mm.), n^{20}D 1.5060, mol. wt., 250; b. p. above 160° (4 mm.), n^{20}D 1.5180, mol. wt., 380.

A small yield of a rubber-like polymer was obtained from the emulsion polymerization technique, which contained approximately one acid group per 10 styrene molecules. The molecular weight of the polymer could not be determined by the freezing point method.

Products Formed from Ethyl Sorbate and Isoprene.— The monomeric, dimeric and trimeric materials obtained from solvent polymerization were partially fractionated by vacuum distillation: b. p. 105° (4 mm.), n^{20}D 1.4741, mol. wt., 200; b. p. 110–130° (4 mm.), n^{20}D 1.4820, mol. wt., 280; b. p. 130–200° (4 mm.), n^{20}D 1.4940, mol. wt., 500.

Approximately 50% yield of a viscous, brown polymer was obtained from the emulsion technique.

Summary

Ethyl sorbate was found to form Diels–Alder addition products in good yield with methyl acrylate, ethyl acrylate, and diethyl fumarate, independent of the method of polymerization or the catalyst employed.

Ethyl sorbate was found to form addition products in poor yield with methyl crotonate and vinyl acetate.

Dimeric and trimeric materials were formed from ethyl sorbate with styrene and isoprene in solvent polymerization. Materials with rubber-like properties were formed by emulsion polymerization of ethyl sorbate and styrene. A very viscous liquid was formed by emulsion polymerization of ethyl sorbate and isoprene.

No polymeric materials were obtained by low temperature polymerization.

Similar dimeric materials were obtained from each of the various methods of polymerization, and it would appear that the catalyst had very little, if any, effect upon the product formed.

2,3-Benzylidene-1,4-anhydro-D-mannitol. A Case of Benzylidene Migration

BY RICHARD E. REEVES

Hockett and co-workers[2] have recently pointed out that the substance of m. p. 162° which was designated by Brigl and Grüner[3] as "1,6-dibenzoyl-2,4-anhydro-3,5-benzal-mannit" is actually a derivative of 1,4-anhydro-D-mannitol (1,4-mannitan). On the basis of a repetition and extension of their work, we have confirmed this ring structure, but we have also acquired new evidence which requires revision of the positions assigned to the substituent groups.[4]

Hockett, et al., removed the benzoyl groups from the compound mentioned above and obtained a crystalline monobenzylidene-mannitan melting at 143–144° to which they assigned the structure 5,6-benzylidene-1,4-mannitan by observing its behavior when subjected to lead tetraacetate oxidation. We have obtained the same substance, but have observed that it is unstable in glacial acetic acid, the medium used for the oxidation, and rearranges into an isomer of levo optical rotation melting at 94–96°. This rearrangement was missed by the workers cited and they were consequently led to several erroneous conclusions. From experimental observations summarized below, it is concluded that our new monobenzylidenemannitan is 2,3-benzylidene-1,4-mannitan. The exact structures

of Brigl and Grüner's dibenzoylmonobenzylidenemannitan and of Hockett's monobenzylidenemannitan remain uncertain at this point, but our observations impose conditions that are not met by the structures that have been proposed.[2,3]
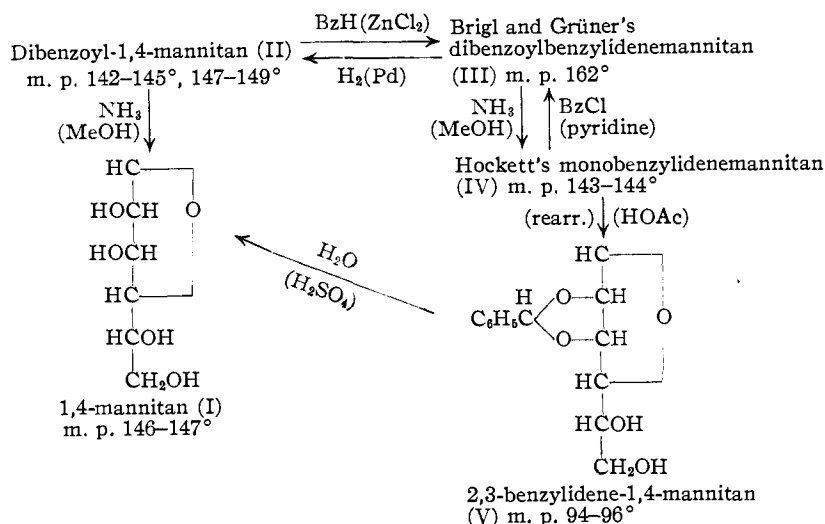
The reactions under discussion are shown in the following chart where structural formulas are used for the substances for which definite assignments are possible.

