[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

cis-trans ISOMERISM IN CYCLOPENTENE DERIVATIVES

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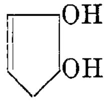
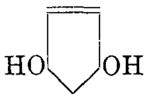
In the course of investigations concerning the stereochemistry of addition reactions of certain conjugated dienes it appeared that the structures and configurations of the four possible stereoisomeric cyclopentenediols had not been completely established. The *cis* and *trans* forms of 3-cyclopentene-1,2-diol (I) have been prepared by Creegie (1) and their configuration established by relating them to the derived *cis*- and *trans*-cyclopentanediols. The latter diols are sufficiently well described by van Loon (2) to serve as reference compounds for stereochemical studies of cyclopentene and cyclopentane derivatives. However, the available data pertaining to the *cis*- and *trans*-2-cyclopentene-1,4-diols (II) are not altogether satisfactory.



I



II

Since it has been clearly demonstrated by Thiele (3) that bromine adds to cyclopentadiene to give *cis*- and *trans*-1,4-dibromo-2-cyclopentene, it should be possible to relate conveniently the configurations of the corresponding 2-cyclopentene-1,4-diols to these dibromides.

In a detailed study of this addition reaction, Thiele showed that the addition of bromine to cyclopentadiene, when carried out in chloroform solution at −10° to −15°, resulted in the formation of two stereoisomeric 1,4-dibromo-2-cyclopentenes which could be separated by fractional distillation under vacuum. By oxidative degradation of the two dibromides to *meso*- and *racemic*-α,γ-dibromoglutaric acid he proved that the lower-boiling liquid dibromide was the labile *cis* isomer and that the higher-boiling solid dibromide (m.p. 45°) was the stable *trans* modification.

Creegie (1) showed that oxidation of cyclopentadiene with tetravalent lead salts gave among other products either *cis*- or *trans*-3-cyclopentene-1,2-diol diacetate depending upon the conditions of the reaction. The *cis* diacetate was obtained when lead tetraacetate was used and the *trans* form resulted in the oxidation with lead tetrabenzoate. He established the configuration of his two diacetates by comparing the properties of the derived 1,2-cyclopentanediols with the properties of *cis*- and *trans*-1,2-cyclopentanediol carefully described by van Loon (2).

Milas (4), who has studied the oxidation of a variety of olefins with the reagent hydrogen peroxide and osmium tetroxide in anhydrous *t*.-butyl alcohol, has obtained the *cis* form of 2-cyclopentene-1,4-diol in the hydroxylation of cyclopentadiene. The structure and configuration of Milas' cyclopentenediol is supported by its chemical behavior and by comparison with the *cis*- and *trans*-3-cyclopentene-1,2-diols of Creegie.

The properties of the cyclopentenediols described by Creegie and Milas are at variance with those given by Dane (5) for two diols prepared through the oxidation of cyclopentadiene with selenium dioxide. Although Dane has not assigned a definite structure or configuration to either of these two cyclopentenediols, it is conceivable that one of them might be the hitherto unknown *trans*-2-cyclopentene-1,4-diol.

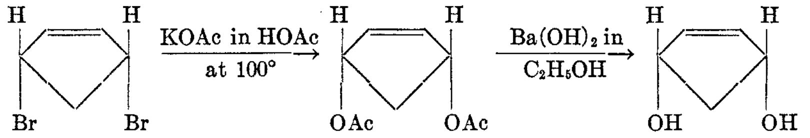
Thiele's preparation of *cis*- and *trans*-1,4-dibromo-2-cyclopentene has been examined. We have found that the formation of the *cis* isomer is favored by a rapid addition of bromine in chloroform at −25°. Slow addition of bromine in petroleum ether gives predominantly the *trans* form. Interconversion of the two *cis-trans* isomers is observed to proceed according to the following:

$$cis\text{-1,4-dibromo-3-cyclopentene} \;\; \underset{\xleftarrow[\text{at } 54\text{–}55^\circ/2\text{ mm.}]{\text{slow distillation}}}{\xrightarrow[\text{absence of light}]{\text{standing at } 0^\circ \text{ in}}} \;\; trans\text{-1,4-dibromo-3-cyclopentene}$$

Slow distillation results in complete conversion of the stable *trans* form into the labile *cis* modification. The *trans* isomer was obtained by direct bromination.

