Notes A department for short papers of immediate interest.

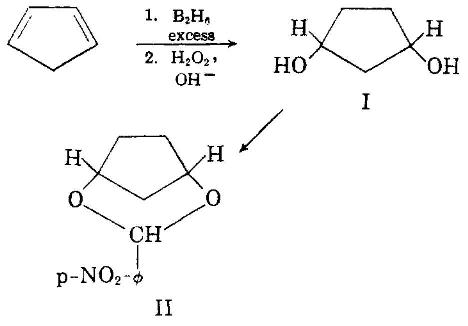
The Bishydroboration of Cyclopentadiene

Klaus A. Saegebarth

Received March 17, 1960

Recent interest in the synthesis of glycols by the bishydroboration-oxidation of dienes[1] prompts us to report on the application of the method to cyclopentadiene which provides a convenient preparation of *cis*-1,3-cyclopentanediol (I).

The hydroboration-oxidation of cyclopentadiene was carried out by H. C. Brown's elegant method,[2] except that an 80% molar excess of diborane was employed to favor glycol formation.[3] In this manner a 41% yield of *cis*-1,3-cyclopentanediol (I) was obtained. The glycol gave a negative periodic acid test for vicinal diol. A high resolution infrared spectrum indicated an intramolecular hydrogen bond as evidenced by the fact that the ratio of the intensities of the two bands, due to the free (3620 cm.$^{-1}$) and bonded (3450 cm.$^{-1}$) hydroxyl is independent of concentration.[4] Treatment of a xylene solution of the diol (I) with *p*-nitrobenzaldehyde in the presence of a trace of *p*-toluenesulfonic acid gave an 80% yield of a *p*-nitrobenzylideneacetal (II). These data make the assignment of the *cis*-1,3-configuration for the cyclopentanediol (I), obtained from the bishydroboration-oxidation process, both unique and compelling.



Our results present serious implications with respect to the steric course and stereochemical assignments of earlier reported preparations of the *cis*-1,3-cyclopentanediol. Owen and Smith[5] prepared the two isomeric *cis*- and *trans*-1,3-cyclopentanediols by treatment of the corresponding *cis*- and *trans*-3,5-dibromocyclopentenes (IV and III) with tetraethylammonium acetate in acetone[6] followed by subsequent hydrogenation and saponification a sequence of transformation which was believed to involve an over-all retention of configuration. More recently Young, Hall, and Winstein[7] have elegantly shown that the previously assigned configurations of the isomeric 3,5-dibromocyclopentenes had been reversed and therefore concluded that the configuration of the two corresponding 1,3-cyclopentanediols, reported by Owen and Smith,[5] were also reversed. The properties of the pure *cis*-1,3-cyclopentanediol, obtained from the hydroboration sequence, are in complete agreement with those of the 1,3-cyclopentanediol derived from *trans*-3,5-dibromocyclopentene (III) *via* the Owen and Smith route.[5] (See Table I). Therefore, an over-all inversion of configuration has occurred in the tetraethylammonium acetate displacement reaction, as the reduction and saponification steps are known to have no effect on configuration. Thus, by the Owen and Smith route, *trans*-3,5-dibromocyclopentene (III) gives *cis*-1,3-

TABLE I

Physical Properties of the Isomeric 1,3-Cyclopentanediols

		Owen and Smith[5] Route *via*	
	Hydroboration of Cyclopentadiene	*trans*-3,5-Dibromocyclopentene (III)[a]	*cis*-3,5-Dibromocyclopentene (IV)[a]
B.p. (mm.)	86–87° (0.5)	92° (0.8)	80–85° (0.1)
M.p.	31–32°	30–32°	40°
n_D (°C.)	1.4832 (25)	1.4835 (21)	—
M.p., bis-*p*-nitrobenzoate	186–187°	186°	153°
M.p., bisphenylurethan	172–173°	172°	162–163°
Configurational Assignment	*cis*	*cis*	*trans*

[a] Configurations based on the assignment made by Young, Hall, and Winstein, ref. 7.

