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).

Anal. Calcd. for $S_2C_2H_{18}O_6Cl_2N_2$: C, 34.21; H, 4.31; N, 6.65. Found: C, 34.2; H, 4.39; N, 6.57.

(L)-Cystine-bis-N-carboxyanhydride (III) was prepared from (II) by heating under reduced pressure at 112° for periods up to 90 minutes; the products decomposed over a wide temperature range (*ca.* 115–150°) and ranged in purity, on the basis of the weight loss from (II), from 93.1 to 97.4%. The purest preparation analyzed 83% cystine by Mecham's modification of the Vassel method[8]; calcd. 82.3%.

Polymerization.—Both II and III polymerized on being heated or treated with moist solvents such as reagent ethyl acetate. The products had no melting points and were insoluble in common neutral organic solvents. They were soluble to varying degrees in solvents having hydrogen bond capacity such as 2-chloroethanol, glycerol dichlorohydrin, 8 *M* aqueous urea and glacial formic acid. The polymeric products were readily soluble in mineral acids, alkalies and in the reducing agent 2-mercaptoethanol. They gave positive biuret tests. X-Ray diffraction photographs[9] indicated that, though amorphous, they showed characteristic peptide chain spacings.

The analyses for carbon, hydrogen and nitrogen deviate considerably from those expected for totally polymerized cystine.

Anal. Calcd. for C_3H_4ONS: C, 35.28; H, 3.95; N, 13.72. Found: C, 34.7–36.8; H, 4.06–4.72; N, 10.1–10.3.

Cystine analyses[8] were low, presumably because of incomplete hydrolysis under the conditions of the determination.

Amino nitrogen values by the manometric Van Slyke procedure[10] ranged from 5.69 to 2.34%, corresponding to polymers of 2.2 to 5.7 cystine units, *i.e.*, molecular weights up to about 1200. On the other hand, ultracentrifuge examination of the polymers dissolved in 2-chloroethanol indicates large molecular-kinetic units, the sedimentation constants of which correspond to minimum molecular weights ranging from 12,000 to 10,000,000. Although the possibility of aggregation of smaller-size units is not excluded, consideration of possible structures of polycystine indicates that high molecular weight polymers are possible which may contain more than two free amino groups per molecule, and this may account for the low values of molecular weights determined from this end-group analysis. This difference between molecular weights determined by physical methods and by end-group analyses, which is probably attributable to aggregation, is also noted in the DL-β-phenylalanine-(L)-leucine copolymer studied by Woodward and Schramm[4] and by Brown, Coleman and Farthing.[6]

That the polymers could be partially fractionated from 2-chloroethanol with ether as precipitant is indicated by the fact that initially precipitated material gives higher sedimentation constants than subsequent fractions. It is significant that reduction of the polycystine with mercaptoethanol gives water-soluble, non-sedimentable products. Moreover, solid polycystine, when treated with small amounts of 2-mercaptoethanol, undergoes plastic flow between parallel plates under high pressure. This seems analogous to the behavior of reduced wool.

Acknowledgments.—We are indebted to Miss G. Secor and Mrs. M. Kilpatrick for the carbon and hydrogen analyses, to Mrs. M. Long for the nitrogen analyses, and to Mr. H. Fujikawa for the cystine analyses.

(8) D. K. Mecham, *J. Biol. Chem.*, **151**, 643 (1943).

(9) K. J. Palmer, unpublished results.

(10) D. D. Van Slyke, *J. Biol. Chem.*, **83**, 425 (1929).

WESTERN REGIONAL RESEARCH LABORATORY
ALBANY 6, CALIFORNIA

RECEIVED JUNE 2, 1951

The Anhydrides of Dimethyl- and Diethylphosphinic Acids

BY GENNADY M. KOSOLAPOFF AND RICHARD M. WATSON

It was of interest to secure some information about the properties of the two lowest members of the series of aliphatic phosphinic anhydrides, in order to supplement the data obtained for the two higher members.[1]

The desired substances were prepared by the reaction scheme used by us in the synthesis of the higher members. However, the preparation of the dimethyl- and the diethylphosphinic acids, the necessary starting materials, could not be accomplished satisfactorily by the reaction of Grignard reagents with dialkyl phosphites owing to the extreme solubility of the acids in water; this method of synthesis apparently is restricted to the relatively insoluble, higher members of the series. The acids were prepared by the reactions of the respective Grignard reagents with thiophosphoryl chloride, following the procedures given by Kabachnik[2] for the dimethyl derivative and by Strecker and Grossmann[3] for the diethyl derivative.

