mature, is similar to the case of buckwheat seed, which contains no rutin. Indeed, rutin appears to be associated with actively metabolizing tissues, and therefore, must play an important role in plant physiology.

TABLE I

RUTIN CONTENT OF FRESH SOPHORA

Date collected 1947	Part of plant	Moisture, %	Rutin content, % (mfb.)
July 15	Panicle with unopened buds	69.0	22.9
July 22	Panicle; a few opened buds	72.7	22.5
Aug. 5	Panicle; one-half of flowers in full bloom	71.7	17.6
Sept. 18	Green seed pods	74.7	None
Nov. 6	Mature seed pods	41.0	None
Dec. 15	Mature seed pods	21.4	None
Sept. 18	Pedicels and flower stalks	61.7	4.6
Nov. 6	Pedicels	56.3	1.5
Dec. 15	Pedicels	43.2	3.7

The rutin content of the pedicels, however, persisted through the season. These flower stalks continued alive while the seed pods were maturing, which may account for this fact. Three collections of leaflets were made during the season. A test for flavonols was positive. On analysis, amorphous deposits unlike crystalline rutin were obtained. Chromatographic analyses on paper[9,10] separated these into three fractions, two of which could readily be identified as rutin and quercetin, respectively. The third fraction unidentified, may be one of the minor glycosides reported by Zemplén and Bognár[11] or Charaux and Rabaté.[12] Approximate values for these constituents were obtained by estimating the size and intensity of the spots in comparison with known quantities of rutin and quercetin. The data are presented in Table II.

TABLE II

RESULTS OF CHROMATOGRAPHIC ANALYSIS OF FLAVONOL FRACTIONS FROM SOPHORA LEAFLETS AND SEED PODS

			Chromatographic results,[a] %		
Sample	Part of plant	Crude flavonols, %	Rutin R_F = 0.05	Flavonol R_F = 0.17	Quercetin R_F = 0.90
47-177	Seed pods	1.5	0.75	0.75	..
47-178	Leaflets	0.4	.2	..	0.2
47-204	Leaflets	0.2	.2	..	0.02
47-205	Seed pods	1.0	.5	0.5	..
47-211	Seed pods	0.4	.2	0.2	..
48-14	Leaflets	4.3	4.1	Trace	Trace
48-16	Woody twigs	0.4	0.4	..	..

[a] The approximate values reported under the chromatographic analysis are based on an estimate of the size of the spots. In most cases, the rutin spot and spot of the flavonol with R_F 0.17 were about the same size and intensity.

When dried, either in air or by heat, sophora behaved like other rutin bearing plants,[7] that is, there was a variable but appreciable loss of rutin during the process, as shown in Table III. In two of the three pairs of experiments, the air-dried sophora appeared to contain slightly more rutin. Considering the difficulties of sampling and the errors in analysis, these differences are not thought to be significant.

TABLE III

EFFECT OF DRYING ON RUTIN CONTENT OF SOPHORA

		Rutin content, %		
Date collected 1947	Conditions of drying	Before drying	After drying	Loss of rutin
July 15	Oven-dried at 110°	22.9	17.9	21.8
July 22	Oven-dried at 110°	22.5	15.7	30.2
July 22	Air-dried	22.5	16.0	28.9
Aug. 5	Oven-dried at 110°	17.6	13.2	25.0
Aug. 5	Air-dried	17.6	15.9	9.7
Aug. 18	Oven-dried at 110°	20.2	16.3	19.3
Aug. 18	Air-dried	20.2	13.3	34.2

PHILADELPHIA 18, PA. RECEIVED JULY 5, 1951

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(9) S. H. Wender and T. B. Gage, *Science*, **109**, 287 (1949).

(10) E. C. Bate-Smith and R. G. Westall, *Biochim. et Biophys. Acta*, **4**, 427 (1950).

(11) G. Zemplén and R. Bognár, *Ber.*, **75B**, 482 (1942).

(12) C. Charaux and J. Rabaté, *Bull. soc. chim. biol.*, **20**, 454 (1938).