This isomerization is of interest in view of the facts which are known regarding the dibromides of butadiene. Only the *trans* form of 1,4-dibromo-2-butene is known (6, 7). All attempts to convert this stable *trans*-1,4-dibromo-2-butene into the labile *cis* isomer resulted in an anionotropic transformation to the compound 1,2-dibromo-3-butene.

Treatment of *cis*-1,4-dibromo-2-cyclopentene with potassium acetate in glacial acetic acid formed a cyclopentenediol diacetate which on careful saponification with barium hydroxide in ethanol gave a cyclopentenediol corresponding to the diol obtained by Milas in the oxidation of cyclopentadiene with hydrogen peroxide and osmium tetroxide.

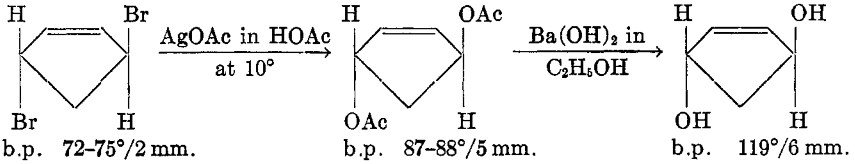


b.p. 53–54°/2 mm. b.p. 81–82°/5 mm. b.p. 110–111°/6 mm.

III

The cyclopentenediol (III) has been assigned the configuration *cis*-2-cyclopentene-1,4-diol on the basis of Milas' work. Further confirmation of the identity of III with Milas' diol was obtained by hydrogenation to *cis*-1,3-cyclopentanediol and the preparation of two solid derivatives of the saturated diol; *bis*-*p*-nitrobenzoate, m.p. 182° (Milas, 179–181°), *bis*-phenylurethan, m.p. 171° (Milas 168–171°). Mixed melting points of the derivatives prepared from the diols by the two methods showed no depressions.

Treatment of *trans*-1,4-dibromo-2-cyclopentene with silver acetate in glacial acetic acid at 10° gave a new cyclopentenediol diacetate. Hydrolysis of this diacetate gave a cyclopentenediol (IV) which differed from Creegie's *cis*- and *trans*-3-cyclopentene-1,2-diol and which also had different properties than *cis*-2-cyclopentene-1,4-diol (III).



IV

This cyclopentenediol (IV) on hydrogenation gives a new cyclopentanediol which does not correspond with any of the three previously described cyclopentanediols; *cis*- and *trans*-1,2-cyclopentanediol and *cis*-1,3-cyclopentanediol. Accordingly we have tentatively assigned to it the structure *trans*-1,3-cyclopentanediol. This saturated *trans*-1,3-diol has been characterized by two solid derivatives which differ from the corresponding derivatives of the *cis*-isomer: *bis*-*p*-nitrobenzoate, m.p. 207°; *bis*-phenylurethan, m.p. 184°.

Attempts to duplicate the selenium dioxide oxidation of cyclopentadiene in order to obtain Dane's cyclopentenediols for purposes of comparison were unsuccessful.

Further work which will establish more conclusively the configurations of the *cis*- and *trans*-2-cyclopentene-1,4-diols is in progress.

Data summarizing the properties of all the isomeric cyclopentenediols and cyclopentanediols are tabulated in the experimental part.

EXPERIMENTAL

All melting points recorded are uncorrected.

BROMINATION OF CYCLOPENTADIENE[1]

cis-1,4-Dibromo-2-cyclopentene. To a well-stirred solution of 66 g. (1 mole) of freshly-distilled cyclopentadiene in 50 cc. of chloroform, maintained below −25°, was added dropwise an ice-cold solution of 160 g. (1 mole) of bromine in 100 cc. of chloroform. The slight excess of bromine was removed by shaking with sodium bisulfite, and the chloroform was removed by heating on a water-bath. The purification of the dibromide was tedious and involved loss of material through decomposition during repeated distillations.