---

(1) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 5832 (1959); K. A. Saegebarth, *J. Am. Chem. Soc.*, **82**, 2081 (1960).

(2) H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **78**, 5694 (1956); **81**, 6428 (1959); *J. Org. Chem.*, **22**, 1136 (1957).

(3) S. Winstein, E. L. Allred, and J. Sonnenberg, *J. Am. Chem. Soc.*, **81**, 5833 (1959); have recently reported that mono-hydroboration of cyclopentadiene, *i.e.* employing excess diene, results in the formation of Δ^3-cyclopentenol.

(4) L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954); **80**, 5950 (1958).

(5) L. N. Owen and P. N. Smith, *J. Chem. Soc.*, 4043 (1952).

(6) J. D. Roberts, W. G. Young, and S. Winstein, *J. Am. Chem. Soc.*, **64**, 2157 (1942); conditions considered to be favorable to S_N2 substitution in allylic systems.

(7) W. G. Young, H. K. Hall, and S. Winstein, *J. Am. Chem. Soc.*, **78**, 4338 (1956).

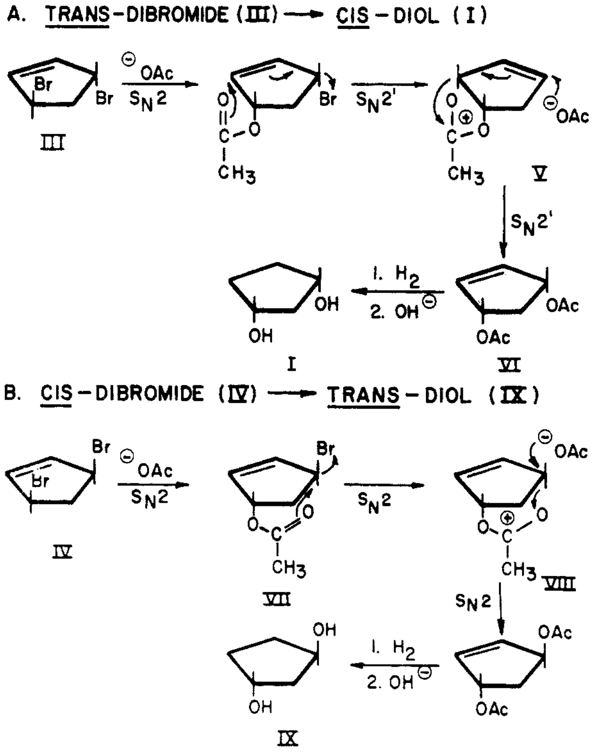


Figure 1

cyclopentanediol (I) and *cis*-3,5-dibromocyclopentene(IV) yields *trans*-1,3-cyclopentanediol (IX). A reasonable scheme by which these conversions could occur is shown in Fig. 1.

In the case of the *trans*-dibromide (III) the formation of V and VI by an internal S_N2' displacement leading to the observed final product (I) appears likely in view of the favorable *cis* relationship between the entering acetoxy group and the leaving halide ion.[8] However, for the *cis*-dibromide (IV) the orientation in (VII) is *trans*, making the acetoxonium ion (VIII) preferred.[9]

EXPERIMENTAL[10]

cis-1,3-Cyclopentanediol. Diborane,[2] 0.36 mole, was passed into a solution of 50 ml. (39.6 g., 0.6 mole) of cyclopentadiene in 100 ml. of dry ether and 150 ml. of dry pentane. The addition required 2.5 hr. during which time a copious white precipitate of the organoborane separated. The solvent was removed under reduced pressure and the solid product treated with a solution of 16.0 g. (0.4 mole) of sodium hydroxide in 250 ml. of ethanol. The slurry was oxidized[2] with 150 ml. of 30% aqueous hydrogen peroxide. Most of the ethanol was removed under reduced pressure, the remaining solution was continuously extracted with ether for 48 hr., and the ether solution was dried over anhydrous magnesium sulfate. Distillation gave 25.0 g. (41%) of *cis*-1,3-cyclopentanediol, b.p. 86–87° at 0.5 mm., n_D^{25} 1.4832, which gave a negative periodic acid test for vicinal glycol.[11] A high resolution infrared spectrum (lithium fluoride prism) exhibited strong absorption at 3620 cm.$^{-1}$ and 3450 cm.$^{-1}$, due to free and bonded hydroxyl bands. The ratio of the two intensities of the two bands was independent of concentration.[4]