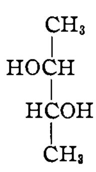
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE BANTING INSTITUTE, UNIVERSITY OF TORONTO, AND THE DEPARTMENT OF BIOCHEMISTRY AND THE INSTITUTE FOR ENZYME RESEARCH, UNIVERSITY OF WISCONSIN]

Synthesis of the Optically Active Enantiomorphic 2,3-Butanediols[1]

BY LEON J. RUBIN,[2] HENRY A. LARDY[3] AND HERMANN O. L. FISCHER[4]

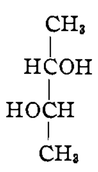
The optically active D- and L-2,3-butanediols have been synthesized from the corresponding D- and L-mannitols by a series of unequivocal reactions. The 2,3-isopropylidene derivatives and the di-*p*-nitrobenzoates of the synthetic butanediols were compared with the same derivatives of the natural, levorotatory butanediol. This proved that the levorotatory butanediol had the D-configuration, the dextrorotatory the L-configuration. The conclusions of previous workers, based on degradative studies, are thus confirmed.

The stereochemical configurations of the optically active 2,3-butanediols have been determined by Morell and Auernheimer[5] as D(−) (I) and L(+) (II). The reactions used by these investigators, namely, esterification and pyrolysis at high temperature, involved extensive racemization. The intermediate methylvinylcarbinol which was reduced to the methylethylcarbinol was moreover a by-product, and not the main product of the reaction. Leroux and Lucas[6] recently confirmed the conclusions of Morell and Auernheimer by degradation of D(−)-2,3-butanediol through 2,3-epoxybutane to the optically pure L(−)-2-butanol.



$$\begin{array}{c} CH_3 \\ | \\ HOCH \\ | \\ HCOH \\ | \\ CH_3 \end{array}$$

D(−)
I



$$\begin{array}{c} CH_3 \\ | \\ HCOH \\ | \\ HOCH \\ | \\ CH_3 \end{array}$$

L(+)
II

However, the final proof of configuration—

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(1) Presented at the XII'th International Congress for Pure and Applied Chemistry, September, 1951, New York, N. Y.

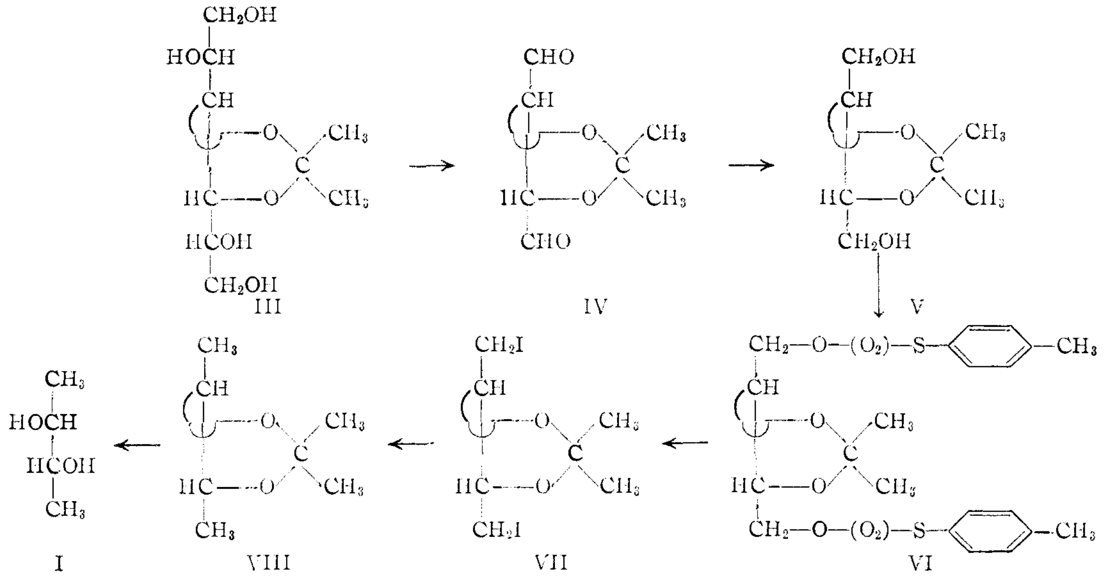
(2) Canada Packers Ltd., Toronto, Canada.

(3) National Research Council Fellow in Chemistry 1944–1945 at the Banting Institute. Present address: Institute for Enzyme Research, University of Wisconsin.

(4) Department of Biochemistry, University of California, Berkeley.

