Table IV

Stilbene X	Stilbene Y	Mp, °C
p-NO$_2$	m-CF$_3$[a]	123
p-NO$_2$	m-Cl[b]	118
p-NO$_2$	p-Cl[b]	185
m-CF$_3$	m-CF$_3$[c]	112
m-Cl	m-Cl[d]	95

[a] *Anal.* Calcd: C, 61.43; H, 3.41; N, 4.77. Found: C, 61.08; H, 4.09; N, 5.40. [b] Reference 15. [c] *Anal.* Calcd: C, 60.76; H, 3.18. Found: C, 61.25; H, 3.52. [d] D. E. Bissings and A. J. Speziale, *J. Amer. Chem. Soc.*, **87**, 2683 (1965).

tion of carbonium and bromonium ion intermediates in stilbene bromination show that the transition states which lead to these intermediates are significantly different in their charge distributions. This confirmation of our previous work is apparently contradictory with the arguments of Yates, *et al.*,[1] who proposed a single transition state structure regardless of the intermediate. In reality, the thermokinetic data signify only that the magnitude of the interactions is retained or slightly increased in passing from the initial to the transition states, *i.e.*, no rotation occurs at this stage.[13] In our opinion, bromine bridging is not the only explanation consistent with strain conservation; counterion effects, interactions between the C–Br bond and the p orbital,[14] or some compensation of substituent–substituent interactions of the ground state by the bromine–substituent interactions of the transition state cannot as yet be excluded.

Experimental Section

Synthesis of Stilbenes. The p-nitro, Y-substituted stilbenes (Table IV) were prepared by condensation of Y-substituted benzaldehydes with p-nitrophenylacetic acid in the presence of piperidine.[15]

The di-m,m'-trifluoromethyl-and di-m,m'-chlorostilbenes were synthesized by pyrolysis of azines obtained from benzaldehydes and hydrazine.[16]

Kinetic Measurements. The bromination rate constants were measured in methanol at 25° for various bromide ion concentration by amperometric titration, as described previously.[17]

Acknowledgments. We are indebted to B. Galland for technical assistance and to J. S. Lomas for helpful discussion.

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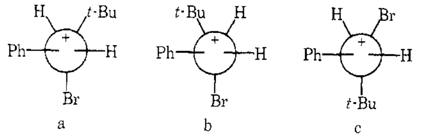

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On the Absolute Configuration of Two *trans-p*-Menthane-2,3-diols

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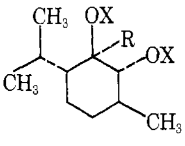
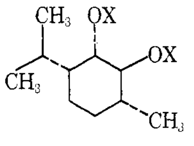
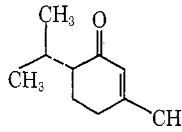
In order to determine the absolute configuration of substituted benzene dihydrodiols obtained in small quantities from enzymatic reactions,[1] it is necessary to employ spectroscopic methods rather than chemical correlations. We have recently applied the dibenzoate chirality rule of Nakanishi[2] (DCR) to ascertain the absolute configuration of a substituted *cis*-cyclohexane-1,2-diol and have verified this assignment by X-ray analysis.[3] Although the dibenzoate chirality rule has been applied to a wide variety of compounds,[2] its extension to the monocyclic *trans*-cyclohexane-1,2-diol system has not previously been reported. The diols **1a** and **2a** were selected for this study, since they can be prepared by hydroboration[4] of piperitone (**3**) whose absolute stereochemistry is known and therefore provides a check of the dibenzoate chirality rule.



1a, R = X = H
b, R = D; X = H
c, R = H; X = COPh



2a, X = H
b, X = COPh



3

Although Klein and Dunkelblum[4] had assigned the relative stereochemistry of **1a** and **2a** from 60-MHz nmr spectra and mechanistic consideration, their published data for **2a** were inconclusive.[5] In our hands, the absorption for carbinol hydrogens in **2a** at 60 MHz overlapped and could not be analyzed. However, these absorptions were separated in the 220-MHz nmr spectrum and the coupling constants so determined (Table I) confirmed the assigned configurations

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Table I[a]

Compd	$\delta_{C\text{-}2}$	$\delta_{C\text{-}3}$	$J_{2,3}$	$J_{3,4}$	$J_{1,2}$
1a	2.94	3.18	9	9	9
1b	2.94			9	
2a	3.37	3.68	8	8	4

[a] Coupling constants given in hertz.

1a and **2a**. The chemical shifts of the carbinol protons for **2a** were assigned from the observed coupling constants, but a similar assignment was not possible for **1a**. The deuterio derivative **1b** was prepared by lithium aluminum deuteride reduction of **3** followed by hydroboration of the resulting allylic alcohol. The disappearance of the multiplet at δ 3.18 in the nmr spectrum of **1b** established the chemical shifts of the carbinol protons.

Since the absolute configuration of (−)-piperitone is known to be 6*R*,[6] the relative stereochemistry of the diols can be used to assign their absolute configurations. From these considerations, (+)-**1a** is (1*S*,2*R*,3*R*,4*R*)-2,3-dihydroxy-*p*-menthane while (+)-**2a** is (1*R*,2*S*,3*S*,4*R*)-2,3-dihydroxy-*p*-menthane.