The product from 132 g. of cyclopentadiene after two fractionations under reduced pressure gave 160 g. of a fraction boiling at 52–58° at 2 mm. The lachrymatory product was only slightly colored when freshly distilled, but darkened slowly on standing.

Physical constants were determined on a specimen of this product: $d_{15.5}^{15.5}$ 1.957; n_D^{20} 1.5822; MR_D, calc'd. 38.2; obs. 38.4.

This corresponds to the compound proved by Thiele (2) to be *cis*-1,4-dibromo-2-cyclopentene.

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[1] Dicyclopentadiene used as a starting material in these studies was furnished through the courtesy of the United States Steel Corporation.

trans-1,4-Dibromo-2-cyclopentene. If the above mentioned *cis* dibromide is allowed to stand for two weeks, crystals begin to separate from the liquid. These crystals continue to grow until the liquid has completely solidified in about three months. When this solid product is recrystallized from petroleum ether, it melts at 45°. This product corresponds to the compound proved by Thiele (2) to be *trans*-1,4-dibromo-2-cyclopentene.

Thiele records for these crystals the boiling point 72–75° at 2 mm. However, it was found that upon slow distillation the substance isomerizes to the *cis* form and boils at 53–54° at 2 mm. The distillate remains liquid and possesses properties established for *cis*-1,4-dibromo-2-cyclopentene.

It was found that *trans*-1,4-dibromo-2-cyclopentene could be formed directly by using petroleum ether as the solvent during bromination. As high as 64% yields of *trans* dibromide could be obtained by carrying out the reaction in petroleum ether. The crystalline dibromide was isolated by removing the solvent and liquid *cis* dibromide with a filterstick. Samples taken from these crystals melted at 45° and proved to be identical with the above mentioned *trans* dibromide by mixed fusion on the microscope slide. Both solid products are characterized by an allotropic change that is identical.

TABLE I

PROPERTIES OF ISOMERIC CYCLOPENTANEDIOLS

DIOLS	B.P., °C./MM.	M.P., °C.	*bis*-*p*-NITROBENZOATE M.P. °C.	*bis*-PHENYLURETHAN M.P. °C.
cis-1,2-Cyclopentanediol[a, b]	132.5/29	29–30	116.5–117.5	205, 197[c]
trans-1,2-Cyclopentanediol[a, d]	136/21.5	54.5–55	145–154.2	221
cis-1,3-Cyclopentanediol[e]	105/5 120–125/12[f]	*ca.* 20	182, 179–181[f]	171, 169–171[f]
trans 1,3-Cyclopentanediol[e]	109/5	—	207	184

[a] *cf.* van Loon (2).

[b] *cis*-Diacetate, b.p. 85.5°/3.5 mm. and *cis*-dibenzoate, m.p. 46.5–47.5° [*cf.* Creegie (1) and also Verkade (8)].

[c] *cf.* Creegie (1)

[d] *trans*-Diacetate, m.p. 62.2–63.2° and *trans*-dibenzoate, m.p. 61.5° [*cf.* Creegie (1) and also Verkade (8)].

[e] Also observed for *cis* isomer: $d_{15.5}^{15.5}$ 1.100, n_D^{20} 1.4792; for *trans* isomer: $d_{15.5}^{15.5}$ 1.119, n_D^{20} 1.4811

[f] *cf.* Milas (4)

CONVERSION OF THE DIBROMIDES TO THE DIACETATES

cis-1,4-Diacetoxy-2-cyclopentene. A mixture of 200 g. of the above *cis* dibromide, 203 g. of freshly fused, finely powdered potassium acetate, and 135 cc. of glacial acetic acid was heated for eighteen hours on a boiling water-bath. The reaction mixture was poured into a liter of water, and the brown oily layer was separated. The water solution was extracted several times with ether, and after removal of the ether this extract was combined with the oily layer and vacuum distilled. Upon careful fractionation 85 g. of product was isolated boiling at 81–82° at 5 mm. The diacetate is a slightly yellow and practically odorless liquid. Physical constants are recorded in Table II.