(5) S. A. Morell and A. H. Auernheimer, THIS JOURNAL, **66**, 792 (1944).

(6) P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951).



namely, synthesis of the individual stereoisomers by unequivocal procedures—has heretofore not been provided. A synthesis of the optically active D- and L-butanediols from corresponding D- and L-mannitols is described in this paper. The route is summarized in the diagram below. The synthesis provides proof of the configurational designation by Morell and Auernheimer and confirms the purity of the levorotatory isomer separated from bacterial cultures.[7]

The optical activity of the synthetic butanediols results from the asymmetry of carbon atoms 3 and 4 of D- and L-mannitol. Reaction conditions were mild and the configuration was guarded throughout (except for the last step) by the protecting isopropylidene group. Danger of racemization was almost completely eliminated. The starting materials were 3,4-isopropylidene-D- and L-mannitols prepared during the earlier part of this project by the procedure of H. O. L. Fischer and Appel.[8] Later the newer and improved procedure of Wiggins[9] was used. The 3,4-isopropylidenemannitols were cleaved by oxidation with lead tetraacetate to the respective 2,3-isopropylidenetartaric dialdehydes of which the D-isomer was first described by H. O. L. Fischer and Appel.[8] The dialdehydes were reduced (without isolation) to the respective 2,3-isopropylidene-D- and L-threitols which are described here for the first time. The specific rotations of the isopropylidenethreitols were found to vary in both sign and magnitude depending upon solvent, concentration and temperature (see experimental). The 2,3-isopropylidene-D-threitol was hydrolyzed to the free D-threitol and converted to the well-known dibenzylidene derivative. The melting point and rotation of this compound left no doubt as to its identity.

The 2,3-isopropylidenethreitols were converted to the corresponding ditosylates in the usual way. These were readily crystallized, well characterized compounds easily prepared in a high state of purity. The D- and L-isomers of 2,3-isopropylidenebutanediol were obtained from the corresponding tosylates by the Freudenberg–Raschig desoxydation procedure. Physical constants of the 2,3-isopropylidene-D- and L-butanediols prepared in this manner agree very closely with those reported by Neish and MacDonald[10] for the corresponding compound prepared from the pure levorotatory butanediol produced by *Aerobacillus polymyxa*.[7] Likewise, the melting points and rotations of the di-*p*-nitrobenzoyl derivatives of the natural[11] and synthetic levorotatory 2,3-butanediols are similar.

The micro carbon and hydrogen analyses were carried out by Mrs. Ena Mason to whom the authors express their thanks.

Experimental

3,4-Isopropylidene-D(or L)-Mannitol (III).—The 3,4-isopropylidenemannitols were prepared from the corresponding D- and L-triisopropylidenemannitols either by the procedure of H. O. L. Fischer and Appel[8] or by the improved method of Wiggins.[9] For the D-isomer, m.p. 85–86°, $[\alpha]^{26.5}\text{D}$ +24.6° (*c* 3, ethanol), Irvine and Paterson[12] reported $[\alpha]^{20}\text{D}$ +23.2° (*c* 3, ethanol). For the L isomer, m.p. 85–86.5°, $[\alpha]^{22}\text{D}$ −24.3° (*c* 3, ethanol).

2,3-Isopropylidene-D(or L)-Threitol (V).—Fifteen grams of 3,4-isopropylidene-D-mannitol was dissolved in 150 ml. of ethyl acetate and 60 g. of lead tetraacetate was added. The mixture warmed up considerably and the reaction was completed in about two minutes. The lead salts were removed with filter aid (Hyflo Supercel) on a precoated funnel and thoroughly washed with ethyl acetate. The filtrate and washings were transferred to the glass liner of a high-pressure reduction apparatus; a settled volume of 25 ml. of Raney nickel catalyst (suspended in ethyl acetate) was added and the reduction of the D-(or L)-tartaric dialdehyde (IV) was carried out at room temperature and at an initial hydrogen pressure of 1000 p.s.i. After 7–12 hours, 15 ml. of fresh Raney nickel was added and the reduction continued for a similar period. The solution then gave after acid hydrolysis, an only faintly positive Fehling test.