Experimental Part

Dimethylphosphinic Anhydride.—Thiophosphoryl chloride (64.4 g., 0.375 mole) was added slowly to the Grignard reagent prepared from 213 g. (1.5 moles) of methyl iodide and 36.4 g. of magnesium in 500 ml. of dry ether. The addition was done with stirring and ice–salt cooling. After 12 hours the mixture was hydrolyzed with ice and 10% sulfuric acid, and the insoluble dimeric reaction product, $(Me_2PS)_2$, was filtered off and dried. The yield was 17 g., or 48.5%. Repetition of the reaction with the same relative ratio of the reactants but carried out on a larger scale (0.5 mole of thiophosphoryl chloride) gave a 62.5% yield. The material was oxidized to dimethylphosphinic acid with nitric acid according to Kabachnik's directions.[2] The yield of dimethylphosphinic acid was 95% and the product melted at 85–87° (Kabachnik and Shepeleva give m.p. 86.5–88.5°).

Dimethylphosphinic acid (34 g.) and 300 ml. of dry benzene, contained in a flask provided with a reflux condenser, were treated slowly with 75 g. of phosphorus pentachloride and the mixture was refluxed for one hour until the evolution of hydrogen chloride ceased. Distillation gave 30.5 g. (75.5%) of dimethylphosphinyl chloride, a very hygroscopic solid, b.p. 202–204°. Kabachnik and Shepeleva give m.p. 66.8–68.4°.[2]

Dimethylphosphinyl chloride (13 g.) in 200 ml. of dry benzene was treated slowly, with stirring and ice-cooling, with a solution of sodium ethoxide prepared from 2.7 g. of sodium and 50 ml. of absolute ethanol. After 12 hours at room temperature the mixture was filtered and distillation of the filtrate gave 8.7 g. (62%) of ethyl dimethylphosphinate, a colorless liquid; b.p. 88–89° at 15 mm., $n^{25}{}_D$ 1.4261, $d^{25}{}_4$ 1.0278.

Anal. Calcd. for $Me_2P(O)OEt$: P, 25.40; *MR*, 30.42. Found: P, 25.22; *MR*, 30.39.

Heating 8 g. of ethyl dimethylphosphinate and 7.4 g. of dimethylphosphinyl chloride for 45 minutes at 145–160° resulted in brisk evolution of ethyl chloride and distillation of the residue yielded 7.5 g. (67%) of dimethylphosphinic anhydride, which boiled at 190–192° at 15 mm., and which showed a considerable tendency to sublime. The substance forms long feathery needles, which melt at 119–121°. The substance is rapidly hydrolyzed by water and titration of the aqueous solution gave the molecular weight of 170.5, against the theoretical value of 170.

Anal. Calcd. for $Me_2P(O)OP(O)Me_2$: P, 36.46. Found: P, 36.31.

Diethylphosphinic Anhydride.—Thiophosphoryl chloride (51 g.), diluted with one volume of absolute ether, was added slowly to ice-cooled solution of the Grignard reagent, prepared from 100 g. of ethyl bromide and 22 g. of magnesium, in 500 ml. of dry ether. The resulting mixture was refluxed for two hours and then was hydrolyzed with 200 g. of ice. Upon acidification with dilute sulfuric acid, the organic layer was separated and the aqueous layer was ex-

---

(1) Kosolapoff and Watson, THIS JOURNAL, **73**, 4101 (1951).

(2) Kabachnik and Shepeleva, *Izvest. Akad. Nauk. S. S. S. R., otdel. khim. nauk.*, **No. 1**, 56 (1949).

(3) Strecker and Grossmann, *Ber.*, **49**, 63 (1916).