The structure of V has been established by the observation that one mole of lead tetraacetate is consumed at the rate characteristic of aliphatic alpha glycols[5] and by its oxidative cleavage with buffered periodate to yield virtually an equimolecular quantity of formaldehyde.

The isomeric monobenzylidenemannitan (IV) is probably not itself actually oxidized by lead tetraacetate since its apparent rate of consumption of this oxidant parallels very closely its rate of conversion into V (Fig. 1, Curve B). Hockett considered it to be oxidized because his observations were made under such circumstances that an unobserved rearrangement had evidently occurred before addition of lead tetraacetate (Fig. 1, Curve A). The conversion of IV into V apparently represents a clear case of benzylidene migration. Since IV does not react rapidly with lead tetraacetate the 5,6-benzylidene-1,4-mannitan structure proposed for this substance[2] is undoubtedly incorrect.

By rebenzoylation of Hockett's monobenzylidenemannitan IV we have obtained Brigl and

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry. Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Hockett, Fletcher, Sheffield, Goepp and Soltzberg, THIS JOURNAL, 68, 930 (1946).

(3) P. Brigl and H. Grüner, Ber., 67, 1582–1589 (1934).

(4) Hockett and co-workers revised Brigl and Grüner's structure to 2,3-dibenzoyl-5,6-benzylidene-1,4-mannitan.

(5) Hockett, Conley, Yusem and Mason, THIS JOURNAL, 68, 922 (1946); cf. Criegee, Büchner and W. Walther, Ber., 73, 571 (1940).

Dibenzoyl-1,4-mannitan (II) $\xrightarrow[\text{H}_2\text{(Pd)}]{\text{BzH(ZnCl}_2\text{)}}$ Brigl and Grüner's dibenzoylbenzylidenemannitan (III) m. p. 162°

m. p. 142–145°, 147–149°

NH$_3$ (MeOH) ↓   NH$_3$ (MeOH) ↓   ↑BzCl (pyridine)

HC———
HOCH   O
HOCH
HC———
HCOH
CH$_2$OH

1,4-mannitan (I)
m. p. 146–147°

Hockett's monobenzylidenemannitan (IV) m. p. 143–144°

(rearr.) ↓ (HOAc)

$\xleftarrow{\substack{H_2O \\ (H_2SO_4)}}$

HC———
H O—CH
C$_6$H$_5$C O
O—CH
HC———
HCOH
CH$_2$OH

2,3-benzylidene-1,4-mannitan (V) m. p. 94–96°

Grüner's dibenzoylbenzylidenemannitan (III). Hence the benzylidene group in III and in IV must occupy the same positions. We have also succeeded in removing the benzylidene group from III by catalytic hydrogenation to regenerate the original dibenzoyl-1,4-mannitan thus demonstrating that there is no benzoyl migration during the course of benzalation of II.

A private communication from Dr. R. C. Hockett indicates that our observed rearrangement of IV to V, the properties of V, and the rate of oxidation of V by lead tetraacetate have been confirmed in the Sugar Research Foundation Laboratory at the Massachusetts Institute of Technology and that he concurs with the structural conclusions reached in this paper. It is also indicated that studies have been initiated to solve fully the structures of III and IV.

Experimental

All melting points were observed between crossed Polaroids on a Fisher–Johns melting point apparatus drilled to allow the passage of a 1 mm. beam of light. The cuprammonium for optical rotations contained 15 g. of copper, 240 g. of ammonia, and 1 g. of glycerol per liter.

Substances I to IV were prepared in the manner described by Hockett and co-workers.[2] Dibenzoyl-1,4-mannitan (II) melted at 147–149°, $[\alpha]^{30}$D $-2°$ (c 2.2, chloroform). The slightly higher melting point was obtained by alternately recrystallizing from xylene and 50% alcohol.

1,4-Mannitan (I), m. p. 145–147°, $[\alpha]^{25}$D $-24°$ (c 0.59, water), $[\alpha]^{25}_{436}$ $-51°$ (c 0.59, water), $-1580°$ (c 0.41, cupra), was prepared by treating II with methanolic ammonia. Its melting point was not depressed when mixed with an authentic sample from the Massachusetts Institute of Technology laboratory.