The catalyst was removed by filtration through a precoated buchner funnel, and the filtrate was stirred with an excess of fused K_2CO_3 for one hour. After filtering, the ethyl acetate was allowed to stand over fresh K_2CO_3 for 36

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[7] (a) G. E. Ward, O. G. Pettijohn, L. B. Lockwood and R. D. Coghill, THIS JOURNAL, **66**, 541 (1944); (b) A. C. Neish, *Can. J. Research*, **B23**, 10 (1945); (c) J. W. Knowlton, N. C. Schieltz and D. Macmillan, THIS JOURNAL, **68**, 208 (1946).

[8] H. O. L. Fischer and H. Appel, *Helv. Chim. Acta*, **17**, 1574 (1934).

[9] L. F. Wiggins, *J. Chem. Soc.*, 13 (1946).

[10] A. C. Neish and F. J. MacDonald, *Can. J. Research*, **B25**, 70 (1947).

[11] F. M. Robertson and A. C. Neish, *ibid.*, **B26**, 737 (1948).

[12] J. C. Irvine and B. M. Paterson, *J. Chem. Soc.*, 907 (1914).

hours. The filtered solution was evaporated to dryness *in vacuo* and the product taken up in anhydrous ether, separating it from a small amount of insoluble material. After evaporation of the ether the product was distilled *in vacuo;* boiling point 91–93° at 0.01–0.02 mm.; bath temperature 110–116°; $n^{25}\text{D}$ 1.4547. The yield in several trials was 73–87% of theoretical.

The clear liquid crystallized on standing in the refrigerator. When recrystallized from diethyl ether by the cautious addition of petroleum ether (b.p. 40–60°)[13] the large glass-like needles melted at 48–51° after drying over P_2O_5. Further recrystallization did not change the melting point. The compound could also be recrystallized from diisopropyl ether (3 ml. per gram).

Optically active 2,3-isopropylidenethreitol is readily soluble in chloroform or diethyl ether, less so in diisopropyl ether, slightly in dibutyl ether and very slightly in petroleum ether.

Anal. Calcd. for $C_7H_{14}O_4$ (162.2): C, 51.8; H, 8.70; acetone, 35.8. Found: C, 51.9; H, 8.80; acetone, 34.8.

Rotation of 2,3-Isopropylidene-D-threitol

Concentration	Solvent	$[\alpha]^{26}\text{D}$
2.09	$CHCl_3$	−0.5°
5.20	$CHCl_3$	−3.1
10.3	$CHCl_3$	−4.8
5.0	Abs. EtOH	−3.7
10.0	Abs. EtOH	−3.1
		αD
In substance at 60°		−1.32° (dcm. tube)
In substance (supercooled liquid) at 26°		+0.50° (dcm. tube)

Hydrolysis of 2,3-Isopropylidene-D-threitol and Preparation of Dibenzylidene-D-threitol.—2,3-Isopropylidene-D-threitol (1.4 g.) was hydrolyzed at 75–80° in 15 ml. of 0.1 *N* sulfuric acid for one hour. The sulfuric acid was removed by stirring with barium carbonate until neutral, and the barium salts were centrifuged off. The solution was evaporated to a clear sirup.

The D-threitol was converted to the dibenzylidene derivative by the method Lucas and Baumgarten[14] used for L-threitol. A crude product (1.75 g., 51.2%) was obtained which melted at 205–212°. One recrystallization from benzene gave 1.45 g. of a fine, cotton-batting-like material; m.p. 221–224° and $[\alpha]^{25}\text{D}$ −79.3° (*c* 0.64, U.S.P. chloroform). Lucas and Baumgarten give for the L-isomer m.p. 221–223° and $[\alpha]^{25}\text{D}$ +79°.

1,4-Ditosyl-2,3-isopropylidene-D(or L)-threitol (VI).—To 8.4 g. of V[15] in 55 ml. of dry pyridine, and cooled to −10°, 21 g. of finely powdered *p*-toluenesulfonyl chloride were added in one portion. The mixture was shaken until homogeneous and held at 0° for 12 hours. The product was crystallized from the reaction mixture by slow addition of water. Once crystals began to form, water was added more rapidly until a total of at least 90 ml. had been added over a period of 3.5 hours. Crystallization was permitted to continue at 0° for a few hours. The product which was washed on the filter with 95% ethanol weighed 18.7 g. It was recrystallized from 63 ml. of ethanol giving 17.7 g. (72.5%; in some trials yields as high as 82% of the pure compound were obtained) of m.p. 91–92°; not raised by further recrystallization.