Anal. Calcd. for $C_5H_{10}O_2$ (102.13): C, 58.8; H, 9.9. Found: C, 58.4, 58.6; H, 9.8, 9.9.

Bis-p-nitrobenzoate, m.p. 186–187° (ethyl acetate).

Anal. Calcd. for $C_{19}H_{16}O_8N_2$ (400.34): C, 57.0; H, 4.0; N, 7.0. Found: C, 56.7, 56.4; H, 4.1, 4.0; N, 6.8, 6.8.

Bisphenylurethan, m.p. 172–173° (toluene).

Anal. Calcd. for $C_{19}H_{20}O_4N_2$ (340.37): C, 67.1; H, 5.9; N, 8.2. Found: C, 67.4, 67.0; H, 6.3, 6.0; N, 8.5, 8.4.

cis-Cyclopentyl-1,3-p-nitrobenzylidene acetal. To a solution of 1.51 g. (0.01 mole) of *p*-nitrobenzaldehyde in 50 ml. of dry xylene was added 1.00 g. (0.01 mole) of *cis*-1,3-cyclopentanediol and a catalytic amount of *p*-toluenesulfonic acid. The solution was distilled until the volume was reduced to 20 ml. and the remaining solvent removed *in vacuo*. The residue was dissolved in 75 ml. of ether and the ether solution passed through a 15 × 300 mm. column of alumina; elution was accomplished with 250 ml. of ether. Evaporation of the solvent gave 2.0 g. (80%) of white, crystalline acetal, m.p. 139.5–140.5° (hexane).

Anal. Calcd. for $C_{12}H_{13}NO_4$ (235.23): C, 61.2; H, 5.7; N, 6.0. Found: C, 61.3, 61.0; H, 6.1, 6.0; N, 6.0, 5.9.

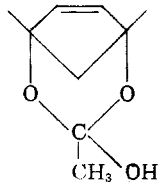
Acknowledgment. The author is indebted to Prof. J. D. Roberts, California Institute of Technology, for his interest and helpful discussions in connection with this work.

E. I. du Pont de Nemours & Co., Inc.
Elastomer Chemicals Department
Wilmington 99, Del.

---

(8) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **75**, 4119 (1953), have demonstrated the *cis* relationship of entering and departing groups in the S_N2' reaction in cyclic allylic systems.

(9) F. V. Brutcher, Jr., and F. J. Vara, *J. Am. Chem. Soc.*, **78**, 5695 (1956), reported the reaction of cyclopentadiene with lead tetraacetate in "wet" acetic acid followed by hydrogenation and saponification to give a 93:7 mixture of *cis*-1,2-cyclopentanediol and *cis*-1,3-cyclopentanediol (previously assigned the *trans*-structure on the basis of the argument presented in ref. (7) in a 75–80% yield. In this conversion the formation of the *cis*-1,3-glycol may arise from the interaction of the intermediate cation (VIII) (see Fig. 1) with water to give



which subsequently would yield the observed product.

(10) Melting points are corrected and boiling points are uncorrected.

(11) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Edition, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 129.

Formation of Cyclopropane Derivatives from 4-Bromocrotonic Esters[1]

Ronald S. Ratney[2] and James English, Jr.

Received May 17, 1960

During the course of another investigation, we were led to examine the reaction of methyl 4-bromocrotonate with phenylmagnesium bromide by