Dibenzoylbenzylidene-1,4-mannitan (III), m. p. 162–163°, $[\alpha]^{25}$D $+39.8°$ (c 1.05, chloroform), was prepared from II.

Hockett's monobenzylidene-1,4-mannitan (IV), m. p. 143°, $[\alpha]^{25}$D $+32°$ (c 0.38, water), $[\alpha]^{25}_{436}$ $+71°$ (c 0.38, water), $+69°$ (c 0.84, cupra), was prepared from III. Substance IV was also compared with an authentic sample from the M. I. T. laboratory and it was found that the mixed melting point was not depressed.

2,3-Benzylidene-1,4-mannitan (V) was prepared by allowing 107 mg. of Hockett's monobenzylidenemannitan (IV) to stand in 3 ml. of purified acetic acid until the specific rotation had changed from $+30°$ to $-88°$, which required five days at room temperature. Evaporation *in vacuo* left a crystalline residue which was recrystallized from acetone–ether–petroleum ether; yield 71 mg., m. p. 94–96°, $[\alpha]^{25}$D $-88°$ (c 0.75, water), $[\alpha]^{25}_{436}$ $-175°$ (c 0.75, water), $-460°$ (c 0.67, cupra).

Anal. Calcd. for C$_{13}$H$_{16}$O$_5$ (252.26): C, 61.89; H, 6.39. Found: C, 61.12, 61.28, 61.17; H, 6.36, 6.46, 6.49.

A similar experiment employing 40.9 mg. of IV in 5.27 ml. of purified acetic acid was allowed to proceed in a thermostat at 25° and the conversion of IV to V at various intervals was calculated from the optical rotation readings and the specific rotations of the two pure substances. The results of this experiment are shown in Fig. 1, curve B.
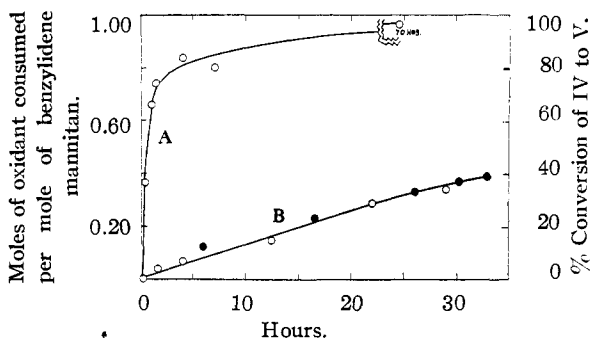

Fig. 1.—Curve A: the rate of oxidation of 2,3-benzylidene-1,4-mannitan with lead tetraacetate; Curve B: (open circles) the rate of oxidation of Hockett's benzylidene-1,4-mannitan with lead tetraacetate; Curve B: (solid circles) the rate of conversion of Hockett's benzylidenemannitan to 2,3-benzylidene-1,4-mannitan (all experiments in purified acetic acid at 25°).

Under standard conditions the new substance consumed 0.97 ml. of lead tetraacetate in seventy hours, the major portion being consumed during the first two hours. Oxidation of 11.3 mg. of the new benzylidenemannitan with periodate buffered with sodium bicarbonate under the conditions for the determination of primary carbinol groups[6] gave 28 mg. of precipitate of m. p. 138–148°. From this mixture 9.7 mg. of pure formaldehyde-dimedon compound (0.74 mole) of m. p. 189–190° was separated by sublimation at 100° and 0.1 mm. pressure. The stability of V in the presence of the bicarbonate buffer was checked in a separate experiment. Hydrolysis of 20 mg. of substance V with 0.5 N sulfuric acid in 50% alcohol overnight at 75° produced a change in specific rotation from -87 to $-23°$ (on the product calculated as 1,4-mannitan) and after neutralization with barium carbonate, filtration, and evaporation to dryness, a crystalline residue was obtained which yielded 1,4-mannitan of m. p. 142–143°.

Reduction of dibenzoylbenzylidene-1,4-mannitan (III) to II was accomplished at room temperature by stirring

(6) R. E. Reeves, THIS JOURNAL, **63**, 1476 (1941).

99.9 mg. of the substance III in 20 ml. of acetic acid with 500 mg. of palladium-on-charcoal (5% Pd) under slightly more than one atmosphere of hydrogen. When 2 moles of hydrogen had been absorbed the reaction was stopped, the solution filtered, and evaporated to dryness. The residue crystallized and after recrystallization three times from dilute alcohol and once from xylene yielded 14 mg. of dibenzoyl-1,4-mannitan of m. p. 145–146°.