For the D-isomer: $[\alpha]^{26.5}\text{D}$ +12.5° (*c* 2.0 or 5.1, chloroform). *Anal.* Calcd. for $C_{21}H_{26}O_8S_2$ (470.5): C, 53.6; H, 5.57; acetone, 12.37. Found: C, 53.7; H, 5.77; acetone, 12.57. For the L isomer: $[\alpha]^{24}\text{D}$ −12.4° (*c* 5, chloroform). *Anal.* Found: C, 53.6; H, 5.71.

1,4-Didesoxy-1,4-diiodo-2,3-isopropylidene-D(or L)-threitol (VII).—16.5 g. of NaI was added to 11 g. of VI and 220 ml. of acetone in a pressure bottle. The mixture was heated for two hours and 40 minutes in a boiling water-bath. The sodium *p*-toluenesulfonate was collected on a filter and washed with fresh acetone; after drying at 110° for 30 hours, its weight corresponded to 105 and 97% (respectively) of theoretical in two separate experiments. The filtrate and washings were evaporated *in vacuo*. The diiodo compound was separated from residual NaI by extracting a water suspension (60 ml.) of the residue with $CHCl_3$. The $CHCl_3$ layer was washed once with dilute sodium thiosulfate to remove iodine, and twice with water. It was dried over Na_2SO_4 and evaporated *in vacuo*. The yellow residue was distilled in high vacuum; b.p. 80–82° at 0.05 mm.; yield 7.8 g. (96% of theoretical) of a pale yellow oil; $n^{26}\text{D}$ 1.5692.

For the D-isomer: $[\alpha]^{24}\text{D}$ +17.5° (*c* 8.5, dry methanol). *Anal.* Calcd. for $C_7H_{12}O_2I_2$ (382.0): C, 22.0; H, 3.16. Found: C, 22.4; H, 3.16.

2,3-Isopropylidene-D(or L)-butanediol (VIII).—A solution of 6.7 g. VII in 60 ml. of methanol was placed in the glass vessel of a hydrogenation apparatus with 50 ml. of 1 *N* potassium hydroxide and 5 ml. of Raney nickel catalyst. The hydrogenation, which was carried out at room temperature, was completed in about five minutes with consumption of the theoretical quantity of hydrogen. The catalyst was removed by filtration and washed thoroughly with diethyl ether and water. The ether layer of the combined filtrate and washings was separated and the aqueous layer (*ca.* 200 ml.) extracted with two additional 100-ml. portions of ether. The combined ether extracts were washed with water and dried over anhydrous sodium sulfate. The ether was distilled off slowly through a 35 cm. insulated Vigreux column, and the product obtained in a fraction which came over at 100–110°. Yields of 40–60% were obtained. After drying pooled samples over anhydrous sodium sulfate the product was fractionally distilled in a smaller apparatus (35-cm. column). A forerun distilling below 106° was discarded (or saved for subsequent refractionation). Small fractions which distilled between 106–108° appeared to be > 95% pure on the basis of their optical rotation. From 75 to 85% of the product was collected in fractions between 108–110°. The specific rotation of these fractions varied no more than 2% in the various runs.

For the D-isomer: b.p. 108° (uncor.); $n^{25}\text{D}$ 1.3908; $[\alpha]^{26}\text{D}$ −28.2° (*c*, 5.01, chloroform).

For the L-isomer: More of this isomer was available. It may therefore have been somewhat purer and was also better characterized; b.p. 109.7° (calibrated thermometer, 734 mm.); $n^{20}\text{D}$ 1.3941; d^{20}_{20} 0.8747; $[\alpha]^{23}\text{D}$ +31.65 ±0.15° (*c* 4.96, chloroform); $\alpha^{20}\text{D}$ +19.72° (1 dcm. in substance) = $[\alpha]^{20}\text{D}$ +22.55°.

Anal. Calcd. for $C_7H_{14}O_2$ (130.2): C, 64.6; H, 10.8. Found: C, 64.7; H, 10.9.

