowed to exceed 6°. After the addition was complete the mixture was stirred for an additional 2.5 hours at ice-bath temperature, and then allowed to stand at room temperature overnight. The aqueous layer was separated and extracted twice with benzene. The combined benzene layers were washed with water, then with saturated sodium bicarbonate solution, and finally again with water. The solution was concentrated (by distillation) to a volume of about 100 ml. On cooling 17.3 g. of *trans*-decalin-1,5-dione, m.p. 164–166°, crystallized. Further concentration and fractional crystallization with added petroleum ether (b.p. 60–68°) yielded an additional 2.9 g. of *trans* isomer, and 14.8 g. of the *cis* compound, m.p. 72–76°.

A pure specimen of the *trans* dione obtained after repeated recrystallization from benzene melted at 166–167° (reported,[5] 165–167°).

Anal.[11] Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.03; H, 8.24.

A sample of the *cis* isomer was purified by repeated recrystallization from petroleum ether (b.p. 60–68°) to give colorless needles, m.p. 79–80°.

Anal.[11] Calcd. for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.11; H, 8.24.

When it was not desired to separate the stereoisomers, the benzene solution containing the mixture was evaporated to dryness. In 10.00-g. runs, yields of 7.6–8.14 g. (71–76%) of solid mixture of ketones were thus realized. Such material gave the characteristic sparingly soluble disemicarbazone in 90% yield indicating a purity of 98% (see below).

The *trans* diketone on treatment with semicarbazide hydrochloride and pyridine in ethanol produced in 92% yield a very sparingly soluble disemicarbazone, m.p. 296–298° (dec.) (uncor.). A satisfactory recrystallization solvent for this derivative was not found. The analytical specimen was especially prepared (by M. Mercury) with semicarbazide in methanol. After thorough washing with hot methanol, hot water, then again with methanol, and drying as usual it melted at 295–296° dec. (inserted at 290°). Although the analysis is not in close agreement, it clearly indicates that the product is largely the disemicarbazone.

Anal.[12] Calcd. for $C_{12}H_{20}O_2N_6$: C, 51.41; H, 7.19. Found: C, 53.06; H, 7.37.

The *cis* diketone also gave in 92% yield a sparingly soluble disemicarbazone which was indistinguishable from that prepared from the *trans* isomer. Thus the purity of the crude mixture of diketones obtained directly from the oxidation described above was easily assayed by conversion to the crude disemicarbazone.

For production of *trans*-decalin-1,5-dione, the benzene solution remaining after crystallizing the first crop of this isomer (see above) was refluxed with a small amount of *p*-toluenesulfonic acid for a few minutes; on concentrating and cooling additional *trans* dione crystallized. Repetition of this process converted essentially all of the material into this form.

---

[9] Large-scale preparation carried out by Peter H. Jackson.

[10] H. Billica and H. Adkins, *Org. Syntheses*, **29**, 24 (1949), see Note 1.

[11] Microanalysis by R. P. Graber.

[12] Microanalysis by C. E. Blades.

LABORATORY OF ORGANIC CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

RECEIVED JULY 5, 1951

Polycystine[1]

BY H. WALTER JONES[2] AND HAROLD P. LUNDGREN[2]

In the course of an investigation directed toward the preparation of model compounds for the study of the mechanical properties of wool, polymers of cystine have been prepared by the method originally employed by Leuchs and Geiger[3] and later, with modification, by many others (*e.g.*[4–7]).

Experimental

Eastman Kodak Co. "white label" grade chemicals were used; the (*l*)-cystine was a sample which had been isolated from human hair. Melting points were determined on the Fisher–Johns apparatus.

N,N′-Dicarboethoxy-(L)-cystine (I) was prepared by the Leuchs procedure[3] from ethyl chloroformate and L-cystine in 42% yield from the cystine. It is a very hygroscopic white solid, m.p. 42°.

Anal. Calcd. for $S_2C_{12}H_{20}O_8N_2$: neut. equiv., 192. Found: neut. equiv., 207.

N,N′-Dicarboethoxy-(L)-cystinyl dichloride (II) was prepared from (I) and excess thionyl chloride in 95.5% yield; m.p. 111.9°.

---

[1] Presented in part before the Division of Colloid Chemistry of the American Chemical Society, San Francisco, Calif., March, 1949. Report of a study made under the Research and Marketing Act of 1946. Article not copyrighted.

[2] Western Regional Research Laboratory, Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[3] H. Leuchs and W. Geiger, *Ber.*, **41**, 1721 (1908).

[4] R. B. Woodward and C. H. Schramm, THIS JOURNAL, **69**, 1551 (1947).

[5] E. Katchalski, I. Grossfeld and M. Frankel, *ibid.*, **70**, 2094 (1948).

[6] C. J. Brown, D. Coleman and A. C. Farthing, *Nature*, **163**, 834 (1949).

[7] P. Alexander, J. L. Bailey and D. Carter, *Textile Research J.*, **20**, 385 (1950).