Rebenzoylation of IV to III was accomplished by dissolving 20 mg. of Hockett's benzylidenemannitan (IV) in 0.3 ml. of dry pyridine, adding 50 mg. of benzoyl chloride and allowing to stand overnight at room temperature. A small amount of water was then added and the crystalline precipitate was filtered off and recrystallized from alcohol; yield 32 mg. of dibenzoylbenzylidene-1,4-mannitan (III), m. p. 161–2°, $[\alpha]^{25}$D +42° (chloroform).

Oxidation of the two benzylideneanhydromannitols with lead tetraacetate was performed under the standard conditions of Hockett, Dienes and Ramsden,[7] in specially purified, anhydrous acetic acid. The results are shown in Fig. 1.

(7) R. C. Hockett, M. T. Dienes and H. E. Ramsden, This Journal, 65, 1474 (1943).

Summary

A new anhydro-D-mannitol derivative, 2,3-benzylidene-1,4-anhydro-D-mannitol is described and doubt is cast on the structures 5,6-benzylidene-1,4-anhydro-D-mannitol and 2,3-dibenzoyl-5,6-benzylidene-1,4-anhydro-D-mannitol previously assigned to two other substances.


[Contribution from the Department of Chemistry of The Ohio State University]

# Configurational Correlation of L-(levo)-Glyceraldehyde with Natural (dextro)-Alanine by a Direct Chemical Method[1]

By M. L. Wolfrom, R. U. Lemieux[2] and S. M. Olin[2]

In order to establish a system of relative configurations among a group of optically active compounds it is absolutely essential that a compound be selected as a standard of reference. Such a standard must be a compound containing only one asymmetric center. The parameters of optical activity are numerous and embrace wave length, temperature, solvent, and concentration. When possible it is convenient to select such parameters that specific rotation is defined as $[\alpha]^{20-25}$D ($c < 5$, water). The form of the standard that is dextrorotatory under these conditions is then arbitrarily assigned the D-configuration and its stereoformula is written in a definitive form. In the sugar series this standard is glyceraldehyde written by agreed convention as shown.[3,4]

D-(dextro)-Glyceraldehyde
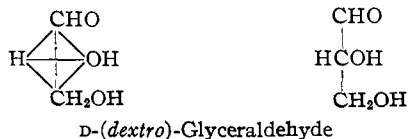
The simplified tetrahedral representation is that suggested by Hudson[5] and this has its counterpart in the Fischer[6] projection formula shown above, the conventions for writing which are little under-

(1) A complete report of this work appeared in Abstracts Papers Am. Chem. Soc., 112, 12Q (1947).
(2) Bristol Laboratories Research Associate (R. U. L.) and Research Fellow (S. M. O.) of The Ohio State University Research Foundation (Project 224).
(3) M. A. Rosanoff, This Journal, 28, 114 (1906).
(4) A. Wohl and K. Freudenberg, Ber., 56, 309 (1923).
(5) C. S. Hudson, J. Chem. Education, 18, 353 (1941).
(6) E. Fischer, Ber., 24, 2683 (1891).

stood by present-day organic chemists.[7] Having established such a standard, it is then feasible to relate it chemically to other compounds containing a like asymmetric center by operations which do not break the bonds attached to the reference carbon. In representing these relations it is essential that the reference center be oriented according to agreed conventions. Thus, in relating D-(dextro)-glyceraldehyde to lactic acid, it is agreed that the carboxyl group of the latter compound arises from the aldehyde group of the former and not from its primary alcohol group.
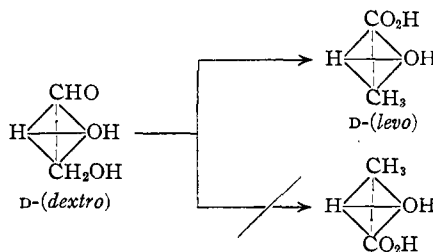
Furthermore, in a compound containing more than one asymmetric carbon, it is necessary to decide which of the centers present represents the standard of reference. In the sugar series, the highest numbered asymmetric center, or the bottom one in the conventional representation, is selected as that standard. In compounds containing more than one asymmetric center and with like terminal groups, an agreed orientation is particularly essential. Some of these substances may have a

(7) See C. S. Hudson, Advances in Carbohydrate Chem., 3, 7 (1948).