2,3-Isopropylidene-D-butanediol from Natural Levorotatory 2,3-Butanediol.—Natural levorotatory butanediol[16] having αD −12.8° (1 dcm., in substance) and $n^{25}\text{D}$ 1.430 was acetonated by the procedure of Neish and MacDonald[10] and the product separated by distillation as above. The purest fraction boiled at 108°: $[\alpha]^{24}\text{D}$ −31.0 ± 0.2° (*c* 5, chloroform); $\alpha^{22}\text{D}$ −19.5° (1 dcm., in substance) = $[\alpha]^{22}\text{D}$ −22.4°. Neish and MacDonald[10] reported $[\alpha]^{25}\text{D}$ −22.1° (in substance).

D(or L)-2,3-Butanediol (I).—One- and four-gram batches (of the D- and L-isomers, respectively) of VIII were hydrolyzed by shaking with 0.5 and 1.0 ml., respectively, of 0.1 *N* HCl until only one phase was apparent. The solution was allowed to stand at room temperature for 2–4 days before separation of the components by distillation.

The quantity of the D-isomer obtained was insufficient for determination of physical constants. The total contents of the receiver were dissolved in dry pyridine and converted to the di-*p*-nitrobenzoate: m.p. 142–44°; $[\alpha]^{25}\text{D}$ −52.7 ± 0.5° (*c* 4, chloroform). Robertson and Neish[11] reported m.p. 143–143.5° and $[\alpha]^{25}\text{D}$ −51.0° for the corresponding derivative of natural levorotatory butanediol.

Of the L-isomer, 0.9 g. were obtained (boiling point approx. 170° but inaccurate because the quantity of vapor was insufficient to maintain a constant temperature). It showed $\alpha^{25}\text{D}$ +12.4° (+6.2° in 0.5-dcm. micro tube, in substance). Since highly efficient columns are required to separate the last traces of water from butanediol it may be inferred that some water but no significant organic impurities were present. The di-*p*-nitrobenzoate melted at 141–143° and showed $[\alpha]^{25}\text{D}$ +52.0 ± 0.5° (*c* 4, chloroform).

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[13] About 2 ml. of each solvent were used per gram of solute.

[14] H. J. Lucas and P. Baumgarten, This Journal, **63**, 1653 (1941).

[15] Either the crystalline, or distilled but not crystallized compound may be used with similar results.

[16] Kindly supplied by Dr. R. W. Watson of the National Research Council, Ottawa, Canada.

Fractional crystallization of mixtures of the di-*p*-nitrobenzoates of optically active and racemic 2,3-butanediols leads to the relative loss of the optically active isomer.[11] Therefore, the high rotations of the di-*p*-nitrobenzoates of the synthetic butanediols indicate the absence of racemized butanediol in the compound showing α_D +12.4° (in substance).

MADISON, WISCONSIN RECEIVED JULY 2, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

The Effect of Solvent on the Pinacol Rearrangement of *cis*- and *trans*-1,2-Diphenyl-1,2-Acenaphthenediols. I. Methyl and Ethyl Alcohols[1,2]

BY RONALD F. BROWN

At room temperature it has been shown that either *cis*- or *trans*-1,2-diphenyl-1,2-acenaphthenenediol reacts in methyl or ethyl alcohol solutions in the presence of sulfuric acid to give high yields of *cis*-2-methoxy- or ethoxy-1,2-diphenyl-1-acenaphthenol. At the solvent boiling point, the principal products were 1,1-dimethoxy- or diethoxy-2,2-diphenylacenaphthene, the acetals of the pinacolone, 2,2-diphenyl-1-acenaphthenone. The pinacolone was present in varying amounts along with varying amounts of the monoether. Aluminum methylate appeared to catalyze these reactions at a slow rate in accordance with the low acidity of this material as compared with the catalyst usually used. The *cis*-monoethyl ether was converted to the *cis*-monomethyl ether and the dimethoxy acetal by reaction in methyl alcohol solutions at the boiling point in the presence of sulfuric acid. The diethoxy acetal was changed into the dimethoxy acetal and at a faster rate, under identical conditions. This is offered as contributory evidence for the assignment of the acetal structure to the dialkoxy compounds. In attempts to prepare the acetal of the pinacolone, the oxime of the pinacolone was prepared. The mono- and dimethyl ethers of the *cis*-diol were made by a Williamson synthesis, and the structure of the *cis*-monoether produced in the acid-catalyzed reaction confirmed. The dimethoxy product from the acid catalyzed reaction has been shown not to be the *cis*-dimethyl ether. The *trans*-diol has been shown to be inert to the action of active metals; the hydrogen of the hydroxyl groups was replaced only by reactive soluble reagents such as lithium aluminum hydride, or the Grignard reagent. The ultraviolet absorption spectra of all the reactants and products have been reported.