Anal. Calc'd for $C_9H_{12}O_4$: C, 58.68; H, 6.57.
Found: C, 58.83; H, 6.63.

trans-1,4-Diacetoxy-2-cyclopentene. Silver acetate (approximately 25% excess of the amount required) was precipitated by adding excess aqueous sodium acetate to aqueous silver nitrate. It was filtered and washed three times with glacial acetic acid on a Büchner funnel. The moist mass was then transferred to a 1-liter flask. Six hundred forty cubic centimeters of glacial acetic acid (100 cc. of acid for each 0.1 mole of dibromide) was added and the mixture cooled to 10°. One hundred forty-four grams of the *trans* dibromide was added stepwise while the reaction vessel was kept in a cooling mixture. The temperature was never allowed to rise above 10° during the entire addition. The reaction flask was shaken intermittently throughout the addition and for several hours thereafter. The reaction mixture was allowed to stand overnight at room temperature. The following day the acetic acid solvent, containing the diacetate, was removed by filtration. The solvent was separated from the diacetate by vacuum distillation. The diacetate (12 g.) boiled at 87–88° at 5 mm. The 8% yield could be accounted for by the fact that the resulting silver bromide coats the silver acetate and prevents further reaction. This could be seen microscopically. The *trans* diacetate is a colorless, practically odorless liquid. The physical properties of the compound are given in Table II.

Anal. Calc'd for $C_9H_{12}O_4$: C, 58.68; H, 6.57.
Found: C, 58.75; H, 6.65.

TABLE II

PROPERTIES OF ISOMERIC CYCLOPENTENEDIOLS

DIOL		DIACETATE
cis-3-Cyclopentene-1,2-diol[a]	b.p. 110–114°/12 mm.; d_4^{17} 1.152	b.p. 106–110°/12 mm.; d_4^{20} 1.137
trans-3-Cyclopentene-1,2-diol[a]	—	—
cis-2-Cyclopentene-1,4-diol	b.p. 110–111°/6 mm. (80–83°/1 mm.)[b]; $n_{15.5}^{15.5}$ 1.182 n_D^{20} 1.4995	b.p. 81–82°/5 mm.; $d_{15.5}^{15.5}$ 1.151; n_D^{20} 1.4650
trans-2-Cyclopentene-1,4-diol	b.p. 119°/6 mm.; $d_{15.5}^{15.5}$ 1.160; n_D^{20} 1.5017	b.p. 87–88°/5 mm.; $d_{15.5}^{15.5}$ 1.168; n_D^{20} 1.4726

[a] *cf.* Creegie (1). No data for *trans* isomer. It was converted to *trans*-1,2-cyclopentanediol and identified as such.

[b] *cf.* Milas (4).

CONVERSION OF THE DIACETATES TO THE DIOLS

cis-2-Cyclopentene-1,4-diol. Eighty-five grams of the *cis* diacetate was refluxed for five hours with twice the theoretical amount of powdered barium hydroxide (306 g.) in 850 g. of ethyl alcohol. The dissolved barium salts separate out nearly completely on cooling and were filtered off. The small amount of dissolved barium salts was then completely removed by passing in carbon dioxide. The resulting barium carbonate cannot be separated by filtration and, therefore, must be removed by centrifuging or long settling. The pure glycol (22 g.) could be recovered from the alcoholic solution by vacuum distillation: See Table II for physical constants.

Anal. Calc'd for $C_5H_8O_2$: C, 59.99; H, 8.05.
Found: C, 59.90; H, 8.13.

trans-2-Cyclopentene-1,4-diol. The above procedure was repeated for the *trans* diacetate. The resulting *trans* diol boiled at 119° at 6 mm. Its physical properties are recorded in Table II.

Anal. Calc'd for $C_5H_8O_2$: C, 59.99; H, 8.05.
Found: C, 59.82, 60.05; H, 8.16, 8.12.

COMPOUNDS DERIVED FROM CIS- AND TRANS-2-CYCLOPENTENE-1,4-DIOL

cis-1,3-Cyclopentanediol. *cis*-2-Cyclopentene-1,4-diol (prepared from the corresponding dibromide) (0.1777 g.) in 15 cc. of ethyl alcohol was reduced catalytically in the presence of

0.02 g. of platinum oxide catalyst. The volume of hydrogen absorbed was 41.3 cc. as compared with the calculated volume of 38.8 cc. A larger amount of the diol was then reduced catalytically and upon purification and fractionation the *cis*-1,3-cyclopentanediol boiled at 105° at 5 mm. This saturated diol solidified at approximately 20°. The physical properties of this compound are listed in Table I.