The dibenzoate chirality rule predicts that the sign of the first Cotton effect around 230 nm is in accordance with the chirality of the dibenzoate groups of a vicinal diol.[2] This chirality is negative for **1** and positive for **2**. The dibenzoates **1c** and **2b**, prepared by treatment of the corresponding diols with excess benzoyl chloride–pyridine, have strong Cotton effects (Figure 1) whose sign is in agreement with that predicted by the rule. The molar ellipticities given in Figure 1 differ by an order of magnitude, although the curves clearly bear a mirror image relationship. The differences in the magnitude of the two effects are probably ascribable to deviations from the parallel alignment of the carbinol carbon–oxygen bond and the long axis transition moment of the benzoate, as well as differences in the relative orientation and separation of the aromatic rings.

In conclusion, the absolute configurations deduced from the CD measurements correspond with those assigned from the known absolute configuration of (−)-piperitone and the relative stereochemistry obtained from the proton nmr spectra. These results coupled with earlier studies[1] support the use of the dibenzoate chirality rule in assigning the absolute configuration of other substituted 1,2-cyclohexanediols.

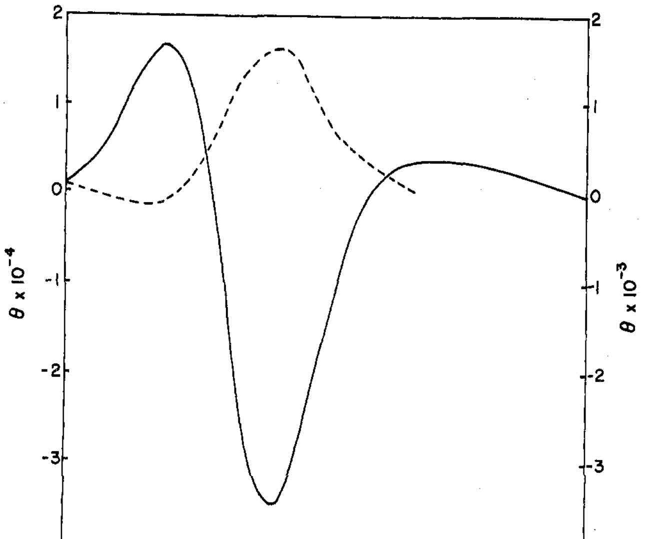

Figure 1. CD curves of diol dibenzoates. The solid line is **1c** legend on left and the dashed line is **2b** legend on right. Optical purity of dibenzoates ~40%.

Experimental Section

(−)-Piperitone, $[\alpha]_D$ −21.1° (reported[7] $[\alpha]_D$ −51.5°, *i.e.*, ~41% optically pure), was hydroborated and oxidized as described by Klein and Dunkelblum.[4] The reaction mixture was distilled and the diol fraction, bp 110–115° (0.1 mm), was collected. Chromatography on silica gel, using ethyl acetate–hexane (1:4) separated the mixture into a faster moving oil (**2a**) and a slower moving oil (**1a**). The specific rotations at the D line in chloroform for **1a** and **2a** were 47.2 and 13.3°, respectively. When these rotations are corrected for the optical purity of (−)-piperitone they become 115 and 32.4°, respectively. The dibenzoate of each diol was prepared by treating the diol in pyridine with excess benzoyl chloride, and the reaction products were purified by preparative thick layer chromatography on silica gel using ethyl acetate in hexane (1:9). The dibenzoates **1c** and **2b** were oils, $[\alpha]_D$ −74° and 42° ($CHCl_3$), respectively. The CD curves of the dibenzoates were determined in isooctane using a Cary 60 spectropolarimeter and are shown in Figure 1. The 220-MHz spectrum of **1c** in $CDCl_3$ showed absorption at δ 5.305 (t, 1 H) and 5.091 (t, 1 H) and complex aromatic absorption (10 H). The spectrum of **2b** showed absorption at δ 5.418 (d, 1 H) and 5.327 (q, 1 H) and complex aromatic absorption (10 H).

Registry No.—**1a**, 51745-19-8; **1b**, 51745-20-1; **1c**, 51705-86-3; **2a**, 51745-21-2; **2b**, 51705-87-4; **3**, 4573-50-6.

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Preparation and Purification of 18-Crown-6[1]

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Of the many crown ethers which have been prepared[2] since the pioneering work of Pedersen[3] first appeared, 18-crown-6 is probably the simplest and most synthetically useful. Its synthesis in low yield was reported by Pedersen in his first paper.[3] Greene[4] and Dale and Kristiansen[5] have reported syntheses of 18-crown-6 from triethylene glycol and the corresponding ditosylate. A variety of bases was examined by Greene[4] but in both cases potassium *tert*-butoxide was favored. We report here a simple synthesis of 18-crown-6 from triethylene glycol and the commercially available (Eastman) 3,6-dioxa-1,8-dichlorooctane (triethylene glycol dichloride) using potassium hydroxide as base in 10% aqueous tetrahydrofuran and purification of the crown *via* its acetonitrile complex.

The Williamson ether synthesis yields crude crown in about 40% yield after a rapid distillation under high vacuum. The distilled material contains an impurity believed to be a vinyl ether and some open-chain, hydroxyl-containing material. Addition of acetonitrile to the crude