A possible explanation of the effect of water on the rate of the pinacol rearrangement of *trans*-1,2-diphenyl-1,2-acenaphthenediol (It) in acetic acid as the solvent and sulfuric or *p*-toluenesulfonic acid as the catalyst, was given in a previous paper[3] on the assumption of an inversion reaction between the conjugate acid of the diol and a molecule of water to yield *cis*-1,2-diphenyl-1,2-acenaphthenediol (Ic), which could be isolated from such a reaction mixture. However, alternate modes of interaction were not excluded by the evidence presented. In order to obtain more conclusive data, a study of this reaction in various alcohols as the solvents has been made.

Since the work of Norris and Rigby[4] had shown that tertiary ethers are easily formed when a tertiary alcohol is heated under reflux with an excess of a primary alcohol in the presence of an acid, it seemed possible that ethers of pinacols would be obtained under similar conditions. Thus, Mamedov[5] was able to prepare the ethers of acetylenic pinacols in 80 to 90% yields by the interaction of the pinacol, an alcoholic solvent, and sulfuric acid as the catalyst. Nevertheless, we were able to find conditions such that rearrangement as well as etherification occurred.

Either the *cis*- or *trans*-diol when allowed to stand at room temperature in absolute methanol containing a small amount of sulfuric acid was converted into the same product during a period of three to five days. If, on the other hand, such solutions were heated under reflux for 30 minutes, a second product was obtained. The presence of small amounts of water did not affect the yields. Analysis showed that there was one methoxyl group in the first product, and two in the second product. Because only one product predominated from either Ic or It under a given set of conditions, and by analogy to the action of water in acetic acid,[3] the first product was tentatively assigned the structure of the *cis*-monomethyl ether of I (*cis*-2-methoxy-1,2-diphenyl-1-acenaphthenol, IIIc), and the second product either that of the *cis*-dimethyl ether of I (*cis*-1,2-dimethoxy-1,2-diphenylacenaphthene, IVc), or the dimethylacetal of 2,2-diphenylacenaphthenone (1,1-dimethoxy-2,2-diphenylacenaphthene, V).

In commercial anhydrous ethyl alcohol, an analogous product was obtained at room temperature, and analysis showed the presence of one ethoxyl group. However, under reflux for 30 minutes, only the pinacolone could be isolated. When the period of reflux was shortened to five minutes, there was obtained a 60% yield of II and a 25% yield of a product which contained two ethoxyl groups as shown by analysis. Again, similar configurations were assigned.

In alcohol which had been dried over magnesium, similar results were obtained except that the proportion of ketone was reduced, and it was possible to isolate some of the monoethoxy product from the reactions carried out under reflux. This disposes of the possibility that the formation of the monoethers at room temperature was due to the removal of an insoluble product.

In order to obtain unequivocal proof of the configurational assignments, it was necessary to prepare the ethers by the reaction of a metallic derivative of the pinacols with an alkylating reagent under neutral or basic conditions to avoid any complication from an acid-catalyzed rearrangement during

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(1) Part of this paper was presented before the Organic Division, American Chemical Society Meeting, New York, N. Y., September 11–15, 1944.

(2) The numbering of the acenaphthene ring system is that recommended in the Ring Index. The 1- and 2-positions correspond with the 7- and 8-positions as used previously.[3]

(3) P. D. Bartlett and R. F. Brown, THIS JOURNAL, **62**, 2927 (1940).

(4) J. F. Norris and G. W. Rigby, *ibid.*, **54**, 2088 (1932).

(5) S. Mamedov, *Trudy Biogeokhim Lab. Akad. Nauk S.S.S.R., azerbaidzhan. filial*, No. 3, 83 (1940); *Khim. Referat. Zhur.*, **4**, No. 1, 49 (1941); See *C. A.*, **37**, 1699 (1943); **38**, 1470 (1944).