Anal. Calc'd for $C_5H_{10}O_2$: C, 58.80; H, 9.87.
Found: C, 58.72; H, 9.98.

The *bis*-*p*-nitrobenzoate of *cis*-1,3-cyclopentanediol was prepared by heating 0.3 g. of the diol for a few minutes with *p*-nitrobenzoyl chloride (1.10 g.). The mixture was then poured into cold water with vigorous stirring. The precipitate was allowed to settle and the supernatant liquid decanted. The residue was stirred thoroughly with 5 cc. of 5% sodium carbonate solution, removed by filtration, and purified by recrystallization from alcohol. The ester melted sharply at 182°.

Anal. Calc'd for $C_{19}H_{16}N_2O_8$: N, 7.02. Found: N, 7.27.

The *bis*-phenylurethan of the saturated diol was prepared by mixing the diol (0.5 g.) with 3 cc. of phenyl isocyanate and bringing the mixture to boiling. After a few minutes the mixture was cooled and washed with a small volume of anhydrous benzene, then dissolved in hot glacial acetic acid to which had been added a small amount of petroleum ether. On cooling, a white crystalline precipitate separated out, which was recrystallized from ligroin; m.p. 170°.

Anal. Calc'd for $C_{19}H_{20}N_2O_4$: N, 8.23. Found: N, 8.39.

cis-1,3-Cyclopentanediol. A quantitative hydrogenation by the above procedure was run on the diol prepared by direct hydroxylation [according to Milas (4)]: 0.0950 g. of the unsaturated diol took up 20.6 cc. of hydrogen. The theoretical amount was 21.3 cc., an error of 3.2%.

The *bis*-*p*-nitrobenzoate derivative melted at 178°, using the procedure previously described, and gave no melting point depression with the *bis*-*p*-nitrobenzoate derived from our *cis*-1,3-cyclopentanediol.

Anal. Calc'd for $C_{19}H_{16}N_2O_8$: N, 7.02. Found: N, 6.90.

The *bis*-phenylurethan derivative melted at 168° and no depression in melting point was observed when mixed with the *bis*-phenylurethan prepared from our *cis*-1,3-cyclopentanediol.

Anal. Calc'd for $C_{19}H_{20}N_2O_4$: N, 8.23. Found: N, 8.50.

trans-1,3-Cyclopentanediol. When the unsaturated *trans* diol was reduced catalytically it absorbed the theoretical amount of hydrogen as determined by the pressure drop in the hydrogenation tank. The *trans*-1,3-cyclopentanediol boiled at 109° at 5 mm. This saturated glycol is a pale yellow, viscous liquid. The physical constants of the compound are given in Table I.

Anal. Calc'd for $C_5H_{10}O_2$: C, 58.80; H, 9.87.
Found: C, 58.53, 58.69; H, 9.95, 10.02.

The *bis*-*p*-nitrobenzoate derivative melted at 207°.

Anal. Calc'd for $C_{19}H_{16}N_2O_8$: N, 7.02. Found: N, 7.18, 7.00.

The *bis*-phenylurethan derivative melted at 184°.

Anal. Calc'd for $C_{19}H_{20}N_2O_4$: N, 8.23. Found: N, 8.31, 8.40.

SUMMARY

1. *cis*- and *trans*-2-Cyclopentene-1,4-diols have been prepared from the known *cis*- and *trans*-1,4-dibromo-2-cyclopentenes.
2. The *cis* configuration is assigned to the diol which is identical with the diol obtained by Milas in the hydroxylation of cyclopentadiene.
3. The *trans* configuration is tentatively assigned to the diol which is unlike any of the known cyclopentenediols of established configuration.

4. Our *trans*-2-cyclopentene-1,4-diol does not correspond to either of the cyclopentenediols obtained by Dane in the selenium dioxide oxidation of cyclopentadiene.

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